

UNIT-II

THERMAL METHOD OF ANALYSIS

Points to be covered in this topic

- ❖ Introduction
- ❖ Thermogravimetric analysis
- ❖ Differential thermal analysis
- ❖ Differential scanning calorimetry

THERMAL METHOD OF ANALYSIS

❑ INTRODUCTION

- Thermal methods of analysis may be defined as those techniques in which **changes in physical and /or chemical properties of a substance are measured as a function of temperature.**
- Thermal analysis used to **quantitative and qualitative analysis** of samples.
- Samples may be identified and characterized by **qualitative investigations of their thermal behaviour.**
- Information concerning the **detail structure and composition of different phases of a given sample** is obtained from the analysis of thermal data.
- Quantitative results obtained from **changes in weight and enthalpy as the sample is heated.**
- The **temperature of phase changes and reaction** as well as the sample is heated.
- The temperature of **phase changes, reactions and heat of reaction** are used to determine the **purity of materials.**
- Three thermal methods discussed in this chapter:
 - **Thermogravimerty (TG):** A technique in which a **change in the weight** of a substance is recorded as function of temperature or time.
 - **Differential thermal analysis (DTA):** A technique in which the **temperature difference between a substance and a reference material** is measured as a function of temperature while the substance and reference are subjected to a **controlled temperature programme.**

➤ **Differential scanning calorimetry (DSC):** A technique in which the difference in energy inputs into a substance and a reference material is measured as function of temperature programme.

Classification of analytical method

S. No.	Name	Property Measured	Apparatus Involved	Graph
1	Thermogravimetric analysis	Change in Weight (mass)	Thermo balance	Mass Vs temp
2	Derivative Thermogravimetric analysis	Rate of exchange of weight(dm/dt)	Thermo balance	dm/dt vs. temp.
3	Differential thermal analysis	Heat absorbed or evolved (AT)	DTA apparatus	AT vs. temperature

❑ THERMOGRAVIMETRIC ANALYSIS (TGA)

❖ Principle

- It is a simple analytical technique that **measures the amount and rate of change in the weight of a material as a function of temperature** or time in a controlled atmosphere.
- Measurement are used primarily to **determine the composition of materials** and to predict their thermal stability at temperatures up to **1000 °C**.
- It is the **most widely used thermal method** which can characterize materials that **exhibit weight loss or gain due to decomposition, oxidation, dehydration**.
- As materials are heated, they can lose weight from a simple process such a **drying, or from chemical reactions that liberate gases**.

- Some materials can **gain weight by reacting with the atmosphere** in the testing environment.
- Since weight loss and gain are disruptive processes to the sample material, **knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps** and holds during those critical reaction periods.
- Such analysis **relies on a high degree of precision in three measurements: weight, temperature, and temperature change.**

➤ **There are three types of thermogravimetry:**

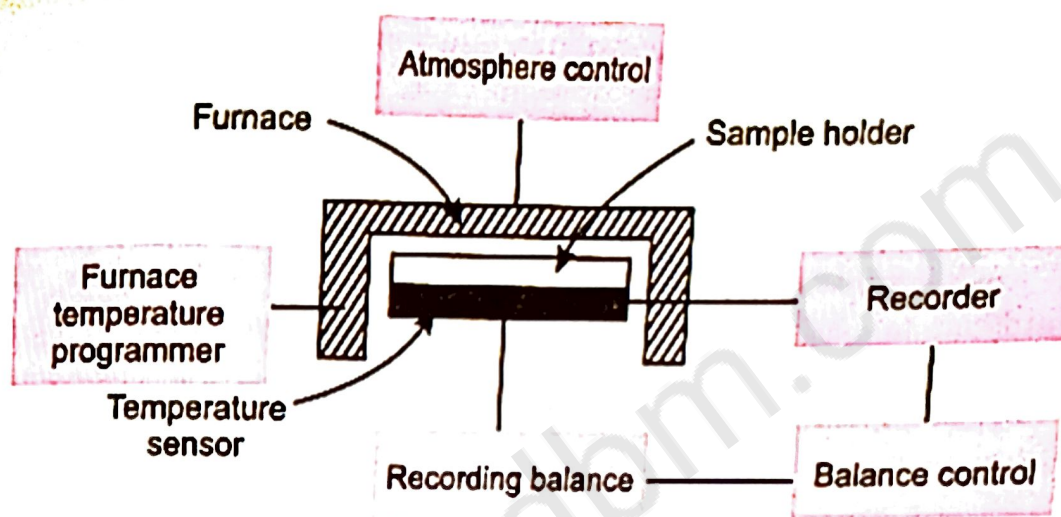
- Isothermal or Static Thermogravimetry:** In this technique the sample weight is recorded as a **function of time at constant temperature.**
- Quasistatic Thermogravimetry:** In this technique, the sample is heated to constant weight at each of a **series of increasing temperatures.**
- Dynamic thermogravimetry:** In this technique, the sample is heated in an environment **whose temperature is changing in predetermined manner, generally at a linear rate.** Most of the studies are carried out with dynamic thermogravimetry. Therefore, generally it is referred to as thermogravimetry.

❖ **Instrumentation**

- The principle of thermogravimetry is based on the **simple fact that the sample weighed continuously as it is being heated to elevated temperatures.**
- In the market both **manual as well as automatic recording balances are available** but for practical reasons, the latter type is preferred.
- However, manual recording is still used for **long term isothermal measurements.**

The various components are as follows

- 1) The balance
- 2) Sample Holder
- 3) The Furnace
- 4) Temperature measurements
- 5) Thermobalance
- 6) Recorder



Schematic representation of Thermobalance

➤ The Balance

It is most important component of the **thermobalance**. A good balance must fulfil following requirements:

- Its **accuracy, sensitivity, reproducibility and capacity** should be similar to those of analytical balance.
- It should have an **adequate range of automatic weight** adjustment.
- It should have a **high degree of mechanical and electronic stability**.
- It should have a **rapid response to weight changes**.
- It should be **unaffected by vibration**.
- The balance should be **simple to operate and versatile**.

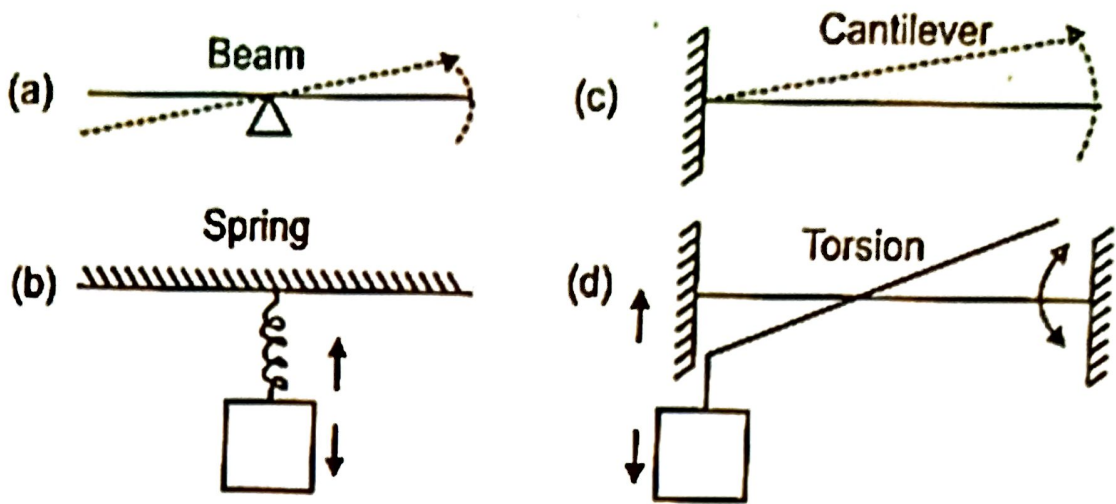
- Recorded balances are mainly of two types:

(a) Deflection type instruments and

(b) Null point instruments.

(a) Deflection Balances: These are of the following types-

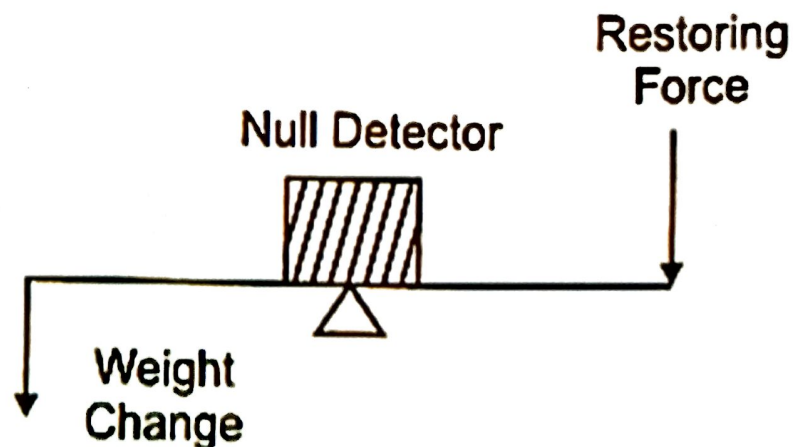
- Beam Type:** In these balances, there occurs a conversion of beam deflection about the fulcrum in a suitably identifiable weight change curves by photographic recorded trace, recorded signals generated by suitable displacement measuring transducers or curve drawn electromechanically.
- Helical Type:** In these balances there occurs an elongation or contraction of the spring with weight change. These changes in the length of the spring may be suitably recorded by use of transducers; the quartz fiber is generally used as a spring. The quartz fiber avoids anomalous results with change of temperature and avoids fatigue problems.
- The Gantlevered Beam:** In these types of balances, one end of the beam is fixed and the other end on which the sample, is placed, is free to undergo deflections. The technique of deflection' measurement are same as in beam type balances.
- Torsion Wire:** In this type of balances, the beam is attached to a taut wire which acts as a fulcrum. The wire is firmly fixed at either or both ends so that the deflections of the beam are proportional to weight changes and the torsional characteristics of the wire. Sometimes, a metallic ribbon is employed instead of a taut wire. In these balances, detection devices used are similar to the beam type.



Deflection Balances

(b) Null Point Balances:

- In these balances, there should be a **sensor to detect the deviation of the balance beam from its null position**.
- Then, a **restoring force, of either electrical or mechanical weight loading**, is applied to the beam to restore its null position from the horizontal or vertical norm,
- This **restoring force is proportional to the weight change** and this force is recorded directly or by transducer of some type.

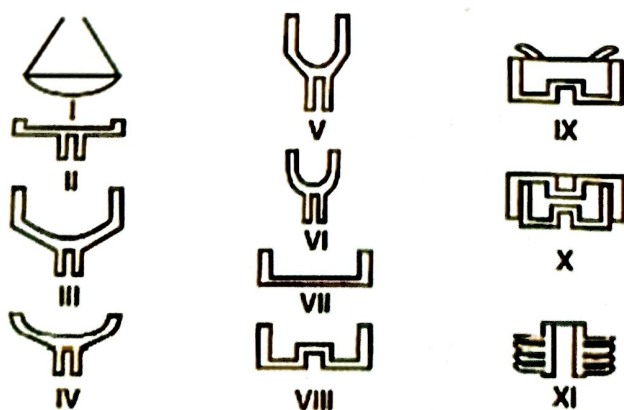


Null Point Balances

➤ Sample Holder

- The geometry, size, and material of sample holder have **important effect on the shape of TG curve**.
- The size and shape of a sample holder **depend upon nature, weight of sample and maximum temperature range** to be used for analysis.
- **Glass, quartz, alumina, stainless steel, platinum, graphite** etc. are used as material for construction of sample holder.
- **The following are the types of sample holder.**

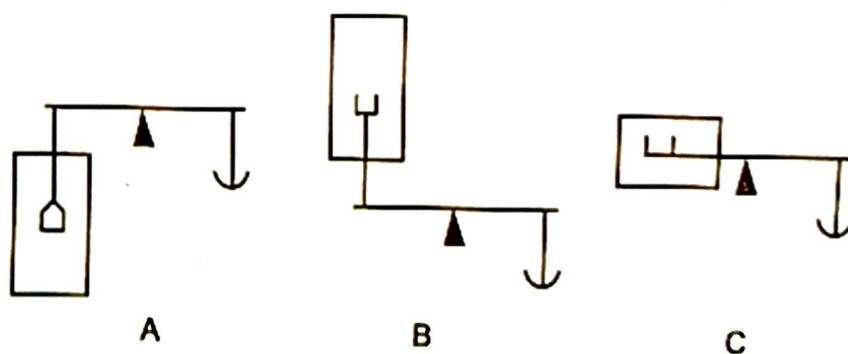
- 1) **Shallow pans:** These are used for such samples in which **diffusion is the rate controlling step**. Volatile substances produced during reaction must **escape out which is determined as weight loss**.
- 2) **Deep crucibles:** These are used in such cases where side reactions are required such as in **study of industrial scale calcinations, surface area measurements, etc.**
- 3) **Loosely covered crucibles:** These are used in **self-generated atmospheric studies**. Rate of temperature or weight loss is not important because the **studies are done isothermally**.
- 4) **Retort cup:** These are used in **boiling point studies**. It provides **single plat of reflux** for a boiling point determination.



Different types of Sample Holder

➤ Furnace

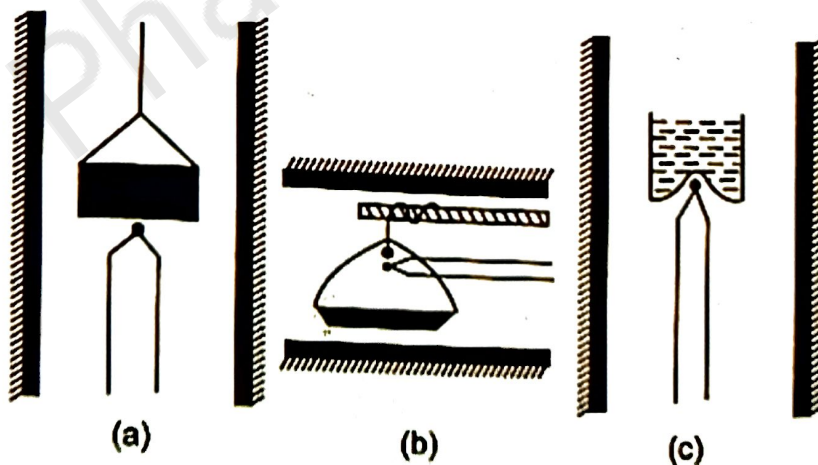
- The furnace should be **designed in such a way that it produces a linear heating range**. It should have a **hot zone which can hold sample** and crucible and its temperature corresponds to the temperature of furnace.
- The temperature ranges can **affect the internal atmosphere of furnace chamber**; therefore, it is necessary to choose specific type of furnace according to temperature ranges.
- There are different **combinations of microbalance and furnace available**. The **furnace heating coil should be wound in such a way that there is no magnetic interaction between coil and sample** or there can cause apparent mass change.
- Coils used are made of **different materials with variant temperature changes viz.**
- **The size of furnace is important**. A high mass furnace may have a **high range of temperature and obtain uniform hot zone** but requires more time to achieve the desired temperature.
- Comparatively, **a low mass furnace may heat quickly but it's very difficult to control rise in temperature and maintain hot zone**. The position of furnace is also important.



The position of furnace with respect to the balance.

➤ Temperature Measurement

- It is done with the help of **thermocouple**.
- Different materials are used for measuring **different ranges of temperatures** i.e. **Chromal or alumel (alloys of platinum)** thermocouples are used for **T-11000°C**,
- **Tungsten or rhenium thermocouples** are used for higher temperature. The position of thermocouple is important.
- It can be adjusted in following ways
 - i. Thermocouple is **placed near the sample container and has no contact with sample container**. This arrangement is not preferred in low-pressures.
 - ii. The **sample is kept inside the sample holder but not in contact with it**. It responds to small temperature changes only.
 - iii. Thermocouple is placed **either in contact with sample or with sample container**. This method is best and commonly employed.



The position of a thermocouple in a thermobalance

➤ Data Recording Unit

- The output from the **thermobalance and furnace** are recorded using either chart recorder or a microcomputer (work station).
- The **advantage of microcomputer over chart recorder** is that the microcomputer comes with **such software which allows data to be saved and plotted while performing mathematical problems.**
- Besides that, **multiple TG curves can be plotted simultaneously.** In such microcomputers, we get plot of **weight change versus temperature or time.** Some other recording systems are also available viz.
- X-Y recorders and Time-Base Potentiometric Strip Chart Recorder. In X-Y Recorder, plot of weight directly against temperature is presented.

❖ Applications

➤ **Thermal Stability:** related materials can be **compared at elevated temperatures under the required atmosphere.**

- The TG curve can help to **elucidate decomposition mechanisms.**

➤ **Compositional analysis:**

- By careful choice of temperature **programming and gaseous environment,** many complex materials or mixtures may be **analyzed by decomposing or removing their components.**

➤ **Simulation of industrial processes:**

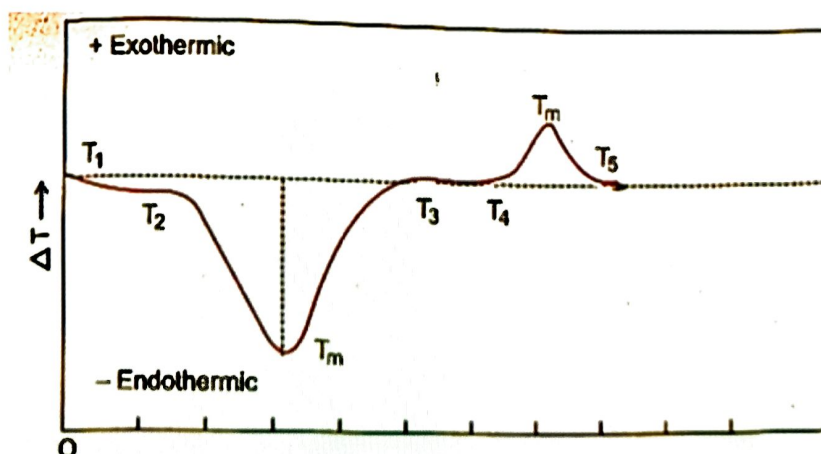
- The thermobalance furnace is **thought as mini-reactor and has ability to perform operations** like some types of industrial reactors.
- **Kinetic Studies:** by understanding the **controlling chemistry or predictive studies,** a variety of methods can be used to analyze the kinetic features of weight loss or gain.

- **Corrosion studies:** TG provides a means of **studying oxidation or some reactions** with other reactive gases or vapors.
- **Evaluation of gravimetric precipitate:** one of the most important application of thermogravimetry is to **determine correct drying temperature of precipitate used in gravimetric analysis.**
- **Evaluation of suitable standard:** A number of experiments on thermogravimetry to find **suitable standards in analytical chemistry.**
- TG studies combined with **infrared absorption spectrophotometric studies** in order to arrive at these conclusions.
- **Testing of Purity of Samples:**
 - As an analytical tool, the thermobalance can be used **determining the purity** of various substances.
 - For example in a research paper **established how an impure sample of calcium oxalate showed an unusual weight loss below 100°C.**
 - When calculations were carried out, it was observed that the weight loss was not **due to adsorbed water but due to some impurity.**
- **Curie Point Determination:**
 - If a ferromagnetic material is kept on a **thermobalance with the pole of a magnet above the sample**, the TG balance will show the weight which will be less than the actual weight.
 - **Ferromagnetic materials lose their magnetism** on heating at exactly reproducible temperatures on Curie points.
- **Other Applications:**
 - One of the first important applications of thermogravimetry was the **determination of correct drying temperatures for precipitates** used in gravimetric analysis.

□ DIFFERENTIAL THERMAL ANALYSIS (DTA)

❖ Principle

- Differential thermal analysis (DTA) involves the technique of **recording the difference in temperature between a substance and a reference material** against either time or temperature.
- Thus, a differential thermogram consists of a record of the **differences in sample and reference temperature (differential temperature, ΔT)** plotted as a function of time t , sample temperature (T_s), Reference temperature (T_r) or furnace temperature. Substance and reference material are subjected to controlled temperature
 - a. Absorption of heat (Endothermic)
 - b. Emission of heat (Exothermic)
- Sharp endothermic peaks give **ideas of changes in crystallinity or fusion processes** whereas broad endothermic peak signify dehydration reactions.
- **Physical changes give rise to endothermic curves whereas chemical reactions** (particularly oxidative nature substances give rise to exothermic peaks).
- DTA allows the **detection of every physical or change** whether or not it is accompanied by a change in weight.



Typical DTA curve

❖ Instrumentation

➤ **Sample Holder**

- This is used to **contain the sample as well as the reference material.**
- Sample and reference crucibles are generally **metallic (Al, Pt) or ceramic (silica)** and may or may not have a lid.
- **Metallic holders give rise to sharp exotherms** and flat endotherms.
- Best results are obtained when the **area of contact between the sample and the pan or crucible is maximized.**
- Samples are generally in the **1-10 mg range for analytical applications.**
- The dimensions of the **two crucibles and of the cell wells are as nearly identical** as possible; furthermore, **the weights of the sample and the reference should be virtually equal.**
- Non metallic materials generally include **glass, vitreous silica or sintered alumina.**

➤ **Furnace**

- This is device for **heating the sample.**
- The sample and reference should be matched **thermally and arranged symmetrically with the furnace** so that they are both heated or cooled in an identical manner.
- The metal block surrounding the wells **acts as a heat sink.** The temperature of the heat sink is slowly increased **using an internal heater.** The sink in turn simultaneously **heats the sample and reference material.**

➤ **Temperature controller**

- Operating temperatures for DTA instruments are **generally room temperature to about 1600°C**, although one manufacturer makes a DTA

capable of operating from **1500°C to 2400°C**.

- To reach the very low sub-ambient temperatures, a **liquid nitrogen cooling accessory is needed**.
- Some **low temperatures (but not -1500°C) may be reached with electrical devices or with forced air-cooling**. When a physical change takes place in the sample, heat absorbed or generated.
- For example, when a **metal carbonate decomposes, CO₂ is evolved** This is an **endothermic reaction**; heat is absorbed and the sample temperature decreases.
- The sample is now at **a lower temperature than the reference**. The temperature difference between the **sample and reference generates a net signal, which is recorded**.

A. Temperature control: The three basic elements are required to control the temperature These are **sensor, control element and heater**.

- The control elements are governs the **rate of heat input required to match heat loss from the system**.
- The location of heater and mode of heat transfer measure **the time elapse between sensing and variation in heat input**.
- If there is adjustment occur between these three components then **successful temperature control is possible**.

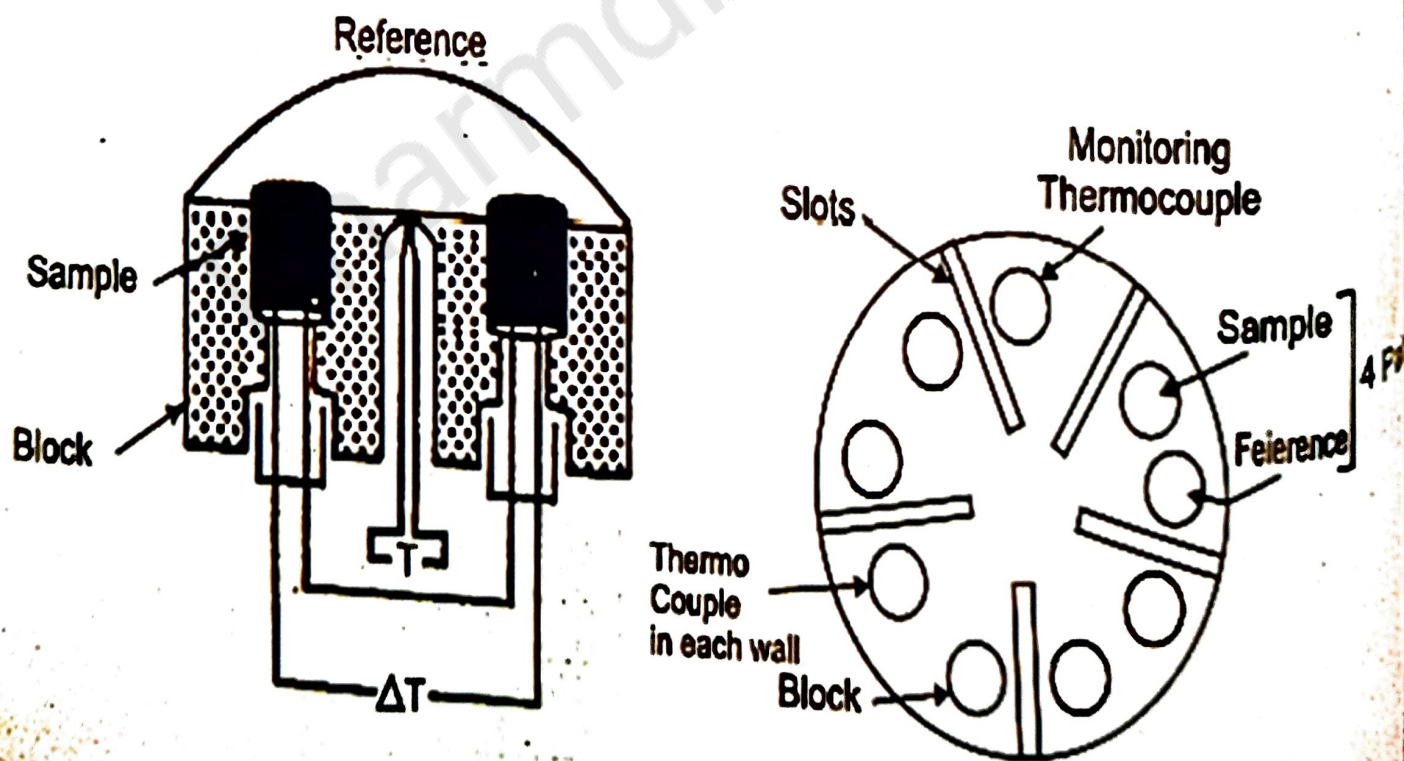
B. Temperature programming: A desired rate of heating or cooling and maintain the constant temperature at any desired value, the thermal apparatus **require a time dependent temperature cycling of the furnace**.

- This can be achieved by employing a temperature programmed which **transmits a certain time based instructions to the control unit**.

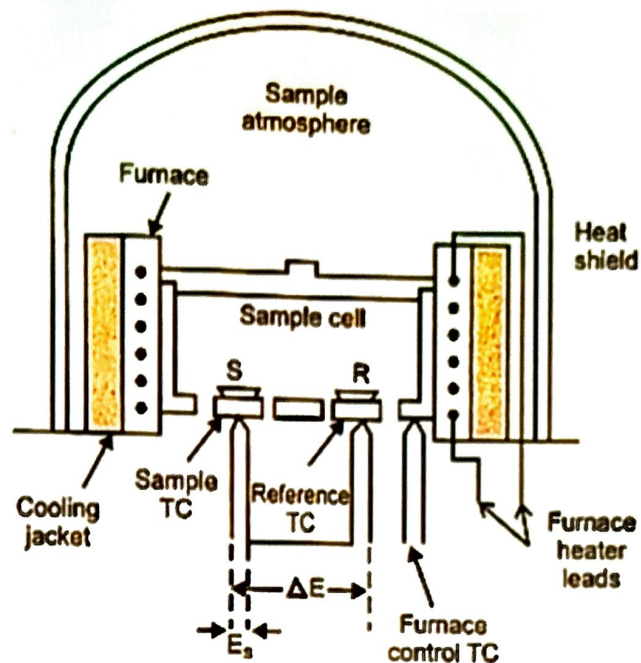
- DTA instrument because one cannot achieve **linear rate of heating or cooling.**
- However one can achieve linearity in the rate of heating or cooling if the autotransformer is driven in a non linear fashion using a special cam - drive.

C. Recorder: This is to record the DTA curve.

- A pair of matched thermocouples is used One pair is in contact with the sample or the sample container, the other pair is in contact with the reference.
- Ts-Tror AT, is amplified and sent to the data acquisition system.
- This allows the difference in temperature between the sample and the reference to be **recorded as a function of the sample temperature, the reference temperature or time.**



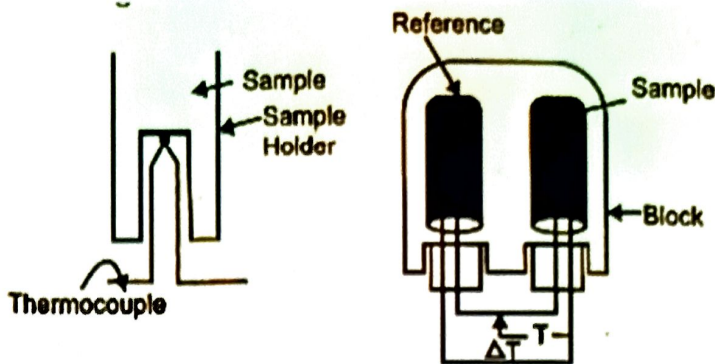
The different Positions of thermocouples in DTA



DTA apparatus

➤ Thermocouples

- In most of DTA and TG instrument **temperature sensor are thermocouples.**
- For more precise temperature measurement the thermocouple terminals were **tapped from time to time.**
- While selecting thermocouple as the temperature sensor one has to consider the following points:
 - 1) Temperature interval
 - 2) Thermoelectric coefficient
 - 3) Chemical compatibility with sample
 - 4) Chemical gaseous environment used
 - 5) Reproducibility of the EMF vs. temperature curve as function of thermal cycling
 - 6) Availability and cost
- Thermocouples are made from chromel P and alumel wire (both nickel-chromium alloys) are used to measure and control temperature upto 1100°C.



Differential Thermocouple

➤ Cooling device

- A simple automatic cooling system is effective in DTA instrument.

❖ Applications

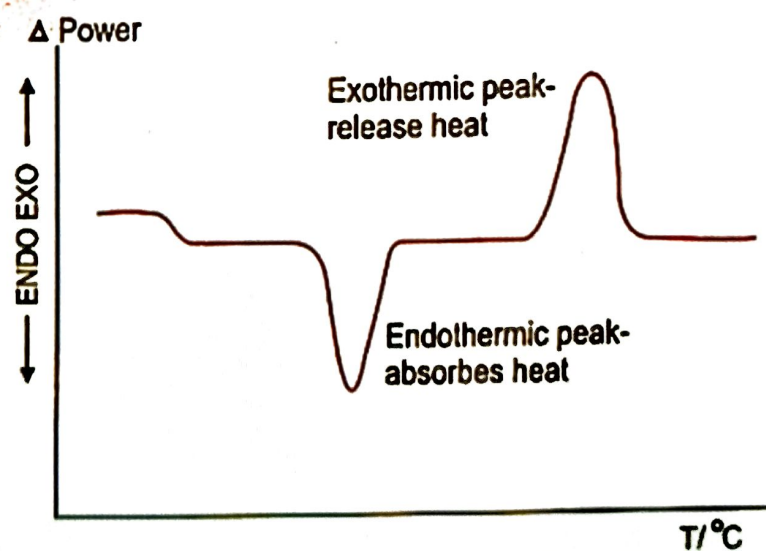
- **Qualitative Identification of Minerals:** Detection of **any minerals in a sample**
- Polymeric Materials:** DTA useful for the **characterization of polymeric materials** in the light of identification of thermo physical, thermo chemical, thermo mechanical and thermo elastic changes or transitions.
- **Measurement of Crystalline:** Measurement of the **mass fraction of crystalline material in semi crystalline polymers.**
- **Analysis of Biological Materials:** DTA curves are used to **date bone remains or to study archaeological materials.**
- **Identification of Substances:** DTA curves for **two substances are not identical, hence they serve as finger prints for various substances.** This technique is used **for testing the purity of the drug sample** and also to **test the quality control of number of substances like cement, soil, glass etc.**
- **Used for the determination of heat of reaction, specific heat and energy change occurring during melting etc.**

- **Trend in ligand stability (thermal stability of the ligands)** gives the information about the **ligands in the coordination sphere**. Whenever there occurs a **change in energy due to chemical as well as physical changes of state in system which is being heated**, DTA yields a signal for this transformation. This generality has widened the scope of DTA compared to TG.
- By DTA, one can study **physical transformations like melting, freezing volatilization changes in crystallinity** and specific heat, adsorption, and desorption as well as changes chemical.
- **Identification of Products:** When a substance reacts with another substance, **the products are identified by their specific DTA curves**. Therefore, this technique has been termed as **Reaction DTA Technique**.
- **Melting Points:** As melting points can be easily determined by DTA, it means that this can be used as a **direct check of the purity of the compound**.
- **Quantitative Analysis:** We know that the area of DTA peak is proportional to the **total heat of reaction and hence to the weight of the sample**. Therefore, the **quantitative analysis is possible with the help of standard curves of peak area vs. weight**.
 - a. **Differential thermal analysis is based on changes of heat flow into the sample**. Using DTA, we can detect the **decomposition or volatilization of the sample**, just as we can with TG.
 - b. It should be noted that a **change in the sample weight does not necessarily take place at a transition temperature** detected by DTA.
 - c. The physical properties, such as **strength and flexibility, of a polymer depend (among other things) on its crystallinity**.

❑ DIFFERENTIAL SCANNING CALORIMETRY (DSC)

❖ Principle

- The DSC has become the **most widely used thermal analysis technique**, in which the **sample and reference material are subjected to a precisely programmed temperature change**.
- When a **thermal transition** (a chemical or physical change that results in the emission or absorption of heat) occurs in the sample, **thermal energy is added to either the sample or reference container to maintain both the sample and reference at the same temperature**.
- Because the transition, the **balancing energy yield a direct calorimetric measurement of transition energy**.
- Energy transferred is exactly **equivalent in magnitude to the energy absorbed or evolved** in since DSC can measure directly both the **temperature and the enthalpy of transition or the heat of reaction**,
- It is often substituted for differential thermal analysis as a mean of determining these quantities except in certain high-temperature application.



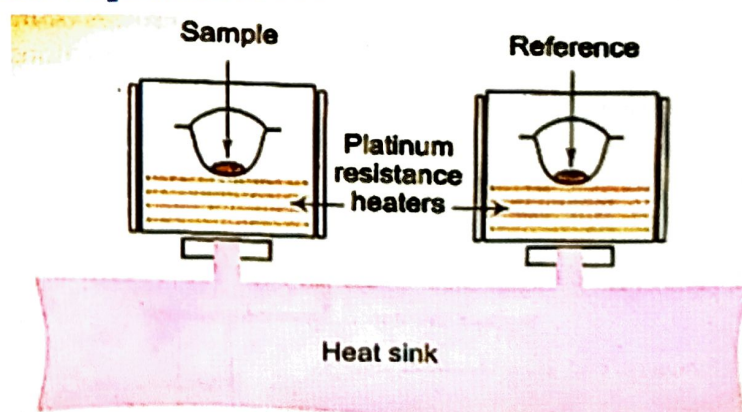
Typical DSC Curve

❖ Instrumentation

- There are three different types of DSC instrument such as **Power Compensated DSC, Heat flux DSC and modulated DSC**. Each produces a plot of power or heat flow versus temperature, **called a thermogram**.

➤ Power compensated DSC

- Theoretical analysis of **two systems of power-compensated DSC** is presented; **one is a system with proportional temperature control** of the sample holder and **the other is with PID** (proportional, integral and differential) temperature control of the sample holder.
- Power-compensated DSC is designed to **measure directly and exactly the enthalpy change of the sample holder** as a function of time.
- When there is an input signal, the **enthalpy change of the sample holder** is a **step function of time**, and the **output signals in both systems are examined**.
- The output signal in the system with **proportional temperature control of the sample holder gradually approaches the input signal** as time increases but does not converge uniformly to the input signal.
- The output signal in the system with PID temperature control of the sample holder **shows time delay and an overshoot or damped vibration depending on the values of control parameters**.
- Proportionality relation between **total enthalpy change of the sample holder and peak area of the output signal is valid in both systems**.

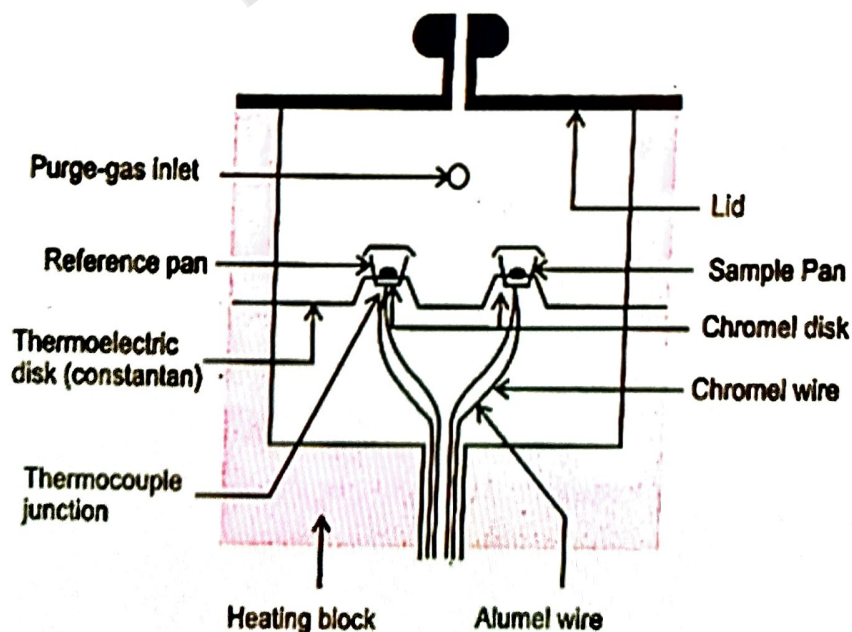


Power-compensated DSC

➤ Heat flux DSC

- The heat flow signal from a differential scanning calorimeter (DSC) includes **significant artifacts related to the instrumentation.**
- They may be categorized as **those due to imbalances in the instrument** or **those resulting from instrument heat capacity effects**, commonly known as **"smearing"**.
- Imbalances cause **instrument baseline defects** that include **offset, slope and curvature.**
- Instrument heat capacity effects **reduce the resolution of transitions and increase uncertainty** when performing partial integrations of transitions.
- A new DSC heat flow measuring technique was developed that **greatly reduces instrument baseline defects resulting from imbalances.**
- It improves resolution and dynamic response by **accounting for the instrument heat capacity effects.**
- There are three components to the new heat flow measurement technique:
 - A. A new heat flow sensor assembly that has **independent sample and reference calorimeters** and incorporates two differential temperature measurements.
 - B. A more comprehensive **heat flow measurement equation** that **includes calorimeter imbalances and differences in heating rates** within the instrument.
 - C. A **calorimetric calibration technique** that **characterizes the imbalances and enables the more comprehensive heat flow equation to be used.** A DSC incorporating the new measurement displays a greatly improved instrument baseline and substantially improved resolution.

- In heat flux DSC, the **difference in heat flow into the sample and reference is measured** while the **sample temperature is changed at the constant rate**.
- The main assembly of the DSC cell is enclosed in a cylindrical, silver heating block, which dissipates heat to the specimens via a constant disc which is attached to the silver block.
- The disk has two raised platforms on which the **sample and reference pans are placed**.
- A **chromel disk and connecting wire** are attached to the underside of each platform, and the resulting **chromel-thermoelectric disk thermocouples** are used to determine the differential temperatures of interest.
- **Alumel wires attached to the chrome discs provide the chromel, alumel junctions** for independently measuring the sample and reference temperature.
- A **separate thermocouple embedded in the silver block serves a temperature controller** for the programmed heating cycle. And inert gas is passed through the cell at a constant flow rate of about 40 ml/min.



Heat flux DSC

➤ **Modulated DSC**

- Modulated DSC (MDSC) uses the **same heating and cell arrangement as heat flux DSC method.**
- In MDSC, a **sinusoidal function is superimposed on the overall temperature programme** to produce a microheating and cooling cycle as the **overall temperature is steadily increased or decreased.**
- **Using Fourier transform methods,** the overall signal is mathematically deconvoluted into two parts, **a reversing heat flow signal and non reversing heat flow signal.**
- The reversing heat flow signal is associated with **the heat capacity component of the thermogram** and **non reversing heat flow is related with kinetic processes.**
- Usually step transition such as the glass transitions, **appear in the reversing heat flow signal and exothermic or endothermic events may appear in either or in both signal.**
- The main advantage of this technique is **the separation of overlapping events in the DSC scans.**
- In MDSC the **normally linear heating ramp is overlaid with the sinusoidal function (MDSC) defined by a frequency and amplitude to produce a sine wave shape temperature versus time function.**

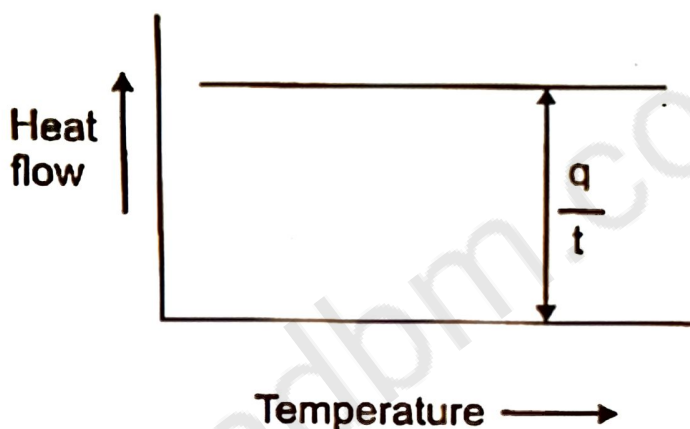
❖ **Applications**

- DSC finds many applications in **characterizing materials.**
- Quantitative applications include the **determination of heats of fusion and the extent of crystallization for crystalline materials.**
- **Glass transition temperatures and melting points** are useful for qualitative classification of materials, although thermal methods cannot be used alone for identification.

- Melting points are also very useful in establishing the **purity of various preparations**. Hence, thermal methods are often used in quality control applications.

➤ **Determination of Heat Capacity**

- DSC plot can be used to **determine Heat Capacity**.
- When a polymer is being heated. When start heating two pans, the computer will plot the **difference in heat output of the two heaters against temperature** that is plot of heat absorbed by the polymer against temperature.



Determination of Heat Capacity

- The heat flow is heat (q) supplied per unit time (t), whereas, The heating rate is temperature increase (ΔT) per unit time (t),

$$\text{Heat flow} = \frac{\text{heat}}{\text{time}} = \frac{q}{t}$$

$$\text{Heating rate} = \text{temperature increase/time} = \Delta T / t$$

- By dividing heat flow (q/t) by the heating rate ($\Delta T/t$). It ends up with heat supplied divided by the temperature increase, which is called heat capacity.

$$(q/t) (\Delta T/t) = q / \Delta T = C, = \text{Heat Capacity}$$

- When a certain amount of heat is transferred to the sample, its temperature increases by certain amount, and the amount of heat it takes to get a certain temperature increase is called the heat capacity, or C_p .

- **Glass Transition Temperatures:** Determination of the glass transition temperature T_g is one of the most important applications of DSC.
- The physical properties of a **polymer undergo dramatic changes at T_g , where the material goes from a glassy to a rubbery state.**
- At the glass transition, the **polymer undergoes changes in volume and expansion, heat flow and heat capacity.** The change in heat capacity is readily measured by DSC.

- **Crystallinity and Crystallization Rate:** With crystalline materials, the level of crystallinity is an **important factor for determining polymer properties.**

- Degrees of crystallinity can be determined **by IR spectroscopy, X-ray diffraction, density measurements, and thermal methods.**
- In most cases DSC is one of the easiest methods for determining levels of crystallinity. The crystallinity level is obtained by **measuring the enthalpy of fusion for a sample (ΔH_f)_{sample} and comparing it to the enthalpy of fusion for the fully crystalline material (ΔH_f)_{Crystal}.** The fractional crystallinity is then given by;

$$\text{Fractional Crystallinity} = \frac{(\Delta H_f)_{\text{Sample}}}{(\Delta H_f)_{\text{Crystal}}}$$

- Calorimetric methods are also used to **study crystallization rates.** **Crystallization is an exothermic event.** The rate of heat release and thus the crystallization kinetics can be followed by DSC.

- **Reaction kinetics:** Many chemical reactions, such as polymer formation reactions, are **exothermic and readily monitored by DSC methods.**

- Here the determination of the **rate of heat release, dH/dt is used to determine the extent of reactions as a function of time.**

- Polymerization kinetics can be studied in **both a temperature scanning and an isothermal mode**. With some polymer systems, **factors such as monomer volatility and viscosity can affect the measured kinetics**.

UNIT-II

X-RAY DIFFRACTION METHODS

Points to be covered in this topic

- ➔ ❖ Introduction
- ➔ ❖ Origin of x-rays
- ➔ ❖ Basic aspects of crystals
- ➔ ❖ Instrumentation
- ➔ ❖ Rotating crystal technique
- ➔ ❖ X-ray diffraction methods
 - Single-crystal x-ray diffraction
 - Powder diffraction method
- ➔ ❖ Applications of x-ray diffraction method

X-RAY DIFFRACTION METHODS

❑ INTRODUCTION

- The alpha-beta and gamma rays given off during **radioactive decay** lose their energy when **they pass through matter by transferring it to the atom molecules, or ions with which they colloid.**
- These collisions may be **elastic in the sense that only K. E. is transferred,** thereby raising the temperature of the exposed material.
- **A variety of X-ray techniques and methods are in use.** But we shall classify all methods in the main **three categories.** These are discussed as follows one by one:

X-Ray absorption methods

- These are analogues to absorption methods in the **other regions of electromagnetic spectrum.**
- In these methods, a **beam of X-rays is allowed to pass through the sample,** and attenuation or fractions of X-ray photons absorbed is **considered to be a measure of the concentration of the absorbing substance.**
- X-ray absorption methods are only helpful in certain cases like **elemental analysis and thickness measurements.** As compared with other X-ray method, these are undoubtedly the least used.

X-Ray diffraction methods

- X-ray diffraction is one of the **earliest methods for studying the structure of solids.**
- In the process of diffraction, **electromagnetic waves of a given frequency but different phases interact to produce constructive interference**

- (bright spots on the film exposed to the light) and **destructive interference** (dark spots).
- By a careful analysis of the diffraction patterns, **very accurate values of the lattice parameters (unit cell dimensions) can be inferred.**
- These methods are based on **scattering of X-rays by crystals.** By these methods, one can identify the crystal structures of various solid components.
- These methods are extremely important as compared with X-ray absorption and X-ray fluorescence methods.

X-Ray fluorescence method

- In these methods, **X-rays are generated within the sample and by measuring the wavelength and intensity** of the generated X-rays; one can perform qualitative and quantitative analysis.
- X-ray fluorescence method is **non destructive and frequently requires very little sample preparation** before the analysis can be carried out.

❑ THEORY

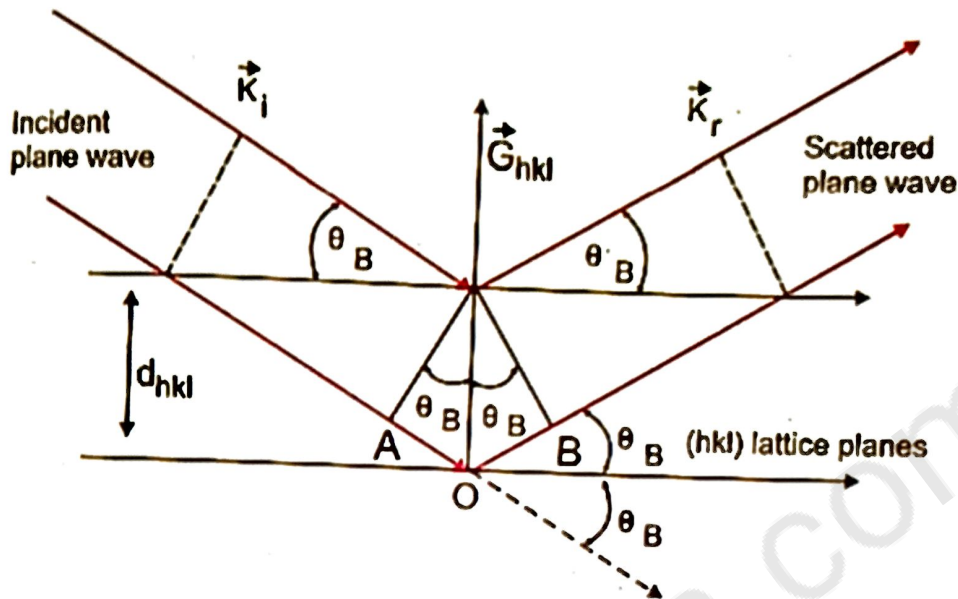
❖ Origin of x-rays

- X-rays make up **X-radiation**, a form of electromagnetic radiation.
- Most X-rays have a wavelength ranging from **0.01 to 10 nanometers**, corresponding to frequencies in the **range 30 pentahertz to 30 hexahertz (3×10^{16} Hz to 3×10^{19} Hz)** and energies in the range **100 eV to 100 keV.**
- For analytical purposes, the **range of 0.07 to 0.2 nanometer is the most useful region.**
- X-ray wavelengths are **shorter than those of UV rays** and typically longer than those of gamma rays.

- In many languages, **X-radiation is referred to with terms meaning Rontgen radiation**, after the German scientist Wilhelm Rontgen, who usually is credited as its discoverer, and who named it **X-radiation to signify an unknown type of radiation**.
- X-rays are generated when **high velocity electrons are impinges on a metal target**.
- The process of **producing X-rays may be visualized in terms of Bohr's theory of atomic structure**. **An atom is composed of a nucleus**.
- X-ray diffraction (XRD) relies on the **dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials**.
- A primary use of the technique is the **identification and characterization of compounds** based on their diffraction pattern.
- The dominant effect that occurs **when an incident beam of monochromatic X-rays interacts with a target material** is scattering of those X-rays from atoms within the target material.
- In materials with **regular structure** (i.e. crystalline), the **scattered X-rays undergo constructive and destructive interference**. This is the process of diffraction.
- The diffraction of X-rays by crystals is described by **Bragg's Law**,

$$n\lambda = 2d \sin \theta$$
- The directions of possible **diffractions depend on the size and shape** of the unit cell of the material.
- The intensities of the diffracted waves depend on **the kind and arrangement of atoms in the crystal structure**.
- However, most materials are not **single crystals**, but are composed of many **tiny crystallites in all possible orientations** called a **polycrystalline aggregate** or powder.

- When a powder with **randomly oriented crystallites** is placed in an **X-ray beam**, the beam will see all possible interatomic planes.
- If the experimental angle is **systematically changed**, all possible **diffraction peaks from the powder will be detected**.



Reflection of X-rays from two different planes of a Crystal

- An **X-ray incident upon a sample will either be transmitted**, in which case it will **continue along its original direction**, or it will be **scattered by the electrons of the atoms in the material**. All the atoms in the path of the **X-ray beam scatter X-rays**.
- We are primarily interested in the peaks formed when **scattered X-rays constructively interfere**.
- Constructive interference occurs when **two X-ray waves with phases separated by an integer number of wavelengths add to make a new wave with larger amplitude**. When two parallel X-rays from a coherent source scatter from **two adjacent planes their path difference must be an integer number of wavelengths** for constructive interference to occur.

$$\text{Path difference} = n\lambda$$

Therefore;

$$n\lambda = 2d \sin \theta$$

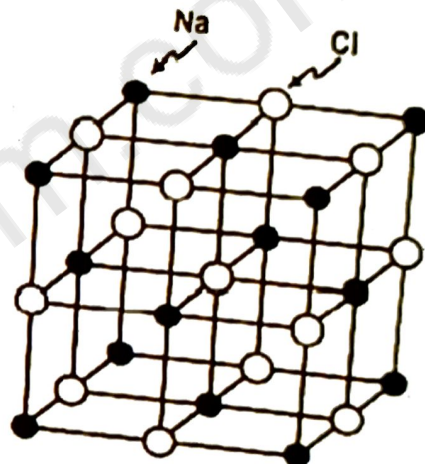
- When X- Rays are scattered from a crystal lattice, peaks of scattered intensity are observed which correspond to the following conditions:
 1. The angle of incidence = angle of scattering.
 2. The path length difference is equal to an integer number of wavelengths.
- The condition for **maximum intensity contained in Bragg's law above allow us to calculate details about the crystal structure**, or if the crystal structure is known, to determine the wavelength of the x-rays incident upon the crystal.

❖ Basic aspects of crystals

- **Lattice:** A 3D translationally periodic arrangement of points in space is called a lattice.

➤ Classification of lattices

- ✓ Lattice
- ✓ 7 Crystal systems
- ✓ 14 Bravais Lattices
- From a morphological view point, a crystal may be defined as the **regular polyhedral form, bounded by smooth surfaces**, which is assumed by a chemical compound under the **influence of its inter-atomic forces** when passing (under suitable conditions) **from gaseous or liquid state to the solid state**.
- The overtly **geometric shapes of crystals reflect an internal symmetry of atoms and molecules arranged** in a regular and repeated pattern.



The Crystal lattice of Sodium Chloride

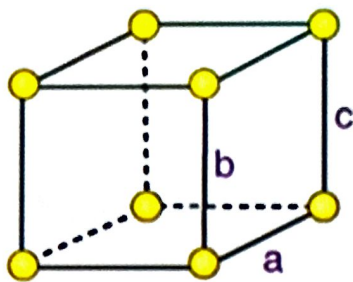
Bravais lattice

In geometry and crystallography, a Bravais lattice, named after **Auguste Bravais** (1850), is an infinite array of discrete points generated by a set of discrete translation operations described in three dimensional space by:

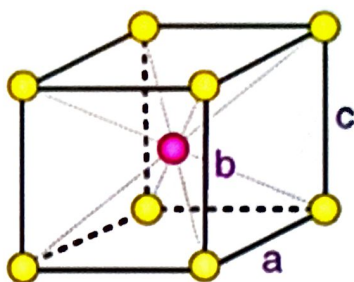
$$R = n_1 a_1 + n_2 a_2 + n_3 a_3$$

Where,

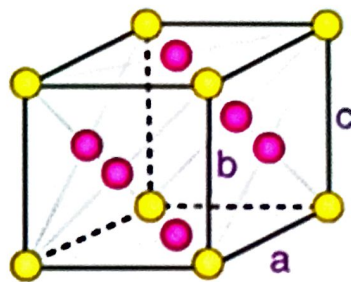
- n_1 are any integers and a_2 are known as the primitive vectors which lie in different directions and span the lattice.
- This discrete set of vectors must be closed under vector addition and subtraction. For any choice of position vector R , the lattice looks exactly the same.
- lattice concept is used to formally define a crystalline arrangement and its (finite) frontiers.
- A When the discrete points are atoms, ions, or polymer strings of solid matter, the Bravais crystal is made up of a periodic arrangement of one or more atoms (the basis) repeated at each lattice point.
- Consequently, the crystal looks the same when viewed from any equivalent lattice point, namely those separated by the translation of one unit cell.
- Two Bravais lattices are often considered equivalent if they have isomorphic symmetry groups.
- In this sense, there are 14 possible Bravais lattices in three-dimensional space. The 14 possible symmetry groups of Bravais lattices are 14 of the 230 space groups.



Simple cubic



Body-centred
Cubic Unit Cell
(BCC)



Face-centred
Cubic Unit Cell
(FCC)

Bravais lattices system

❖ X-Ray Crystallography

- It is a technique used for **determining the atomic and molecular structure of a crystal**, in which the crystalline structure causes a **beam of incident X-rays to diffract into many specific directions**.
- By measuring the **angles and intensities** of these diffracted beams, a crystallographer can produce a three-dimensional picture of **the density of electrons within the crystal**.
- From this **electron density**, the **mean positions of the atoms in the crystal can be determined**, as well as their chemical bonds, their crystallographic disorder, and various other information.
- Since many materials can form crystals such as **salts, metals, minerals, semiconductors**, as well as **various inorganic, organic, and biological molecules** X-ray crystallography has been fundamental in the development of many scientific fields.
- The method also **revealed the structure and function of many biological molecules**, including vitamins, drugs, proteins and nucleic acids such as DNA.
- X-ray crystallography is still the **primary method for characterizing the atomic structure of new materials**.

❖ Instrumentation

The instrumentation used in crystallography consists of following components.

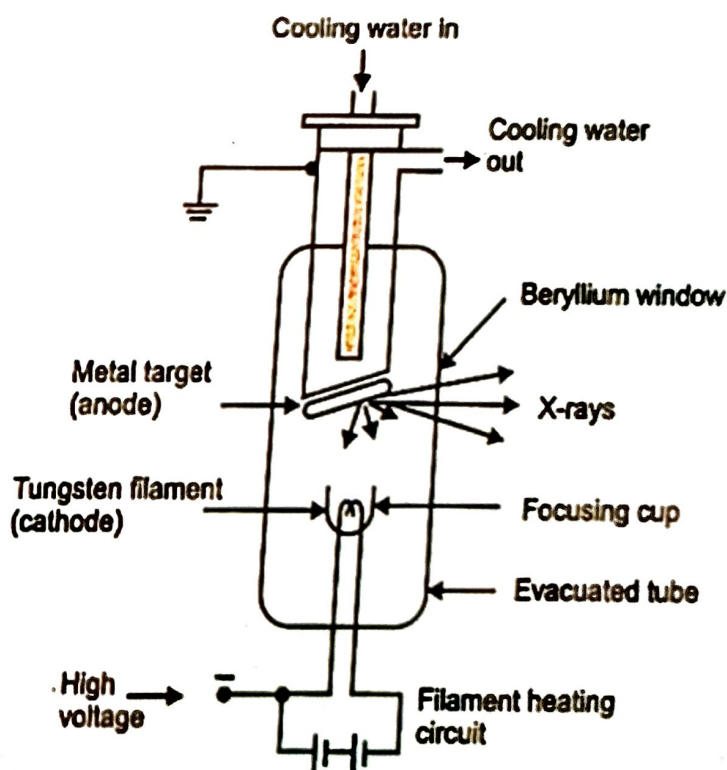
1. A source
2. A wavelength selector
3. A sample holder
4. A detector
5. A recorder

➤ Source

Two major sources used to obtain X-radiation are as follows.

✓ Production of X-rays using an X-ray tube

- The X-ray tube, also called as a **Coolidge tube**, is the most **common source of X-ray radiation**. It consists of an **evacuated tube made up of glass, fitted with glass, fitted with a cathode and an anode**.
- The cathode is a **tungsten filament** which is heated by using a high voltage.
- An anode is a **heavy block of copper** which is coated with a target material (which emits X-rays) such as **tungsten, cooper, molybdenum, rhodium, silver, iron or cobalt**. Cold water can be circulated/ in some areas of anode to avoid its excessive heating.



X-ray tube or Coolidge tube

- The cathode in the form of **heated tungsten filaments** emit **electrons**, which are accelerated towards anode due to its **positive potential**.
- **Accelerated electrons hit the metallic target**, used in the form of an anode. When the **electrons hit the target material**, **X-rays are emitted out**.
- The **voltage applied for heating the cathode decides the number of electrons emitted** by the cathode.
- The accelerating potential i.e. the **positive potential applied to anode determines the force with which emitted electrons** hit the target metal and therefore, decides the energy or wavelength of the emitted X-rays.
- The **greater the accelerating force**, the higher is energy of X-rays and **shorter is their wavelength**.
- The **emitted X-rays come out of beryllium** window fitted on one side of a Coolidge tube.

Advantages

- An electron bombardment on some target material like **molybdenum or tungsten** is that it produces continuous spectrum in the X-ray region.

Disadvantages

- X-rays produced by bombarding high energy electrons on a **metal having poor output efficiency**.

✓ Production of X-rays using Radioisotopes

- Certain radioactive substances produce X-rays as a **result of their radioactive decay process and can acts as a source for X-rays**.
- The elements such as ${}_{26}\text{Fe}^{55}$, ${}_{27}\text{Co}^{57}$, ${}_{48}\text{Cd}^{109}$, and ${}_{51}\text{I}^{125}$ produce X-rays by **electron capture or K-capture**.
- **Tritium (1H^3), lead (${}_{82}\text{Pb}^{210}$) produce X- rays by β -emission process.**

➤ Wavelength selector

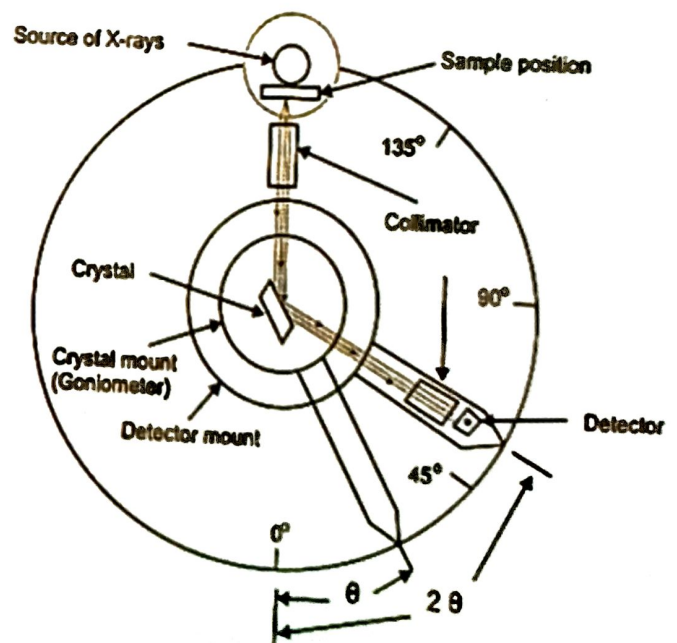
- The isolation of a **narrow range of wavelength** (monochromatic X-Rays) from the full range can be achieved by using following devices.

1. Filters

- The instruments which make use of filters are called as **X-rays photometers**.
- X-rays filters are specific materials of **definite thickness or they are thin metallic strips**.
- A molybdenum target produces a continuous spectrum in the **range of 0.4 to 0.6 Å**.
- It also produce **two lines (K_{β} and K_{α}) at around $0.62\text{Å} - 0.75\text{Å}$** .
- If X-rays from this target are allowed to **pass through a thin strip (0.01cm thickness) of zirconium (zirconium filter)**, it absorbs K_{β} line and most of continuous radiation from it, thus a pure K_{α} line is isolated by this filter.

2. Monochromator

- Those using monochromator are called as **Spectrophotometers**.
- X-rays monochromator nothing but **the crystals which can diffract X-rays according to their wavelengths**. The useful wavelength range from a crystal is determined by its **lattice spacing**.
- A crystal is placed on a **rotating table or a goniometer**. A crystal monochromator works on the principle of Bragg's equation.



Crystal monochromator

➤ Sample holder

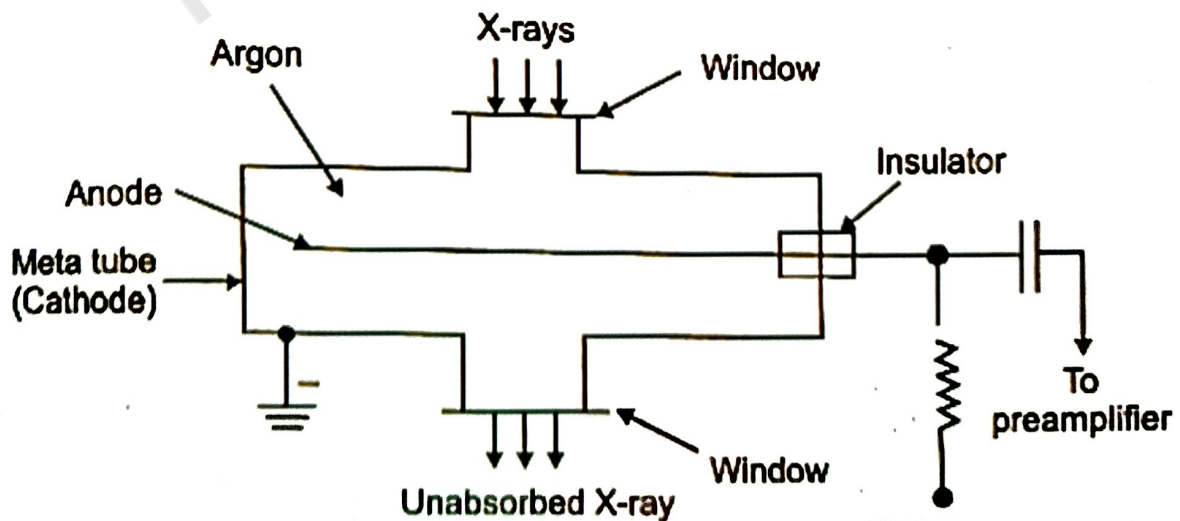
- The sample holder is nothing but a **rotating table called as a crystal mount**.
- A sample crystal is placed at the center of a crystal mount, **which is kept rotating at a particular speed**.

➤ X-ray detector

Three types of detectors are used for X-rays detection.

1. Gas filled detectors

- Gas filled detectors consist of a **metal tube filled with an inert gas as argon, krypton or xenon**.
- The tube is provided with **two transparent windows on opposite sides**. Windows are **made up of mica, beryllium, aluminum or Mylar**.
- The tube contains a **centrally placed anode in the form of a wire**.
- The **lower side of the tube is negatively charged** and acts as a cathode.
- X-rays are passed through one of the **windows into the gas**.
- The interaction of X-rays with the atoms of an inert gas **results in their excitation and the loss of one of the outer electrons**.



Gas filled detector

- The number of electrons reaching the anode for each entering X-ray photon depends on the **potential applied to anode and is listed below.**

- 1) Potential of anode less than 200 volts.
- 2) Potential between 200-400 volts (Ionization chamber region).
- 3) Potential between 800-1000 volts (Proportionate counter region).
- 4) Potential between 1100-1600 volts (Geiger counter region).

2. Scintillation counters/ Detectors

- Scintillation counter consists of **transparent, cylindrical crystal of sodium iodide (NaI)**, 3-4 inches in length and breadth.
- **Thallium iodide is added to sodium iodide in 0.2% in quantity** for the purpose of ease of activation of electron in the crystal.
- When **X-rays strike the crystal**, the electrons in the crystal are **excited**.
- When the electrons **fluorescent material**. A large number of **electrons are produced in the photomultiplier tube**, come back to their original position, **they give out photons and produce scintillations on the which results in the production of a large number of photons**, which are collected ultimately at one electrode.
- The amount of energy released by the electrons while coming back from **the excited state is called scintillation energy**.
- This energy is converted to an **electric energy to get that equivalent current**, the value of which depends on the intensity of X-rays striking the surface.

3. Semiconductor detector

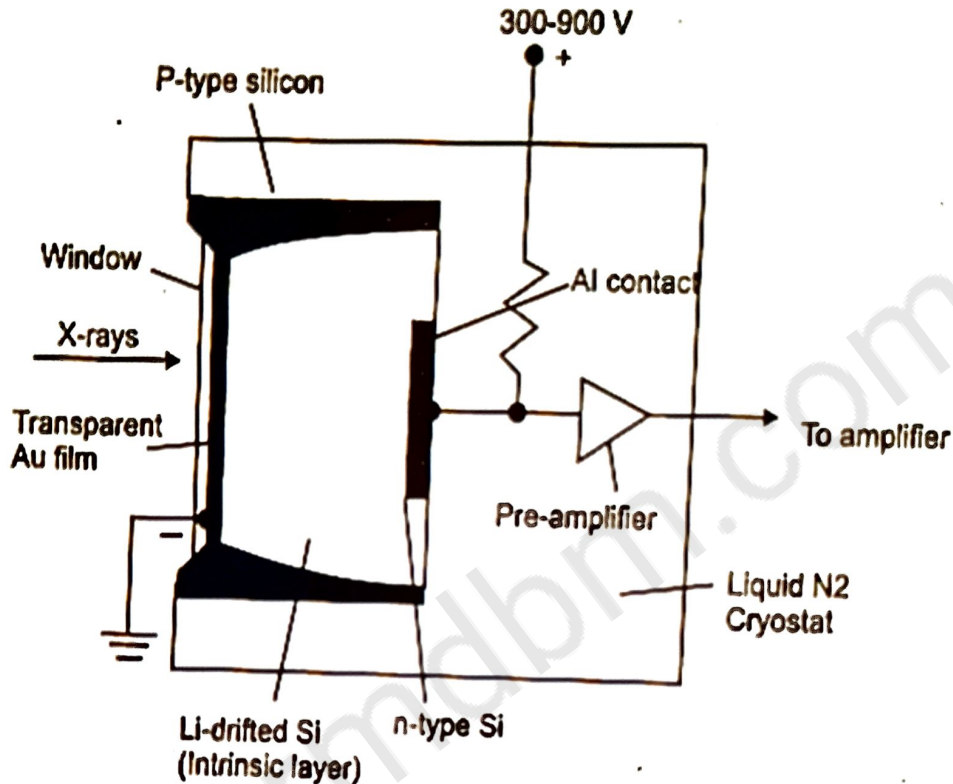
Semiconductor detectors find major application in X-ray crystallography, these are called as:

- 1) Lithium drifted silicon detector-Si (Li).
- 2) Lithium drifted germanium detector-Ge (Li).

✓ Lithium drifted silicon detector

Lithium drifted silicon detector-Si (Li) consist of following three layers.

- i) P-type semiconducting layer.
- ii) Central intrinsic layer.
- iii) n-type semiconducting layer.



Lithium drifted silicon detector

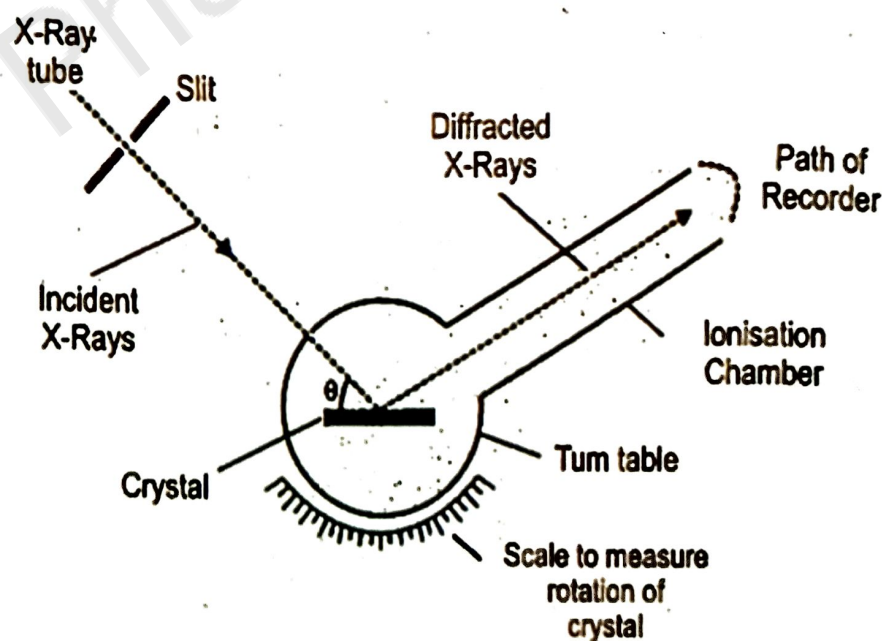
- An outer layer of **p-type semiconductor** is coated on its outer side with a thin layer of gold for electric contact, which in turn is covered with a thin beryllium window.
- This window is transparent to X-rays. On the other side of the **p-type semiconductor** is present an intrinsic layer of lithium drifted silicon. At the end of this intrinsic layer is present n-type of semiconductor, which is coated externally with a thin layer of aluminum for the electric contact.
- This aluminum sheet is connected to a preamplifier, which in turn is connected to an amplifier and a recorder.

✓ Lithium drifted germanium detector- Ge (Li)

- These detectors are exactly same as that of Lithium drifted silicon detector, but in this case **instead of silicon as a semiconductor germanium is used**. These detectors are mainly used to detect X-radiation **shorter than 0.3\AA** .

❖ Rotating crystal technique

- A beam of X rays of known wave length falls on a **face of crystal** mounted on graduated turn table.
- The diffracted rays **pass in to the ionization chamber of the recorder**.
- Here they **ionize the air and a current flow between the chamber wall and an electrode** inserted in it which is connected to an electrometer.
- The electrometer **reading is proportional to the intensity of X-rays**.
- As recorder along with **crystal is rotated, the angles maximum intensity is noted on the scale**.
- Thus the values of θ for $n=1, 2, 3$ etc. are used to calculate the distance d between the lattice planes parallel to the face of crystal.



Rotating Crystal method

❖ X-ray diffraction methods

- X-ray diffraction studies have provided very large wealth of information about the **arrangement and the spacing of atom in crystalline substances both organic and inorganic.**
- Such studies are very useful in the **field of science, technology, industry, biomedical sciences** and complex natural products like steroids, vitamins and in antibiotics.
- X-ray diffraction studies have also provided a very clear understanding of the **properties of metals polymeric substances, alloy mineral** and other solids.
- All diffraction methods are based on **generation of X-rays in an X-ray tube.** These X-rays are directed at the sample, and the diffracted rays are collected.
- A key component of all diffraction is the **angle between the incident and diffracted rays.**

➤ **Single-crystal x-ray diffraction**

- A beam of x-rays strikes a single crystal, producing **scattered beams.**
- When they land on a piece of film or other detector, these **beams make a diffraction pattern of spots;** the strengths and angles of these beams are recorded as the crystal is **gradually rotated.**
- Each spot is called a **reflection,** since it corresponds to the reflection of the X-rays from one set of **evenly spaced planes within the crystal.**
- For single crystals of **sufficient purity and regularity,** X-ray diffraction data can determine the **mean chemical bond lengths and angles to within a few thousandths of an angstrom** and to within a few tenths of a degree, respectively.

- The atoms in a crystal are **not static, but oscillate about their mean positions**, usually by less than a few tenths of an angstrom. X-ray crystallography allows measuring the size of these oscillations.

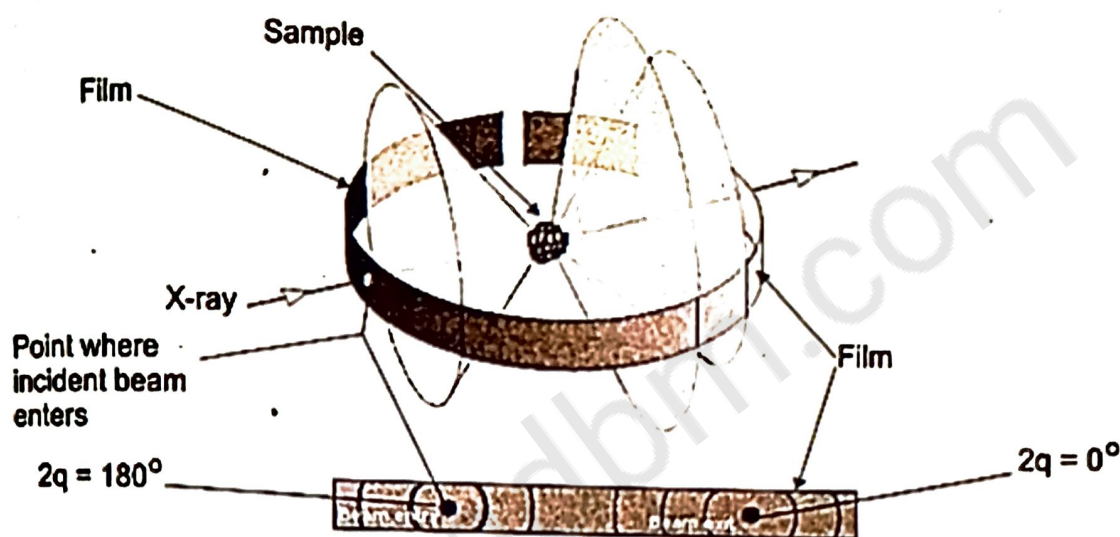
Procedure

- The technique of single-crystal X-ray crystallography has **three basic steps**.
- The first and crystal should be **sufficiently large** (typically larger than 0.1 mm in all dimensions), **pure in composition and regular in structure**, with no significant internal imperfections such as cracks or twinning.
- In the second step, **the crystal is placed in an intense beam of X-rays, usually of a single wavelength** (monochromatic X-rays), producing the regular pattern of reflections.
- The angles and intensities of **diffracted X-rays are measured, with each compound having a diffraction pattern**. As the crystal is gradually rotated, **previous reflections disappear and new ones appear**; the intensity of **every spot is recorded at every orientation of the crystal**. **Multiple data sets may have to be collected**, with each set covering slightly more than half full rotation of the crystal and typically containing tens of thousands of reflections. unique
- In the third step, these data are **combined computationally with complementary chemical information to produce and refine a model of the arrangement of atoms** within the final, refined model of the atomic arrangement now called a **crystal structure is usually stored in a public database**.

➤ Powder diffraction method

- The powder diffraction method is only analytical method which is **capable of furnishing both qualitative and quantitative information** about the compounds present in a solid sample.

- The rotating crystal method could only be used if a single undistorted crystal is available.
- To overcome this limitation, **the powder method was devised**. In this method the crystalline material contained in capillary tube is placed in camera containing a film strip.
- The sample is rotated by means of a motor. The X-ray pass through the gap between ends of film.



Powder diffraction method

- The powdered sample contains small crystals arranged in all orientations some of these will reflect X-ray from each lattice plane at the same time.
- The reflected X-rays will make an **angle 2θ** with the original direction.
- Hence on the photo are **obtained lines of constant θ** . From **geometry of the camera, θ can be calculated for different crystal plane**.

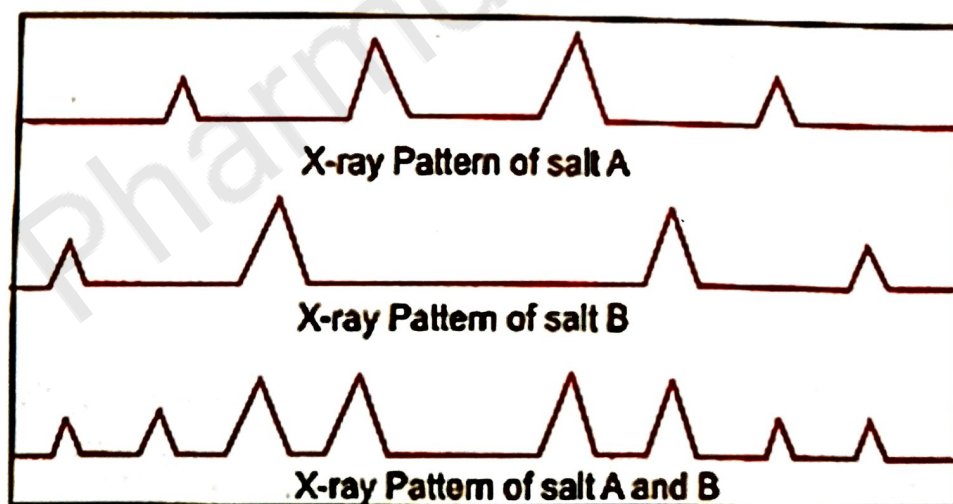
Applications

1. X-ray powder diffraction is most widely used for the **identification of unknown crystalline materials** (e.g. minerals, inorganic compounds).
2. Determination of **unknown solids is critical to studies in geology, environmental science, material science, engineering and biology**.

❖ Applications of x-ray diffraction method

➤ Structure of crystals

- The analytical applications of X-ray diffraction are numerous. The method is **non destructive and gives information on the molecular structure** of the sample.
- It also used to measure the **size of crystal planes**.
- The patterns obtained are **characteristic of the particular compound from which the crystal was formed**.
- For example; **NaCl crystals and KCl crystals give different diffraction patterns**. A mixture containing 1% KCl in NaCl would show a diffraction pattern of NaCl with a weak pattern of KCl. On the other hand, a mixture containing 1% NaCl in KCl would show the diffraction pattern of KCl with a weak pattern of NaCl.

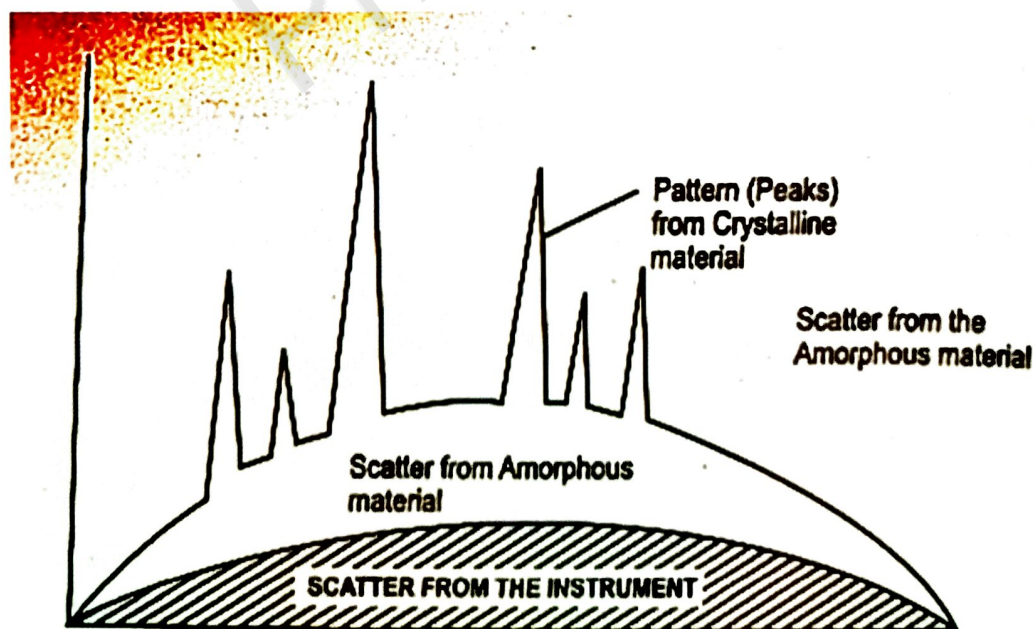


Hypothetical X ray patterns of two salts

- Comparing diffraction patterns from crystals of unknown composition with patterns from crystals of known compounds permits the identification of unknown crystalline compounds.

➤ Polymer characterization

- Powder method can be used to **determine degree of crystallinity** of the polymer.
- The non crystalline portion simply **scatters the X-ray beam to give continuous background**, while the crystalline portion causes diffraction lines that are not continuous.
- The amorphous material in the polymer will scatter at all wavelengths and give a scattered pattern however the **crystalline material will include crystal structures and will produce definite diffraction lines or spots**.
- The ratio of the **area of diffraction peaks to scattered radiation is proportional to the ratio of crystalline to non crystalline material** in the polymer.
- The ultimate quantitative analysis must be confirmed by using **standard polymers with known crystallinities** and basing the calculations on known ratio of crystalline diffraction to amorphous scattering.
- By measuring the **intensity of diffraction patterns in several directions of crystals of a polymer** or a metal are oriented in any particular direction.



Diffraction pattern of a polymer showing crystalline amorphous and scattered radiation components

➤ State of anneal in metals

- Properties of metals that can be **determined by X-ray diffraction is the state of anneal**. Well annealed metals are in well ordered crystal form and give sharp diffraction lines.

➤ Particle size determination

The variety of X-ray techniques may be used to determine the size of particles or crystallinities.

a) Spot counting method - This method is useful for **determining size of particle larger than 5 microns**. If the powder diffraction pattern of such specimen is obtained, it will **consist of a series of lines or rings having a spotty appearance**. From this diffraction patterns, one can determine the size of particles by applying the following relation:

$$v = \frac{V \cdot \delta\theta \cdot \cos\theta}{2n}$$

Where,

v - The volume or size of an individual crystallite

V - The total volume of the specimen irradiated

n - The number of spots in a diffraction ring at Bragg angle of θ

$\delta\theta$ - the divergence of the X ray beam and is a function of the apparatus used.

b) Broadening of diffraction lines - This method is used for particles in the range **30-1000 Å**.

- This method is based upon the simple fact that **there is broadening of the powder diffraction lines**.
- For a powder composed of **perfect crystalline particles** in this range is size range, we know.

$$L_{hkl} = \frac{K\lambda}{\beta_o \cos\theta}$$

Where,

L_{hkl} = the mean crystalline dimension (size) perpendicular to the plane, (hkl)

β_o = the breadth at half maximum of a pure diffraction profile in radians

K = a constant, generally taken as unity

➤ Miscellaneous applications

Other applications of x-ray diffraction include:

- 1. Soil classification based on crystallinity.** Different types of soils, such as various types of **clays and sands**, exhibit different types and **degrees of crystallinity**. Knowledge of this crystallinity gives valuable information concerning **soil structure**. It also tells us the **effects of rain and drought** and indicates the mechanism of soil erosion.
- 2. Analysis of industrial dusts** can be affected, and their relationship to industrial disease ascertained, by means of x-ray diffraction studies.
- 3. X-ray diffraction** can also be used to **assess the weathering and degradation of natural and synthetic minerals**. By designed experiments, the factors responsible for the degradation can be revealed. The same type of study can be carried out on **polymers**. It is possible to investigate the **effects of temperature, humidity, direct sunlight, or corrosive gases** on polymers. Based on the results, stable polymers have been developed that are suitable for outdoor use.
- 4. Tooth enamel and dentine** have been examined by X-ray diffraction.

5. Corrosion products can be studied by this method. When metal samples are exposed to atmosphere, they are susceptible to corrosion. If the corrosion is rapid, it leads to a short life for metal product. The products of **corrosion can be identified by X-ray diffraction studies also by research the factors** that affect the corrosion rate can be determined.