III BSc CHEMISTRY

SUBJECT: ANALYTICAL CHEMISTRY –I

Analytical chemistry studies and uses instruments and methods used to separate, identify, and quantify matter. In practice, separation, identification or quantification may constitute the entire analysis or be combined with another method. Separation isolates analysis. Qualitative analysis identifies analysis, while quantitative analysis determines the numerical amount or concentration.

UNIT –I

1.1 Data analysis;

ERRORS

1) **error** refers to the difference between a measured value and the "true" or "known" value.
2) **error** often denotes the estimated uncertainty in a measurement or experiment. " We can only hope to minimize **errors** and estimate their size with acceptable. Accuracy The formula for calculating percent error is:

$$\text{percent error} = \frac{|\text{experimental value - accepted value}|}{\text{accepted value}} \times 100\%$$

TYPES OF ERROR:

It is classified into two types (i)determinate error , (ii)Indeterminate error

Systematic (determinate) errors:

1. Instrument errors - failure to calibrate, degradation of parts in the instrument, power fluctuations, variation in temperature, etc. Can be corrected by calibration or proper instrumentation maintenance.

2. Method errors - errors due to no ideal physical or chemical behavior - completeness and speed of reaction, interfering side reactions, sampling problems Can be corrected with proper method development.

3. Personal errors - occur where measurements require judgment, result from prejudice, color acuity problems. Can be minimized or eliminated with proper training and experience.

Random (indeterminate) Error: No identifiable cause; Always present, cannot be eliminated; the ultimate limitation on the determination of a quantity. • Ex. reading a scale on an instrument caused by the finite thickness of the lines on the scale; electrical noise • The accumulated effect causes replicate measurements to fluctuate randomly around the mean; Give rise to a normal or Gaussian curve; Can be evaluated using statistics

CORRECTION OF ERROR:

1. Analysis of standard samples

2. Independent Analysis: Analysis using a "Reference Method" or "Reference Lab"

3. Blank determinations

4. Variation in sample size: detects constant error only

How do we determine error :

1.2 Accuracy : closeness of measurement to its true or accepted value Systematic or determinate errors affect accuracy

Precision : agreement between 2 or more measurements of the sample made in exactly the same way Random or indeterminate errors affect precision.

Absolute error (E) : diff. between true and measured value $E = xi - xt$ where xi = experimental value, xt = true value Ex. xi = 19.78 ppm Fe & xt = 20.00 ppm Fe $E = 19.78 - 20.00$ ppm = -0.22 ppm Fe (-) value too low, (+) value too high

Relative error (Er) : expressed as % or in ppt Er = (as %); Er = (as ppt)

Find the mean, median, mode for the following list of values:

8, 9, 10, 10, 10, 11, 11, 11, 12, 13

The mean is the usual average, so I'll add up and then divide:

(8 + 9 + 10 + 10 + 10 + 11 + 11 + 11 + 12 + 13) ÷ 10 = 105 ÷ 10 = 10.5

The median is the middle value. In a list of ten values, that will be the (10 + 1) ÷ 2 = 5.5-th value; the formula is reminding me, with that "point-five", that I'll need to average the fifth and sixth numbers to find the median. The fifth and sixth numbers are the last 10 and the first 11, so:

(10 + 11) ÷ 2 = 21 ÷ 2 = 10.5

The mode is the number repeated most often. This list has two values that are repeated three times; namely, 10 and 11, each repeated three times.

The largest value is 13 and the smallest is 8, so the range is 13 – 8 = 5.

mean: 10.5
median: 10.5
modes: 10 and 11

Standard Deviation

The Formula for Standard Deviation**=(∑*i*=1*n*(*xi*−*x*)2/n-1)2**

where:

xi=Value of the *ith* point in the data set

x=The mean value of the data set

n=The number of data points in the data set

CONFIDENCE LIMITS:

A confidence interval, in statistics, refers to the probability that a population parameter will fall between two set values for a certain proportion of times. Confidence intervals measure the degree of uncertainty or certainty in a sampling method. A confidence interval can take any number of probabilities, with the most common being a 95% or 99% confidence level.

1.3 PURIFICATION OF ORGANIC COMPOUNDS:

Purification in a **chemical** context is the physical separation of a **chemical** substance of interest from foreign or contaminating substances. Pure results of a successful **purification** process are termed isolate.

(1) SOLVENT EXTRACTION:

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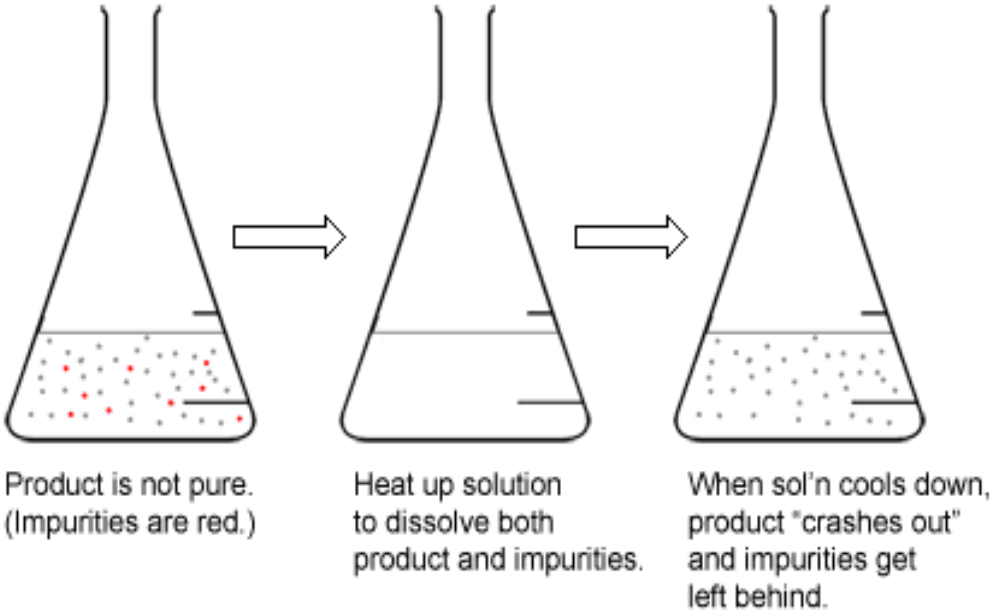
Solvent extraction, also called **liquid-liquid extraction** (LLE) and **partitioning**, is a method to separate compounds based on their relative solubilities in two different immiscible liquids. **Immiscible liquids** are ones that cannot get mixed up together and separate into layers when shaken together. These liquids are usually water and an organic solvent. **LLE** is an extraction of a substance from one liquid into another liquid phase. The most common use of the distribution principle is in the extraction of substances by solvents, which are often employed in a laboratory or in large scale manufacturing. Organic compounds are generally much more soluble in organic solvents, like benzene, chloroform, and ether, than in water and these solvents are immiscible with water. Organic compounds are then quite easily separated from the mixture with inorganic compounds in aqueous medium by adding benzene, chloroform, etc. Upon shaking, these separate into two layers. Since organic compounds have their distribution ratio largely in favor of the benzene phase, more of them would pass into a non-aqueous layer. Finally this non-aqueous layer is removed and distilled to obtain the purified compound

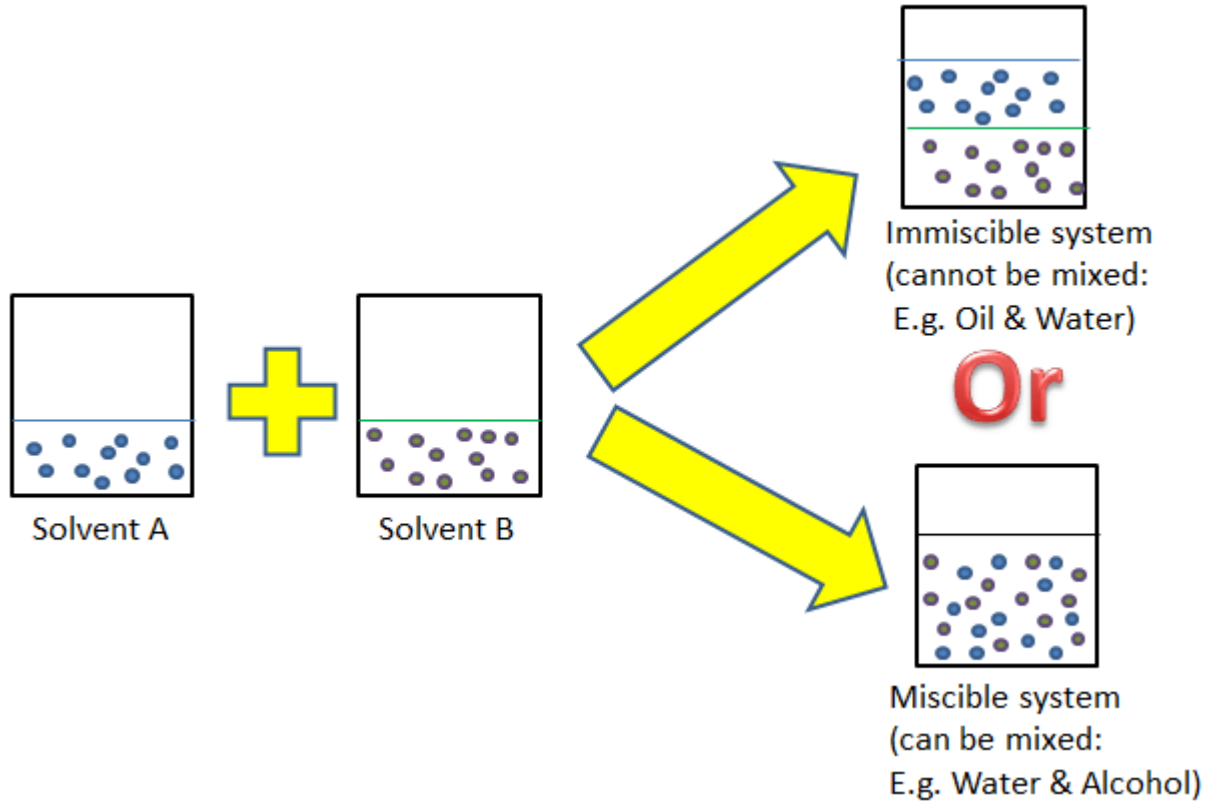
(2) RECRYSTALISATION

Recrystallization is a technique used to purify solid compounds. [1]. Solids tend to be more soluble in hot liquids than in cold liquids. During **recrystallization**, an impure solid compound is dissolved in a hot liquid until the solution is saturated, and then the liquid is allowed to cool.

Recrystallization in a nutshell:



IMMISCIBLE SOLVENT:



Immiscible liquids are those which won't mix to give a single phase. Oil and water are examples of **immiscible liquids** - one floats on top of the other

USES OF IMMISCIBLE LIQUIDS

i)The ability to confine and position the boundary between **immiscible liquids** inside microchannels leads to a broad range of **applications** in microfluidic systems.

ii)which is exemplified by fabrication of a semipermeable membrane in a surface-patterned channel via interfacial polymerization.

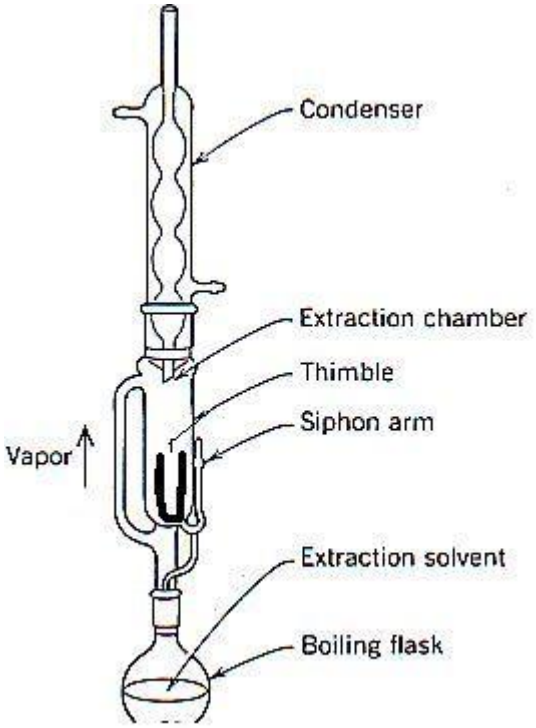
MISCIBLE SOLVENT:

Those liquids which mix together in all proportions and form a single layer are called miscible liquids.

Ex. **Alcohol** and **water** are miscible liquids because they mix together in all proportions and form a single layer on mixing. A mixture of miscible liquids is separated by the process of fractional distillation.

(3) Soxhlet extraction :

A **Soxhlet extractor** is a piece of laboratory apparatus invented in 1879 by Franz von Soxhlet. It was originally designed for the extraction of a lipid from a solid material. Typically, Soxhlet extraction is used when the desired compound has a *limited* solubility in a solvent, and the impurity is insoluble in that solvent. It allows for unmonitored and unmanaged operation while efficiently .



The solvent is heated to reflux. The solvent vapour travels up a distillation arm, and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapour cools, and drips back down into the chamber housing the solid material. The chamber containing the solid material slowly fills with warm solvent. Some of the desired compound dissolves in the warm solvent. When the Soxhlet chamber is almost full, the chamber is emptied by the siphon. The solvent is returned to the distillation flask. The thimble ensures that the rapid motion of the solvent does not transport any solid material to the still pot. This cycle may be allowed to repeat many times, over hours or days.

During each cycle, a portion of the non-volatile compound dissolves in the solvent. After many cycles the desired compound is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled.

After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound. The non-soluble portion of the extracted solid remains in the thimble, and is usually discarded.

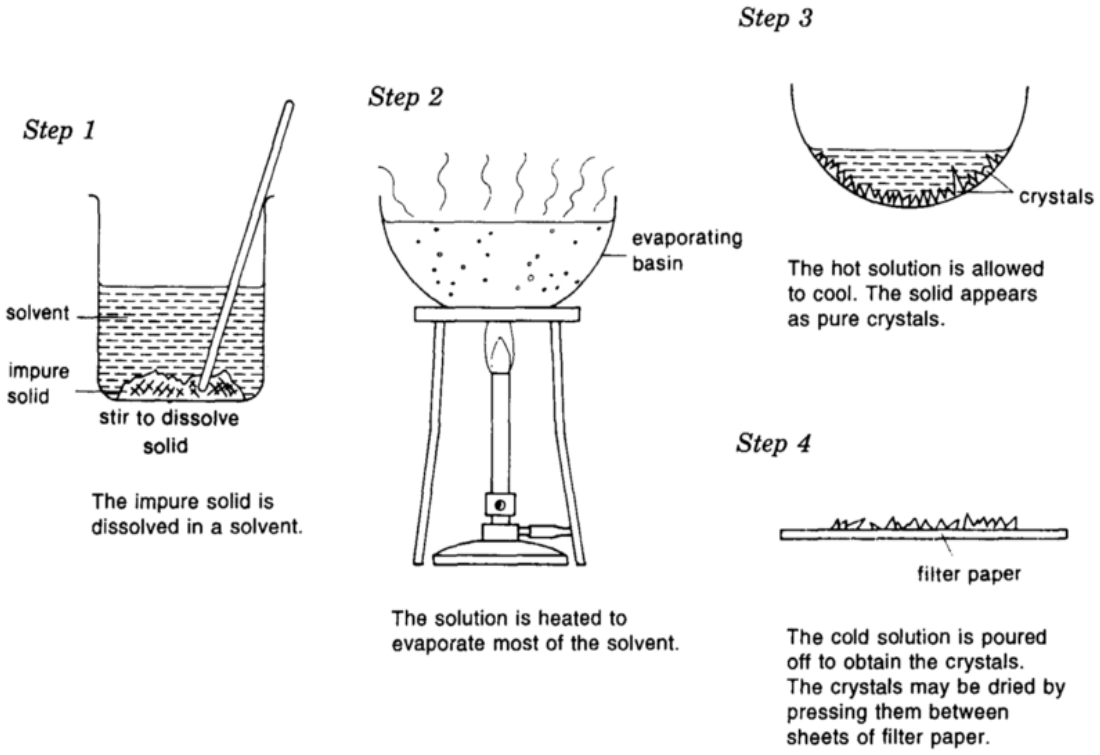
USES

i) soxhlet extraction is also known as the hot continuous extraction process the main advantage of this method is complete extraction in minimum amount of solvent.

ii) Use the separation of plant oils.

(4) CRYSTALLIZATION:

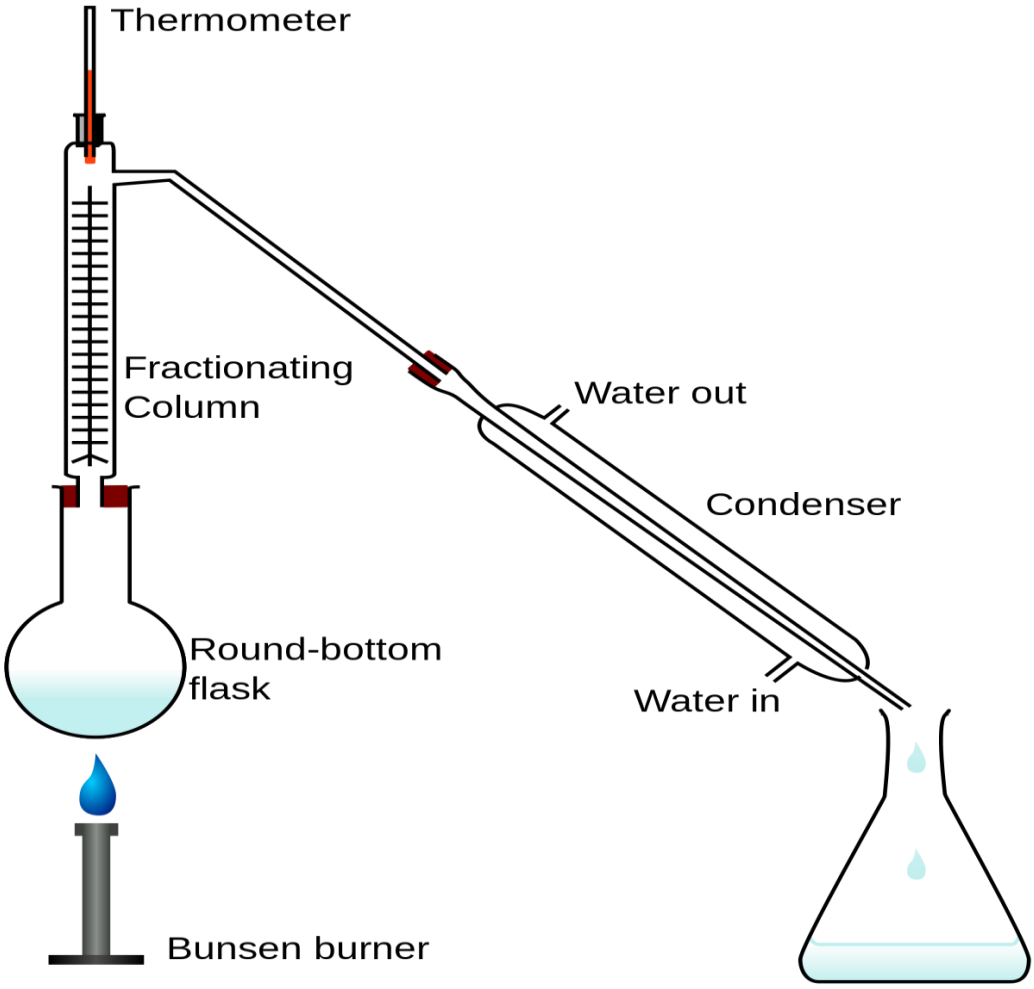
Crystallization is the solidification of atoms or molecules into a highly structured form called a crystal. **Crystallization** can also refer to the solid-liquid separation and purification technique in which mass transfer occurs from the liquid solution to a pure solid crystalline phase.



(5) FRACTIONAL CRYSTALLIZATION:

A **process** by which a chemical compound is separated into components by **crystallization**. In **fractional crystallization** the compound is mixed with a solvent,

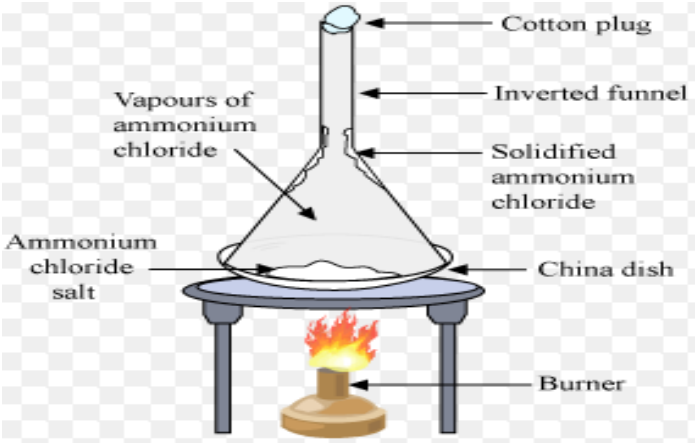
heated, and then gradually cooled so that, as each of its constituent components crystallizes, it can be removed in its pure form from the solution.

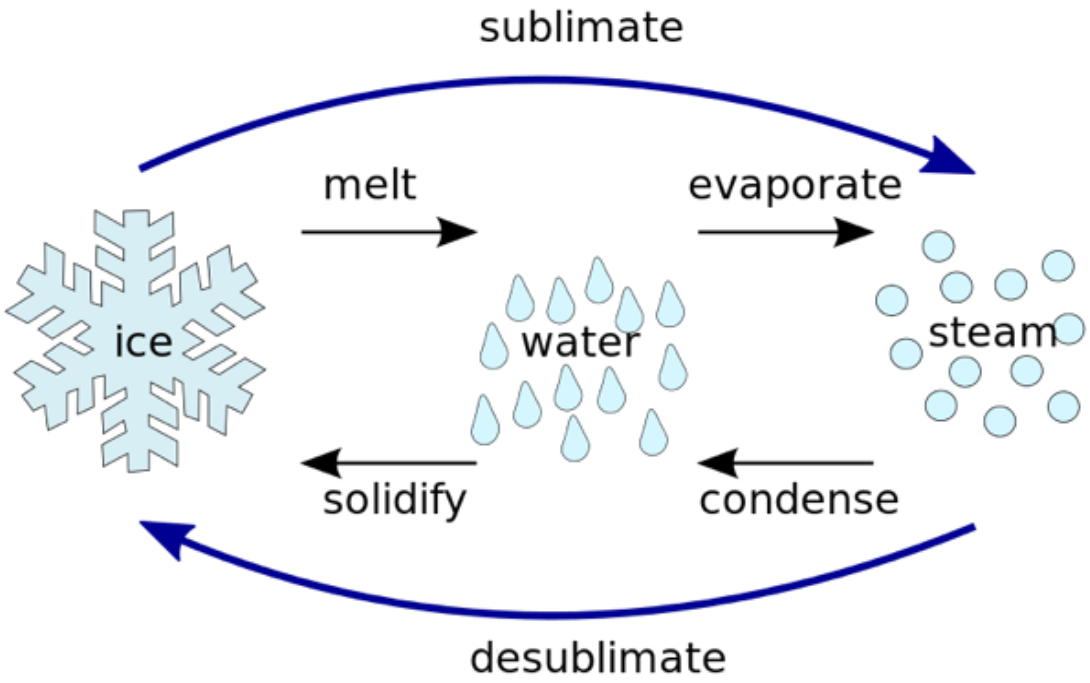


fractional crystallization is a method of refining substances based on differences in their solubility. It fractionates via differences in crystallization (forming of crystals). If a mixture of two or more substances in solution are allowed to crystallize, for example by allowing the temperature of the solution to decrease or increase, the precipitate will contain more of the least soluble substance. The proportion of components in the precipitate will depend on their solubility products. If the solubility products are very similar, a cascade process will be needed to effectuate a complete separation. This technique is often used in chemical engineering to obtain very pure substances, or to recover saleable products from waste solutions. Fractional crystallization can be used to separate solid-solid mixtures. An example is separating KNO_3 and KClO.

(6) SUBLIMATION:

sublimation. ... **Sublimation** is a chemical **process** where a solid turns into a gas without going through a liquid stage. An **example** of sublimiation is when ice cubes shrink in the freezer.





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