Chapter II

THEORETICAL ASPECTS

This chapter deals with theoretical aspects and various methods of measurements of surface tension and viscosity. In this chapter, theoretical aspect of electrical conductivity and spectroscopic studies such as vibrational, rotational and vibrational-rotational are also discussed. A brief theory of urine albumin, creatinine, bilirubin, glucose and urea are discussed.
The physical properties of a system are those properties which can be investigated without any chemical changes in it. These properties are divided into two types. i) Additive property. ii) Constitutive property.

An additive property is a sum of corresponding properties of the system, for example molar mass, specific gravity etc. The total mass of a system is the sum of the constituents of the system. The constituent property depends on the arrangement of constituents of the system, for example refractive index, surface tension, viscosity etc.

The physico-chemical analysis of a system provides information concerning the composition of the system and behavior of its molecules. To obtain an insight into the problem of structure determination the techniques such as molar refractive index, optical activity, dipole moment, analysis of emission and absorption spectra are required. The spectroscopic techniques UV-VIS, Infrared, Raman, NMR and ESR techniques are widely used for bio-physical substances.

2.1 Theory of Surface Tension

The surface tension is a property of liquid that has no counterpart in solids or gases. It is a property of surface of liquid, causes the surface portion of liquid to be attracted to another surface. The surface tension is caused by cohesion. The cohesive forces among the liquid molecules are responsible for surface tension. A molecule in the bulk of a liquid is equally attracted and pulled by the surrounding molecules in all directions results a net zero force.
A molecule of the liquid at its surface does not have other like molecules on all sides of it. Therefore, it coheres more strongly to those directly associated with them on the surface.

Fig 2.1 Force acting on two molecules of liquid

Hence the molecule of the liquid at its surface is pulled sideways and downwards, but there is no molecule above it to balance the downward pull. As a result, the molecules at the surface are subjected to a force acting inwards at right angles to the surface. So the surface of the liquid is always in a tension and behaves like a stretched membrane. This property of a liquid is known as surface tension. Another way to view this is that a molecule which is in contact with a neighbour will be in a lower state of energy compared to that which does not have neighbours. All the molecules which are present in the interior of the liquid will have a large neighbour than those present at the surface or boundary. So the boundary or surface molecule will be in a higher state of energy. If the curvature on the surface of the liquid has a greater area then it has a higher energy. So in order to keep the
surface energy low, the surface will be pushed back against the curvature to minimise its gravitational potential energy.

The surface of a liquid is defined as the tangential force acting on unit length of a line drawn on the surface of a liquid, tending to pull it apart. Also it can be defined as the force acting at right angles along the surface of liquid per unit length. It is expressed in dynes/Cm (or) Newton /meter. 1 dyne/cm = 1 m N/m

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface tension (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>28.9</td>
</tr>
<tr>
<td>Acetone</td>
<td>23.7</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>22.3</td>
</tr>
<tr>
<td>Carbon tetra chloride</td>
<td>27.0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>63.4</td>
</tr>
<tr>
<td>Methyl alcohol</td>
<td>22.6</td>
</tr>
<tr>
<td>Normal Human urine</td>
<td>68.0</td>
</tr>
</tbody>
</table>

**Angle of contact:**

The surface of any liquid is an interface between that liquid and some other medium, and hence the surface tension is not a property of liquid alone, but a property of liquid’s interface with other medium. If a liquid is in some container, then besides the liquid-air interface at its top surface, there is an interface between the walls of container and liquid. The surface tension between the liquid and air is different and greater than that of between liquid and walls of the container. As the surface of liquid and container meets, their geometry is such that
all the forces are balanced and they form a contact angle, which is defined as the tangent to the surface makes with the solid surface.

![Diagram of liquid contact angle](image)

**Fig 2.2 Angle of contact**

The rise and fall of a liquid in a container depends on the interaction between the liquid surface and the walls of the container. If the intermolecular forces between liquid molecules are weaker than the force between the liquid and solid surface, the liquid will rise and wet the solid surfaces. If the solid-liquid interactions are weaker than intermolecular forces in the liquid its level will fall. The angle between the tangent to the liquid surface at the point of contact and the solid surface inside the liquid is known as Angle of Contact ‘$\theta$’ for the pair of liquid and solid surface. It can have any value from 0 to 180.

When a liquid is poured in a container, the various forces acts are the liquid-air interface tension force $F_{la}$, the solid-air interface force $F_{sa}$ and liquid-solid interface force $F_{ls}$. If the cohesive forces between the liquid molecules are greater than the adhesive forces between liquid-solid containers, then at point of contact both the vertical and horizontal forces will be exactly cancel each other. The horizontal component of force between liquid-air interfaces $F_{la} \sin\theta$ is cancelled.
by the adhesive force. The difference of forces between $F_{ls} - F_{sa}$ is equal to vertical component of $F_{la}$.  
\[ F_{ls} - F_{sa} = -F_{la} \cos \theta \]

As these forces are directly proportional to surface tension then their surface tensions  
\[ \gamma_{ls} - \gamma_{sa} = -\gamma_{la} \cos \theta \]

And the angle of contact is more than $90^\circ$ an obtuse angle, the difference between liquid-solid and solid-air surface tension is less than the liquid–air surface tension and both are positive  
\[ \gamma_{la} > \gamma_{ls} - \gamma_{sa} > 0 \]

and if the adhesive forces between the liquid molecules and solid container are greater than the cohesive forces between the liquid molecules then, the angle of contact is less than 90. And the liquid air surface tension is positive, while the difference between the liquid-solid surface tension $\gamma_{la}$ and solid–air surface tension is negative. The angle of contact is less than $90^\circ$. 

Fig 2.3 Forces acting on the liquid in a container
2.1.1 Various Methods for Measurement of Surface Tension

There are various methods for the measurement of surface tension of liquids. These methods depend on the nature of liquid being measured; the condition under which it being measured and the stability of surface when it is deformed and the temperature. The various methods that are being used in the laboratory are:

1. Capillary rise method: When the capillary tube is immersed in the liquid, the height at which the liquid rise in the capillary depends on the surface tension of the liquid.

2. Spinning drop method: The diameter of spinning drop is related to the surface tension. This technique is suitable for measuring low interfacial tensions.

3. Wilhelmy plate method: In this method a vertical plate of known perimeter is attached to a balance and the force due to wetting is measured, which depends on the surface tension. This method ideal to check surface tension of liquids over long intervals.

4. Pendent drop method: This method can used at higher temperature and pressure and the surface tension and interfacial tension can be measured with this method. The shape of the falling drop is analyzed in this technique.

5. Drop volume method: In this method liquid of one density is pumped in to second liquid of different density and the between drops is measured. This method is suitable for determining interfacial tension as a function of interface age.
6. Stalagmometer method: With stalagmometer the surface tension can measured with two techniques: i) drop weight method ii) drop number method.

7. Du Noüy ring detachment method: This is a commonly used method for the measurement of surface or interfacial tension of liquids, in which the wetting properties of the surface have a little effect on the measuring technique.

The simple and economical generally used methods in the laboratory are:

2.1.2 Stalagmometer method

The stalagmometer consist of a bulbed capillary tube having marks on capillary above and below the bulb. The tube is cleaned with chromic acid then with distilled water and dried and filled with the liquid for which surface tension is to found by sucking with rubber tube from one end of the capillary. A drop of a liquid is allowed to form at the end of capillary tube. The drop is supported by upward force of surface tension acting at the outer circumference of the tube, the weight of the ‘mg’ (where ‘m’ is mass of the drop and ‘g’ is acceleration due to gravity) pull it downward. When the two forces are balanced, the drop breaks. At the point of break, \( mg = 2 \pi r \gamma \), where ‘r’ is the radius of the capillary.

i) Drop weight method

This method generally used for the comparing of the surface tension of a liquid with another of which the absolute value of surface tension is already known. After cleaning the tube, it is filled with the liquid
whose surface tension is to be found up to a mark above the bulb by sucking the liquid from one end of the tube. A weighing tube is kept under the stalagmometer and about 20 drops of the liquid are dropped in to the weighing tube. The rate at which drops fall are adjusted in such a way that there are 20 drops falls per minute. The weight of each drop is found. The apparatus is again cleaned and dried, and filled with other reference liquid say water and weight of one drop is determined as before, then

\[ m_1 \, g = 2 \pi r \, \gamma_1 \]
\[ m_2 \, g = 2 \pi r \, \gamma_2 \]

Therefore,

\[ \frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} \]

If the surface tension of the reference liquid is known then that of other liquid can be found.

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Fig 2.4 Stalagmometer

Fig 2.5 A drop forming from a tube of radius \( r \)
ii) Drop number method

In this case, the stalagmometer is filled up to the mark “A” with a liquid whose surface tension has to be found. The liquid is allowed to flow until the lower mark ‘B’ below the bulb is reached. The number of drops \( (n_1) \) is counted. The purpose of small graduated portion of the tube is to enable fraction of a drop to judge. The same procedure is repeated with other reference liquid for example distilled water for number of drops \( (n_2) \). The average weight of the drop of liquids is given by

\[
W_1 = \frac{m_1 g}{n_1} = \frac{V \rho_1 g}{n_1}
\]
and
\[
W_2 = \frac{m_2 g}{n_2} = \frac{V \rho_2 g}{n_2}
\]

Where \( n_1 \) is the number of drops of one liquid in volume \( V \), \( n_2 \) is the number of drops of reference liquid of volume \( V \). \( \rho_1 \) and \( \rho_2 \) are their densities, and \( g \) is acceleration due to gravity. Dividing the above equations

\[
\frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2} = \frac{(V/n_1) \rho_1 g}{(V/n_2) \rho_2 g}
\]

Therefore,

\[
\frac{\gamma_1}{\gamma_2} = \frac{n_2 \rho_1}{n_1 \rho_2}
\]

If the surface tension of reference liquid say water is known, that of the liquid can be found.

1. **Du Noüy ring detachment method:**

This technique was proposed by French Physicist Pierre Lecomte du Noüy. This method involves slowly lifting a ring made up of platinum from the surface of the liquid, whose surface tension is to be found. The force \( (F) \) required to lift the ring is exactly equal to the downward pull due to surface tension.
The apparatus consist of a long torsion wire; one end is fixed while other end is attached to a knob carrying a pointer. The pointer moves on a graduated fixed scale. The scale has to be calibrated by taking different weights on the beam and noting the scale reading when it is lifted from horizontal position.

Fig 2.6 du Nouy platinum ring with a suspending hook

Fig 2.7 du Nouy Tensiometer
The liquid whose surface tension is to be determined is kept in a watch glass so that the platinum ring just touches the surface. The knob of the torsion wire is then slowly turned till the ring is just detached from the surface. The reading shown by the pointer on the scale gives the force ‘F’ required to detach the ring from the surface. If R is the radius of the, and since the liquid is in contact with both the inside and outside of the ring, there by \( F = 2(2 \pi r \gamma) \).

Therefore, the surface tension \( \gamma = \frac{F}{4 \pi R} \)

### 2.1.3 Maximum Bubble Pressure Method

In this method gas or air pressure is applied slowly through a capillary tube immersed in a liquid whose surface tension is to be found. Air bubbles are formed at the end of the capillary at constant rate. Slowly the bubble grows and become hemispherical and then it breaks away when the pressure is recorded by manometer is noted, which is the maximum pressure required to make a bubble at the end of capillary. At the moment of breaking, the force due to this maximum pressure ‘P’ equals to the sum of forces due to hydrostatic opposing pressure ‘\( P_h \)’ and the surface tension ‘\( \gamma \)’ at the circumference of the capillary.

If ‘\( \rho \)’ is the density of the liquid, ‘\( r \)’ is the radius of the capillary tube and ‘\( h \)’ is the depth it is immersed, then the force due to maximum pressure ‘P’ is \( P \pi \rho r^2 \), that due to hydrostatic opposing pressure ‘\( P_h \)’ is \( P_h \pi r^2 \) and the force due to surface tension is equal to \( 2 \pi r \gamma \).

Therefore, \( P \pi \rho r^2 = P_h \pi r^2 + 2 \pi r \gamma \)
\[ P = P_h + 2 \gamma / r \]

or \[ P = h \rho g + 2 \gamma / r \]

Knowing the values of \( P, h, \rho \) and \( r \), the surface tension can be found.

2.2 Theory of Electrical Conductivity

The conductors obey Ohm’s law. The current \( i = E / R \), where ‘\( E \)’ is the e.m.f applied and ‘\( R \)’ is the resistance, which is directly proportional to length ‘\( l \)’ and inversely to the area of cross-section ‘\( A \)’. The resistance \( R = \rho l / A \) where ‘\( \rho \)’ is resistivity or specific resistance, which is defined as the resistance of a conductor of unit length and unit area of cross-section, or it is the resistance of one centimeter cube of a material.
The specific conductance or conductivity \( \kappa \) of a conductor is defined as the reciprocal of specific resistance \( \kappa = 1/\rho = \ell/(R \times A) \). The conductance \( L \) is defined as the reciprocal of resistance \( L=1/R= \kappa A/\ell \). The specific conductance is a conductance of a material of a unit length and unit area of cross-section.

Like metals the solutions conduct electrical current through them by the migration of ions under the influence of an electric field, obeying Ohm’s law. For an applied electromotive force \( E \), maintained constant but at a value that exceeds the decomposition voltage of the electrolyte, the current \( I \) flowing between the electrodes immersed in the electrolyte will vary inversely with the resistance of the electrolyte \( R \). The electrical conductance of a solution is a summation of contributions from all the ions present. It depends upon the number of ions per unit volume of the solution and upon the velocities with which these ions move under the influence of the applied electromotive force. As a solution of an electrolyte is diluted, the specific conductance \( \kappa \) will decrease and fewer ions to carry the electric current are present in each cubic centimeter of solution. As the conductivity is due to large number of ions, in order to express the ability of individual ions to conduct, a function called Equivalent conductance \( \Lambda \) can be used. The equivalent conductance of a volume of an electrolyte is defined as the conductance of a volume of a solution containing one gram equivalent of electrolyte placed between two parallel electrodes one centimeter apart. It is also defined as the...
conductance of an electrolyte obtained by dissolving one gram-equivalent of it in $V_{cc}$ volume of water.

The equivalent conductance is the product of specific conductance $\kappa$ and $'V'$ in cubic centimeters containing one gram-equivalent of electrolyte.

Equivalent conductance $\Lambda = \kappa \times V$

If an electrolytic solution containing $N$ grams-equivalent in 1000 cc of the solution, then the volume of solution containing 1 gram equivalent will be $1000/N$

Therefore, $\Lambda = \kappa \times 1000/N$

The unit for equivalent conductivity is ohm$^{-1}$ cm$^2$ eqvt (or) siemen-cm$^2$.

**Effect of dilution**

The equivalent conductivity of a solution depends on concentration and nature of electrolyte. The strong electrolytes are completely ionized at all concentrations or dilutions. The equivalent conductance of a strong electrolyte increases linearly with dilution, and that of weak electrolyte increases exponentially with dilution or square root of concentration. The increase in the equivalent conductance is not due to increase in the number of current carrying charged ions, but due to the decrease in force of attraction between the ions of opposite charges with decrease in concentration or increase in dilution. At higher concentration the force of attraction between the opposite charged ions increases, thereby it affects the speed and mean free path of ions with which they move towards electrodes. In strong
electrolytes as a solution becomes more dilute the equivalent conductance increases.

Weak electrolytes have low ionic concentrations, thereby interatomic forces are negligible. The increase in the equivalent conductance with increase in dilution is due to the number of current carrying ions. In case of weak electrolytes the degree of ionization at some temperature is ‘Λ’ is given by \( \alpha = \Lambda / \Lambda_\infty \) where ‘\( \Lambda_\infty \)’ is equivalent conductance when the ionization is complete.

The equivalent conductivity at infinite dilution is sum of equivalent conductivity due to anions and that due to cations called ionic conductance \( \Lambda_\infty = \lambda_+ + \lambda_- \).

**Effect of temperature**

The conductance of a solution increases by a small amount with rise in temperature. Generally the conductance of a given solution increases by 2 to 3 % for every degree rise in temperature. Since the conductivity depends on two factors i) the number of ions present in unit volume of solution ii) the speed with which these ions moves towards electrodes. As the ions in the solution remains same at a given temperature, the increase in conductivity with rise in temperature is due to the motion of ions. With rise in temperature the viscosity of the solvent decreases there by the ions moves freely and hence increases in the conductivity.

**Principle of Measurement of electrical conductivity**

Various types of cells have been designed and are in practice for the measurement of conductivity of a solution. The basic principle is
Wheatstone bridge, as the conductance of a solution amounts to the determination of its resistance. For this direct current cannot be used, as it cause polarization and hence changes the resistance of the solution.

Fig 2.10 Principle for Measurement of conductance

The apparatus consists of two arms. ‘C’ is a cell containing the electrolyte whose conductivity is to be found called conductivity cell, ‘Rs’ is a resistance box with which the resistance can be varied and ‘S’ is a source of alternating current. The current can be measured Galvanometer ‘G’. ‘AB’ is a uniform resistance slide wire on which contact point ‘X’ moves. The bridge is balanced by moving X on AB until no current or deflection in the galvanometer is zero. Hence the resistance of arm in the bridge are related by \( R_c/R_s = AX/BX \), where \( R_c \) is the resistance of the cell containing electrolyte and ‘Rs’ is the standard resistance. As the ratio of AX/BX can be found, the resistance of the cell can calculated.
The conductance cells are made up of Pyrex glass fitted with electrodes of platinum or gold, and to overcome the outside interfering effects, the electrodes are coated with a layer of finely divided platinum black. The distance between the electrodes is determined by the conductance of the solution to be measured. For low conducting solution the electrodes are fitted near to each other, and for highly conducting solution the electrodes are widely spaced.

**Cell Constant**

Since \( \kappa = 1 / \rho = \ell / (R \ A) \), the resistance of the solution in the conductance cell as measured by the Wheatstone bridge can be converted in to specific conductance by using above equation and

\[
\kappa = \frac{1}{R} \ (X) \quad \text{Where} \quad X = \frac{\ell}{A}
\]

is called Cell Constant.

\[
\text{Cell Constant} \ (X) = \frac{\text{Distance between the electrodes}}{\text{Area of the electrodes}}
\]

Therefore, Specific Conductance \( (\kappa) \) = \( \frac{1}{R} \) (Cell Constant)

\[
= (\text{Observed Conductance})(\text{Cell Constant})
\]
The actual measurement of ‘ℓ’ and ‘A’ for a given cell is difficult. So the cell constant can be determined by a solution of known specific conductance. Kcl solution can be used for this purpose. A given solution of Kcl of specific conductance κ is placed in the cell and its resistance is ‘R’ is measured. Then the cell constant = κ x R. If the resistance of unknown solution is ‘R’ then the specific conductance is given by

\[
\kappa = \frac{\text{Cell Constant}}{\text{Resistance}}
\]

And hence the equivalent conductance can be found by

\[
\Lambda = \kappa \left( \frac{1000}{N} \right)
\]

2.4 Theory of Viscosity

The viscosity is an inherent property of a liquid, which determines its resistance to shear stress. It measures the internal fluid friction which causes the resistance to flow of the liquid. The viscosity occurs due to cohesion and molecular movement between fluid layers.

A perfect or ideal fluid has no viscosity. But in practice there is no perfect fluid. All the fluids are compressible, and when they flow, they are capable of shearing stress on account of friction between the adjacent layers of the fluid. The temporary resistance offered by fluid to the shearing stress is called viscosity. A liquid may be considered as a pile of thin sheet or layers placed one on other. The velocity gradient between the two the adjacent layers is \((dv/dx)\), caused by a force acting parallel to upper layer in the direction of motion. In the absence of this force i.e. if there is no viscosity, this velocity gradient
is zero. This tangential force ‘F’ is proportional to velocity gradient and area.

\[ F \propto A \frac{dv}{dx} \]

\[ F = \eta A \frac{dv}{dx} \] is called Newton’s law of viscous flow.

where ‘\( \eta \)’ is called coefficient of viscosity

The viscosity is temperature dependent. In gases the viscosity increases with increasing temperature. In liquids the viscosity decreases with increasing temperature and decreasing pressure. The viscosity of a solution changes with concentration of the solution, it depends on the amount of cohesive and adhesive forces between the same kind of molecule and different kind of molecules respectively.

The cgs unit of viscosity is gm/cm/Sec it is called ‘poise’. Centipoise and mill poise are also used. 1 poise=0.1kg m\(^{-1}\) s\(^{-1}\)

**Poiseuille’s equation**

Let a liquid is flowing in a capillary of length ‘\( \ell \)’ and radius ‘\( r \)’. Let the velocity of liquid along the walls of the tube is zero and is maximum along the axis of the tube. The liquid can be considered as consist of different cylindrical layers. In each cylindrical shell the velocity of the liquid is same and one. Consider a cylindrical a layer of liquid of radius \( r = x \) and outer radius \( x+dx \), the velocity of liquid a distance from \( x \) from the axis of capillary is \( v \) and at a distance \( x+dx \) is \( v-dv \), the velocity gradient is \(-\frac{dv}{dx}\). The tangential viscous force according to Newton’s law of viscous flow \( F = -\eta A \frac{dv}{dx} \)
Fig 2.12 Liquid flowing through surface area A of thin a cylindrical shell of radius $x = r$

The surface area $A$ for the cylindrical cell of radius $x$ is $A = 2 \pi x \ell$

Therefore $F = - \eta 2\pi x \ell \frac{dv}{dx}$ For the forward push of the liquid is due to pressure difference 'p' at the end of capillary. At the steady state, there is no acceleration of the liquid and the viscous force is equal and opposite to the driving force.

$$- \eta 2\pi x \ell \frac{dv}{dx} = P\pi x$$

$$dv = -\frac{P}{\eta} \frac{dx}{2\ell}$$

The volume 'V' of liquid flowing through the tube per second is area of cross-section time velocity of liquid. The equation can be solved to as

$$\eta = \frac{P\ell^4 r}{8V}$$ called Pioseulle’s equation.

**Types of Viscometers**

Different types of viscometers, which are being used for the study of viscometric parameters of many biological liquids and non-biological fluids are Dead-load viscometers, Gas viscometers or constant pressure viscometers, Counter pressure viscometers, Constant Rate capillary viscometers, Dead-Load viscometers with variable loads,
Glass viscometers, Rotational viscometers, Falling cylinder viscometer, Ostwald viscometer.

**Dead-load viscometers**

In this type of viscometer a load mass $M$ is applied as constant load to a specimen placed in the reservoir of the apparatus, the load causes the specimen to be forced through a capillary under the cylinder. The shear stress $T_R$ is evaluated as

$$T_R = \frac{Mgr}{2\pi R^2 (L+mr)}$$

Where $R$ and $r$ are the radii of the cylinder and the capillary, respectively $m$ is the end correction, and “g” is acceleration due to gravity. This viscometer can be used for shear rates up to 100 s$^{-1}$, and of stresses $T_R$ up to $10^6$ Pa, and temperatures up to 350°C. The approximate limits with respect to the viscosity are $10^2$ to $10^5$ Pa. S. From one to two grams of the material are needed for tests. This technique is intended for a comparative technological appraisal of plastics. The volumetric flow rate is measured in this according to the displacement of piston. Knowing the applied load ($m$), flow rate ($Q$) and density ($d$) of the liquid, the coefficient of viscosity can be calculated using the relation,

$$\text{Viscosity (}\eta\text{)} = \frac{0.5Md}{Q}$$

**Glass Viscometers**

The glass viscometers are widely used for determination of viscosity of dilute solutions like polymers and low molecular weight liquids. There are a variety of dead-lead capillary viscometers used for measurement
of viscosity at low pressure. These viscometers are used to measure the viscosity of opaque, highly volatile liquids.

The general glass viscometers are Ostwald viscometer and Ubbelohde viscometer, both of this viscometer consists of a calibrated capillary and measuring reservoir of a fixed volume. In these viscometers the liquid flows through the capillary under action of liquid column of varying height, and consequently by the pressure difference. The time required to empty the reservoir is found by the marks on the capillary. The mean pressure $p$ can be found by $P = (h_1-h_2)\rho g/\ln(h_1/h_2)$ Where $h_1$ and $h_2$ are the initial and final heights of the liquid column $\rho$ is density of the liquid and $g$ is acceleration due to gravity.

![Fig 2.13 Different types of glass viscometers](image)

where, A, B and C - Marks, M - Measuring reservoir.

The viscosity $\eta$ is proportional to the density $\rho$ and time $t_0$ the time required for the flow of a liquid through calibrated volume.
\[ \eta \propto \rho \ t_0 \]
\[ \eta = C \rho \ t_0 \]

Where ‘C’ is constant of proportionality depends on the apparatus, it can be determined by the calibration of the apparatus. The viscosities of two liquids \( \eta_1 \) and \( \eta_1 \) can be compared as \( \eta_1/\eta_2 = \rho_1 t_2/\rho_2 t_2 \), where \( \rho_1 \) and \( \rho_2 \) are their viscosities and \( t_1 \) and \( t_2 \) are their time of flow through the capillary.

**Falling ball viscometers**

The Stokes law is the basis for the falling ball viscometer, in which the fluid is stationary in a vertical glass tube. The resistance to motion of a body in a viscous liquid depends on the viscosity of the liquid. The viscosity of the liquid can be found by measuring the speed of the body. This method of measuring the viscosity is in great favour for low-molecular liquids.

When a ball of radius \( R \) made up of a material of density \( \rho_1 \) moves in a liquid whose density is \( \rho_2 \) and whose viscosity is \( \eta \), the driving force \( F \) is given by

\[ F = \frac{4}{3} \pi R^3 (\rho_1 - \rho_2) g \]

This formula is valid for Reynolds number less than 0.1.

Shear stress \( T_m = \frac{R (\rho_1 - \rho_2) g}{3} \)
Correction for Non-Newtonian effect

If the viscosity of a liquid under study depends on the rate of shear, then the viscosity depends on velocity of the ball falling. By varying the material with which the falling balls are made from, and can vary the stresses within the range from 1 to 100 pa. For this, the method of extra-polation of the results is obtained to a zero stress. The viscosity of the non-Newton liquids is given by

$$\eta = \frac{\eta_0}{1 + C T^2}$$

Where C is an empirical constant and $\eta_0$ is the initial Newtonian viscosity that can be found by plotting $\eta^{-1}$, versus $T^2$ with $T = 0$.

Rolling Ball Method

The cylindrical tube can be arranged at a certain angle $\phi$ with respect to the vertical axis, so that the driving force is given by

$$F = 4\pi R^2 (\rho_1 - \rho_2) g \cos \Phi$$
A ball in an inclined tube rolls down along a wall over its entire length. The resistance to motion of the ball \( \eta \propto \frac{C_1 P}{U} \)

\[
\eta = \frac{C_1 P}{U}
\]

Where \( p \) is the pressure produced by the weight of the ball or by an external force, \( u \) is the speed, and \( C \) is the constant of the apparatus.

**Falling cylinder viscometer**

In the laminar flow of a body of any shape in a viscous Newtonian liquid, the force of resistance \( F \) is proportional to the viscosity of the liquid \( \eta \). This allows one to replace a ball with a different geometrical shape, for example a cylinder.

The longitudinal motion of a cylinder of radius \( R_i \) in a coaxial cylindrical tube of radius \( R_0 \), the velocity profile described by

\[
U(r) = u_1 \left( \frac{\ln(r/R_0)}{\ln(R_0/R_i)} \right)
\]

where \( u_1 \) is the speed of the inner cylinder, and \( r \) is the radial position in the gap.

This gives the following expression for the force \( F \) per unit cylinder length

\[
F = 2\pi R_1 \eta \left. \frac{du}{dr} \right|_{r = R_1} = \frac{2\pi \eta u_1}{\ln(R_0/R_i)}
\]

The above equation allows finding only the component of the total force of resistance to motion of the cylinder associated with friction, when the liquid flows between the cylinder and the tube. The expression for the speed \( u_1 \) of a body falling under the action of a density difference \( (\rho_1 - \rho_2) \) has the form
\[ U_1 = \eta g (\rho_1 - \rho_2) \frac{R_i^2}{2} \left[ \ln K^{-1} + \frac{K^2 - 1}{K^2 + 1} \right] \Phi \]

where \( k = R_i/R_0 \) and \( \Phi \) is a correction factor, taking into account, the boundary effects appear owing to the features of the velocity field near the cylinder ends.

Although, there is a strict theory of falling cylinder viscometers, they are commonly treated as relative instruments and viscosity is calculated from the values of \( u_1 \) with the aid of the formula

\[ \eta = \frac{B U_1}{\rho_1 - \rho_2} \]

Where \( B \) is a constant determined in calibration of the instrument according to reference liquids with a known viscosity.

**Theoretical considerations**

The most traditional method for measuring the viscosity and surface tension of a liquid is the capillary viscometer. In the lab a theory is developed for the dynamics of a liquid column in an open capillary tube, in which there is no external pressure, is applied on the liquid column and the pressure at the two ends of the capillary tube is the atmospheric pressure.

Let a liquid column of length ‘L’ flows through a capillary tube of radius ‘R’.

The forces acting on the liquid column are:

1. Viscous force (\( F_v \))
2. Force due to surface tension (\( F_s \))
3. Gravitational force (\( F_g \))
From Poiseuille’s equation, viscous force \( F_v \) acting on the fluid column can be obtained as

\[
\text{Viscous force } F_v = 8\pi \eta LV
\]

Where \( \eta \) = coefficient of viscosity of the fluid, \( V \) = velocity of the fluid column, and \( L \) = length of the fluid column.

and force due to surface tension \( F_s = 2\pi RT \cos \theta \)

Where \( T \) is surface tension of the liquid, \( \theta \) is the angle of contact of the liquid.

When the liquid column in the vertical capillary tube is in motion, it is assumed that the lower surface doesn’t experience the force due to surface tension.

The gravitational force, \( F_g \), acting on the fluid column \( L \) is

\[
F_g = nR^2L \rho g
\]

Where \( L \) = length of the fluid column, \( \rho \) = density of the fluid column, \( R \) = radius of the capillary tube, and \( g \) = acceleration due to gravity.

The liquid column in the vertical capillary tube has two free surfaces (upper and lower) in which the upper surface experience a force due to surface tension of the liquid, which can be given as

\[
F_s = 2\pi RT \cos \theta
\]

The inertial force \( F_a \) is acting on the liquid column due to the accelerated motion of the liquid when the external pressure is applied on it. This force is given by the equation
When the liquid is flowing through the capillary tube, the free-body diagram of the forces acting on the liquid column in a vertically held capillary tube is as shown below.

![Free-body diagram of the liquid column](image)

There are two upward forces i) Viscous force \( F_v \) and the force due to surface tension \( F_s \) and two downward forces i) the Inertial force \( F_a \) ii) the gravitational pull \( F_g \)

From free-body diagram, the resultant force \( \sum F_Y = F_a \). \( F_Y \) represents the vertical component of the force.

\[
\sum F_Y = F_g - F_v - F_s = F_a
\]

Here it is observed that flow of the liquid is steady. Hence, \( F_a = 0 \)

Therefore,
\[
\sum F_Y = F_g - F_v - F_s = 0
\]

Hence,
\[
\Pi R^2 \rho g L - 8 \Pi \eta L v + (-2 \Pi R T \cos \theta) = 0
\]

When divided by \( \Pi L \) throughout
\[
R^2 \rho g - 8 \eta v \frac{2 R T \cos \theta}{L} = 0
\]
\[ 8\eta v = -2R T \left( \frac{1}{L} \right) + R^2 \rho g \]

Thus, coefficient of viscosity and surface tension of the liquid can be obtained by measuring velocity for different lengths of liquid column and plotting a graph between \( L^{-1} \) on x-axis and velocity on y-axis.

\[ V = - \frac{2RT \cos \theta}{8\eta} \left( \frac{1}{L} \right) + \frac{R^2 \rho g}{8\eta} \]

The above equation fits into the equation of a straight line,

\[ Y = -mx + C \]

From the above two equations, we get

\[ V_0 = \frac{R^2 \rho g}{8\eta V} \]

Then the coefficient of viscosity, \( \eta = \frac{R^2 \rho g}{8V_0} \)

The slope of the straight line is given as

\[ \tan \alpha = \frac{2\pi RT \cos \theta}{8\eta} \]

The surface tension of the liquid can be obtained as

\[ T = \frac{4\eta \tan \alpha}{R \cos \theta} \]

Therefore, if the parameters, \( L^{-1} \) and \( V \) related to the liquid column are plotted as X-axis and Y-axis respectively, the response would be a straight line. The intercept of the straight line on Y-axis gives the characteristic velocity \( v_0 \) the velocity of continue flow, of the liquid.
2.5 Albumin in Urine

The protein in urine is called albumin. Proteins are the building blocks of the body parts, such as muscles, bones, hair and nails. The proteins in the blood performs important functions like protect the body from infections, help blood clotting and keep the right amount of fluid circulating through the body.

When the blood gets filtered in the glomerulus in the Bowman’s capsule, all the large proteins, platelets and cells will be circulated to veins. The filtered Glomerulus filtrate consists of small portion of proteins beside other waste. Some time, when glomerulur filtration called glomeruli is damaged, large proteins from blood can leak in to Bowman’s space and in to urinary tract and then in to urine. The presence of large proteins in the urine is called Proteinuria also called albumineria. The proteinuria is a sign of Chronic Kidney Disease (CKD), which could be due to diabetes, high blood pressure (hypertension) and disease that cause inflammation of kidneys.

The normal range of albumin in urine 0 to 7 mg/dl, and for a collection of 24hour urine the normal range is 150 mg/24 hr urine. The albumin in urine called albuminuria, can be classified in to 2 stages: i) Micro albuminuria ii) proteinuria.

The presence of small amount of albumin in urine is called microalbunminuria. As the kidney damage progress and the amount of albumin in urine increases at the end stage of renal disease it is called proteinuria. The proteenuria or albuminuria is not always due to CKD, but it could be due to defect in the re-absorption process that occurs
in the tubule. The diminished re-absorption occurs due to pyelonephritides (acute and chronic) cystinosis, renal tubular disease and interstitial nephritis. The proteinuria may also result from the change in the glomerular blood flow; it could be due to non-renal diseases. This state of proteinuria is called functional proteinuria occurs in the diseases like lukemia, hematologi disorders toximia, hyperthyroidisim, acute infection specticemia, trauma and stress etc.

If there is an infection at some level in the urinary tract, then large number of lenkocytes accompanies with proteinuria. The non-infectious inflammatory disease of glomerulus will have large number of both leukocytes and erythrocytes associated with the findings of casts on sediment examination of urine, because protein is necessary for cast formation. The excretion of proteins by some patients, when they stand or move is called postural proteinuria. The postural proteinuria is intermittent and disappear when the patient lies down. This type of proteinuria occurs in 5 to 15% of health young adults. It is also called as orthostatic proteinuria.

**2.6 Creatinine in Urine**

The creatinine is the byproduct of muscle energy metabolism and is produced at a constant rate. The break-down of high energy phosphate present in the muscle produce creatinine and is excreted by kidneys. The endogenous creatinine production is constant as long as the muscle mass is constant. Since all the creatinine filtered by kidneys in a given time interval is excreted, so the creatinine levels are
equivalent to Glomerular filtration rate (GFR). The disorders in the kidney function lowers or prevent maximum excretion of creatinine.

The creatinine clearance test gives the rate at which kidneys clears the creatinine from the blood, which is a measurement of kidneys function and glomerular filtration rate (GFR). The creatinine clearance test is defined as the imaginary volume (in ml) of plasma from which the creatinine has to be completely excreted in order for the kidney to excrete that amount in 1 minute. Since the excretion of creatinine in a human being is constant, weighed 24 hour urine is used to measure creatinine in urine.

The normal value of creatinine in urine in men is 15 to 25 mg/kg/24 hour & in women it is 10 to 20 mg/kg/24 hour, where the blood creatinine value is generally ranges from 0.8 to 1.2 mg/dl. The increased urine creatinine is found in diabetic mellitus, acromegaly, hypothyroidism. And the decreased value is found in anemia, lukemia, renal stenosis and hyperthyroidisim. Some drugs, excessive physical exercise, pregnancy may increase the urine creatinine.

The National Kidney Disease Education program me (NKDEP) in collaboration with International Society of Nephrology and other professional organization & laboratory working groups have given method for measuring GFR and defined Chronic Kidney Disease (CKD). It has developed a plan that enables standardization and improved accuracy of serum creatinine measurement in clinical labs that includes the use of estimating equation for GFR based on serum
creatinine concentration which is developed from Modification of Diet in Renal Diseases (MDRD) study.

The MDRD equation is based on variables such as age, sex and serum creatinine. It does not require a body weight as variable, because it normalizes GFR for a standard body surface area 1.73m\(^2\), but has some limitations such as it cannot be used in advance stage of CKD.

The GFR in ml/min/1.73m\(^2\)=186 x (sCr)-1.54 x (age)-0.203 x (0.742) for females, and for males is GFR in ml/min/1.73m\(^2\)=186 x (sCr)-1.54 x (age)-0.203 x (1.201).

The CKD is defined as either kidney damage or GFR is less than 60ml/min/1.7m\(^2\) for three months or more irrespective of case, and also abnormal high value albumin excretion. The ratio of urine albumin to creatinine ratio is greater than 30mg/dl. According to the joint conference of NKDEP and International Federation of Clinical Chemistry and laboratory medicine (IFFC) convened to address standardization of urine albumin/creatinine measurement, this ratio can be used to find the protein excretion rate in urine, because the rate of excretion of creatinine is constant through the kidney in to the urine. So the urine albumin to creatinine ratio is a surrogate for the albumin excretion rate (AER). Random samples can be collected at any time of the day to find ACR. A urine sample containing more than 30mg of albumin for each gram of creatinine the person is more likely to have CKD.
2.7 Bilirubin in Urine

The Bilirubin is a byproduct of the human body. As the red blood cells (RBC’s) that carry oxygen to the body breaks down into hem and globin, the hem is converted into bilirubin. The bilirubin will be carried by the albumin in the blood to the liver. In the liver most of bilirubin is chemically attached to another molecule and is released into the bile. This attached or conjugated bilirubin is called direct bilirubin. The unconjugated bilirubin is indirect bilirubin. The total serum bilirubin is sum of direct and indirect bilirubin.

The conjugated bilirubin is released into the bile by the liver and stored in the bladder and then transferred into the intestine. The breakdown of bilirubin in the intestine contribute to the color of feces, small percentage of these breakdown compound are taken by the body and eventually appear in the urine. When the liver does not function properly, the direct bilirubin increases in the blood and filtered by the kidneys and appears in the urine.

The bilirubin is light sensitive, it break down in the strong light. The normal range of total bilirubin in the urine is 0.3 to 2 mg/dl. The increased level of bilirubin in urine is the indication of liver disease and hepatitis, which gives the yellow color to skin and eyes.

The abnormal bilirubin in the urine could be due to blocked of common bile duct. The liver creates the bile and releases the enzyme into the intestine, but when the common bile duct is blocked, the bile and bilirubin cannot go into the intestine and will be expelled from the body through urine.
2.8 Glucose in Urine

The glomerulus filtrate from the Bowman’s capsule contains waste products like urea, electrolytes, amino acids and glucose. When the filtrate passes in to the proximal convoluted tubule (PCT), the glucose is re-absorbed in to the back in to the blood stream. The PCT can only absorb a limited amount of glucose. As and when blood glucose level exceeds 165 to 185 mg/dl, the PCT becomes over loaded and begins to excrete glucose in the urine. This point is called renal threshold of glucose (RTG). This glucose is a simple sugar called corn sugar or blood sugar, which is an important carbohydrate in biological systems. The cells in the human body use glucose as a source of energy, and metabolic intermediate.

The glucose molecule exists in two mirror images called stereo-isomers forms. D-glucose and L-glucose. Only D-glucose (C₆H₁₂O₆) which is right-handed polarized i.e. turning the polarized light to right hand side presents in the biological systems. It is also called as dextrose monohydrate or dextrose. The L-glucose also called glycolysis, cannot be metabolized by cells in the biological system. The D-glucose in the food industry is used as precursor to make vitamin-C. The normal glucose ranges in human urine is 0 to 20 mg/dl in the timed 24 hour urine. The excretion of abnormally large amount of glucose in urine is called ‘glycosuria’. It may be due to renal glycosuria, a genetic defect in renal absorption. The increased glucose in urine also occurs in diabetic mellitus, endocrine disorders such as
acromegaly, liver and pancreatic disorders, pregnancy with possible latent diabetic and central nervous disorders.

2.9 Urea in Urine

The urine urea nitrogen is a measure of protein breakdown in the body. Besides waste nitrogen carrier, the urea also play an important role in the counter current exchange system at loop of henle of the nephrons that allows the reabsorption of critical ions and water from the excreted urine. Urea is reabsorbed at the collecting duct of the nephron, but some amount flows back in to the ascending limb of loop of henle through the collecting duct and then in to the urine. This process is controlled by ADH and allows the body to create hyperosmotic urine which has large concentration of dissolved substance than the blood plasma.

The amount of urea in urine ranges from 15-25 gm/24 hour collections. For normal human being it is from 60 to 100 mg/dl in random collection. The urine urea nitrogen test is performed to measure protein breakdown in the body to find the protein intake and also find the kidney function.

The low level of urea excretion by kidney indicates the kidney problem and malnutrition. The elevated value of urea is an indication of too much protein intake and protein breakdown. Urea is also measured in the blood as Blood Urea Nitrogen (BUN) test. The increased value of BUN is called uremia, occurs in both acute and chronic renal failure, congestive heart failure, where there exist a
faulty urine formation and excretion. Where there is low urea in the urine and large BUN.

2.8 Different Spectroscopic Methods
Spectroscopy is the interaction of matter and electromagnetic radiation which falls on it and as well as with the particle radiation. The spectroscopy is the measurement of absorption, scattering and emission of electromagnetic radiations by atoms or molecules. Absorption is a transfer of electromagnetic energy from a source to atom or molecule. Scattering is the redirection of light as a result of interaction with matter and emission is the transmission of electromagnetic energy from one energy level to another that results in the emission of photon.

When atoms or molecules absorb the electromagnetic energy then they are transferred to higher energy levels. The electrons are promoted to higher orbital by visible or ultra violet radiations, vibrations are excited by infrared radiation and rotations are excited by microwaves. The atomic absorption spectroscopy measures the concentration of an element in a sample; whereas atomic emission spectroscopy measures the concentration of elements in samples.
The electromagnetic wave travels with the speed of light ($c$) has frequency ($\nu$) and wavelength ($\lambda$) and are related by $c = \nu \lambda$ and has energy $E = h \frac{c}{\lambda}$. Very energetic radiations from UV to X-ray region of the electromagnetic spectrum may cause ejection of electrons form molecules and gives the spectra in that region. The photons in the infrared region of the spectrum have much less energy than that resent in the UV-visible region. The infrared photons excite vibrations in the molecules; there could be many possible vibrational levels within each electronic state. The microwave radiation is even less energetic than infrared radiations; it neither excites electrons in the atoms nor produces vibrations, but cause molecules to rotate and hence gives rotational spectra.
The molecules of gases and liquids possess different types of energies viz. the translational energy ($E_t$) due to translational motion; the electronic energy ($E_e$) as the electron is associated with each atom or band are in a state of continuous motion; the vibration energy ($E_v$) is due to periodic motions of atoms from their equilibrium position and the rotational energy ($E_r$) by virtue of bodily rotation of a molecule about its centre of gravity.

The translation energy ($E_t$) is not quantized. As the atom undergo a small displacement about its mean point because of restoring forces of the bond; the vibrational energy is quantised. A molecule can rotate about its centre of gravity and can move utmost in the volume occupied by it. So the rotational energy can be quantized. These energies of atoms are independent of each other.
The total energy \[ E = E_e + E_v + E_r \]

Each electronic level \((E)\) consists of number of vibrational energy level \((v)\) and each vibrational level consist of number of rotational energy level \((J)\). A spectral line is emitted when a molecule absorbs radiation of energy \((h\nu)\) and get excited or when it de-excites to lower energy level. A transition between electronic energy level gives spectrums in the visible or ultra violet region and it is called electronic spectra; while the transition between vibrational levels within the same electronic level is known as vibrational spectra it falls in infrared region and transition between rotational levels within the same vibrational level gives rotational spectra which falls in far infrared or microwave region.

A nucleus or electron can give interaction energies when placed in magnetic field gives nuclear magnetic resonance (NMR) or electron spin resonance (ESR) respectively, which occurs in the radio frequency and microwave frequency regions.

**Infrared Spectra**

The vibration spectra occur in infra red region. When infrared radiations of some frequency falls on molecules; the molecules absorbs energy and get excited to higher vibrational levels. The molecules absorb a quantum of energy give rise to characteristic based of the molecules from 50 to 12000 cm\(^{-1}\). It is generally subdivided into three regions. Far IR 400 – 50 cm\(^{-1}\), mid IR 4000 to 400 cm\(^{-1}\), and near IR 12,500 to 4000 cm\(^{-1}\). The mid IR region is the most commonly used for standard research investigations. For solid
samples the Far IR is also equally important requires special instruments & techniques.

2.9 Rotational Spectra

When a diatomic molecule rotates about its axis perpendicular to the bond length, the dipole moment changes continuously and produced fluctuating electric filed. When this fluctuating electric field interacts with the electric field of e. m radiation then pure rotational spectrum occurs. Those molecules which do not possess permanent dipole moment do not show rotational spectrum. Rotation about bond axis for a diatomic and linear molecule does not produce any change in dipole moment and hence they do not possess rotational spectra.

2.9.1 Rotational spectra of rigid diatomic molecule

A diatomic molecule consisting of atoms of masses \( m_1 \) and \( m_2 \) at a distance ‘\( r \)’ apart can be considered as a rigid rotator.

Fig 2.18 Diatomic molecules as rigid rotator
The moment of inertia of this molecule about an axis passing through its centre of mass and perpendicular to bond length \( r \) is moment of inertia \( I = m_1r_1^2 + m_2r_2^2 \)

\[
I = \frac{m_1m_2}{m_1 + m_2} r_1^2 + \frac{m_2m_1}{m_1 + m_2} r_2^2
\]

Since \( r_1m_1 = m_2r_2 \) \& \( r = r_1 + r_2 \)

\[ I = \mu R^2 \]

Where \( \mu = \frac{m_1m_2}{m_1 + m_2} \) is called reduced mass of the system.

The angular moment \( L \) of the rotating molecular is \( L = I \omega \), where ‘\( \omega \)’ is angular frequency, in quantum theory the angular moment can be written as

\[
L = \sqrt{J(J+1)} \hbar \quad J = 0.1.2.3 \ldots \ldots \ldots \ldots
\]

\( J \) is called rotational quantum number

For free rotation the P.E \( V(r) = 0 \). The Schrödinger wave equation for relative motion is

\[
\frac{-\hbar^2}{2\mu} \nabla^2 \psi(r) = E \psi(r)
\]

The energy Eigen values is given by \( E_J = \frac{\hbar^2}{2I} J(J+1) \) or the rotation, K.E of the diatomic molecule is \( \frac{1}{2} I\omega^2 \).

The wave number \( \varepsilon_J = \frac{1}{\lambda} = \frac{E_J}{hc} \)

Since \( E = hu \Rightarrow E_J = hc/\lambda \Rightarrow 1/\lambda = E_J/hc \)

or rotational energy
\[ \varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I C} J(J+1) \text{ cm}^{-1} \]

\[ \varepsilon_J = B J(J+1) \text{ cm}^{-1} \]

Where \( B = \frac{h}{8\pi^2 I C} \) is called rotational constant.

The rotational spectra are always obtained in absorption. For a transition from lower energy that \( J'' \) to the higher energy state \( J' \).

\[ \Delta \varepsilon_J = \varepsilon_J - \varepsilon_J = B [J'(J'+1)-J''(J''+1)] \]

\[ = 2B (J+1) \text{ Cm}^{-1} \]

The selection rule for rotational transition is \( \Delta J = \pm 1 \). The frequency difference between two successive lines in the pure rotational spectrum of a diatomic molecule is given by \( \frac{h}{2\pi I} \). Therefore, by measuring \( \Delta \varepsilon_J \), the frequency difference, the moment inertia and hence the bond length can be found.

### 2.10 Vibrational Spectra

The diatomic molecule consisting of two atoms of mass \( m_1 \) and \( m_2 \) is analogous to a spring mass system at masses either ends of executing SHM. The fundamental frequency of vibration \( \nu_0 \) is given by

\[ \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

Where \( \mu \) is the reduced mass of the system \( \left( \mu = \frac{m_1 m_2}{m_1 + m_2} \right) \).
Fig 2.19 Two atoms of masses $m_1$ and $m_2$ coupled by chemical bond

This is a linear harmonic oscillator where the potential is continuous function of the coordinate ‘$x$’. The potential $V = \frac{1}{2} k x^2$

Where $k$ is restoring force per unit displacement called force contract and is given by $k = 4 \pi m \nu^2 = m \omega^2$.

The time independent Schrödinger wave equation for this system is

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - \frac{m\omega^2 x^2}{2}) \psi = 0$$

In terms of new variables

$$\frac{d^2 \psi}{d\rho^2} + (\lambda - \rho^2) \rho = 0$$

Where

$$\rho = \left( \frac{m\omega}{\hbar} \right)^{1/2} x \quad \text{and} \quad \lambda = \frac{2E}{\hbar\omega}$$

The energy Eigen value for such a system is $E_\nu = (\nu + \frac{1}{2}) \hbar \nu_0$

Where $\nu = 0, 1, 2, 3, \ldots$ called vibrational quantum numbers express as $\text{cm}^{-1}$. The vibrational energy $\varepsilon_\nu = \frac{E_\nu}{\hbar c} = \left( \nu + \frac{1}{2} \right) \nu_0^2$

$$\therefore \varepsilon_\nu = \left( \nu + \frac{1}{2} \right) \nu_0^2 \text{ cm}^{-1}$$

Where $\nu_0$ is frequency in cm$^{-1}$.

The vibrational energy levels are equally space. When $\nu=0$, $\varepsilon_0 = \frac{1}{2} \nu_0^2$ is the lowest energy called zero-point energy. Even though at lowest vibration level, the vibrational energy is not zero i.e. the
molecules always vibrate. The vibrational spectra occur in infra red region.

**Selection Rules for Infrared Spectra**

The condition for absorption of a quanta of radiation of energy $h\nu$ by the molecules is that the energy difference between the two states represented by wave function $\psi_i$ & $\psi_j$ must be equal the $h\nu$. It depends on the interaction of electric fields of electric dipole and that of incident radiation.

For a plane electromagnetic wave moving in $z$ direction, the electric field vector $E_x$ is given by $E_x = E_o \cos (wt-kx)$. For visible light $kx = (2\pi /\lambda) x = 10^{-3} << 1$ and for infra red region it the spatial variation of electric field can be neglected compare with $wt$.

\[ \therefore E_x = E_o \cos wt \]

The electric field is the force per unit charge; then the force on charge $q_i$ is $q_i E_x$. Therefore, $-dv/dx = q_i E_x \Rightarrow dv = -q_i E_x dx$

For a system of large number of charges $v = -\sum q_i x_i E_o \cos wt$. Writing $\cos wt$ in the form of exponential and then the Hamiltonian will be

\[ H'_{mn} = -\frac{1}{2} E_o (e^{iwt} + e^{-iwt}) \int \psi_0^m \sum (q_i x_i) \psi_0^n dx \]

Let $\sum q_i x_i = \mu$ electric dipole moment operator of the system, then the Hamiltonian, where the electric dipole moment operator is given as

\[ \mu = \int_0^\infty \mu^0_0 dt \]
Electric dipole moment

\[ \mu_{ij} = \mu_o \int \psi_i^* \mu_o \psi_j \ d\tau + \int \psi_i^* \left( \frac{\partial \mu}{\partial Q_k} \right) Q_k \psi_j \ d\tau \]

\[ \mu_{ij} = \int \psi_i \mu \psi_j \ d\tau, \text{ where } \mu_{ij} \text{ is a function of normal coordinates } Q_k \text{ and can be expressed in Taylor series. The } \mu_{ij} \text{ can be written as} \]

\[ \mu = \mu_o + \left( \frac{\partial \mu}{\partial Q_k} \right) Q_k + \ldots \]

\[ \mu_{ij} = \mu_o \int \psi_i^* \mu_i \psi_j \ d\tau + \int \psi_i^* \left( \frac{\partial \mu}{\partial Q_k} \right) Q_k \psi_j \ d\tau \]

\[ \mu_{ij} = \mu_o \int \psi_i^* \psi_j \ d\tau + \int \psi_i^* \left( \frac{\partial \mu}{\partial Q_k} \right)_o \int \psi_i^* Q_k \psi_j \ d\tau \]

The first term in the above equation vanishes due to orthogonality condition and the conditions for the second term to be non-zero are:

i) The term \( \left( \frac{\partial \mu}{\partial Q_k} \right)_o \) is finite for one component of dipole moment.

Hence for a mode of vibration to be IR active, there should be a change in the dipole moment.

ii) \( \int \psi_i^* Q_k \psi_j \ d\tau \) must be finite, which is possible only, when, the \( \Delta u = \pm 1 \), for harmonic oscillator and for anharmonic oscillator \( \Delta u = \pm 1, \pm 2, \pm 3, \pm 4 \ldots \). Therefore, the selection rule for transition to be vibrational spectra is \( \Delta u = \pm 1 \), i.e. the change in vibrational quantum number must be \( \pm 1 \).
2.12 Vibrational-Rotational Spectra

Pure vibrational spectra are observed only in liquids, because the interaction between the neighboring molecules doesn’t allow the rotational motion. In solids a molecule rotates while executing vibrational motion and therefore rotational energy change is accompanied by vibrational energy change. Therefore each vibrational bond is found to contain rotational fine structure. A diatomic molecule can execute both rotation and vibration independently.

The total energy $\varepsilon_{\text{total}} = \varepsilon_r + \varepsilon_v$ i.e. $\varepsilon_{jv} = \varepsilon_j + \varepsilon_v$

$$\varepsilon_{\text{total}} = \left(\frac{\nu + \frac{1}{2}}{\nu_o}\right) + B\nu (J+1)$$

The selection rules for the combined motion are same as those for separate motion. $\Delta \nu = \pm 1, \pm 2, \pm 3, \pm 4\ldots$ and $\Delta J = \pm 1$. $\varepsilon_v$ is larger than $\varepsilon_j$. Even at higher temperatures only the vibrational states corresponding to $\nu = 0$ and $\nu = 1$ are excited. The $\nu = 0 \quad \nu = 1$ transition falls in to two categories.

i) P- branch: The lines corresponding $\Delta J = -1$ are called P-branch. The frequencies of the spectral lines in this branch are given by

$$u_P = u_o - J\left(\frac{\hbar}{2\pi I}\right)$$

where $J = 1, 2, 3, 4, 5\ldots$

ii) R- branch: The lines corresponding to $\Delta J = +1$ are called R-branch, the frequency corresponding to these lines are $u_R = u_o + (J+1)\left(\frac{\hbar}{2\pi I}\right)$

$J$ takes values $0, 1, 2, 3 \ldots$
2.13 Modes of Vibrations

The IR spectra of polyatomic molecules are much complex, because different modes of vibration of molecules containing due to many atoms leads to several bands. A molecule containing \(n\) atoms has \(3n\) degrees of freedom. The translational and rotational moments use \(3\) each, therefore a non-linear molecule of \(n\) atoms has \((3n-6)\) degrees of freedom. A linear molecule doesn’t have rotation about the bond axis and has \((3n-5)\) degrees of freedom. The \((3n-6)/(3n-5)\) vibrations are called normal or internal modes are also called fundamental vibrations of molecules, during which the centre of gravity remains unchanged. The position of the atoms in the molecules are not fixed, they are subjected to number of different vibrations. These vibrations of a molecule are generally two types.

i) Stretching, ii) bending or deforming vibration.

i) Stretching Vibration Mode: This is the simplest mode of vibration in which the atoms moves along the bond axis, such that the bond length increases and decreases in regular intervals, but the atom remains in the same bond axis. These modes of vibrations does not cause any change in dipole moment in the symmetrical molecules and is not IR active. These vibrations are also two types:

a) Symmetrical stretching and b) asymmetrical stretching
a) **Symmetrical stretching:** In this type of stretching, with respect to a particular atom, other type of atom moves in the same direction keeping the bond angles same. For example, in case of methylene
group, H-C-H, the two hydrogen atoms move away from the carbon atom without change in the bond angle.

b) **Asymmetrical stretching**: In this type of stretching one atom moves away from the central atom, while other atom moves towards the central atom. For example in methylene group one hydrogen atom approaches the carbon, while the other atom moves away from carbon.

ii) **Bending or deforming vibration mode**: The vibrations cause a change in the bond angle between the bonds with a common atom or the moment of group of atoms with respect to the remaining atoms or the reminder of the molecule. The bending vibrations are of four types.

   a) **Scissoring**: In this mode, the two atoms concerned to a molecule moves towards and away from each other with deformation of the valency angle, (in-plane bending).

   b) **Rocking**: In this the structural units swing back and forth in the plane of molecule (in plane bending)

   c) **Wagging**: In wagging, the structural units swings back and forth out of plane of the molecule (out of plane bending)

   d) **Twisting**: In this type of bending vibration the structural unit rotates about the bond which joins it to the remaining of the molecule (out of plane bending).

**2.14 Vibrational Spectra- Group Frequencies**

The vibrational spectra of molecules consist of two major regions, the group frequency region and the finger print region.
2.14.1 Group frequency region

The group frequency region extends up to 1450 Cm\(^{-1}\) in the mid IR region, where the vibrations are associated with some structural frequencies. The group frequency region can further divided into three regions.

i) X-H stretching region: The fundamental vibrations in this region are from 4000-2500 Cm\(^{-1}\) are generally due to O-H, C-H and N-H stretching. The O-H stretching produces a broad band that occurs in the range from 3700-3600 Cm\(^{-1}\). The N-H stretching is observed between 3400-3300 Cm\(^{-1}\). The C-H stretching extends from 3200-2600 Cm\(^{-1}\). This is hetero attachment group.

ii) Triple bond region: This occurs in the region from 2500-2000 cm\(^{-1}\) because of high force constant of the C=\(=\)C bonds. The C=\(=\)C bond absorbs between 2300 and 2050 cm\(^{-1}\) and C=\(=\)N bond occurs between 2300 - 2200 cm\(^{-1}\). The massive silicon and phosphorus – H occurs in 2400 - 2200 cm\(^{-1}\).

iii) The principal band in the region 2000-1500 cm\(^{-1}\) is due to C=C and C=O stretching. The carbonyl stretching is the most intense band in the spectrum and depending on C=O bond and occurs in 1830-1650 cm\(^{-1}\) region. For identification and determination of molecular structure in mid-IR, one has to look first at high-wave number end of the spectrum > 1500 Cm\(^{-1}\), and concentrate initially on the major bands.
The finger print region

The region from 900 – 1450 cm$^{-1}$ is called finger print region, which is very rich in absorption bands and contains bending and certain stretching vibrations. The structural moiety can be identified by assignment of bands in the region. Even though the molecules having similar group shows similar spectra outside the region, they also shows bands of the molecule in the regions and hence called finger print region.