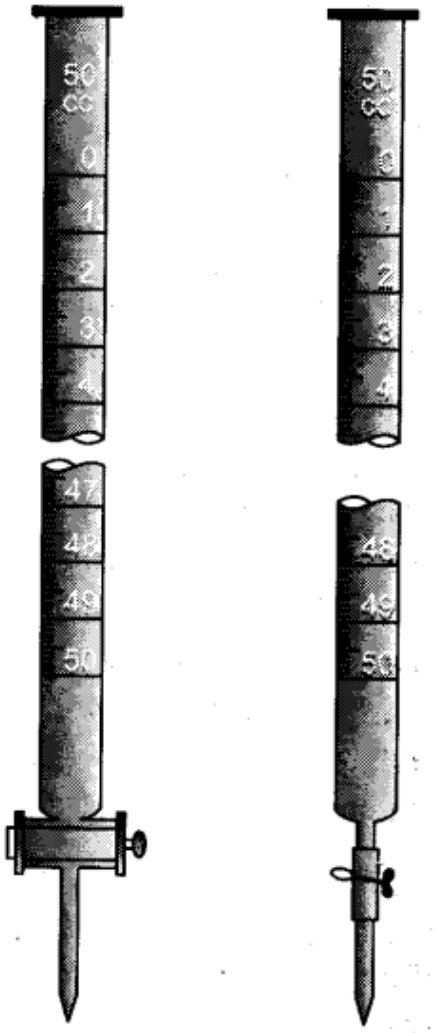
Volumetric Analysis

In volumetric analysis, the quantities of the constituents present in the given unknown solution are determined by measuring the volumes of the solutions taking part in the given chemical reaction. The main process of this analysis is called titration which means the determination of the volume of a reagent required to bring a definite reaction to completion.

Apparatus Used in Volumetric Analysis

In volumetric analysis, the apparatus required is as follows:
(i) Graduated-burette, pipette, measuring flasks and measuring cylinders.
(ii) General-titration flasks, beaker, tile, glass-rod, funnel, weighing bottle, wash bottle.
(iii) A chemical balance for weighing.
It is a long, cylindrical tube of uniform bore fused at the lower end with a stop cock (Fig). It is graduated in millilitres from 0 to 50. Each division is further sub-divided into ten equal parts. Therefore, each sub-division reads 0.1 ml.



Before a burette is filled with the solution, it is thoroughly washed, so that no greasy matter is sticking inside or outside the burette. No drops should adhere to the inner wall of a clean burette. Take a small volume of solution to be taken in it, close the upper mouth of the burette with the thumb and hold in horizontal position as shown in Fig. Rotate the burette so as to wet the inner walls of the burette. Reject this solution through the stop-cock. This process is known as rinsing. Then the burette is filled with the help of a funnel inserted in the top Fig. The funnel must then be taken out after filling the burette. The solution in the burette is called titrant. Care must be taken that no air bubbles remain in the narrow bottom tip of the burette. To remove this air, the stop-cock is opened and the liquid is allowed to run out rapidly into the beaker or flask.
Burette reading forms the most important aspect of the experiment, therefore, burette should be read very carefully, after removing parallax.

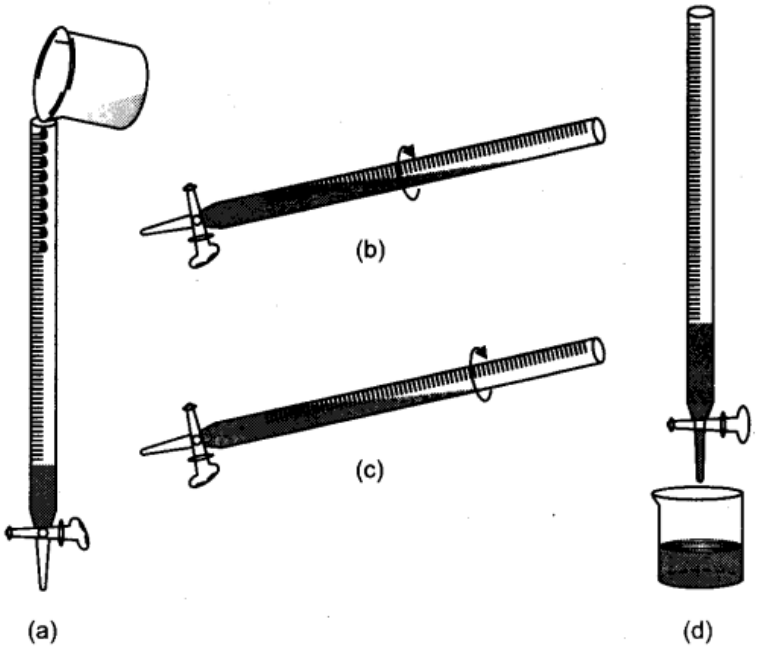


Fig. Rinsing the burette.

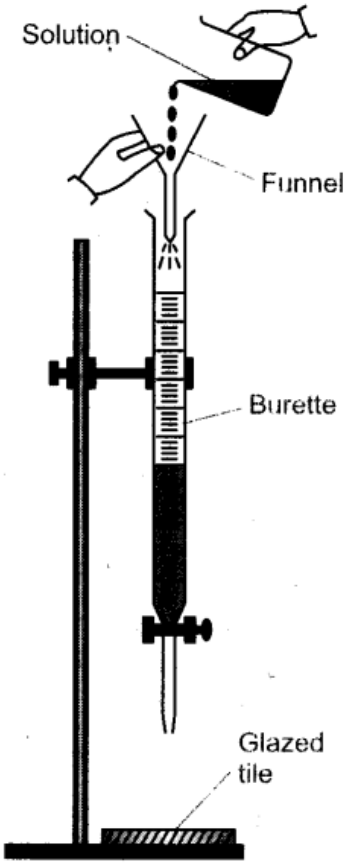


Fig. Filling the burette.

To read the burette, hold behind the level of the liquid and in contact with the burette, a piece of white paper to illuminate the surface of the liquid. This paper, called antiparallax card, eliminates errors in reading due to parallax. In order to prepare an anti-parallax card take a rectangular piece of paper and fold it half. Give two cuts as shown in Fig. Open the fold and mount it on the burette.

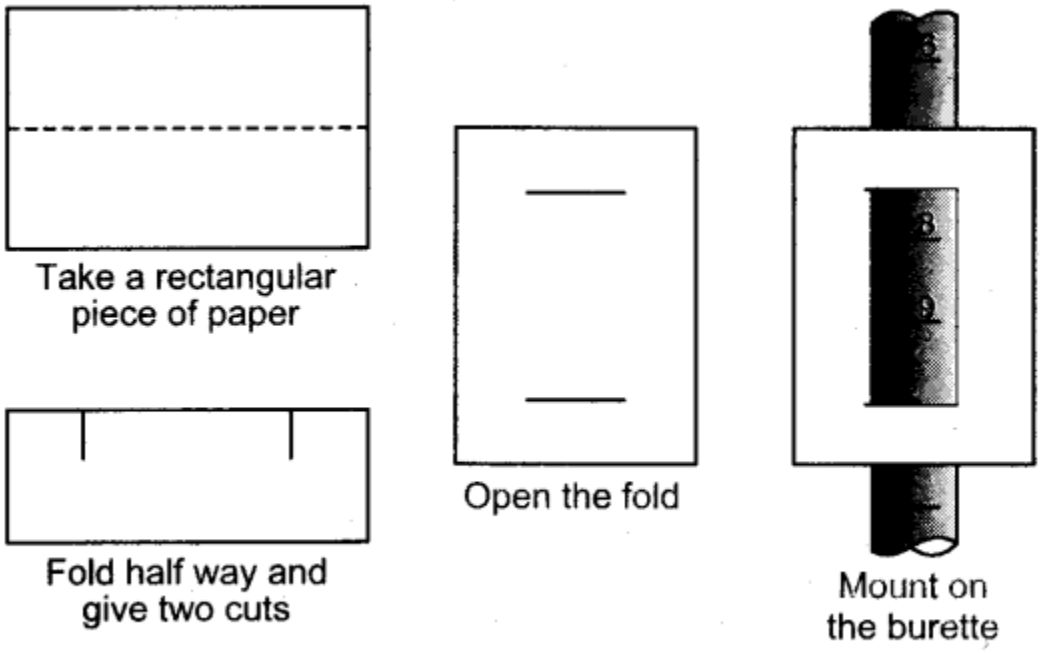


Fig. Making and mounting an antiparallax card.

It is to be remembered that in case of colourless solutions lower meniscus is read, while in case of coloured solutions, level is read from the upper meniscus. This is due to the reason that in case of coloured solutions lower meniscus is not visible clearly.
Take reading of the burette placing your eye exactly in front of meniscus (Fig.) of the solution.

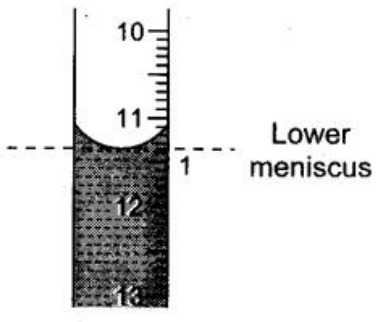


Fig. Lower meniscus.

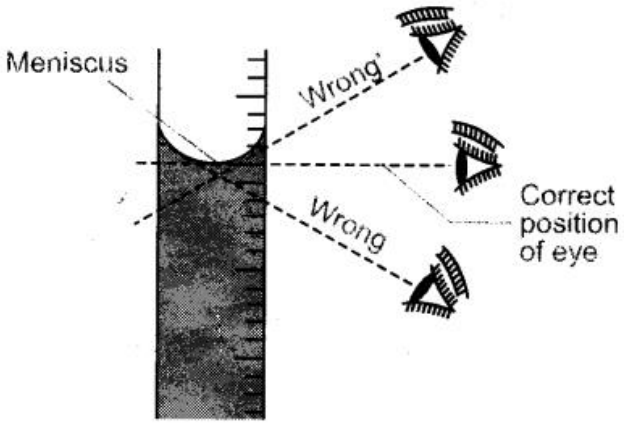


Fig. Correct way of reading burette.

Precautions

1. See that stop-cock does not leak.
2. Remove the funnel immediately after filling the burette.
3. Do not allow any air bubble to remain inside the burette.
4. Always use antiparallax card and place the eye exactly in the level of meniscus.
5. Let no drops of solution be hanging at the tip of the burette at the end point.

Pipette

This apparatus is used for accurate measurements of definite volume of solution. It consists of a long narrow tube with cylindrical bulb in the middle and a jet at its lower end.

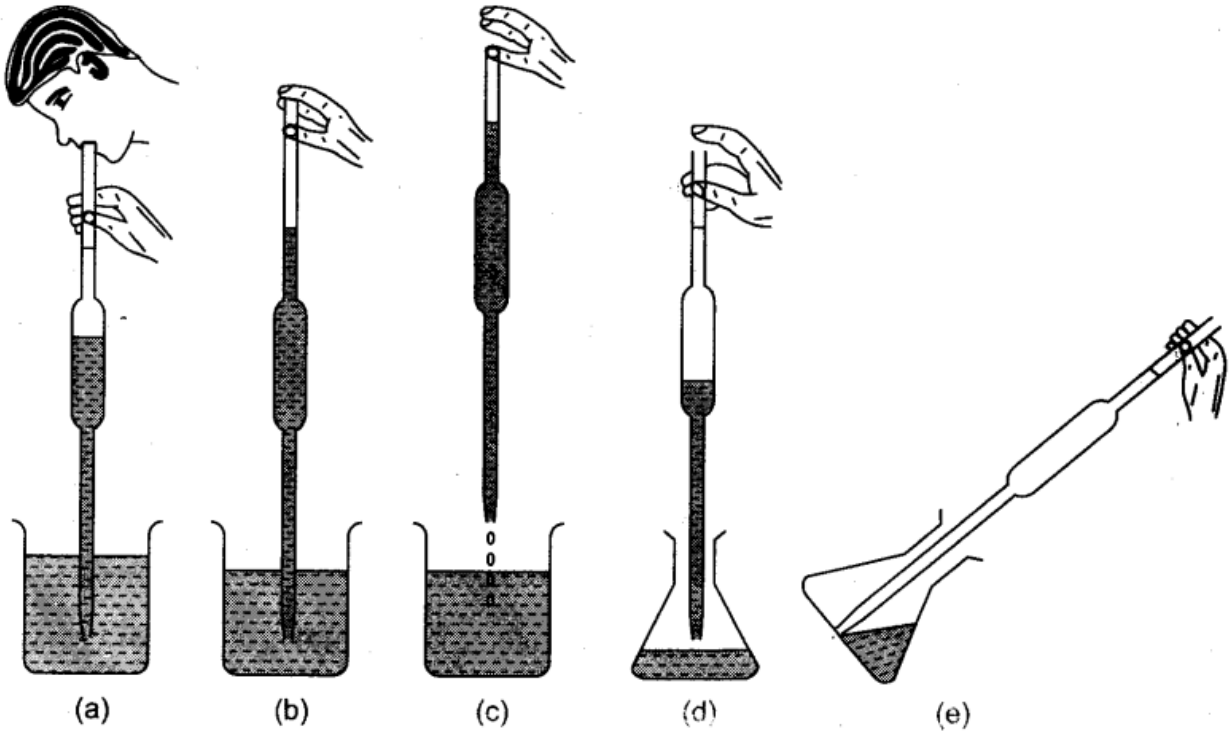


Fig. Use of pipette

On the upper part of the stem, there is an etched circular mark. On the bulb is marked the volume which the pipette can deliver when filled up to the circular mark [Fig]. Before a pipette is filled with the solution, it is washed and thoroughly rinsed with the solution to be measured with it. The upper part of pipette is then held by the thumb and middle finger of the right hand, the lower end is dipped into the liquid and the solution is sucked into the pipette until the liquid level is about 2 cm above the mark. The open end of pipette is then closed with index finger. The liquid is allowed to run slowly until the lower edge of meniscus just touches the mark. The solution is then allowed to run freely out of the pipette in the titration flask.

Precautions

1. Never close the pipette with the' thumb.
2. Keep the lower end always dipping in the liquid while sucking the liquid.
3. Never pipette out hot solutions or corrosive solutions.
4. Do not blow out the last drop of the solution from the jet end.

Chemical Balance

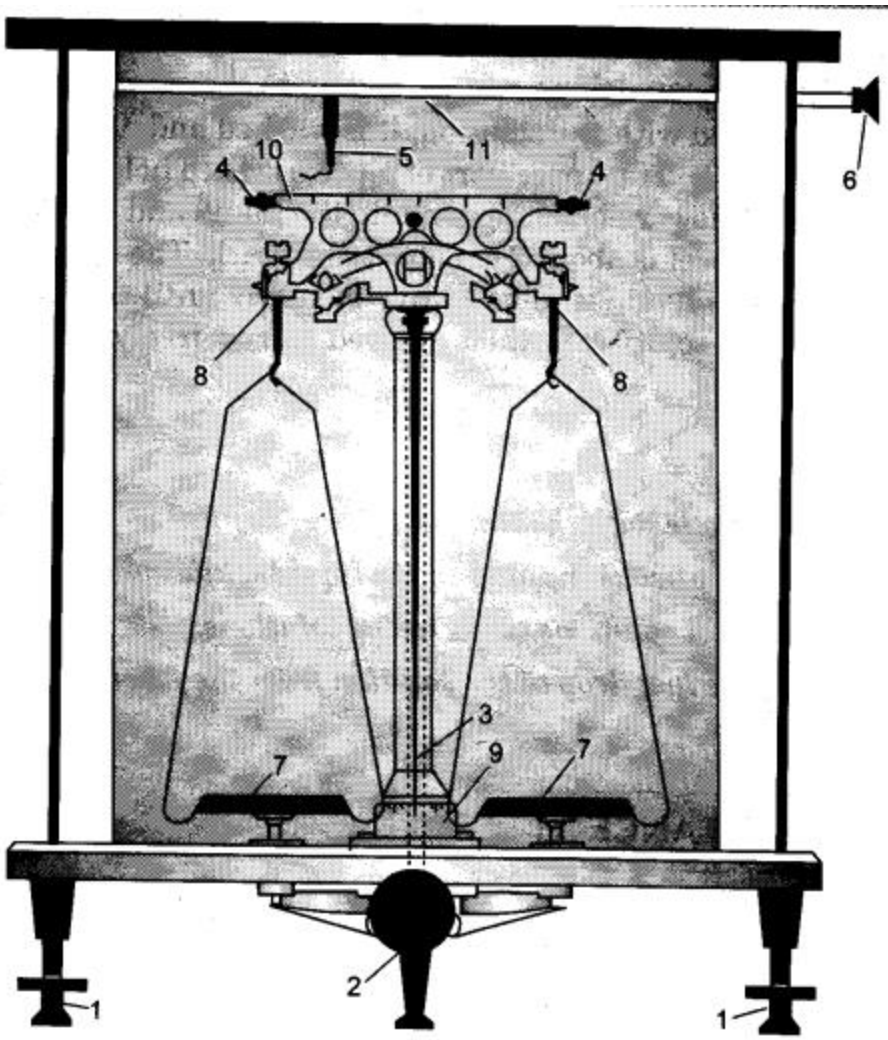
The balance is the principal instrument used in quantitative analysis. One of the most important requirements in quantitative analysis is a sufficiently high degree of precision. The analytical balance used in quantitative analysis can be used for weighing objects not heavier than 100-200 g to a precision of 0.0002 g, i.e., 0.2 mg. The most usual design of a balance of this type is shown in Fig.
The most important part, the beam, has three knife edges made of agate or very hard steel [Fig]. The central knife edge rests on a special very smooth agate plate on the top of the balance column. The balance pans are suspended from the terminal knife edges by means of stirrups [Fig].

A pointer is fixed to the centre of the beam; as the balance swings the lower end of the pointer moves the scale, at the bottom of the column. All the three knife edges must be strictly parallel and in the same plane for correct operation of the balance. The knife edges and plates gradually wear out and the balance becomes less precise. To reduce wear and tear as much as possible the balance is provided with an arrest device whereby the balance beam can be raised and the balance "arrested". The balance must be arrested when not in use.

The balance is enclosed in a glass case which protects it from dust, air movements, the operator's breath, etc.

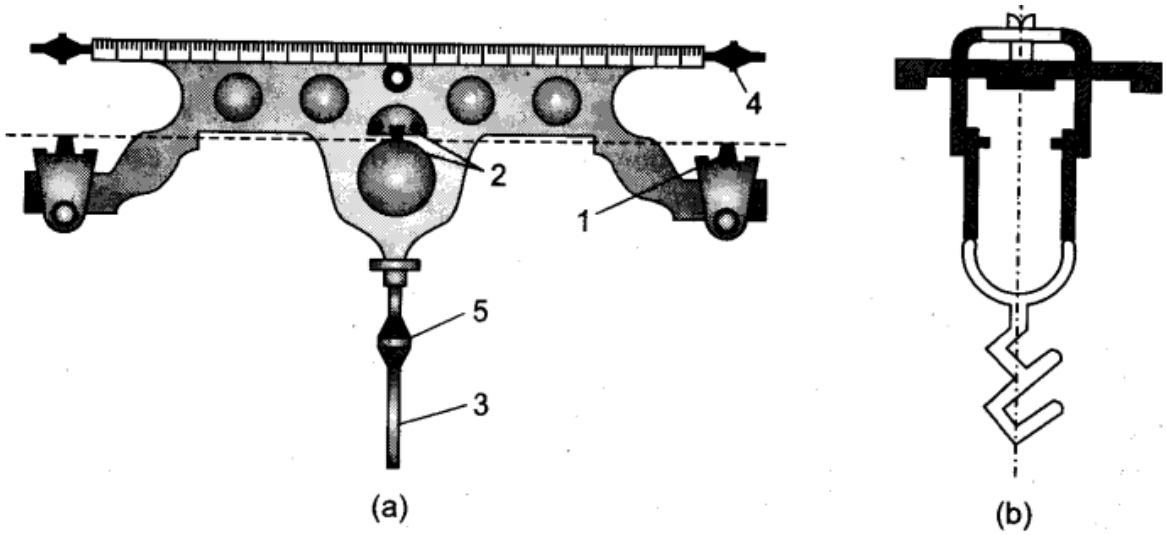
The base of the balance rests on screws 1 (Fig), whereby the knife edges and agate plates on which they rest are brought into horizontal position by means of a plumb bob attached to the balance column (at the back).

The balance pans are made of some light metal which is nickel-plated or coated with gold or platinum to prevent oxidation. Obviously substances should never be put directly on the balance pans because this spoils the balance. Therefore, substances are weighed either in special weighing bottles with ground-glass lids [Fig] or on watch glasses [Fig] or in crucibles, test tubes, etc.



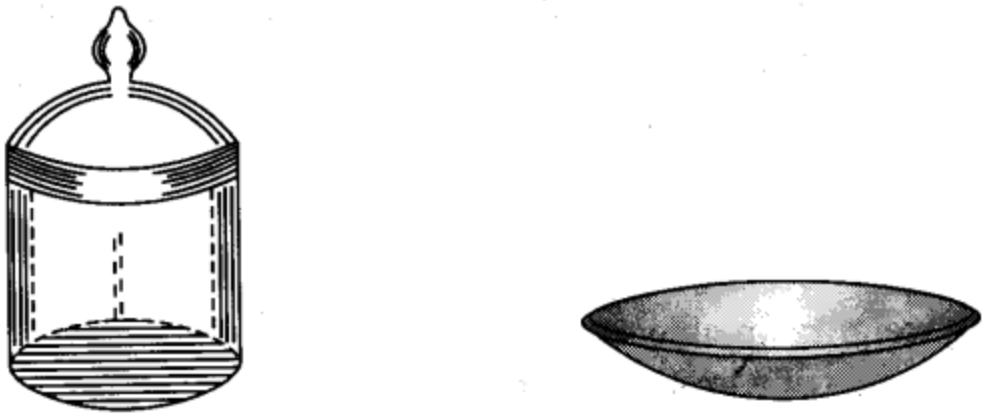
1. Adjusting screws; 2. Arrest knob; 3. Pointer;
4. Screws for zero point adjustment; 5. Rider hook;
6. Knob of rider carrier; 7. Balance pans; 8. Stirrups;
9. Scale; 10. Graduated beam; 11. Rider carrier.

Fig. Analytical balance.



1. Terminal knife edge; 2. Central knife edge; 3. Pointer;
4. Screw for zero point adjustment; 5. Weight for sensitivity adjustment.

Fig. Parts of analytical balance.



(*a*) Weighing bottle. (*b*) Watch glass.

Fig.

For the results of weighing to be accurate the weighed object must be of the same temperature as the balance. If a hotter (or colder) object is placed on a balance pan, this has the effect of lengthening (or shortening) the corresponding arm of the beam resulting in incorrect readings. The weights used with analytical balance are contained in a special box as shown in Fig.

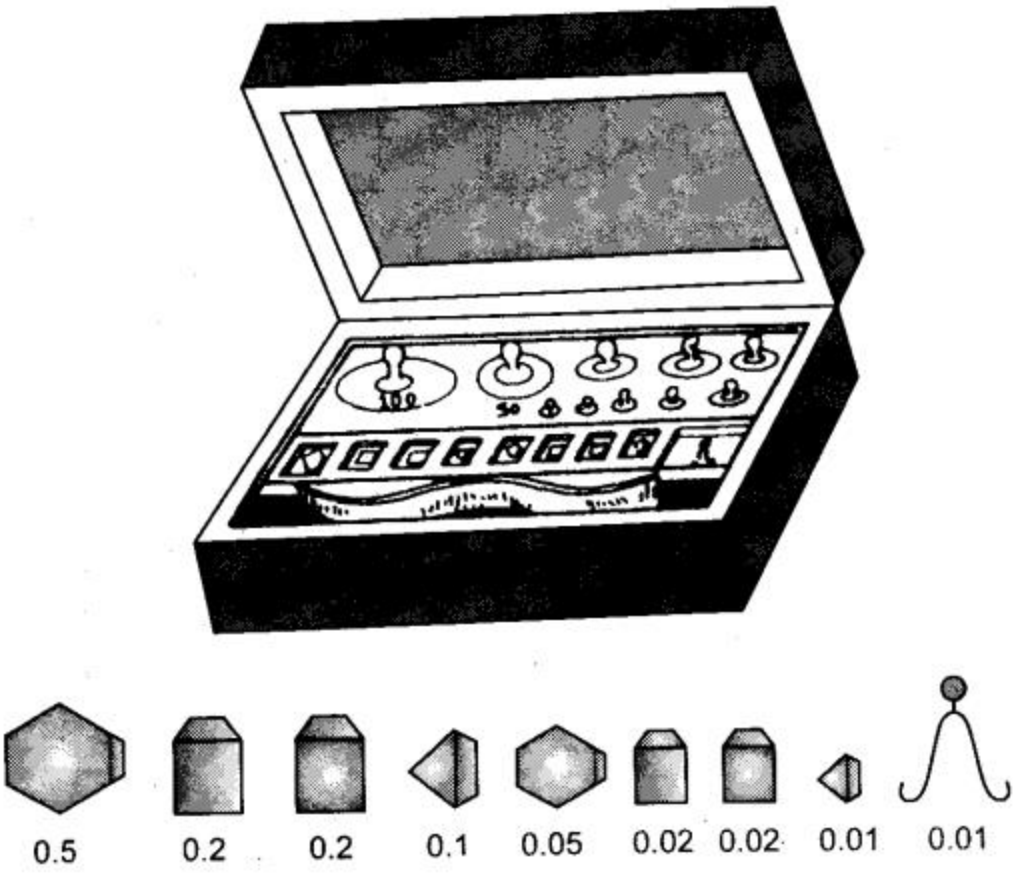


Fig. Weight box and fractional weights.

Box also contains a pair of forceps for lifting the weights and putting them on and off the balance pans. The forceps should be ivory-tipped. The weights must never be touched by hand.

The weights are coated with gold or platinum to prevent corrosion and consequent changes of weight. The small weights (fractions of a gram) are made of some metal which is not corroded in air, e.g., aluminium or platinum.

The weights are arranged in the box in definite order. There are two usual systems corresponding to the numbers 5 :2 : 2 :1 or 5:2:1:1. In accordance with the first system, the box would contain weights of 50, 20, 20, 10, 5, 2, 2, 1 g and in accordance with the second, weights of 50, 20,' 10,10,10, 5, 2,1,1,1 g. Fractions of a gram follow the same systems and are •made of different shapes so that small weights are easier to distinguish. For example, fractional weights of 0.5 and 0.05 g are made in shape of regular hexagon, weights 0.2 and 0.02 g are squares and weights 0.1 and 0.01 g are triangles. Each fractional weight has an edge bent at right angle by which it is lifted with the forceps.

By means of the weights an object can be weighed to an accuracy of 0.01 g. Thousandth and ten-thousandth fractions of a gram are weighed by means of the so called rider. The rider, as shown in Fig. 11.12, is a thin bent wire (usually of aluminium) weighing 0.01 g or 0.005 g, it is attached with the aid of the forceps by its loop on hooks. This hook is fixed to the horizontal rod 11 with the knob 6 outside the balance case. This rod is rotated or moved to place the rider at any desired point on the beam. The beam has a scale, the graduations of which differ in different balances. If the rider is moved from the zero division to the fifth (i.e., exactly over the central knife edge), this is equivalent to removal of 0.005 g from the left-hand pan or a similar increase of the load on the right-hand pan.

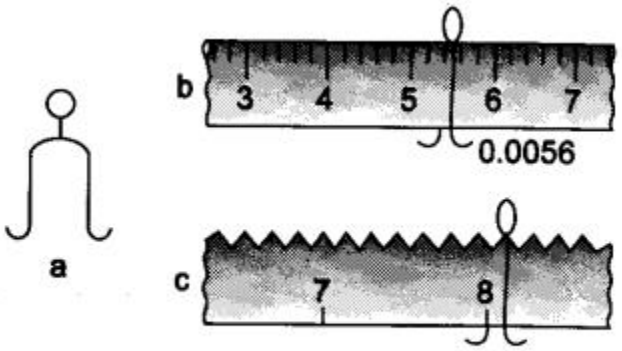


Fig. **Rider and readings along the balance beam.**

Setting the Balance

Before the substance can be weighed in a balance it has to be first set in proper order. The following steps are followed for setting the balance:

1. Clean the pans of the balance with a hair-brush or a clean handkerchief.
2. Level the balance by adjusting the levelling screws. See that the pointer rests at zero. Close the front door of the balance.

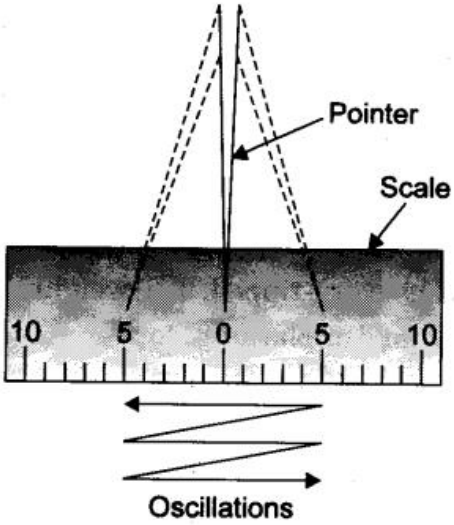


Fig.

3. Now rotate the key arrest knob to raise the beam and see that the pointer swings or oscillates equal divisions on both sides of the zero mark as shown in Fig. If it does not oscillate equally on both the sides arrest the beam and move the adjusting screws (4) till on rotating the arrest knob, the pointer oscillates equally on both sides of the zero mark. Again arrest the beam.

Weighing the Substance

1. Take a clean and dry watch glass or weighing bottle and place it carefully on the left hand pan of the balance.
2. Pick out an appropriate gram weight from the weight box with the help of forceps and place it on the right hand pan. If the gram weight is heavier as compared to the weight of the watch glass, remove it and try lower weight. The gram weight should be slightly less than the weight of the watch glass (less than 1 gram).
3. After placing the correct gram weight start placing fractional weights.
4. Use rider for weights lighter than 10 mg.
5. Record the correct weight of empty watch glass.
6. Now add weights (gram weights and fractional weights), equal to the amount of the substance to be taken, in the right hand pan.
7. Now add required quantity of the substance to be weighed on the watch glass.
8. Take out the watch glass along with the substance.
9. Clean the balance and close it.

Precautions While Handling the Analytical Balance

In weighing it must be remembered that the analytical balance is a precise physical instrument which must be handled with great care.
To avoid damage to the balance and to ensure accurate weighing the following rules must be strictly observed:

1. Check the state of the balance before each weighing. Remove dust from the pans with a soft brush and find the zero point of the balance.
2. The unarrested balance must not be touched. The balance must be arrested before the object and weights are put on the pans or taken off them. The balance must be arrested before the rider is moved along the beam. The knob must be turned slowly and carefully.
3. Do not move the balance from its place.
4. Never overload the balance above the permitted load (usually 100 g) as this causes damage.
5. Do not place wet or dirty objects on the balance. Do not spill anything inside the balance case.
6. Do not put the object to be weighed directly on the balance pan. Do not use pieces of paper; put the substance on a watch glass, or in a weighing bottle, crucible, test tube, etc.
7. Hygroscopic substances and liquids (especially if they give off corrossive vapours) must be weighed in closed weighing bottles.

8. Do not weigh hot (or very cold) objects. The object to be weighed must reach the temperature of the balance. It must, therefore, be left for at least 20 minutes in a dessicator near the balance.
9. Always use only the side doors of the balance case when weighing. The front door, must be kept shut all the time.
10. Do not touch the balance, weights or rider with the fingers. The weights must be handled by special forceps.
11. Do not muddle the weights. Each weight must be put in its proper place in the box.
12. Remain in the balance room only while weighing.

Some Important Terms

1. Standard Solution

A solution whose concentration is known, is called a standard solution. Concentration of a solution is generally expressed in terms of normality or molarity.

2. Normality

Normality of a solution is defined as the number of gram-equivalents of solute per litre of solution. It is denoted by N. Mathematically, it may be expressed as:

$$\text{Normality} = \frac{\text{Number of gram-equivalents of solute}}{\text{Volume of solution (in litres)}}$$

or

$$= \frac{\text{Mass of solute (in grams) per litre of solution}}{\text{Gram-equivalent mass of the solute}}$$

Number of gram equivalents of solute = Normality x Volume of solution (in litres).
A solution containing one gram-equivalent of solute per litre of solution is called normal solution.

3. Molarity

Molarity of a solution may be defined as the number of gram moles of solute per litre of the solution. It is denoted by M. mathematically, it may be expressed as:

$$\text{Molarity} = \frac{\text{Gram moles of solute}}{\text{Volume of solution (in litres)}}$$

or

$$= \frac{\text{Mass of solute (in grams) per litre of solution}}{\text{Gram molecular mass of the solute}}$$

$\therefore$ Gram moles of solute = Molarity × Volume of solution (in litres)

A solution containing one gram mole of solute per litre of solution is called **molar solution.**

4. End Point
It is the point where the reaction between the two solutions is just complete.

5. Indicator
A substance which indicates the attainment of end point. Indicator undergoes a change in colour at the end point.

Equivalent Masses of Oxidizing and Reducing Agents

According to electronic concept, oxidation is the process which results in the loss of one or more electrons by atoms or ions and reduction is the process which results in the gain of one or more electrons by atoms or ions. The oxidising agent is the substance which gains one or more electrons and gets reduced. The reducing agent is the substance which loses one or more electrons and gets oxidised.

The equivalent mass of an oxidising agent is equal to its molecular mass (or formula mass) divided by the number of the electrons gained by one molecule or ion of the substance in the reaction.

$\therefore$ Eq. mass of an oxidising agent $= \dfrac{\text{Molecular mass or formula mass}}{\text{No. of electrons gained by one molecule}}$

Eq. mass of a reducing agent $= \dfrac{\text{Molecular mass or formula mass}}{\text{No. of electrons lost by one molecule}}$

Equivalent Mass of Potassium Permanganate

In the acidic medium, permanganate (active ion) is reduced as follows:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O.$$

Here, the number of electrons gained by one permanganate is 5.

$\therefore$ Eq. mass of $KMnO_4$ in acidic medium $= \dfrac{\text{Molecular mass}}{5} = \dfrac{158}{5} = 31.6.$

Equivalent mass of Ferrous Ammonium Sulphate $FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr's salt).

$$FeSO_4(NH_4)_2SO_4.6H_2O \equiv FeSO_4 + (NH_4)_2SO_4 + 6H_2O$$

$$FeSO_4 \rightleftharpoons Fe^{2+} + SO_4^{2-}$$

Fe^{2+} is oxidised to Fe^{3+} by losing one electron

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

Number of electrons lost per molecule of Mohr's salt is 1.

$\therefore$ Eq. mass of Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O = \dfrac{\text{Molecular mass}}{1} = \dfrac{392}{1} = 392.$

Equivalent mass of Oxalic Acid

During reaction with acidified $KMnO_4$, oxalic acid is oxidised to CO_2.

Here the reaction takes place as:

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow 2CO_2 + 2H^+ + 2e^-$$

The number of electrons lost per molecule of oxalic acid = 2.

$$\therefore \text{ Eq. mass of crystalline oxalic acid, } \begin{matrix}\text{COOH}\\ |\\ \text{COOH}\end{matrix}\cdot 2H_2O = \frac{\text{Molecular mass of crystalline oxalic acid}}{2} = \frac{126}{2} = 63$$

The equivalent masses of some common substances which we come across during redox titrations at this level are given in Table

Table Molecular Masses and Equivalent Masses of Some Substances

Substance	*Molecular mass*	*Ionic equation*	*n*	*Eq. mass = Mol. mass / n*
Pot. permanganate ($KMnO_4$)	158	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	5	31.6
Mohr's salt [$FeSO_4(NH_4)_2SO_4.6H_2O$]	392	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	1	392
Ferrous Sulphate (anhydrous) ($FeSO_4$)	152	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	1	152
Ferrous Sulphate (crystals) ($FeSO_4.7H_2O$)	278	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	1	278
Oxalic acid (anhydrous) ($H_2C_2O_4$)	90	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	2	45
Oxalic acid (crystals) ($H_2C_2O_4.2H_2O$)	126	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	2	63

Preparing a Standard Solution

A standard solution is prepared by dissolving a definite weight of substance (a primary standard), in a definite volume. A substance is classified as a primary standard if it has following characteristics:

1. It is easily available in state of high purity.
2. It is neither hygroscopic nor deliquescent.
3. It shows high solubility in water.
4. It does not dissociate or decompose during storage.
5. It should react instantaneously with another substance in stoichiometric proportion.

Substances whose standard solutions cannot be prepared directly are called secondary standard substances. These include those substances which are not available in the pure form, for example, potassium permanganate or those which are hygroscopic like NaOH, KOH, etc. The solutions of secondary standards are standardized by titrating against solution of some primary standard. For preparing a standard solution, student must remember that he is working on precise experiments, where the slightest inaccuracy may distort the analytical results which may have taken a great deal of work and time to obtain. It is, therefore, specially important to follow strictly the usual rules concerning orderly and clean work. The apparatus required for a given determination must be procured beforehand and washed thoroughly and the weighing must be done accurately.