B.Sc CHEMISTRY - I SEMESTER

GENERAL CHEMISTRY - I

NEW SYLLABUS

(PERIYAR UNIVERSITY)

UNIT - I

MATERIALS

DEPARTMENT OF CHEMISTRY

Unit - I

HANDLING OF CHEMICALS AND VOLUMETRIC ANALYSIS

Importantance of analytical methods in qualitative and Quantitative analysis

Analytical chemistry is concerned with the identification of substances, the elucidation of its structure and quantitative analysis of its composition. It is an inter disciplinary branch of science which deals with various disciplines of chemistry such as inorganic, organic, physical, industrial and bio chemistry. It finds extensive applications in other fields of science like environmental agricultural, biomedical and clinical chemistry. Solid state research electronics, oceanography, forensic science and space research.

Chemical analysis

It involves the resolution as a chemical compound into its proximate or ultimate parts, the determination of its elements or of foreign substance it may contain. The first requirement in a completely unknown sample is to ascertain what substance is presence in it and which type of impurities are contained in the sample. The solution of such problems lies within the province of qualitative analysis. Having ascertained the nature of the constituents of a given sample, the next step is to determine how much of each or specified component is present. Such determinations lie within the realm of quantitative analysis and to supply and required information a variety of techniques is available.

Advantages of chemical methods

1. Chemical methods are based on absolute measurements.
2. Procedure is simple and accurate.
3. Equipment required is cheap and reading available.

Limitations of chemical methods

1. Procedure is time consuming.
2. Accuracy decreases with decreasing concentration.
3. Lack of specifying and versa tiling.

Instrumental methods

The methods dependent upon measurement of an electrical property and those based upon determination or the extent to which radiation is absorbed (or) upon assessment of the in tensing of emitted radiation, all require the use of a suitable instrument. Eg., polar graph and spectrometer, etc. and in consequence such methods are referred to as instrumental methods. These methods are based on the theory of relation between the content and the corresponding physical – chemical and physical properties of the chemical system being analyses.

Advantages of instrumental methods:

1. Instrumental methods are normally applicable at concentrations far too small to be amenable of determination as chemical methods.
2. Determination is much faster than purely chemical procedure.
3. Measurements obtained are reliable.
4. Even complex samples can be handled easily.
5. Accuracy is obtained.
6. Find wide application in industry.

Limitations of instrumental methods

1. With instrumental methods it is necessary to carryout a calibration operation using a sample of material of known composition as reference substance.
2. Many instruments are highly expensive and their use will only be justified, if numerous samples have to be analyzed.

3. Instrumental methods is ideally suited to the performance of a large number of routine determination.
4. The sensitives and accuracy depends on the instrument.
5. Sizable space is required.
6. Specialized training is needed.

Types of chemical analysis

1. ***Proximate analysis :*** In which the amounts each elements in a sample is determined with concern as to the actual compound present.
2. ***Partial analysis :*** it is dealers with the determination of selected constituents into sample.
3. ***Trace constituents analysis :*** A specialized instance of partial analysis deals with the determination of specified compounds presence in very minute quantity.
4. ***Complete analysis :*** When the proportion of each component of the sample is to be determined.

Safety measures

Laboratory is a place where a student practises what he learns in the class room. A chemistry laboratory is a place where a student has to store and handle chemicals. Chemicals are, by and large, dangerous substances. There are several chemicals which are corrosive, flammable, explosive, toxic, carcinogenic and poisonous. So a student's health will be spoiled if he or she does not know how to store and handle these substances carefully.

Hygiene means conditions or practices conductive to maintaining health. so if a student does not want to spoil his or her health while doing experiments he or she has to follow certain conditions and practices in

the laboratory. Thus laboratory hygiene and safety assume importance in the life of a student who practises chemistry.

Storage and Handling of Chemicals

1. Corrosive Chemicals

Chemicals which corrode or destory gradually, skin, wood, cloth, metal etc. are called corrosive chemicals.

Examples :

Acids, alkalis, chlorine, bromine, phenols etc.

Storage :

They must be stored in corrosive resistant chambers or in pits containing sand.

Handling :

Acids should not be poured directly from their containers. Instead, a siphon or funnel must be used to transfer them from their containers without spilling them on the floor, table or person. Rubber gloves and rubberised apron may be used to avoid accidental spillage on the body or the cloth. Sodium hydroxide pellets or sticks should not be hand picked. A pair of forceps is to be used for this purpose. Chlorine and bromine must be handled infume cupboards only without allowing their vapours to come into contact with nose, eyes or skin.

2. Flammable chemicals

Chemicals which catch fire on exposure to air or on heating over a naked flame or in a warm surrounding are called flammable chemicals.

Examples :

Ether, benzene, acetone, carbon disulphide, alcohol, sodium, potassium, etc.,

Storage :

They should be kept in bottles with tight lids in a cool place. Sodium and potassium are to be stored under kerosene only.

Handling :

They should not be handled near burning burners, heaters etc. They should not be heated directly, over a flame. They should be heated in a flask using a reflux condenser, on a water bath or steam bath. While heating them in this way the near by burners must be put off. Buring Sodium or Potassium metal can be extinguished using foam or sand. Water should not be used.

3. Explosive chemicals

Chemicals which explode violently on heatng, grinding or pressing are called explosive chemicals.

Examples :

Chlorates, perchlorates, nitrates, ethers, peroxides, poly nitro compounds etc.

Storage :

They should be kept in such a way that there is no empty space above them in the container in which they are kept. They must be stored in a cool place.

Handling :

They must be handled with all windows open and wit exhaust fan on. They must be very carefully heated or ground.

4. Toxic chemicals.

They are substances related to poison. When taken in, they produce ill effects creating health problems.

Examples :

Benzene, toluene, chloroform, carbon tetra chloride, naphthalene etc.

[Note : Almost all the chemicals are toxic].

Storage :

They must be stored in well sealed bottles.

Chloroform is stored in dark brown / blue bottles to prevent the formation of highly poisonous phosgene.

$$CHCl_3 + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{Phosgene}}{COCl_2} + HCl$$

Handling :

They must be handled with all windows open and in fume cup - boards. They must not be inhaled directly. Smellingtest must be done by keeping the test tube containing the toxic subtance away from the nose and waving the vapours towards the nose and inhaling slowly and in small quantities. They should not be handled by naked hands. Gloves must be used while handling them.

5. Carcinogenic Chemicals

Chemicals which cause cancer are called carcinogenic.

Examples :

Naphthyl amines, salts of napthyl amines, aziridine, methyl iodide, benzene (causes blood cancer), benzphyrene, thiourea, diazomethane, dimethyl sulphate, N - nitrosocompounds, etc.

Storage :

They should be stored in locked containers inside fume cup - boards. Warning lables showing a skill and a pair of crossed bones should be pasted onthe container.

Handling :

They must be handled only with gloves on. The vapours should not be inhaled. They should not be allowed to come into contact with the skin. They must be handled in fume cup - boards with the exhaust fan on.

6. Poisonous chemicals

Chemicals which when introduced into or absorbed by a living organism causes death or injury expecially one that kills by rapid action even in small quantity are called poisonous chemicals.

Actually their is no great difference between toxic and poisonous chemicals. We can distinguish between them by saying that those chemicals whcih cause death realtively quickly are poisonous. Chemicals which are injurious to health in someway, which may lead to death in course of time are toxic.

Examples :

Benzene, toluene, xylenes, napthalene, anilines, $CHCl_3$, CCl_4, DDT, hydrazine, salts of Pb, selinium compounds, cyanides, tellurium compounds, chromium compounds, vanadium compounds, arsenic compounds etc.

Storage :

They must be stored in well sealed tubes. They should be labelled as poisons.

Handling :

They must be handled only with gloves on. The vapours should not be inhaled. They should not be allowed to come into contact with the skin.

Definitions of molarity

In volumetric analysis we react solutions and determine the volume of one solution required to react completely with a given volume of another solution. From these volumes and the concentration of one of the two reacting solutions, the concentration of the other is calculated. This is the basic principle of volumetric analysis.

Standard Solution :

Definition :

A solution whose strength or concentration is known is called a standard solution.

Units of concentration of Solutions :

The concentration of solutions are expressed in different units. Generally the concentrations of solutions are expresses in terms of

1. Molarity
2. Molality
3. Normality
4. Molefraction

Molarity : (M)

The molarity of a solutions is defined as the number of moles of the solute present in one litre of the solutions. It is denoted as M.

$$M = \frac{W_2}{M_2} \times \frac{1}{V(dm^3)}$$

$$M = \frac{\text{No of moles of solute}}{\text{Volume of solution in litres } (dm^3)}$$

M = molarity, W_2 = weight of the solute, M_2 = molecular weight of the solute, V = volume of the solution (litre)

Examples :

6 g of glucose is present in one litre of the solution. Calculate molarity of the solution.

W_2 = weight of the glucose = 6 gram

M_2 = molecular weight of the glucose $(C_6H_{12}O_6) = 180$

V = volume of the solution (litre)

$$M = \frac{6}{180} \times \frac{1}{1} = 0.0333$$

Molarity of the solution = 0.0333 m

Molality : (m)

The molality of a solution is defined as the number of moles of the solute present in 1000 g of the solvent. It is denoted as M.

$$\text{Molality (m)} = \frac{\text{No.of moles of solute x 1000}}{\text{Mass of solvent in grams}} = \frac{W_1}{M_2} \times \frac{W_2}{1000}$$

m = molality, W_1 = weight of the solvented, W_2 = weight of the solute, M_2 = molecular weight of the solute.

Examples :

6 g of urea is present in one litre of the solution. Calculate molality of the solution.

W_2 = weight of the urea = 6 gram

W_1 = weight of the water = 1000 gram

M_2 = molecular weight of the urea = 60

$$m = \frac{1000 \times 6}{60 \times 1000} = 0.1$$

Normality : (N)

The normality of a solution is defined as the number of gram equivalents of the solute present in one litre of the solution. It is denoted as N.

$$N = \frac{\text{Weight in litre}}{\text{Equivalent weight}} = \frac{W_2}{E_2}$$

N = Normality, W_2 = weight of the solute in litre E_2 = equivalent weight

Examples :

40 g of NaOH dissolved in 400 ml of the solution.Calculate normality of the solution.

Weight of the NaOH present in 400 ml = 40 g

Weight of the NaOH present in one litre = $\frac{40}{400} \times 1000 = 100$ gram

E_2 = Equivalent weight of the solute = 40

W_2 = Weight of the solute = 100

$$N = \frac{100}{40} = 2.5N$$

Mole fraction (x_2)

$$\text{Mole fraction} = \frac{\text{Number of moles of solute}}{\text{Total number of moles of solvent + solute}}$$

$$x_2 = \frac{n_2}{n_1 + n_2}$$

Here

x_2 = mole fractionof solute

n_1 = Number of moles of solvent

n_2 = Number of moles of solute

Volumetric principle :

In volumetric analysis we titrate two solutions and use the formula.

$$V_1N_1 = V_2N_2$$

During titration we take a fixed volume of solution i.e., V_1 is known. We titrate this against another solution and find out the volume of the second solution which is required to react completely with the first i.e., V_2 is found out

by titration. Now if the strength of any one solution is known that of the other can be calculated. Thus we need to know the strength of one of the solutions that we titrate in volumetric analysis.

A solution whose strength or normality is known is called the standard solution.

Primary Standard :

Definition : It is a substance which could be directly weighed and dissolved in a known volume of solvent to give a standard solution.

Examples :

Oxalic acid ($H_2C_2O_4 .2H_2O$), sodium carbonate (Na_2CO_3), potassium dichromate ($K_2Cr_2O_7 .7H_2O$), ferrous sulphate ($FeSO_4.7H_2O$), copper sulphate ($CuSO_4 .5H_2O$), arsenious oxide (As_4O_6).

Explanation :

One way to prepare a standard solution is to accurately weigh the substance, dissolve it in a small quantity of water and to dilute the solution carefully to a known volume in a standard flask. Such a substance which could be directly weighed and dissolved in a known volume of solvent to give a standard solution is called a ***primary standard.***

Secondary Standard :

A secondary standard is a substance which can not be used to prepare a standard solution by weighing it and dissolving it in a given volume of the solvent. It should be standardised with a primary standard.

E.g. Standard sodium hydroxide solution cannot be prepared directly because it is not a primary standard substance. This is because it is

deliquescent. However this may be used as a secondary standard. It can be standardised with oxalic acid using phenolphthalein as indicator.

$KMnO_4$, HCl, H_2SO_4, HNO_3 etc the other secondary standards. **Basic requirements of a primary standard.**

A chemical must fulfil the following requirements if it is to be selected as a primary standard.

1. It should be pure and dry at room temperature.
2. During weighing it should not undergo any change by air. In other words, it should not be hygroscopic. It should not be oxidised by air or affected by CO_2.
3. It should have constant composition for equite a long time, for more than several months.
4. It should be 100% pure, although some impurity is acceptable provided it is accurately known.
5. Its equivalent weight must be high so as to minimise weighing errors. Normally the precision in weighing is about 0.001 to 0.002 g. For an accuracy of 999 parts in 1000, the minimum weight of the sample should be 0.2g.
6. It should be readily soluble in water under laboratory conditions.
7. Its reaction with the other titrant should be stoichiometric and practically complete immedicately.

Titration theories

Titration : Definition :

It is a process used to determine the volume of a solution of a substance required to react completely with a known volume of another solution containing another substance.

Explanation :

To estimate the amount of a given substance in a given solution we react that solution with a standard solution and apply the formula, $V_1N_1=V_2N_2$. Let us say that solution number 1 is the standard solution. i.e., N_1 is known. We have to find out, the strength of the experimental solution. i.e., N_2 is to be determined. It is obvious that knowing N_1, if we want to determine N_2, then we require V_1 and V_2. i.e., the volume V_1 of the standard solution required to react completely with V_2 ml of the experimental solution. For this purpose we adopt a procedure called titration. We pipette out say 20 ml of the experimental solution in a conical flash. Now V_2 is fixed i.e., 20 ml. Now the standard solution is taken in a burette. It is added in small quantities to the experimental solution from the burette till all the 20 ml of the experimental solution has reacted. Now the burette reading is noted which gives the volume of the standard solution viz., V_1 requried to react completely with 20 ml of the experimental solution. This process of adding one solution from the burette to determine the volume of that solution required to react completely with a particular volume of another solution is known as **titration.**

Equivalence point

During titration a stage will be reached at which the amount of the reagent added is exactly and stoichiometrically equivalent to the amount

of the reacting substance in the titrated solution. This point is called **equivalence point.**

End point

It is a stage during the titration where the reaction between the titrated solutions become completed.

The end point and the equivalence point should normally be the same. In practice this does not happen. They normally differ. The difference is the titration error.

To get precise results we repeat the titration till we get concordant titre values.

Indicator

It is a substance used to fix the end point in a titration. E.g., Methyl orange, phenolphthalein.

Basic requirements of a titrimetric reaction

1. The reaction should be rapid.
2. The reaction should follow a stoichiometric equation. Then only we can calculate exactly the amount of the reacting substance.
3. The reaction must proceed to nearly 100% completion on addition of the stoichiometric amount of the standard solution.
4. The completion of the reaction as indicated by the end point should be easily determinable.
5. The reaction should not be reversible.

Types of titrations :

Titrimetric analysis is broadly classifed into two types. In one type the oxidation state of various substances do not change during the reaction. These reactions depend on the combination of ions. In the

second type there is a change in the oxidation state. i.e., these involve transfer of electrons. There are further subdivided into the following :

1. Acid - base titration

In these titrations an acid is neutralised by a base or vice versa. If a standard alkali is titrated against an aicd, to estimate the latter, then the titration is known as alkalimetry. On the other hand, if a standard acid is titrated against a base, to estimate the latter, the titration is known as acidimetry.

Principle :

The purpose of titration of a solution of a base with a standard solution of an acid is to determine the volume of the standard acid required exactly to neutralise a given volume of the base. The point at which the acid neutralises the base completely is known as the **equivalence point, stoichiometric point or the end point.** At the end point an aqueous solutions of the corresponding salt is obtained. In the titration between a strong acid and a strong base, the resultant solution at the end point will be neutral and will have pH 7. In the titration between a strong base the resultant solution will be basic and its pH will be more than 7. Thus during a titration, near the end point, there will be a sudden change in the pH of the solution undergoing titration. This fact helps us to select an indicator which will change its colour within the range of pH change occurring during a titration. We can measure the pH of the solution undergoing titration after each addition of the titrant and plot pH against the milli - litres of titrant added. Such a curve will have a sharp rise or fall in it which will indicate the end point. Determination of pH at the various stages of the titration may be done with a potentiometer or it may be drawn theoretically.

Thus the end point in an acid - base titration is determined by using indicators or using a potentiometer.

A third method is to measure the conductivity of the solution that is undergoing titration and to draw a graph between the conductivity and the milli - litres of the titrant added. A break in the graph indicates the end point.

2. Redox - titration :

Principle / Theory :

When a titration involves a change in the oxidation number of the reacting species, i.e., if it involves transfer of electron from one reacting substance to the other, then it is known as a **redox titration**.

Examples : The titration between $KMnO_4$ and $FeSO_4$, $K_2Cr_2O_7$ and $FeSO_4$, $Ce(SO_4)_2$ and $FeSO_4$ and so on.

Explanation with example :

Let us consider the titration between $FeSO_4$ and $Ce(SO_4)_2$. In this titration electrons are transterred to Ce^{4+} from Fe^{2+} as shown below :

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$Ce^{4+} + e^- \longrightarrow Ce^{3+}$$

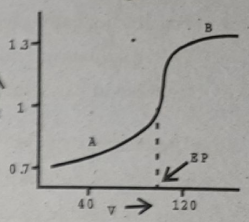
$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

Ferrous Ceric Ferric cerous

Here Ce^{4+} is the oxidising agent. It oxidises Fe^{2+} to Fe^{3+} getting it self reduced to Ce^{3+}.

The equivalence point or the end point is determined in two ways :

1. The potential of the system changes abruptly in the neighbourhood of equivalence point. In our example, when we add Ce^{4+} solution to a given volume of Fe^{2+} solution, in the neighbourhood of the equivalence point an abrupt change in the potential of the system will be noticed.



E = EMF in volts ;
V = Volume of ceric solution in ml ;
EP = End Point ;
A = Excess Fe^{2+},
B = Excess Ce^{4+}

If we plot the **emf** of the system against the volume in ml of the ceric solution, we get a curve as shown in figure (1). Near the end point there is a sudden change in the potential of the system.

2. We can use indicators to determine the end point in redox titrations. The indicators used to determine the end point in redox titrations are called **redox indicators**. They indicate the sudden change in the oxidation potential in the neighbourhood of equivalence point during a redox titration. During the titration these indicators are also oxidised or reduced. The oxidised from will have one colour while the reduced form will have a different colour. Therefore, at the equivalent point (end point) in the titration there will be a colour change.

Oxidised from + ne^- $\rightleftharpoons$ Reduced form

Colour I Colour II

E.g.

i. Diphenyl amine is the redox indicator used as an internal indicator used for titrations of Fe^{2+} against $K_2Cr_2O_7$. It is used as 1% solution

in conc. H_2SO_4. The end point is the apperance of intense bluish violet colour.

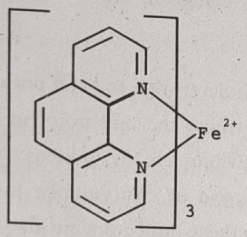
ii. Ferroin indicator (Figure - 2) is used when Fe^{2+} is titrated against Ce^{4+} in sulphuric acid medium. The end point is the change of colour from red to pale blue.

The complex of Fe^{2+} with the ligand orthophenanthroline is called ferroin. Its formula is $(Ph)_3Fe^{2+}$. The complexed iron in the ferroin undergoes reversible oxidation - reduction reaction as follows:

$$(Ph)_3Fe^{3+} + e^- \rightleftharpoons (Ph)_3Fe^{2+}$$

Pale blue — Red

The structure of ferroin is as follows:



3. Precipitation titration

What is it? It is a titration in which precipitates are formed. One of the reacting species is converted into a precipitate.

Example :

Estimation of chloride using $AgNO_3$. Here AgCl is precipitated.

$$Cl^- + AgNO_3 \longrightarrow AgCl^- + NO_3^-$$

Explanation :

When chloride solution is titrated against $AgNO_3$ chloride ions are precipitated as AgCl. Such a titration is known as precipitation titrations.

Principle :

In precipitation titrations, the formation of precipitates is used as the basis of the titration. The point at which a stoichiometric amount of the titrant is added to precipitate completely the ion to be estimated present in a given volume of the solution is the end point.

Conditions for precipitation titrations:

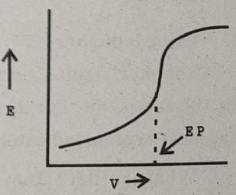
1. The precipitation reaction must attain equilibrium very rapidly after each addition of the titrant to the analyte.
2. Co - precipitation, occlusion, adsorption of foreign ions should not interfere with the reaction involved in precipitation titration.
3. A suitable indicator which can indicate the stoichiometric equivalence point should be available.

Different procedures involved in precipitation titrations :

We can conduct precipitation titrations potentiometrically, conductometrically, by using suitable indicators to fix up the end point etc.,

i. Potentiometric method :

When the titrant is added to the analyte, the potential of the system changes abruptly in the neighbourhood of the equivalence point. If we plot the emf of the system against the volume of the titrant in ml, we get a curve as shown in the figure 3. Near the end point there is a sudden change in the potential of the system.



E = EMF in volts;
V = Volume of the titrant

ii. Conductometric method :

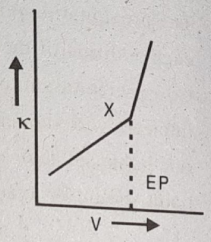
When the titrant is added to the analyte, progressively the ions are removed from the reaction mixture e.g.,

$$AgNO_3 + NaCl \longrightarrow AgCl^- + NaNO_3$$

i.e., $Ag^+ + NO_3^- + Na^+ + Cl^- \longrightarrow AgCl^- + Na^+ + NO_3^-$

If $AgNO_3$ is the analyte and NaCl is the titrant, then, during the titration the less mobile Ag^+ ions are replaced by more mobile Na^+ ions.

Thus during the titration when more and more of NaCl is added, more and more of Na^+ is introduced and so the conductance increases regularly. At the end point we have Na^+ and NO_3^- only. If we add any more amount of NaCl, conductance increases rapidly. It is because NaCl is a strong electrolyte and the addition of it causes an increase of Na^+ and Cl^- ions. The curve obtained in such a titration is shown figure - 4. The end point is given by the break in the curve X.



k - Conductance ;
V = Volume of NaCl,
EP = End Point

3. Using indictors :

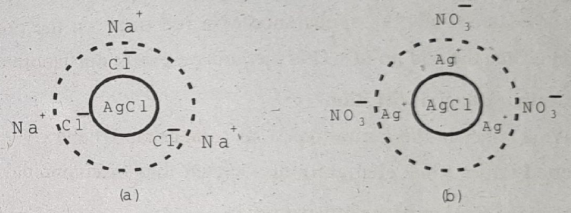
The precipitation titrations are also conducted using indicators to fix the end point. For this purpose we use a special type of indicators called **adsorption indicators.**

What are they? They are indicators which change their colour at the end point because of adsorption.

Explanation with example :

Fluorescein is used as indicator during the titration of chloride with $AgNO_3$ [Fajan's method].

When a chloride solution is treated with a solution of silver nitrate, the precpitated silver chloride adsorbs chloride ions (primary adsorbed layer). These negatively charged chloride ions adsorb positively charged sodium ions present in sodium chloride ions adsorb positively charged sodium ions present in sodium chloride solution (secondary adsorbed layer) (Fig a)



a) AgCl precipitated in the presence of excess of Cl^-
b) AgCl precipated in the presence of excess of Ag^+

At the equivalence point, silver ions are present in excess. These will now be primarily absorbed and nitrate ions will be held by secondary adsorption (Figure b)

If fluorescein is also present in the solution, the negative fluorescein ions, which are much more strongly adsorbed than the nitrate, are immediately adsorbed. This gives red colour due to the formation of complex of silver and fluoresceinate ion on the surface. Thus at the end point red colour is obtained.

Conditions for the choice of suitable adsorption indicator :

1. The indicator ion must be of opposite charge to the ion of the precipitating agent.

2. The indicator ion should not be adsorbed before the particular compound has been completely precipitated. But it should be strongly adsorbed immediately after the equivalence point.
3. The precipitate should separate, as for as possible, in the collodial condition.
4. Formation of a coloured precipitate - The Mohr method :
   In the titration of a neutral solution, for example, chloride ions with silver nitrate solution, a small quantity of potassium chromate solution is added to serve as indicator. At the end point, the chromate ions combine with silvelr ions to form the sparingly soluble red silver chromate. Thus the appearance of a red tinge on the precipitate indicates the end point. This method we use in our laboratory.

4. Complexometric titration

What is it ? In these titrations, ions (other than H^+ and OH ions) are converted into a soluble, slightly dissociated ions or compounds.

Description / Explanation with example :

When $AgNO_3$ is titrated against KCN, Ag^+ is converted into the soluble complex $Ag[(CN)_2]^-$ ion which dissociates slightly.

$$2CN^- + Ag^+ \rightleftharpoons [Ag(CN)_2]^-$$

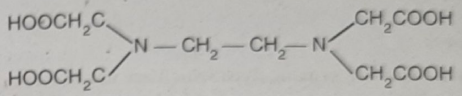
Principle :

Metal ions can be determined by titrating them with a reagent that complexes them in solution. The solution to be titrated is buffered at a suitable pH, an indicator is added and the metal ion is titrated with a standard solution of the complexing agent. A sharp colour change marks the end point of the titration.

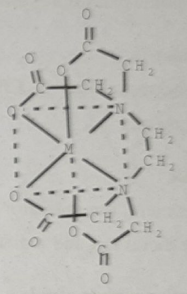
complexometric titrations are convenient and accurate. They have replaced time consuming gravimetric procedures. Except for the alkali metals most metal cations can be determined by titration with a suitable complexing agent.

A suitable complexing agent is EDTA. It forms stable chelates with a large number of metal ions. It is used as a primary standard in complexometric titrations.

EDTA is ethylene diamine tetracetic acid. It is a hexa dentate ligand and it is an important chelating agent. Its structure is as follows :



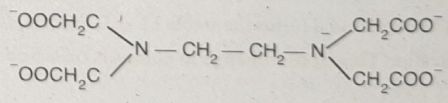
EDTA complexes with a large number of metallic ions such as Ca^{2+}, Mg^{2+}, Ba^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Co^{3+} etc. It binds through two nitrogen and four oxygen atoms to the central metal ion. The complexes formed by EDTA are highly stable. The M-EDTA complex is as shown.



M = Ca^{2+}, Mg^{2+}, Ba^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Co^{3+} etc.

EDTA is assigned the formula H_4Y, Where Y^{4-} refers to the anion of EDTA.

The disodium salt of EDTA is therefore represented as Na_2H_2Y. The complex forming ion is therefore H_2Y^{2-}. This ion reacts with all metals in a 1:1 ratio.



The 1:1 complexes are extremely stable because all co - ordination valencies on a metal ion upto 6 may be satisfied by a single molecule of Y^{4-}.

The reactions with cations, e.g., M^{2+} may be written as

$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+$$

Determination of end points in complexometric titrations :

In complexometric titrations, the end points are determined with a help indicators called metal ion indicators.

Metal ion indicators :

What are they ? They are organic dyes which are used to determine the end point in complexometric titrations.

Examples :

i. Eriochrome Black T (EBT)
ii. Murexide

Principle :

The metal ion indicator exhibits one colour when they are complexed with the metal ion and a different colour when they are free.

Explanation with example :

Let us take the example of the titration of Mg against EDTA using Eriochrome Black T (EBT) as indicator. The Mg^{2+} ion complexes with EBT and forms Mg - EBT comples.

During the titration the free metal ions are complexed by EDTA until all the metal is displaced. Near the end point, the EDTA reacts with the less stable Mg. EBT complex and forms the stable M - EDTA complex and leaves the free indicator. Therefore a change in colour is observed at the end point.

In the pH range 7 - 11, Mg - EBT complex is red and the free indicator is blue in colour.

$$\underset{\text{Red}}{\text{Mg - EBT}} + \text{EDTA} \longrightarrow \text{M - EDTA} + \underset{\text{Blue}}{\text{EBT}}$$

Requirements of a metal ion indicator :

1. The indicator must have a different colour from metal - indicator complex.
2. The metal indictor complex must be formed under the same conditions as metal - EDTA complex.
3. The indicator must be very sensitive to metal ions so that colour change occurs as near to the equivalence point as possible.
4. The metal indicator complex, must be less stable than the metal - EDTA complex, to ensure that at the end point EDTA removes metal ions from metal - indicator complex. The change in equilibrium from metal - indicator complex to metal - EDTA complex should be sharp and rapid.

Applications :

Complexometric titrations are used to i) determine hardness, ii) determine Ni and many other ions.

1. Determination of Hardness of water :

The hardness of water is due to the presence of calcium and magnesim salts. To estimate the total hardness of water, the sum of Ca^{2+} and Mg^{2+} ions present must be known. First by titrating a standard EDTA solution against a measured quantity of hard water using EBT, the total hardness of water can be estimated. In the second titration magnesium is converted into its hydroxide and is removed. From the second titration the amount of Ca^{2+} is determined. From these two values the total amount of Mg^{2+} is determined.

Procedure :

40 ml of water samples is taken in a conical flask and 20 ml of ammonium buffer is added to keep the pH between 8 - 10. It is diluted to100 ml with distilled water and a pinch of Eriochrom black T is added. The solution is warmed to 60°C and it is titrated against standard EDTA (0.01 M). The end point is the change of colour from wine red to blue. Let the titre value be x ml.

Another 40ml of the sample is taken in a conical flask and 10 ml of 2M NaOH is added followed by a pinch of murexide indicator. The solution is diluted to 100 ml with distilled water and it is titrated against EDTA. The end point is the change of colour from pink of blue. Let the titre value be y ml.

Calculation :

Factor value for calcium F_{Ca} is

1 ml of EDTA = 0.4 mg of calcium

Factor value for magnesium F_{Mg} is

1 ml of EDTA = 0.243 mg of magnesium

X Amount of Ca in 1000 ml of the

$$\text{Sample} = \frac{0.4 \times y \times 1000}{40} = A \text{ mg} = A \text{ ppm}$$

Amount of Mg in 1000 ml of the

$$\text{Sample} = \frac{0.243 \times (x - y) \times 1000}{40} = B \text{ mg} = B \text{ ppm}$$

Total hardness = A + B ppm.

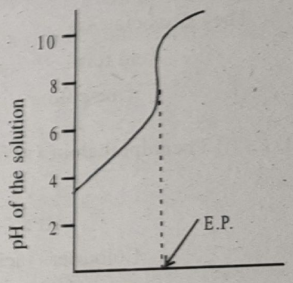
2. Determination of Ni :

Nickel can be estimated by titrating a solution of nickel against standard EDTA. Murexide is used as indicator for this titration. The pH is to be maintained between 10 and 11.The end point is the change of colour from yellow to blue violet.

The same titration can be done with Eriochrome black T incicator also. In that case, the endpoint is the change of colour from blue to red. The pH range is 7 to 11.

Titration Curves

These are graphs drawn to find out the end point in a titration. In these graphs, the volume of the titrant (the solution added from the burette) is plotted against a measurable properly. E.g. In acidimetry - alkalimetry titrations, the pH values of the reaction mixture are plotted against the volume of the titrant added. We get a graph as shown in figure 6. A major change in the pH gives the end point.



E.P. = End Point

Plots of analogous data for titrations involving redox, precipitation and complexometric titrations also are similar to the one shown in the diagram.

Indicators

Indicators are substrances which are used to fix the end point in a titration. The choice of indicator depends on the nature of the titration.

i. Acid - base indicators

What are they ? Indicators that are used to indicte the end point in an acid - base titration are called acid base indicators.

Example :

Methyl orange and phenolphthalein.

Theories of (acid - base) indicator

The acid base concept of indicators (Ostwald's Theory)

According to this concept, the indicators themselves are considered as acids or bases.

They dissociate as

Acid form $\rightleftharpoons$ H^+ + Basic form

One colour another colour

E.g., (i) Phenolphthalein (written as HPh) is assumed to dissociate as acid.

$$HPh \rightleftharpoons H^+ + Ph^-$$

Colourless (acid form) Pink (basic form)

Due to common ion effect, the equilibrium shifts to the left in acid solution (e.g., HCl). Therefore the indicator exists as undissociated. Therefore phenophthalein is colourless in acid solutions.

In alkaline solution (e.g., NaOH), the OH^- ions of the base combine with H^+ ions and form water. Therefore the equilibrium shifts to right. Ph^- ions are produced. Therefore phenolphthalein is pink in alkaline solutions.

ii) Methyl orange (written as MeOH) is assumed to dissociate as a base.

$$MeOH \rightleftharpoons Me^+ + OH^-$$

Yellow (basic form) Red (acid form)

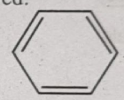
In acid solutions, (e.g., HCl), the OH ions combine with the H^+ ions of the acid and form water. Therefore the equilibrium shifts to the right. Me^+ions are produced. Therefore methyl orange is red in acid solutions.

Due to common ion effect, the equilibrium shifts to the left in alkaline solutions (e.g., NaOH). Therefore the indicator remains as undissociated. Therefore methyl orange is yellow in alkaline solutions.

Quinonoid Theory :

Principle :

Compounds having benzenoid (benzene like). structure are colourless or light coloured and compounds having quinonoid (quinone like) structure are coloured.



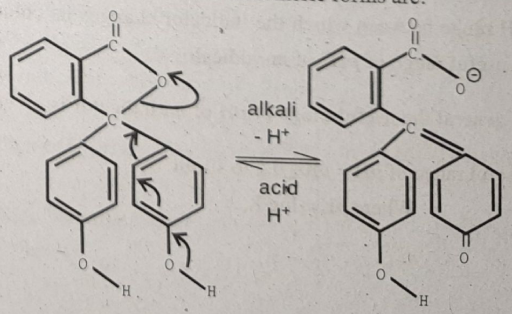
Benzenoid structure

Quinonoid structure

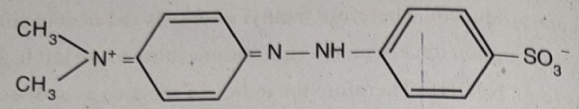
Theory :

An indicator exists as an equilibrium mixture of the two, tautomeric forms, viz., the benzenoid form and the quinonoid form. The quantity of a particular form varies with the *p*H of the solution. Therefore the colour also changes with *p*H.

E.g., (i) Phenolphthalein : The two tautomeric forms are:

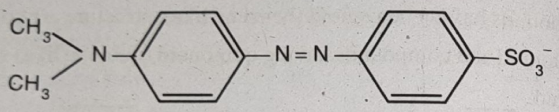


(ii) Methyl orange : The tautomeric forms are :



Quinonoid from - Red (in acid)

acid $+ H^+$ ⇌ alkali $- H^+$



Benzenoid form - Yellow (in alkali)

Criteria for choosing an indicator for a given acid-base titration :

In an acid-base titration, at the end point there is a sudden change in the *p*H value of the reaction mixture. The *p*H change that occurs near the end point various from titration to titration. We have to choose a suitable indicator that changes its colour within the range of change in *p*H that occurs around the end point of the particular titration.

Each indicator changes its colour between two specific *p*H values. This *p*H range between which the indicator changes its colour is known as 'the useful range of *p*H" of an indicator.

In general the useful range of *p*H of an indicator is given by

Useful range of $pH = pK \pm 0.5$ to 1 unit.

Where $pK = -\log K$.

and K is the dissociation constant of the indicator E.g.,

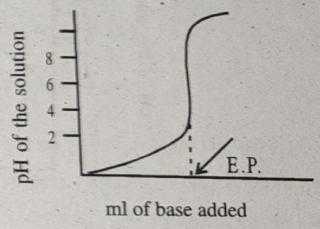
Indicator	pK	Useful range of pH
Methyl orange	3.5	3.0 to 4.0
Phenolphthalein	9.3	8.0 to 9.8

In other words, phenolphthalein will show the acid colour (viz., colourless) in solutions whose *p*H is below 8 and it will show the base colour (viz. pink) in solution whose *p*H is above 9.8.

Similarly methyl orange will show the acid colour (viz., red) in solutions whose *p*H is below 3.0 and it will show the base colour (viz., yellow) in solutions whose *p*H is above 4.0.

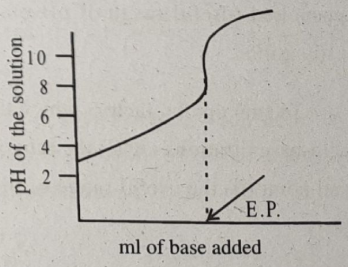
Examples : (i) Titration of a strong acid versus a strong base.

At the neutralisation point the *p*H changes from 3 to 9.5. All the indicators whose useful range of *p*H is between 3 and 9.5 can be used for such titrations. Both phenolphthalein and methyl orange can be used for titration between a strong acid and a strong base.



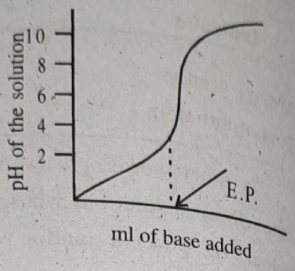
(ii) Titration of a weak acid versus a strong base :

At the neutralisation point the *p*H changes from 7 to 10. Therefore we have to choose an indicator whose useful range of *p*H is between 7 and 10 for such titrations. Phenolphthalein, whose useful range of pH is 8 to 9.8 can be used for titration between a weak acid and a strong base.



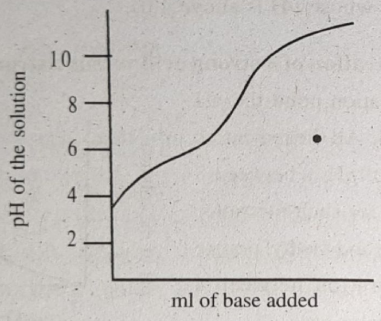
(iii) Titration of strong acid versus a weak base :

At the neutralisation point the *p*H changes from 4 to 7.



Therefore we have to choose an indicator whose useful range of *p*H is between 4 and 7 for such titrations. Metyl orange, whose useful range of *p*H is 3 to 4.5 can be used for titration between a strong acid and a weak base.

(iv) Titration of a weak acid versus a weak base :



At the neutralisation point there is no sharp change in the *p*H value. Therefore they cannot be titrated using normal indicators. Anyhow, phenolred (useful range of pH 6.8 to 8.4) can be used for approximate estimations.

To sum up, the factors which decide the choice of an indicator for an acid-base titrations are (i) the range of change of *p*H of the solution at the end point (ii) the useful range of *p*H of the indicator.

The principle is that the useful range of *p*H of the indicator shoud fall with the in the in the range of change of *p*H at the end point.

2. Mixed indicators :

They are mixtures of usual acid base indicators and orange dyes. They are used to increase the sharphness of the visible end point.

The added dye is not affected by *p*H. It blocks out certain wavelengths of light common to the colours of indicators before and after the end point, so that there is a marked difference between them.

E.g. Methyl purple. It is mixture of methyl red and an inert blue dye. It has a very pronounced colour change. Further the colour change occurs over a very narrow *p*H range.

3. Fluorescent indicators :

They are substances which fluoresce in ultraviolet light and change colour or have their fluorescene quenched with change in *p*H.

Example : Fluorescein and eosin (tetrabromo fluorescein)

Explanation : The intensity and colour of the fluoresence of many substances depend upon the *p*H of the solution. Indeed, some substances as so sensitive to *p*H that they can be used as *p*H indicators. These are termed fluorescent or luminescent indicators. Fluorescent indicators are used in acid-base titrations. These indicators can be employed in the titration of coloured (and sometimes of intensely coloured) solutions in which the colour changes of the usual indicators would be masked. Titrations are performed in a silica flask.

Eosin and florescein are frequently employed as adsorption indicators also. Fluorescein is used in the *p*H range 4-6, when the colour change is from colourless to green. Eosin changes its colour in the *p*H range 3-4 from colourless to green.

Data Analysis

In analytical chemistry were are going to get a lot of data. How to analyse and interpret these data? This we shall see in this chapter.

1. ERRORS IN CHEMICAL ANALYSIS

Definition of Error :

The difference between the measured value of a property and its accurate value is called the error.

Explanation :

During chemical analysis we measure the value of a particular property. E.g., we measure the weight of an object or the volume of a solution. Accurate results will be got when persons with great skill do the measurements with best instruments. This is nearly impossible. Usually the measured value of the property will never be the accurate value of the property. The difference between these two is called the error. Such errors in measurement will affect the accuracy and precision of the property that is measured. So, the analytical data so obtained becomes unreliable. In the following pages we shall study about such errors in chemical analysis.

Classification of Errors :

The errors that arise in a chemical analysis are classified into two types. They are

i. Determinate errors
ii. Indeterminate errors (or) Random errors.

It should be remembered that it is difficult or impossible to be certain of the type to which a given error belongs. Never the less the classification is useful for discussing analytical errors.

Determinate Errors (or) Systematic errors

These are errors which have a definite value and an assignable cause. The analyst can measure and account for these errors. These can be avoided. They are unidirectional i.e., the errors will be either more or less than the accurate value. From this, they can be identified.

Sources of these errors :

i. Defective instruments
ii. Careless operation
iii. Procedural defects

Classification :

i. Instruments errors.
ii. Method errors .
iii. Personal errors.

i. Instrument Errors :

When we use balances, weights, pipettes, burettes etc., we must make sure that they are not defective. For example, a weight marked 10g may not be 10g after all. So to avoid these errors one must use best instruments. Periodic calibration of apparatus and weights is a must. These errors may be identified by changing the instrument, the error will also change.

ii. Methods Errors :

These are introduced by defective expermental procedures. E.g.,

a. Co - precipitation or post precipitation in gravimetric analysis.
b. Usage of improper indicators in volumetric analysis.

These are difficult to identify. So these are the most serious of the three types of determinate errors. So to avoid these, one must be thorough with the theoretical part of the experiment.

iii. Personal Errors (or) Operative Errors

These are introduced by personal defects or carelessness. The Sources of this error are human defects in eyes, mind etc., In colorimetric

experiments errors will be introduced by a person who is colourblind. A person with defective eyes will invariably note readings erraneously. Carelessness, fatigue and improper instructions from the teacher also introduce these errors. Several mistakes may creap in E.g., Wrong calculations, wrong placement of decimals, noting wrong signs, cooking results etc. These can be avoided if one works scrupulously in the laboratory. These are identified by the fact that these errors change when the measurement is repeated.

Determinate errors may also be classified as being either

1. Constant Errors and 2. Proportional Errors.

1. Constant Errors :

These are errors whose magnitude is independent of the size of the sample taken for analysis. For example, let us say that 0.5 mg of percipitate is lost when washed with 200ml of the wash liquid. Now, if we wash 500mg of precipitate with 200 ml of wash liquid 0.5 mg of the precipitate will be lost. So the loss is $(0.5 \times 100) \div 500 = 0.1\%$. Let us assume that we wash 50mg of the precipitate with 200ml of wash liquid, here also 0.5mg will be lost. So the loss is $(0.5 \times 100)\ 50 = 1\%$.

Thus we find that a constant error will become more serious as the size of the quantity measured decreases. So to minimize the effect of constant error we have to use a large, sample. [Please remember that in our experiments in gravimetric analysis the solution to be estimate is so prepared that the weight of the precipitate is around 0.2g].

2. Proportional Errors :

These are errors whose magnitude increases or decreases in proportion to the size of the sampel taken for analysis. Invariably impuritites in the sample. If not removed, will cause a proportional error.

Correction of Determinate Errors :

Determinate instrumental errors are corrected by calibrating the

instruments concerned. The equipments are to be calibrated periodically. This is because instrumental errors arise due to wear corrosion or mistreatment.

Determinate personal errors can be minimised by care and self discipline. Instrument readings, note book entries and calculations should be checked systematically.

Determinate method errors are particularly difficult to detect. They may be corrected by one or more of the following procedure.

1. Analysis of standard samples :

A method may be tested for determinate error by analysis of a synthetic sample whose over all composition is known and which closely resembles the material to be tested by the particular method.

2. Independent analysis :

When samples to be analysed are not available in a pure state this method is used. The sample is analysed in a particular method. Then it is anlysed by a different method of established reliability.

3. Blank determinations :

Constant errors affecting physical measurements can be frequently evaluated with a blank determination in which all steps of the analysis are performed in the absence of the sample. The result is then applied as a correction to the actual measurement. This method is useful to correct errors that the due to the introduction of interfering contaminants from reagents and vessels employed in the analysis. This method is useful to correct titration data in volumetric analysis.

4. By taking large sample size :

We know that a constant error decreases as the size of the sample is increased. So, to correct such type of errors large sample size is used for analysis.

Random Errors or Indeterminate Errors or Accidental Errors

They are errors arising from uncertainities in a measurement that are

unknown and not controlled by the person doing an experiment.

Sources :

i. Instrument uncertainities

ii. Method uncertainities

iii. Personal uncertainities.

Identification :

Indentification of indeterminate errors is difficult. Scatter of data about the mean is the effect of an indeterminate error.

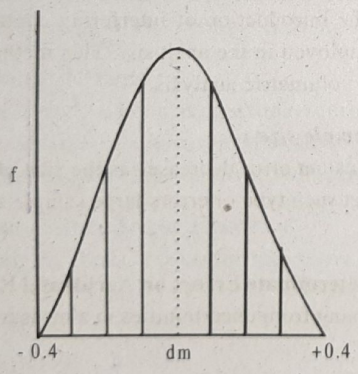
Error Analysis :

When indeterminate error or deviation from mean (dm) is ploted against its frequency (f) we get a curve as shown in figure. This bell shaped curve is called Gaussian of normal error curve. The properties of this normal curves are

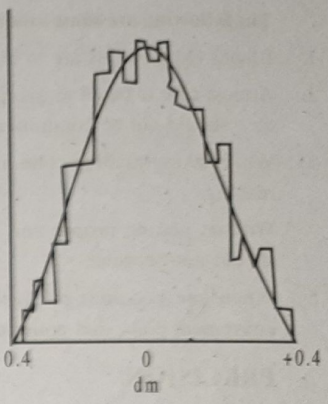
i. The frequency is maximum where the indeterminate error is nil.

ii. There is a symmetry about this maximum, suggesting that positive and negative errors occur with equal frequency.

iii. As the magnitude of the error increases, the frequency decreases exponentially.



In chemical analysis, indeterminate errors follow this Gaussian type distribution. For e.g., if the deviation from the mean (dm) of hundreds of repetitive weighing measurements on a single object, are plotted against the frequency (f) of occurrence of each deviation we get a curve a shown in figure. This curve proves the fact that a number of small independent and uncontrolled uncertainities are there in our normal measurements.



These uncertainities manifest in the result.

This Gaussian distribution of most analytical data, permits us to use statistical techniques to estimate the extent of indeterminate errors. Thus we use several statistical techniques like mean, median, average deviation, standard deviation etc., while analysing our experimental results.

Minimising Errors :

From the above discussion it is clear that, if we want to minimise error we have to minimise determinate as well as indeterminate errors.

To minimise determinate errors we will have to use standard, internationally accepted instruments. The various measuring aids must be calibrated periodically and got certified according to international standards. All reagents must be properly maintained. Dependable procedures must be adopted to avoid methodic errors. To avoid personal errors one must be careful and honest in recording the observation. It is human tendency to manipulate results to get high degree of precision. This tendency must be avoided.

We know that indeterminate errors are uncontrollable. So, to minimise these errors, we repeat the experiments several times and adopt statistical techniques to get maximum precision.

The following are some other specific suggestions to minimise error.

1. Blanks experiments are to be conducted along with regular ones.
2. Atmost care is taken to avoid personal errors. Arithmatic mistakes, etc., should not be committed.
3. While taking readings one must be very careful to note the correct reading.
4. Without getting proper and complete instructions, the experiment should not be done.
5. When one becomes tired, the experiment must be stopped in a convenient place and continued after taking sufficient rest.

2. PRECISION

Definition :

It is the degree of aggrement between two or more measured values of a property measured under identical condition.

Explanation with example :

Let the weight of a beaker be 20.0326g when weighed ina particular set of conditions. If the same beaker is weighed under identical conditions and if the weight got is the same 20.0326g then we say that there is precision in the weighing. Thus if a value is reproducible then it called a precise value.

Precision and range of a set of value :

The differenses between the highest and lowest values in a set of values is called the range (w). This range is a measure of precision. If the range is wids then it means that the measurement is less precise.

3. ACCURACY

Definition :

It is the degree agreement between the measured value and the expected or true value of a property.

Explanation with example :

As per analytical data available the solubility product of AgCl is 1.8×10^{-10}. If an analyst gets this same value while determining the same

in an experiment, then. It is said accuracy of the result is excellent. If it differs, we calculate the deviation. This deviation gives a measure of the accuracy of experiment.

Methods of expressing accuracy :

Accuracy is expressed in terms of absoulte error or relative error. The lower these values are, the more will be the accuracy.

Absolute Error (E) :

Definition :

It is defined as the difference between the accepted value (x_t) and the observed values (x_i). Mathematical expression : $E = x_i - x_t$.

Relative Error (RE) :

Defnition :

It is the error percentage the accepted value.

Mathematical expression :

$$RE = \frac{E}{x_t} \times 100$$

Advantage of relative error over absolute error :

Absolute error depends onthe reliability of the accepted value it self as a lot of uncertainity may be there about the accepted value. So relative error is used more often to express accuracy.

Distinctions between Absolute Error (E) and Relative Error (RE)

		E	R E
1.	Definition	$E = x_i - x_t$	$RE = (E/x_i) \times 100$ $= (x_i - x_t / x_i) \times 100$
2.	Usefulness	Not much useful as E depends on x_t which itself is subject to uncertainty.	More useful

Difference between Precision and Accuracy

	Precision	Accuracy
1.	Degree of agreement between a value and other values obtained under substantially the same condition.	Degree of agreement between a measured value and the true value or expected value
2.	Precision may be achieved.	Accuracy is never known. It is known within certain limits only. Accuracy can be approached but never attained.
3.	Expresses the reproducibility of the results.	Expresses correctness of a measurement.

One must clearly understand the connotations of the terms precision and accuracy. An understanding of the two terms will make it clear that high precision does not imply accuracy. We can prove this with an example. In a volumetric estimation one may get concordant titre values. Yet the result may turn out to be wrong. Here, as concordant titre values have been got, the result is precise.

But as the answer doesnot agree with the expected value, it is not accurate. Thus as precise value may not be an accurate value. The reason for this may be a determinate error like instrumental error or operative or personal error like personal carelessness or even some unknown indeterminate error.

Confidence limits :

Definition :

They are the limits, which may be set, about the experimentally measured mean (x), with in which we may expect to find the true mean (μ) with a given degre of proabability.

Explanation :

Only the mean of an infinite number of measurements can be true or accurate mean. This true mean is represented by μ. This is unattainable as an infinite number of measurements is impossible. i practice, we make a finite number of measurements and calculate the experimental mean ($\bar{x}$) How near or how far away is $\bar{x}$ from μ ?. This can be determined by setting limits. Within these limits we can find μ with a given degree of probability. The interval between these limits is called the confidence interval. The size of this interval depends on the degree of probability that we need. If we want 99% probability, the intervel will be small 99% probability means that 99 times out of 100, the true mean will be within this intervel. Similarly we can choose 95% probability, 90% probability etc., depending upon our needs. This percentage probability is called confidence level.

Mathematical expression of confidence limits :

a. When the standard deviation is for a small number of measurements, σ (standard deviation, applicable only when the number of measurements is large) the confidence limit for a single measurement for μ is given by

$$\mu = \bar{x} \pm Z\sigma$$

$$\text{Where } Z = \frac{\bar{x} - \mu}{\sigma}$$

The confidence limit for the μ of N measurements is given by

$$\mu = \bar{x} \pm \frac{Z\sigma}{\sqrt{N}}$$

When σ is unknown : Confidence limit for μ of N measurements is given by

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$$

Where $t = \frac{\bar{x} - \mu}{s}$

Thus we find by applying statistical methods we can fix the confidence limits within which the true average of a set of experimental results can be found for various confidence levels of probabilities. For this we must known the values of Z and t which are readily available in literature.

Rejection of Results :

In a set of data we come across one or two values that are suspicious. Whether to reject such a data or not would become difficult. In such cases we employ a test called Q - test. In this test we compare two Q - values.

i. Q_{exp} and ii. Q_{crit} If $Q_{exp} > Q_{crit}$ then we reject the data. If not, we retain the data.

To get Q_{exp} the difference between the suspicious value and its nearest neighbour is divided by the spread of the entire set.

To get Q_{crit} the following table giving various Q_{crit} values is used.

Number of observations	Q_{crit}		
	90% confidence	96% confidence	99% confidence
3	0.94	0.98	0.99
4	0.76	0.85	0.93
5	0.64	0.73	0.82
6	0.56	0.64	0.74
7	0.51	0.59	0.68
8	0.47	0.54	0.63
9	0.44	0.51	0.60
10	0.41	0.48	0.57

Let us illustrate how to decide whether to reject or retain a data.

Let us say that the experimentally determined percentages of CaO in a calcite sample are 55.95, 56.00, 56.04, 56.08, 56.23. Now we suspect that the last value and so we have to decide whether to reject it or not.

For this set of data Q_{exp} = (Suspecious value – Its nearest neighbour) ÷ the spread of the entire set.

$= (56.23 - 56.08) \div (56.23 - 55.95)$

$= 0.15 \div 0.28 = 0.54$

Now let us say we want our results in 90% confidence level i.e., our result should be 90% as near to the correct value then we look under 90% confidence column of the table. Since we have 5 observations we look for Q_{crit} against number of observations 5 and under 90% confidence. The value is 0.64.

Since $Q_{exp} < Q_{crit}$ we conclude that the value is to be retained.

Though the Q - test is superior to other methods one must be careful while deciding to either reject or retain a particular data using this test. One has to use one's good judgement in deciding. Where the number of observations are small the reliability of Q - test decreases. So, to reject a value in a small set a cautious approach is desirable.

4. SIGNIFICANT FIGURES

They are figures in a number which contains only digits known with certainty plus the first uncertain one.

Explanation :

A measured value has some uncertainty about it. There is a convention to give the measured value as a number such that it contains only one figure about which there is uncertainty. The practice is called significant figure convention.

Example :

If the weight in a weighing is known with certainty only upto three decimals, the value should be reportes only upto four decimals.

Salient features ? Points to be borns in mind while using the concept of significant figures :

The number of significant figures in a given number is found out by counting the number of figurs from left to right in the number begining with the first non - zero digits and continuing till reaching the digit that contains the uncertainty.

Examples :

1. Each of the following has three significant figures. 583. 0.234, 1.67, 0.00987 and 65.4.
2. Zero is a siginificant figure when used as a number. It is not a significant figure when it is used to locate decimal points in very small and very large numbers. E.g., 0.02670 has four siginificant figures. The two zeros before 2 are used to imply only the magnitude. So they are not significant. The zero beyond 7 is significant.
3. The value 6.030×10^{-1} has four significant figures while 1.45×10^{5} has three significant figures.

Using the above, one can determine the number of significant figures in a given number.

Its importance or Uses :

In presenting scientific data, one comes across a set of values. For this set of values, one gives their mean or median as the best value. Now the uncertainty about this best value must also be indicated while presenting the data. To achieve this, usage of significant figures is very helpful. On several occasions one has to round off numbers to give meaningful results. For this, the practise of rounding off to a numer which contains only one uncertain figure in it, is adopted. Thus significant figures become important.

Methods of expressing Precision :

Precision is expressed by two methods.

i. Absolute Method

ii. Relative Method.

i. Absoulte Method :

In this method the precision is expressed in terms of average mean deviation. The smaller the value of average mean deviation the greater will be the precision.

ii. Relative Method :

In this method the precision is expressed in terms of percentage deviation from the mean of a set of values.

$$\text{i.e., Percentage deviation from the mean} = \frac{\text{Mean of a set of values minus a particular value}}{\text{The mean}} \times 100$$

$$= \frac{\bar{x} - x_i}{\bar{x}} \times 100$$

To understand the above two methods let us learn some terms used in statistics.

Mean / Artithemetic mean / Average :

Mean is the quotient obtained when the sum of a set of replicate measurements by the number of individual results in the set. The following worked out unversity problem would illustrate mean.

Problem :

Calculate the mean for the following set of values 20.21, 20.04, 20.13 and 20.19

Solution :

Mean = $(20.21 + 20.04 + 20.13 + 20.19) \div 4 = 80.57 \div 4 = 20.14$.

Median :

It is the value about which all other values are equally distributed. Half the values will be greater and the other half smaller than the median.

The median is obtained by arranging the set of values in increasing or decreasing order. If there are odd number of values then the middle

value gives the median. If there are even number of values than the average of the middle pair gives the median. The following worked out university problems would illustrate the median.

Problem :

Calculate the median for 20.20, 20.08 and 20.02.

Solution :

Arranging the values in increasing order we get 20.01, 20.08 and 20.20. This set contains odd number of values. Therefore the median of this set is the middle value i.e., 20.08.

Problem :

Calculate the median for the following set of values 20.21, 20.04, 20.13 and 20.19.

Solution :

Arranging the values in increasing order we get 20.04, 20.13, 20.19 and 20.21. This set contains even number of values. Therefore the median of this set is the average of the middle pair of values, i.e., (20.13 + 20.19) ÷ 2 = 40.32 ÷ 2 = 20.16

Difference between Mean and Median

		Mean	Median
1.	Definition	It is the quotient obtained when the sum of a set of replicate measurements by the number of individual results in the set.	It is the value about which all other values are equally distributed 20.08
2.	Examples Date : 20.20 20.08, 20.01	20.09	20.08
3.	Precission	Better than median	Less than mean

Mean deviation or Average deviation

Definition :

The average deviation of a value in a set of values is the average of the divations of all the individual values from their average.

Explanation :

To get the average deviation.

i. The average of the given set of values is calculated.

ii. The deviation of each value from the average is calculated.

iii. The average of all these deviations (ignoring signs) give the average deviation. The following worked out University problems would illustrate average deviation.

Problem :

Calculate the mean (average) deviation for the following set of values : 20.21, 20.04, 20.13 and 20.19.

Solution :

Average of this set = (20.21 + 20.04 + 20.13 + 20.19) ÷ 4
= 80.57 ÷ 4 = 20.14.

Value	Deviation from average
20.21	20.14 – 20.21 = 0.07
20.04	20.14 – 20.04 = 0.10
20.13	20.14 – 20.13 = 0.01
20.19	20.14 – 20.19 = 0.05
Total of deviation from average	= 0.07 + 0.10 + 0.01 + 0.05
	= 0.23
Mean deviation	= 0.23 ÷ 4 = 0.575

Its usefulness :

If the mean deviation of a set of measure ments is small it means that the average of that set is nearly precise.

Standard Deviation :

Definition :

It is the square root of the quotient obtained by dividing the sum of the squares of the individual deviations from their mean by the number of measurements made.

or

Standard deviations = $\sqrt{\text{Sum of squares of individual deviation from their mean} \div \text{Number of measurements made}}$

Explanation :

To obtain standard deviation.

i. The average $(\bar{x})$ of the measurements (x_{ii}) is calculated.
ii. The individual deviation of each measurement from the average $(x_i - \bar{x})$ is calculated.
iii. Each individual deviations is squared $(x_i - \bar{x})^2$
iv. All the individual deviation square are added $\sqrt{\Sigma(x_i - \bar{x})^2}$.
v. The value obtained in step.
vi. It is divided by the number of measurements made $\Sigma(x_i - \bar{x})^2 \div N$.
vii. The square root of the value obtained in step.
v. Gives the standard deviation. Thus standard deviation $\sigma = \sqrt{\Sigma(x_i - \bar{x})^2 \div N}$.

σ is applicable only when the number of measurements is large. But in analytical chemistry we make only a small number of measurements. so in step (v) instead of dividing by N the value obtained in step (iv) is divided by N – 1. The standard deviation for a small number of measurements $s = \sqrt{\Sigma(x_i - \bar{x})^2 \div (N - 1)}$.

Example / Illustration :

The following worked out university problem would illustrate how standard deviations is obtained from a set of data.

Problem :

Find the standard deviation for a subset having the following six values.

7.720, 7.725, 7.736, 7.719, 7.742 and 7.751

Solution :

i. Calculation of average $\bar{x}$

$(7.720 + 7.725 + 7.736 + 7.719 + 7.742 + 7.751) \div 6$

$= 46.393 \div 6 = 7.732$

ii. Calcualtion of $\Sigma(x_i - \bar{x})^2$

x_i	$(x_i - \bar{x})$	$(x_i - \bar{x})^2$
7.720	0.012	1.44×10^{-4}
7.725	0.007	0.49×10^{-4}
7.736	0.004	0.16×10^{-4}
7.719	0.013	1.69×10^{-4}
7.742	0.010	1.00×10^{-4}
7.775	0.043	18.49×10^{-4}

iii. $\therefore \Sigma(x_i - \bar{x})^2 = 23.37 \times 10^{-4}$

iv. $\dfrac{\Sigma(x_i - \bar{x})^2}{N - 1} = \dfrac{23.27 \times 10^{-4}}{5} = \dfrac{4.82}{5} = 0.96$

v. $\sqrt{\Sigma(x_i - \bar{x})^2 \div (N - 1)} = 0.98$

Standard deviation = 0.98.

Exercises : (University Problems)

1. Calculate the standard deviation for the subset of the values : 25.32, 25.07, 25.18, 25.26
   [Ans : 0.1082]

2. The percentage of a constituent M in a compound MA are found to be 62.42, 62.28, 62.46, 62.32 and 62.22. Calculate the mean, median and standard deviation.
   [Ans : i. 62.34, ii. 62.32, iii. 0.099]

Advantages of standard deviation : Standard deviation is more reliable than average or mean deviation to express precision as it has theoretical foundation.

Its usefulness :

If the standard deviation of a set of measurements is small, it means that the average of the set is nearly precise.

Difference between Mean deviation and Standard deviation

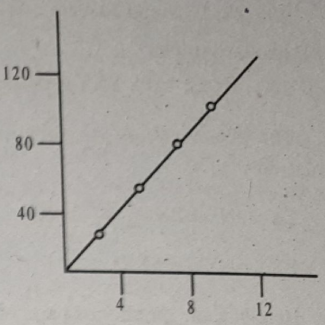
		Mean deviation	*Standard deviation*
1.	Definition	It is the average of the deivation of all the individual values from their average.	Sum of squares of individual deviation from their mean ÷ number of meansurements made.
2.	Formula	$\sqrt{\Sigma(x_i - \bar{x}) \div N}$	$\sqrt{\Sigma(x_i - \bar{x})^2 \div (N-1)}$
3.	Precision	Less than standard deviation but better than average	Better than mean deviation, It is the best way of expressing precission.

Curve Fitting - Method of Least Squares

If we want to present a trend or relationship we draw a graph. A graph is obtained by plotting two variables X and Y against each other. Let us consider the following data.

x	y
2	20.20
4	40.4
6	60.6
8	80.2
10	100.8
12	120.0

A graph may be drawn using these data (figure). By convention we plot the independent variable, i.e., the cause of the value based on which a particular prediction is made along the axis (horizontal axis) and the dependent variable. i.e., the effect on the predicted property, along the Y axis (vertical axis).



The graph gives the trend or relationship between X and Y. The above graph indicates a linear relationship between X and Y. In the above graph linearity is good. Usually for the data obtained in experiments, linearity will not be as good as shown in figure. In such cases we have to draw a best fit line. This is called curve fitting. For this purpose we use the method of least squares. By this method we get a straight line for which the algebraic sum of the vertical deviations is less then that from any other straight line. There will be only one such line i.e., it will be the best fit line. This best fit line cannot be drawn just by observing the points on the graph. For drawing the best fit line we have to use the method. of least squares.

Let us consider the following data :

X	Y
1	1.5
2	1.8
3	2.7
4	4.0

To draw the best fit line for the above data the following steps are followed.

i. ΣX, ΣY, ΣXY and ΣX^2 are calculated.

In our example,

$\Sigma X = 10$, $\Sigma Y = 10$, $\Sigma XY = 29.2$ and $\Sigma X^2 = 30$

ii. The above values are substituted in the following simultaneous equations.

$\Sigma Y = aN + b\Sigma X$

$\Sigma XY = a\Sigma X + b\Sigma X^2$

Here N = the number of pairs of data = 4

i.e., $10 = a \times 4 + b \times 10$ - (1)

and $29.2 = a \times 10 + b \times 30$ - (2)

multiplying (1) by 3 we have

$30 = 12a + 30b$ - (3)

substracting (2) from the (3) we have

$0.8 = 2a$

$\therefore a = 0.4$ - (4)

Substituting (4) in (1) we have $b = 0.84$

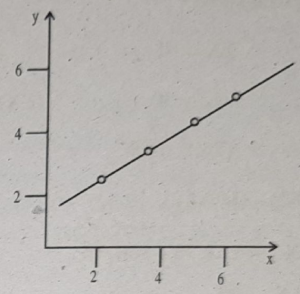
iii. Now for the given values of X, Y values are calculated using the equation

$Y_{cal} = a + bX$

The calculated Y values for two values of X from our data are calculated.

X	$Y_{cal} = (0.4 + 0.8)\,X$
1	1.2
4	3.6

iv. Two points corresponding to these two pairs of values are marked on the graph and they are joined. We get the best fit line for our data. The following will be the graph for the data given.



Correlation Coefficient :

It is a quantity that indicated the extend of linearity of a given set of data. It is denoted by r.

Mathematical expression.

$$r = \frac{N\Sigma XY - (\Sigma X)(\Sigma Y)}{\{[N\Sigma X^2 - (\Sigma X)^2]\,[N\Sigma Y^2 - (\Sigma Y)^2]\}^{1/2}}$$

Where X and Y are vaiables or two properties, N is the number of pairs of data.

Explanation :

It helps us find out whether there is any linear relationship between two properties X and Y from N pairs of data relating X and Y.

If **r** is 1.0 is means that there is perfect linearity relationship between X and Y.

If r is between 0.99 and 0.75 it means that there is excellent linearity relationship between X and Y.

If r is between 0.75 to 0.50. If means that their is good linearity realtionship between X and Y.

If it is less than 0.50 we can conclude that there is poor linearity relationship between X and Y.

In our example given above

$N = 4$ $\quad \Sigma X = 10$ $\quad \Sigma Y = 10$

$\Sigma XY = 29.2$ $\quad \Sigma X^2 = 30$ $\quad (\Sigma X)^2 = 100$

$\Sigma Y^2 = 28.78$ $\quad (\Sigma Y)^2 = 100$

$$r = \frac{(4 \times 29.2) - (10 \times 10)}{\{[4 \times 30 - 100]\,[4 \times 28.78 - 100]\}^{1/2}}$$

$$= \frac{116.8 - 100}{\{[120 - 100]\,[115.12 - 100]^{1/2}}$$

$$= \frac{16.8}{\{[20]\,[15.12]\}^{1/2}} = \frac{16.8}{304^{1/2}}$$

$$= \frac{16.8}{17.44} = 0.96$$

That is, as per our data, there is excellent linear relationship between X and Y.

Thus correlation co - efficient givens us and idea about the extent of linearity of a given set of data.

Chemical and single pan balance

Precautions in using an analytical balance

1. Center the load on the pan as well as possible.
2. Protect the balance from corrosion.
3. Consult the instructor if the balance appears to need adjustment.
4. Keep the balance and its case scrupulously clean. A camel – hair brush is useful for removing spilled materials or dust.

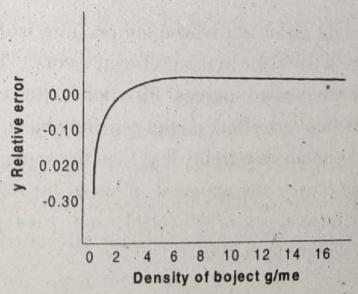
5. Always allow an object that has been heated to return to room temperature before weighing it.
6. Use tongs of finger pads to prevent the uptake of moisture a by dried object.

Buoyancy effect

A buoyancy error is the weight error that develops when the object being weighed has a significantly different density them the masses. The buoyancy error will affect data if the density of the object being weighted differs significantly from that of the standard masses. This error has its origin in the difference in buoyant force exerted by the medium (air) on the object and on the masses. Buoyancy corrections for electronic balance may be accomplished use the equation.

$$W = W_1 + W_2 \left(\frac{d_{air}}{d_{obj}} - \frac{d_{air}}{d_{wts}} \right)$$

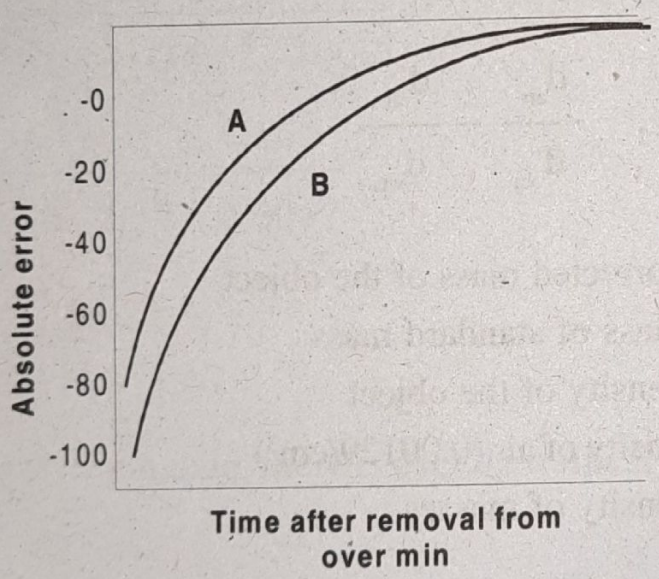
W_1 - Corrected mass of the object
W_2 - Mass of standard mass
d_{obj} - Density of the object
d_{air} - Density of air ($0.00129/cm^3$)
d_{wts} - Density of masses



The consequence of equation are shown in figure in which the relative error due to buoyancy is plotted against the density of object weighted in air against stainless steel masses. Note that this error is less than 0.1% for objects that have a density of $2g/cm^3$.

The density of masses used in single plan balance ranges from 7.8 to 8.4g /cm^3 depending on the manufacture. Use 8 g /cm^3 is adequate for most purpose is greater accuracy is required the specifications for the balance to be used should be consulted for the necessary density data.

Temperature effects



Affects to weight an object whose temperature is difference from that of its surroundings will result in a significant errors. Errors due to a difference in temperature have two sources. First convection currency within the balance case exert a buoyant effect on the pan and object. Second warm air trapped in a closed container weights less than the same volume at low temperature both effects cause the apparent mass of the object to be low. The error can amount to as much of 10 (or) 15 mg for typical porcelain filtering crucibles (or) weighting bottle.