# Quantitative Estimation (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. During volumetric analysis we have to prepare solutions of known concentrations. In this chapter we shall study how to prepare solutions of substances with known concentrations. We shall also learn about the process of titration.

## 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 macroanalysis 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. 8.1.

The most important part, the beam, has three knife edges made of agate or very hard steel [Fig. 8.2. (a)]. 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. 8.2 (6)].

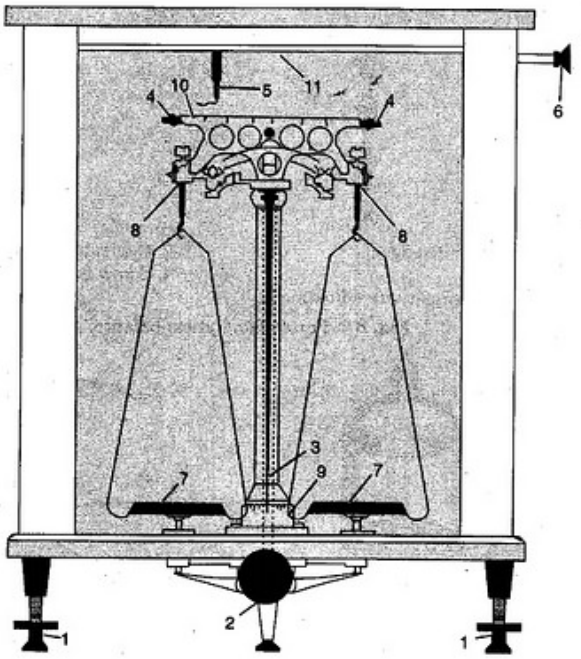
A pointer is fixed to the centre of the beam ; as the balance swings the lower end of the pointer moves along the scale, at the bottom of the column. All the three knife edges must be strictly parallel and in the same plane for correct operation of the balance. The knife edges and plates

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. 8.1), 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 7 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. 8.3 (a)] or on watch glasses [Fig. 8.3 (6)] or in crucibles, test tubes etc.

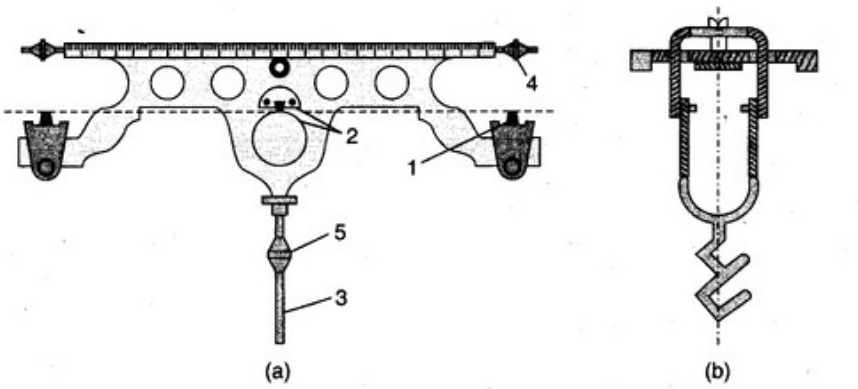



1. Adjusting screws ;
2. Arrest knob ;
3. Pointer ;
4. Screws for zero point adjustment ;
5. Rider hook ;
6. Knob of rider carrier ;
7. Balance pans ;
8. Stirrups ;
9. Scale ;
10. Graduated beam ;
11. Rider carrier.

**Fig. 8.1.** Analytical balance.

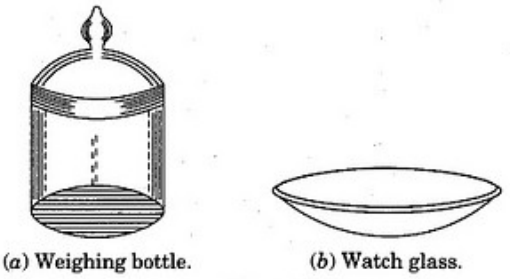
For the results of weighing to be accurate the weighed object must be of the same temperature as the balance. If a hotter (or colder) object is placed on a balance pan, this has the effect of lengthening (or shortening) the corresponding arm of the beam resulting in incorrect readings.

The weights used with analytical balance are contained in a special box as shown in Fig. 8.4. 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.




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

**Fig. 8.2.** Parts of analytical balance.



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

**Fig. 8.3.**

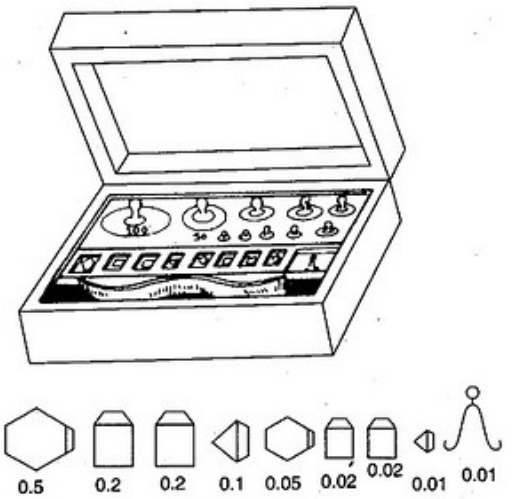



**Fig. 8.4.** Weight box and fractional weights.

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, frac-tional 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. 8.5, 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 10 the graduations of which differ in different balances. If the rider is moved from the zero division to the fifth (i.eexactly 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.

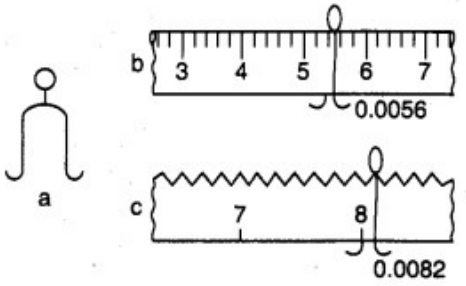



**Fig. 8.5. Rider and readings along the balance beam.**

## 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.
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. 8.6. 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.

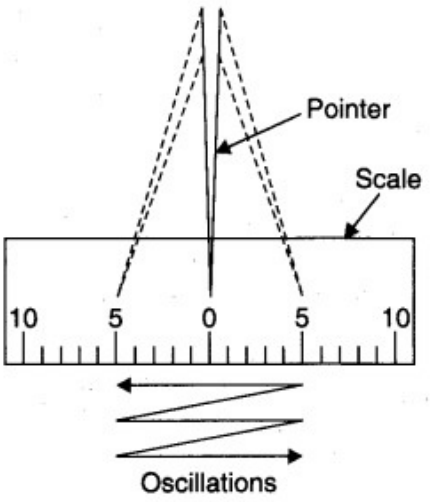



**Fig. 8.6.**

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 for Handling the Analytical Balance

In weighing it must be remembered that the analytical balance is a precise physical instru¬ment 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.

## Some Important Terms

### 1. Standard Solution

A solution whose concentration is known is called a **standard solution**.
Concentration of a solution is generally expressed as 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.

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

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

$$\therefore \quad \text{Number of gram equivalents of solute} = \text{Normality} \times \text{Volume of solution (L)}.$$

**solution**.

Equivalent mass of a substance can be obtained from its molecular mass.

**Equivalent mass of an acid** is defined as the mass of the acid which can furnish one mole of hydrogen ions.

$$\text{Equivalent mass of an acid} = \frac{\text{Molecular mass of acid}}{\text{Number of available hydrogen ions per molecule}} = \frac{\text{Molecular mass of acid}}{\text{Basicity of acid}}$$

Similarly, equivalent mass of a base is defined as the mass of the base which can furnish one mole of hydroxyl ions. It may also be defined as the mass of the base which is completely neutralized by one equivalent of the acid.

$$\text{Equivalent mass of a base} = \frac{\text{Molecular mass of base}}{\text{Number of hydroxyl ions per molecule}} = \frac{\text{Molecular mass of base}}{\text{Acidity of base}}$$

In case of salts,

$$\text{Equivalent mass of a salt} = \frac{\text{Molecular or formula mass of salt}}{\text{Total valency of metal ion in the formula unit}}$$

Equivalent masses of some compounds (acids, bases and salts) are given in Table 8.1.

**Table 8.1. Equivalent Masses of Some Compounds**

| Name of Compound | Formula | Molecular Mass | Equivalent Mass |
|---|---|---|---|
| 1. Hydrochloric acid | HC1 | 36.5 | 36.5 |
| 2. Sulphuric acid | $H_2SO_4$ | 98 | 49 |
| 3. Acetic acid | $CH_3COOH$ | 60 | 60 |
| 4. Oxalic acid | COOH<br>\| . $2H_20$<br>COOH | 126 | 63 |
| 5. Sodium hydroxide | NaOH | 40 | 40 |
| 6. Sodium carbonate | $Na_2CO_3$ | 106 | 53 |
| 7. Sodium bicarbonate | $NaHCO_3$ | 84 | 84 |

### 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 :

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

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

Gram moles of solute = Molarity x Volume of solution (L)

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

## Preparing a Standard Solution

A standard solution is prepared by dissolving a definite weight of substance (a primary standard), in solvent to prepare a definite volume of solution. 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 with another substance instantaneously and in stoichiometric proportion.

Oxalic acid, mohr's salt, potassium dichromate and sodium thiosulphate are some exam¬ples of primary standards.

Substances whose standard solutions cannot be prepared directly are called **secondary standards**. For example, potassium permanganate, sodium hydroxide and potassium hydroxide. A secondary standard cannot be used for preparing a standard solution by direct weighing.

## Apparatus Used In Volumetric Analysis

In volumetric analysis, the volumes of the various solutions should be measured accurately. 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.

### Burette

It is a long, cylindrical tube of uniform bore fused at the lower end with a stop cock (Fig. 8.8). 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 remains sticking inside or outside the burette. Take a small volume of solution (to be taken in it as titrant), close the upper mouth of the burette with the thumb and hold in horizontal position as shown in Fig. 8.10. 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

through a funnel inserted in the top Fig. 8.9. The funnel must then be taken out after filling the burette.

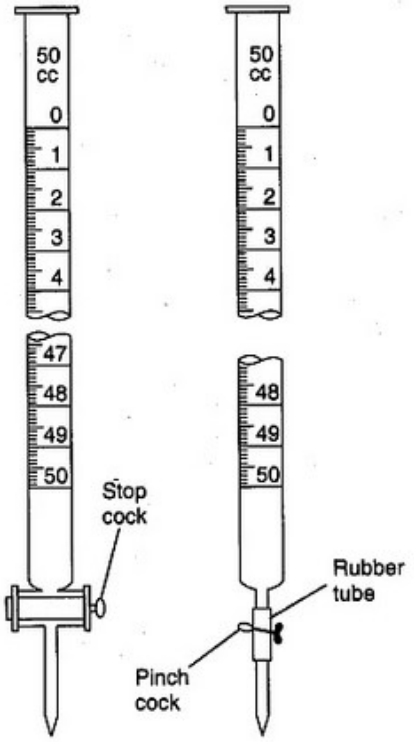



Fig. 8.8. Burettes.

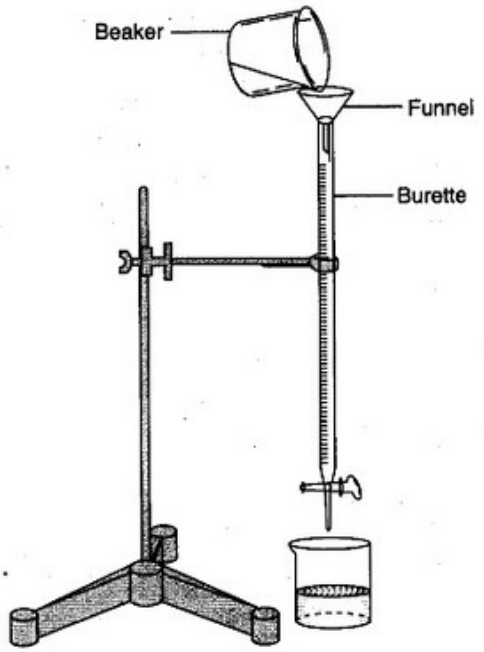



Fig. 8.9. Filling the burette.

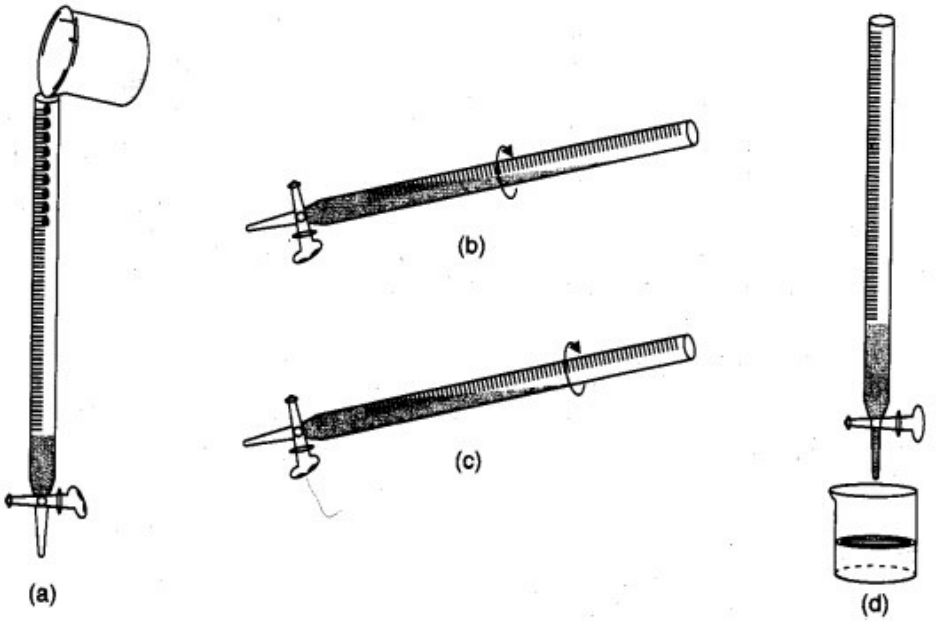



Fig. 8.10. Rinsing the burette.

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.

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. 8.11. Open the fold and mount it on the burette.

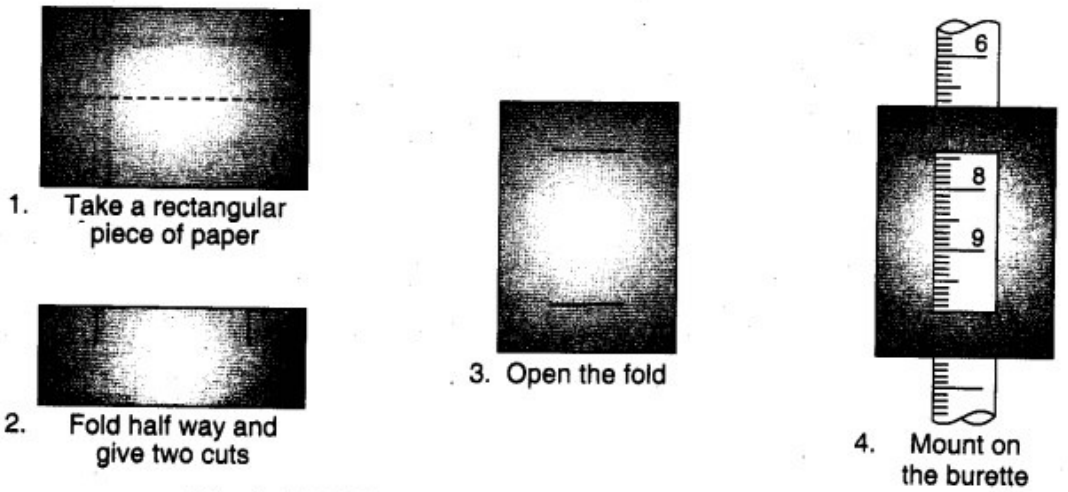



**Fig. 8.11.** Making and mounting an antiparallax card.

**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 clearly visible.

Placing your eye exactly in front of meniscus (Fig. 8.13) of the solution take initial reading and then final reading at the end. Find out the difference between two readings to obtain the volume of solution consumed.

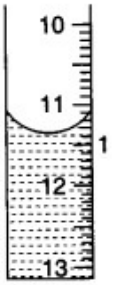



**Fig. 8.12.** Lower meniscus.

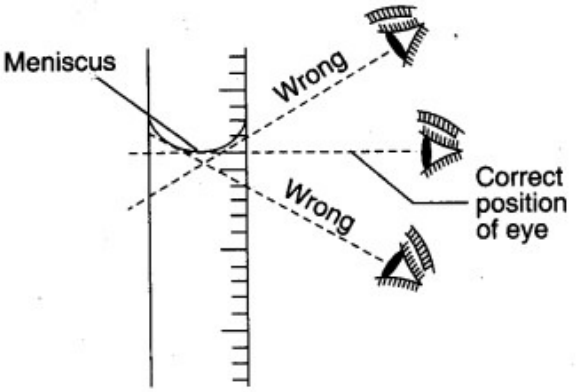



**Fig. 8.13.** Correct way of reading burette.

## 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 is a small and handy apparatus 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.

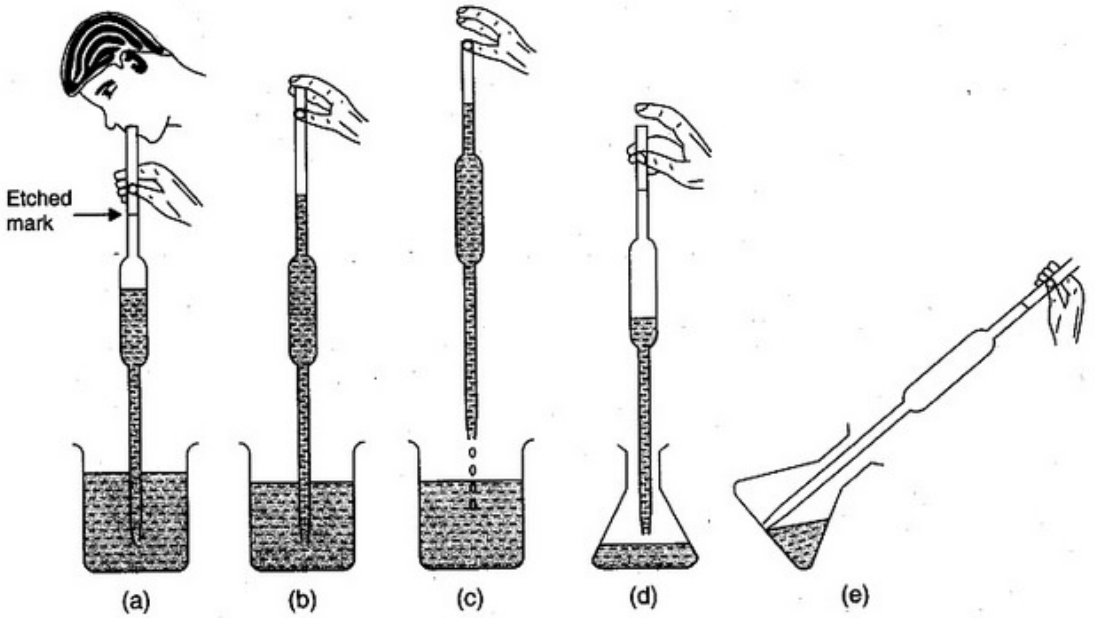



**Fig. 8.14.** Use of pipette.

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. 8.14 (a)]. Before a pipette is filled with the solution, it is washed thoroughly and rinsed. 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 [Fig. 8.14 (d)L When no more of the liquid flows out, touch the tip of the pipette with the bottom of the flask [Fig. 8.14 (e)]. Some liquid will still remain in the pipette. Do not remove it by blowing because the pipette is calibrated taking this liquid into account.

### 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 or corrosive solutions.
4. Do not blow out the last drop of the solution from the jet end.

## Process Of Titration

The process of titration is carried out to find the volume of one solution required to react completely with a certain known volume of solution of some other substance. This is the most important step in volumetric analysis. The process of titration is carried out as under :

1. Place a glazed white tile below the burette and place the titration flask on the glazed tile below the burette nozzle. Adjust the height of the burette so that the nozzle tip just enters the mouth of the titration flask.
2. Note initial reading of the burette after filling it with the solution and run out the solution from the burette (one ml at a time) by opening the stop cock with the left hand. The titration flask is kept in the right hand as shown in Fig. 8.15.
3. Give rotatory motion to the titration flask throughout the titration.

4. Continue running more of the solution from the burette into the titration flask, keeping it all the time shaking. The solution should fall directly into the solution of titration flask. It should not fall on the walls of flask.
5. Stop addition of the solution when the end point is reached and take final reading of the burette. The difference between the final and initial readings gives rough volume of the solution used for completion of the reaction.
6. The solution from the titration flask is thrown away and the titration flask is washed thoroughly first by keeping it under tap water and then with a little of distilled water. Do not rinse the titration flask.
7. Pour more solution in the burette.
8. Pipette out 20 ml of the solution into the titration flask and add 1-2 drops of the indicator solution.

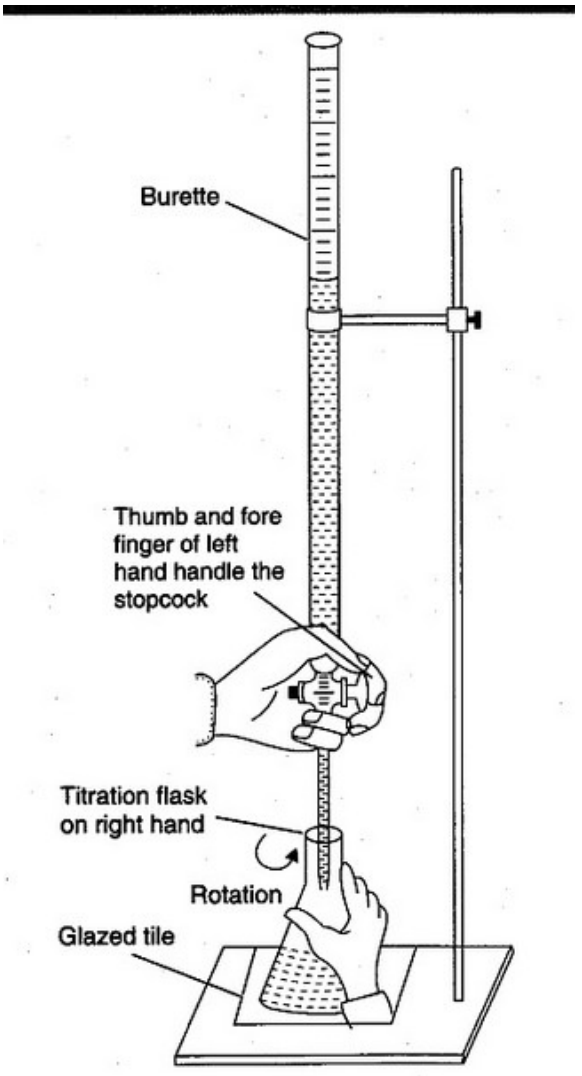



**Fig. 8.15.** Correct way of handling a burette.

9. Take initial reading of the burette. Run solution from the burette into the titration flask slowly with constant shaking. Continue adding the solution till the volume added is 1 ml less than the rough volume found out in the first titration. Now add solution from the burette dropwise.
10. Continue adding solution dropwise from the burette, till by addition of last single drop, the end point is attained.
11. Note down the final reading of the burette. The difference between the final and initial readings of the burette gives the exact volume of the solution required for completion of the

reaction.

12. Check the correctness of the end point by adding one drop of solution (taken in the titration flask) with the help of a pipette. Restoration of original colour confirms the correctness of the end point.

13. Perform 5 to 6 titrations so that at least three concordant readings (difference not more than 0.05 ml) are obtained.

**Recording of Volumetric Analysis in the Practical Note-Book**

| *Left hand Page (with pencil)* | *Right hand Page (with ball pen)* |
|---|---|
| Date | Date |
| Experiment | Experiment |
| Chemical equation | Requirement |
| Indicator | Theory |
| End point | Procedure |
| Observations | |
| Calculations | General calculations |

# Law Of Equivalents

According to this law, the number of equivalents of the substance to be titrated (titre) is equal to the number of equivalents of the titrant used.

Derivation of the normality equation. Consider an acid-alkali neutralization reactions. Let $V_1$ $cm^3$ of an acid solution of $N_1$ normality require $V_2$ $cm^3$ of base of $N_2$ normality. We know that 1000 $cm^3$ of 1 N acid solution contains acid = 1 gram equivalent.

$V_1$ $cm^3$ of 1 N acid contains acid = $\frac{1}{1000}$ x $V_1$ gm equivalents.

Thus, number of gram equivalents of acid in $V_1$ $cm^3$ of $N_1$ acid solution = $\frac{V_1N_1}{1000}$

Similarly, number of gram equivalents of base in $V_2$ $cm^3$ of its $N_2$ solution = $\frac{V_2N_2}{1000}$

By the law of equivalents, at the end point,

$$\frac{V_1N_1}{1000} = \frac{V_2N_2}{1000}$$

$$N_1V_1 = N_2V_2$$

It is known as normality equation. If three factors ($V_1$,$V_2$, $N_1$) are known, N2 can be calculated by using above formula.

In terms of molarities we can proceed as

$$\frac{[Molarity(M1) \times Volume(V1)]of\ Acid}{[Molarity(M2) \times Volume(V2)]of Base} = \frac{Stoichiometric\ coefficient\ of\ the\ acid\ in\ the\ balanced\ equation}{Stoichiometric\ coefficient\ of\ the\ base\ in\ the\ balanced\ equation}$$

For a reaction between HCl and $Na_2C0_3$

$$\underset{1\ \text{mole}}{Na_2CO_3} + \underset{2\ \text{moles}}{2HCl} \longrightarrow 2NaCl + CO_2 + H_2O$$

Thus,

$$\frac{(Molarity \times Volume)\ \ of\ \ HCl}{(Molarity \times Volume)\ \ of\ \ Na_2CO_3} = \frac{2}{1}$$

## Acid-Base Titrations

In acid-base titrations the amount of the substance is determined by titrating it against a standard solution of acid or base (depending upon the titrant). The chemical reaction involved in acid base titration is called neutralisation reaction. Neutralisation involves

$$\underset{\text{(Acid)}}{H_3O^+(aq)} + \underset{\text{(Base)}}{OH^-(aq)} \longrightarrow \underset{\text{(Water)}}{2H_2O(l)}$$

To know the end point or the neutralisation point, an indicator is used.
An **indicator** is a substance whose solution helps in locating the end point by undergoing a colour change. Common indicators used are organic compounds.

| *Indicator* | *Colour in Basic Medium* | *Colour in Acidic Medium* |
|---|---|---|
| Phenolphthalein | Pink | Colourless |
| Methyl orange | Yellow | Pink or red |

Selection of indicator is made according to the solutions used for titration.
For **strong acid** and **strong alkali** titration **phenolphthalein** is the best choice.
For **strong acid** and **weak alkali** titration **methyl orange** suits the best.
**Weak acid** and **strong alkali** titrations **phenolphthalein** is most suitable.

**Note**

1. An indicator should be added by means of glass dropper.
2. Always use one or two drops of the indicator. Large amount of indicator will not give sharp end point.
3. The same number of drops of indicator should be used for each titration.