

Physical Chemistry of Milk



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Lesson 1

Composition of Cow Milk

1.1 INTRODUCTION

Milk derived from cattle species is an important food. It has many nutrients and the precise nutrient composition of raw milk vary by species and by a number of other factors. Cow milk is available for marketing and utilization in the preparation of various products world over in a large proportion. Globally milk from other species like ovine, caprine, is utilized in a very insignificant proportion. For millennia, cow's milk has been processed into dairy products such as cream, butter, fermented milk products like dahi & yogurt, ice cream, cheese etc.

1.2 GROSS COMPOSITION OF COW MILK

Majority of the people utilize cow milk for their day to day needs. As such it is necessary to study the gross composition of cow's milk. It could be observed from the Table 1.1 that the major constituent of milk is water which ranges from 85.5 % to 88.7%. Lactose, the milk sugar, is high in its concentration ranging from 3.8 % to 5.3%. There is considerable variation in fat content and it ranges from 2.4 % to 5.5%. The building block of the living cells, the proteins, range between 2.3 % and 4.4%. The concentration of the major protein of milk, casein ranges from 1.7% to 3.5%. The remaining constituents although less in their concentration play an important role in maintaining the subtle balance among the various constituents in milk. Organic acids and other miscellaneous substance such as vitamins, citrate, etc. play a vital role both in the nutrition of the young calves and in humans.

Table 1.1 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
Lactose	4.6	3.8-5.3	36
Fat	3.9	2.4-5.5	31
Protein	3.25	2.3-4.4	26
Casein	2.6	1.7-3.5	20
Mineral substances	0.65	0.53-0.80	5.1
Organic acids	0.18	--	1.4
Miscellaneous	0.14	--	1.1

(Source: Dairy Chemistry and Physics, Walstra and Jenness, 1984)

A considerable variation in the composition of milk from various mammals is observed as evident from the data presented in table 1.2. Buffalo milk and sheep milk has highest fat percentage while human milk has highest lactose content. The casein content is low in human milk when compared with other milks.

Table 1.2 Gross Composition of Milk from different-Species of mammals

Species	Scientific name	COMPOSITION (g/100g)					
		Water	Fat	Casein	Whey proteins	Lactose	Ash
Human	<i>Homo sapiens</i>	87.1	4.5	0.4	0.5	7.1	0.2
Cow	<i>Bos Taurus</i>	87.3	3.9	2.6	0.6	4.6	0.7
Zebu	<i>Bos indicus</i>	86.5	4.7	2.6	0.6	4.7	0.7
Buffalo	<i>Bubalus bubalis</i>	82.8	7.4	3.2	0.6	4.8	0.8
Goat	<i>Capr hircus</i>	86.7	4.5	2.6	0.6	4.3	0.8
Sheep	<i>Ovis aries</i>	82.0	7.2	3.9	0.7	4.8	0.9
Horse	<i>Equus caballus</i>	88.8	1.9	1.3	1.2	6.2	0.5
Camel	<i>Camelus dromedaries</i>	86.5	4.0	2.7	0.9	5.0	0.8

(Source: Jenness and Sloan,1970, Dairy science abstracts,32,599-612)

1.3 MAJOR CONSTITUENTS OF MILK

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

1.3.1 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 collogative properties of milk.

1.3.2 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.

1.3.3 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.

1.3.4 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).

1.3.5 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.

1.3.6 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.

1.3.7 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.



Lesson 2

Classification of Colloids

2.1 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. The term colloid is not applicable to a given substance but rather to a specific state of a matter endowed with certain characteristic properties.

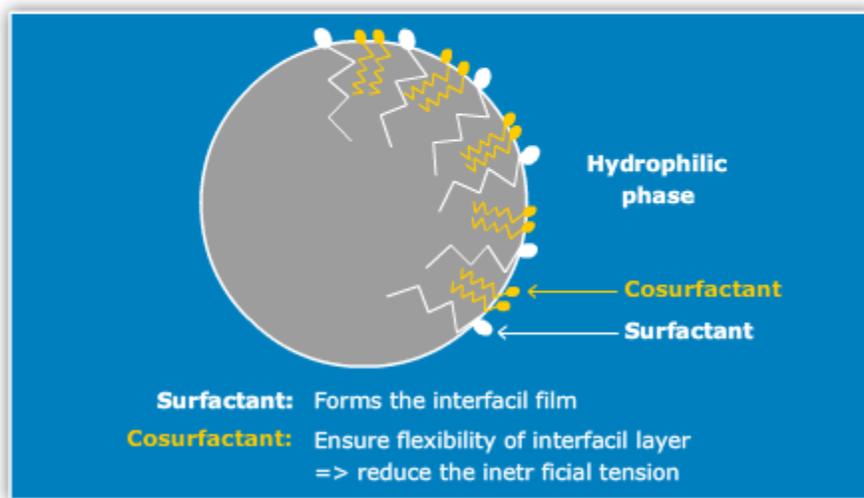
2.2 CHARACTERISTIC FEATURES

A colloid is a substance microscopically dispersed evenly throughout another substance. 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). The dispersed phase consists of the suspended particles and dispersion medium surrounding the suspended particles. As such all dispersions are heterogeneous systems. A colloidal system may be solid, liquid or gaseous condition. Colloids are specific form of disperse system in which the particle sizes ranges from 10 to 2000 Å. In some cases, a colloid can be considered as a homogeneous mixture. This is because the distinction between "dissolved" and "particulate" matter can be sometimes a matter of approach, which affects whether or not it is homogeneous or heterogeneous.

Considering the degree of dispersion, colloids will be between the coarse dispersions and molecular dispersions or true solutions. In solutions, the solute is dispersed in the solvent (dispersion medium) in the form of separate molecules or ions. The colloids are micro heterogeneous in nature and in these colloids dispersed particles comprise a separate phase that is divided by an interface from the dispersion medium. In a colloid system, the particle size is larger than dissolved molecules but smaller than settleable solids since the particles are having fine dimensions and greater surface area. The size of the

particles in a colloidal system ranges approximately 1 to 10^5 nm. The dispersed particles are large enough to scatter the light and do not dissolve.

Colloids



Colloids

2.3 CLASSIFICATION

Colloids could be classified on the basis of the affinity of dispersed molecules with dispersing media. If the affinity on dispersion medium is more it is lyophilic or reversible sol. If the affinity on dispersion medium is less it is lyophobic or irreversible sol. Lyophilic colloidal systems with aqueous continuous phase are known as hydrophilic while the lyophobic systems with aqueous dispersion medium are known as hydrophobic. Reversible colloids are thermodynamically stable. They are either macromolecules (such as proteins) or association of colloids (micelles). Irreversible colloids constitute a true phase in aqueous medium. The classification of their physical state of dispersed phase and dispersions presented in Table 2.1

Table 2.1 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

2.4 DIFFERENCES BETWEEN THE TWO TYPES OF COLLOIDS

The major differences between lyophilic and lyophobic colloids are presented in Table 2.2. The lyophilic (solvent attracting) colloid is one whose particles have a strong attraction for the molecules of dispersion medium and binding large number of them into so called solvent shells. On the contrary in lyophobic (solvent repelling) colloid, the particles do not interact so strongly with the molecules of the surrounding medium. The terms hydrophilic and hydrophobic are used in case of aqueous colloid solution. Lyophobic colloids are heterogeneous and highly dispersed colloid systems. Removal of the dispersion medium would result in the formation of powdery deposit by the dispersed phase and there will be insignificant amount of dispersion medium in it.

Table.2.2 Differences between the lyophilic and lyophobic colloids

LYOPHYLLIC	LYOPHOBIC
Reversible	Irreversible
Can be prepared by simple methods of mixing	Needs special methods for preparation
More solvated because of which it is more stable	Not solvated hence less stable but can be made stable by adding small quantity of lyophilic colloid
Viscosity is more for sol than for dispersion medium	Viscosity of sol is similar to dispersion medium
Surface tension is less than dispersion medium	Surface tension of colloid sol is same for dispersion medium
Exhibit weak tyndall effect	Exhibit strong tyndall effect

2.5 DISTINCTION BETWEEN THE TRUE AND COLLOIDAL SOLUTIONS

The distinguishing differences between colloid and true solution are given in Table 2.3 and depicted in fig 2.1. 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.

Table 2.3 Differences between True and Colloidal Solutions

Property	True solutions	Colloidal solutions
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



Lesson-3

Milk as a Colloidal System

3.1 INTRODUCTION

Milk, when secreted by the epithelial cells of the mammary glands is a mixture of various substances which exist in different states. It is necessary to maintain similar conditions continuously to maintain the stability of substances in native state. Accordingly, the constituents like casein micelles and minerals exist in the form of a colloidal suspension and exists in that condition as long as favorable conditions prevail. It is necessary to study the conditions that influence colloidal stability of milk which could be used to obtain different milk products by suitably modifying the conditions.

3.2 CHARACTERISTIC FEATURES OF A COLLOIDAL SYSTEM

Particles larger but definitely too small to be visible are said to exist in colloidal state. The size range is approximately 1 to 10^5 nm. A colloidal solution will have a continuous phase and a discontinuous phase. Depending on the affinity of the particles towards the dispersion phase colloids are divided (grouped) as lyophilic or hydrophilic and lyophobic or hydrophobic colloids. The reversible colloids such as macromolecules like proteins or association of colloids like micelles are thermodynamically stable. Irreversible colloids constitute a true phase in aqueous environment such as oil in water emulsions.

3.3 MILK AS COLLOIDAL SYSTEM

It is a well known fact that milk is not a homogeneous fluid. At the same time milk is also not a pure colloidal system. It could be even observed that in some milk products, the fat globules exist as hydrophobic colloids along with air bubbles, and crystals of fat and lactose. The hydrophobic colloids are thermodynamically unstable.

3.3.1 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. A phenomenon in solid

solutions or liquid sols which describes the change of an inhomogeneous structure over time during which small crystals or sol particles dissolve and redeposit onto larger crystals or sol particles is known as Oswald's ripening. This happens due to the difference in solubility larger particles which tend to grow at the expense of smaller ones and the latter disappears. Generally, the radii should be below $0.1\mu\text{m}$ to exhibit this effect for solids or liquids or below $100\ \mu\text{m}$ for gasses. Further, it is necessary that the substance in the particles be at least slightly soluble in the surrounding medium. In milk the hydrophobic colloids are subjected to this Oswald's ripening particularly when they are very small. In the normal conditions the hydrophobic colloidal particles sediment or cream. Brownian motion prevails when the particles are so smaller than $< 1\ \mu\text{m}$. The smaller particles show a tendency to flocculate which could effectively be prevented by the steric repulsion caused by their surface material.

- 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

3.3.2 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

3.4 SEDIMENTATION AND COAGULATION OF COLLOIDAL SYSTEMS

Colloidal systems widely differ with respect to the stability.

- Disintegration of the colloid system could be by two processes namely sedimentation and coagulation
- 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
- 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
- Coagulated particles can be redispersed by adding certain substances
- 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)



Lesson-4

Emulsions

4.1 INTRODUCTION

The characteristic and most useful feature of milk is the presence of a very important constituent namely the fat. This constituent being hydrophobic has to exist in emulsion form. Knowledge about the behavior and characteristics of an emulsion will help in effective and economic utilization of this component in the preparation of different milk and food products.

4.2 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). Many emulsions are oil/water emulsions, with dietary fats being one common type of emulsion encountered in everyday life. Examples of emulsions include butter and margarine, milk and cream. In butter and margarine, fat surrounds droplets of water (a water-in-oil emulsion). In milk and cream, water surrounds droplets of fat (an oil-in-water emulsion). Emulsification is the process by which emulsions are prepared.

The two liquids that involve in the formation of emulsion must be insoluble in each other. The formation of the interface always requires work to be done and as such greater is the interfacial tension, greater is the amount of work required. Addition of emulsifying agents will reduce the interfacial 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.

4.3 PROPERTIES OF EMULSIONS

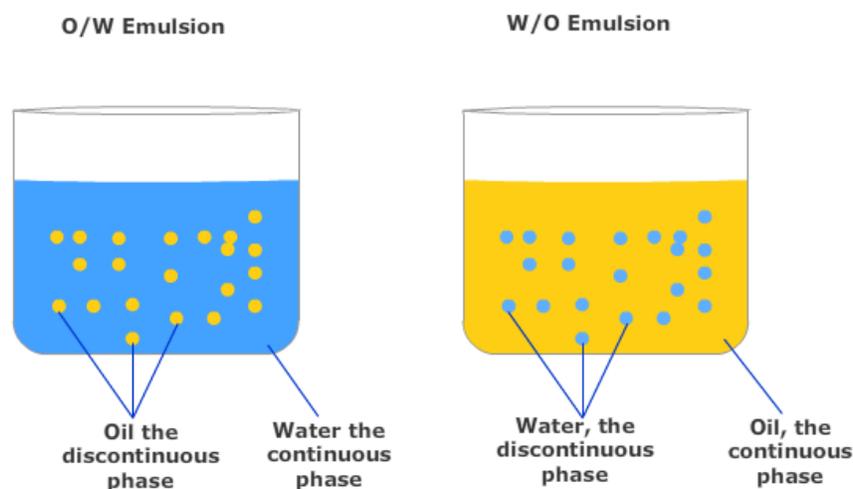
Several factors influence the properties of emulsions. Some of the important factors are

- 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

The two important properties of emulsions are the stability against creaming, and the flow properties, in other words their rheology. Stability against creaming relates to shelf life of commercial products. In food, the rheological property contributes to the mouth feel apart from the ease with which the product pours out of the containers.

4.4 TYPES OF EMULSIONS

There are two types of emulsions. A system consisting of water and non-polar organic liquid, is known as oil-in-water and is denoted by O/W. The other type of emulsion is water-in-oil type of emulsion and is denoted as W/O. In oil-in-water emulsion the lipid droplets are dispersed in water whereas in water-in-oil emulsion, the water droplets are dispersed in continuous oil phase.



Types of Emulsions

Food emulsions may possess solid particles (coagulated protein clumps) and gas bubbles in addition to the two liquid phases. Example for food emulsions are Butter (W/O), margarine (W/O), mayonnaise (O/W), salad dressing (O/W), milk (O/W), cream (O/W), non dairy creamer (O/W) and ice cream (O/W).

4.5 FUNCTIONAL ATTRIBUTES OF FOOD EMULSIONS

Acceptability of food emulsions is dependent on attributes such as appearance (colour and opacity), texture (viscosity, plasticity, and oiliness) and flavour. Certain features of food emulsions prove to be advantageous for modifying some these attributes.

It is possible to incorporate oil, soluble flavouring and coloring matter or vitamins in an oil- in- water emulsion. Similarly, by dispersing droplets of particles with a diameter of 0.05 to 1.0 μ m into the continuous phase, it is possible to create opacity in the fluid product. By increasing the concentration of the dispersed liquid to about 60% or more it is possible to introduce the oil into an emulsion without imparting any oily sensation e.g. mayonnaise.

4.6 PHYSICAL PROPERTIES OF EMULSIONS

The physical properties of an emulsion are discussed here under

4.6.1. Droplet size distribution: In coarse low concentration of emulsions, with differences in their densities of the dispersed and dispersion phases, the phases either tend to rise to the surface or settle at the bottom of the vessel. In highly concentrated emulsions the dispersion medium remains as a thin film between the particles of the emulsion. In such systems, it is the strength of this film that prevents the coalescence of the particles. The geometrical form of the particles in highly concentrated emulsions may not be spherical in shape.

4.6.2. Optical properties: The light scattering property of the emulsion systems is the greatest for the shorter wave lengths i.e. for the blue and violet rays. Light scattering property is effectively studied by using the spectrophotometers.

4.6.3. Rheology: The rheological properties of emulsions play an important role in the practical utility of the emulsions. This property helps in removing the product from the containers. The pouring out

property of the emulsions depends on the size distribution of the suspended particles. Butter being an emulsion of water- in- oil type has to be modified to get a product, butter spread by modifying its rheological property.

Colloidal particles are heterogeneous mixture of two phases namely the dispersed phase and dispersion phase and the particles remain in their own boundary surfaces which separate them from the dispersion medium. Colloid is a solution in which the particle size ranges between 10^{-7} and 10^{-5} cm and the particles can be seen under a powerful microscope.

The particles in true solution will not settle down but the particles in colloidal suspension can settle upon high speed centrifugation.

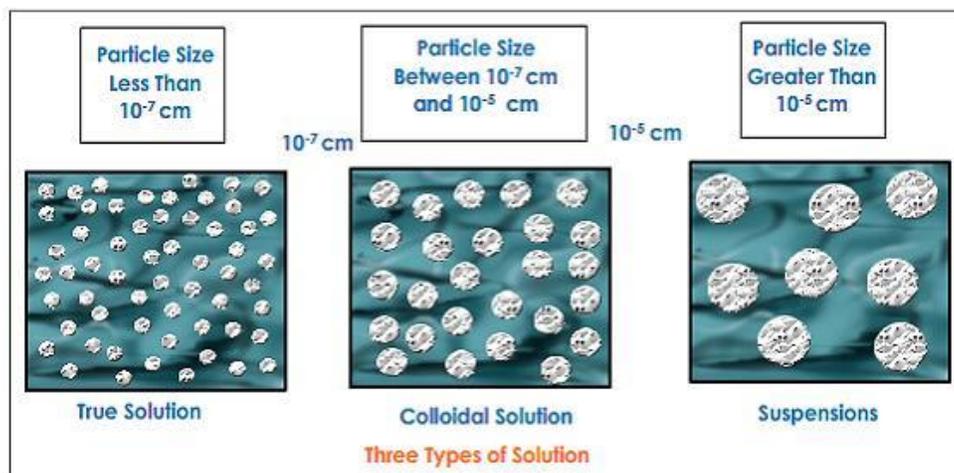


Fig 2.1 Types of Solutions

True solutions will not form any residue when filtered through a filter paper/ parchment paper or animal membranes whereas colloids can pass through ordinary filter paper but do not pass through animal membranes.

The composition and properties of a true solution are same throughout and is clear and transparent. True solution does not scatter the light whereas colloidal solution always reflects the light. The phenomena known as the "Tyndall Effect" is used to differentiate between the effects of colloids and true solutions.

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.



Lesson-5

Gels

5.1 INTRODUCTION

Gels play a very important role not only in the food system but also in the industrial application. The cross linking of the molecules give the typical three dimensional structure to these gels. This has increased their usefulness in various fields of application.

5.2 DEFINITION

Gels are defined as a substantially dilute cross linked system, which exhibits no flow in steady-state. Gels are mostly liquid, yet they behave like solids due to a three-dimensional cross linked network within the liquid. It is the cross links within the fluid that gives structure to a gel (hardness) and contribute to stickiness (adhesiveness). In other words, a gel is formed when particles aggregate to such an extent forming a continuous network throughout the liquid.

A gel has an elastic behavior similar to a solid and is deformed when stress is applied to it but recovers to its original shape after removal of the stress as deformation has left the bonds between the particles intact. A gel also has viscous properties because part of the deformation is not recovered after the stress is removed and the gel flows since the bonds are broken and new bonds are formed as in a liquid when stress is applied.

If the stress is applied for a very short duration the elastic deformation will be predominant i.e. recoverable. If the stress lasts long the viscous deformation is most conspicuous i.e. flow.

A gel thus shows the visco -elastic behavior which is characterized by the two rheological parameters.

Gels exhibit an elastic or storage module (G') and the viscous or loss module (G''). If the G' is greater than the G'' the elastic properties prevail, and if the G' is less than the G'' the viscous properties prevail. The overall resistance to deformation is expressed in the combined modulus G^* . The moduli give the ratio

of the stress to the relative deformation and thus have the dimension of stress e.g N.M^{-2} or Pa. They often strongly depend on the timescale of deformation.

The above reasoning holds when the deformation is about proportional to the stress (so called linear behaviour). Gels unlike solids often can be deformed considerably (e.g. by 10%) and still show linear behaviour. At larger deformation this relationship breaks down and as the bonds in the net work are broken that do not reform within the time scale of the experiment. A still larger deformation soon causes yielding or breaking of the gel and the net work is locally destroyed. The stress needed to do this may be called 'yield stress' It is not a well defined quantity as it depends much on conditions like geometry of the measuring instrument and time scale. The rheological properties will be altered when the deformation of the gel results in permanently breaking of the bonds.

5.3 TYPES OF GELS

There are two types of gels

1. Elastic gels and
2. Non elastic gels

5.3.1 Elastic Gels: Gradual removal of water from elastic gel becomes elastic solids. By adding water they can again be transformed into a gel, eg. gum used for pasting. The linkages between the particles of a gel are due to electrical attraction and they are not rigid or strong.

5.3.2 Non Elastic Gels: These non elastic gels are rigid and upon dehydration they set in to become glossy powder and thus lose their elasticity. The glossy powder cannot be converted back to gel by addition of water. These are prepared by suitable chemical action such as addition of concentrated hydrochloric acid to sodium silicate solution of correct concentration makes silica gel. Initially silicic acid is formed which gradually polymerizes to silica gel. This has a strong rigid covalent structure.

5.4 FOOD GELS

A food gel consists of a continuous phase of inter connected particles and/ or macro molecules intermingled with a continuous liquid phase such as water. Gels possess various degrees of rigidity,

elasticity and brittleness depending on the type and concentration of the gelling agent, salt content and pH of the aqueous phase and temperature. Gelling agents present at levels of 10% or less may be polysaccharides, proteins or colloidal complex particles such as casein micelles. Firm gels can be prepared by few types of gums, pectins, and gelatin at levels of 1% or lower. Gels prepared with colloidal particles are generally not very rigid even when the solids content is considerably higher than 1%. Some of the gels can be melted (liquefied) and reset with the addition or removal of thermal energy and these have been designated as thermo reversible. Gels with covalent bonds between the molecules or complex particles however are generally thermo irreversible.

Conditions for the transformations of a sol into a gel are:

- Temperature change
- Chemical alteration of gelling agent
- Reduction in number of charged groups by adjustment of pH or addition of salt and addition of a water competitive compound such as sugar

During the sol gel transformation a three dimensional network is formed involving interaction of groups of polymer chains or particles to form cross linkages at the site of junction zones. The aqueous phase is entrapped in the interstitial areas of the structure. In some gelling agents, the junction zones consist of microcrystallites involving specific chain units arranged in a crystal like fashion. Bonds in the junction zones are electrostatic, hydrophobic, covalent and hydrogen bonds. Thermo reversible gels have preponderance of intermolecular hydrogen bonds whereas in a protein gel a few disulfide linkages per polymer chain may be sufficient to render them thermo irreversible

5.5 PROPERTIES OF GELS

5.5.1 Hydration: Elastic gels after complete dehydration can be regenerated by adding water while non elastic gels cannot be hydrated.

5.5.2 Swelling: Partially dehydrated gels when dipped in water absorb water resulting in increase in the volume of gel and this process is called swelling.

5.5.3 Syneresis: Most of the inorganic gels on standing shrink and exude water and discharge water in the form of tear. This is known as syneresis. During storage of a gel ,the system may shift to a more stable

state with changes in the junction zones and solvent solute relationships. This process leads to syneresis which involves spontaneous release of water and contraction of gel volume.

5.5.4 Thixotropy: Some gels liquefy on shaking and reset when allowed to stand. This reversible sol gel transformation is known as thixotropy.



Lesson-6

Density

6.1 INTRODUCTION

Density is one the important physical property of a matter. Density has a direct relationship with weight and volume of a substance. The knowledge about density is helpful in understanding the behavior of substance when placed in a different environment. The density of milk and milk products is used to convert volume into mass and vice versa, to estimate the solids content of milk and to calculate other physical properties (e.g. kinematic viscosity). The relationship of this property with the temperature will also be helpful in developing various processing techniques of milk products.

6.2 DEFINITIONS

6.2.1: Density: Density is defined as the mass of a certain quantity of material divided by its volume. It is expressed in kg.m^{-3} (SI units) or g.ml^{-1} . The symbol ρ used to express density. Since density closely depends on temperature it is usually denoted with temperature ρ^{20} meaning the density at 20°C .

6.2.2 Specific Gravity: The mass or weight of a certain volume of the product divided by the mass of an equal volume of water is known as specific gravity. Thus specific gravity (s.g) of a product can be obtained by using the formula.

$$\text{s.g} = \rho_{\text{product}} / \rho_{\text{water}}$$

The density of substance varies with temperature and pressure so it is necessary to specify the temperatures and pressures at which the densities or weights are determined. Usually the density measurement is made nominally at 1 atmosphere (1013.25 millibars /hectopascal) pressure. As the substances for which density is measured are incompressible liquids, the effect of atmospheric pressure on this property is negligible. As such the variations caused by changes in pressure are neglected. For true (*in vacuo*) specific gravity calculations, air pressure must be considered. Temperatures are specified by the notation T_s/T_r with T_s representing the temperature at which the sample's density was determined and T_r the temperature at which the reference (water) density is specified. For example, s.g ($20^{\circ}\text{C}/4^{\circ}\text{C}$) would be understood to mean that the density of the sample was determined at 20°C and of the water at 4°C .

Relative density or specific gravity: It is customary to represent specific gravity or relative density of any liquid as below:

$$8.15 \frac{20^{\circ}\text{C}}{4^{\circ}\text{C}}$$

Where the superscript indicates temperature at which the density of the material is measured, and the subscript indicates temperature of the reference substance to which it is compared. There is appreciable variation in specific gravity with the change in temperature of both the fluids. As such it is necessary to know both the temperatures to get more reliable information.

6.3 DIFFERENCES BETWEEN THE DENSITY AND SPECIFIC GRAVITY

- Specific gravity i.e. relative density is a dimensionless quantity. It is mostly useful as a comparison but not in absolute units. Whereas density can be measured in specific units.
- Specific gravity does not provide the actual difference in the mass of two substances since it is only on a relative basis. It tends to be rather vague while the density will help in giving the exact mass of the product per unit volume.
- Specific gravity is more suitable for only liquids while density is for both solids and liquids.
- Measuring the specific gravity is simple and more convenient, less laborious and does not require any sophisticated equipment and quick results can be obtained, while the density needs specific equipment like pycnometer, sensitive balance and other materials.
- Specific gravity can be measured by people with minimum skill but density measurement requires specially trained individuals for this purpose.
- In a given time, a large number of samples could be tested for specific gravity whereas only limited samples for density could be determined.
- Determination of specific gravity is more economical in comparison to the density determination.

6.4 METHODS FOR THE DETERMINATION OF THE DENSITY AND SPECIFIC GRAVITY OF MILK

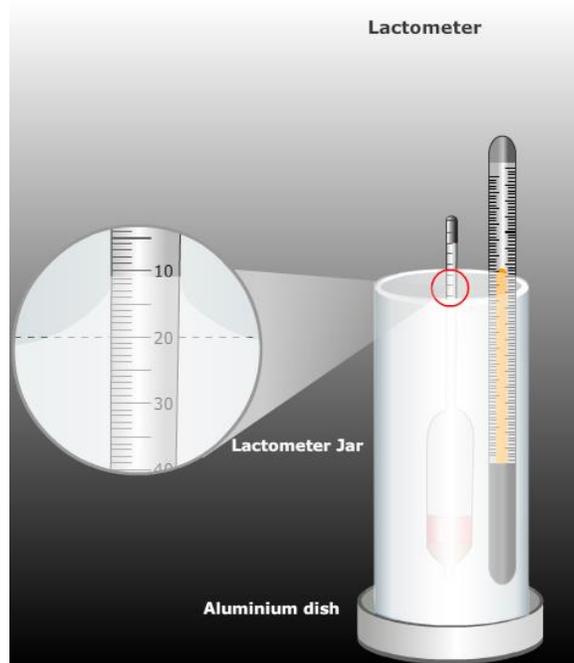
A very common instrument for direct measurement of density of a liquid is the hydrometer, which measures the volume displaced by an object of known mass. A common laboratory device for measuring fluid density is a pycnometer; a related device for measuring the absolute density of a solid is a glass pycnometer. Another instrument used to determine the density of a liquid or a gas is the digital density meter - based on the oscillating U-tube principle.

6.4.1 Hydrometer: Hydrometer is an instrument used to measure the specific gravity (or relative density) of liquids; that is, the ratio of the density of the liquid compared to the density of water. The operation of the hydrometer is based on the Archimedes principle that a solid suspended in a fluid will be buoyed up by a force equal to the weight of the fluid displaced. Thus, the lower the density of the substance, deeper the hydrometer will sink.

A hydrometer is usually made of glass and consists of a cylindrical stem and a bulb filled with mercury or lead shot to make it float upright. The liquid to be tested is poured into a tall jar or measuring cylinder and the hydrometer is gently inserted / lowered into the liquid until it floats freely. The point at which the surface of the liquid touches the stem of the hydrometer is noted. Hydrometers usually contain a paper scale inside the stem, so that the specific gravity can be read directly. The scales may be Plato, Oechsle, or Brix, depending on the purpose.

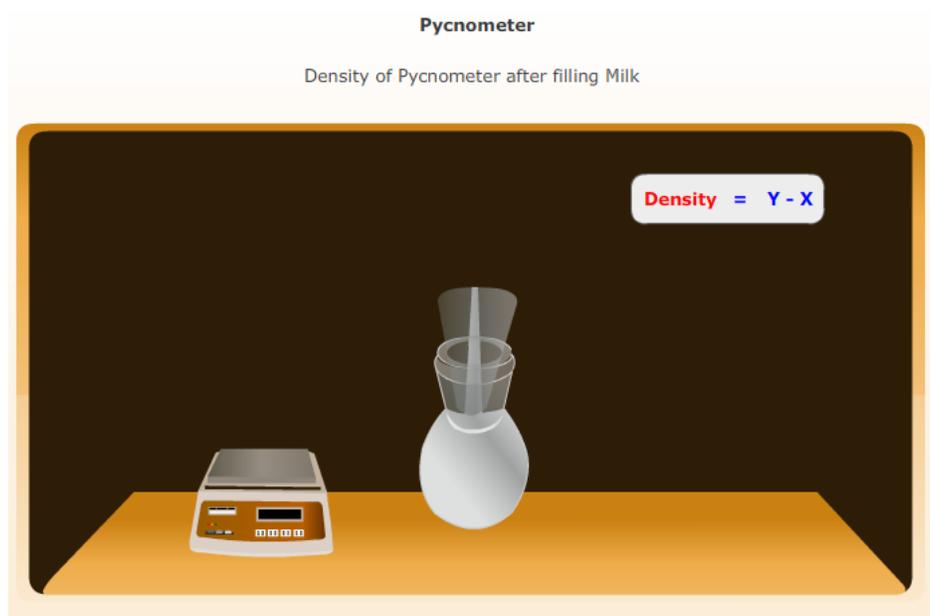
Hydrometers may be calibrated for different uses, such as a lactometer for measuring the density (creaminess) of milk, a saccharometer for measuring the density of sugar in a liquid, or an alcohol meter for measuring higher levels of alcohol in spirits

6.4.2 Lactometer: A lactometer (or galactometer) is a hydrometer used to test relative density of milk. The specific gravity of milk does not give a conclusive indication of its composition since milk contains a variety of substances that are either heavier or lighter than standard substance i.e. water. Additional tests for fat content are necessary to determine overall composition of milk. Another instrument, invented by Doeffel, is two inches long, divided into 40 parts, with division beginning at the point to which it sinks when placed in water.



lactometer

6.4.3 Pycnometer: A pycnometer (from Greek: πυκνός (puknos) meaning "dense"). A pycnometer is usually made of glass, with a close-fitting ground glass stopper with a capillary tube through it, for facilitating the escape of air bubbles from the apparatus. This device enables accurate measurement of a liquid's density in reference to an appropriate working fluid, such as water or mercury, using an analytical balance.



Pycnometer

The specific gravity of the liquid can easily be calculated if the weight of empty flask, flask with full of water, and flask with full of an experimental liquid are known. The particle density of a powder, for which the usual method of weighing cannot be applied, can also be determined with a pycnometer. The powder is added to the pycnometer and is then weighed, to get weight of the powder sample. The pycnometer is then filled with a liquid of known density, in which the powder is completely insoluble. The weight of the displaced liquid can then be determined, and hence the specific gravity of the powder.

6.4.4 Westphal Balance: This balance is used to measure the specific gravity (or density) of liquids. This is usually supplied in its box, along with the characteristic U-shaped balancing masses and the plummet in the upper right-hand corner. The sliding top of the box has the decorative molding attached to it.

The arm is first balanced with the plummet totally immersed in water at 15.5°C. The plummet has a built-in thermometer and has a known volume (equal to 5 gms of water at 15.5°C) and mass (15 g). A 5 g mass is placed on the hook holding the plummet, and screw on the foot is adjusted until the index pointer on the end of the beam lines up with the point on the frame. The plummet is then completely immersed in the unknown liquid, and the system is rebalanced, using a series of riders on the nine equally paced notches on the beam, thus giving the value of the added mass for each decimal place. This gives the buoyant force of the liquid relative to water, and hence the specific gravity, which may be obtained to four decimal places.



Lesson-7

Factors affecting Density and Specific Gravity of Milk

7.1 INTRODUCTION

Milk is often subjected to various processes before being allowed for marketing. During processing of milk there will be change in the density or the specific gravity of milk. A number of factors influence density or specific gravity of milk such as addition or removal of water, cream or other components etc. and temperature and pressure used during the processing of milk.

7.2 FACTORS AFFECTING THE DENSITY/SPECIFIC GRAVITY OF MILK

Density of milk is influenced by the combined effect of densities of its various components. As such it is dependent on the amount of dissolved or suspended matter, changes in the constituents and the physical state of components in milk. Milk density is further influenced by the various factors such as temperature history of samples, biological differences of micelles and processing conditions of milk. Among the various milk constituents, milk fat content is known to be the main cause for variation in the density of milk. The physical state of the milk fat was observed to have greater influence on density.

7.2.1 Recknagel Phenomenon: Recknagel, observed that the density of specific gravity of milk as soon as milking is lower than the same milk held for long periods of time, especially of milk under cold storage. Such phenomenon is known as Reckngel phenomenon. He attributed the increase in the hydration of the protein at low temperature as the major cause for such a phenomenon rather than the escape of the air bubbles. Subsequent work carried out by other scientists attributed this phenomenon to the ratio between the liquid and solid.

7.2.2 Temperature: Density and specific gravity decreases with increase of temperature and decreased with increase in temperature. This is the reason for obtaining corrected lactometer reading while calculating the specific gravity of milk at designated temperature of the lactometer. Sp. gravity of milk is $= 1 + \text{CLR} / 1000$, Where CLR is Corrected lactometer reading at a particular temperature expression. For attaining the maximum density and to avoid the Recknagel phenomenon it is suggested that milk

should be heated to a temperature of 40⁰ C and specific gravity is determined when cooled to 20⁰C to ensure reproducible state of milk fat.

7.2.3 Type of the Milk and Breed: These two factors influence the density/specific gravity of milk since there is variation in the composition which would otherwise influence this property. As the milk fat is lighter constituent, the milk with higher fat content will have lower the specific gravity and vice versa. However, although buffalo milk contains more fat than cow milk, its specific gravity is higher than the latter. This is because buffalo milk contains more solids-not-fat as well, which ultimately results in a higher specific gravity.

The specific gravity of milk is decreased by:

- Addition of water
- Addition of cream (fat)
- Increased temperature.

The specific gravity of milk is increased by:

- Addition of separated milk
- Removal of fat
- Reduction of temperature.

7.2.4 Processing and other factors: There will be an increase in the milk density due to refrigerated storage. Slow crystallization of the fat and change in the hydration of the globule membrane is responsible for this increase in the density.

- Fat content and temperature have been related to the density of creams.
 - Homogenization slightly increases the density of whole milk but not of skim milk. Sterilization decreases the density of both milks. These changes are very small and negligible due large variations observed from sample to sample.
 - The specific gravity of cream decreases regularly with increase in the fat content. Skim milk has specific gravity of 1.0320 to 1.0365 at 15⁰C /15⁰C. The removal of water in the manufacture of concentrated milk products raises the specific gravity.
 - Baume hydrometer is widely used for this purpose. The Baume's reading is related to specific gravity as follows :
1. Sp. Gravity at 60⁰F/60⁰F = 145/145-Be Where Be = Baume scale reading at 60⁰F
 2. The concentrated milk products will have high viscosity as such the Baume's reading is often taken at 120⁰ F instead of 60⁰F.

- The milk with higher SNF content will have higher density. Similarly the processes in which water is removed will have similar effect on the density of milk.
- Densities of the liquid dairy products such as whey, evaporated milk, sweetened condensed milk and freshly frozen ice cream vary in similar way as to milk.



Lesson-8

Liquid State - Surface Tension

8.1 INTRODUCTION

The surface tension of a solid is a characteristic of surface properties and interfacial interactions such as adsorption, wetting or adhesion. The knowledge of surface tension is helpful in understanding these mechanisms and more specifically in milk and food packaging industry in relation with wettability of systems.

8.2 DEFINITION AND CONCEPT OF SURFACE TENSION

Surface tension is a property of the surface of a liquid that allows it to resist an external force. In other words surface tension is the property of a liquid that makes it stretch like elastic. The cohesive forces among liquid molecules are responsible for the phenomenon of surface tension and are responsible for many behavioral properties of liquids. Surface Tension may be defined as the force along a line of unit length where the force is parallel to the surface but perpendicular to the line.

The area of contact between two phases is called the interface and is known as surface when one of the two phases is gaseous phase. The properties of interfaces and surfaces are determined by the number, kind, and orientation of the molecules located in them. Cohesion or the tension of molecules in the surface resulting from the imbalance of forces acting on them causes the surface to act as though it is covered with a film or skin. As a result of this property the surface portion of liquid to be attracted to another surface or another portion of liquid as in connecting bits of water or as in a drop of mercury that forms a cohesive ball. In the bulk of the liquid, each molecule is pulled equally in every direction by neighboring liquid molecules, resulting in a net force of zero. The molecules at the surface are pulled inwards as they do not have other molecules on all sides of them creating some internal pressure and thus forcing liquid surfaces to contract to the minimal area. Surface tension is responsible for the shape of liquid droplets. In terms of energy, a molecule in contact with a neighbor is in a lower state of energy than when it is not in contact with a neighbor. The molecules in the interior of liquid have as many neighbors. The molecules at boundary are having some missing neighbors and therefore have a higher energy. For a liquid to minimize its energy state the number of higher energy boundary molecules must be minimized and this results in a minimized surface area.

8.2.1 Units of Surface tension: Surface tension has the dimension of force per unit length or of energy per unit area. Surface tension, represented by the symbol γ is defined as the force along a line of unit length, where the force is parallel to the surface but perpendicular to the line. Its SI unit is newton per meter but the cgs unit of dyne/cm is also used. An equivalent definition is work done per unit area and is measured in SI system as joules per square meter and in the cgs system as ergs per cm². Although these two expressions are equivalent, but it is customary to refer the term surface energy when the energy per unit of area is to be mentioned. The term surface energy is more of a general term in the sense that it also applies to solids and not just liquids

8. 2.2 Interfacial Tension

The tension caused across the two phases in a liquid is known as interfacial tension. The more effective depressants of interfacial tension tend to be concentrated at the interface to the exclusion of other substance present there. In many cases the amount of material concentrated at the interface is greater than would be predicted.

In milk the important interfaces are those between the liquid product and air and between the milk plasma and the fat globules. Studies on the surface tension (liquid / air) have been made to ascertain the relative effectiveness of the milk components as depressants, to understand the release of the surface active components as a result of processing and the release of the free fatty acids during lipolysis and to explain the characteristic foaming phenomenon of the milk. Interfacial tensions between milk fat and solutions of milk components have been measured during the stabilization of fat globules in raw and processed milks.

8.3 MEASUREMENT OF SURFACE TENSION

The methods used for measuring the surface and interfacial tension may be grouped as dynamic and static. In dynamic method the measurements are made on freshly formed surfaces during the period required for equilibrium. Such methods enable the rate of orientation of molecules in the interfaces to be followed. The method of vibrating jets is a dynamic method.

Majority of the information on surface and interfacial phenomena in milk has been obtained with various static methods. The major principles involved in the determination are :

- Rise in the height of liquid in a capillary tube
- Weight of drops formed by specific volume of liquid flowing from a capillary tip. Some times this method is considered to be semi dynamic method
- Force required to pull a ring or plate out of the surface
- Maximum pressure required to force a bubble of gas through a nozzle immersed in the liquid
- Shape of a drop hanging from a capillary.

Among these methods the method involving pulling of a ring or plate from the surface is most widely employed. This method is rapid, simple, more reliable and give an accurate result $\pm 0.25\%$. The result could be more accurate when the force is measured with an analytical balance. Apparatus employing tension balance with various degrees of sensitivity (du Nouy balances) are also available.

8.3.1. Principle of surface tension measurement: There are several methods of measuring surface tension including those based on the following principles.

- The duNouy ring method is one technique by which the surface tension of a liquid can be measured. The method involves slowly lifting a ring, often made of platinum, from the surface of a liquid. The force required to pull the ring from the liquid's surface is measured and related to the liquid's surface tension
- Number of drops formed when a given amount of liquid is allowed to fall from a pipette
- The pressure required to force a bubble through a nozzle immersed in the liquid

8.3.2 Factors influencing surface tension determination of milk: The factors which influencing the measurement of surface tension are.

- Temperature history of the milk
- Age of the milk
- Time required for measurement and
- Correction factors required for individual instruments

The surface tension of milk is influenced by several factors and it is difficult to specify with any certainty an average value. Values ordinarily fall within the extremes of 40 – 60 dynes / cm measured at 20°C and the mid value of this range will give the average value. This may be compared with water which has a surface tension of 72.75 dynes/cm at that temperature. The milk proteins, fat, phospholipids and free fatty acids are the principal surface active components that contribute to the surface properties. The surface active substances tend to concentrate in the surface in proportion to their concentration and ability to lower the surface tension and. Soluble constituents like salts and sugars do not tend to concentrate at the surface because they do not lower the surface tension. Various dilution studies of milk, skim milk, whey, and solutions of milk proteins reveal that casein and whey proteins of lactalbumin

fraction (β -lactoglobulin, α -lactoglobulin and bovine serum albumin) are powerful depressants while immunoglobulin fraction are not having greater influence on this property of milk. The shorter chain fatty acids contribute more to the rancid flavour and the larger ones are more effective surface tension depressants. The fatty acids released by lipolysis are very effective depressants of surface tension. Butyric acid has little action on reducing the surface tension, acids with longer chain lengths particularly caprylic, capric and possibly mono and di glycerides are responsible for lowering of surface tension due to lipolysis.

Homogenization of raw whole milk or cream stimulates lipolysis and thus leads to a decrease in surface tension of the product which has been pasteurized previously. However, the exact reason for such behaviour is not known. It is suggested that the denaturation or other changes in the lipoprotein complex or a reduction in the amount of protein available to the milk air interface because of the adsorption on the extended fat surface are responsible for decreased surface tension. Another suggestion for such behaviour of milk is that the homogenization reduces the amount of free fat in the product.

Heat treatment has little effect on the surface tension except that sterilization treatments cause an increase by few dynes cm^{-1} coinciding with grain formation. This effect undoubtedly results from denaturation and coagulation of the proteins so that they are no longer effective surface active agents.

Table 8.1 Surface tension of various milk products

Milk product	Surface Tension (dynes/cm)
Rennet whey	51-52
Skim milk	52-52.5
Whole milk	46-47.5
25% cream	42-45
Sweet cream butter milk	39-40

From the data presented in the Table 8.1 it could be observed that the proteins of whey are not effective surface tension depressants. The fat globules in milk and cream (as well as traces of free fat on the surface) serve to reduce the surface tension significantly below that of skim milk. The fat globule membrane

material released from the fat globules during churning of cream are exceedingly surface active and are responsible for the very low surface tension of butter milk.



Lesson-9

Viscosity, Newtonian and Non-Newtonian Behavior of Fluids

9.1 INTRODUCTION

Viscosity is an important physical property of fluids. Viscosity is influenced by temperature and pressure exerted in the system. Moreover, the nature, concentration and type of milk components have a direct bearing on the viscosity. Therefore it is necessary to have some knowledge about this property of fluids and it is also necessary for designing various equipment of the milk processing.

9.2 DEFINITION OF VISCOSITY AND ITS UNITS

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear or tensile stress. In simple terms taking example of fluids, viscosity is termed as "thickness" or "internal friction". Thus, water is "thin", having a lower viscosity, while milk is "thick", having a higher viscosity. In others words it could simply be defined as the resistance of liquid to flow or pour, meaning the less viscous the fluid is, the greater its ease of movement or fluidity.

Viscosity of liquids can be defined as the resistance of a liquid to the motion of its layers relative to one another. Viscosity is also defined as ratio of shearing stress (S) to the shear rate which pertains to simple shear flow (i.e. laminar flow with parallel streamlines). In such fluids the shear rate is then equal to the velocity gradient G which is perpendicular to the direction of flow.

9.2.1 Units of Viscosity:

The usual symbol for dynamic viscosity is the Greek letter μ . The symbol η is also used by chemists. The SI physical unit of dynamic viscosity is the pascal-second (Pa s) which is equivalent to N s/m², or kg/(m s). The c.g.s physical unit for dynamic viscosity is the *poise*. It is more commonly expressed as *centi poise* (cP)

9.3 TYPES AND FORMS OF VISCOSITY:

Newton's law of viscosity is not a fundamental law of nature but an approximation that holds in some materials and fails in others. Thus there exist a number of forms of viscosity:

9.3.1 Newtonian Fluids: Fluids for which the viscosity coefficient depends only on temperature and pressure and is independent of the rate of shear are called "Newtonian". Newtonian fluid is the fluid in which the viscosity remains constant for all rates of shear if constant conditions of temperature and pressure are maintained. In common terms, this means the fluid continues to flow, regardless of the forces acting on it. For example, water is Newtonian, because it continues to exemplify fluid properties no matter how fast it is stirred or mixed. Other examples may be aqueous solutions, emulsions. Gases, pure liquids, and solutions of materials of low molecular weight exhibit behavior of this type. E.g. Skim milk and whole milk do not differ appreciably from Newtonian behavior. For a Newtonian fluid, the viscosity depends only on temperature and pressure not on the forces acting upon it if the fluid is a pure substance or else it will also be influenced by the chemical composition if it is not a pure substance.

9.3.2 Non Newtonian Fluids: A non-Newtonian fluid is a fluid whose flow properties differ in any way from those of Newtonian fluids. Generally speaking, a non-Newtonian fluid is defined as one in which the relationship between shear stress and shear rate (S/R) is not constant. Most commonly the viscosity of non-Newtonian fluids is dependent on shear rate or shear rate history. The viscosity of non-Newtonian fluids changes as the shear rate is varied. Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient than simple linearity. There are several types of non-Newtonian flow behavior, characterized by the way a fluid's viscosity changes in response to variations in shear rate.

1. Shear thickening: viscosity of the substance increases with the shear rate is increased.
2. Shear thinning: viscosity of the substance decreases with the shear rate is increased.
3. Thixotropic: It is the property of certain gels or fluids that are viscous under normal conditions, but become thin, less viscous and flow over time when shaken, agitated, or otherwise stressed. Shear thinning liquids are very commonly, but misleadingly, described as thixotropic.

4. Rheopectic: It is the rare property of some non-Newtonian fluids to show a time-dependent change in viscosity; the longer the fluid undergoes shearing force (shaken, agitated, or otherwise stressed) the higher its viscosity
5. A Bingham plastic is a material that behaves as a solid at low stresses but flows as a viscous fluid at high stresses.
6. A magnetorheological fluid is a type of "smart fluid" which, when subjected to a magnetic field, greatly increases its apparent viscosity, to the point of becoming a viscoelastic solid.

Many materials also exhibit hysteresis, where by the coefficient of viscosity at a particular shear rate depends upon whether the shear rate is being decreased or increased. The cream, concentrated milks, butter and cheese exhibit varying degree of non-Newtonian behavior

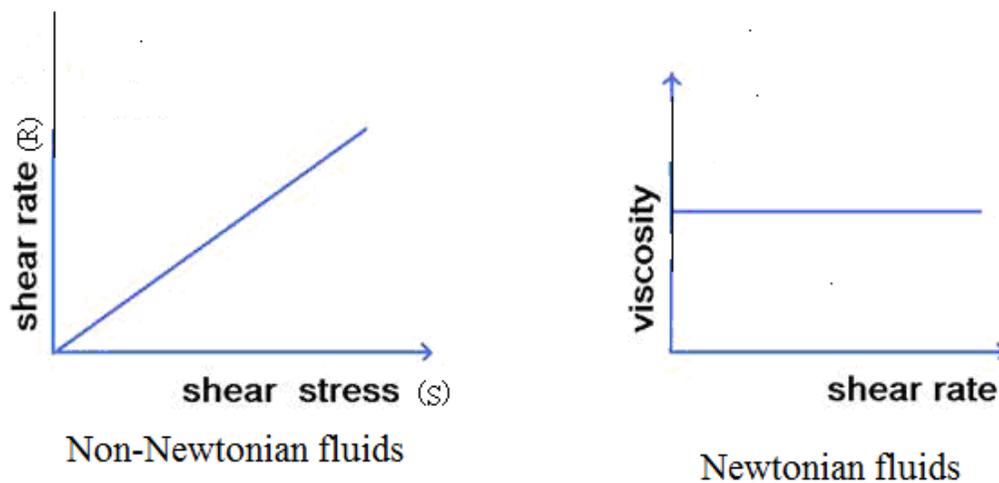


Fig.9.1 Relationship between Shear stress(S) and Shear rate(R)

Fig 9.1 shows the relationship between shear stress S and shear rate R and the fluid's viscosity at a varying shear rate R . At a given temperature the viscosity of a Newtonian fluid remains constant regardless of which viscometer model, spindle or speed is used to measure it.

9.3.3 Apparent viscosity: It is the viscosity of a fluid measured at a given shear rate at a fixed temperature. In order for a viscosity measurement to be meaningful, the shear rate must be stated or defined. This type of viscosity is ordinarily met in concentrated fluid milk products particularly in ice cream mix. It

refers to a thickened condition of the product which can be dispelled by agitation. It results from the formation of gel structure in the medium.

9.3.4 Plasticity: The property exhibited by a complex, non-newtonian fluid in which the shear force is not proportional to the shear rate. This property is ordinarily differentiated from viscosity on the basis of the force necessary to cause flow. Liquids of substantial fluidity start to flow and continue to do so by driving force of their own weight. However, certain relatively non fluid substances will only start to flow after application of initial external pressure. These substances are said to exhibit plastic flow.

9. 4. STOKE'S LAW

When small spherical bodies move through a viscous medium, the bodies drag the layers of the medium that are in contact with them. This dragging results in relative motion between different layers, which are away from the body. Therefore, a viscous drag comes into play, opposing the motion of the body. It is found that this backward force or viscous drag increases with increase in velocity of the body.

According to Stoke, the viscous drag 'f', depends on the coefficient of viscosity 'η' of the medium, the velocity (v) of the body and radius (r) of the spherical body

$$f \propto \eta v r$$

$$f = k \eta v r$$

Where k is found to be 6π



Lesson-10

Viscosity of Milk

10.1 INTRODUCTION

The viscosity of a substance refers to, its resistance of flow. It is a measure of the friction between molecules as they slide past one another. The viscosity of a heterogeneous substance such as milk at a given temperature depends upon its composition and the physical state of its colloidal dispersed substances, including milk fat. The viscosity of fluids is influenced by various factors and knowledge of which is of immense value in understanding the behavior of these fluids during processing.

10.2 FACTORS INFLUENCE INFLUENCING THE VISCOSITY OF MILK

Viscosity of milk and milk products is important in determining the flowing rate of cream, rates of mass and heat transfer, the flow conditions in dairy processes. Milk and skim milk, excepting cooled raw milk, exhibit Newtonian behavior in which the viscosity is independent of the rate of shear. The viscosity of these products depends on the temperature and pH. An increase or decrease in pH of milk also causes an increase in casein micelle voluminosity.

Important factors that influence the viscosity of milk are as follows:

1. State and concentration of protein
2. State and concentration of fat
3. Temperature of milk
4. Age of the milk

10.2.1 State and concentration of the protein: The viscosity of colloidal systems depends upon the volume occupied by the colloidal particles. Changes in the caseinate micelles produced by either raising or lowering the pH results in increased viscosity. The viscosity is approximately doubled by the addition of 10 ml of 1.4 to 3.8 N ammonia to 90 ml milk. Addition of alkali (pH up to 11.7), urea (up to 4.8M) and

calcium complexing agents to concentrated (22.7% solids) skim milk causes a marked transient increase of several folds in viscosity followed by a sharp decline. This is due to the swelling of the micelles followed by their disintegration.

10.2.2 State and concentration of fat: Viscosity increases with increasing concentration of fat and solids-not -fat, but consistent general relationship could not be established

10.2.3 Temperature: The viscosity of milk and dairy products depends up on the temperature and on the amount and state of dispersion of the solid components. Cooling temperature increase viscosity due to the increased voluminosity of casein micelle and temperatures above 65° C increase viscosity due to the denaturation of whey proteins

Cooled raw milk and cream exhibit non-Newtonian behavior in which the viscosity is dependent on the shear rate. Agitation may cause partial coalescence of the fat globules (partial churning) which increases viscosity. Fat globules that have under gone cold_agglutination may be dispersed due to agitation, causing a decrease in viscosity.

The viscosity of milk and other products at 20° C is given in the Table 10.1

Table.10.1 Viscosity of whey and Various Types of Milk

Type of Milk	Viscosity (centi poise)
Whey	1.2
Skim Milk	1.5
Whole milk	2.0

From these values it is evident that the caseinate micelles and the fat globules are the most important contributors to the viscosity. The effect of temperature on the viscosity of normal fluid milk and in comparison to the various other fluids is given in table 10.2.

Table.10.2 Viscosity of Milk, skim milk and lactose at Various Temperatures

Temperature (°C)	Viscosity (cp)			
	Whole milk	Skim milk	5% lactose	Water
5	3.254	3.96	1.76	1.519
10	2.809	2.47	1.50	1.308
15	2.463	2.10	..	1.140
20	2.127	1.79	1.15	1.005
25	1.857	1.54	1.03	0.894
30	1.640	1.33	0.91	0.894
35	--	1.17	. --	0.723
40	--	1.04	0.74	0.656

The viscosity of 5% lactose solution at a given temperature is not much greater than that of water but skim milk has an appreciable viscosity approaching to that of whole milk. The difference in the viscosity between 5% lactose and skim milk indicates the role of milk proteins on the viscosity of milk. Lactose, whey proteins and milk salts have relatively small contribution towards the viscosity of milk whereas the casein alone is contributing substantially towards this property. The tendency of milk to increase the viscosity upon heating as it will approach to a point of coagulation of proteins. This tendency of milk is the basis for producing high viscosity super heated condensed milk. Conditions and treatments that affect the stability of casein are very significant in the viscosity of milk. Acidity, salt balance, heat treatment and the action of various enzymes and bacteria are some of the factors which affect the stability of caseins.

Heating of skim milk to such a degree that most of the whey proteins are denatured causes an increase in viscosity by about 10%. Homogenization has little effect volume fraction of fat increases (because of the larger surface covered with protein volume fraction of casein and whey decreases (by providing material for the surface layers)

10.3 DETERMINATION OF VISCOSITY

The unit of viscosity is poise. It is defined as the force required to maintain a relative velocity of 1cm/sec between two parallel planes placed 1 cm apart. The unit commonly used for milk is centi poise (10^{-2} poise)

A useful quantity in fluid flow calculations is the kinematics viscosity or viscosity/density.

In dealing with the solutions and colloidal dispersion the following quantities are often used

Relative viscosity: $\eta_{rel} = \eta_{soln} / \eta_{solv}$

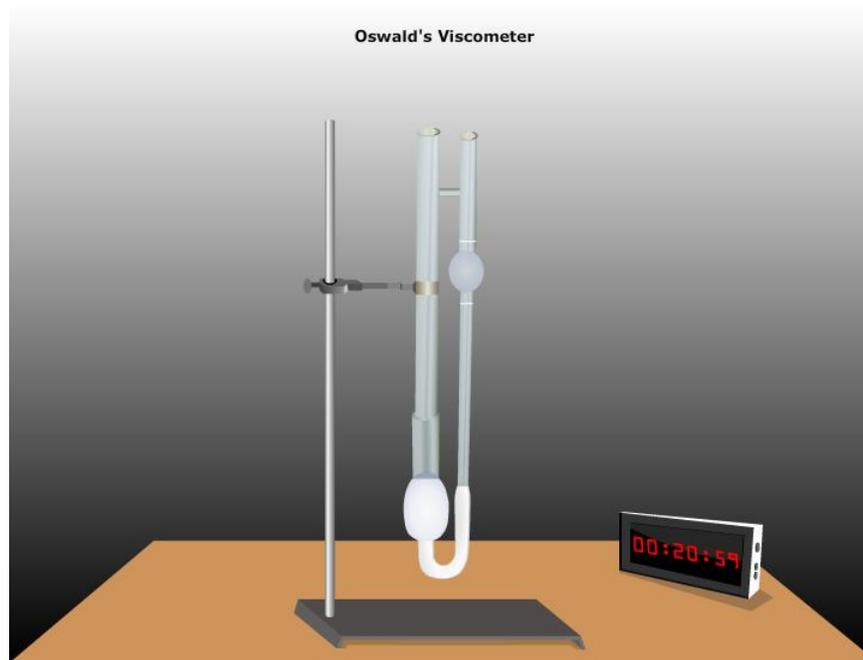
Specific viscosity: $\eta_{sp} = \eta_{rel} - 1$

Reduced viscosity : $\eta_{red} = \eta_{sp}C$ where c is the concentration of the solute

Intrinsic Viscosity: $[\eta] = \lim (\eta_{sp}/C)$ as c goes to zero

10.3.1 Types of Viscometers: Three types of viscometers that are used for determination of viscosities of dairy products are

- Coaxial cylinders: e.g. Mc Michaecouetter and Brookfield
- Falling sphere e.g. Hoeppler
- Capillary tubes e.g. Ostwalds, McKennell



Ostwald's Viscometer

Falling sphere and capillary tube viscometers are not suitable for measurements of non-Newtonian fluids because of the correction for non uniform shear rates. These methods are not only tedious but the results obtained are not accurate. A Mobil meter, which has some features of both the coaxial cylinder and falling sphere viscometers, has been used to measure viscosities of evaporated milk. A sealed micro viscometer of the falling sphere type in which the specimen can be sterilized has been proposed for studies of changes occurring in sterilization of concentrated milk products.



Lesson-11

Colligative Properties of Dilute Solutions-01

11.1 INTRODUCTION

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent. The dilute solutions show more or less ideal behavior as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as colligative properties. Historically, colligative properties have been one of the means for determining the molecular weight of unknown compounds.

11.2 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.

Colligative properties are the physical changes that result from adding solute to a solvent. Colligative Properties depend on how many solute particles are present as well as the solvent amount, but they do NOT depend on the type of solute particles. For example, the freezing point of salt water (solution) is lower than that of pure water, due to the presence of salt dissolved in it. It does not matter whether the salt dissolved in water is sodium chloride or potassium nitrate; if the molar amounts of solutes are the same and the number of ions is the same, the freezing points will be the same. For example, (AlCl_3) aluminium chloride and potassium phosphate (K_3PO_4) would exhibit essentially the same colligative properties, since each compound dissolves to produce four ions per formula unit.

The four commonly studied colligative properties are freezing point depression, boiling point elevation, lowering of vapor pressure, and 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.

Colligative properties are the properties of dilute solutions, that these properties are related to one another. Thus, if one is measured, the other can be calculated. The importance of these properties lies in the fact that they provide methods for the determination of molecular masses of dissolved solutes. The results are excellent if the following three conditions are satisfied.

- The solution should be very dilute
- The solute should be non-volatile
- The solute does not dissociate or associate in solution

11.3 COLLIGATIVE PROPERTIES

A colligative property is one that depends only on the number of particles in solution rather than the type of particle. Molecular solutes have only one particle per formula, but ionic materials come apart into their ions and have almost as many particles in the solution as there ions are available. Sometimes re-association of the ions decreases the number of particles. The effect of the ionic pair depends upon the properties of the species dissolved and the concentration of solute. The more concentrated the solute, the greater percentage of ion pairing takes place.

The colligative properties of solutions are;

- 1) The solution shows an increase in osmotic pressure between it and a reference solution as the amount of solute is increased. A semi permeable membrane is one which allows only water from the solution but not the solutes. When two solutions are separated by such a membrane osmotic pressure will develop across the membrane, consequently due to the process of osmosis the water from the solution having lesser solute will pass through the semi permeable membrane and dilutes the solution with more solutes. Semi permeable membranes are an important part of any living thing. Cell membranes are semi permeable. The membranes on the outside of eggs are semi permeable. Trees pull up water from their roots by osmosis.
- 2) Solution of a solid (non-volatile) solute in a liquid solvent shows a decrease in vapor pressure above the solution as the amount of solute is increased.

- 3) The solution shows an increase in boiling point as the amount of solute in it is increased. The boiling point of a liquid is just the point at which the vapor pressure of the liquid equals the surrounding pressure. If the vapor pressure decreases, it will take a greater temperature to boil the liquid.
- 4) The solution shows a decrease in melting point as the amount of solute is increased.
- 5) It may be observed that the dissolved materials block the water molecules from attaching onto the rest of the water in the crystal or possibly that the dissolved material holds onto the water molecules more tightly than the water in the crystals. Whatever the cause, you have seen this in action in the making of home made barrel ice cream. The barrel on the outside of the ice cream container has ice and salt (sodium chloride) in it. The ice melts (grabs up the heat) at a temperature lower than the usual melting point of ice. Just ice in the barrel would not work, because it does not get cold enough to freeze the ice cream inside that has dissolved materials in it itself.
- 6) Refractive index also called index of refraction is the measure of the bending of a ray of light when passing from one medium into another. If i is the angle of incidence of a ray in vacuum (angle between the incoming ray and the perpendicular to the surface of a medium, called the normal), and r is the angle of refraction (angle between the ray in the medium and the normal), the refractive index n is defined as the ratio of the sine of the angle of incidence to the sine of the angle of refraction; *i.e.*, $n = \sin i / \sin r$. Refractive index is also equal to the velocity c of light of a given wavelength in empty space divided by its velocity v in a substance, or $n = c/v$. Measurement of this bending gives a direct measure of refractive index, $n = \sin i / \sin r$. Where ' i ' is the angle of the ray to the surface as it approaches (incidence) and ' r ' is the exit angle (refraction). Since the refractive index varies with the sample temperature and the wave length of the light these must be critically controlled and specified. Thus n^{20_D} refers to the index at 20°C with D line of the sodium spectrum (589.0 and 589.6nm). The refractive index of water is $n^{20_D} = 1.33299$, the value of n^{20_D} for cow's milk generally falls in the range of 1.3440 to 1.3485. Buffalo milk is similar to that of cow's milk while human, goat, and ewe milk appear to have higher refractive index values. Since refractive index increments contributed by each solute in a solution are additive, much consideration has been given to the possible use of refractive index as a means of determining total solids or added water in milk. The refractive index of milk itself is somewhat difficult to determine because of the opacity but by using a refractometer such as Abbe's instrument which employs a thin layer of sample, it is possible to make satisfactory measurement particularly of skim milk products and sweetened condensed milk.

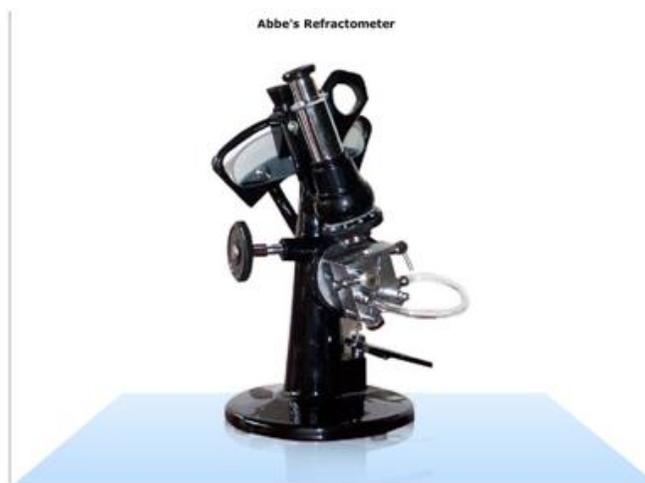


Fig.11.1 Abbe's Refractometer

The relation between solids content (on the basis of weight per unit volume) and refractive index is linear and the contributions of the several components are additive. The individual components of milk differ in specific refractive increment $\Delta n(\rho c)$ where ' ρ ' is the density of the sample and ' c ' is the weight / weight concentration specific refractive increment ' n ') of the component. Thus the relation between percent solids and refractive index will vary between lot of milk. Studies by the researches have revealed the following specific refractive increments (mn g^{-1}).

- Casein complex 0.207
- Soluble proteins 0.187 and
- lactose 0.140

The total contribution to the refractive index for milk containing 2.34% casein complex, 0.83% serum proteins, and 4.83% lactose becomes $0.00500 + 0.00159 + 0.00695$ or 0.01354 . The residue 0.95% contributes 0.00166 to the total difference between the refractive indices of water and the milk. The refractive index of milk fat is 1.4537 to 1.4578 at 40°C . Fat does not contribute to the refractive index of whole milk because refraction occurs at the interface of air and the continuous phase. Sterilization and storage does not alter the refractive index.



Lesson-12

Colligative Properties of Dilute Solutions -2

12.1 INTRODUCTION

Osmosis is one of the most important colligative properties of liquids. Osmosis is influenced by the pressure exerted by the liquid on the membrane. It is helpful in isolating some of the constituents of milk.

12.2 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.

When a solution and the pure solvent used in making that solution are placed on either side of a semi permeable membrane, it is found that more solvent molecules flow out of the pure solvent side of the membrane than solvent flows into the pure solvent from the solution side of the membrane. That flow of solvent from the pure solvent side makes the volume of the solution rise. When the height difference between the two sides becomes large enough, the net flow through the membrane ceases due to the extra pressure exerted by the excess height of the solution chamber. Converting that height of solvent into units of pressure gives a measure of the osmotic pressure exerted on the solution by the pure solvent. 'P' stands for 'pressure,' ρ is the density of the solution, and 'h' is the height of the solution.

More solvent molecules are at the membrane interface on the solvent side of the membrane than on the solution side. Therefore, it is more likely that a solvent molecule will pass from the solvent side to the solution side than vice versa. That difference in flow rate causes the solution volume to rise. As the solution rises, by the pressure depth equation, it exerts a larger pressure on the membrane's surface. As that pressure rises, it forces more solvent molecules to flow from the solution side to the solvent side. When the flow from both sides of the membrane is equal, the solution height stops rising and remains at a height reflecting the osmotic pressure of the solution.

The equation relating the osmotic pressure of a solution to its concentration has a form quite similar to the ideal gas law: $PV=inRT$

This form of the equation has been derived by realizing that n / V gives the concentration of the solute in units of molarity, $M.P = iMRT$

12.3 RAOULT'S LAW

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

12.3.1 Vapor Pressure: When a nonvolatile solute is added to a liquid to form a solution, the vapor pressure above that solution decreases. To understand why that might occur, let's analyze the vaporization process of the pure solvent then do the same for a solution. 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 vapor pressure above the pure liquid.

If we add a nonvolatile 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 vapor pressure for a solution relative to the pure solvent. That statement is only true if the solvent is nonvolatile. If the solute has its own vapor pressure, then the vapor pressure of the solution may be greater than the vapor pressure of the solvent.

Note that we need not identify the nature of the solvent or the solute (except for its lack of volatility) to derive that the vapor pressure should be lower for a solution relative to the pure solvent. That is what makes vapor pressure lowering a colligative property it only depends on the number of dissolved solute particles.

On the surface of the pure solvent (shown on the left) there are more solvent molecules at the surface than in the right-hand solution flask. Therefore, it is more likely that solvent molecules escape into the gas phase on the left than on the right. Therefore, the solution should have a lower vapor pressure than the pure solvent.

12.3.2 Raoult's law: The law that mathematically describes the vapor pressure lowering phenomenon.

Raoult's law is given in:

$$P = c_{\text{solvent}} P^{\circ}$$

P - vapor pressure of a solution

c_{solvent} - Vapour pressure of the solvent above a solution

P° - vapor pressure of the pure solvent

12.4 LOWERING OF VAPOR PRESSURE

The vapour Pressure of a given solution is lower than that of the pure solvent. This fact is being explained by using the Raoult's as explained below.

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

The reason for the deviation stems from a defect in our consideration of the vapor pressure lowering event--we assumed that the solute did not interact with the solvent at all. That, of course, is not true most of the time. If the solute is strongly held by the solvent, then the solution will show a negative deviation from Raoult's law because the solvent will find it more difficult to escape from solution. If the solute and solvent are not as tightly bound to each other as they are to themselves, then the solution will show a positive deviation from Raoult's law because the solvent molecules will find it easier to escape from solution into the gas phase.

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 behavior. 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.



Lesson-13

Colligative Properties of Dilute Solutions - 3

13.1 INTRODUCTION

The physical properties which are influenced by the concentration of the soluble components in the system are known as colligative properties. These properties play an important role in the processing of milk and preparation of milk products. Among these properties for milk, the freezing point and boiling point are important in detecting the adulteration of milk.

13.2 BOILING POINT

Boiling point of a solution is the temperature at which the vapour pressure of the liquid equals to the external (Atmospheric) pressure. 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. 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. Pure water boils at 100°C. Milk constituents are responsible for the elevation of the boiling point of milk. The normal Ionic ↔ molecular ↔ colloidal equilibrium is altered due to heating. 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°C.

13.3 FREEZING POINT

The freezing point of milk, like that of any aqueous systems depends on the concentration of water soluble components. The mathematical relationship between depression of freezing point and concentration of the solute was determined by Raoult and is expressed in the below mentioned equation.

$$T_f = K_f M$$

Where T_f is the difference between the freezing points of the solvent and the solution, K_f is the molal depression constant (1.86°C for water) and M is the molar concentration of the solute. This relationship

is valid only for dilute solution of undissociated solutes. The freezing point is a property controlled by the number of particles rather than the kind and nature of the particles in the solvent.

In the dairy field, the objective of freezing point measurement is virtually restricted to determination of the water content of the product in order to detect the illegal addition of water. Its value rests on the fact that the freezing point of authentic bovine milk varies within very narrow limits. Since the depression of freezing point is directly proportional to the number of particles in solution it is obvious that it is primarily determined by the major constituents of low molecular weight, the lactose, and the salts and is nearly independent of variation in the concentrations of colloidal micelles and fat globules. Since there is complimentary relationship between the lactose and sodium chloride in milk such that the osmotic pressure and hence the freezing point is maintained within a narrow range.

The temperature at which the solid, liquid and vapour pressure exists in equilibrium with each other a solution freezes at a lower temperature than the pure solvent and the depression of the freezing point depends on the concentration of the dissolved substances. The freezing point depression is the function of osmotic pressure as that of the solution. Since milk is having same osmotic pressure as that of the blood on physiological grounds and has fairly constant value.

Since the concentration of the total dissolved substances influences the freezing point and as milk is a physiological secretion of the mammary gland it is the most constant physical property. The mean freezing point for milk being -0.545°C . The addition of water will decrease the concentration of the dissolved substances the freezing point will raise (below -0.53°C). This property will help in detecting the adulteration of milk. The freezing point of milk can be determined by using Hortvet cryoscope. Although the Hortvet method has been accepted as the official method a number of modifications have been developed such as replacing the ether cooling system with mechanical refrigeration and adding mechanical stirring and tapping devices. Cryosopes employing thermistors in place of mercury -in -glass thermometers have been developed. Regardless of the method used, determination of the freezing point of solutions is empirical. As such it is necessary to use standardized equipment and technique. The Hortvet method involves measurement of the differences between the freezing point of a standard solution and the freezing point of milk. Any systematic error should be reflected in both the observed values and should thus be eliminated.

The average freezing point of bovine milk is usually within the range- 0.512 to - 0.550°C the average value is close to -0.522°C, buffalo milk -0.560°C, sheep milk -0.588°C and goat milk -0.575°C. Freezing point depression of milk is inversely proportional to the amount of water added. Colostrums is having a freezing point -0.605°C which is slightly less than normal milk. The composition of milk is altered by the udder diseases like mastitis, but in order to maintain the osmotic pressure in equilibrium with blood the lowering of the lactose content is compensated by increase in the sodium chloride. As such the milk obtained from the animal affected with mastitis will not alter the freezing point.

The major components affecting the freezing point are lactose and soluble salts. 75 to 80% of the depression of the freezing point is due to these two constituents. Fat, protein, colloidal calcium phosphate, casein colloids and fat globules have negligible effect on the freezing point of milk because of their high molecular weight. Souring of milk, fortification of milk with lactose or non fat solids or addition of sugar will increase the depression of the freezing point.

Environmental factors associated with the variation in freezing point have been studied by several workers. Some of the variations have been attributed to seasonal effects, feed, water intake, stage of lactation, breed of the cow, heat stress and time of the day (i.e. morning or evening milk).If the net number of osmotically active particles are changed due to the handling of milk from the time it is drawn from the udder and the freezing point depression will also be changed.

The general principle employed for the determination of the freezing point is to super cool a sample slightly to induce crystallization and then to observe the maximum temperature attained. The temperature of cooling bath must be controlled otherwise the rate of heat loss will be greater than the rate of heat transfer to the bath by the heat of fusion of the solution and the observed freezing point will be too low. Control of temperature of super cooling and seeding techniques is extremely important. If it varies the amount of solvent that crystallizes out and consequently the observed freezing point also varies. Attempts have been made to apply a correction factor to the observed freezing point in order to enable calculation of the true freezing point.



Lesson-14

Electrolytes and Non-Electrolytes, Ionic Mobility

14.1 INTRODUCTION

It is very interesting to note that the electrical current will pass through the medium when certain substances are dissolved in it but in certain situations it will not allow the current to pass through. To understand such phenomena we need to study the nature of these substances.

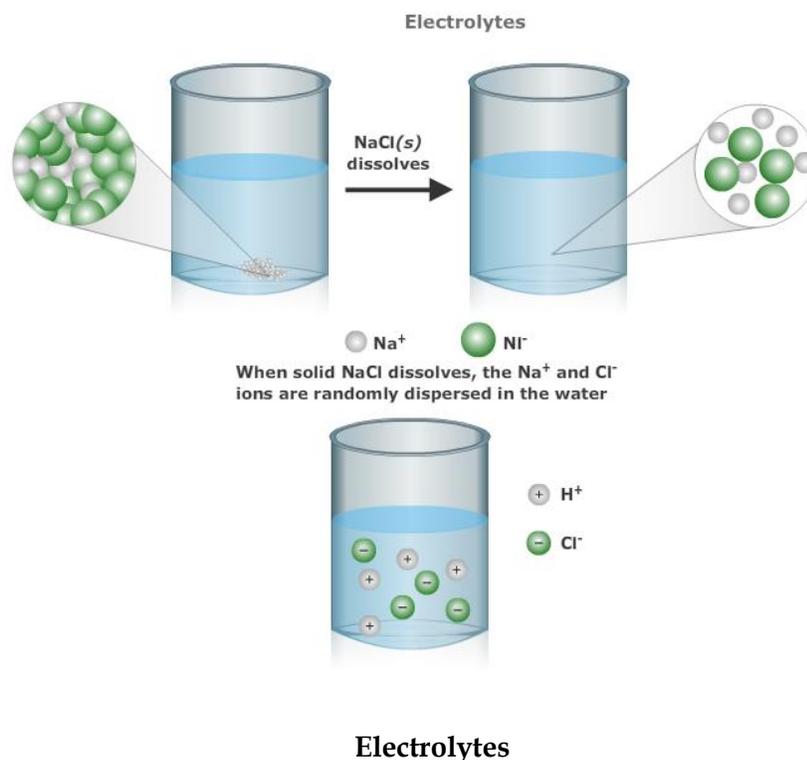
14.2 DEFINITION

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).

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.

14.3 ELECTROLYTIC DISSOCIATION

Non electrolytes behave in a definite manner with respect to osmotic pressure, freezing point and boiling point and this behavior 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.

14.4 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⁺ (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.

14.5 THE THEORY OF ELECTROLYTIC DISSOCIATION

The theory of electrolyte dissociation explains

- The abnormal behaviors of electrolytes with respect to osmotic pressure, freezing point and boiling point.
- The electrical conductivity of solutions, and
- The facts of electrolysis.

Since ions play such an important role part in chemical behavior let us examine the extent of dissociation and the equilibrium conditions more closely. 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.

14.6 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 cm²/ volt. The mobilities are very low having values of only 0.0005 – 0.003 cm²/ 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



Lesson-15

Kohlrawsch Law and Ostwald's Dilution Law and Electrical Conductance of Milk

15.1 INTRODUCTION

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 Kohlrawsch's Law explain the behaviour of these ions and help in calculating their ionic mobility.

15.2 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

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

Where:

K_p = constant of protolysis

α = degree of dissociation (or degree of protolysis)

$C(A^-)$ = concentrations of anions

$C(K^+)$ = concentration of cations

C_0 = overall concentration

$C(KA)$ = concentration of associated electrolyte

Concerning conductivity, this results in the following relation:

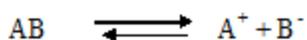
Where:

K_c constant of dissociation

- Λ_c equivalent conductivity
- Λ_0 boundary conductivity
- C concentration of 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⁺ and B⁻ ions and the equilibrium state is represented by the equation:



Initially t = 0 C 0 0

At equilibrium C C α C α

So, dissociation constant may be given as

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{(C\alpha \times C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \quad \dots\dots (i)$$

For very weak electrolytes,

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

$$\therefore K = C\alpha^2 \quad \dots\dots (ii)$$

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

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

From equation (ii) it is clear that degree of ionization increases on dilution.

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

15.3 LIMITATIONS OF OSTWALD'S DILUTION LAW

The law holds good only for weak electrolytes and fails completely in case of strong electrolytes. The value of 'α' is determined by conductivity measurements by applying the formula Λ/Λ_∞ . The value of

' α ' 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 CH_3COOH , NH_4OH , 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 Λ/Λ_∞ does not give accurate value of ' α '.
- 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.

15.4 KOHLRANSCH'S LAW

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", i.e., anions and cations.

$$\Lambda_\infty = \lambda_a + \lambda_c$$

Where λ_a is the equivalent conductance of the anion and λ_c that of the cations.

The ionic conductances are proportional to their ionic mobilities. Thus, at infinite dilution,

$$\lambda_c = k u_c \text{ and } \lambda_a = k u_a$$

Where u_c and u_a are ionic mobilities of cation and anion respectively at infinite dilution. The value of k is equal to 96500 c, i.e., one Faraday.

Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte, it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionized at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

$$\text{Degree of dissociation } \alpha = \Lambda / (\Lambda_\infty)$$

$$= (\text{Equivalent conductance at a given concentration}) / (\text{Equivalent conductance at infinite dilution})$$



Lesson-16

Ionic Equilibria Dissociation of Ionic Product of Water

16.1 INTRODUCTION

Chemical reactions mostly take place in solutions. Solution chemistry plays a very significant role in chemistry. All chemical substances are made up of either polar units (called ions) or non-polar units. The activity of these entities is more evident and pronounced in solution. The behavior of these substances depends upon their nature and conditions of the medium in which they are added. It is therefore necessary to understand the principles that govern their behavior in solution.

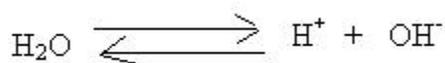
16.2 IONIC EQUILIBRIUM

This type of equilibrium is observed in substances that undergo ionization easily, or in polar substances in which ionization can be induced. Ionic and polar substances are more easily soluble in polar solvents because of the ease of ionization taking place in the solvent medium. With the dissolution of ionic and polar substances in the solvent, these solutions become rich in mobile charge carriers (ions) and thus can conduct electricity. Substances, which are capable of conducting electricity, are called as electrolytes while those substances which are non-conducting are called as non-electrolytes.

In a water molecule the electrons are shared unevenly between the oxygen & hydrogen making it a polar molecule. Because of this water molecules have a partial negative charge on Oxygen, and a partial positive charge on Hydrogen Accordingly the water molecules can form strong electrostatic attractions with other water molecules, polar molecules and ions

16.3 DISSOCIATION OF WATER

Water is frequently regarded as a substance that practically does not dissociate into ions. It is observed that it will dissociate to a small extent according to the following equation



The hydrogen ion in water always forms hydroxonium H_3O^+ . For the sake of simplicity, we consider only the hydrogen ion H^+ since this will not influence the results.

In solutions containing acids, the hydrogen ions formed will affect the equilibrium in the above equation. A similar effect could also be seen in solutions containing bases which form the hydroxyl ions (OH^-). The equilibrium is determined by the dissociation constant which is expressed in the following equations.

$$K_{d,a} = \frac{a_{\text{H}^+} \times a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}}$$

For pure solutions or for pure water the activities (a) can be replaced by concentration (c), then the above equation could be expressed as:

$$K_d = \frac{c_{\text{H}^+} \times c_{\text{OH}^-}}{c_{\text{H}_2\text{O}}}$$

In the water dissociation reaction equilibrium which greatly shifts the direction of undissociated water but it is readily established and this imparts considerable importance to the role played by the reaction of water dissociation and also in many properties of aqueous solutions. Dissociation of water being very slight is considered that either the activity of undissociated water molecule or its concentration is regarded as constant. We can now combine the dissociation constant and rearrange the above two formulae as follows

$$a_{\text{H}^+} \times a_{\text{OH}^-} = K_w$$
$$c_{\text{H}^+} \times c_{\text{OH}^-} = K_w$$

Where the constant $K_w = K_{d,a} \times a_{\text{H}_2\text{O}}$ or

$$K_w = K_{d,c} \cdot c_{\text{H}_2\text{O}}$$

This is called the ionic product of water

Table. 16.1 Ionic product k_w , concentration c_{H^+} and c_{OH^-} of ions in water and pH of water at various temperatures

Temperature (°C)	Ionic product (k_w)	$c_{H^+} = c_{OH^-}$	pH
0	1.139×10^{-15}	3.38×10^{-8}	7.472
18	5.702×10^{-15}	7.64×10^{-8}	7.117
25	1.008×10^{-14}	1.004×10^{-7}	6.998
50	5.474×10^{-14}	2.339×10^{-7}	6.631
100	5.9×10^{-13}	7.7×10^{-7}	6.12

At 25°C the ionic product of water $k_w = 1.008 \times 10^{-14}$

Since pure water as in any other neutral medium $a_{H^+} = a_{OH^-}$ (or $c_{H^+} = c_{OH^-}$) for 25° C

$a_{H^+} = a_{OH^-} = \sqrt{K_w} = 1.004 \times 10^{-7}$ g ions per litre and hence the degree of dissociation

$$\alpha = \frac{a_{H^+}}{55.5} = \frac{1.004 \cdot 10^{-7}}{55.5} = 1.8 \times 10^{-9}$$

Where 55.5 = C_{H_2O} i.e the number of moles of water per litre at 25°C

In non neutral media the a_{H^+} and a_{OH^-} are not equal to each other. As it could be observed from the above equations these two ions are intimately connected and are inversely proportional to each other. Thus upon adding acid to water we increase the concentration of hydrogen ions and therefore augment the value of a_{H^+} but this accelerates the opposite side of the reaction, some of the added H^+ ions bind an equal amount of OH^- to form H_2O and reduction in acid a_{OH^-} ions occur. Equilibrium is established again when the product of ion activities once more acquires the value it had prior to addition of the acid. Hence, any increase in hydrogen ion concentration causes a corresponding decrease in the hydroxyl ion concentration and vice versa.



Lesson-17

pH and pOH Scales

17.1 INTRODUCTION

When water molecule dissociates and attains ionic equilibrium the concentration of both $[H^+]$ and $[OH^-]$ ions will be equal. Increase of either H^+ or OH^- would result in the imbalance of the equation. As such this phenomenon is used to measure the acidic or alkaline condition of the solution. This is referred as pH scale. Due to the large range of proton concentration values $[H^+]$ in aqueous solution (typically from 10^{-15} to 10 M), a logarithmic scale of acidity makes the most sense to put the values into manageable numbers.

17.2 DEFINITIONS

The pH is a quantity characterizing the activity (or concentration) of hydrogen ions and is numerically equal to the negative common logarithm of the activity or concentration expressed in g-ions/l

The pH scale of acidity defines pH as the negative common logarithm of the concentration of H^+ : $pH = -\log [H^+]$

A common logarithm is a function that computes what exponent would be on 10 to obtain the input number. For example, the logarithm of 100 (written "log 100") is 2 because $10^2 = 100$

Although water is frequently regarded as a substance that practically does not dissociate into ions it is in fact always dissociated to a small extent according to the following equation



In solutions containing acids the hydrogen ions form will affect the equilibrium of the above reaction. Similarly in solutions containing bases the hydroxyl ions will affect the equilibrium. The equilibrium is determined by the dissociation

constant which in general is expressed in terms of their activities

$$K_{d.a} = \frac{(a_{H^+}) \times (a_{OH^-})}{a_{H_2O}} \quad \text{----- (2)}$$

For dilute solutions or for pure water, the activities can be replaced with concentrations. Consequently the above reaction could be written as follows

$$K_d = \frac{c_{H^+} \times c_{OH^-}}{c_{H_2O}} \quad \text{----- 3}$$

In the water dissociation reaction, equilibrium greatly shifts in the direction of undissociated water, but it is very readily established and this imparts considerable importance to the role played by the reaction (1) in many properties of aqueous solutions. Since the dissociation of water being very slight, the activity or concentration of undissociated water molecule is regarded as constant and combining this constant with the dissociation constant we write the following equations.

$$a_{H^+} \times a_{OH^-} = K_w$$

$$c_{H^+} \times c_{OH^-} = K_w$$

Where the constant $K_w = K_{d.a} \cdot a_{H_2O}$ (or $K_d c_{H_2O}$)

This constant is called the ionic product of water. At 25°C the ionic product of water.

$$K_w = 1.008 \times 10^{-14}$$

since in pure water as in any other neutral medium

$$a_{H^+} = a_{OH^-} \text{ or } (c_{H^+} = c_{OH^-}) \text{ for } 25^\circ\text{C}$$

$a_{H^+} = a_{OH^-} = \sqrt{K_w} = 1.004 \times 10^{-7}$ g ions per litre and hence the degree of dissociation

$$\alpha = \frac{a_{H^+}}{55.5} = \frac{1.004 \times 10^{-7}}{55.5} = 1.8 \times 10^{-9}$$

Where 55.5 = C_{H_2O} i.e the number of moles of water per liter at 25°C.

In non neutral media, the activities a_{H^+} and a_{OH^-} are not equal to each other. And they are inversely proportional to each other. Thus on adding the acid to water we increase the concentration of hydrogen ions and therefore augment the value of a_{H^+} but this will accelerate the opposite direction of reaction. Some of the added hydrogen ions bind an equivalent amount of OH^- to form H_2O and a reduction in a_{OH^-} occurs. Equilibrium is established again when the product of the ion activities once more acquires the value it had prior to the addition of the acid. Hence any increase in hydrogen ion concentration causes a corresponding decrease in hydroxyl ion concentration and vice versa.

The simple reaction between these two quantities may be used to characterize the acidity and alkalinity of media. The acid properties are due to the hydrogen ion and can be expressed quantitatively by the activity of a_{H^+} . Similarly the alkalinity of a medium can be expressed by the activity of a_{OH^-} . Owing to the single valued relation between these two only one of them can be used to characterize both acidity and alkalinity. Although both are equivalent in this respect it is customary to use the activity of the hydrogen ions as the parameter utilized by convention.

In acid solution a_{H^+} is greater than in pure water, the difference increasing as the acidity increases. In alkaline media the Value of a_{H^+} is less than for pure water again the difference increasing as the alkalinity increases. In practice instead of a_{H^+} the so called hydrogen ion exponent of pH is used which is defined as

$$pH = -\log_{10} a_{H^+}$$

For a dilute solutions $pH = -\log_{10} C_{H^+}$

Hence pH is a quantity characterizing the activity (or concentration) of hydrogen ion and is numerically equal to the negative common logarithm of the activity of concentration expressed as g⁻ ions per litre.

At 25°C the pH of a neutral medium is 7, acidic solution has a pH value less than 7 because $[H^+]$ is greater than that of pure water. This is known as neutral pH. This value is not randomly selected, but rather it comes from the fact that the $[H^+]$ in pure water is 10^{-7} (recall that $K_w = 10^{-14}$). A basic solution has a pH greater than 7 because there is a lower $[H^+]$ than that of pure water (and consequently a larger OH).

Chemists use a pOH scale analogous to the pH acidity scale to gauge hydroxide ion concentrations of aqueous solutions. pOH is defined as the negative common logarithm of the concentration of OH^- : $pOH = -\log [OH^-]$. In the pOH scale, 7 is neutral, less than 7 is basic, (acidic) and greater than 7 is (basic) acidic. A useful relationship (which you should be able to derive using the definition of K_w) is that $pH + pOH = 14$. This formula will allow you to readily convert values of pH and pOH. A comparison of the pH and pOH scales is provided in Fig 17.1. Note that because K_w is constant, the product of $[H^+]$ and $[OH^-]$ is always equal to 10^{-14} .

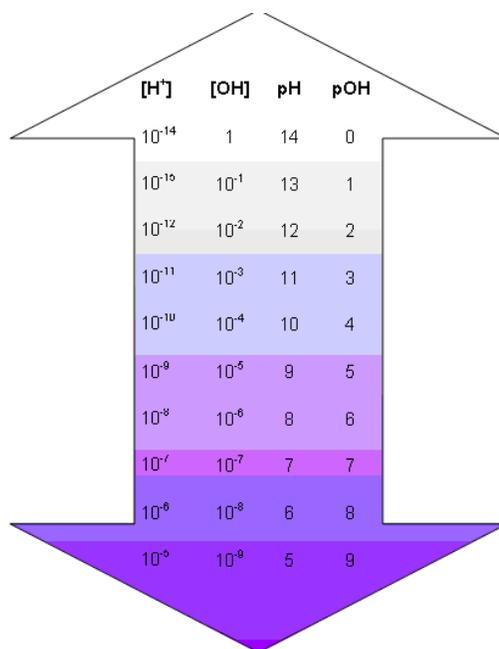


Fig. 17.1 comparison of the pH and pOH scales of acidity

(Source: Text book of Dairy Chemistry, Mathur.et.al., 2005.)

The prefix "p" in front of a symbol means "take the negative log". We have defined pH and pOH as values to describe the acidic or basic strength of solutions. Now we can talk about pK_a ($-\log K_a$) and pK_b ($-\log K_b$) as measures of acidity and basicity, respectively, for standard acids and bases. An acid with a pK_a less than zero is called a strong acid because it almost completely dissociates in water, giving an aqueous

solution a relatively low pH. Acids with pK_a 's greater than zero are called weak acids because they only partially dissociate in water, to make solutions with larger pH's than those strong acids produce at the same concentration. Similarly, bases with pK_b 's less than zero are strong bases and bases with pK_b 's greater than zero are called weak bases.



Lesson-18

Lewis Concepts of Acids

18.1 INTRODUCTION

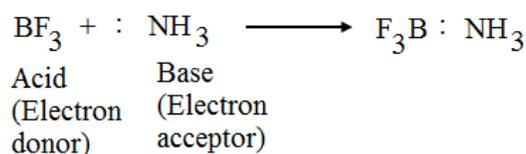
Various scientists have attempted to explain the concept of acids and bases. Lewis tried to give his conceptual definition to these acids and bases basing upon their electronic configuration. Similarly Arrhenius and Bronsted and Lewis have also explained the concept of acids and bases taking in to consideration several other parameters of the reactions between an acid and a base. The concepts proposed by Arrhenius and Bronsted and Lowry are limited to such substance which contain protons where as the Lewis proposed more general and broader concept for acids and bases.

18.2 LEWIS CONCEPT

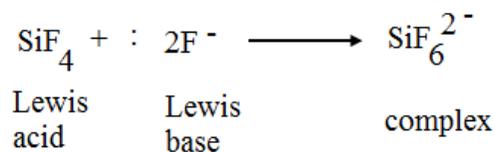
According to this concept an acid is any species which is capable of accepting a pair of electrons and a base is a species having lone pair of electrons for donation. Thus all the Bronsted - Lowry Acids and bases are also Lewis acids and Lewis bases but all the Lewis acids and bases are not Bronsted - Lowry Acids and bases respectively. Lewis acids also include some other compounds like BF_3 , AlCl_3 , ZnCl_2 , FeCl_3 , SO_3 etc. According to Lewis an acid may also be a species without any proton.

18.2.1 Types of Lewi's Acids: Lewis acids have been grouped based on certain criteria. The criteria for such grouping are discussed here under.

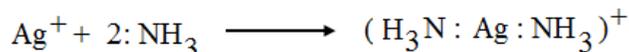
- Compounds whose central atom has an incomplete octet. In other words Lewi's acids of this type are the electro deficient molecules such as BF_3 , AlCl_3 , GaCl_3 etc.



- Compounds in which the central atom has available d-orbital and may acquire more than that of an octet of valence electrons.



- Some other examples of this type are PF₃, PF₅, SF₄, Se F₄, Te Cl₄ etc.
- All simple cations e.g; Na⁺, Ag⁺, Cu²⁺, Al³⁺, Fe³⁺ They can combine with an electron pair.



Molecules with a multiple bond between atoms of dissimilar electro negative charge.

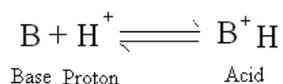


18.2.2 Lewis Bases: Bases are also being grouped similar to acids on the basis of certain criteria. The criteria and the groups of bases are discussed here under. These are the following types

- All the simple negative ions such as Cl⁻, F⁻ etc.
- Molecules with one or two unshared pair of electrons ex: H₂O, NH₃, R OH, R₂O, R₂S Pyridine etc.
- Multiple bonded compounds which form coordination compounds with transition metals Eg. CO, NO, Ethylene, Acetylene.

18.3 BRONSTED - LOWRY CONCEPT

Bronsted - Lowry defined an acid, as a substance which gives up proton (proton donor) and a base as a substance which accepts proton (Proton acceptor). In the following cases the species B accepts a proton and thus behaves as a base while the species BH⁺ gives up a proton and thus acts as an acid



Such related pairs of an acid and a base is said to conjugate to one another i.e in the above example B is the conjugate base of the acid B⁺H and B⁺H is the conjugate acid of the base B. On the whole we can say that every base has its conjugate acid and every acid has a conjugate base. Hence, strong acid has a weak conjugate base and a weak acid has a strong conjugate base some examples of conjugate acids and bases is given in Table 18.1

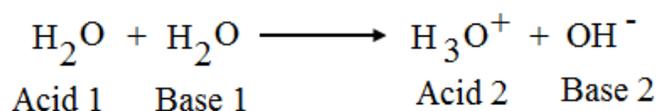
Table: 18.1 Conjugate Acids and Bases

Acid	Base		Conjugate acid	Conjugate base
H ₂ SO ₄	+ H ₂ O	→	H ₃ O ⁺	HSO ₄ ⁻
H ₂ O	+ NH ₃	→	NH ₄ ⁺	OH ⁻
HCl	+ OH ⁻	→	H ₂ O	Cl ⁻
H ₃ O ⁺	+ OH ⁻	→	H ₂ O	H ₂ O
NH ₄ ⁺	+ H ₂ O	→	H ₃ O ⁺	NH ₃

Thus according to Bronsted -Lowry concept neutralization is a process in which a proton is transferred from an acid to a base.

A substance acts as an acid only when another substance capable of accepting a proton (i.e Base) is present. For eg. HCl or CH₃COOH solution in benzene is not acidic because benzene is not in a position to take up protons. On the other hand HCl or CH₃COOH solutions in water are definitely acidic because HCl or CH₃COOH can ionize in water.

Water the most common solvent can act both as an acid as well as a base because it can give up a proton as well as can receive a proton Such compounds as water can function both as an acid and base is are known as amphoteric or amphiprotic. Its dual behaviour may be represented by the following equation



Lesson-19

Dissociation Constants of Acids and Bases

19.1 INTRODUCTION

The dissociation constant quantifies the tendency of a compound or an ion to dissociate. Dissociation is the process by which the compound or ion is split into two components that are also ions and or compounds. In chemical language the acids and bases are the frequent terms used as such it is necessary to know their definition and their behavior under various conditions especially when they are dissociated.

19.2 DISSOCIATION CONSTANT

A general example is the dissociation of the compound AB into A+B which can be written as

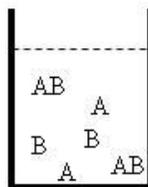


Fig. 19.1 Dissociation of Compounds

Observing the above figure it could be noticed that when a solution is prepared by adding AB, it is possible to calculate from the dissociation how much of the material added is in the form of AB, A and B which are constant. . However, before calculation it is important to know that dissociation of AB into A and B is a reversible process. A and B can assemble back to AB. The dissociation constant can be written as

$$K_a = \frac{[A] \times [B]}{[AB]}$$

If the dissociation constant of this process is e.g 10^{-7} , 1 mol of AB dissolved in to a solution of water will result in a concentration of both A and B of approximately 0.000316 moles and a concentration of AB of 0.999684. This gives us an idea that AB is not very soluble. This equation does not give much information unless we take into consideration the concentration. We have to set a second degree equation to understand this aspect of the equation. The process is as follows

$$10^{-7} = \{ [A] \times [B] \} / [AB]$$

When AB dissolves x concentration is lost from AB and x concentration of A and B. So the equation is rewritten to

$$10^{-7} = (x \times x) / 1 - x \text{ this could be rewritten as}$$

$$10^{-7} \times (1 - x) = (x \cdot x)$$

$$10^{-7} - 10^{-7} \cdot x = x^2$$

$$10^{-7} = x^2 + 10^{-7} \cdot x$$

$$0 = x^2 + 10^{-7} \cdot x - 10^{-7}$$

The result obtained after calculating using this second order reaction is approximately 0.000362 which is x or [a] and [b]. The concentration of AB is 1-x or 1- 0.000362. More complicated cases are calculated using the same method and in most cases the problem is more complicated. The above equation is actually a simplification of a general equation. The general equation is written as follows.



In this case the dissociation constant is written as: $K_a = ([A]^x \cdot [B]^y) / [A_x B_y]$

19.3 DEFINITIONS FOR ACIDS AND BASES

Arrhenius has proposed that acids are the substances that produce protons H^+ in aqueous solutions while bases are the substances which produce OH^- . But the behaviour of some acids and bases in aqueous solutions was different. The definition given by Bronsted and Lowry for acids was that the compounds

which are capable of donating protons. Similarly bases are the substance which accepts protons. This definition being independent of the solvent explains the behavior of most acids and bases

19.4 DISSOCIATION CONSTANTS FOR AN ACID

The dissociation constant of an acid is used to study the dissociation of weak or strong acids. Dissociation constants are often denoted as K_a -values.

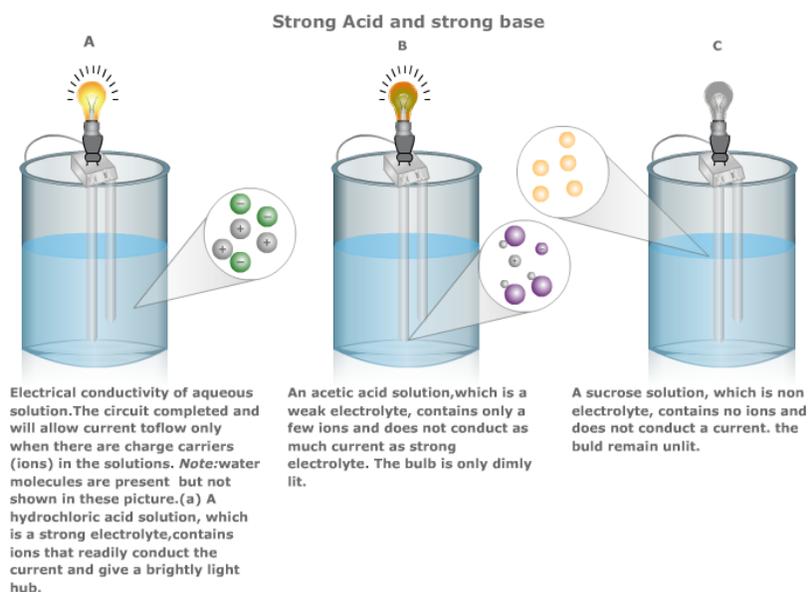
A simple example on how to use K_a -values is given here:

Consider ammonium (NH_4^+) dissociating reversibly into ammonia (NH_3)



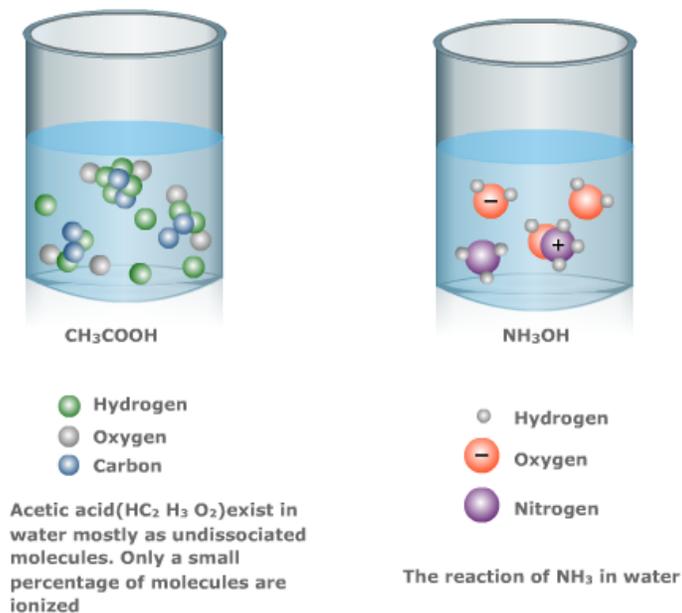
19.5 REACTIONS OF ACIDS AND BASES WITH WATER

In the equations showing the reaction of acids and bases, we show the arrows in both the directions indicating that they are in equilibrium process. The proportion of the reagents and products at equilibrium are described by equilibrium constant.



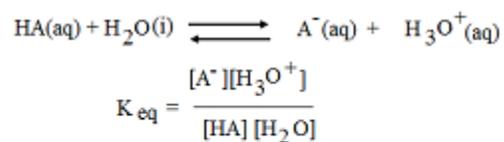
Reaction of Strong acids and Strong bases

Weak acid and weak base

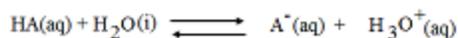


(Animation of Reaction of Weak acids and Weak bases)

For the reaction of an acid HA with water is shown as



We can observe in the above equation that water is the reactant and belongs in the equilibrium constant. Its value is 55.5M in aqueous solution. This is very large when compared with the change in water concentration at equilibrium. So it is assumed that the value of [H₂O] with this assumption we will define the dissociation constant K_a as follows



$$K_{\text{eq}} [\text{H}_2\text{O}] = K_{\text{a}} = \frac{[\text{A}^{\ominus}][\text{H}_3\text{O}^{\oplus}]}{[\text{HA}]}$$

From this equation we can see that the acids which dissociate to a greater extent will have larger value of K_{a} are stronger acids while those which have a smaller values of K_{a} are weaker acids. The dissociation constants for acids (K_{a}) range from 10^{-12} to 10^{13} this shows that the weakest acid is having the lowest equilibrium constant while the strongest acid will have the highest value of equilibrium constant. Further by deriving the equilibrium constant for any acid we will be in a position to know whether a given acid is a strong or a weak acid.

Similarly equilibrium constant for bases K_{b} with the following equation



$$K_{\text{eq}} [\text{H}_2\text{O}] = K_{\text{b}} = \frac{[\text{BH}^{\oplus}][\text{OH}^{\ominus}]}{[\text{B}]}$$

Higher equilibrium constant of a base indicates that it is a strong base while the smaller value a weak base. These values range from 10^{-11} to 10^3 .



Lesson-20

Acidity of Milk

20.1 INTRODUCTION

The acidity of a solution results from the ionization of groups that split off or bind protons. Milk being a biological fluid secreted from mammary cells (gland) has to maintain isotonicity with the blood plasma. Further the proteins in milk exist in its native colloidal state only when the pH of milk is maintained constantly within the given range. Any change in the pH would destabilize the proteins and result in precipitation and gelation. The determination of acidity of milk is a rapid measure to understand the stability of milk during heat processing.

20.2 ACIDITY OF MILK

The hydrogen ion concentration of milk is about $10^{-6.6}$ per litre which means that pH value for milk is 6.6. Freshly drawn milk is amphoteric to litmus paper that is to say that it will turn the red litmus to blue and blue litmus to red. The pH of normal healthy cow milk will range between 6.4 to 6.6 while the pH of buffalo milk is in the range of 6.7 – 6.8. If the animal is suffering from udder disease like mastitis the pH would be higher than the normal milk.

Due to the variation in the composition which is the result of the mammary gland activity a difference in the pH and buffering capacity of individual lots of fresh milk was observed. In general the pH is lower in colostrum (pH 6.0) and higher in cases of mastitis (Up to pH 7.5) than normal milk of mid lactation. Colostrums and mastitis milk differs radically from normal milk in the proportion of proteins, and certain salts. (A radical difference in the colostrum and mastitis milk from normal milk could be observed in which the proportion of proteins and certain salts were observed to be different). Milks of low phosphorus, casein, and Ca^{2+} tend to be low in titratable acidity while excessive acidity is related to hyperketonemia, inadequate calcium and excessive concentrates in the ration.

Table.20.1 Titratable Acidity and pH of Milk

Breed	Titratable Acidity (% lactic acid)		Mean PH
	Range	Mean	
Ayrshire	0.08-0.24	0.160	--
Holstein	0.10-0.28	0.161	6.71
Guernsey	0.12-0.30	0.172	6.65
Jersey	0.10-0.24	0.179	6.66
Pooled	0.12-0.21	0.134	6.66

(Source: Fundamental of Dairy Chemistry Wong.et.al.,1988)

Perusal of the Table 20.1 reveal that there appears to be a reduction in the mean titratable acidity over a period of study. The drop in the maximum values is consistent with an improvement in the microbiological quality of milk supply.

20.3 TYPES OF ACIDITY

There are two types of acidity observed in milk

- a. Natural acidity or apparent acidity
- b. Developed acidity or true acidity

20.3.1 Natural acidity: Milk freshly drawn from the udder of a cow shows acidity due to its normal constituents. Such acidity is known as Natural acidity or apparent acidity. The constituents that contribute to this acidity are Casein, acid phosphates and citrates and to some extent the albumins and globulins, carbon dioxide. Colostrum is having high natural acidity due to its protein content. In early lactation also this value is higher which slowly returns to normal level during the second month of lactation. This level is maintained upto the last month of lactation. At that stage of lactation a slight decline in the acidity is observed. This is the normal phenomenon during the lactation of an animal. The variation in the natural acidity of fresh milk is also observed between the species, breed, individual animal, physiological condition of the udder etc. An increase in the solids non fat content of milk would also increase the natural acidity.

20.3.2 Developed acidity: During the microbial multiplication in milk the lactose would be converted into lactic acid which would result in increase in the acidity of milk and decrease in the pH value. This acidity is known as developed acidity. The sum of natural acidity and developed acidity is known as titratable acidity. The normal acidity of individual cow Milk ranges from 0.10 to 0.26% lactic acid. Milk having titratable acidity more than 0.18% Lactic acid is not suitable to prepare heat treated products as the milk will coagulate at or above that acidity. Heated milk will show an increase in acidity due to the changes in the casein complex and formation of acids by the degradation of lactose. Dilution of milk will decrease the acidity and increases the pH. The acidity of milk cannot be increased through feeding.

20.4 METHODS OF DETERMINATION OF ACIDITY OF MILK

As a routine method the total titratable acidity is determined by using the titration method where the milk sample is titrated against standard alkali to the phenolphthalein end point. This corresponds to the pH 8.3 or 8.4. and at this end point the color of the phenolphthalein would change from colourless in the acidic medium to pink in the alkaline medium. The milk is being titrated using the standard sodium hydroxide and the acidity is determined by calculating the acidity using the volume of the standard sodium hydroxide used for the titrating to the phenolphthalein end point. The total titratable acidity of milk is expressed as percent lactic acid. The pH of the milk does not truly represent the titratable acidity because of the non availability of the ionic groups to titration in the normal milk. It is also a matter of interest that the titratable acidity of a milk sample will vary depending upon the buffering capacity of the milk. The natural constituents protect the milk from developing acidity. Mastitis, even in mild or sub-clinical form, causes the acidity of the milk to be lower. In rare cases mastitis causes a high acidity in the milk

20.5 IMPORTANCE OF ACIDITY OF MILK

Titratable acidity of milk could be used in several stages during milk processing, however we have to use it with considerable discretion.

- It is mostly used as a method to grade raw milk at the plant while the milk is received at the milk reception dock (RMRD). While using this we have to take into consideration the variation in the natural acidity of the milk and the buffering capacity of milk. The conditions of storage of milk would also influence the initial acidity which means that if the milk is held under room conditions for long time and there is higher microbial count in the milk the initial increase in the

acidity cannot be detected. It is necessary that higher SPC count should also be associated with high acidity

- Titratable acidity could also be of use in monitoring the udder health of an animal. A change in the titratable acidity indicates the change in the udder health
- It could also be used as a measure to study the heat stability of milk during processing. Acidity of more than 0.18% lactic acid would result in the curdling during heat processing



Lesson-21

Salts and Their Hydrolysis

21.1 INTRODUCTION

Salts are ionic compounds containing cations and anions except hydrogen and hydroxide ions. All ions in aqueous solution are hydrated i.e., they are surrounded by water molecules in aqueous solution some ions undergo only hydration while other ions react with the water molecules and result in the formation of acidic and alkaline solutions. Salt is formed when an acid comes in contact with a base and when dissolved in water it gets dissociated and forms ions. This process is known as hydrolysis.

21.2 DEFINITION OF SALT

Salts are defined as ionic compounds that result from the neutralization reaction of an acid and a base. They are composed of positively charged cations and negatively charged anions in such a proportion that the product formed is electrically neutral i.e without a net charge.

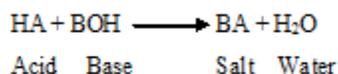
There are several varieties of salts. Salts that hydrolyze to produce hydroxide ions when dissolved in water are *basic salts* and salts that hydrolyze to produce hydronium ions in water are *acid salts*. *Neutral salts* are those that are neither acid nor basic salts.

21.3 HYDROLYSIS OF SALTS

Dissolving salts in water would result in the interaction of its ions viz. cations and anions with water. This is called hydrolysis. This interaction would affect the pH of the solution. The cations (e.g., Na^+ , K^+ , Ca^{2+} , Ba^{2+} , etc.) of strong bases and anions (e.g., Cl^- , SO_4^{2-} , Br^- , NO_3^- , ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse. Therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7 for e.g., Na_2SO_4 , KCl , KNO_3 etc. Salts formed by reactions of strong acid and weak -base will give acidic aqueous solutions and for e.g., NH_4Cl , CuSO_4 , $\text{Al}(\text{NO}_3)_3$ etc. This is due to the interaction of the ions produced from the salt with the ions formed from water. Hydrolysis is quite opposite of neutralization process.

21.4 NEUTRALIZATION

Reaction between acid and base would result in salt formation. This reaction is known as neutralization. In this reaction water is also formed along with salt This reaction could be represented as follows:



Depending on the solubility of the salt, it may remain in ionized form in the solution or it may precipitate out of solution. Neutralization reactions usually proceed to completion.

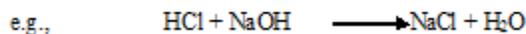
21.5 TYPES OF COMBINATIONS FOR THE SALT FORMATION

The interaction between acid and base could be grouped in to four categories basing on their type These categoriесе are

- a. Strong acid and strong base
- b. Strong acid and weak base
- c. Strong base and weak acid
- d. Weak base and weak acid

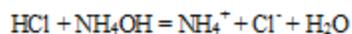
21.5.1 Strong acid with a strong base: Interaction between a strong acid and a strong base would result in the formation of salt. When strong acid like hydrochloric acid (HCl) reacts with an equally strong base like sodium hydroxide(NaOH) sodium chloride (NaCl) would be formed .

This reaction is represented in the following equation:

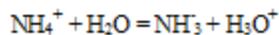


The acid and base neutralize each other with the resulting solution will be neutral (pH=7) and there is no interaction between the ions and water.

21.5.2. Strong acid with a weak base: The interaction between a strong acid and a weak base would also result in the formation of salt. The following equation expresses this reaction. :

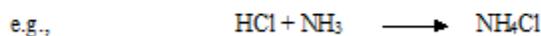


In the solution, the NH_4^+ ion reacts with water as shown below

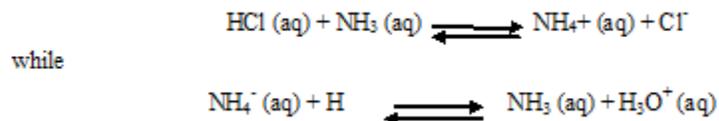


Ammonia ions formed in this reaction would result in the lowering of pH since they react with water. As such the resulting salt which is in the form of a solution is acidic.

Similarly when hydrochloric acid (HCl) reacts with a weak base like ammonia would form ammonium chloride which is a salt, but in this reaction water molecule is not formed. The solvent water interacts with the ammonia which is the cation of the salt to reform the weak base :



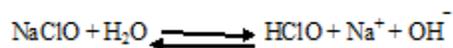
The reaction between a strong acid and a weak base also produces a salt, but water is not usually formed because weak bases tend not to be hydroxides. In this case, the water solvent will react with the cation of the salt to reform the weak base. The equation below represents this reaction. :



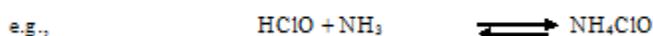
21.5.3. Weak acid with a strong base : Interaction between a weak acid like bleaching powder with a strong base like sodium hydroxide would result in the formation of sodium hypochloride which is a salt. The basicity of this salt is due to the hydrolysis of the conjugate base of the (weak) acid used in this reaction. Similarly sodium acetate formed by the interaction between acetic acid which is a weak acid and sodium hydroxide (NaOH) a strong base will be formed which is a basic salt. When salt is dissolved, ionization takes place: The bleaching powder being a weak acid when it reacts with sodium hydroxide



When a weak acid reacts with a strong base the resulting solution will be basic. The salt will be hydrolyzed to form the acid, together with the formation of the hydroxide ion from the hydrolyzed water molecules.



21.5.4: By the reaction of a weak acid with weak base: The reaction between the bleaching powder with a weak base like ammonia would form ammonium hypochloride



pH of the solution formed from the reaction of a weak acid with a weak base depends on the relative strengths of the reactants. For example, if the acid HClO has a K_a of 3.4×10^{-8} and the base NH_3 has a $K_b = 1.6 \times 10^{-5}$, then the aqueous solution of HClO and NH_3 will be basic because the K_a of HClO is less than the K_a of NH_3 .

When a salt is formed between a weak acid and a weak base it could be neutral, acidic, or basic depending on the relative strengths of the acid and base.

If $K_a(\text{cation}) > K_b(\text{anion})$, the solution of the salt is acidic.

If $K_a(\text{cation}) = K_b(\text{anion})$, the solution of the salt is neutral.

If $K_a(\text{cation}) < K_b(\text{anion})$, the solution of the salt is base



Lesson-22

Buffers, Types of Buffer Solutions, Solutions of Single Substance, Solutions of Mixtures, Importance.

22.1 INTRODUCTION

There is often a need of having a solution whose pH does not change appreciably with a change in conditions. A study of such solutions is essential to understand their behaviour. This will help in utilizing such buffer solutions to resist change in pH for maintaining product stability.

22.2 DEFINITION

Solutions with stable hydrogen ion concentration and therefore usually with no change in pH which is almost independent of dilution and changing very little with small additions of a strong acid or alkali are called buffers. In simple terms it can also be defined as a solution which resists any change of pH when a small amount of a strong acid or a strong base is added to it, is called a buffer solution or simply as a buffer. Thus, buffers have acidity and reserve alkalinity

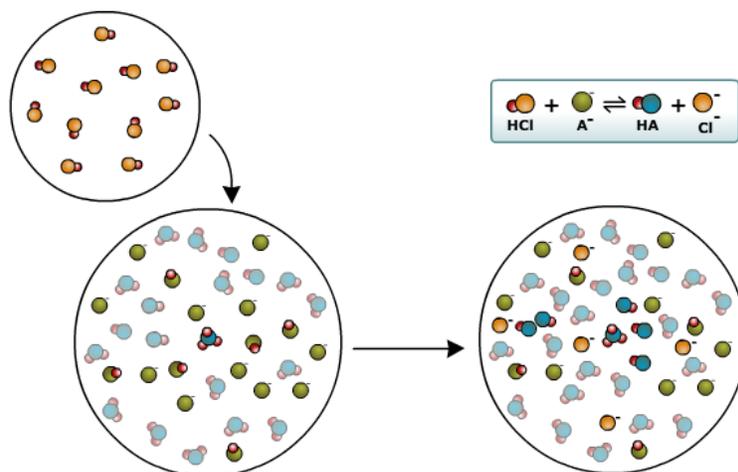
Certain solutions, such as that of ammonium acetate, have a tendency to resist any change in its hydronium ion concentration or pH, whenever a small amount of a strong acid or a strong base is added to it. This property of a solution is known as buffer action.

Buffer solutions usually consist of a mixture of a weak acid and its salt with a strong base e.g., CH_3COOH and CH_3COONa , or that of a weak base and its salt with a strong acid e.g., NH_4OH and NH_4Cl . The solution of any salt of a weak acid and a weak base e.g., ammonium acetate, also shows buffering property.

22.3 TYPES OF BUFFERS

There are two types of buffers, acid buffer and basic buffer.

Addition of a strong acid to the buffer solution



Acid Buffer

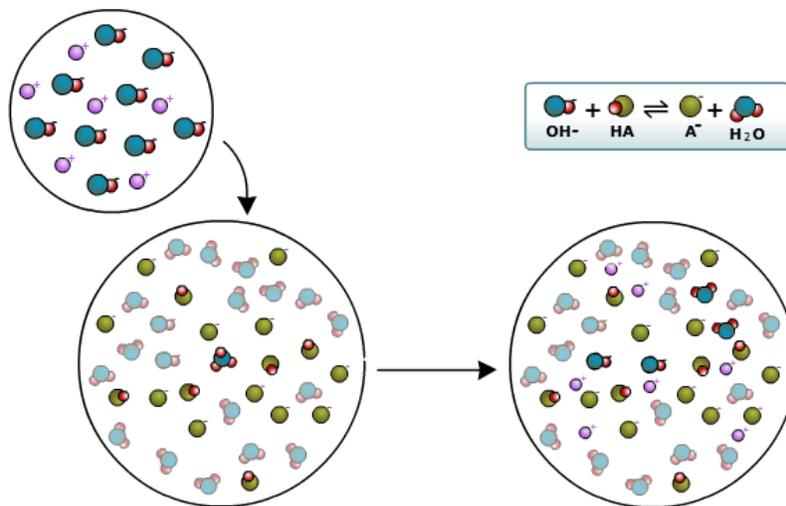
22.3.1: Acid buffer: A buffer solution containing large amounts of a weak acid, and its salt with a strong base, is termed as an acid buffer. Such buffer solutions have pH on the acidic side i.e., pH is less than 7 at 298 K. The pH of an acid buffer is given by the equation. CH₃COOH and CH₃COONa

$$\text{pH} = \text{pK}_a + \ln \frac{[\text{salt}]}{[\text{acid}]}$$

Where K_a is the acid dissociation constant of the weak acid

22.3.2: Basic Buffer: A buffer solution containing relatively large amounts of a weak base and its salt with a strong acid is termed as a basic buffer. Such buffers have pH on the alkaline side i.e., pH is higher than 7 at 298 K. e.g.: NH₄OH and NH₄Cl

Addition of a strong base to the buffer solution



Base Buffer

The pH of a basic buffer is given by the equation

$$\text{pOH} = \text{pK}_b + \ln \frac{[\text{salt}]}{[\text{acid}]}$$

Where K_b is the base dissociation constant of the weak base.

These equations are called **Henderson Hasselbalch equations**

22.4 BUFFER-CAPACITY AND BUFFER-RANGE

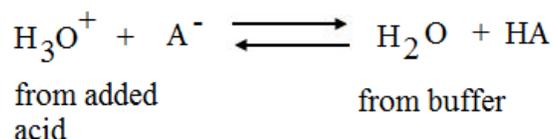
The effectiveness of any buffer is described in terms of its buffer capacity. It is defined as, 'the number of equivalents of a strong acid (or a strong base) required to change the pH of one litre of a buffer solution by one unit, keeping the total amount of the acid and the salt in the buffer constant.

The buffer capacity of a buffer is maximum when acid to salt or base to salt ratio is equal to 1 i.e., it contains equal number of moles of acid (or base) and the salt. All buffer solutions remain effective over a small pH range: this pH-range is characteristic of the buffer and is termed as the buffer-range.

22.5 MECHANISMS

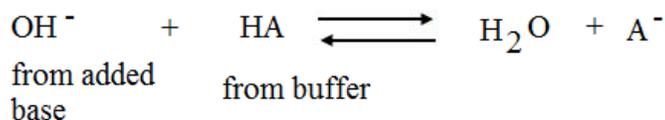
22.5.1 Action of an acid buffer: An acid buffer contains relatively large amounts of a weak acid (HA) and its salt with a strong base (say NaA). The buffer solution thus contains large concentration of HA and A⁻ (due to the dissociation of the salt), apart from H₃O⁺ and OH⁻.

An addition of small amount of a strong acid causes the reaction, to proceed in such a direction that an equivalent amount of A⁻ combines with H₃O⁺ to give the same amount of undissociated weak acid, HA. Thus, the added acid is picked up by the anions (from the salt) present in large concentrations in the buffer. As long as the added strong acid is in smaller amounts, the changes in the concentrations of salt and that of the weak acid, (HA) are small. Therefore, the acid to salt ratio does not change appreciably by the addition of strong acid to the buffer solution. As a result, no noticeable change is seen in the pH value of the buffer.



Similarly addition of a strong base to an acid buffer on the other hand causes the reaction

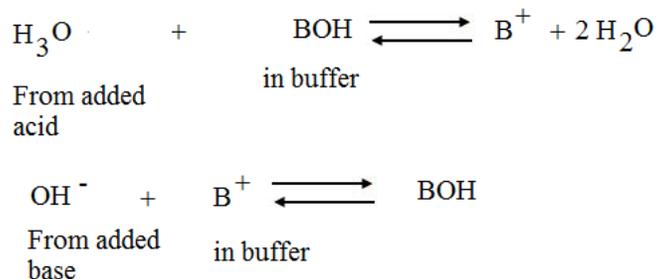
to proceed in the forward direction, resulting in the formation of an equivalent amount of the salt at the cost of the buffer acid. As long as the added base is in small amounts, the ratio of weak acid to salt remains virtually unchanged. As a result, no observable change in the pH value is seen.



22.5.2 Action of basic buffer

A basic buffer contains a weak base (BOH), and its salt with strong acid (BX). The buffer solution thus contains large amounts of the weak base BOH, and the cation B⁺ (coming from the dissociation of the salt BX), in addition to H₃O⁺ and OH⁻.

The addition of an acid or a base to the basic buffer causes the following reactions:



The reactions proceed in the forward direction. It is clear that the addition of an acid or a base to any buffer solution does cause a change in the concentrations of the buffer acid (or base) and the salt. But, because of the relatively much larger concentrations of these in the buffer solution, for all practical purposes, the ratio, [Salt] / [Acid] or [Salt] / [Base] remains constant. Hence, the pH does not change.

22.6 IMPORTANCE OF BUFFERS

Many chemical reactions are affected by the acidity of the solution in which they occur. In order for a particular reaction to occur or to occur at an appropriate rate, the pH of the reaction medium must be controlled. Such control is provided by buffer solutions, which are solutions that maintain a particular pH. Biochemical reactions are especially sensitive to pH. Most biological molecules contain groups of atoms that may be charged or neutral depending on pH, and whether these groups are charged or neutral has a significant effect on the biological activity of the molecule.

In all multi cellular organisms, the fluid within the cell and the fluids surrounding the cells have a characteristic and nearly constant pH. This pH is maintained in a number of ways, and one of the most important is through buffer systems.



Lesson-23

Derivation of Henderson and Hasselbalch Equation

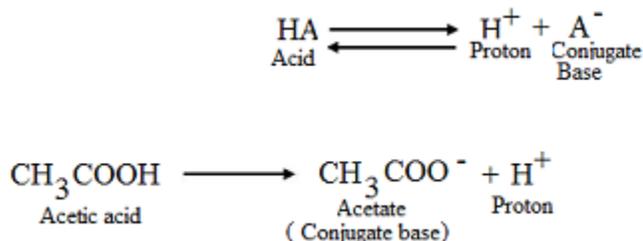
23.1 INTRODUCTION

Henderson-Hasselbalch equation describes the derivation of pH as a measure of acidity using the acid dissociation constant (pK_a) in biological and chemical systems. The equation is also useful for estimating the pH of a buffer solution and to ascertain the equilibrium pH in acid-base reactions which will be of use to calculate the isoelectric point pI of proteins.

23.2 DERIVATION OF HENDERSON-HASSELBALCH EQUATION

As per the theory of Bronsted-Lowry an acid (HA) is capable of donating a proton (H^+) and a base (B) is capable of accepting a proton. After the acid (HA) has lost its proton, it is said to exist as conjugate base (A^-). Similarly, a protonated base is said to exist as conjugate acid (BH^+).

The dissociation of an acid can be described by an equilibrium expression:



Consider the case of acetic acid (CH_3COOH) and acetate anion (CH_3COO^-):

Acetate is the conjugate base of acetic acid. Acetic acid and acetate is a conjugate acid/base pair. We can describe this relationship with equilibrium constant:

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

In this simulation, we will use K_A for the acid dissociation constant. Taking the negative log of both sides of the equation gives:

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

This can be rearranged:

$$-\ln K_A = -\ln[H^+] + \left(-\ln \frac{[A^-]}{HA} \right)$$

By definition, $pK_a = -\ln K_a$ and $pH = -\ln[H^+]$,

so for acid solutions the equation is

$$pK_a = pH - \ln \frac{[A^-]}{HA}$$

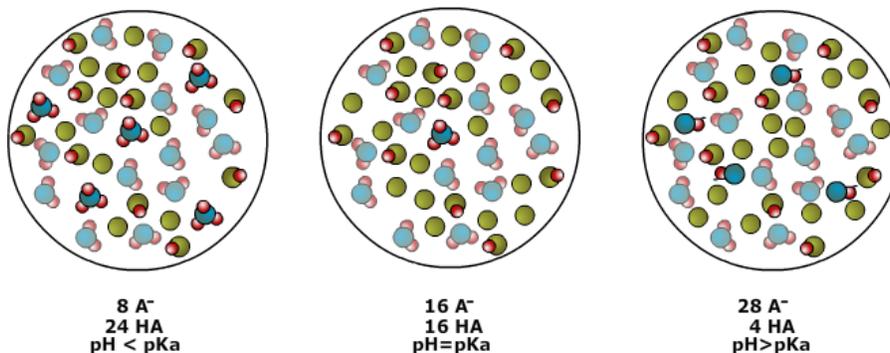
For solutions of a weak base the equation below can be used

$$pOH = pK_b + \log \left[\frac{(B)}{(BOH)} \right]$$

Both equations are perfectly equivalent and interchangeable. So this equation can be rearranged to give the Henderson-Hasselbalch equation

$$pH = pK_a + \ln \frac{[A^-]}{[HA]} = pK_a + \ln \frac{[\text{Conjugate base}]}{[\text{Conjugate acid}]}$$

Henderson-Hasselbalch equation



Henderson-Hasselbalch equation

23.3 LIMITATIONS OF HENDERSON-HASSELBALCH EQUATION

Henderson-Hasselbalch equation is used mostly to calculate pH of solution which is obtained by mixing known amount of acid and conjugate base (or neutralizing part of acid with strong base). When we prepare a solution by mixing 0.1 M of acetic acid and 0.05 M NaOH half of the acid is neutralized by the alkali and resulting in the equal concentrations of acid and conjugate base, thus quotient under logarithm is 1, logarithm is 0 and $\text{pH} = \text{pK}_a$.

However, this approach is justifiable in many cases, it creates false conviction that the equation could be applied in all the situations which is not true

Henderson-Hasselbalch equation is valid only when it contains equilibrium concentrations of acid and conjugate base. In the case of solutions containing not-so-weak acids (or not-so-weak bases) equilibrium concentrations can be far from those predicted by the neutralization stoichiometry.

When we replace acetic acid in the above example with a stronger acids like dichloroacetic acid, with $\text{pK}_a = 1.5$. Repeating the same reasoning we used earlier we will arrive at $\text{pH} = 1.5$ - which is wrong. By determining the pH using either an equation or by pH meter we find the pH will be 1.78. It is because dichloroacetic acid is strong enough to dissociate on its own and equilibrium concentrations of acid and

conjugate base are not 0.05 M (as we expected from the neutralization reaction stoichiometry) but 0.0334 M and 0.0666 M respectively.

As a rule of thumb you may remember that acids with pK_a value below 2.5 dissociate too easily and use of Henderson-Hasselbalch equation for pH prediction can give wrong results, especially in case of diluted solutions. For solutions above 10 mM and acids weaker than $pK_a \geq 2.5$, Henderson-Hasselbalch equation gives results with acceptable error. The same holds good for bases with $pK_b \geq 2.5$. However, the same equation will work perfectly regardless of the pK_a value if you are asked to calculate ratio of acid to conjugate base in the solution with known pH.

Similar problem is present in calculation of pH of diluted buffers. Let's see what happens when you dilute acetic buffer 50/50:

Table: 23.1 pH of diluted solutions of acetic buffer 50/50 (ionic strength ignored)

C_a (M)

	Buffer pH (pH Calculator values)
0.1	4.76
0.01	4.76
10^{-3}	4.79
10^{-4}	4.95
10^{-5}	5.47
10^{-6}	6.31
10^{-7}	6.89

The more diluted the solution is, the more solution pH is dominated not by the presence of acetic acid and its conjugate base, but by the water auto dissociation. pH of 1 mM solution is close enough to the expected (from pK_a) value, more diluted solutions deviate more and more. It is worth noting here that 1 mM buffer solution has so low capacity, that it has very limited practical use.

Henderson-Hasselbalch equation can be also be used for pH calculation of polyprotic acids, as long as the consecutive pK_a values differ by at least 2 (better 3). Thus it can be safely used in case of phosphoric buffers ($pK_{a1}=1.963$, $pK_{a2}=7.199$, $pK_{a3}=12.35$), but not in case of citric acid ($pK_{a1}=3.128$, $pK_{a2}=4.761$, $pK_{a3}=5.40$). It is necessary to determine the pH of the solution directly rather than depending on the above equation.

Using known pH and known pK_a you can calculate the ratio of concentrations of acid and conjugate base, necessary to prepare the buffer. Further calculations depend on the way you want to prepare the buffer.



Lesson-24

Buffering Capacity and Buffering Index

24.1 INTRODUCTION

Constituents in any biological fluid retain their native state so long the pH of the solution is maintained unchanged. For effective utilization and to perform the designated functions by that fluid the constituent exist in different forms e.g., in milk the fat exists as an emulsion while the major protein casein exists in the form of micelles. Maintenance of uniform pH becomes possible when buffers are present in that solution. Milk also has some normal constituents which are having buffering action which prevents the changes due to variations in the milk such as microbial population in it or atmospheric changes environment in the pH of milk within a given pH range.

The buffering capacity of milk products is an important physico-chemical characteristic that corresponds to the ability of the product to be acidified or alkalinized. The parameters of this value depend on several compositional factors including small constituents (inorganic phosphate, citrate, organic acids) and milk proteins (caseins and whey proteins). Natural and induced variations in the composition of milk affect this physico-chemical parameter. Thus, some processing treatments and physico-chemical changes, such as heat treatment, membrane separation technology, high-pressure treatment and salt addition, results in a buffering capacity specific to the transformed product (heated milk, retentate, fermented milk). In cheese manufacture, the preparation of cheese milk and the cheese making parameters have major influences on the buffering capacity of the curd at mould removal and during ripening. Cheese quality is therefore affected during ripening, via enzymatic activities and microbial growth.

The maximum buffer index of skim milk, standardized milk (4.5% fat) and whole milk are 0.0290, 0.0283 and 0.0270 for buffalo and 0.0333, 0.0283 and 0.0277 for cow respectively. Both milks exhibit a maximum buffering at pH 5.3 to 5.4 and show the same buffer intensity curve between pH 4.5 and 10.0. Sodium citrate and pyrophosphate are favourable stabilizers shifting the maximum buffering of milk towards the normal pH of the milk. These additives cause an increase in milk pH and higher rate of dispersion.

24.2 BUFFERING CAPACITY

In milk aggregation or dispersion of protein micelles and fat globules is dependent up on its buffering capacity, pH, acidity and electrical conductivity. Determination of these properties and range of variation will help in assessing the technological properties of milk. The natural range of variation of this property in milk and milk products will determine several technological properties of milk. Stability of milk suspension is mainly controlled by the acid base equilibrium in milk. Substances which liberate protons (acid) and of those that combine with them (Bases) are responsible for maintaining this stability of milk constituents. The ionized and ionizable constituents of milk are in a state of rather delicate physical balance. The treatments such as heating or changing in milk compositional qualities alter the state of dispersion of proteins and salts which is reflected in protons. Buffers resist changes in pH. The Buffering Capacity increases as the molar concentration (molarity) of the buffer salt/acid solution increases. The closer the buffered pH is to the pKa, the greater the Buffering Capacity. Buffering Capacity is expressed as the molarity of Sodium Hydroxide required to increase pH by 1.0 unit / litre of solution.

$$\beta = d_n/dpH$$

Where n is number of equivalents of added strong base. Note that addition of dn moles of acid will change pH by exactly the same value but in opposite direction.

24.3 THE BUFFER INDEX

This can be defined as the differential ratio of the increase in the amount of strong acid or strong base added, to pH variation. The field of application of both notions is different: the buffer capacity is used in the quantitative chemical analysis and the buffer index in studying biological systems.

24.4 CONSTITUENTS CONTRIBUTING TO THE BUFFERING CAPACITY OF MILK

Milk contains many acidic and basic groups. Because of the presence of acidic and basic groups the pH changes much less than when titrating with water: these groups have a buffering action. The buffering capacity of solution can be expressed in the buffer index which is the molar quantity of acid or base needed to change the pH of 1 litre of solution by one unit; it is thus the derivative of the titration curve. The buffering index of an ionizable group is given by the following formula

$$pH-pK=\pm 2. \quad \frac{dB}{dpH} \approx 2.3cK_a \frac{H^+}{(K_a+H^+)^2}$$

Where C is the total molar concentration of the group (dissociated plus associated). Again, it concerns intrinsic constants, but the above equation also holds for monoprotic acids if K_a is the stoichiometric dissociation constant. This equation implies that the buffering capacity is maximal (0.58 c) for the $pH=pK$; it is reduced to 33% of the maximal values for $pH-pK=\pm 2$.

The buffering groups of milk are given in Table 24.1.

Table: 24.1 Buffering Groups In Milk

Group	Concentration (mM)	pK _a value
Protein-Bound residues		
Aspartic acid	19	4.1
Glutamic acid	50	4.6
Histadine	6	6.5
Tyrosine	12	9.7
Lysine	20	10.5
Ester-phosphate	7	2.6
N-Acetyl Neuraminic Acid	0.5	5
Terminal group	1.5	3.7,7.9
Salts		
Phosphate	21	3.,5.8,6.6
Citrate	9	3.,4.1,4.8
Phosphate ester	2.5	1.7,5.9
Carbonate	2	6.4,10.1
Various carboxylic acids	2	4.8
Various amines	1.5	7.6
Lactic acid	50-120	3.95

The ionizable groups of the proteins, the phosphates, and the citrates mainly determine the acidity and the buffering capacity of milk. There will be variation in the titration curves due to the considerable variation in the concentration of these substances. Some of the ionizable groups in a protein may even be unavailable for titration, as they are buried in the hydrophobic interior of the molecules. Ionizable groups of the whey proteins and casein molecules. are not exposed The presence of Ca^{2+} ions strongly modifies the ionization of di and triprotic acids such as phosphoric acid and citric acids they will behave as if they are titrated by $\text{Ca}(\text{OH})_2$ instead of NaOH or HCl . Lowering of the pH of milk will make calcium phosphate soluble because it is not soluble in normal pH of milk whereas colloidal phosphate will increase when the pH is increased. The Magnesium citrate and protein affect the composition and quantity of colloidal phosphate. Consequently the buffering index of various groups is not strictly additive.



Lesson-25

Electrolyte Equilibrium And pH Indicators

25.1 INTRODUCTION

Electrolytes when added to water will dissociate into charged particles and can pass electric current while nonelectrolytes although dissolve in water but cannot pass electric current. The number of dissociated and undissociated ions attain equilibrium which is necessary for the stability of the solution.

25.2 DISSOCIATION OF IONS IN SOLUTIONS

Some of the compounds like sodium chloride (NaCl), hydrochloric acid (HCl), acetic acid (CH₃COOH) etc dissolve in water by dissociating into ions. To begin this process the ions require some energy which they obtain by the process known as hydration.

25.3 HYDRATION

This is a process in which opposite charges attract one another. In the present example the partial positive charge on the hydrogen molecule of H₂O is attracted to the anion and the partial negative charge on oxygen is attracted to cations. In this way during hydration each ion is surrounded by a group of opposite charges thereby lowering the overall energy of the solution. It may be mentioned that these substances in their pure state are not separated ions, are electrically neutral and do not conduct electricity.

25.4 CONDUCTIVITY

The molecular compounds such as pure acetic acid do not conduct electricity. Under the influence of water and during the process of hydration these compounds can be broken down into ionic species due to which the solution conducts electricity. Ionic compounds are also poor conductors of electricity when not in solution.

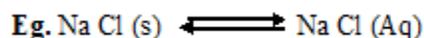
25.5 REVERSIBLE REACTIONS AND EQUILIBRIUM

Hydration is an example of a reversible reaction. Most chemical reactions are the equilibrium of the hydration process is largely influenced by the type of electrolyte i.e, strong or weak electrolyte. Weak electrolytes upon introduction into water begin to dissociate into ions but most of the particles remain in molecular form. But the tendency of the particles in the molecular form to dissociate is same as those molecules that have already dissociated into ions. What could be the reason for these molecules to continue to exist in their undissociated form? In fact, these molecules have also been dissociated but they immediately get associated into their molecular form. In this way, the total number of ions and molecules stays the same while each is constantly becoming the other. In the case of strong electrolytes the molecules dissociate to a great extent than weak electrolytes and the equilibrium shifts to one side of the reaction where there are more ions and no molecular particles are found in the solution. The situation or the stage in which the number of ion pairs and molecular particles stay the same is called Equilibrium. Equilibrium should not be thought of as the end of a reaction but rather a stage or point at which no net change occurs.

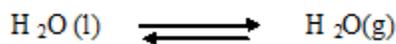
25.6 KINDS OF EQUILIBRIUM

Many kinds of equilibrium could be observed in solutions

- Physical equilibrium can be reached between a solid salt and a saturated solution of that salt



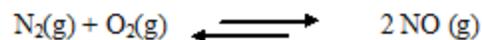
- Physical equilibrium between liquid water and gaseous water in a closed container



- Physical equilibrium can be reached between molecular particles and ions in solution



- Chemical equilibrium can be reached between reactants and products



25.7 NON EQUILIBRIUM SYSTEMS

Some reactions have an end point and due to the formation of precipitate. These reactions are not considered equilibrium because a product formed by this reaction does not become available to react in the reverse direction, a precipitate is insoluble and will not react with ions in solution a gas escapes to the atmosphere and is no longer even physically present to react.

25.7 Le CHÂTELIER'S PRINCIPLE

Reversible reactions will reach equilibrium which is a point at which no net reaction is occurring or the reaction is progressing backward at the same time it is progressing forward. if it is left undisturbed. It is possible to disturb this equilibrium causing the reaction to progress more in one direction than another until a new equilibrium is reached. There are many conditions which will disturb this equilibrium which are

- Change in temperature i.e., any addition or subtraction of energy from the system
- A change in pressure
- The removal or addition of a product or reactant

As mentioned by Le Chatelier “any change in one of the variables that determines the state of system in equilibrium causes a shift in the position of equilibrium in the direction that tends to counteract the change in the variable under consideration

25.8 pH INDICATORS

A **pH indicator** is a chemical compound that is added in small amounts to a solution so that the pH (acidity or alkalinity) of the solution can be determined easily. A pH indicator is a chemical detector for protons (H^+). Normally, the indicator causes the colour of the solution to change depending on the pH, of the solution.

pH indicators themselves are frequently weak acids or bases. When introduced into a solution, they may bind H^+ (Hydrogen ion) or OH^- (hydroxide) ions. The different electronic configuration of the bound indicator causes indicator's colour to change.

Since determination of colour change is subjective in nature the results obtained by using pH indicators are most likely approximate and not precise. However, for applications requiring precise measurement of pH, a pH meter is frequently used.

pH indicators are frequently employed in titrations in analytic chemistry and biology experiments to determine the extent and magnitude of a chemical reaction.

Tabulated below are several common laboratory pH indicators. Indicators usually exhibit intermediate colour at pH values inside the listed transition range. For example, phenol red exhibits an orange colour between pH 6.6 and pH 8.0. The transition range may shift slightly depending on the concentration of indicator in solution and on the temperature at which it is used.

Table.25.1 Common Laboratory pH Indicators.

Indicator	Colour at low pH	Transition pH range (approximate)	Colour at high pH
Methyl violet	blue-violet	0.0-1.6	yellow
Thymolblue(first transition)	Red	1.2-2.8	yellow
Methyl yellow	Red	2.9-4.0	yellow
Bromophenol blue	yellow	3.0-4.6	violet
Congo red	Blue	3.0-5.2	red
Methyl orange	Red	3.1-4.4	yellow
Litmus	Red	4.5-8.3	blue
Bromocresol purple	yellow	5.2-6.8	violet
Bromothymol blue	yellow	6.0-7.6	blue
Phenol red	yellow	6.6-8.0	red
Thymol blue (second transition)	yellow	8.0-9.6	blue

Phenolphthalein	colorless	8.2-10.0	pink
Thymolphthalein	colorless	9.4-10.6	blue
Alizarin Yellow R	yellow	10.1-12.0	red
Indigo carmine	blue	11.4-13.0	yellow

Universal Indicator is a blend or mixture of different indicators that exhibits several smooth colour changes over wide range of pH values.

Anthocyanins are a class of compounds that occur in many different plants; they appear red in acidic solutions and blue in bases. Extracting anthocyanins from red cabbage leaves to form a crude acid-base indicator is a popular introductory chemistry demonstration.

Lesson-26

Oxidation Reduction Potential, Nernst Equation and Electrochemical Cell

26.1 INTRODUCTION

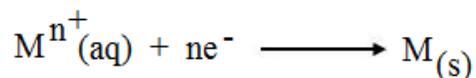
Oxidation is defined as the process, in which a substance takes up positive, or parts with negative charges, while reduction is the process in which a substance takes up negative or parts with positive charges. Oxidation reduction potential (ORP) covers a large pH range. It is an electrochemical test and can easily measured using simple and portable instruments.

26.1 DEFINITION

Oxidation Reduction Potential is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. Reduction potential is measured in volts (V), millivolts (mV), or E_h ($1 E_h = 1 \text{ mV}$). Each species has its own intrinsic reduction potential; the more positive (negative) the potential is, the greater the species' affinity for electrons and tendency to be reduced.

26.3 NERNST EQUATION

For a general reduction reaction,



Nernst developed an equation, known as: Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{[M(\text{s})]}{[M^{n+}(\text{aq})]}$$

Where

E is the electrode potential

E^0 is the standard electrode potential (for 1M solution of metal ions at 298 K)

R is gas constant

T is temperature

n is the number of electrons accepted during the change and

F is Faraday of electricity (96500 coulombs).

The molar concentration of solids in the pure state is assumed to be unity i.e. $[M_{(s)}] = 1$. Substituting the values,

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$, $F = 96500 \text{ coulombs}$,

the quantity $\frac{2.303RT}{F}$ becomes a constant.

$$\frac{2.303RT}{F} = \frac{2.303 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(96500 \text{ C mol}^{-1})} = 0.059$$

Therefore, the Nernst equation for the general reduction reaction at 25°C is:

$$E = E^0 - \frac{0.059}{n} \ln \frac{1}{[M^{n+}(\text{aq})]}$$

26.4 ELECTRO CHEMICAL CELL

Immersion of a metal plate in water or in a solution containing ions of that metal, a double electric layer is formed at the interfacial boundary between the metal plate and solution resulting in the establishment of a potential difference between them. The magnitude of potential difference established between the metal plates and the solution of the salts of that metal depends upon.

- a) Properties of the metal and the solution in particular,
- b) On the concentration of the ions of the metal in the solution
- c) On the nature of the interaction between the particles of the double layer.

Now, let us assume instead of one, two metal plates *i.e.*, zinc and copper are dipped in solutions of their salts separated by a porous membrane. Each of the metals emits a certain quantity of ions into the solution

corresponding to its equilibrium state. Since the equilibrium potential for all the metals is not similar, there is greater tendency for the zinc to give off its ions in to solution than copper. Due to this release of zinc ions in to the solution it acquires more negative charge.

$Zn = Zn^{2+} + 2e^{-}$ at the negative electrode

$Cu = Cu^{2+} + 2e^{-}$ at the positive electrode.

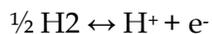
If the plates are now connected through a wire this difference in the potential between the plate and its will allow the electrons to glow from the zinc plate to the copper plate. This would result in the disturbance of equilibrium of the double layer at both the plates. Consequently another proton of zinc ion will pass from the zinc plate to the solution and corresponding number of copper ions are discharged on the copper plate. This would further difference in the charge of the plates causing transition of the electrons from the zinc plate (negative electrode) to the copper (Positive electrode) resulting in the further transport of the ions. Consequent to this spontaneous process taking place with the dissolving of the zinc plate (Oxidation) and deposition of copper on the copper plate due to the discharge of the copper ions (reduction) there will be passage of electrons along the wire from zinc to the copper plate. This passage is responsible for the electric current. By applying the maximum work and the equilibrium conditions of the process can be determined by applying a potential difference of the same magnitude but of opposite sign is applied to the system the process will take place under practically reverse conditions. The electrical work that is obtained by means of redox potential is maximum when the cell is operating under close to reversible conditions. This maximum potential difference is called the Electro motive force (EMF) The appliances which could be designed to create electrical current by means of chemical reactions are known as galvanic cell. Galvenic cells involve in the reaction of oxidation reduction potential.

26.5 ELECTRODES

Hydrogen electrode is the reference electrode universally used the standard galvanic cell.

26.5.1 Hydrogen Electrode: The electrode potential of a given electrode is the quantity of its potential (EMF) with that of the standard hydrogen electrode. This quantity is known as **electrode potential** and is designated by the letter **E**, which is similar to the EMF of the cell. The hydrogen electrode usually consists of a platinized platinum foil immersed in a solution containing hydrogen ions and around which

a current of hydrogen gas flows. In the standard hydrogen electrode the concentration of the hydrogen ions in solution corresponds to the activity $a_{\text{H}^+} = 1$ and a gaseous hydrogen pressure of 1 atmosphere. It functions on the basis of the reaction.



This reaction is similar to the one occurring on the surface of the metallic electrode reversible with respect to cations. Platinum here plays only the part of an inert carrier and may be replaced by palladium, iridium, gold and certain other metals. The hydrogen electrode may be used at any hydrogen pressure at any hydrogen ion concentration in the solution and any temperature. It's potential depends on the operating conditions. Such a hydrogen electrode is taken as a reference electrode (to which 0 potential is assigned) for which the activity of the hydrogen ion in solution is unity ($a_{\text{H}^+} = 1$) and the hydrogen gas pressure is one atmosphere, both the hydrogen electrode and the other electrode of the cell being at the same temperature. Hence $E_{\text{H}^+} = 0$.

Hydrogen electrode is very sensitive to the operating conditions as such, it is necessary to maintain high purity with respect to the hydrogen and platinum surface. When correctly used hydrogen electrode gives very sensitive results, reproducible to 0.00001V. The high sensitivity of this electrode to the environmental conditions greatly hampers its utilization.

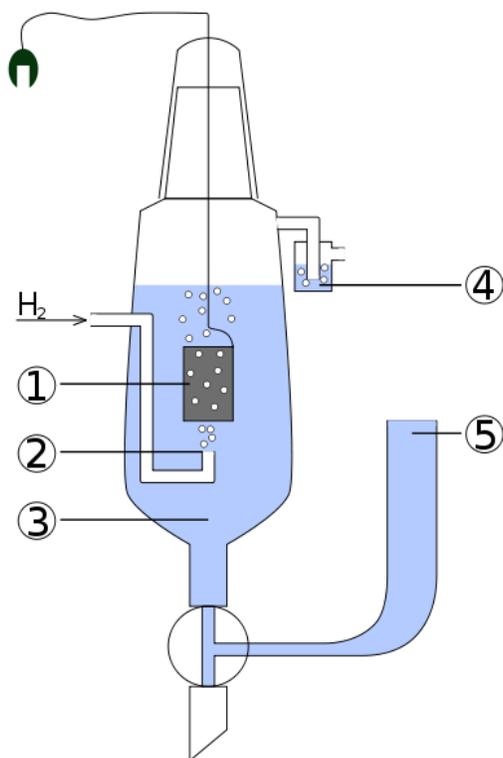


Fig.26.1 Standard hydrogen electrode scheme:

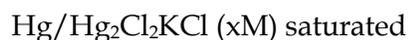
1. Platinized platinum electrode
2. Hydrogen gas
3. Acid solution with an activity of $H^+=1$ mol/l
4. Hydroseal for prevention of oxygen interference

5. Reservoir via which the second half-element of the galvanic cell should be attached

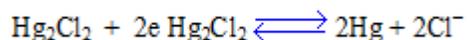
26.5.2 Reference electrodes: A **reference electrode** is an electrode which has a stable and well-known electrode potential. The high stability of the electrode potential is usually reached by employing a redox system with constant (buffered or saturated) concentrations of each participants of the redox reaction. These electrodes are reversible, have little hysteresis, follow Nernst equation and have stable potential with time.

26.5.3 Saturated calomel electrode: A diagram of the calomel electrode is shown in figure 9. It consists of an outer glass tube fitted with a frit at the bottom to permit electrical contact with the outside solution.

In side there is another tube, the bottom of which is packed with glass wool to allow further electrical connection between the contents of the inner tube and the contents of the outer tube. The inner tube is packed with a paste of mercury and mercurous chloride dispersed in a saturated solution of potassium chloride represented by



And the reaction for the electrode will be,



The electrode potential will depend on the concentration of the potassium chloride and, thus, the electrode potential must be reported together with the potassium chloride concentration. Thus, for the saturated calomel electrode the common reference voltage is +0.244 V. The calomel electrode operating temperature is restricted to below 80°C due to the mercurous chloride disproportioning into mercury and mercuric chloride at higher temperatures. Unfortunately due to its design and the thermal characteristics of the materials from which it is made, it's rate of progress towards equilibrium after a temperature change is rather slow.

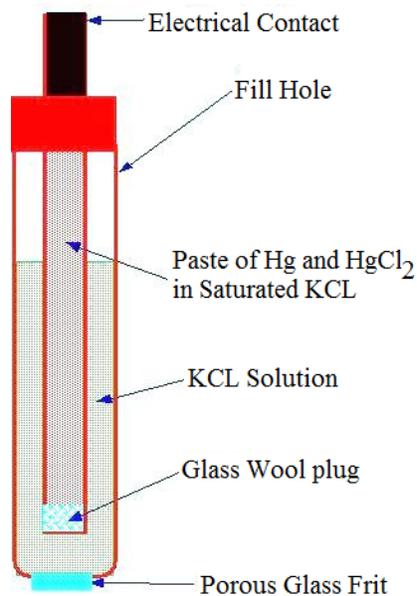
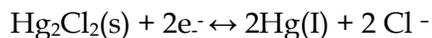


Fig.26.2. The Calomel Electrode

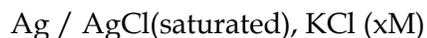


Half cell for calomel electrode :



Position of equilibrium affected by a_{Cl^-} from KCl, so E^0 depends on a_{Cl^-} for a most common saturated calomel electrode SCE $[(\text{Cl}^-)] \sim 4.5\text{M}$

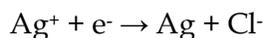
26.5.4 Silver /silver chloride electrode: The silver/silver chloride electrode is the most common and popular electrode used in electrochemistry. The electrode consists of a silver wire coated with silver chloride and immersed in a solution of potassium chloride saturated with silver chloride. Thus,



And the half reaction is,



The actual "redox" action occurring at the electrode is



And the potential developed will be a function of the (Ag^+) concentration. Now as the (Ag^+) concentration depends on the solubility product equilibrium of AgCl then the electrode potential will also depend on the chloride ion concentration. The standard potential of the Ag/AgCl electrode at 25°C is 0.2223 V. The silver/silver chloride electrode is easily constructed, can be used over a relatively wide range of temperatures and can be used in non-aqueous solutions.

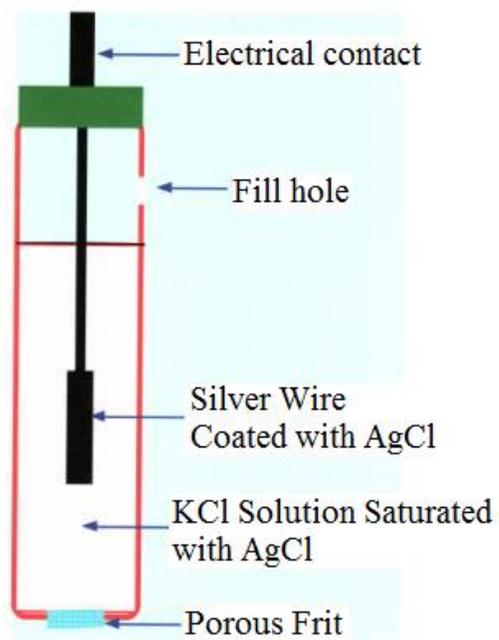
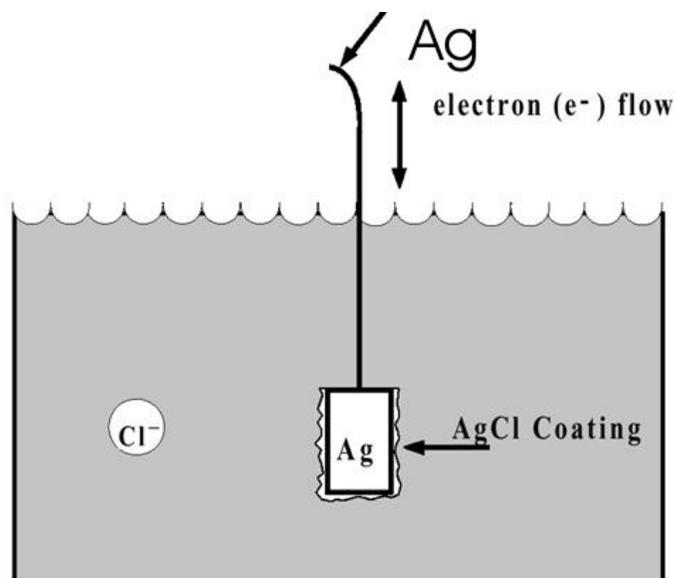


Fig: 26.3 Silver electrodes



Electrode reaction:



This reaction can also be presented by:

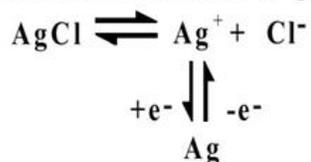
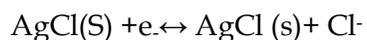
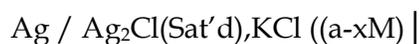


Fig: 26.4 Silver electrodes



Again depends on a_{Cl^-} but commonly sat (~3.5M)

Ag/AgCl better for uncontrolled temperature (lower T coefficient) Ag reacts with more ions

26.5.5 Indicator electrodes for ions: Electrodes used with reference electrodes to measure potential of unknown solutions. Potentials are proportional to ion activity. These electrodes may be specific (one ion) or selective (Several ions)

$$E_{\text{cell}} = E_{\text{indicator}} - E_{\text{reference}}$$

Generally there are two types of electrodes are available in this type. They are

Metallic and membrane electrodes

26.5.6 Metallic Indicator Electrodes: Electrodes of the first kind respond directly to changing activity of electrode ions Eg. Copper indicator electrode but other ions can be reduced at Cu surface. The metals with higher +ve E^0 and having better oxidizing agents than Cu such as Ag, Hg, Pd can also be used . In general electrodes of first kind are simple, they are not very selective, and some metals are easily oxidized (Deaerated solutions) some metals like Zn and Cd dissolve in acidic solutions. The electrodes of the second kind respond to changes in ion activity through formation of complex. e.g. Silver wire in KCl (Sat'd) forms Ag Cl layer on the surface of the Electrodes of the third kind respond to changes of different ion than metal electrodes.

26.5.7 Membrane (Or Ion Selective) Electrodes: Membranes are of low solubility which may be solids, semisolids and polymers, since part of membrane binds/reacts with analyte so they are selective. Generally there are two types of membranes are used crystalline and non-crystalline. Non crystalline membranes are Glass silicate glasses for H^+ , Na^+ liquid ion exchanger for Ca^{2+} immobilized liquid - liquid /PVC matrix for Ca^{2+} NO_3^- . Crystalline membranes could be single crystal or polycrystalline or mixed crystals - AgS for S^{2-} and Ag^+

26.5.8 Biosensor Membrane Electrodes: These are very important and are being developed after extensive research on this aspect. Immobilized enzymes bound to gas permeable membrane and the catalytic enzyme reaction produces small gaseous molecules (H^+ , NH_3 , CO_2) then gas sensing probe will measure the change in the gas concentration in the internal solution. The advantages of these electrodes are they are fast, very selective, used in vivo but the disadvantages of these electrodes include that they are expensive, only few enzymes alone could be immobilized, immobilization would change the activity, the operating conditions are limited (pH, temperature, ionic strength).



Lesson-27

Redox System in Milk

27.1 INTRODUCTION

The oxidation reduction reactions involve transfer of electrons between atoms or molecules. Transfer of oxygen (O) or hydrogen (H) or both also may occur. Oxidation is loss of electrons while reduction is the gain of electrons. In a redox system when half of the system is having oxidation reaction and the other half is having a reduction reaction there will be no flow of electrons either in to the system or go out of the system. In normal milk there are several complicated biological systems with varying composition and concentration. In addition to this microorganism gaining entry in to milk contribute certain redox systems to it depending upon the type of the organisms.

27.2 REDOX SYSTEM IN MILK

A reversible system give a potential at a metal electrode is the intensity factor which is the measured potential. Potential measured for the reversible systems is similar to the potential measured at the hydrogen electrode while determining the hydrogen ion concentration i.e.,pH. The quantity factor for the oxidation reduction is the overall concentration of active substances $[Ox] + [Red]$.

Several factors influence this potential in a system. These factors are

- Reversibility of the system
- Standard potential of the system(e_0)
- Or the position on the scale of the potential
- Concentration of the active components of this system.

Methylene blue is reduced by freshly drawn milk when it is drawn from udder anaerobically indicating a more negative potential than methylene blue system. Exposure to oxygen will change this potential to

be more positive than the methylene blue system. Apart from this the chief oxidation and reduction systems present in milk are Ascorbate, lactate and riboflavin.

The ascorbic content of fresh milk is about 0.25 meq litre⁻¹ the milk is drawn from the udder all the ascorbate present in milk will be in its reduced form but reversible oxidation to dehydro ascorbate occurs at rates dependent on temperature, copper (Cu) and oxygen (O₂) concentration. In order to inhibit growth of microorganisms milk is held at temperature between 1 to 4°C, and the reduced form of ascorbate gradually decreases over several days as dehydro ascorbate levels are constant (0.05 mEq Litre⁻¹) their ratio remains large until the system disappears. Preventing the contamination with copper (Cu) and by deaeration the ascorbate content can be preserved. The concentration of free riboflavin is only 4µM. It plays an important role in the photo oxidation. It does not contribute significantly either to the O-R potential *i.e.*, E_h or poisoning action. Milk contains only low concentration of small molecular weight thiols. Thiols of the native proteins are not active in oxidation reduction systems. Due to heat denaturation of proteins unfolding and uncoiling would occur due to which these thiols groups contribute to the O-R potential of milk. The concentration of such activated thiols in milk heated under UHT conditions may attain 0.18 mEq.liter⁻¹.

The redox potential E_o of milk and standard potential E₀ of some important systems in milk are plotted against pH is presented in the Fig.27.1. Individual milk samples in equilibrium with air generally have E_h's in the range of +0.25 to +0.35 V at 25°C at their normal pH of milk *i.e.* 6.6 to 6.7. Not much information is available on the capacity of the oxidation – reduction system in milk. Fresh raw whole milk will reduce 0.6 to 0.8 m mol of ferricyanide to ferrocyanide per liter at 50° C for 20 min.

Besides redox potential which pertain to equilibrium conditions the kinetics of the oxidation reduction reactions is also important. Some reactions are very slow because of a high free energy of activation(ΔG^{*}) which implies that it may take considerable time before equilibrium is reached. Accurate measurement of E_h of milk takes considerable time as there are several systems in milk which overlap and these reactions are either slowly reversible or even irreversible. Measuring OR potential of milk is complicated due to entry of oxygen during determination. In milk oxidation reduction systems resist change in the potential when the oxidant and reductant are near equilibrium state. This phenomenon is similar to the buffering action in acid base equilibrium. This phenomenon is known as 'poising'. It is difficult to obtain meaningful data on the poisoning index though milk has considerable poisoning capacity.

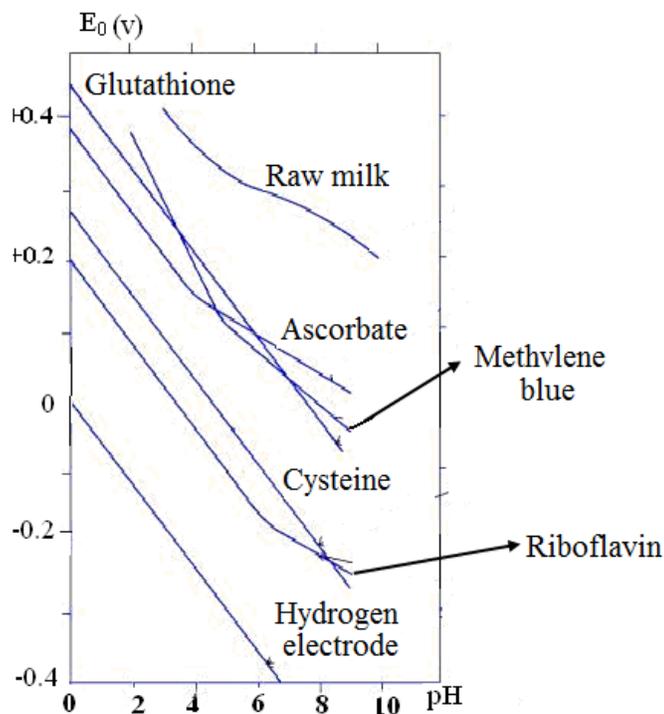


Fig.27.1 The redox potential (E_0) of milk and the standard potential (E_h) of various systems in relation to pH

(Source: Dairy chemistry and physics, Walstra and Jenness,1984)

Concentration of lactate-pyruvate system in milk is negligible. Enzymatic activation of this system would influence the redox system. At higher pH the aldehyde group of lactose is oxidizable to carboxyl group, but this reaction is not a reversible and hence it will not influence the E_h at pH of 6.6.

Redox reactions in milk systems are influenced by heat treatment, by concentration of O_2 and metal ions such as Cu^{2+} , by exposure to light and by oxido reductases of milk and or micro organisms. The redox potential of metal ions may depend closely on their binding to various ligands, including some (Metallo) proteins.



Lesson-28

Nuclear Chemistry, Isotopes

28.1 INTRODUCTION

In any compound the electrons around the atom's nucleus are involved in various chemical reactions. Discovery of radiation emitted by uranium has expanded this field to nuclear changes. Marie Sklodowska Curie has initiated the study of radioactivity and contributed much to the study of nuclear changes. In the present lesson we will be learning what the isotopes are their nature and about the radio isotopes.

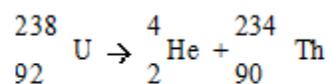
28:2 RADIATION AND NUCLEAR REACTIONS

According to the theory proposed by Frederic Soddy "radioactivity is the result of a natural change of an isotope of one element into an isotope of a different element." In nuclear reactions, the particles in an atom's nucleus will change and thus changing the atom itself due to nuclear reactions. In chemical reactions the molecules are formed whereas due to the nuclear reactions there will be transmutation of one element into a different isotope or a different element altogether. All elements heavier than bismuth (Bi) exhibit natural radioactivity and thus can "decay" into an altogether lighter elements. Normally the number of protons in an atom will determine a particular element. As the protons are changing in the nucleus due to radiation the atom of that element will also change.

28.3 TYPES OF RADIATION

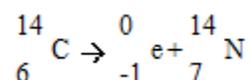
There are three common types of radiation and nuclear changes.

28.3.1: Alpha radiation (α) : Emission of an alpha particle from an atom's nucleus is called the alpha radiation. An alpha particle contains 2 protons and two neutrons and is similar to He Nucleus (${}^4_2\text{He}$). When an atom emits α particle the atom's atomic mass will decrease by four units (because two protons and two neutrons are lost) and the atomic number (z) will decrease by two units. The element is said to "transmute" into another element that is two z units smaller. e. g. Uranium decays into Thorium by emitting alpha particle.



(Note: in nuclear chemistry, element symbols are traditionally preceded by their atomic weight (upper left) and atomic number (lower left).

28.3.2: Beta Radiation (β): The transmutation of a neutron into a proton and an electron followed by the emission of the electron from the atom's nucleus. When an atom emits β particle the atom's mass will not change since there is no change in the total of nuclear particles. There will be an increase in the atomic number by one because of the transmutation of a neutron to an additional proton. e.g. Carbon -14 an isotope of Carbon into the element Nitrogen.



28.3.3: Gamma Radiation (γ): It is the emission of electromagnetic energy (Similar to light energy) from an atom's nucleus. There will be no emission of particles during gamma radiation and gamma radiation does not itself cause the transmutation of atom. It is often observed that γ radiation during the transmutation of atoms to, α or β radioactive decay. e.g. X-rays emitted during the beta decay of Cobalt -60.

28.4 ISOTOPES

Isotopes may be defined as the atoms having the same nuclear charge but are having different masses. Such atoms have practically same structure of their electrons shells and belong to the same chemical element of the periodic system. Consequent to the development of mass spectroscopy, it became possible to discover isotopes among the naturally occurring compounds of non radio active elements. Further with the development of nuclear physics it has become possible to obtain different isotopes for different elements artificially.

28.4.1: Nature of Isotopes: The composition of Isotopes of naturally occurring elements is markedly constant.

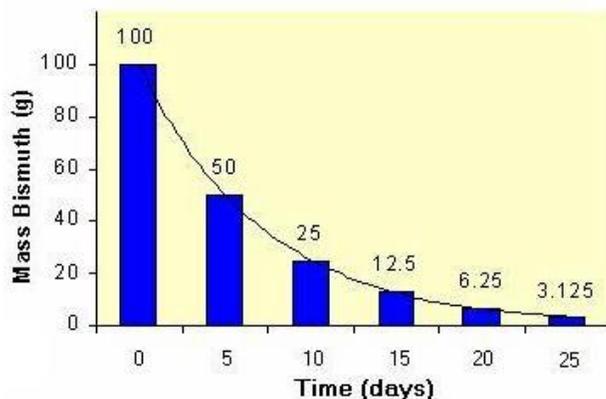


Fig.28.1 Radioactive Decay of Bismuth-210 (T_{1/2}=5 DAYS)

(Source: www.vissionlearning.com)

28.5 HALF-LIFE

Radioactive decay proceeds according to a principle called the half-life. The half-life (T_{1/2}) is the amount of time necessary for one-half of the radioactive material to decay. For example, the radioactive element bismuth (²¹⁰Bi) can undergo alpha decay to form the element thallium (²⁰⁶Tl) with a reaction half-life equal to five days. If we begin an experiment starting with 100 g of bismuth in a sealed lead container, after five days we will have 50 g of Bismuth and 50 g of Thallium in the jar. After another five days (ten from the starting point), one-half of the remaining bismuth will decay and we will be left with 25 g of Bismuth and 75 g of Thallium in the jar. As illustrated in fig. 28.1, the reaction proceeds in halves, with half of whatever is left of the radioactive element decaying every half-life period.

The fraction of parent material that remains after radioactive decay can be calculated using the equation:

$$\text{Fraction remaining} = \frac{1}{2^n}$$

(where n = number of half-lives elapsed)

The amount of a radioactive material that remains after a given number of half-lives is therefore:

$$\text{Amount remaining} = \text{Original amount} * \text{Fraction remaining}$$

The decay reaction and T_{1/2} of a substance are specific to the isotope of the element undergoing radioactive decay. For example, Bi210 can undergo decay to Tl206 with a T_{1/2} of five days. Bi215, by comparison, undergoes decay to Po215 with a T_{1/2} of 7.6 minutes, and Bi208 undergoes yet another mode of radioactive decay (called electron capture) with a T_{1/2} of 368,000 years!

28.5 STIMULATED NUCLEAR REACTIONS

While many elements undergo radioactive decay naturally, nuclear reactions can also be stimulated artificially. Although these reactions also occur naturally, we are most familiar with them as stimulated reactions. There are two such types of nuclear reactions:

28.5.1: Nuclear fission: Reactions in which an atom's nucleus splits into smaller parts, releasing a large amount of energy in the process. Most commonly this is done by "firing" a neutron at the nucleus of an atom. The energy of the neutron "bullet" causes the target element to split into two (or more) elements that are lighter than the parent atom.

During the fission of U235, three neutrons are released in addition to the two daughter atoms. If these released neutrons collide with nearby U235 nuclei, they can stimulate the fission of these atoms and start a self-sustaining nuclear chain reaction. This chain reaction is the basis of nuclear power. As uranium atoms continue to split, a significant amount of energy is released from the reaction. The heat released during this reaction is harvested and used to generate electrical energy.

Two Types of Nuclear Chain Reactions.

Concept simulation – Reactions controlled and uncontrolled nuclear chain reactions.

28.5.2: Nuclear fusion: Reactions in which two or more elements "fuse" together to form one larger element, during the process energy is being released. A good example is the fusion of two "heavy" isotopes of hydrogen (deuterium: ^2H and tritium: ^3H) into the element helium. fig.28.2 shows such reaction.

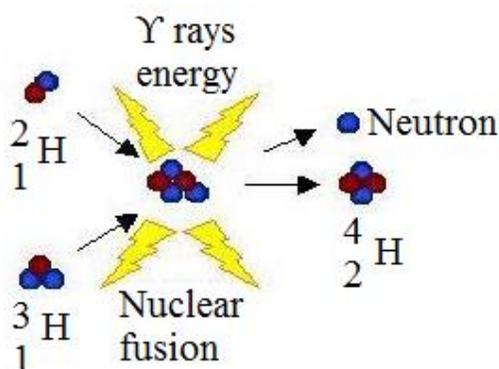


Fig.28.2 Nuclear Fusion of Two Hydrogen Isotopes

(Source: Vission Learning.com)

28.5.3 Nuclear Fusion: Fusion reactions release tremendous amounts of energy and are commonly referred to as thermonuclear reactions. Although many people think of the sun as a large fireball, the sun (and all stars) is actually enormous fusion reactors. Stars are primarily gigantic balls of hydrogen gas under tremendous pressure due to gravitational forces. Hydrogen molecules are fused into helium and heavier elements inside of stars, releasing energy that we receive as light and heat.



Lesson-29

Half Life Period of Radio Isotopes and Measurement of Radio Activity

29.1 INTRODUCTION

The radioactive materials are of use in several research activities especially to monitor the movement of substances across the body and as a diagnostic tool for some of the abnormalities in the body. These radio isotopes are also of some use in the dairy field, because of the fact that they are often found in milk in traces.

Radioactive material will lose its radio activity by emitting the radiation into the atmosphere. Consequently the ability to emit radiation by a given radioactive material progressively gets reduced. The time taken for half of the radionuclide's atoms to decay is commonly referred as half life. This property is related to decay constant. The radioactivity of any radionuclide is based on its half-life. A radio nuclide is said to be highly radioactive if the half life is short while a radionuclide having longer half-life is considered to radioactively weak. There is wide variation in half-life of known radionuclides which ranges from 10^{19} years to 10^{-23} seconds.

29.2 MEASUREMENT OF RADIOACTIVITY

29.2.1: Radiation Detection: The oldest principle for detecting radiation is by darkening photographic emulsion. This principle is used in the personnel dosimetry. The film badge is most popular and cost-effective for personnel monitoring and gives reasonably accurate readings of exposures from beta, gamma and x -ray radiations. The film badge consists of a radiation sensitive film held in a plastic holder. Filters of copper and lead are attached to the holder to differentiate exposure from different types and energies of radiation.

29.2.2 Thermoluminescence: Thermoluminescence is another principle for detecting the radiation. Several inorganic crystals (e.g. LiF) can accumulate radiation energy and hold it. If the crystal is heated from 300 to 400°C, it emits light in amounts proportional to the absorbed energy. Thermoluminescent dosimeters, so called TLD, are mostly used as finger dosimeters, so inorganic crystals are held in a plastic holders and plastic rings. It gives an accurate exposure reading and can be reused.

29.2.3: Converting the Energy of Radiation to Electric Current: Converting the energy of radiation to electric current is also used for detecting the radiation. There are two basic principles which are based on ionization and excitation. First principles are based on ionization of gas molecules, while the second is based on excitation and ionization of solid, liquid or plastic material in a Scintillator, which emits photons of light after absorbing radiation. Light is then converted to the electric current by means of photomultiplier tube, and is measured.

29.3 GAS-FILLED DETECTORS

In gas-filled detectors voltage is applied between two electrodes and the ion pairs formed due to excitation are collected as a current. The measured current is proportional to the applied voltage and the amount of radiation.

In ionization chambers lower voltage ranging from 50 to 300 V is applied resulting in the formation of primary ion pairs by the initial radiation. Gas-filled detectors are cylindrical chambers with a central wire filled with air or different gases. These detectors are primarily used for measuring high intensity radiation. Dose calibrators and pocket dosimeters are the common ionization chambers used in nuclear medicine. The dose calibrator is one of the most essential instruments in nuclear medicine for measuring the activity of radionuclides and radiopharmaceuticals. It must be regularly checked for constancy, accuracy, linearity and geometry.

At higher voltages from 1000 to 1200 V, the current becomes identical regardless of how many ion pairs are produced by the incident radiation. Geiger-Müller counters operate in this region. They are used to monitor the radiation level in different work areas and they are called area monitors or survey meters. They are more sensitive than ionization chambers but cannot discriminate between energies. They are almost 100% efficient for counting alpha and beta particles but have only 1 to 2% efficiency for counting gamma and x rays.

29.4 SCINTILLATION DETECTORS

The detectors of this type consist of scintillator emitting flashes of light after absorbing gamma or x radiation. The light photons produced are then converted to an electrical pulse by means of a photomultiplier tube. The pulse is amplified by a linear amplifier, sorted by a pulse-height analyzer and then registered as a count. Different solid or liquid scintillators are used for different types of radiation.

In nuclear medicine, sodium iodide solid crystals with a trace of Thallium sodium iodide (NaI(Tl)) are used for gamma and x ray detection.

29.5 HALF LIFE OF RADIO ACTIVE ELEMENTS

The formula useful for calculating the half life of radio isotopes is

$$N_t = N_o \times (0.5)^{\text{number of half-lives}}$$

Where:

N_t = amount of radioisotope remaining

N_o = original amount of radioisotope

number of half-lives = time ÷ half-life

Table.29.1 Calculated Half Life of Radio Active Isotopes

Number of half-lives	Time (Years)	% Strontium -90 Remaining	% Strontium -90 that has decayed
0	0	100	0
1	28	50	50
2	56	25	75
3	84	12.5	87.5
4	112	6.25	93.75
5	140	3.125	96.875
6	168	1.5625	98.4375

29.5.1 Half Life of Radioactive Elements: The half life of some of the commonly used isotopes is being shown here under:

Please note that some of the longer half-lives are written in scientific notation (i.e., 7.2E1 is equal to 7.2 x 10, or 72.)

Barium: Ba^{137m} - 2.552 minutes, Ba¹³⁹ - 82.7 minutes, Ba-140 - 12.74 days, Ba-141

Carbon: C-11 - 20.38 minutes, C-14 - 5730 years

Cesium: Cs-134 - 2.062 Years, Cs-134m - 2.90 Hours, Cs-135 - 2.3E6 Years, Cs-136 - 13.1 Days, Cs-137 - 30.0 years Cs-138 - 32.2 minutes

Iodine ; I-123 - 13.2 hours ,I-125 - 60.14 days ,I-129 - 1.57E7 years ,I-130 - 12.36 hours I-131 - 8.04 days ,I-132 - 2.30 hours ,I-133 - 20.8 hours ,I-134 - 52.6 minutes ,I-135 - 6.61 hours

Plutonium: Pu-238 - 87.74 Years, Pu-239 - 24065 years, Pu-240 - 6537 years, Pu-241 - 14.4 years, Pu-242 - 3.76E5 years, Pu-243 - 4.956 hours, Pu-244 - 8.26E7 years

Potassium: K-40 - 1.27E9 Years, K-42 - 12.36 Hours, K-43 - 22.6 hours,

Radium: Ra-223 - 11.434 Days, Ra-224 - 3.66 Days, Ra-225 - 14.8 days, Ra-226 - 1600 years, Ra-228 - 5.75 years

Rubidium: Rb-86 - 18.66 Days, Rb-87 - 4.7E10 Years, Rb-88 - 17.8 Minutes, Rb-89 - 15.2 minutes

Selenium: Se-75 - 119.78 Days, Se-79 - 65000 years

Sodium: Na-22 - 2.602 Years, Na-24 - 15.00 hours

Strontium: Sr-85 - 64.84 Days, Sr-87m - 2.81 Hours, Sr-89 - 50.5 Days, Sr-90 - 29.12 years Sr-91 - 9.5 Hours, Sr-92 - 2.71 hours,

Sulfur: S-35 - 87.44 days

Thallium: Tl-201 - 73.06 hours, Tl-207 - 4.77 minutes, Tl-208 - 3.07 minutes, Tl-209 - 2.20 minutes

Thorium: Th-227 - 18.718 Days, Th-228 - 1.913 Years, Th-229 - 7340 years ,Th-230 - 7.7E4 years ,Th-231 - 25.52 hours ,Th-232 - 1.41E10 years ,Th-234 - 24.10 days

Tin: Sn-119m - 293.1 days, Sn-123 - 129.2 days, Sn-125 - 9.64 days, Sn-126 - 1.0E5 years

Tungsten; W-181 - 121.2 days, W-185 - 75.1 days, W-187 - 23.9 hours

Uranium: U-232 - 72 Years, U-233 - 1.59E5 years, U-234 - 2.445E5 years, U-235 - 7.03E8 years, U-236 - 2.34E7 years, U-237 - 6.75 days, U-238 - 4.47E9 years,

Vanadium: V-48 - 16.238 days

Xenon: Xe-131m - 11.9 days, Xe-133 - 5.245 days, Xe-133m - 2.188 days, Xe-135 - 9.09 hours, Xe-135m - 15.29 minutes, Xe-138 - 14.17 minutes

Zinc: Zn-65 - 243.9 days, Zn-69 - 57 minutes,



Lesson-30

Occurrence of Radio Nuclides in Milk and Milk products

30.1 INTRODUCTION

Utilization of nuclear energy for beneficial purpose has become more common in the recent past. Radio nuclides are often secreted into the milk by the consumption of contaminated feed and water and are ultimately found in milk and milk products.

30.2 SOURCE OF RADIO NUCLIDES IN MILK

There are different pathways through which radionuclides enter the human body. A general path of such contamination could be diagrammatically represented as below

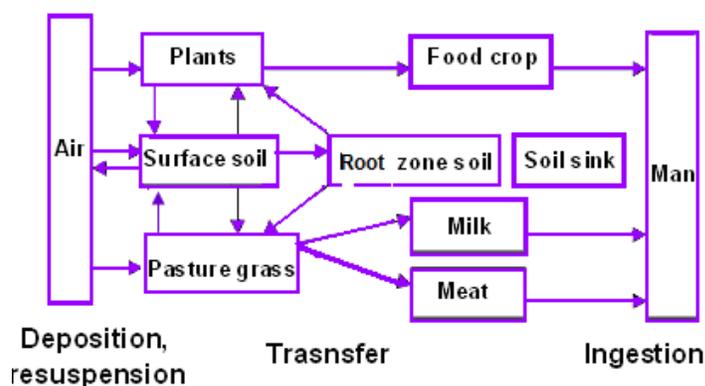


Fig.30.1 Typical set of path ways through the environment from radiation

Greatest contamination would occur during nuclear fallout periods when cows graze ingesting grass from contaminated soil. Even if they are kept indoors, contamination of milk may occur by inhalation of radionuclides or ingesting them through contaminated drinking water and feed. Milk from goat and sheep, should be checked periodically over a longer period because of their ranch system of grazing.

Environmental radionuclide contamination is primarily man made. Nuclear explosions, manufacture and processing of nuclear fuel, accidents and or operation of nuclear reactors, increasing use of nuclear

and disposal of radioactive waste will discharge radionuclide elements into the biosphere. This will further result in the contaminate the natural resources like soil, plants and water.

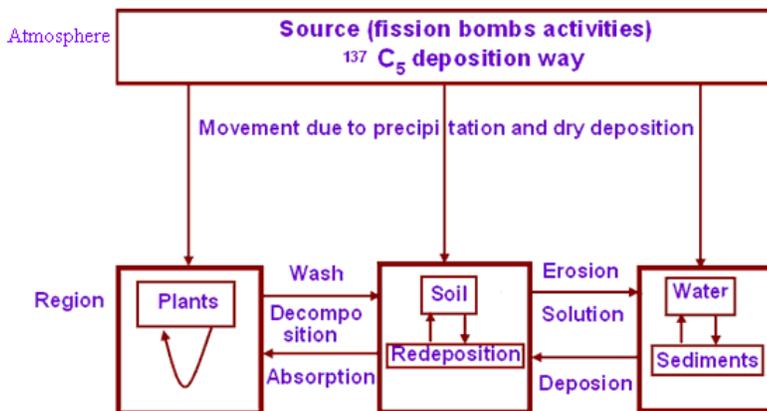


Fig.30.2 ^{137}Cs incorporation cycle diagram in the nature

Fig. 30.2 diagrammatically shows the incorporation of ^{137}Cs in the nature. Vegetation when decomposed will result in the entry of radionuclides into the soil. Erosion of soil by rain, rivers etc., would result in the contamination of water. Sediments from contaminated water will in turn contaminate the soil. The plants growing in such a soil absorb the radionuclides.

30.3 COMMON RADIONUCLIDES FOUND IN MILK

The most important radionuclides associated to internal radiation exposure (due to ingestion of contaminated water and food by the animal) and the contamination of the environment, are ^{134}Cs , ^{137}Cs , $^{137\text{m}}\text{Ba}$, ^{131}I , ^{89}Sr , ^{90}Sr , ^{238}Pu , ^{239}Pu , ^{241}Am , ^{242}Cm and tritium. With regard to milk, radionuclides of specific interest are ^{134}Cs , ^{137}Cs , ^{131}I , ^{89}Sr , ^{90}Sr . As they decay at different rates, the doses from these elements and other radionuclides are delivered in different manners.

Table.30.1 Distribution of Radio Nuclides in Milk and Their Half Life

Radio nuclide	Physical half life*	Biological half life**	Distribution
⁸⁹ Sr	52 Days	1-50 years	80% in casein micelles
⁹⁰ Sr	28 years	1-50 years	80% in casein micelles
¹³¹ I	8 days	100 days	Serum
¹³³ I	21 hrs		
¹³⁷ Cs	33 years	230 days	Serum
¹⁴⁰ Ba	13 days	< 3 years	plasma

(Source: Dairy chemistry and Physics, Walstra and Jenness, 1984)

* Physical half life is the period needed to reduce the concentration / amount of radioactive emission by an isotope to half of its original level, outside the biological system (i.e *in-vitro*).

** Biological half life is the time taken for a radioactive isotope to be reduced to half of the amount in the body of after ingestion by an animal/ person.

Strontium accumulates in bone and remains there for a long time.⁹⁰Sr uptake causes a prolonged exposure to harmful radiation as it has a long physical half life. It is distributed in milk in much similar way to calcium. However, strontium phosphate in milk is less soluble than calcium phosphate and a greater proportion of it associated with the casein micelles.

Barium behaves more nearly like calcium. Iodine accumulates in the thyroid gland where it attains high concentration and radioactive isotopes of ¹³¹I are considered hazardous as they produce intense radiation. Small portions of ¹³¹I are being strongly bound to protein while about 2% of it is found in the fat globules. Cesium chemically behaves like Na⁺ and K⁺ ions.

Atomic Energy Regulation Board (AERB) standards for radio activity are based on an annual exposure of 10 mrem when all items of food are contaminated to the recommended levels and intake is throughout the year. From milk and milk products alone exposure would be 1.6MR/year which is quite small compared to the natural and other radiation exposure that is received during the day to day activities.

Radio nuclides in milk and milk products observed in different countries are invariably lower than that of recommended limits in those countries. Presence of radio nuclides in milk and milk products varies from country to country.

^{40}K is some what more hazardous due to higher energy of radiation compared to ^{137}Cs . Natural radioactivity due to ^{40}K present in milk powder is in the range of 600 – 800 Bq/kg while in liquid milk in the range of 30-40 Bq / l in Indian milk and 50-80 Bq/l in foreign milk. It has also been reported that cow milk contains 44 Bq/l and buffalo milk contains 38Bq/l. Since potassium salts are very soluble ^{40}K being retained in liquid phase in the preparation of butter and it contains only 1.3Bq/kg. Cheddar cheese is reported to have 41Bq/kg of ^{40}K .

The ratio of $^{90}\text{Sr} / ^{137}\text{Cs}$ in European milk is 1.8 while it is 0.5 – 1.58 in Indian milk. The mean value for ^{90}Sr is reported to be 3.9pCi / l

In India ^{137}Cs has been reported to be 0.02 Bq/ l in milk and 0.6 Bq/l kg in milk powder which is far below than the prescribed levels of 30Bq/l in milk and 210 Bq/l kg in milk powder. Most of the dairy products in general contain ^{137}Cs to the extent of 40Bq/1 kg. ^{131}I present in milk is to an extent of 20 Bq/l.



Lesson-31

Spectrum of Electromagnetic Radiation

31.1 INTRODUCTION

Human eye perceives the difference in the colour of various compounds and things around them e.g. quinone is yellow; chlorophyll is green; 2,4-dinitrophenylhydrazone derivatives of aldehydes and ketones range in color from bright yellow to deep red, aspirin is colourless. So human eye is functioning like a spectrophotometer analysing the light reflected from the surface of solid or passing through a liquid. Sunlight seen as single white colour is in fact composed of a wide range of radiation with different wavelengths in the ultraviolet, visible and infrared portions of the spectrum. The electromagnetic spectrum of an object is the characteristic distribution of electromagnetic radiation emitted or absorbed by that particular object. In principle this spectrum is infinite and is continuous.

31.2 CLASSIFICATION OF ELECTROMAGNETIC RADIATION

When sunrays are passed through a prism, the rays bend in accordance to their wave lengths. Electromagnetic radiation such as visible light is commonly treated as a wave phenomenon, characterized by a wavelength or frequency. Wavelength is defined as distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or nanometers (10^{-9} meters). Frequency is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz).

Generally electromagnetic radiation is classified on basis of its wave length. Visible wavelengths cover a range from approximately 400 to 800 nm. The spectrum along with the wave length for the visible light is shown in Fig.31.1.

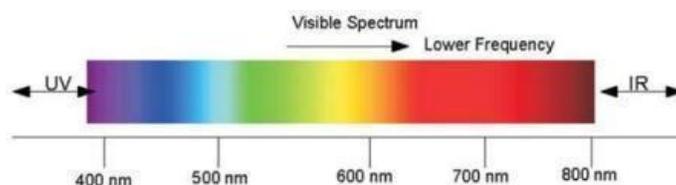


Fig.31.1 Wavelength in nm -visible spectrum

It could be observed that red colour has the longest wavelength while violet has the shortest wavelength, while the remaining colours are in decreasing order of wavelengths. People perceive this radiation as the visible light, ultraviolet (UV) rays, x-rays and gamma rays. The behaviour of electromagnetic radiation depends on its wavelength and on the amount of energy it carries with when it interacts with single atoms and molecules. This energy is measured per quantum (photon).

31.3 ELECTROMAGNETIC SPECTRUM

Spectrum of electromagnetic radiation is shown in Fig. 31.2 and presented in Table 31.1

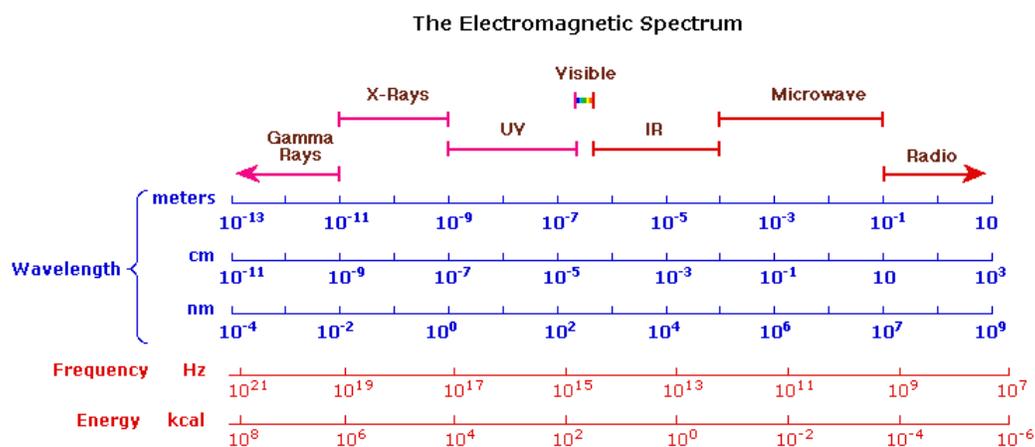


Fig 31.2 Spectrum of electromagnetic radiation

Electromagnetic spectrum can broadly be grouped into non-ionizing and ionizing radiation. The non ionizing radiation when obtained by low induced current is non thermal while high induced current generates heat which is effectively used in the microwave ovens. Photo electric excitation is used for producing photochemical effect.

Table.31.1 Regions of the Electromagnetic Spectrum

The Electromagnetic Spectrum			
Wave Type	Wavelength (m)	Frequency (Hz)	Energy (J)
Radio waves	> 0.1	< 3×10^9	< 2×10^{-24}
Microwaves	10^{-3} - 0.1	3×10^9 - 3×10^{11}	2×10^{-24} - 2×10^{-22}
Terahertz waves	10^{-3} - 10^{-4}	3×10^{11} - 3×10^{12}	2×10^{-22} - 2×10^{-21}
Infrared	7×10^{-7} - 10^{-3}	3×10^{11} - 4×10^{14}	2×10^{-22} - 3×10^{-19}
Optical(visible light)	4×10^{-7} - 7×10^{-7}	4×10^{14} - 7.5×10^{14}	3×10^{-19} - 5×10^{-19}
Ultraviolet	10^{-8} - 4×10^{-7}	7.5×10^{14} - 3×10^{16}	5×10^{-19} - 2×10^{-17}
X-rays	10^{-11} - 10^{-8}	3×10^{16} - 3×10^{19}	2×10^{-17} - 2×10^{-14}
Gamma rays	< 10^{-11}	> 3×10^{19}	> 2×10^{-14}

Source: <http://csep10.phys.utk.edu/astr162/lect/light/spectrum.html>

The ionizing radiation is more useful in medical field. Rays generated during ionization produce several effects such as damage to the DNA and also breaking of the bonds which are of immense help in treatment of cancer, correcting birth defects and also causing mutation.

In non-ionizing radiation, the extremely low frequency rays and very low frequency are included. These are generally referred as radio waves. The next range of frequency is categorized as microwave, which is followed by infra red rays. The visible range is forming the next group of rays. The ultra violet rays, X-rays and gama rays are considered under the category of ionizing radiation.

31.4 LAMBERT-BEER LAW

This law relates to the absorption of light and to the properties of material through which the light travels. Transmittance is the term used to the amount of light penetrating a solution. It is expressed as the ratio between the intensity of transmitted light (I_t) to the intensity of initial light of light beam (I_0).

$$T = I_t / I_0$$

Where: T - Transmittance

I_t - Intensity of the transmitted light

I_0 - Intensity of the initial light beam

The law states that there is a logarithmic dependence between transmission (or transmissivity) of light through a substance, T , and the product of absorption coefficient of substance, a , and the distance the light travels through the material (i.e. the path length), ℓ . The absorption coefficient can, in turn, be written as a product of either a molar absorptivity of the absorber, ϵ , and the concentration c of absorbing species in the material, or an absorption cross section, σ , and the (number) density N' of absorbers.

For liquids, these relations are usually written as:

$$T = \frac{I}{I_0} = 10^{-a\ell} = 10^{-\epsilon lc}$$

The transmission (or transmissivity) is expressed in terms of an absorbance which, for liquids, is defined as

$$A = -\ln\left(\frac{I}{I_0}\right)$$

Thus, if path length and molar absorptivity (or the absorption cross section) is known and if the absorbance is measured, then the concentration of the substance (or the number density of absorbers) can be deduced. If the concentration is expressed as a mole fraction i.e. a dimensionless fraction, the molar absorptivity (ϵ) takes the same dimension as the absorption coefficient, i.e. reciprocal length (e.g. m^{-1}). However, if the concentration is expressed in moles per unit volume, the molar absorptivity (ϵ) is used in $\text{L mol}^{-1} \text{cm}^{-1}$, or sometimes in converted SI units of $\text{m}^2 \text{mol}^{-1}$. The absorption coefficient a' is one of many ways to describe the absorption of electromagnetic waves.

31.5 MASS SPECTROMETRY

The mass spectrometer is an instrument which can measure the masses and relative concentrations of atoms and molecules. It makes use of the basic magnetic force on a moving charged particle. This is an analytical technique that measures the mass-to-charge ratio of charged particles. This technique is useful

for the determination of mass of particles, elemental composition of a sample or a molecule, in finding out the chemical structure of molecules such as peptides and other chemical compounds. Main principle of this technique consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios. Mass spectrometer is the instrument used for this analytical technique. Mass spectrophotometer has three associated components. They are

- **The ion source:** This component of the instrument will help in ionization of the sample in which an electron is removed from cations.
- **The Mass analyser:** This component of the instrument will sort out ions and separate them according to their mass and charge
- **The detector :** The sorted and separated ions are then measured and the results are recorded

The mass spectroscopy is useful in (1) measuring the size of nano particles in the absence of sophisticated transmission electron microscopy or x-ray diffraction; (2) detecting toxins in pharmaceuticals, biotechnology, and other foods and (3) can identify multiple compounds of pesticides at once that enter the food supply.

31.6 NUCLEAR MAGNETIC RESONANCE (NMR)

Nuclear magnetic resonance (NMR) is a physical phenomenon in which magnetic nuclei in a magnetic field absorb and re-emit electromagnetic radiation. Nuclear magnetic resonance spectroscopy is a research technique which is used for determining physical and chemical properties of atoms or the molecules of a compound. It also gives information about the structure, dynamics, reaction state, and chemical environment of the molecules. The technique is based on the nuclear magnetic resonance of the atomic nuclei in the molecules. In the scientific field this technique is being used to investigate properties of the organic molecules. Samples for which this technique is used range from small compounds with one dimensional protons or carbon-13 to large protein or nucleic acids using 3 or 4 dimensional techniques. This technique provides a wide range of information for a large number of samples including solutions and solids.

NMR spectroscopy is employed in a wide range of food safety areas broadly aimed at averting significant chemical, biological or microbiological threats to the food chain. This technique is more useful about new

or immersing threats. Under such circumstances the analysis of specific compounds using traditional methods is time-consuming, expensive and often unsuccessful in reaching the goal of controlling risk. NMR is focussed on the development of non-targeted methods that are able to rapidly determine the presence of unspecified hazards.

NMR spectroscopy has also been used to study the effect of microbes on food composition. Applications include monitoring maturation processes, shelf-life determination and the measurement of freshness like storage history of a food product may be determined by considering the biochemical composition.

NMR methodologies can be used for food authentication i.e for the verification of geographical and botanical origin, and for the verification of labelling claims such as “organic” and those relating to more direct health implications including the characterisation of pronutrients.

NMR spectroscopy increasingly is playing a role in understanding a range of activities, for example, assessing ingredient purity, characterising functional ingredients and investigating the effect of novel processes on final product composition.



Lesson-32

Visible and Ultraviolet Spectrophotometers

32.1 INTRODUCTION

The electromagnetic radiation and its spectra are of immense value in developing instruments useful for the analysis of various compounds. Development of spectrophotometer is an outcome of the study of this spectrum. The absorption or reflectance tested using the visible light or near Ultra violet (UV) and Near Infrared (NIR) is referred as absorption spectroscopy or reflectance spectroscopy. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy. In fluorescence transition from excited state to ground state is measured, whereas in absorption transition from the ground state to the excited state is measured.

32.2 PRINCIPLE OF SPECTROPHOTOMETER

Molecules containing π -electrons or non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The energetically most favorable $\pi \rightarrow \pi^*$ excitation occurs from the highest energy bonding pi-orbital (HOMO) to the lowest energy antibonding pi-orbital (LUMO). The more easily the electrons excited the higher wavelength of light it can absorb.

Accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum are made to understand why some compounds are colored and others are not and also to determine the relationship of conjugation in the compounds to color. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both near ultraviolet and visible portions of the spectrum.

The visible region of the spectrum comprises of photon energies of 36 to 72 kcal/mole, and in the near ultraviolet region this energy increases to 143 kcal/mole. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is rarely used as a routine tool for structural analysis. The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital.

Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy".

Different compounds may have different absorption maxima and absorbance. Intensely absorbing compounds must be examined in dilute solutions, so that significant light energy is received by the detector, and this requires the use of completely transparent (non-absorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane. Solvents having double or triple bonds, or heavy atoms (e.g. S, Br & I) are generally avoided. Because the absorbance of a sample will be proportional to its molar concentration in the cuvette, a corrected absorption value, known as the molar absorptivity, is used when comparing the spectra of different compounds.

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown Fig 32.1. Since isoprene is colorless, it does not absorb light in the visible part of the spectrum and this region is not displayed on the graph. Absorbance usually ranges from 0 (no absorption) to 1 (99% absorption), and is precisely defined in context with spectrometer operation. Because the absorbance of a sample will be proportional to the number of absorbing molecules in spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). Molar absorptivity (ϵ) is defined as:

Molar Absorptivity, $\epsilon = A / c l$

(where A = absorbance, c = sample concentration in moles/liter & l = length of light path through the sample in cm.)

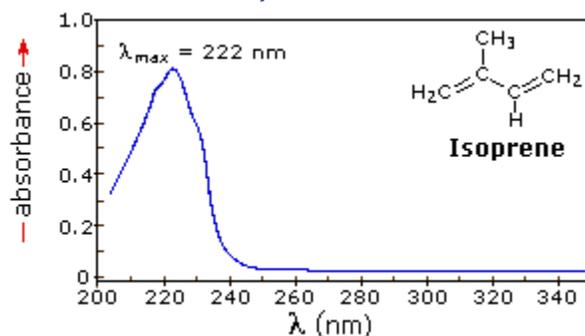


Fig.32.1 UV-visible spectrum of isoprene showing maximum absorption at 222 nm.

(Source: www.pharmaxchange.info)

The UV visible spectrum for isoprene Fig 32.1 shows maximum absorptivity (λ max) of 222nm, and as there is no absorbance in the visible spectrum, the compound will not have any colour. Absorption of light in 200 to 800 nm region by molecular moieties is due to the function of pi-electron and hetero atoms having non-bonding valence-shell electron pairs. Such light absorbing groups are referred as chromophores. The oxygen non-bonding electrons in alcohols and ethers do not give rise to absorption above 160 nm. Consequently, pure alcohol and ether solvents may be used for spectroscopic studies. Though UV-Visible spectroscopy can detect the presence of these chromophores in a molecule, most instruments cannot provide absorption data for wavelengths below 200nm. Conjugation will help in moving the absorption maxima to longer wavelength as observed in the isoprene spectra. By UV-visible spectra it is possible to identify these structural features.

Molar absorptivities may be very large for strongly absorbing chromophores (>10,000) and very small if absorption is weak (10 to 100). The magnitude of ϵ reflects both the size of the chromophore and probability that light of a given wavelength will be absorbed when it strikes the chromophore. The terms used to define shifts in absorption are shown in Table 32.1. Thus extending conjugation generally results in bathochromic and hyperchromic shifts in absorption. The appearance of several absorption peaks or shoulders for a given chromophore is common for highly conjugated systems, and is often solvent dependent. This fine structure reflects not only different conformations that conjugated systems may assume, but also electronic transitions between different vibrational energy levels possible for each

electronic state. Vibrational fine structure of this kind is most pronounced in vapor phase spectra, and is increasingly broadened and obscured in solution as the solvent is changed from hexane to methanol.

Table 32.1 Terminology for Absorption Shifts

Nature of Shift	Descriptive Term
To longer wavelength	Bathochromic
To shorter wavelength	Hypsochromic
To greater absorbance	Hyperchromic
To lower absorbance	Hypochromic

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

32.3 MILK AND DAIRY APPLICATIONS

There is increasing awareness among consumers about the quality and safety of milk and milk products. The concentrations of constituents such as water, protein, fat and carbohydrate can in principle be determined using classical absorption spectroscopy. Routine analytical methods used for measuring various milk components are sample destructive, expensive and time & labour intensive. Most commonly used instrument for milk analysis is Milko-scan which is based on the infra red spectroscopy.

The analysis of water by near infrared spectroscopy (NIRS) was the first successful application of this rapid technology. NIR spectroscopy is used routinely for the compositional, functional and sensory analysis of food ingredients, process intermediates and final products. Studies carried on NIR spectroscopy have made it possible to analyze milk for adulteration and for several constituents like fat, protein and lactose etc. The greatest advantage of NIR spectroscopy is that it is rapid and accurate. This

technique can be used for analyzing various dairy products like milk powders, whey, cheese etc. An additional advantage of NIR spectroscopy is that it could be used online in the process of milking for effective farm management.

Atomic absorptive spectroscopy is helpful in the study of essential micronutrients such as iodine content in infant milk formulae and milk powder samples.

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