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CHEMISTRY

UNIT-2- INORGANIC CHEMISTRY

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CHEMISTRY

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UNIT-2: INORGANIC CHEMISTRY

SEPARATION AND PURIFICATION TECHNIQUES

Analytical chemistry–separation, spectroscopic, electro-and thermo analytical methods.

INTRODUCTION

The separation of mixtures of compounds to give the pure components is of great practical importance in chemistry. Separation techniques constitute an important aspect of experimental chemistry. Almost all compounds of biochemical interest occur naturally as components of very complex mixtures from which they can be separated only with considerable difficulty. Separations can be achieved by differences in physical properties, such as differences in boiling point, or by chemical means, wherein differences in physical properties are enhanced by chemical reactions. In this chapter we will consider some separations of compounds based on differences in physical properties. The chemical and physical aspects of purification of matter are interesting. The purification techniques have undergone vast improvements with the development of modern technology. Though expensive instruments are sometimes used for purifying a compound, the well-known principle of adsorption-desorption is used in chromatography. In spite of the availability of modern gadgets for separation and purification of chemicals, the simple and inexpensive techniques like distillation, filtration, sublimation, etc., continue to remain indispensable in all laboratories.

Separation Techniques:

Definition:

- It consists of important aspects of experimental chemistry.
- The quest for isolating a chemical in a 100% pure form has resulted in the invention and perfection of innumerable separatory methods.
- The low cost technique is filtration and the computer aided technique are HPLC etc., which are expensive.

Types: Precipitation:

It is an important method of separation in various analytical techniques.

In qualitative analysis, the principle of separation of cations is based on by adding suitable reagents. Eg:

- HCl precipitates Hg, Pb & Ag.
- Thus the separation of these ions from $Cu^{2+,}$ Al^{3+}, Zn^{2+} etc., is possible.
- Mn ions can be separated from Zn ions by adding NaOH.
- In a mixture of Cu & Ni ions, Cu ions are precipitated as sulphide and removed before Ni is estimated gravimetrically using DMG(dimethyl glyoxime).
- A carbonyl compound can be precipitated by adding Borsche's reagent).

Solvent Extraction:

- Extraction with solvents is used as a method for separation of dissolved substances from solutions.
- It can also be used for the separation of one constituent from a solid mixture as well as for the removal of undesired soluble impurities from mixtures.
- Extraction with a second solvent is an application of the Nernst distribution law which states that “at constant temperature a solute distributes itself between two immiscible solvents only in a particular ratio”.
- When a substance distributes itself between two solvents without the complications of dissociation or association, it is possible to calculate the weight of the substance that can be removed by a series of extractions.
- If v_1 ml of a solution contains Wg of a substance and if the substance is repeatedly extracted with v_2 ml of another solvent, the weight of the substance W_n remaining in the first solvent after n extractions is given by,

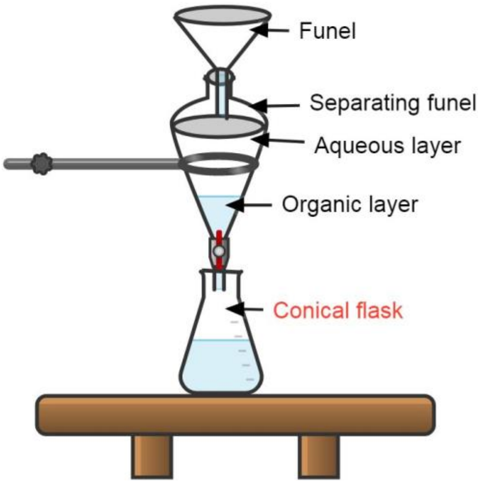
$$W_n = W [K v_1 / K v_1 + v_2]^n$$

Solvent Extraction Using Separating Funnel:

- The extraction with a second solvent can be carried out in the laboratory with a separating funnel.
- It is provided with a ground glass stopper and a stop-cock.
- It is mounted in a ring on a stand.
- When an aqueous solution is shaken with ether in a separating funnel and allowed to settle, two sharply defined layers are formed.
- The two layers can be separated by opening the stop-cock and allowing the lower aqueous layer to drain slowly into a beaker.

Continuous Extraction:

- When one has to separate a component which is slightly soluble in the extracting solvent from a mixture whose other components are essentially insoluble, large quantities of solvent would have to be used.
- The method of continuous extraction can be used in such cases with a smaller quantity of the solvent.
- The apparatus used for continuous extraction when the extracting solvent is lighter than the original solution containing the solute.
- The extracting solvent is kept in a flask which is heated.
- The vapours condense and the liquid solvent drains into the vessel containing the solution to be extracted.
- After extracting a little of the solute, the extracting solvent being lighter rises to the top.
- When the level exceeds a certain limit, it drains once again into the original flask from where it is vaporised and then utilised for extraction once again.



Separating Funnel

Soxhlet Extraction:

- For separation of the components of a solid mixture by continuous extraction, a Soxhlet apparatus is used.
- The solid is kept in the porous thimble.
- The extracting solvent is taken in the boiling flask.

- When the solvent is heated to reflux, the distillate drains into the porous thimble and extraction occurs.
- As more and more solvent collects in this chamber, the solution drains into the boiling flask by a siphoning action.
- Pure solvent continuously gets vapourized from the boiling flask and the cycle of condensation of the vapour takes place.
- Simultaneously the extraction of the components and draining of the solution into the boiling flask will goes on.

The common solvents used are:

- Diethyl ether
- Benzene
- Petroleum ether
- $CHCl_3$
- CCl_4

Conditions for a good Solvent:

- The substance extracted should be highly soluble in water.
- After the extraction the solvent should be easily separable from the solute.

Note: Normally diethyl ether is used as solvent because organic substances generally soluble in ether and ether has low boiling point.

Electrophoresis:

Definition:

It is a separation technique that is based on the migration of charged particles under the influence of an electric field.

Principle:

The principle describes that any charged ion or molecule migrates when placed in an electric field, the rate of migration depend upon its net charge size, shape and the applied electric current. This system consists of two electrodes of opposite charge (anode, cathode), connected by a conducting medium called an electrolyte.

Types:

- Gel electrophoresis.
- Capillary tube electrophoresis.
- Disc electrophoresis.
- Pulsed field electrophoresis.

Process:

- Positively charged ions migrate towards a negative electrode and negatively charged ions migrate towards positive electrode.
- Anions have different migration depending on the total charge, size and shape. For safety reason one electrode is usually at around and the other is based on positive or negative ion.
- This technique is used particularly for macro molecules such as protein, DNA etc.
- A negative charge is added to these molecules so they move towards the positive electrode.
- An gel electrode apparatus consists of a high voltage supplied (DC power), electrodes consist of a buffer and a support for the buffer such as filter paper, cellulose acetate strip, polyacryl amide gel or capillary tube.
- Open capillary tubes are used for many types of samples and other supports like gel are used for biological samples such as protein, DNA etc.

- After separation is completed the support is strained to visualize the separated component.
- Resolution can be improved by isoelectric focussing in this technique and the support gel maintains the pH gradient.
- As the protein migrates down the gel it reaches a pH that is equal to its isoelectric point and at this pH the protein is neutral and no longer migrates which is focussed into a sharp based on the gel.

Applications:

Electrophoresis plays an important role in the field of,

- Pharmaceutical
- Forensic
- Foods
- Bioscience
- Agricultural field
- Pesticide analysis
- Surfactant analysis
- Transition metal analysis
- Organic compound analysis

Purification Techniques:

Sublimation:

Definition:

It is a process of converting a solid directly into its vapour on heating without becoming a liquid.

Principle:

It works on the principle that solids have weak intermolecular forces hence a higher vapour pressure which converts it into directly vapour state.

Process:

- The substance to be sublimed is placed in a crucible.
- A narrow ring of pyrex glass is fitted near the rim which support a filter paper with a number of small holes made in upward direction.
- A funnel with a pinch of glass wool or cotton in the stem is kept inverted over the paper.
- The crucible is heated gently.
- The vapours escaped to the holes in the paper and condense on the upper surface of the filter paper and also on the walls of the funnel.
- Heating is stopped when the most of the material in the crucible has vapourized.
- Supply of the heat should be such that the does not become hot and the rate of sublimation is increased by applying suction at the stem of the funnel.
- This will draw the vapour into the condensing chamber.

Types of sublimation:

- ➢ Simple sublimation
- ➢ Sublimation under reduced pressure
- ➢ Vacuum sublimation

Advantages:

- ➢ Convenient method for purification of solids containing impurities.
- ➢ Apparatus is simple and inexpensive.
- ➢ Impurities can be easily removed as vapours forming pure crystals of a substance.

Distillation:

Definition:

It is the process of separating the components or substances from a liquid mixture by using selective boiling and condensation.

Principle:

- A liquid present in a closed space will evaporate giving off vapour until the vapour attains a definite pressure.
- This pressure depends on the temperature and the vapour pressure of a liquid in contact with its own liquid is a constant at given temperature.
- It is independent of the absolute amount of liquid and vapour pressure in the system.

The distillation apparatus consists of,

- Distillation flask
- Thermometer
- Round bottom flask
- Liebig condenser
- Funnel
- Condenser tube

Process:

- The liquid is boiled in the distillation flask, condensing the vapour produced by means of a Liebig condenser.
- The condensed pure liquid is collected in a receiver.
- All the joints in the distillation unit must be interchangeable standard joints.
- A small amount of silicone grease may be used at the joints so that dismantling will be easy.
- Sometimes lubrication may contaminate the liquid.
- Bumping of the liquid during boiling may be avoided by adding unglazed porcelain bits.
- These bits should be added before the boiling process and never to be a heated liquid.

Aspects to be followed while distilling a liquid,

- A round bottom flask should be used and not the flat bottom flask.
- Heating must be slow and uniform using a bunsen flame or electric heater.
- The distillate should be collected separately.
- Reject the last portion of the liquid in the flask itself.
- The clamp should hold the coolest part of the neck of the flask.
- The bulb of the thermometer should be below the position where the side tube is fused into the neck of the flask.
- The thermometer tube should not be immersed inside the liquid.
- The glass units must be assembled tightly to avoid loss of vapour or liquid.

- The distillation should be stopped when some liquid is left in the flask.
- Flammable liquids like ethanol, benzene, carbon disulphide etc., should never be heated with a bunsen burner.
- They must be distilled with a steam-bath or controlled electric heating mantle.

Fractional Distillation:

Definition:

It is a method of separating two or more liquids having different boiling points.

Principle:

When a mixture of two liquids is boiled, the vapour phase is richer in the more volatile component than the boiling liquid with which it is in equilibrium at any given temperature.

Eg: If the component A is more volatile than B then,

Partial pressure of A/ Partial pressure of B > 1

or

mole fraction of A in the V.P/ mole fraction of B in the V.P >

mole fraction of A in the L.P/ mole fraction of B in the L.P

∴ it is a method used to separate liquids which are miscible with one another and the boiling point of two liquids should be far from each other.

Eg: A mixture of benzene and toluene have boiling point at 80°C and 110°C can be separated by fractional distillation.

Procedure:

- The mixture of liquids is distilled by heating the flask electrically.
- Care should be taken that the condensed liquid does not drop into the receiver at rapid rate than one drop per second.
- In this distillation a special type of fractionating column is attached to the top of the distillation flask.
- As a mixture of vapour of the two liquids rises in the column the vapours of the higher boiling liquid will condense and fall back into the flask.
- Whereas the vapours of the lower boiling liquid will alone go the top of the column and escape into the condenser.
- The process will proceed slowly and eventually.
- Separate fractions are collected at 3 or 5°C.
- Any distillate passing over between 80.2°C and 81.2°C will be rich in benzene.
- Pure toluene will distills at 110.6°C.
- Each component must be collected at closed temperature ranges as possible.
- Complete separation is not possible at one distillation process.
- The fractionalized liquid should be separately distilled for effective purity of a component.
- Repeated fractionations will give pure component.

Conditions for good fractionation:

- There should be large amount of liquid continuously running through the column.
- Thorough mixing of liquid and vapour should occur.
- A large effective surface area between liquid and vapour should be available.
- There should not be excess cooling in the column.

Steam Distillation:

Definition:

It is a process in which the separation and purification of volatile organic compounds which are immiscible in water is distilled by steam distillation.

Principle:

In this method a current of steam is blown through the substances to be distilled.
The steam escapes from the substance carrying with it only the volatile component which is being separated from the impurities.

Eg: Mixture of benzene and water.

As the temperature is raised the sum of the two pressures reaches the atmospheric pressure and at this temperature the mixture boils. But this temperature is less than 80°C which is the boiling point of the benzene. Actually the temperature is 69.3°C and partial pressure of benzene is 533mm and for water is 227 mm. ∴ a mixture of benzene and water distills at 69.3°C until one or the other material is exhausted in the distillation flask. Thus passing steam through the benzene will remove as a distillate and this operation is called steam distillation.

Process:

- The organic compound to be distilled is placed in a round bottom flask with a claisen head, which is equipped with a head connected to a water cool condenser?
- The claisen head prevents splattering of the mixture into the condenser during distillation.
- Steam is produced externally in a steam generator and passed through a long tube reaching almost the bottom of the distillation flask.
- Water may condense in the distillation flask filling into the inconvenient levels.
- This problem is avoided by heating the flask gently using bunsen burner or connecting with a bent adapter.
- Instead of passing through the liquid water can be added to the organic compound to be distilled in the distillation flask. This mixture is heated directly to generate steam inside and it is best suitable for steam distillation of small amount of soft liquids.

Precautions:

Steam should be turned off only after opening the pinch clamp on the bent adapter exit tube otherwise due to the development of vacuum in the distillation flask the distilled liquid from the receiver will go back into track.

Uses:

- ➢ Used in chemical industries for separating turban oil from crude pine oil.
- ➢ Used for separating volatile components of several classes.
- ➢ Provides a method of separation of volatile liquids and volatile solids which are insoluble in water from non-volatile substance under mild conditions.

Vacuum Distillation:

Definition:

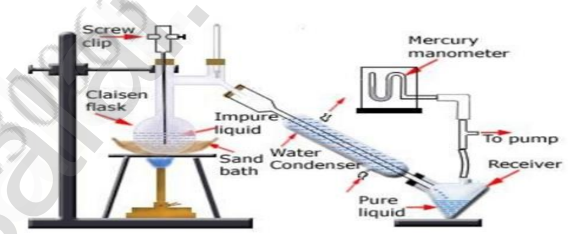
It is technique for distilling organic liquids having high boiling temperature.

Principle:

The boiling point of the liquid is that the temperature at which the total vapour pressure is equal to the atmospheric pressure from this it follows that when the external pressure increases the pressure above the liquid is reduced. Hence the boiling point will be decreased. When vacuum is applied (no pressure) the boiling point should be minimum at intermediate pressure. ∴ the boiling will be intermediate and hence normal distillation is effective under diminished pressure.

Need to adopt under diminished pressure:

- A certain liquids have high boiling points ∴ distillation of these under vacuum is easy.
  In many cases boiling temperature at atmospheric pressure ae too high because the compound being distilled may get oxidised or decompose or undergo molecular rearrangements.
- Sometimes impurities present in the liquid may catalyse some reactions at high temperature.



Vacuum Distillation Apparatus

Process:

- For distillation under reduced pressure the distillation apparatus consists of a distillation unit having provision for as aspirator(water pump) or a mechanical oil pump.
- An aspirator commonly reduces the pressure to above 25mm and oil pump to below 1mm.
- The flask should be made up of stout glass otherwise low pressure due to insight it may collapse.
- The distillation apparatus should be tightly assembled with no leakage or loose joints.
- The ground glass joints surfaces of the distillation unit may be lubricated using vaseline or silicon grease.
- Bumping is much more pronounced in distillation under diminished pressure than in ordinary distillation this is avoided by the introduction of a bit of porcelain materials.
- Another way of avoiding bumping is to have a glass tube fitted to the neck of the flask.
- This tube drawn out at its lower end to a capillary which dips into the liquid and closed using a piece of rubber and small screw clamp at its upper end.
- With this arrangement the passage of air into the distilling flask is easily regulated.
- The pressure inside can be read using manometer which is connected to the system between the pump and the distillation unit.

Approximation need to follow for vacuum distillation:

- ➢ When the pressure is reduced from 760mm to 25mm, the boiling of a high boiling liquid(250-300°C) is reduced by about 100-125°C.
- ➢ Below 25mm,each time the pressure is halved, the boiling point is reduced by about 10°. The exact boiling points at different pressures can also be calculated using the Clausius-Clapeyron equation.

Crystallization:

Definition:

It is a process by which a solid forms, where the atoms or molecules are highly organized into a structure known as a crystal.

Process:

- The solution is heated in an open container
- The solvent molecules start evaporating, leaving behind the solutes.
- When the solution cools, crystals of solute start accumulating on the surface of the solution
- Crystals are collected and dried as per the product requirement
- The undissolved solids in the liquid are separated by the process of filtration.
- The size of crystals formed during this process depends on the cooling rate.
- A large number of tiny crystals are formed if the solution is cooled at a fast rate
- Large crystals are formed at slow cooling rates.

Application of Crystallization:

- Purification of seawater.
- Separation of alum crystals from impure samples.
- In the pharmaceutical industry, crystallization is used as a separation and purification process for the synthesis and isolation of co-crystals, pure active pharmaceutical ingredients (API), controlled release pulmonary drug delivery, and separation of chiral isomers.

Fractional Crystallization:

Definition:

It is a physical separation process used for purification of organic compounds from a multicomponent mixture by crystallization without addition of a solvent.

Principle:

- Fractional crystallization is the method of refining substance based on difference in solubility. The proportion of components in then precipitate will depend in their solubility products.
- $Na_2O + K_2O$ (A), $FeO + Fe_2O_3$ (F), and MgO (M) - Magma

Procedure:

- Add about 25g of the unknown mixtures to a pre-weighed 250ml beaker.
- Weigh the beaker and mixture to determine the mass of the mixture.
- Add 60ml of DI water to the beaker.
- Heat the mixture to 85^0C while stirring.(do not boil)
- Keep the mixture near 85^0C for 5 minutes with stirring.
- While the mixture is heating, setup a vacuum filtration system.
- If a mixture of two or more substances in solution is allowed to crystallize.
- Eg; By allowing the temperature of the solution to decrease, the precipitate will contain more of the least soluble substances.

Application:

- Used in crystal production and purification.
- Used in salt industry.
- Used in silicon wafer production.

Test for Purity:

The substance purified distillation, sublimation etc., has to be checked for its purity by the following methods:

1. Melting Point
2. Boiling Point
3. Refractive Index
4. Density measurements

Melting Point:

- The melting point of a substance is a temperature at which liquid and solid phase exists in equilibrium with each other.
- The melting point of a pure substance is constant and not affected by experimental conditions.
- It is an intrinsic property (i.e) it is not dependent on the quantity of substance used.
- The pressure of impurity lowers the melting point of a substance.

Determination of Melting Point:

The melting point of the substance can be determined with the help of the following apparatus:

- A beaker containing a liquid and a stirrer
- A thistle melting point apparatus
- A electrically heated metal block

Electrically heated metal block:

- ➢ The substance is taken in a capillary tube.
- ➢ It is heated by placing in the cavity of a metal block.
- ➢ A hole is provided to insert the thermometer which helps to note down the temperature accurately.
- ➢ The metal block is heated.
- ➢ The change in substance is observed through the magnifying glass.
- ➢ The rate of heating can be controlled by rheostat.

Precautions:

- Only a small of the substance is used.
- Thermometer should be calibrated before use.
- The temperature of the bath must be raised slowly by means of a microburner because rapid heating may lead to inaccurate melting points.
- Since the thermometer is not immersed completely, the temperature correction should be carried using the formula, $t_{corr} = t + 0.000156\alpha(t-t_0)$

0.000156 = apparent coefficient of expansion of mercury in glass, α= length of thread measured in degrees not immersed in the hot liquid, t= melting point as measured

t_0 = mean temperature of the thread above the liquid

When a short thermometer (50^0C) is used, this correction is not required

Factors affecting melting point:

- Sample Size
- Heating rate
- State of subdivision of the sample

Boiling Point:

- When the vapour of a liquid becomes equal to the atmospheric pressure then the liquid starts boiling.
- The boiling point of a pure substance under a particular pressure is constant and therefore this property can be used to check the purity of the liquid.
- The boiling point of a liquid can be determined using the apparatus as shown below.
- The correct boiling point will be recorded by the thermometer only when there is a constant passage of the boiling liquid from distilling flask to the outlet.
- This is achieved by a steady heating, so that a thermometer bulb comes into contact with sufficient boiling vapour.

Precautions:

- The whole of the thermometer bulb should be exposed to the hot vapours during distillation.
- The thermometer is arranged such that the bulb is just below the side tube.
- The bulb should not be immersed in the liquid .
- Bumping should be avoided by adding four to five porcelain bits.

Refractive Index:

- The velocity with which light travels in different media is not a constant.
- This leads to the bending of beam of light as it passes through the interfaces of two different media.
- The angle of refraction is dependent on the density, type of molecules, temperature of medium and also on the wavelength of light.
- Air is chosen as the standard medium with reference to this medium and different media bend light to different angles.
- When all the angles of refraction are measured at the same temperature with same wavelength of light with reference of air, then the measured angle is a property of second medium.
- This property is used as identifying characteristics of the substance constituting the medium.
- Instead of angle of refraction another quantity called refractive index(μ) is actually reported.
- The refractive index is given by the equation,

$$\mu = \text{Sin } i / \text{Sin } p$$

- Monochromatic light gives more precise value of Θ than white light and
- ∴ Refractive indices for the "D" line of sodium are 589.3 nm.
- This fact is indicated by a subscription and the temperature by a superscription.
- A typical notation of refractive index is "μ^{20}_{D}".
- i.e., the index is measured at 20^0C for Na D line.
- It is measured with an instrument called the refractometer.

Density:

- The density of a substance is used to check the purity of the sample it is the measure of concentration of the matter its unit is g/ml at 20^0C.
- The density of a liquid is measured using a small apparatus for picnometer whose volume is known accurately.
- The pycnometer is weighed accurately and then filled with liquid whose density is to be determined.
- The temperature of this is brought to 20^0C and the volume is readjusted.
- If necessary it is also weighed the density may be calculated by dividing the weight in grams by volume in mm.

Thermo Analytical Techniques

Introduction

Thermal analysis is the analysis of a change in a property of a sample, due to temperature. The sample is usually in the solid state and the changes that occur on heating include melting, phase transition, sublimation, and decomposition.

Thermo Gravimetric Analysis Technique Principle

TGA measures the amount of weight change of a material, either as a function of increasing temperature, or as a function of time (temperature of the sample is increased), in an atmosphere of nitrogen, helium, air, other gas, or in vacuum. A plot of mass or mass percent as a function of time is called a thermogram, or a thermal decomposition curve.

Instrumentation

Requirements:

(i) **Sensitive analytical balance:**

The most common type of balance is capable of weighing the sample range from 5 to 20 mg.

(ii) **Furnace :**

The sample holder of the balance must be placed inside the furnace.The temperature range for most furnaces is zero to 1500^{0}C.

(iii)**A purge gas system providing an inert atomosphere . Nitrogen or Argon are usually used to purge the furnace and prevent oxidation of the sample.**

(iv)**A microcomputer /microprocessor for instrument control and data acquitistion and display.**

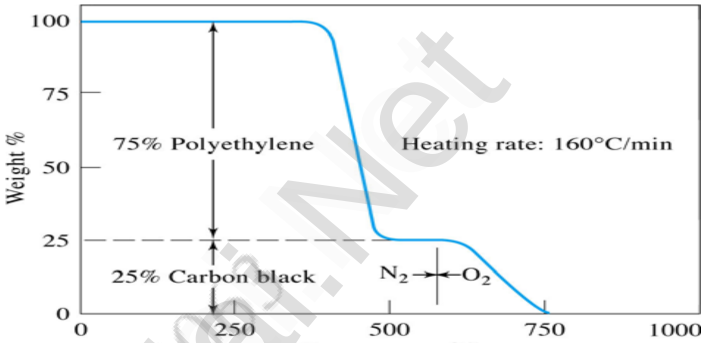
In this analysis, the sample is placed in a sample holder (which is made up of platinum) of a microbalance. The entire arrangement is placed within a small oven, temperature of which is controlled and monitored. This temperature is measured by immersing a small thermocouple close to the sample container.The recorded temperatures then lead or lag the actual sample temperature.

Modern thermobalances use a computerized temperature control unit which finds the difference between the temperature of the thermocouple and the temperature specified in read only memory (ROM) to adjust the voltage to the heater. Analysis is carried out by raising the temperature of the sample gradually in a flow of air or inert gas such as N_2, Ar or He and the sample weight (or percentage) is plotted against temperature.

The parameters affecting the TGA are: heating rate, amount of sample, carrier gas flow, nature of carrier gas etc.

Applications

1. Thermograms provide information about decomposition mechanisms for various polymeric preparations. Decomposition patterns are characteristics for each kind of polymer and in some cases can be used for identification of various polymers.
2. Following Fig. illustrates how a thermogram is used for quantitative analysis for a polymeric material.



The sample is polyethylene that has been formulated with fine carbon –black particles to inhibit degradation from exposure to sunlight.

3. Thermogravimetric analysis of Calcium oxalate monohydrate. Successive plateaus correspond to the formation of anhydrous salt,calcium carbonate and calcium oxide.

$CaC_2O_4 .H_2O$ (s) $CaC_2O_4 + H_2O$
CaC_2O_4(s) $CaCO_3$ (s) + CO(g)

$CaCO_3$ (s)   CaO (s) + CO_2(g)

Thermogram indicates that loss of water begins at 100^0C,loss of CO at 400^0 C and loss of CO_2 at 600^0C.

Differential Thermal Analysis (DTA)

Principle

In DTA, the difference in temperature is measured between a sample and an inert reference material, which are subjected to a controlled temperature programme. The difference in temperature

DTA peaks result from:

1) Physical changes

* Endothermic: fusion, vaporization, sublimation, absorption, desorption.

* Exothermic: adsorption, crystallization.

2) **Chemical reactions**

* Endothermic: dehydration, reduction, decomposition.

* Exothermic: oxidation in air or O_2, polymerization, catalytic reactions.

Instrumentation

The sample (few mg) and an inert reference are placed in small aluminium dishes that are located above sample and reference thermocouples in an electrically heated furnace. Reference material is an inert substance such as alumina,silicon carbideor glass beeds. The furnace is controlled under a temperature program and the temperature of the sample and the reference are changed. During this process, a differential thermocouple is set up to detect the temperature difference (ΔT) between the sample and the reference. Also, the sample temperature (T_s) is detected from the thermocouple on the sample side.

In a differential thermogram, (T_s) is served as abscissa (X-axis) and (ΔT) is served as ordinate(Y-axis).

The temperature should be the same until thermal event occurs, such as melting, decomposition or change in the crystal structure. In an endothermic event takes place within the sample, the temperature of the sample will lag behind that of the reference and a minimum will be observed on the curve. On the contrary, if an exothermal event takes place, then the temperature of the sample will exceed that of the reference and a maximum will be observed on the curve. The area under the endotherm or exotherm is related to the enthalpy of the thermal event, ΔH.

Differential thermogram for heating a polymer is shown below.

The initial decrease in $(\Delta T)$is due to the glass transitition, (T_g) at which glassy amorphous polymer becomes flexible or rubber like nature. During this process heat will neither be absorbed nor be released.i.e $(\Delta H = 0)$

.Two maxima are the result of exothermic process (heat evolved from the analyte) and two minima are the result of endothermic process (heat absorbed by the analyte).The first exothermic peak is due to the crystal formation. The second exothermic peak is possible when the heating is performed in the presence of oxygen or air.

The first endothermic peak arises due to the melting of the microcrystals which are formed in the previous exothermic process.The final negative change in (ΔT) results from the endothermic decomposition of the polymer to produce a variety of products.

Applications

1.To determine the thermal behaviour and composition of naturally occurring and manufactured polymers.

2.To determine the thermal behaviour of pure Inorganic compounds.

3.To study the phase transitions.

Ex: Differential thermogram for sulfur.
The peak at 113^0C corresponds to the change from the rhombic to the monoclinic.

The peak at 124^0C corresponds to the melting point of the element.

The peak at 179^0C corresponds to the liquid phase transition of sulphur.

The peak at 446^0C corresponds to the boiling point of the sulphur.

4. To determine the melting ,boiling and decomposition points of organic compounds.

Ex: Differential thermogram for benzoic acid.

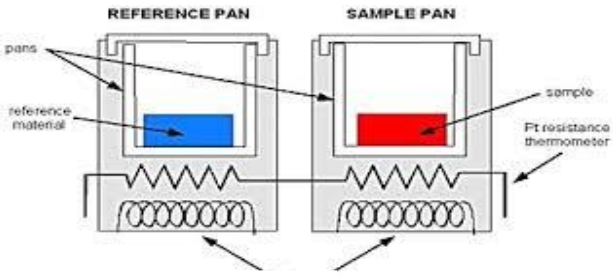
The first peak corresponds to the melting point and the second to the boiling point of the acid.

Differential Scanning Calorimetry (DSC)

Principle

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature while the two are subjected to a controlled temperature programme. In DSC, the differences in energy are measured.

Instrumentation



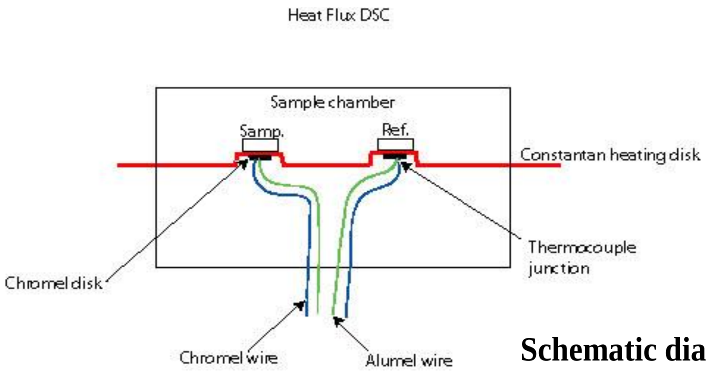
Power Compensated DSC

Power Compensated calorimeter has two independent furnaces, one for heating the sample and the other for heating the reference. The furnaces are small and imbedded in a large temperature controlled heat sink. Above the furnaces are the sample and reference holders, which have platinum resistance thermometers imbedded in them to monitor the temperatures of the two materials continuously. Two control circuits are employed, one for average temperature control and one for differential temperature control.

Average temperature control is used to maintain the same temperature of the sample and the reference. Differential temperature control is used to find the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature .

The average temperature of the sample and the reference is taken as the abscissa (X-axis), difference in the amount of heat (i.e) heat flow is taken as ordinate (Y-axis) in the thermogram.

Heat flux DSC



Schematic diagram of Heat flux DSC

Heat flows in to sample and reference material via an electrically heated constantan (constantan is an alloy with 60% copper and 40% nickel.) thermoelectric flask. A platinum pan is placed on constantan disc. Heat is transferred through the discs and upto the sample and reference via pan. Sample holder and the reference holder are connected by a low resistance heat path. The differential heat flow to the sample and the reference is monitored by constantan / chromel (chromel is an alloy made of 95%Ni,1%Si ,2%Mn and 2%Al)thermocouple. Thermocouple is a junction between two metal that produces voltage due to a temperature difference. The differential heat flow into the two pans directly proportional to the difference in output of the two thermocouple junction. The sample temperature is measured by means of chromel /alumnel junction under the disc.

Temperature of the sample is taken as the abscissa (X-axis), difference in the amount of heat (i.e) heat flow is taken as ordinate (Y-axis) in the thermogram.

Applications

1. To determine the thermal behaviour of polymers

The DSC curve for an amporphous sample of polyethylene Terephthalate is shown

DSC curves shows peak for glass transition, crystallization and melting. It does not show peak for oxidation, because the experiment was carried out in an atmosphere of nitrogen

2. It is used in the pharmaceutical industry to check the purity of drug samples.

Thermometric Titrations

In the thermometric titration, titrant is added at a known constant rate to a titrand until the completion of the reaction is indicated by a change in temperature. The endpoint in a thermometric titration is indicated by sharp break in the temperature versus volume curve.

Conditions for thermometric titration

1. Thermometric titrations are carried out in adiabatic conditions.

2. The reaction should be accompanied by sufficient heat change that can be measured.
3. Heat of dilution of the product should be negligible.

4. The reaction should be simple, one step change.

Instrumentation

Titration Instrument:

A simple schematic representation of thermometric titration unit is shown above. It consists of motor-driven thermostated burette, thermally insulated adiabatic titration vessel [Dewar flask]. Aknown volume of the solution to be estimated is taken in the Dewar Flask. The tip of the burette is dipped into the solution in the vessel. The vessel is covered by a thick, insulating material containing holes for inserting the thermistor., the burette and the stirrer. The titrant is added at a constant rate which the solution in the Dewar flask is constantly stirred.

The thermistor assembly is connected to one arm of a wheatstone bridge and its resistance is recorded directly on a recorder. The temperature measuring thermistor unit should be capable of measuring temperature change of 0.01 ^{0}C. The titrant should be 10-100 times more concentrated than the solution in the Dewar flask, so that the titration can be done by the addition of only a small quantity of the titrant.

Titration of Hydrochloric Acid with Sodium Hydroxide:

A known volume of hydrochloric acid to be estimated is taken in the Dewar flask. The titrant NaOH solution is added from the burette. Temperature readings are recorded for different volume of the titrant added. The thermogram is obtained by plotting temperature versus titrant volume .

The neutralization point is indicated by a sharp, inflexion point C. Thermometric Titrimetry is one of the few methods of titration not based solely on considering of the free energy change ΔG and hence on the equilibrium constant of the reaction. is measured in this method. Hence this titration may give useful results even when positive

Complexometric titrations:

Consider, for example, the titration of calcium and magnesium with EDTA. The stability constants of the chelates differ by less than two orders of magnitudes, so that titration based on an indicator can give only the sum of the concentrations of the two ions. However, for the reaction of Mg^{2+} with EDTA the enthalpy is +5.5 kcal/mole whereas that for the Ca^{2+} reaction is ΔH and ΔG , not ΔG

ΔG is zero or -5.7kcal/mole. This distinct difference in ΔH values makes it possible for the adoption of thermometric titration for estimating these two ions.

Application of Thermometric Titrations:

Several types of titrations have been followed successfully by the thermometric method. These include neutralizations of both and strong and weak acids, precipitations, redox reactions and complex formations. These titrations can be carried out in aqueous or non-aqueous medium. Besides in water, titration have been reported in acetic acid, carbon tetrachloride, benzene and nitrobenzene. The precision of a thermometric titration is usually + or - 1%.

ELECTROANALYTICAL TECHNIQUES AND FLUORESCENCE SPECTROSCOPY

ELECTROCHEMISTRY

Electrochemistry deals with the transfer of electrons from one substance to another. This transfer creates a current, the magnitude of which can give us clues about the analyte.

ELECTROCHEMICAL SENSOR

A chemical sensor can be defined as a device that provides continuous information about a specific chemical species in the environment. All chemical sensors consist of a transducer, with transforms the response into a detectable signal on modern instrumentation, and a chemically selective layer, which isolates the response of the analyte from its immediate environment. Electrochemical sensors are designed to detect and respond to an analyte in the gaseous, liquid or solid state. Eelectrochemical sensors are especially attractive because of their remarkable detectability, experimental simplicity and low cost. There are three main types of electrochemical sensors: potentiometric, amperometric and conductometric.

POTENTIOMETRIC: For potentiometric sensors, a local equilibrium is established at the sensor interface, where either the electrode or membrane potential is measured, and information about the composition of a sample is obtained from the potential difference between two electrodes.

There are three basic types of potentiometric devices: ion- selective electrodes (IES), coated wire electrodes (CWES) and field effect transistors (FETS).

ION-SELECTIVE ELECTRODE

Ion-selective electrode also known as a **specific ion electrode** (SIE), is a transducer (or sensor) that converts the activity of a specific ion dissolved in a solution into an electrical potential. The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. Ionselective electrodes are used in analytical chemistry and biochemical/biophysicalresearch, where measurements of ionic concentration in an aqueous solution are required.

Ion-selective electrodes possess a high degree of selectivity. The selectivity of the ISE is determined by the composition of the membrane. Ideally the membrane allows the uptake of only one specific ion into it. The analyte ion may be a cation or an anion. The three main components of making a measurement at an ISE are an inner reference, or standard, solution and an outer analyte, or sample, solution separated by a thin membrane.

Ion-selective electrode: Different strategies for producing an electrode that is selective to one species are based primarily on the nature and composition of the membrane material. Depending on the nature of the membrane, ISEs can be divided into three groups: glass, liquid or solid electrodes.

TO BE CONTINUED...

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