CHAPTER-2.
GENERAL THEORETICAL CONSIDERATION.

2.1 X-RAY DIFFRACTION ANALYSIS:

With the help of X-rays, the order of arrangement of atoms in a crystal can be understood. The X-ray method is the most suitable technique for use in crystal structure study. The space lattice arrangement of atoms (or ions) in a crystal implies the existence of innumerable parallel planes containing the lattice points or atoms. Each face of the crystal must have lattice planes parallel to itself. When the sample either single crystal or a poly crystalline material is irradiated by a narrow beam of monochromatic X-rays, scattering of X-rays occurs and that can be represented as diffraction from the plane of atoms parallel to a given face on which X-rays are incident. These beams emerge out from various planes of the specimen as cones with different semi vertical angles with respect to incident beam. These can be recorded as circles on the flat film or as rows of powder lines on a strip of film encircling the specimen.

For a given wave length (\(\lambda\)) of the incident X-ray beam, the crystals of the specimen be so oriented with respect to the incident beam that a family of the crystal planes (hkl) satisfy the Bragg’s condition:

\[2d_{hkl} \sin \theta = n\lambda\]  \(1\)

Where \(d_{hkl}\) = distance between successive planes of the crystal (interplanar spacing)

\(\theta\) = Glancing angle i.e. angle between the direction of the incident beam and the crystal planes (Bragg angle)
n=Order of reflection (1,2,3,...)
λ=wave length of the incident X-ray beam.

In case of polymers, the reflection with the strongest intensity is usually found for n=1. Reflections from crystal planes occur only when the Bragg’s condition is satisfied.

There are two basic techniques used in X-ray diffraction analysis
(i) X-ray photography
(ii) Counter diffractometry

2.1.1 X-RAY PHOTOGRAPHY TECHNIQUE:

To-day this technique is applied, not only to structure determination, but to many diverse problems such as chemical analysis, the study of phase equilibria, particle size measurements and crystalline orientation in poly crystalline aggregates etc. The study of long chain molecular alignment of natural and synthetic fibres can be successfully made with this technique.

Each crystallographic substance has its own set of definite plane-spacings and hence each substance gives its own characteristic diffraction patterns by interpretation of which crystalline substances can be identified.

The interpretation for the inter-planar spacings \(d\) of a parallel plane set of incidence \((hkl)\) is given by:

\[
d^2(hkl) = \frac{1}{(h/a)^2 + (k/b)^2 + (l/c)^2} = \cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3 \quad (P)
\]

Where \(a\), \(b\) and \(c\) are lattice parameters and \(\cos \theta_1\), \(\cos \theta_2\) and...
**Cos** \( \theta \) are direction cosines of the normal to the plane with respect to the crystallographic axes.

For a body-centred lattice, the crystallographic axes form an orthogonal set. Thus

\[
\cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3 = 1 \quad \text{and} \quad a = b = c
\]

Hence from equation (2)

\[
d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3)
\]

Thus, Bragg's equation can be written as

\[
\lambda = 2d_{hkl}\sin \theta = \frac{(2a \sin \theta)}{\sqrt{(h^2 + k^2 + l^2)}}
\]

Hence,

\[
\sin^2 \theta \sqrt{(h^2 + k^2 + l^2)} = \frac{\lambda^2}{4a^2} \quad (4)
\]

For an orthorhombic lattice \( a \neq b \neq c \) and \( \alpha = \beta = \gamma = 90^\circ \)

Hence,

\[
d_{hkl} = \sqrt{\frac{a^2}{h^2} + \frac{b^2}{k^2} + \frac{c^2}{l^2}} \quad (5)
\]

and \( \sin^2 \theta = \frac{\lambda^2}{4d^2} \)

\[
= \frac{\lambda^2}{4} \left[ \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right]
\]

\[
= A_1 h^2 + A_2 k^2 + A_3 l^2 \quad (6)
\]

Thus, knowing the values of the constants \( A_1, A_2 \) and \( A_3 \) all possible values of the \( \sin^2 \theta \) can be computed taking all possible combinations of \( h,k,l \). Comparing with the experimentally observed values of \( \sin^2 \theta \), the powder lines from an unknown crystal can be indexed for its lattice parameters.
2.1.1(a) Debye-Scherrer Method:

In this method, a fine beam of X-ray is allowed to pass through the powder sample placed on the path of the beam. The specimen is mounted at the axis of the cylindrical film in such a manner that it becomes perpendicular to the incident X-ray beam. The essential features of this method is shown in Fig. (1A). The diffracted X-rays radiate from the specimen as a family of coaxial hollow cones whose apical angles are each \( 4\theta \) and are intercepted by the cylindrical film. The \( \theta \) values for each pair of diffraction arcs thus recorded can then be determined from measurements on the developed strip of film by the relationship:

\[
\theta = \frac{S}{4R} \quad \text{for low angle region} \quad (7a)
\]

\[
\theta = \frac{\pi}{2} - \frac{S}{4R} \quad \text{for high angle region} \quad (7b)
\]

Where \( R \) is the radius of the cylindrical film and \( S \) is the distance between corresponding pairs of arcs or spots registered on the film.

2.1.1(b) Forward Reflection Method:

In this method, the photographic film is placed vertically and perpendicular to the incident X-ray beam Fig. (1B). The entire diffraction circles are recorded making it easy to detect circumferential variations in intensity.

In case of semi-crystalline sample, some spots, instead of continuous circles, are obtained. Each set of such spots lies in a circle of definite radius.
A. Debye-Scherrer photography principle.

B. Forward reflection photography principle.
If 'D' is the distance between the specimen and the film and 'S' is the diameter of any circle formed on the film or the distance between two similar spots on both sides of the centre, then half cone angle (in radians) for the particular reflections is given by

$$\tan 2\theta = \frac{S}{D}$$  \hspace{1cm} (8)\]

Now knowing the values of '\theta' the interplanar spacings ($d_{hkl}$) for the specimen can be evaluated from equation (1).

2.1.2 COUNTER DIFFRACTOMETER (XRD) TECHNIQUE:

The diffractometer directly measures the intensity of X-rays diffracted at any particular angle $2\theta$. The dependence of the diffracted rays on the angle $2\theta$ is continuously recorded in the graphical form with the help of a strip-chart recorder. By measuring the spacings between the corresponding symmetric maxima on the diffraction pattern, $2\theta$ values can be determined and hence the interplanar spacings ($d_{hkl}$) can be calculated from equation (1).

2.1.3 RELATIVE INTENSITY OF X-RAY DIFFRACTION:

The intensity of x-ray diffraction recorded either as arcs or spots on cylindrical film or as peaks on diffractograms, vary greatly some of them are very intense and some are barely visible, due to certain factors—such as structure factor, absorption factor etc. Thus we have the relation between them and the observed relative intensities on powder photograph taken with a cylindrical film and the specimen on its axis as:
Where \( I_{(hkl)} \) is the observed intensity, \( F_{(hkl)} \) is the structure amplitude, \( P \) is the number of equivalent planes contributing to the reflection, \( T \) is the temperature correction factor and \( A \) is the absorption factor. In some point groups, there are non-equivalent planes with equal \( d_{(hk1)} \) values having different \( F_{(hk1)} \) values. For these intensities will be superimposed on photographs. The relative intensities of the X-ray diffraction may be obtained in terms of heights of the diffractogram peaks with respect to background shifts from the base.

X-ray diffractometer analysis helps to determine the degree of crystallinity of the sample under study from the measurement of areas under the diffractograms. The degree of crystallinity percent \( (K) \) is given by the relation

\[
K = 100 \frac{S_c}{S}
\]  

Where \( S_c = \) area of the crystallinity fields, 
\[\text{i.e., areas of the diffractogram maxima} \]
\( S = \) total area under the diffractogram.

2.2 INFRARED SPECTROSCOPY:

Infrared (IR) spectroscopy is one of the most powerful analytical techniques which offers the possibility of chemical identification. This technique when coupled with intensity measurements may be used for quantitative analysis. One of the
most important advantages of infrared spectroscopy over the other usual methods of structural analysis is that it provides useful information about the structure of molecule quickly, without tiresome evaluation methods.

2.2.1 ORIGIN OF IR SPECTRA:

The (IR) spectra originate from the different modes of vibration and rotation of a molecule. Due to vibration and rotation, the substance shows selective absorption in the infrared region. Therefore this technique is based upon this simple fact of selective absorption. After absorption of IR radiations, the molecules of a substance vibrate at many rates of vibration, giving rise to close-packed absorption bands, called an IR absorption spectrum, which may extend over a wide wavelength range. Various bands will be present in IR spectrum which will correspond to the characteristic functional groups and bonds present in a substance. Thus an IR spectrum of a substance is a finger-print for its identification. Band positions in an IR spectrum may be expressed conveniently by the wave number whose unit is $\text{cm}^{-1}$. Band intensities in IR spectrum may be expressed either as transmittance ($T$) or absorbance ($A$). Transmittance is defined as the ratio or radiant power incident on the sample. On the otherhand absorbance ($A$) is defined as: $A = \log_{10}(1/T)$ where $T$ = transmittance.

A molecule absorbs radiation only when the natural frequency of vibration of some part of a molecule (i.e. atoms or group of atoms comprising it) is the same as the frequency of the incident radiation. After absorbing the correct wavelength of
radiation, the molecule vibrates at an increased amplitude. This occurs at the expense of the energy of the IR radiation which has been absorbed. There is another condition for a molecule to absorb IR radiation. A molecule can only absorb IR radiation when its absorption causes a change in its electric dipole (dipole moment). When the molecule having electric dipole is kept in the electric field (as in the case when the molecule is kept in a beam of IR radiation), this field will exert forces on the electric charges in the molecule. Opposite charges will experience forces in opposite directions. This tends to decrease or increase separation. As the electric field of the IR radiation is changing its polarity periodically it means that the spacing between the charged atoms (electric dipoles) of the molecule also changes periodically. When these charged atoms vibrate, they absorb IR radiation from the radiation source. If the rate of vibration of charged atoms in a molecule is fast the absorption of radiation is intense and, thus the IR spectrum will have intense absorption bands. On the other hand when the rate of vibration of the charged atoms in a molecule is slow, there will be weak bands in the IR spectrum.

2.2.2 MODES OF VIBRATIONS OF ATOMS IN POLYATOMIC MOLECULES:

In a polyatomic molecule, each atom is having three degrees of freedom in three directions which are perpendicular to one another. Consequently a polyatomic molecule is requiring three times as many degrees of freedom as the number of its atoms. Thus a molecule of 'n' atoms has 3n degrees of freedom. For a non-linear molecule, three of the degrees of freedom describe
rotation and three describe translation, the remaining $3n-6$ degrees are vibrational degrees of freedom or fundamental vibrations. In a linear molecule, only two degrees of freedom are required to describe rotation. Thus a linear molecule has $3n-5$ vibrational degrees of freedom.

According to the character of vibration, normal vibrations can be divided into two principal groups—Stretching Vibration and Bending Vibration.

In stretching vibration, the atoms move essentially along the bond axis, so that the bond length increases or decreases periodically. As this type of vibrations corresponds to one-dimensional motion, it means that there will be $(n-1)$ stretching vibrations for non-cyclic systems. During stretching vibrations, bond angles change only if it is required to do so by the centre of gravity resisting displacement.

In bending vibrations, there occurs a change in bond angles between bonds with a common atom or there occurs the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another. The bending vibrations are also called deformation vibrations. As these vibrations are describing two-dimensional motions, there will be $(2n-5)$ bending vibrations for non-cyclic and linear molecules. These appear at lower frequencies, whereas stretching vibrations at higher frequencies. The force constants of deformation vibrations are generally less than those of the stretching vibrations. Due to the smaller force constants, the deformation vibrations are more sensitive to environmental
in a polyatomic molecule, the same bond can perform stretching and deformation vibrations simultaneously. Stretching vibrations are of two types, Symmetric and Asymmetric. Deformation vibrations are also of two types: In-plane deformation vibrations (Scissoring and rocking) and Out-of-plane deformation vibrations (Wagging and Twisting).

2.2.3 MATHEMATICAL EXPRESSION FOR IR SPECTRA:

The basic problem of vibrational spectroscopy is to correlate the experimentally observed energy levels with the structure and force function of the molecule. The energy states of infrared transitions may be obtained from solutions of the Schrodinger wave equation in co-ordinates of the nuclei. The potential energy function corresponds to a fixed electron configuration of lowest energy. Infrared frequencies are determined mainly by the mechanical motions in the molecule while the intensities are related to the electrical properties. Vibrational transitions without rotation may be discussed in terms of the harmonic oscillator model and pure rotational transitions may be understood in terms of rigid rotator model.

In the harmonic oscillator model, the restoring force is proportional to the first power of the displacement (Hooke's Law) and the potential energy function is proportional to the square of the displacement. This model can account for fundamental vibrations occurring between the non-vibrating state and the next vibrationally excited state. By applying Hooke's Law, the vibrational energy of a diatomic molecule is,
\[ E_{vib} = \frac{\hbar}{2\pi} \sqrt{\frac{f}{\mu}} \left( n + \frac{1}{2} \right) \]  \hspace{1cm} (11)

\[ n = 0, 1, 2, \ldots \]

Where

- \( \hbar = \) Planck's constant
- \( n = \) Vibrational quantum number
- \( f = \) force constant of the bond
- \( \mu = \) reduced mass of the molecule.

\( \mu \) is defined by

\[ \mu = \frac{m_1 m_2}{(m_1 + m_2)} \]  \hspace{1cm} (12)

Where \( m_1 \) and \( m_2 \) are the masses of two atoms of a vibrating diatomic molecule.

The energy change, \( \Delta E_{vib} \) for the absorption process, \( n = 0 \rightarrow 1 \) is

\[ \Delta E_{vib} = \frac{\hbar}{2\pi} \sqrt{\frac{f}{\mu}} \]  \hspace{1cm} (13)

By applying Bohr relation, we get

\[ h\nu' = h\nu = \frac{\hbar}{2\pi} \sqrt{\frac{f}{\mu}} \]  \hspace{1cm} (14)

Where

- \( \nu' = \) Vibrational frequency in sec\(^{-1}\)
- \( \nu = \) Vibrational frequency in Cm\(^{-1}\)

Thus, the Vibrational frequency in Cm\(^{-1}\) is given by

\[ \nu = \frac{1}{(2\pi c)} \sqrt{\frac{f}{\mu}} \]  \hspace{1cm} (15)
The value of 'f' is of the order of $5 \times 10^5$ dynes cm\(^{-1}\) for single bonds and is about twice and thrice this value for double and triple bonds. Vibrations of individual bonds in more complex molecules may also be treated similarly although the absorption frequencies are influenced by several other factors. Since both the reduced mass and force constant of the bond determine the vibrational frequency, the effects of neighbouring atoms are prominent in case of complex molecules.

2.3 THERMAL ANALYSIS:

A body suffers transformations both physically and chemically under the action of heat. These transformations can be studied by measuring some physical property of the body recorded as a function of temperature. The technique for relating the property of temperature data to possible thermal events in the sample material is called thermal analysis technique. In general a differential thermal technique is used where the difference between some property (temperature) of the sample and that of a standard material is observed. Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are two main differential thermal analysis techniques.

2.3.1 Differential Thermal Analysis (DTA):

In DTA, both the test sample and an inert reference material (usually $\alpha$-alumina) undergo a controlled heating or cooling programme which is usually linear with respect to time. The sample and the reference material are separately heated in identical environments. The reference material undergoes no
thermal event in the temperature range under study, and therefore its temperature is the same as the programmed temperature throughout the heating. The difference of temperature between the sample and the reference material is zero when the former does not undergo any chemical or physical change. However, if reaction takes place then a temperature difference $\Delta T$ will occur between the sample and reference material.

P.3.1 (a) Mathematical expressions:

With change of temperature of the ceramic block of a DTA apparatus, temperature of the reference material and the sample also change, and in absence of any thermal anomaly in the sample,

$$\Delta T = T_1 - T_2 = 0 \quad (16)$$

Where $T_1$ and $T_2$ are temperature of the sample and the reference material respectively, when an anomaly occurs, $\Delta T$ would vary and its variation with time or temperature is called the thermogram.

The magnitude $T_2 - T_3$, where $T_3$ is the temperature of the block, is proportional to the rate of heating $H_2$, the mass $m$ of the reference material, its heat capacity $C$ and inversely to the thermal conductivity $K$.

i.e.,

$$T_2 = T_3 - H_2 mc/K$$

Similarly for the sample
\[ T_1 = T_3 - H_1 (mc/K)_1 \]

Thus
\[ \Delta T = T_1 - T_2 = H_2 (mc/K)_2 - H_1 (mc/K)_1 \]

\[ = H \left( (mc/K)_2 - (mc/K)_1 \right) \]  \hspace{1cm} (17)

\[ \therefore H_2 = H_1 \]

If the variation of \( mc/K \) with temperature is same for both, then \( \Delta T = 0 \) at all temperatures and the thermogram is a horizontal straight line. If any one of these quantities varies with temperature, the thermogram will have either endothermic or exothermic peaks depending upon the nature of reaction.

Thus in an endothermic change, e.g. when the sample melts or is dehydrated, the sample temperature is lower than that of the reference material. This condition is only transitory because on completion of the reaction the sample will again show zero temperature difference compared with the reference.

In DTA, temperature difference \( \Delta T \) is plotted against furnace temperature. In idealised DTA curve both the shape and size of the peaks can give a large amount of informations about the nature of the sample. Generally phase transitions, dehydration and reduction produce endothermic effects where as crystallization, oxidation and some decomposition reactions produce exothermic effects.

2.3.2 Differential Scanning Calorimetry (DSC):

The same phenomena may be studied by DSC as by DTA. Differential Scanning Calorimetry instruments measure the energy change in the sample directly not as a temperature change and it
is consequently more suitable than DTA instruments for quantitative measurements of heats of reaction and transition, specific heats etc.

The DSC system measures the differential energy required to keep both the sample and reference material at the same temperature throughout the analysis. When an endothermic transition occurs, the energy absorbed by the sample is compensated by an increased energy input to the sample in order to maintain a zero temperature difference between the sample and reference. Because this energy input is precisely equivalent in magnitude to the energy absorbed in the transition, the direct calorimetric measurement or energy of the transition is obtained from this balancing energy. DSC measurements may be made isothermally or at very low heating rates without loss of sensitivity. A DSC curve is a plot of differential power (i.e., difference in rate of energy supply) against temperature or time. The ordinate signal, the rate of energy absorption by the sample, is proportional to the specific heat of the sample. Any transition accompanied by the change in specific heat produces a discontinuity in the power signal and endothermic or exothermic enthalpy changes gives peaks whose areas are proportional to the total enthalpy change.

2.3.2 (a) The DSC Signal $H:

The heat flow $H$ to the sample ($H$ in order to express that the heat flow is the change in sample enthalpy) is equal to the difference between the two heat flows $Q_s$ and $Q_r$. 

\[ H = Q_s - Q_r \]  

(18)

here \( Q_s \) — heat flows for sample  

\( Q_r \) — heat flows for reference

According to the thermal analogue of Ohm's law it is

\[ Q = \frac{(T_2 - T_1)}{R_{th}} \]  

(19)

where \( (T_2 - T_1) \) is the temperature difference

\( R_{th} \) is the thermal resistance

When this is applied to the DSC cell, it follows that

\[ H = Q_s - Q_r = \left( \frac{(T_c - T_s)}{R_{th}} \right) - \left( \frac{(T_c - T_r)}{R_{th}} \right) \]  

(20)

Where \( T_c \) = furnace temperature  

\( T_r \) = reference temperature  

\( T_s \) = sample temperature

For reasons of Symmetry, the two \( T_c \) and the two \( R_{th} \) values are identical.

It follows that

\[ H = -\frac{(T_s - T_r)}{R_{th}} \]  

(21)

In order to avoid problems with signs, an effect is defined as exothermic or endothermic and the sign is omitted. As the temperature difference, \( \Delta T = T_s - T_r \), is measured by the gold/nickel thermopile it follows from the thermo-couple equation, \( \Delta U = \Delta T \cdot S \)
From (21)

\[ H = \frac{\Delta U}{(R_{th} \cdot S)} \]  \hspace{1cm} (22)

Where \( S \) is the entropy.

As the two terms in the denominator are functions of the actual temperature, they can be combined as the calorimetric sensitivity \( E = R_{th} \cdot S \) which can be divided into a temperature dependent (relative) term \( E_{rel} \) and a temperature independent term \( E_{In} \), specific to the measuring cell being used. \( E = E_{rel} \cdot E_{In} \). Thus it follows that the heat flow to the sample is

\[ H = \frac{\Delta U}{(E_{In} \cdot E_{rel})} \]  \hspace{1cm} (23)

The temperature dependence of \( E_{rel} \) is contained in the TA processor as a hard programmed polynomial \( E_{rel} = A + BT + CT^2 \). On the other hand \( E_{In} \) is determined by calibration using the known heat of fusion of indium.

In general change of enthalpy between two states is

\[ \Delta H = \int H \, dt \]  \hspace{1cm} (24)

The process in which the enthalpy of a body increases is called entothermal as heat is drawn from the surroundings.

2.3.2(b) Basic Equations of Reaction Kinetics:

The kinetic parameters are usually evaluated through expressions derived from the basic equation—

\[ \dot{\alpha} = K (1 - \alpha)^n \]  \hspace{1cm} (25)

where \( \dot{\alpha} = \text{rate of reaction in } S^{-1} \).
\[ K = \text{reaction rate constant in } S^{-1} \]
\[ \alpha = \text{degree of conversion} \]
\[ n = \text{order of reaction} \]

for \( n \neq 1 \),
\[ \alpha = 1 - e^{-kt} \quad \text{(26)a} \]
\[ \therefore \alpha = k e^{-kt} \quad \text{(26)b,} \]

where \( t = \text{time of reaction} \).

for \( n \neq 1 \),
\[ \alpha = 1 - (kt(n-1)+1)^{1/(1-n)} \quad \text{(27)a} \]
\[ \therefore \alpha = k(kt(n-1)+1)^{(n/(1-n))} \quad \text{(27)b} \]

Thus the course of reaction can be calculated with known rate constant and order of reaction for any given temperature.

The temperature dependence of rate constant is given by Arrhenius equation,

\[ K = K_0 e^{\left( \frac{-E_A}{RT} \right)} \quad \text{(28)} \]

Where \( K_0 = \text{reaction rate constant at infinite temperature (frequency factor or pre-exponential factor in } S^{-1}) \)
\[ e = \text{basis of natural logarithm } 2.718 \]
\[ E_A = \text{activation energy in } J/mol \]
\[ T = \text{temperature in kelvin} \]
\[ R = \text{gas constant } = 8.31 \text{ J/mol K} \]

In logarithmic form of the Arrhenius equation-

\[ \ln K = \ln K_0 - (E_A/R) \cdot (1/T) \quad \text{(29)} \]
The linear curve ln K versus 1/T gives the slope \(-E_A/R\) and ordinate intersection ln \(K_0\).

The temperature function of the reaction rate (from equation 25 and 28) is

\[ \alpha = K_0 e^{(-E_A/RT)} (1 - \alpha)^n \]  (30)

2.3.2 (c) Relation between DSC Signal and Reaction Kinetics:

Each reacting molecule \(d\alpha\) produces a certain enthalpy change \(dH\):

\[ d\alpha = dH \cdot (1/\Delta H_{tot}) \]  (31)

Where \(\Delta H_{tot}\) = measured enthalpy of reaction in mJ = total peak area.

Differentiating equation (31) with respect to time yields

\[ \dot{\alpha} = H(1/\Delta H_{tot}) \]  (32)

Thus the rate of reaction is directly proportional to the DSC signal.

From the proportionality of the degree of conversion and the respective enthalpy change (equation 31) it follows.

\[ \alpha = (\Delta H_{\text{part}}/\Delta H_{\text{tot}}) \]  (33)

and for the term \(1 - \alpha\) of the kinetic equation,

\[ 1 - \alpha = (\Delta H_r/\Delta H_{\text{tot}}) \]  (34)

where \(\Delta H_r\) is the remaining area of the DSC peak substituting of \(\alpha\).
and \((1-\alpha)\) in equation (30) by equation (32) and (34) and conversion to the logarithmic form gives,

\[
\ln(\frac{H}{\Delta H_{\text{tot}}}) = \ln K_0 + E_A(\frac{1}{RT}) + n \ln(\Delta H_r/\Delta H_{\text{tot}}) \tag{35}
\]

The three terms \(\ln K_0\), \(E_A\) and \(n\) are unknown. Choosing three points out of the several points of the DSC curve, the three unknown could be determined.

From the multiple linear regression analysis the accuracy of the results is substantially increased because any number of curve points may be evaluated. The confidence limits are computed for 95% probability. They allow to judge the validity of the equation (25) and (26) for the investigated reaction. They should have a value below 10% of the corresponding kinetic data.

2.3.2 (d) Practical use of the kinetic parameters:

The computation of the adiabatic course of the reaction is based on numeric integration of the following equation,

\[
\frac{dT}{dt} = \dot{\alpha} \frac{\Delta H_{\text{spec}}}{C_p}
\]

\[
= K_0 e^{-\frac{E_A}{RT}} (1-\alpha)^n \frac{\Delta H_{\text{spec}}}{C_p} \tag{36}
\]

The total adiabatic temperature rise \(\Delta T_{\text{adi}}\) is

\[
\Delta T_{\text{adi}} = \frac{\Delta H_{\text{spec}}}{C_p} \tag{37}
\]

Where \(\Delta H_{\text{spec}}\) = Specific reaction enthalpy in J/g

\(C_p\) = Mean specific heat during reaction. As an approximation, a \(C_p\) value measured
before the onset of the reaction is sufficient.

2.3.3 Thermogravimetry Analysis (TGA):

Thermogravimetry Analysis (TGA) is a technique where a sample is continuously weighing as it is heated at a constant preferably linear rate. The resulting weight change against temperature curve is known as TG curve and gives information concerning the thermal stability and composition of the original sample.

The weight of a sample remains constant or decreases on heating unless the sample combines with its immediate atmosphere. Such combinations do occur, e.g. in oxidising atmospheres, and a weight increase is then observed, but they are not often encountered. TG curve is therefore known as weight-loss curve. The change in sample weight may be recorded as the actual weight or weight-loss in grams, milligrams etc. or as the percentage or fractional weight-loss. Unless trapped gas is released or volatiles are desorbed, physical transitions are not accompanied by weight losses and therefore cannot be detected by TG. Thus TGA is a useful technique for differentiating between thermal events arising from physical changes and those arising from chemical changes in a sample. The TG curve records a series of weight-loss steps as successive reactions producing volatile materials occur at various temperatures during the programmed heating. Isothermal weight loss measurements, giving weight/time curves, are also used, particularly for kinetic studies of dehydration for hygroscopic materials and decomposition reactions in general. TGA
measurements can be made either in the presence or absence of gases (in vacuum), air, oxygen, nitrogen etc.

In addition to a thermogravimetric curve (TG), the results of TGA study may also be presented as a Derivative Thermogravimetric (DTG) curve. In DTG, the rate of weight loss of the sample is recorded as a function of the sample temperature. A DTG curve shows better resolution of two or more processes occurring at similar temperature than a TG curve. DTG curve consists of a series of peaks corresponding to the various stages in the decomposition, the peak maximum being equivalent to the point of inflection on the TG curve. Moreover DTG curves, often bear a strong resemblance to DTA curves and permit comparison to be made.

The horizontal portions (plateaus) of the TG curve indicate the regions where there is no weight change and the curved portions are indicative of weight losses. If the rate of change of weight with time, \( \frac{dw}{dt} \) is plotted against temperature, a DTG curve is obtained.

2.3.3 (a) Kinetic Studies From TG Curves:

For kinetic measurements it is essential that the weight loss accurately reflects the reaction rate and the sample temperature should be calibrated. Reactions accompanied by large heat changes often give unreliable values for kinetic parameters since the sample temperature is liable to go away considerably from the programmed temperature as the reactions occur.

The kinetic parameters are usually evaluated through expressions derived from the basic equation —
\[
\frac{da}{dt} = K(1-a)^n
\]  \hspace{1cm} (38)

where  
\( a \) = the fraction of sample decomposed  
\( K = \) a rate constant  
\( n = \) the order of reaction  
\( t = \) the time of reaction.

This may also be expressed in terms of the weight of remaining sample 'W'

\[
\frac{dW}{dt} = -K W^n
\]  \hspace{1cm} (39)

This equation is not applicable to all types of reaction and this is one of the major limitations of the method. An equation of this form should be applied separately to every step in the weight loss curve, and the fractional weight loss during each step referred to the total weight loss for that step. Such a procedure can be applied only to those curves giving a reasonable plateau between each stage.

The rate constant depends, as usual on temperature \( T \), the activation energy \( E \), the pre-exponential factor \( A \) and the gas constant \( R \), which is derived as:

\[
K = A e^{-E/RT}
\]  \hspace{1cm} (40)

These relationships can be manipulated to give equations relating the experimental quantities (weight, temperature, heating rate etc.) to the kinetic parameters and the parameters evaluated graphically. The procedure of Freeman and Carroll eliminates the heating rate giving differential equation as:
\(-E/2.3R\) \(\Delta(T^{-1})/\Delta\log W_r = -X + (\Delta \log (dW/dt))/(\Delta \log W_r)\) \(\Delta T^{-1}/\Delta \log W_r\) \(\Delta T^{-1}/\Delta \log W_r\)

Where \(W_r = W_e - W\)

\(W_r\) = the total weight loss for the particular reaction step.

\(W_e\) = weight change at the completion of the reaction.

\(W\) = weight of that reactive portion which remains at time \(t\).

\(R\) = gas constant in KJ/mol.

Calculation of the activation energy \('E'\) from the above equation consists of the following steps.

(i) Plot of weight \((W)\) against time \((t)\) and the slope of this curve gives \(dW/dt\).

(ii) Plot of \('\log (dW/dt)\)', against \('\log W_r'\) at the points corresponding to curve (i) and the slope of this curve gives \((\Delta \log (dW/dt))/(\Delta \log W_r)\).

(iii) Plot of \('T^{-1}'\), against \('\log W_r'\) at the points corresponding to curve (i) and the slope of this curve gives \(\Delta T^{-1}/\Delta \log W_r\).

(iv) Finally plot of \((\Delta \log (dW/dt))/(\Delta \log W_r)\) against \(\Delta T^{-1}/\Delta \log W_r\) and the slope of this straight line gives \(+ or - E/2.3R\), where from \('E'\) can be calculated.

The various slopes (i), (ii), (iii) and (iv) are calculated using the following computed Fortan Programme of second degree polynomial.
Program to calculate activation energy

integer n,m,flag

common d(50, 50), a(50, 50), sol(50)

write (*) 'no of observations (n), order of polynomial (m).
read (*) n,m

write (*) 'Enter (% weight, time, temp )'
read (*) (d(i,1), d(i,2), d(i,3), i=1, n)

do 10 i=1, n
    d(i,4) = (d(i,1) - d(n,1))
    if (d(i,4) .ne. 0.0) then
        d(i,5) = alog10(abs(d(i,7)))
    endif
    d(i,6) = 1.0/d(i,3)
10 continue

flag = dydx(n, m, 1, 2, 7)
do 44 i=1, n
    if (d(i,7) .ne. 0.0) then
        d(i,8) = alog10(abs(d(i,4)))
    endif
44 continue

flag = dydx(n-1, m, 8, 5, 9)
flag = dydx(n-1, m, 6, 5, 10)
flag = dydx(n-1, m, 9, 10, 11)
do 55 i=1, n-1
    avr = avr + d(i,11)
55 continue

avr = avr/(n-1)
e = avr * 2.3 * 8.3256
write(*,*), E = ', e, 'Kj per mol'
write(*,222)
222 format (1x, //6x,'%wt', 8x, 'time', 4x, 'temp', 8x, 'wr', 8x,
* 'log10wr', 3x, '1/T', 6x, 'dw/dt', 5x, 'log10dw/dt',
* 4x, 'slope3', 4x, 'slope4')
do 66 i = 1, n
   write(*,111)(d(i,j),j=1,11)
111        format(4x,11f10.4)
66 continue
   stop
end
integer function dydx(n,m,cx,cr)
integer cy,cx,cr,i,flag,polyreg,gauss
common d(50,50),a(50,50),sol(50)
flag=polyreg(n,m,cx,cr)
flag= gauss(m)
do 88 i=1,n
   d(i,cr)= sol(2)+2*sol(3)*d(i,cx)
88 continue
   dydx = 0
return
end
integer function polyreg(n,m,cx,cr)
integer n,m,cx,cr,l
common d(50,50),a(50,50),sol(50)
do 20 i = 1, m+1
   do 10 j = 1,m+l

k = i+j-2

do 10 1 = 1,n

   a(i,j) = a(i,j) + d(1,cx) ** k

10 continue

right hand side vector linear system of equations

do 20 1 = 1,n

   a(i,m+2) = a(i,m+2) + d(1,cy)*d(1,cx)*(i-1)

20 continue

polyreg = 0

return

end

integer function gauss(m)

integer m,i,k,j

common d(50,50), a(50,50), sol (50)

n=m+1

do 10 k = 1, n-1

   do 20 i=k+1,n

      qt = a(i,k)/a(k,k)

   20 continue

   do 30 j = k+1, n+1

      a(i,j) = a(i,j) - qt*a(k,j)

30 continue

20 continue

   do 40 i=k+1,n

      a(i,k) = 0.0

40 continue

10 continue

back substitution

sol (n)=a(n,n+1)/a(n,n)
2.4 STUDY OF DIELECTRIC PROPERTIES:

Dielectric constant is a dielectric properties of an insulating material used as a dielectric medium. The dielectric properties of the polymeric materials (fibres) were studied by capacity measuring method in which an alternating electric field was used.

2.4.1 DIELECTRIC CONSTANTS:

The dielectric constant or relative permittivity ($\varepsilon'$) of a substance is defined as the ratio of the capacity of an electric capacitor ($C$) filled with the substance to that of the same capacitor ($C_0$) in vacuum at a definite external field frequency as

$$\varepsilon' = \frac{C}{C_0} \quad (42)$$

In case of a cylindrical condenser, if the inner cylinder is charged to $'Q'$ e.s. units of charge per unit length, then
potential difference at a distance \( r' \) from the axis of the cylinder according to Gauss's theorem will be \( \frac{2Q}{\varepsilon' r} \).

Hence, capacity per unit length of the cylindrical condenser is given by

\[
\frac{Q}{2 \log_e (b/a)} = \frac{\varepsilon'}{2 \log_e (b/a)} \text{ e.s.u} \quad (43)
\]

where \( a \) = the radius of the inner cylinder

\( b \) = the radius of the outer cylinder

\( \varepsilon' \) = the dielectric constant of the medium.

Now, the capacity for cylindrical condenser of length \( l \) cm is

\[
C = \frac{\varepsilon' l}{2 \log_e (b/a)} = \frac{2.413 \varepsilon' l}{10^7 \log_{10} (b/a)} \quad \text{mfd.} \quad (44)
\]

\[
= \frac{0.2413 \varepsilon' l}{\log_{10} (b/a)} \quad \text{pfd} \quad (44)
\]

Hence, the dielectric constant of the medium is

\[
\varepsilon' = \frac{\log_{10} (b/a)}{\log_{10} (b/a)} C = K \cdot C \quad (45)
\]

\[
= \frac{0.2413 l}{0.2413 l}
\]

If \( \varepsilon \) is the permittivity of the medium and \( \varepsilon_0 \) is the
permittivity of free space then the relative permittivity of the medium defining dielectric constant as
\[ \varepsilon' = \frac{\varepsilon}{\varepsilon_0} \]  

(46)

2.4.2 DIELECTRIC POLARIZATION AND DIELECTRIC LOSS:

The polarity of the substance can be judged from the chemical structure of its molecules. The experimental definition of the dipole moment \( \mu (=qI) \) leads us to conclusions regarding to structure of the molecules of matter. Symmetrically arranged molecules are nonpolar since in this case the centres of gravity both of positive and negative charges of a molecule coincide with the centre of the symmetry of the molecule. Conversely asymmetric molecules are always polar.

The majority of polymers (cellulose) are typical dielectric materials. When a dielectric is placed in an electric field, an electric moment arises in the dielectric i.e. electrical polarization takes place. The polarization of the unit volume of a dielectric 'P', can be represented by the following sum:

\[ P = P_{or} - P_{def} \]  

(47)

Where \( P_{or} \) - is the polarization due to the orientation of permanent dipoles (orientational polarization).

\( P_{def} \) - is the polarization due to the distortion of electronic shells or to the displacement of atomic nuclei (deformational polarization).

Deformational polarization is practically unaffected by the temperature of the dielectric and is not connected with an irreversible dissipation of energy. The electric energy required
to polarize a molecule is completely returned to the electric energy source after voltage is removed. For this reason deformational polarization does not entail any dielectric losses. Dielectric loss is the part of the energy of an electric field that is dissipated per irrecoverably as heat in the dielectric. The energy dissipated unit volume of dielectric as heat (dielectric loss) is proportional to the field frequency \(f\) and to \(\tan \delta\), the angle \(\delta\) is usually called the loss angle. Besides \(\tan \delta\), dielectric loss is characterised by the loss factor

\[
\varepsilon'' = \varepsilon' \tan \delta.
\] (48)

Where \(\varepsilon'\) is the dielectric constant of the material.

On the other hand the dipole or orientational polarization is connected by its nature with the thermal motion of molecules, and temperature must exert an appreciable effect on the phenomenon of dipole polarization.

A dielectric material (e.g. Cellulose fibre) is characterised by its dielectric constant and dielectric loss, both of which are function of frequency \(f\) and temperature \(T\).

When a low frequency alternating electric field is applied the polarization follow the field. As the frequency becomes higher, the polarization cannot follow the field and there is a lag in attaining equilibrium. This lag is known as relaxation.

A characteristic feature of polymers is independent movement of chain sections consisting of a large number of monomeric units (segments). Besides segments, smaller and more mobile kinetic units are also moving in polymers. Such kinetic independent units
may be side chains or individual atomic groups, e.g. polar substituents. The relaxation time of the orientation moment of such groups is smaller than the relaxation time of main-chain segments and for this reason they can retain their mobility at lower temperatures, where the segments of the main chain are practically immobile.

If a polymer containing polar groups is placed in an electric field, orientation of its segments and smaller kinetic units will be observed at definite relaxation time/field frequency ratios and this gives rise to definite values of dielectric constant and dielectric loss.

In crystal bodies at a temperature below the melting point the dipoles secured in their places so tightly that they can not be oriented and dipole polarization can not occur in them. For all that dipole polarization sometimes manifests itself in some crystal bodies with loose packing of molecules. In some cases specially in cellulose and its derivatives, there may take place a rotation of not whole molecules but of their separate parts.

2.5 STUDY OF ELECTRICAL CONDUCTIVITY (6):

The electrical conductivity of a polymeric material (fibre) depends on the presence of free ions not connected chemically with the macromolecules. The molecular chain proper does not participate in the transfer of electric charges. Therefore, the conductivity of polymers depends largely on the presence of low molecular mass impurities that can serve as sources of ions. The
chemical constitution has only an indirect effect on the mobility of the ions.

Polymers containing no polar impurities possess high dielectric strength and break-down voltages. The break-down voltage of a given polymer (cellulose) may be much lower if the material contains moisture or air inclusions, which ionise in an electric field. The conductivity of a polymer decreases with increasing crystallinity.

2.5.1 Mathematical Expression of \( \sigma \)

In case of a cylindrical condenser used for the measurement of electrical resistivity (hence conductivity) of a dielectric material the volume conduction plays vital role. If the axial length of the electrodes be \( 'l' \) and the outer radius of the inner electrode (cylinder) and the inner radius of the outer electrode be \( 'a' \) and \( 'b' \) respectively, then the electrical resistance of a thin layer of the dielectric having thickness \( 'dx' \) and radius \( 'x' \) will be given by:

\[
dR = \rho \frac{dx}{2\pi x}
\]

\( \rho \) — electrical resistivity.

Integrating from \( x = a \) to \( b \), we get the total resistance of the dielectric as:

\[
R = \int_{a}^{b} \frac{\rho}{2\pi x} dx
\]

\[
= \frac{\rho}{2\pi} \ln \frac{b}{a}
\]

\[
\therefore \rho = \frac{8\pi R l}{\ln \frac{b}{a}}
\]
Where, \( K = \frac{2\pi l}{\ln b/a} \)

The reciprocal of the value of \( \rho \) gives the electrical conductivity of the material as-

\[
\sigma = \frac{1}{\rho} \quad (51)
\]

2.5.2 ACTIVATION ENERGY \((E)\):

At high temperature, ionic mobility increases owing to the considerable mobility of the chain units and hence the conductivity rises. With increasing temperature, the conductivity of polymers increases according to an exponential law-

\[
\sigma = Ae^{-E/KT} \quad (52)
\]

Where \( \sigma \) = electrical conductivity,

\( A \) = a constant,

\( E \) = activation energy,

\( K \) = Boltzmann constant,

\( T \) = absolute temperature.

The slope of the curve \( \log \sigma \) vs \( 1/T \) gives \( E/K \) and hence \( E \), the activation energy can be calculated.