Contents

CHAPTER
1

IMPORTANT FACTS IN EXPERIMENTAL CHEMISTRY

✣ [I] CONCENTRATION OF SOLUTION

A homogeneous mixture of two or more substances is called a solution. The concentration of a dissolved substance (solute) in a solution is determined by its amount contained in a definite weight (or volume) of the solvent (or solution). The concentration of a solution can be expressed in a number of following different ways :

✣ [A] EXPRESSING CONCENTRATION IN PHYSICAL UNITS

(1) In terms of percentage composition : It is expressed by the number of weight units (g) of the solute in 100 weight units (g) of the solution. For example, 10% aqueous glucose solution contains 10 g of glucose in 100 g of solution. For preparing this solution, 10 g of glucose is dissolved in 90 g of water to form 100 g of solution.

(2) In terms of weight of solute per unit volume (litre or dm^2) of solution : In such a case, we can express 1 g of glucose per dm^3 of the solution, *i.e.*, 1 g of glucose is dissolved in water and the total volume is made 1000 cm^3 or a litre of solution.

(3) By weight of solute per weight of solvent : For example, 5 g of NaCl in 100 g of water.

(4) In terms of parts per million (ppm) : This is usually used for solutions when the substance is present in a very small amount. It is defined as,

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 10^6$$

✣ [B] EXPRESSING CONCENTRATION IN CHEMICAL UNITS

(1) In terms of normality : Normality (N) of a solution is defined as the *number of gram equivalent weight of the solute in one litre (dm^3) of the solution.* For example, 1N solution of sodium chloride (eq. wt. =58.5) contains $1 \times 58.5 = 58.5$ g of sodium chloride in 1 litre (dm^3) of the solution. Similarly, 0.1N solution of oxalic acid (eq. wt. = 63) contains $0.1 \times 63 = 6.3$ g of oxalic acid in 1 litre (dm^3) of the solution.

(2) In terms of molarity : Molarity (M) of a solution is defined as the *number of moles of the solute in 1 litre (dm^3) of the solution.* For example, 0.2M solution of oxalic acid (mol. wt. = 126) contains $0.2 \times 126 =$ 25.2 g oxalic acid in one litre (dm^3) of solution.

(3) In terms of molality : Molality (m) of a solution is defined as the *number of moles of the solute per kilogram (1000 g) of the solvent.* For example 1 m solution of glucose (mol. wt. =180) contains $1 \times 180 = 180$ g of glucose in 1 kg (1000 g) of water.

(4) In terms of mole fraction or mole percent : Mole fraction of a substance in a solution is defined as the *number of moles of that substance divided by the total number of moles of all the substances in the solution.* The sum of the mole fractions of all the components in a solution is always unity. In a binary solution,

$$\text{Mole fraction of solute} = \frac{\text{Moles of solute}}{\text{Moles of solute + Moles of solvent}}$$

Similarly,

$$\text{Mole fraction of solvent} = \frac{\text{Moles of solvent}}{\text{Moles of solute + Moles of solvent}}$$

For example, if a solution contains 1 mole of A and 2 moles of B, then mole fraction of A will be $\frac{1}{1+2} = \frac{1}{3}$. Similarly, mole fraction of B will be $\frac{2}{1+2} = \frac{2}{3}$.

✦ [II] CALIBRATION OF WEIGHTS

The accuracy of weighing depends on the accuracy of the weights used even with the use of sensitive and accurate balance. Normally, the weights deteriorate by using them for a long time in a chemical laboratory. Even in costly weights sets, errors of quite appreciable degree are sometimes found. So, it becomes necessary to determine the errors in the weights, *i.e.,;* to calibrate the weights before carrying out accurate weighting. Therefore, for the calibration of weights, the following two methods are used :

(1) Method using standarised weights : If a complete set of standardised weights is available, the calibration can be easily carried out by available, the calibration can be easily carried out by weighing the individual weights against the standardised ones by the method of substitution to eliminate the error which might creep in due to inequality of balance arms.

In order to calibrate the weights by the substitution method, place the standard weight on the left hand scale pan and adjust a tare on the right hand scale pan. For the exact balancing, use a rider (It is always advisable to use the rider in the middle of the arm by keeping an extra 5 mg weight on the left hand pan throughout the whole operation of calibration). Replace the standard weight by the weight to be calibrated and obtain the same rest point by moving the rider, if necessary. In this way, a relation between the standard weight and the weight to be calibrated can easily be found. Similarly, other weights can be compared.

(2) Kohrausch's method : When only one set of unstandardised wieghts is given, the weights can be calibrated with respect to one another, taking one of the weights (*e.g.,* 50 g) as an arbitrary standard. Although calibration is in relative terms, not absolute mass, but this relative calibration serves the purpose in several chemical usuages, such as volumetric and gravimetric analysis.

This method consists in comparing each weight in the set in turn with a suitable selection of others. So, in a set of brass weights of 50, $20'$, $20''$, 10, 5, $2'$, $2''$, 1 g (the sign $'$ and $''$ distinguish duplicates), the 50 can be compared with $(20' + 20'' + 10)$, $20'$, with $20''$. $20''$, with $10 + 5 + 2' + 2'' + 1$, 10 with $(5 + 2' + 2'' + 1)$ and so on upto 10 mg. The 10 mg weight can be compared by placing a rider on 10th mark on the balance arm. Let $a_1, a_2, a_3, \ldots g$ etc. be the small differences determined very accurately using a rider between normally equal collection of weights. Then we have the following simultaneous equations :

$$50 = 20' + 20'' + 10 + a_1 \qquad \ldots(1)$$

$$20' = 20'' + a_2 \qquad \ldots(2)$$

$$20'' = 10 + 5 + 2' + 2'' + 1 + a_3 \qquad \ldots(3)$$

$$10 = 5 + 2' + 2'' + 1 + a_4 \qquad \ldots(4)$$

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$$0.05 = 0.02' + 0.02'' + 0.01 + a_{n-3} \qquad \ldots(n-3)$$

$$0.02' = 0.02'' + a_{n-2} \qquad \ldots(n-2)$$

$$0.02'' = 0.01 + \text{rider on the 10th mark} + a_{n-1} \qquad \ldots(n-1)$$

$$0.01 = \text{Rider on the 10th mark} + a_n \qquad \ldots(n)$$

For $(n+1)$ weights (including the rider) there will be n equations. For the sake of calculation, take 0.01 g as a temporary internal standard and the equations are then solved as follows :

From equations (n) and $(n-1)$, we get

$$0.02' = 2 \times (0.01) + a_{n-1} - a_n$$

On substituting the value of $(0.02')$ in equation $(n-2)$, we get

$$0.02' = 2 \times (0.01) + a_{n-1} - a_n + a_{n-2}$$

This procedure may be adopted upto 50 g weight.

The numerical a values with their proper sign are summed up step-by-step and apparent wiehgt of each piece is calculated in terms of (0.01) piece and the results are tabulated. Then the different values are converted taking 50 g weight as standard instead of 0.01 g piece.

Suppose, the apparent weight of 50 g piece is found to be 50.0124 g. In order to standardise the various weights with reference to 50 g piece as the internal standard multiply the apparent weight of each piece by $\frac{50}{50.0124}$.

◆ [III] CLEANING OF VOLUMETRIC APPARATUS

All the volumetric apparatus, *e.g.* pipette, burette, volumetric flasks etc must be perfectly clean, free from dust and greasy impurities. If the apparatus is dirty, unreliable results are liable to be obtained. The cleanliness of a glass vessel can be easily tested by filling it with distilled water and then pouring it out. If an unbroken film of water remains on the walls, the vessel is clean, the formation of droplets shows the presence of impurities which means that the vessel needs cleaning.

Following methods can be adopted for cleaning the glass apparatus.

(a) Soak the apparatus in warm solution (about 10%) of soap or detergent for nearly 20-25 minutes. Wash it with tap water, then with HCl and finally with distilled water.

Or, **(b)** Soak the vessel in cleaning mixture (equal volumes of concentrated H_2SO_4 and saturated solution of $Na_2Cr_2O_7$ or $K_2Cr_2O_7$, (preferably the former) for a few hours. Pour off the mixture and wash the apparatus throughly with tap water and finally with distilled water. Preserve the cleaning mixture for subsequent use.

Or, **(c)** Soak the apparatus in a mixture of concentrated sulphuric acid and nitric acid. Pour off the mixture and wash the apparatus thoroughly with tap water and then with distilled water. This method is very efficient for cleaning very dirty and greasy apparatus.

After cleaning, the apparatus may be dried by rinsing it with a littel acetone/alcohol and then passing a current of warm air filtered thorough the cotton wool plug. *It must be noted that the volumetric apparatus should never be dried in an oven, because the volume of the apparatus is likely to change.* Apparatus made of pyrex or borosilicate glass may be dried in an oven at 100-120°C.

◆ [IV] CALIBRATION OF VOLUMETRIC APPARATUS

Now-a-days, all the volumetric apparatus are calibrated in cm^3 (one thousandth part of a litre. 1 litre = 1000 ml = 100.028 cm^3) at room temperature (average) of 20°C. For orindary purposes, the volume marked on the apparatus by the manufacturer may be treated as reliable. Moreover, in relative measurements, such as double titrations, any error in the volume, if present, gets cancelled. However, for accurate work, even small error must be determined and hence the apparatus must be calibrated.

(1) Calibration of volumetric flask : Weigh accurately a thoroughly cleaned and dried flask on a balance. Fill the flask with air-free distilled water (water boiled and then cooled) so that the lower edge of the meniscus stands at the fixed mark of the neck. Remove any drop of water above the amark by a piece of filter paper. Dry the outer surface and weigh the flask again. After having calculated the weight of water contained in the flask upto the mark obtain the true volume of the vessel from the following table. In case the error is appreciable, etch a new ring on the neck.

Table 1. Apparent specific weight and apparent specific volume of water weighed in air.

Temp. (°C)	Apparent weight of 1 cm^3 of water (g)	Volume corresponding to an apparent weight of 1 g of water (cm^3)	Temp. (°C)	Apparent weight of 1 cm^3 of water (g)	Volume corresponding to an apparent wieght of 1 g of water (cm^3)
10	0.9986	0.0013	14	0.9982	1.0018
11	0.9985	0.0014	15	0.9981	1.0019
12	0.9984	1.0015	16	0.9979	1.0021
13	0.9983	1.0017	17	0.9977	1.0023
18	0.9976	1.0024	23	0.9965	1.0035
19	0.9974	1.0026	24	0.9963	1.0037
20	0.9972	1.0028	25	0.9960	1.0040
21	0.9970	1.0030			
22	0.9967	1.0033			

(2) Calibration of pipettes : Calibration of a pipette can be done by weighing the water it delivers from the fixed mark. Thoroughly clean the pipette to be calibrated by *cleaning mixutre* and then wash it with tap water and finally with distilled water. Suck the air-free distilled water into the pipette upto the mark and transfer it by keeping it almost upright, into a previously weighed small flask. When the water stops running, allow the pipette to drain for about 12-15 second, touch the tip of the piepette against the side of the flask so as to remove the last drop of water which collects at the tip. Determine the weight of water thus run out by weighing the flask again. From the weight of water, calculate the true volume of the pipette from table-1.

(3) Calibration of burettes : Burettes are generally calibrated by means of Ostwald's method with the help of a small pipette (capacity 10 cm^3), the volume of which has been accurately determined. Alternately, it can be calibrated as follows :

First, clean the burette, which is to be calibrated by *'cleaning mixture'* and wash it with tap water and finally with distilled water. Then fill the cleaned burette with air-free distilled water, taking care that no air bubble remains in the jet of the burette. Clamp it in vertical position and deliver 1 cm^3 water from zero mark into a previously weighed small flask. Determine the weight of water delivered by weighing the flask again. Withdraw successively 1 cm^3 water and weigh the flask after each delivery. From the weights of 1, 2, 3, ..., 10 cm^3 etc. from the burette, calculate the correct volumes. Tabulate the corrections (differences) corresponding to 1, 2, 3, ..., 50 cm^3. Now plot a graph between the burette readings as abscissa (X-axis) and corrections. as ordinates (Y-axis), positive corrections above and the negative corrections below the abscissa axis.

❖ [V] PREPARATION OF STANDARD SOLUTIONS

A solution whose concentration is known is called a *standard solution. Such a solution can be prepared by dissolving a known amount of the solute in a known amount of solvent or in a known volume of the solution. This method of preparing the standard solution is restricted only to substances of primary standard, i.e.,* whose concentration is exactly known and which does not change with time, *e.g,* oxalic acid, $K_2Cr_2O_7$, $AgNO_3$, $CuSO_4$ *etc.* such a procedure cannot be adopted for substances of secondary standard *i.e.,* whose concentration changes with time, *e.g.,* sodium hydroxide, sodium thiosulphate etc. or whose concentration is not exactly known, *e.g.,* HCl, HNO_3, H_2SO_4, NH_4OH etc. The standard solution of such substances can be obtained by preparing first a solution (known as stock solution) of concentration higher than that required (about 1.5-2.0 times concentrated) by approximate weighing or taking the required volume by means of a graduated pipette and then standardising it by titration. Then a solution of particular concentration (on dilution side) can be prepared by dilution of the stock solution (using the formula $N_1V_1 = N_2V_2$). Standard solution of some substances of secondary standard can be prepared as follows :

(1) Standard solution of caustic soda (200 cm^3 0.1 N) : We know that sodium hydroxide is hhygroscopic in nature, so it is always contaminated with water. So, its standard solution cannot be prepared by dissolving a weighed amount in a known volume of solution. A solution of higher concentration (stock solution) is first prepared by approximate weighing and is then standardised with a standard solution of oxalic acid (primary standard). A standard solution of any desired strength (less than that of stock solution) can be preapred easily by proper dilution of the stock solution.

The amount of NaOH required to prepare 200 cm^3 of 0.1M solution $= \frac{40 \times 200}{1000} \times 0.1 = 0.8$ g. Dissolve about 1.5 g of NaOH in 200 cm^3 water. Prepare 100 cm^3 of standard solution (0.1 N) of oxalic acid by accurately weighing $\left(\frac{63 \times 100}{1000} \times 0.1 = 0.63 \text{ g}\right)$. Titrate 20 cm^3 of the acid solution with alkali using phenolphthalein as an indicator. The exact strength of the alkali is thus found by using the formula, $N_1V_1 = N_2V_2$. Let the concentration be 0.1754 N. Then the volume of the alkali required to repare 200 cm^3 0.1 N solution of NaOH may be calculated as,

$$0.1754N \times V_1 = 0.1N \times 200$$

or

$$V_1 = \frac{0.1N \times 200}{0.1754N} = 114.02 \text{ cm}^3$$

By means of a calibrated burette take 114.02 cm^3 of the alkali (NaOH) into a 200 cm^3 measuring flask and make the solution upto the mark. This gives *0.1 N solution of* NaOH. *Similarly, solutions of other* alkalis, *e.g.*, KOH *etc.* can be prepared.

***(2) Standard solutions of acids, e.g.,* HCl, H_2SO_4, HNO_3 etc. (Suppose 200 cm^3 0.1 N HCl solution is to be prepared) :** The concentration of concentrated solution of different acids, *e.g.*, HCl, H_2SO_4, HNO_3, CH_3COOH *etc.* is approximately known. For preparing a standard solution of any desired concentration, a stock solution of some nearly known concentration about 1.5 to 2 times higher than the concentration of the standard solution required, is prepared. Its exact concentration is then determined by titrating it with a standard slolution of NaOH. The solution of any required concentration (dilute one) can then be prepared by proper dilution of the stock solution.

For preparing 200 cm^3 of 0.1N HCl solution, the volume of concentrated HCl (~ 11.6N) required will be given by,

$$11.6N \times V_1 = 0.1N \times 200$$

or

$$V_1 = \frac{0.1N \times 200}{11.6} = 1.7 \text{ cm}^3 \text{ (approx)}$$

By means of a graduated pipette take about 3 to 4 cm^3 of concentrated HCl and dilute it to 200 cm^3. Titrate the acid solution with a standard alkali and find the exact concentration of the stock solution. Suppose the correct concentration is found to be 0.1876N. The volume of stock solution to be diluted to 200 cm^3 is

$$0.1876N \times V_1 = 0.1N + 200$$

or

$$V_1 = \frac{0.1N \times 200}{0.1876} = 106.6 \text{ cm}^3$$

Take 106.6 cm^3 of the acid solution into a 200 cm^3 measuring flask and make the solution upto the mark to get the desired solution of HCl. Similarly, standard solutions of H_2SO_4, HNO_3, CH_3COOH etc. can also be obtained.

(3) Standard solution of ammonium hydroxide : Suppose 1000 cm^3 of 0.1 N solution is to be prepared. The strength of concentrated solution of ammonia available in the laboratory is nearly 14.8 N. The volume of concentrated solution of ammonia required is thus

$$V_1 = \frac{0.1N \times 1000}{14.8N} = 6.7 \text{ cm}^3 \text{ (approximately)}$$

Dilute about 15 cm^3 of concentrated ammonia to about 1000 cm^3. (The bottle of ammonia should be properly cooled in a bath of ice, before it is opened). Standardise the above ammonia solution by titrating it with a standard HCl solution, say 0.1N, using methyl orange, as an indicator. Suppose the concentration of ammonia solution is nearly 0.25N. The volume of stock solution to be diluted to 1000 cm^3 is,

$$0.25N \times V_1 = 0.1N \times 1000$$

or

$$V_1 = \frac{0.1N \times 100}{0.25N} = 400 \text{ cm}^3$$

Now take 400 cm^3 of the stock solution and dilute it with distilled water to make the solution up to 1000 cm^3 mark to get the solution of desired concentration.

Table 2. Concentration of aqueous solutions of common acids and ammonia

Reagent	Normality of concentrated solution	Molarity of concentrated solution	Volume required to make 1 dm^3 0.1N solution (approximately cm^3
Hydrochloric acid	11.6	11.6	8.6
Sulphuric acid	17.8	35.6	2.8
Nitric acid	15.4	15.4	6.5
Acetic acid	17.4	17.4	5.8
Phosphoric acid	43.8	14.6	2.3
Ammonia	14.8	14.8	8.6

(4) Standard solutions of $KMnO_4$ and $Na_2S_2O_3$: First, solutions of $KMnO_4$ and $Na_2S_2O_3$ (concentration higher than that required) are preapred. $KMnO_4$ solution is standardised by titrating it with a standard oxalic acid solution (self indicator). The $Na_2S_2O_3$ (hypo) solution is standardised with standard copper sulphate solution iodometrically, using starch solution as an indicator. The standard solution on the dilution side can be obtained by proper dilution of the stock solution.

(5) Preparation of a mixture of two miscible liquids, composition in mole fraction being known : The mole fraction of each liquid is multiplied by the respective molecular weight and mix the amounts so obtained to get the required mixture. If the densities of the liquids are known, their volumes to be mixed can be calculated by dividing the above amounts by their respective densities. Suppose M_1 and M_2 are the molecular weights and d_1 and d_2 are the densities (in g cm^{-3}) of the two liquids. Let the respective mole fractions of the liquids be x_1 and x_2. The amounts (m_1 and m_2) of the liquids to be mixed will be :

$$m_1 = M_1 x_1 \text{ g}; \quad m_2 = M_2 x_2 \text{ g}$$

The respective volumes will be given by,

$$V_1 = \frac{M_1 x_1}{d_1} \text{ cm}^3; V_2 = \frac{M_2 x_2}{d_2} \text{ cm}^3$$

So, to prepare the required mixture of the two liquids mix either m_1 and m_2 g or V_1 and V_3 cm^3 of liquids 1 and 2, respectively. If a mixture of CH_3OH and C_2H_5OH (respective mole fractions being 0.4 and 0.6) is to be prepared then,

Amount of methyl alcohol $= 0.4 \times 32 = 12.8$

$$=\frac{12.8}{0.75}\approx 17.1\ \text{cm}^3 \text{ at } 20°\text{C}$$

Amount of ehtyl alochol $= 0.6\times 46 = 27.6$ g

$$=\frac{27.6}{0.79}\approx 34.9\ \text{cm}^3 \text{ at } 20°\text{C}$$

So mix 12.8 g (or 17.1 cm^3) of methyl alcohol and 27.6 g (or 34.9 cm^3) of ethyl alcohol or multiples of these amounts to obtain the desired mixture.

THERMOSTAT (OR TEMPERATURE CONTROL)

Several physical properties such as osmoatic pressure, vapour pressure, rate constant, equilibrium constant, surface tension, viscosity etc. depend on temperature and so their values must be measured at a knwon temperature controlled to within ±0.01°C. Ice bath (ice in equilibrium with water at 0°C), mixture of crushed ice with salt (freezing mixtures), liquid nitrogen at its normal boiling point (77.2K or − 195.8°C), dry ice-acetone bath, solid carbon dioxide in equilibrium with CO_2 vapours at 1 atmosphere (~ 78.5°C) are some of the low tempeature baths.

An important method of obtaining temperature control is to use a thermosensing device with a feedback *system to control the input of heater or refrigerator to* a bath such that the temperature is maintained at any desired arbitrary value within a narrow range. Such a device is known as a **thermostat.** It consists mainly of the following different parts :

(i) Bath, (ii) Stirrer, (iii) Heater or refrigerator, (iv) Thermoregulator and (v) Relay.

(1) Bath : It consists of a large rectangular tank of suitable size. The most commonly used size in 45 cm deep and 45 × 75 cm in horizontal area. The bath is made of glass or stainless steel metal with glass windows in two or more sides. The tank is filled with water for temperature upto ~ 70 − 80°C or a suitable oil such as heavy cylinder oil up to ~ 300°C or silicone oil for still higher temperatures.

(2) Stirrer : *To provide a good stirring of the liquid* in the tank, a metallic stirrer or a centrifugal liquid circulation driven by an electric motor is used.

(3) Heater or refrigerator : To heat the bath, an electric heater of suitable wattage is used. For more accurate work, an auxilliary heater is also provided. If two heaters are used, one may be *constantly switched* on and the other is intermittent under the control of a thermoregulator or both may be intermittent depending upon their power rating. If a thermostat working at low temperatures is required, then a refrigerating device instead of a heater is used. The thermostat is then known as a ***cryostat.***

(4) Thermo-regulator : A thermo-regulator or a *thermosensing element* is a thermometric instrument which provides an electric signal. For laboratory temperature control, the most commonly used devices are *off-on thermoswitch type.* Four types of devices based on the principle of thermoswitch *viz.* (a) toluene bulb regulator, (b) vapour-liquid type regulator, (c) mercury-in-glass regulator and (iv) bi-metallic strips type regulator, are commonly used.

Fig. (1) shows a toluene bulb regulator. It consists of a J-type glass tube having a bulb at its one end and a capillary at the other. The bulb is filled with toluene (a *liquid of large thermal expansion coefficient*) in contact with mercury ending as a capillary column. A mercury reservoir is connected by means of a side tube having a stopcock to the main mercury column. For making electrical contacts, two platinum wires are used, one Pt. wire is directly inserted into the main mercury column by fusion through the glass, while the other to mercury

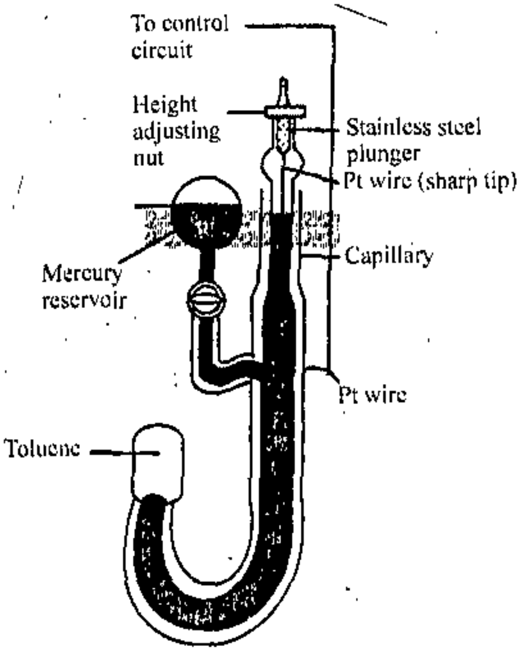

Fig. 1. Toluene thermo-regulator

meniscus in the capillary when temperature has attained the desired value. The regulator is set to the desired temperature either by lowering or raising the central wire in the capillary using a screw or by adjusting the height of the mercury column.

Fig. (2) shows a vapour-liquid type regulator in which the bulb is partly filled with a liquid in equilibrium with its saturated vapour and partly with mercury. The liquid is so chosen as to have a boiling point close to the desired temperature. In a mercury-in-glass thermo-regulator, the bulb is filled completely with mercury. A bimetallic strip type regulator is useful only where the temperature regulation better than 1° is not required. This type of regulator is commonly used for temperature control in electric ovens used in laboratory.

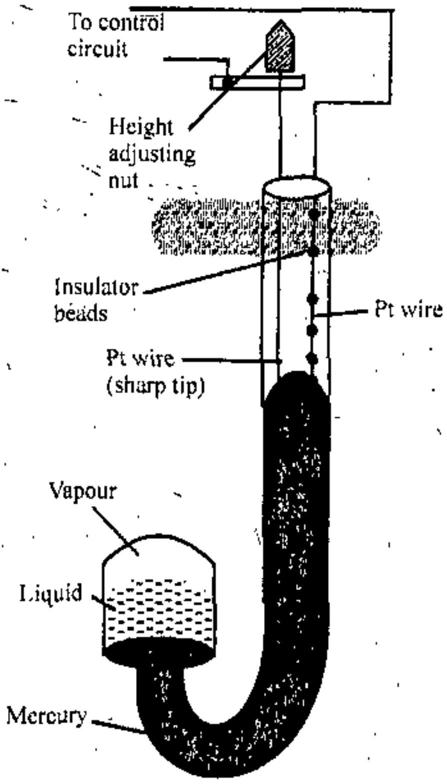

Fig. 2. Vapour-liquid thermo-regulator

(5) Relay : It is an electronic or electromechanical device which *'makes'* or *'breaks'* the electrical circuit of heater or refrigerator. In electromechanical relay, an electromagent gets energised when its circuit is closed through the thermoregulator. The electromagnet attracts a piece of soft iron which then breaks the circuit of the heater. When the circuit of the relay is borken through the regulator and temperature falls below the desired value due to heat loss, the piece of iron is released by the electromagnet which then makes the circuit of the heater.

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CHAPTER

2

CHEMICAL ANALYSIS

◆ PHYSICO-CHEMICAL PRINCIPLES INVOLVED IN QUALITATIVE ANALYSIS

The branch of chemistry which deals with the analysis of inorganic substances, identification of its component etc., is called Inorganic Analytical Chemistry. It may be classified into following two categories :

1. Qualitative Analysis : Qualitative analysis deals with the determination of nature and quality of the substance.

2. Quantitative Analysis : Quantitative analysis deals with the determination of the respective amounts of any of the constituents of the substance. It may be divided into following categories :

(a) Gravimetric Analysis : In gravimetric analysis the given substance is changed into precipitate of a known composition and then weighed. In other words it depends upon the measurement of weight.

(b) Volumetric Analysis : In volumetric analysis the given solution is titrated with a known solution. It is based on the determination of volumes of solution of interacting substances that are required for complete reaction.

Qualitative Analysis : Qualitative analysis is that branch of analytical chemistry in which we analyse the given salt or mixture to know the presence of different radicals. Each and every salt has two radicals :

(i) Basic radical

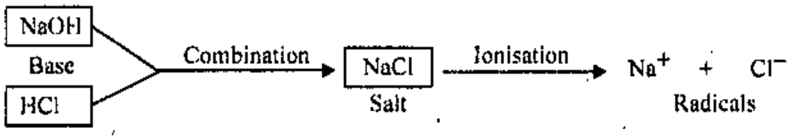
(ii) Acid radical

A salt is formed by the reaction of an acid and a base.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \longrightarrow \underset{\text{Salt}}{NaCl} + \underset{\text{Water}}{H_2O}$$

Every salt consists of two parts, usually called **radicals** known as the **basic radical** and the **acid radical.** Sodium chloride is formed by the interaction of hydrochloric acid and sodium hydroxide, as is evident from the above equation. In sodium chloride (NaCl), Na^+ radical has come from sodium hydroxide (a base), hence it is known as basic radical. The basic radical is also called the **positive radical** since it always bears a positive charge. The Cl^- radical in sodium chloride has come from hydrochloric acid (an acid), hence it is known as acid radical. The acid radical is also called the **negative radical** since it always bears a negative charge.

When a salt is dissolved in water it undergoes ionisation giving positive and negative ions, e.g.,



$$\underset{\substack{\text{Sodium}\\\text{Chloride}\\\text{Salt}}}{NaCl} \rightleftharpoons \underset{\substack{\text{Sodium}\\\text{ion}\\\text{Basic radical}\\\text{(Cation)}}}{Na^+} + \underset{\substack{\text{Chloride}\\\text{ion}\\\text{Acid radical}\\\text{(Anion)}}}{Cl^-}$$

The success of inorganic analysis is based on some physico-chemical principles which are described here.

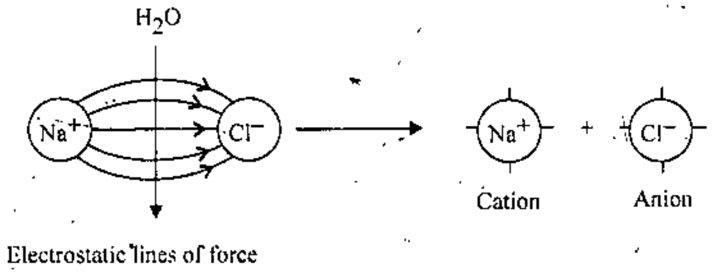


Fig. 1. Ionisation of sodium chloride

PHYSICO-CHEMICAL PRINCIPLES INVOLVED IN QUALITATIVE ANALYSIS

(1) Ionisation Equilibrium : When any electrolyte is dissolved in water it gives two types of charged particles. According to ionisation theory an equilibrium is established between ionised and unionised molecules. For example, the ionisation of ammonium hydroxide may be represented as :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

According to law of **mass action**

$$K = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

where, K is called ionisation constant.

(2) Common Ion Effect : The phenomenon of lowering the degree of ionisation of a weak electrolyte by adding to it solution of a strong electrolyte having a common ion is called *common ion effect.* For example, ammonium hydroxide dissociates in solution as :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

According to law of mass action

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K$$

On the addition of ammonium chloride (a strong electrolyte), NH_4^+ ions are added to the solution. Thus the concentration of NH_4^+ ions increases. Since K is constant at a particular temperature, hence on increasing the concentration of NH_4^+ ions the concentration of OH^- ions decreases.

Thus the ionisation of NH_4OH decreases in the presence of NH_4Cl which furnishes the common ion, NH_4^+.

Importance of Common Ion Effect in Qualitative Analysis

Consider the ionisation of H_2S is presence of HCl, *i.e.*,

$$\begin{array}{lcccc} H_2S & \rightleftharpoons & 2H^+ & + & S^= \\ HCl & \rightleftharpoons & H^+ & + & Cl^- \\ & & \text{Common ion} & & \end{array}$$

Thus the ionisation of the H_2S is suppressed. Similarly, we may explain the suppression of ionisation of NH_4OH in the presence of NH_4Cl due to common ion, NH_4^+.

$$\begin{array}{lcccc} NH_4OH & \rightleftharpoons & NH_4^+ & + & OH^- \\ NH_4Cl & \rightleftharpoons & NH_4^+ & + & Cl^- \\ & & \text{Common ion} & & \end{array}$$

Evidently, the common ion effect is really of immense importance in qualitative analysis. It provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte.

(3) Solubility Product and Precipitation : When a sparingly soluble substance, say AB is kept in contact with water for some time at a definite temperature the following equilibrium is attained.

$$\mathrm{AB(s)} \rightleftharpoons \mathrm{AB} \rightleftharpoons \mathrm{A^+ + B^-}$$

According to law of mass action,

$$\frac{[\mathrm{A^+}][\mathrm{B^+}]}{[\mathrm{AB}]} = \mathrm{K}$$

If AB is in large excess at a definite temperature then [AB] may be considered as constant. Therefore,

$$[\mathrm{A^+}][\mathrm{B^-}] = \mathrm{K\,[AB]} = \mathrm{K_{sp}} = \text{constant}$$

"In equilibrium, the product of the ionic concentration $[\mathrm{A^+}][\mathrm{B^-}]$ *is constant at a given temperture; which is known as solubility product,* K_{sp}*."*

When the ionic product exceeds the solubility product, the solution is supersaturated and precipitation takes place. If the ionic product is less than the solubility product, solution will be unsaturated and the precipitation will not take place.

Since precipitation is related with solubility product, hence it has great importance in qualitative analysis.

Precipitation of the sulphides of Group II and IV

Since the solubility product of the sulphides of group II radicals is low, hence we require low concentration of S^{2-} ions which may be obtained by passing H_2S gas in the presence of acid (HCl) (common ion effect). Therefore, in acidic medium only the radicals of group II are precipitated as their sulphides.

$$\mathrm{H_2S} \rightleftharpoons \mathrm{2H^+ + S^{2-}}$$

$$\mathrm{HCl} \longrightarrow \mathrm{H^+ + Cl^-}$$

On the other hand, the solubility product of the sulphides of group IV radicals is high. We require high concentration of $S^{=}$ ions which may be obtained by passing H_2S gas in alkaline solution. Therefore the radicals of group IV are precipitated in the presence of NH_4OH.

$$\mathrm{NH_4OH} \rightleftharpoons \mathrm{NH_4^+ + OH^-}$$

$$\mathrm{H_2S} \rightleftharpoons \mathrm{S^{2-} + 2H^+}$$

$$\mathrm{H^+ + OH^-} \rightleftharpoons \mathrm{H_2O}$$

In the same way we may explain the precipitation of the radicals of different groups on the basis of common ion effect and solubility product.

The solubility products of different compounds are given below :

$PbCl_2$	2.4×10^{-4}	MnS	2.5×10^{-13}
Hg_2Cl_2	2.0×10^{-21}	ZnS	1.6×10^{-24}
AgCl	1.2×10^{-10}	$Fe(OH)_3$	4.0×10^{-28}
PbS	8.0×10^{-28}	$Al(OH)_3$	1.3×10^{-33}
HgS	1.6×10^{-52}	$Cr(OH)_3$	6.3×10^{-31}
Bi_2S_3	1.6×10^{-72}	$Ni(OH)_2$	2.0×10^{-15}
CuS	6.3×10^{-26}	$Co(OH)_2$	1.5×10^{-15}
CdS	8.0×10^{-27}	$Mn(OH)_2$	1.9×10^{-13}
NiS	1.0×10^{-24}	$Zn(OH)_2$	1.2×10^{-17}
CoS	2.0×10^{-25}	$Mg(OH)_2$	1.8×10^{-11}

(4) Complex Ion Formation : Complex ion formation is of immense importance in qualitative analysis (i) to dissolve a precipitate alone or from a mixture of two or more (ii) to check the precipitation of a particular cation by complex ion formation.

(i) In the separation of AgCl and Hg_2Cl_2 in the group I, which is based upon the capacity of Ag^+ ion to form complex with NH_3.

$$AgCl + 2NH_3 \rightleftharpoons \underset{\text{Complex salt}}{[Ag(NH_3)_2]Cl}$$

$$Ag^+ + 2NH_3 \rightleftharpoons \underset{\text{Complex ion}}{[Ag(NH_3)_2]^+}$$

(ii) Separation of Cu^{2+} and Cd^{2+} ions is also based on complex formation with potassium cyanide solution. The complexes formed are :

$$K_3[Cu(CN)_4] \text{ and } K_2[Cd(CN)_4]$$

These complexes ionise as follows :

$$K_3[Cu(CN)_4] \rightleftharpoons 3K^+ + [Cu(CN)_4]^{3-}$$

$$[Cu(CN)_4]^{3-} \rightleftharpoons Cu^+ + 4CN^-$$

$$K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + [Cd(CN)_4]^{2-}$$

$$[Cd(CN)_3]^{--} \rightleftharpoons Cd^{2+} + 4CN^-$$

According to law of mass action,

$$\frac{[Cu^+][CN^-]^4}{[Cu^+(CN)_4^{3-}]} = K = 5\times 10^{-28}$$

$$\frac{[Cd^{++}][CN^-]^4}{[Cd(CN)_4^{2-}]} = K = 1.4\times 10^{-17}$$

K is the instability constant of the complex ion and determines its stability. The value of instability constant for copper complex ion is less than that of cadmium complex ion and hence more Cd^{2+} ions are available in the solution than Cd^{2+} ions. When hydrogen sulphide gas is passed through a solution containing copper and cadmium cyanide complex ions, copper complex remains unaffected while cadmium complex ion gives cadmium ions which combine with S^{2-} ions (available form H_2S) to form a yellow *precipitate of* CdS.

Thus, we get the precipitate of Cd^{2+} as cadmium sulphide even in the presence of Cu^{2+}.

$$[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^-$$

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$Cd^{2+} + S^{2-} \rightleftharpoons \underset{\text{(Yellow ppt.)}}{CdS\downarrow}$$

(5) Hydrogen Ion Concentraton, pH Value : The acidity of the solution can be quantitatively determined by its pH value (p means *potenz i.e.*, power and H stands for hydrogen ions). This value plays an important part in the precipitation of cations. It may be defined as, *''the numerical value of the negative power to which 10 must be raised in order to express the hydrogen ion concentration.''*

Mathematically, it is expressed as :

$$[H^+] = 10^{-pH}$$

or

$$pH = -\log[H^+] = \frac{1}{\log[H^+]}$$

Therefore, pH may be defined as, *''the logarithm of the reciprocal of H^+ ion concentration.''*

If $[H^+] = 10^{-6}$, then pH = 6

If $[H^+] = 10^{-11}$ then pH = 11

$$\text{pH} = \underbrace{0\ \ 1\ \ 2\ \ 3\ \ 4\ \ 5\ \ 6\ \ 7}_{\text{Acidic}}\ \underset{\text{Neutral}}{\downarrow}\ \underbrace{8\ \ 9\ \ 10\ \ 11\ \ 12\ \ 13\ \ 14}_{\text{Alkaline}}$$

(6) Buffer solution : Buffer solutions are those solutions which have reserve acidity or alkalinity *i.e.* their pH values are constant. For example :

$$CH_3COOH + CH_3COONa,\ NH_4Cl + NH_4OH \text{ etc.}$$

(7) Salt Hydrolysis : A reaction in which a salt reacts with water to produce acidity or alkalinity is known as salt hydrolysis. For example, an aqueous solution of sodium carbonate is alkaline due to the excess of OH^- ions in solution.

$$\begin{array}{rccc} Na_2CO_3 \rightleftharpoons & 2Na^+ & + CO_3^{-2} & \\ 4H_2O \rightleftharpoons & 2OH^- & +2H_3O^+ & \\ & \upharpoonleft\downharpoonright & \upharpoonleft\downharpoonright & \\ & 2NaOH & H_2CO_3 & +2H_2O \\ & \text{(highly ionised)} & \text{(feebly ionised)} & \end{array}$$

(i) Hydrolysis of salts of weak acid and strong base : The examples of such salts are $NaHCO_3$, Na_2CO_3, KCN, CH_3COONa etc., which produce alkaline solution on hydrolysis.

$$\begin{array}{rcc} CH_3COONa \rightleftharpoons & CH_3COO^- & + Na^+ \\ 2H_2O \rightleftharpoons & H_3O^+ & + OH^- \\ & \upharpoonleft\downharpoonright & \upharpoonleft\downharpoonright \\ & CH_3COOH + H_2O & NaOH \\ & \text{(feebly ionised)} & \text{(highly ionised)} \end{array}$$

(ii) Hydrolysis of the salt of strong acid and weak base : The examples of such salts are NH_4Cl, NH_4NO_3, $CuSO_4$, $FeCl_3$ etc. which produce acidic solution on hydrolysis.

$$\begin{array}{rccc} NH_4Cl \rightleftharpoons & NH_4^+ & + Cl^- & \\ 2H_2O \rightleftharpoons & OH^- & + H_3O^+ & \\ & \upharpoonleft\downharpoonright & \upharpoonleft\downharpoonright & \\ & NH_4OH & HCl & + H_2O \\ & \text{(feebly ionised)} & \text{(highly ionised)} & \end{array}$$

(iii) Hydrolysis of the salt of a weak acid and a weak base : The examples of such salts are $(NH_4)_2CO_3$, CH_3COONH_4 etc. which produce acidic or alkaline solution on the basis of strength of acid and base.

$$\begin{array}{rcc} CH_3COONH_4 \rightleftharpoons & CH_3COO^- & + NH_4^+ \\ 2H_2O \rightleftharpoons & H_3O^+ & + OH^- \\ & \upharpoonleft\downharpoonright & \upharpoonleft\downharpoonright \\ & CH_3COOH + H_2O & NH_4OH \end{array}$$

(8) Oxidation-Reduction or Redox Reaction : Ionic reactions in aqueous solution which involve the loss or gain of electrons are called oxidation-reduction or redox reactions.

(i) Oxidation : In oxidation one or more electrons are furnished by an atom or ion of the substance, *e.g.*,

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \qquad \textit{(Oxidation)}$$

$$Zn \longrightarrow Zn^{++} + 2e^- \qquad \textit{(Oxidation)}$$

(ii) Reduction : In reduction one or more electrons are accepted by the atom or ion of the substance, *e.g.*,

$$Cl + e^- \longrightarrow Cl^- \qquad \textit{(Reduction)}$$

$$Co^{3+} + e^- \longrightarrow Co^{2+} \qquad \textit{(Reduction)}$$

Both the reactions simultaneously take place, *i.e.*, if one substance is oxidized then the other is definitely reduced.

$$Zn + 2H^+ \longrightarrow Zn^{++} + H_2$$

$$Fe + Cu^{++} \longrightarrow Cu + Fe^{++}$$

(iii) Oxidising agent : The substance which accepts electrons or gets reduced is known as oxidising agent, *e.g.*, $KMnO_4$, $K_2Cr_2O_7$, HNO_3, H_2O_2, Cl_2 are good oxidising agents.

(iv) Reducing agent : The substance which loses electrons or gets oxidised is known as reducing agent *e.g.* $FeSO_4$, H_2S, $H_2C_2O_4$, KI, $SnCl_2$, H_2, SO_2 etc.

(v) Oxidation-reduction reactions

$$\begin{array}{r}
2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \\
[2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5 \\
\hline
2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O \\
\hline
\end{array}$$

or,

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

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

In the above reaction, MnO_4^- ion is oxidising agent while Fe^{2+} ion is reducing agent because MnO_4^- ion reduces into Mn^{2+} ion, while Fe^{2+} ion is oxidised to Fe^{3+} ion.

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CHAPTER
3
IDENTIFICATION OF ACID RADICALS

Although it has not been possible to categorise the acid radicals, even then these may be divided into following three groups depending upon their reaction with certain reagents—

Group	Name and formula of the radical	Group reagent	Inference of the group
Group I	Carbonate (CO_3^{2-}) Sulphite (SO_3^{2-}) Sulphide (S^{2-}) Acetate (CH_3COO^-) Nitrite (NO_2^-)	Dil. HCl or Dil. H_2SO_4	Evolution of gases with characteristic colour and smell.
Group II	Chloride (Cl^-) Bromide (Br^-) Iodide (I^-) Nitrate (NO_3^-) Oxalate ($C_2O_4^{2-}$) Borate (BO_3^{3-}) Fluoride (F^-)*	Conc. H_2SO_4	Evolution of gases with characteristic colour and smell.
Group III	Sulphate (SO_4^{2-})	Dil. HCl + $BaCl_2$	White ppt.
	Phosphate (PO_4^{3-})	Conc. HNO_3 + Ammonium molybdate	Canary yellow ppt.

*Conc. H_2SO_4 + Sand

Group I

(Group reagent : dil. HCl or dil. H_2SO_4)

S. No.	Experiment	Observation	Inference	Confirmation
1.	Take mixture in a dry test tube and add dil. HCl. Warm gently.	Brisk effervescence with the evolution of colourless and odourless gas (CO_2)	CO_3^{2-} (Carbonate)	Pass the evolved gas into lime water, $Ca(OH)_2$. It turns milky. In excess of CO_2 gas it becomes clear solution.

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* Acidified $K_2Cr_2O_7$ Solution may be prepared by dissolving about 0.1 g $K_2Cr_2O_7$ (solid) in 5 ml of water and add 2-4 ml dil. H_2SO_4.

2.	Take mixture in a dry test tube and dil. HCl. Warm gently.	Evolution of colourless gas with suffocating odour of burning sulphur (SO_2)	SO_3^{2-} (Sulphite)	The evolved gas turns paper moistened with acidified* $K_2Cr_2O_7$ sol. green.
3.	Take mixture in a dry test *tube and add dil. HCl. Warm* gently.	Evolution of colourless *gas with smell of rotten* eggs (H_2S)	* S^{2-} (Sulphide)	(i) The evolved gas turns *paper dipped in lead* acetate solution $(CH_3COO)_2Pb$ black. (ii) The evolved gas turns paper dipped in alkaline sodium nitroprusside solution violet.
4.	Take mixture in a dry test tube and add dil. HCl. Warm gently.	Evolution of brown fumes (NO_2) with Pungent odour.	NO_2^- (Nitrite)	(i) The evolved gas turns paper dipped in starch +KI solution *blue.* (ii) Add 2-3 drops of KI and starch solution in the *test tube* →*deep blue* or violet colour appears.
5.	Take mixture in a dry test tube and add dil. HCl. Warm gently.	Smell of vinegar (CH_3COO^-)		(i) A water extract of the substance gives blood-red colour in cold with neutral* $FeCl_3$ solution. (ii) Rub a small amount of the substance + oxalic acid with a few drops of water between your fingers → Smell of vinegar.

* Many sulphides specially native ores are not decomposed by *dil. acids; some H_2S is evolved upon* warming with conc. HCl alone or with a little *zinc.*

* Neutral $FeCl_3$ solution may be prepared by adding dropwise dil. NH_4OH solution in $FeCl_3$ solution taken in a test tube till permanent turbidity appears. The filtrate of this is neutral $FeCl_3$ solution.

REACTIONS INVOLVED IN THE TEST OF GROUP I RADICALS

1. Carbonate

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{Milky}}{CaCO_3\downarrow} + H_2O$$

$$\underset{\text{Insoluble}}{CaCO_3} + H_2O + CO_2\ (\text{excess}) \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

2. Sulphite

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2\uparrow$$

$$\underset{\text{Orange yellow}}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$$

3. Sulphide

$$FeS + H_2SO_4 \longrightarrow H_2S\uparrow + FeSO_4$$

$$(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\text{Black}}{PbS\downarrow} + 2CH_3COOH$$

$$Na_2S + \underset{\text{Sod. nitroprusside}}{Na_2[Fe(NO)(CN)_5]} \longrightarrow \underset{\text{Violet}}{Na_4[Fe(NOS)(CN)_5]}$$

4. Nitrite

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO\uparrow + H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2\uparrow \text{ (Brown)}$$

$$2KI + 2NO_2 \longrightarrow 2KNO_2 + I_2$$

$$I_2 + \text{Starch} \longrightarrow \text{Blue colour}$$

5. Acetate

$$2CH_3COONa + H_2SO_4 \longrightarrow \underset{\text{Smell of vinegar}}{2CH_3COOH} + Na_2SO_4$$

$$3CH_3COONa + FeCl_3 \longrightarrow \underset{\text{Blood red colour}}{(CH_3COO)_3Fe} + 3NaCl$$

$$2CH_3COONa + H_2C_2O_4 \longrightarrow \underset{\text{Smell of vinegar}}{2CH_3COOH} + Na_2C_2O_4$$

Group II

(Group reagent : Conc. H_2SO_4)

S. No.	Experiment	Observation	Inference	Confirmation
1.	Heat the mixture with 1-2 ml. conc. H_2SO_4 in dry test-tube.	Colourless pungent gas (HCl) is evolved.	Cl^- (Chloride)	(i) White dense fumes of NH_4Cl are formed on bringing a rod dipped in NH_4OH near the mouth of the test-tube. (ii) Greenish-yellow (Cl_2) pungent gas is evolved on heating the given mixture with conc. H_2SO_4 and MnO_2. (iii) **Chromly Chloride Test-** Heat the given mixture (a very small portion of it) + $K_2Cr_2O_7$ solid (3 times of the substance taken) + conc. H_2SO_4. Orange *yellow vapours of* chromyl-chloride (CrO_2Cl_2) are evolved. These vapours are now collected in a test-tube containing NaOH. This is acidified with CH_3COOH and treated with $(CH_3COO)_2Pb$ solution. A *yellow* ppt. of lead chromate is formed.
				(iv) In the solution of the mixture in water or dil. HNO_3 or sodium carbonate extract acidified with dil. HNO_3 add $AgNO_3$ solution. A white ppt. of AgCl is formed which is soluble in NH_4OH. If conc. HNO_3 is added in it, a white ppt. of AgCl is again obtained.

2.	Heat the mixture with 1-2 ml conc. H_2SO_4 in the dry test-tube.	Colourless pungent gas (HBr) is evolved. (Some times brown fumes are evolved.)	Br^- (Bromide)	(i) On heating the given mixture with MnO_2 conc. H_2SO_4 red brown vapours of bromine (Br_2) are evolved. (ii) In the solution of the mixture in water or dil. HNO_3 or sodium carbonate extract acidified with dil. HNO_3 add $AgNO_3$ solution a pale yellow ppt. of AgBr is formed which is hardly soluble in NH_4OH.
3.	Heat the mixture with 1-2 ml conc. H_2SO_4 in a dry test tube.	Dark violet fumes (I_2) are evolved.	I^- (Iodide)	(i) On heating the given mixture with MnO_2 and conc. H_2SO_4, violet vapours (I_2) in excess are evolved. These vapours turn a paper dipped in starch, *blue*. (ii) In the solution of the mixture in water/dil. HNO_3 or sodium carbonate extract acidified with dil. HNO_3 add $AgNO_3$ solution. A yellow ppt. of AgI is formed which is insoluble in NH_4OH.
4.	Heat the mixture with 1-2 ml conc. H_2SO_4 in a dry test-tube.	Pungent light brown gas (NO_2) is evolved.	NO_3^- (Nitrate)	(i) ON heating the given mixture with copper turnings and conc. H_2SO_4 deep brown fumes (NO_2) in excess are evolved. (ii) Add freshly prepared solution of $FeSO_4$ to aqueous extract of the given substance or to the solution of it in dil. HCl. Shake well, gradually add conc. H_2SO_4 by the side of the test tube. A brown ring. ($FeSO_4.NO$) is formed at the junction of the two liquids. This test is known as ring test.
5.	Heat the mxiture with 1-2 ml of conc. H_2SO_4 in a dry test-tube.	Colourless, odourless gas is evolved which burns with blue flame at the mouth of the test-tube.	$C_2O_4^{--}$ (Oxalate)	Take sodium carbonate extract* of the mixture in a test-tube. Acidify it with excess of CH_3COOH and then add $CaCl_2$ solution. A white ppt. of CaC_2O_4 is formed. The ppt. is dissolved in dil. H_2SO_4 and warm it. Now add few drops of $KMnO_4$ solution and shake it. The colour of $KMnO_4$ solution is discharged.

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* Mix one part of the solid substance with 3 parts by weight of Na_2CO_3 and not more than 10-20 ml. of distilled water and boil it for 10 minutes in a beaker or conical flask. Filter while hot. The filtrate is known as sodium carbonate extract.

6.	Take a little mixture in a procelain dish add, a little conc. H_2SO_4; 1/2 ml of ethyl alcohol or methylated spirit, stir well by a glass rod and ignite.	A green edged flame is developed.	BO_3^{3-} (Borate)	Copper and Barium salts intefere *because they also give a positive* test. So this test should be performed in a test-tube instead of procelain dish and the vapour-evolved on heating the test-tube should be burnt at the mouth of the test-tube which will burn with a green edged flame.
7.	Take a little mixture with some sand in test-tube, add conc. H_2SO_4 to it and heat. Bring a glass rod moistened with water at the mouth of the test-tube.	A waxy white deposit of H_2SiO_3. *Note* : Mecury chloride and ammonium chloride also leave a white deposit on the rod, but this deposit is crystalline in stead of waxy.	F^- (Fluoride)	This is the confirmatory test for fluoride. (After perofrming the test, *contents of the test-tube* should not be thrown in the sink without cooling and diluting the contents of the tube.)

Reactions involved in the test of Group II Radicals

1. Chloride

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{Pungent smell gas}}{HCl\uparrow}$$

$$HCl + NH_4OH \longrightarrow \underset{\text{White fumes}}{NH_4Cl\uparrow} + H_2O$$

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + \underset{\text{Yellowish green}}{Cl_2\uparrow}$$

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White}}{AgCl\downarrow} + NaNO_3$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\substack{\text{Diammine}\\ \text{silver (I) chloride}}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

$$[Ag(NH_3)_2]Cl + 2HNO_3 \longrightarrow AgCl + 2NH_4NO_3$$

Chromyl Chloride Test—

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow \underset{\substack{\text{Orange yellow gas}\\ \text{(chromyl chloride)}}}{2CrO_2Cl_2} + 2Na_2SO_4 + K_2SO_4 + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{Yellow}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

$$(CH_3COO)_2Pb + Na_2CrO_4 \longrightarrow \underset{\text{Yellow}}{PbCrO_4\downarrow} + 2CH_3COONa$$

2. Bromide

$$KBr + H_2SO_4 \longrightarrow KHSO_4 + HBr\uparrow$$

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2\uparrow + \underset{\text{Reddish brown}}{Br_2\uparrow}$$

$$2KBr + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + \underset{\text{Reddish brown}}{Br_2\uparrow}$$

$$NaBr + AgNO_3 \longrightarrow \underset{\text{Pale yellow}}{AgBr\downarrow} + NaNO_3$$

$$AgBr + 2NH_4OH \longrightarrow \underset{\substack{\text{Diammine}\\ \text{silver (I) bromide}}}{[Ag(NH_3)_2]Br} + 2H_2O$$

3. Iodide

$$NaI + H_2SO_4 \longrightarrow HI + NaHSO_4$$

$$H_2SO_4 + 2HI \longrightarrow \underset{\text{Violet vapours}}{I_2 \uparrow} + SO_2 \uparrow + 2H_2O$$

$$2NaI + MnO_2 + 3H_2SO_4 \longrightarrow I_2 \uparrow + 2NaHSO_4 + MnSO_4 + 2H_2O$$

$$I_2 + \text{Starch} \longrightarrow \text{Blue colour}$$

$$NaI + AgNO_3 \longrightarrow \underset{\text{Yellow}}{AgI\downarrow} + NaNO_3$$

4. Nitrate

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$4HNO_3 \longrightarrow \underset{\text{Brown}}{4NO_2 \uparrow} + O_2 \uparrow + 2H_2O$$

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2 \uparrow$$

Ring Test—

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO\uparrow$$

$$FeSO_4 + NO \longrightarrow \underset{\text{Brown ring}}{[FeSO_4.NO]SO_4 \downarrow}$$

5. Oxalate

$$Na_2C_2O_4 + 2H_2SO_4 \longrightarrow 2NaHSO_4 + H_2O + CO_2 \uparrow + CO\uparrow$$

$$2CO + O_2 \longrightarrow 2CO_2 \uparrow$$

$$Na_2C_2O_4 + CaCl_2 \longrightarrow \underset{\text{White ppt}}{CaC_2O_4 \downarrow} + 2NaCl$$

$$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4 + \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$5\begin{array}{c} COOH \\ | \\ COOH \end{array} + 5O \longrightarrow 10CO_2 \uparrow + 5H_2O$$

6. Borate

$$Na_3BO_3 + 3H_2SO_4 \longrightarrow 3NaHSO_4 + H_3BO_3$$

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\substack{\text{Ethyl borate} \\ \text{(Burns with green edged flame)}}}{(C_2H_5)_3BO_3 \uparrow} + 3H_2O$$

$(C_2H_5)_3BO_3$ may also be written as $(C_2H_5O)_3B$.

7. Fluoride

$$2NaF + H_2SO_4 \longrightarrow Na_2SO_4 + 2HF\uparrow$$

$$SiO_2 + 4HF \longrightarrow \underset{\text{Oily drops}}{SiF_4} + 2H_2O$$

$$3SiF_4 + 3H_2O \longrightarrow \underset{\text{Fluoro silicic acid}}{2H_2SiF_6} + \underset{\text{Silicic acid}}{H_2SiO_3}$$

White deposit like wax

Group III

Experiment	Observation	Inference	Confirmation
In the soln. of the mixture in *dil.* HNO_3 *add* $BaCl_2$ *soln.*	A curdy white ppt. is *formed.*	SO_4^{2-} (Sulphate)	(i) White ppt. so obtained is insoluble *in all the concentrated acids.* Take a portion of the sodium carbonate extract and acidify it with dil. HCl. Now add $BaCl_2$ soln. in it A white ppt. is formed which is insoluble in all the concentrated acids. (ii) In the soln. of the mixture add lead acetate $(CH_3COO)_2Pb$ soln. A white ppt. of $PbSO_4$ is formed.
The mixture is boiled with conc. HNO_3. Now add ammonium molybdate $(NH_4)_2MoO_4$ soln., boil and cool.	A canary yellow ppt.	PO_4^{3-} (Phosphate)*	(i) The ppt. is soluble in ammonium hydroxide and alkali hydroxides. (ii) This test can also be performed with sodium carbonate extract in the usual manner.

* Arsenic (As^{3+}) also responds to this test of phosphate. Hence phosphate must be tested as above from the filtrate of the 2nd group which is free from arsenic.

Reactions involved in the test of SO_4^{2-} ***and*** PO_4^{3-} **Radicals**

1. Sulphate

$$Na_2SO_4 + BaCl_2 \longrightarrow \underset{\text{White}}{BaSO_4} \downarrow + 2NaCl$$

$$(CH_2COO)_2Pb + Na_2SO_4 \longrightarrow \underset{\text{White}}{PbSO_4} + 2CH_3COONa$$

2. Phosphate

$$Ba_3(PO_4)_2 + 6HNO_3 \longrightarrow 3Ba(NO_3)_2 + 2H_3PO_4$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\substack{\text{Canary yellow} \\ \text{(Ammonium phospho molybdate)}}}{(NH_4)_3PO_4.12MoO_3} \downarrow + 12H_2O + 21NH_4NO_3$$

SODIUM CARBONATE EXTRACT

An extract of salt or mixture obtained after boiling the salt or mixture with an excess of sodium carbonate solution is called **extract or Sodium carbonate extract.** *It is usually prepared for testing some of the acidic radicals and also for identifying the basic radicals of insoluble substances.*

✣ PREPARATION OF SODIUM CARBONATE EXTRACT

Mix one part of the given substance with 2-3 parts by weight of solid Na_2CO_3, add nearly 15-20 c.c. distilled water and boil for about 15-20 minutes in a beaker or conical flask. Now filter* it. The filtrate so obtained is known as **sodium carbonate extract.**

The excess of sodium carbonate taken reacts with the salts or mixture of the salts whereby the cations (metals, basic, radicals) are converted into their corresponding carbonates which are insoluble in water and therefore remain as residue and the anions (acidic radicals) to their corresponding sodium salts which are water soluble and can be filtered. So that acid radicals come down in the filtrate along with the excess of sodium carbonate. Let X represent the basic radical and Y the acid radical of any salt and both are divalent. When such a salt is heated with excess of sodium carbonate, the following reactions take place.

$$XY + Na_2CO_3 \longrightarrow \underset{\text{Insoluble}}{XCO_3} + \underset{\text{Soluble}}{Na_2Y}$$

$$SnCl_2 + Na_2CO_3 \longrightarrow \underset{\text{Insoluble}}{SnCO_3} + \underset{\text{Soluble}}{2NaCl}$$

$$CaC_2O_4 + Na_2CO_3 \longrightarrow \underset{\text{Insoluble}}{CaCO_3} + \underset{\text{Soluble}}{Na_2C_2O_4}$$

Mixture ($XY, SnCl_2, CaC_2O_4$) + Na_2CO_3

Water, heat & filter

Residue

(i) $XCO_3, SnCO_3, CaCO_3$ etc.

may be

(2) Unchanged salts

Filtrate

(1) $Na_2Y, NaCl, Na_2C_2O_4$ etc.

may be

(2) Excess of Na_2CO_3 solution.

The filtrate so obtained after neutralization with suitable acid, can be used for the identification of certain acidic radicals. The acid is to be added in excess till bubbles cease to evolve. This indicates complete neutralization of the solution.

The advantages of preparing sodium carbonate extract are :

(i) It removes the basic radicals which may interfere in the systematic identification of acid radicals, by converting them into insoluble carbonates.

(ii) The identification of acid radicals becomes easier in the case of compounds insoluble in water and dil. acids.

(iii) It helps in the identification of certain basic radicals of compounds insoluble in water, conc. HCl, HNO_3 etc e.g., $BaSO_4$, $SrSO_4$ etc.

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** The residue may be dissolved in water or dil. HCl and tested for basic radicals whose salts are insoluble both in dil. and conc. HCl.

CHAPTER 4

TESTS FOR SPECIAL COMBINATIONS OF ACIDIC RADICALS

Sometimes a mixture contains combination of two or more such acidic radicals which cannot be tested by their usual tests because the presence of one radical interferes in the test of other radicals. Such cases are :

(1) Carbonate and Oxalate,
(2) Carbonate and Sulphite,
(3) Sulphide, Sulphite and Sulphate,
(4) Chloride, Bromide and Iodide,
(5) Nitrate and Bromide,
(6) Nitrate and Iodide,
(7) Nitrite and Iodide,
(8) Nitrite and Nitrate.

❖ TESTS

(1) Carbonate and Oxalate : Carbonates and oxalates both are decomposed by conc. H_2SO_4. Carbonates are also decomposed by dil. acids. Hence, oxalates can be tested only by first destroying the carbonates.

The mixture is treated with dil. H_2SO_4 if effervescence takes place and CO_2 is evolved which turns lime water milky. This confirms the presence of CO_3^{2-}. Warm the solution till no effervescence appears.

Now add MnO_2. Fresh effervescence confirms the presence of oxalate. Oxalate can also be confirmed by its usual **sodium carbonate extract test.**

$$Na_2C_2O_4 + MnO_2 + 2H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + 2CO_2\uparrow$$

(2) Carbonate and Sulphite: Sulphite interferes in the lime water test of carbonate as SO_2 also turns lime water milky. Hence, they can be tested as follows :

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{Milky}}{CaCO_3} + H_2O$$

$$Ca(OH)_2 + SO_2 \longrightarrow \underset{\text{Milky}}{CaSO_3} + H_2O$$

Take 1 part of the mixture and mix it with 2 parts of $K_2Cr_2O_7$ in a test tube and heat it with dil. H_2SO_4. Pass the evolved gas in lime water and observe the changes :

(i) Solution in test tube turns green and lime water turns milky → CO_3^{2-} and SO_3^{2-} both.

(ii) Solution in the test tube turns green and lime water remains unaffected → SO_3^{2-} only.

(iii) Solution in the test tube remains unaffected and lime water turns milky → CO_3^{2-} only.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$$

phide, Sulphite and Sulphate : When the mixture is treated with dil. H_2SO_4, it becomes difficult to identify sulphite and sulphide (if both are present together) only by the smell of gases as well as SO_2 and H_2S react together producing sulphur.

$$SO_2 + 2H_2S \longrightarrow 3S\downarrow + 2H_2O$$

Test a portion of sodium carbonate extract with freshly prepared sodium nitroprusside solution. The appearance of violet colour indicates the presence of sulphide. If a positive test is indicated remove the sulphide by adding excess of solid cadmium carbonate or lead carbonate to the sodium carbonate extract. Shake it and filter it.

Acidify the filtrate with dil. HCl, add excess of $BaCl_2$ solution. If white precipitate is obtained filter it. If this precipitate is insoluble in mineral acids then sulphate is confirmed. Now add Br_2 water in the filtrate. If again white precipitate is obtained then sulphite is confirmed.

$$Na_2S + PbCO_3 \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + Na_2CO_3$$

$$Na_2S + CdCO_3 \longrightarrow \underset{\text{Yellow ppt.}}{CdS\downarrow} + Na_2CO_3$$

$$Na_2SO_4 + BaCl_2 \longrightarrow \underset{\text{White ppt.}}{BaSO_4\downarrow} + 2NaCl$$

$$Br_2 + H_2O \longrightarrow 2HBr + O$$

$$Na_2SO_3 + O \longrightarrow Na_2SO_4$$

$$Na_2SO_4 + BaCl_2 \longrightarrow \underset{\text{White ppt.}}{BaSO_4\downarrow} + 2NaCl$$

(4) Chloride, Bromide and Iodide :

(i) First Method : Confirm chloride by **chromyl chloride test.**

Take sodium carbonate extract in a test tube, acidify it with dil. HNO_3, then add a few drops of $CHCl_3$ or CCl_4 and then chlorine water drop-by-drop with constant shaking.

(a) Orange yellow colour of $CHCl_3$ or CCl_4 layer confirms **Bromide.**

(b) Pink violet colour of $CHCl_3$ or CCl_4 layer confirms **iodide.**

(c) If iodide is present add more of chlorine water drop-by-drop and shake. If the pink colour disappears, and $CHCl_3$ or CCl_4 layer assumes orange-yellow colour, then **bromide** is also present. If no colour is developed, then bromide is absent.

(d) If CCl_4 or $CHCl_3$ layer remains colourless then both iodide and bromide are absent.

(ii) Second Method : Acidify the sodium carbonate extract with dil. H_2SO_4 and solid $NaNO_2$. Violet vapours of iodine are liberated which confirm the presence of **iodide.**

Now boil the solution till it becomes colouress and add $AgNO_3$ solution. A white ppt. of AgCl soluble in NH_4OH confirms the presence of **chloride.**

$$KI + H_2SO_4 \longrightarrow KHSO_4 + HI$$

$$2NaNO_2 + H_2SO_4 \longrightarrow 2HNO_2 + Na_2SO_4$$

$$2HNO_2 + 2HI \longrightarrow I_2\uparrow + 2NO\uparrow + 2H_2O$$

$$KBr + H_2SO_4 \longrightarrow KHSO_4 + HBr$$

$$2HBr + Na_2CO_3 \longrightarrow 2NaBr + H_2O + CO_2\uparrow$$

$$2NaBr + 4HNO_3 \longrightarrow 2NaNO_3 + 2NO_2\uparrow + 2H_2O + Br_2\uparrow$$

(5) Nitrate and Bromide : These radicals interfere in the usual tests of each other if present together.

Nitrate : Take a portion of sodium carbonate extract and acidify it with dil. H_2SO_4. Add a piece of zinc and boil it. Now add KI and starch solution. Appearance of blue colour indicates the presence of **Nitrate.**

Bromide : Take a portion of sodium carbonate extract and acidify it with dil. HNO_3 and add a few drops of $CHCl_3$ or CCl_4. Now add freshly prepared chlorine water with vigorous shaking. Bromide is present if $CHCl_3$ or CCl_4 layer turns orange yellow in colour otherwise not.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$
$$NaNO_3 + 2H \longrightarrow NaNO_2 + H_2O$$

(6) Nitrate and Iodide : Take a portion of sodium carbonate extract and acidify it with dil. H_2SO_4, Add a piece of zinc and boil it. Now add a drop of starch solution into it.

(a) A deep blue colour indicates the presence of both **nitrate and iodide.**

(b) If no blue colour is obtained, add a little **KI** solution. Now, if a blue colour appears then only **nitrate** is present.

$$2NaI + 2NaNO_2 + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + I_2\uparrow + 2NO\uparrow + 2H_2O$$

(7) Nitrite and Iodide : Take a portion of sodium carbonate extract and acidify it with dil. H_2SO_4 and add starch solution. A blue colour indicates the presence of **nitrite and iodide** in the mixture.

(8) Nitrate and Nitrite : If nitrite is present in the mixture it is not possible to test for nitrate, until nitrite is decomposed. First of all nitrite is tested by usual test. Now in a portion of sodium carbonate extract add excess of solid urea or NH_4Cl and boil it. Nitrite will be decomposed. Test it by bringing a KI and starch paper at the mouth of the test tube. If it turns blue, it means nitrite is not completely decomposed and hence add more urea or NH_4Cl till the vapours cease to give blue colour with KI and starch paper.

When the nitrite has been decomposed completely as above add to it dil. H_2SO_4 and a piece of zinc. Boil it and then add to it KI and starch solution. Blue colouration indicates **nitrate.**

$$NaNO_2 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_2$$
$$\underset{\text{Urea}}{NH_2CONH_2} + 2HNO_2 \longrightarrow 2N_2\uparrow + 3H_2O + CO_2\uparrow$$
$$NaNO_2 + NH_4Cl \longrightarrow NaCl + NH_4NO_2$$
$$NH_4NO_2 \longrightarrow N_2\uparrow + 2H_2O$$
$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$
$$HNO_3 + 2HI \longrightarrow HNO_2 + H_2O$$
$$2HNO_2 + 2KI \longrightarrow 2KOH + 2NO\uparrow + I_2\uparrow$$

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CHAPTER
5
INTERFERING ACIDIC RADICALS AND THEIR REMOVAL

Oxalate, borate, fluoride and phosphate are known as **interfering acid radicals.** Their presence in the mixture stands in the usual procedure of analysis of basic radicals after second group. Actually salts of these radicals are soluble in acid medium but are insoluble in neutral or alkaline medium. Upto 2nd group, the medium remains acidic, hence they are not precipitated and thus they do not interfere. But in and after 3rd group the medium is made akalkine by the addition of NH_4OH in which majority of the salts of these interfering radicals are insoluble. So in the 3rd group oxalates, phosphates, fluorides and borates of metals of 3rd group and subsequent groups get precipitated. The hydroxides of analysis will be disturbed therefore — it is essential to remove the interfering radicals before adding NH_4OH for the test of 3rd group and subsequent group radicals.

CAUSE OF INTERFERENCE

The interference can be explained on the basis of electrolytic dissociation theory. For example, consider magnesium phosphate which is a salt of weak acid. In acidic medium (*i.e.*, upto 2nd group) it dissociates as Mg^{2+} and PO_4^{3-}.

$$\begin{array}{rcc} Mg_3(PO_4)_2 \rightleftharpoons & 3Mg^{2+} & +\,2PO_4^{3-} \\ 6HCl \rightleftharpoons & 6Cl^- & +\,6H^+ \\ & \updownarrows & \updownarrows \\ & 3MgCl_2 & 2H_3PO_4 \\ & \text{(Highly Ionised)} & \text{(Feebly Ionised)} \end{array}$$

Hydrochloric acid dissociates to produce large number of H^+ ions which react with PO_4^{3-} ions to give feebly ionised H_3PO_4. As a result, the concentration of PO_4^{3-} ions becomes less and the ionic product of concentration of Mg^{2+} and PO_4^{3-} also becomes much less than the solubility product of magnesium phosphate. Magnesium phosphate therefore goes in the solution.

On addition of NH_4Cl and NH_4OH in the third group, medium becomes alkaline. NH_4OH dissociates to yield OH^- ions which combine with H^+ ions to give feebly ionised water. PO_4^{3-} ions are, therefore, formed and consequently the ionic product of concentration of Mg^{2+} and PO_4^{3-} ions exceeds the solubility product of $Mg_3(PO_4)_2$ resulting in its precipitation along with the hydroxides of Fe, Al and Cr (if present) *in III group.*

$$\begin{array}{rcc} 3NH_4OH \rightleftharpoons & 3OH^- & +\,3NH_4^+ \\ H_3PO_4 \rightleftharpoons & 3H^+ & +\,PO_4^{\cdots} \\ \text{Phosphoric acid} & \updownarrows & \updownarrows \\ & 3H_2O & (NH_4)_3PO_4 \\ & \text{(Feebly Ionised)} & \text{(Highly Ionised)} \end{array}$$

(i) Removal of Oxalate : Take 2 g of the mixture in a procelain dish and heat it strongly for 5-10 ml of conc. nitric acid and evaporate to dryness. ***Repeat the process four to five times when all oxalic acid gets oxidised to CO_2.***

$$MgC_2O_4 \longrightarrow MgCO_3 + CO\uparrow$$

$$MgCO_3 \longrightarrow MgO + CO_2\uparrow$$

$$2HNO_3 \longrightarrow H_2O + 2NO_2\uparrow + O$$

$$H_2C_2O_4 + O \longrightarrow 2CO_2\uparrow + H_2O$$

The residue is dissolved in a little conc. HCl diluted with water and it can be used as the original solution. ***Oxalate can also be removed from the III group precipitate in similar manner described above.***

(ii) Removal of borate : Take 2 g of the mixture in a proclain dish and add 2-4 ml of conc. HCl. Evaporate the solution to almost dryness. Repeat this operation five to six times. The residue is dissolved in little conc. HCl, diluted with water and can be used as the original solution. **It can be removed from the 3rd group precipitate in the manner described above :**

$$\underset{\text{Sodium borate}}{2Na_3BO_3} + 6HCl \longrightarrow \underset{\text{Orthoboric acid (Volatile)}}{2H_3BO_3\uparrow} + 6NaCl$$

(iii) Removal of fluoride : Fluoride is also removed by the same method as **Borate** forming hydrofluoric acid which volatilizes. It can be removed from the III group precipitate in the manner described above.

$$NaF + HCl \longrightarrow HF\uparrow + NaCl$$

(iv) Removal of Phosphate[*] **:** Boil the filtrate of 3rd group to remove H_2S. Add 2 drops of conc. HNO_3 and again boil, to convert ferrous salt into ferric one. Now add NH_4Cl and NH_4OH (excess) till a clear smell of ammonia is obtained. If no ppt. is obtained then there is no need of removing phosphate. Now in this solution, containing ppt. add to it sodium acetate and acetic acid in excess till the smell of acetic acid is noticed. If whole of the ppt. dissolves then 3rd group is supposed to be absent, if not then proceed as follows :

Residue :	Filtrate :	
III group is present. Test as usual. If no residue is left behind III group is usually absent.	Now take the filtrate or the total solution in a beaker and add[*] neutral $FeCl_3$ solution slowly with constant shaking until tea colour is obtained. Boil for 5-10 minutes and filter.	
	Filtrate : Add NH_4Cl and NH_4OH (excess) till it gives smell of ammonia. Filter it.	Residue : Reject residue of $FePO_4$ and $Fe(OH)_2$ CH_3COO and Basic ferric acetate.
	Filtrate : Test the 4th and subsequent group radicals as usual.	*Residue :* Reject it.

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1. [*] In the case of nickel, cobalt and zinc the presence of phosphate does note trouble in the usual analysis.

2. [*] Neutral Ferric Chloride Solution : Take shelf ferric chloride solution and add in it NH_4OH dropwise. Shaking each time a drop is added till a precipitate appears. This is filtered and the filtered ferric chloride solution is used as neutral ferric chloride sodium. Solid $NaHCO_3$ (pinch by pinch) may be used in place of NH_4OH. A large excess of neutral $FeCl_3$ is not to be added.

Theory of Phosphate removal : The phosphates of iron, aluminium and chromium are insoluble in acetic acid and sodium acetate buffer medium and therefore they remain in the form of precipitate while the phosphates of the metals of IV, V and VI group are soluble in this buffer medium and therefore metals of these groups remain as ions in the solution. Addition of $FeCl_3$ precipitates phosphate ion completely from the solution as $FePO_4$.

$$FeCl_3 + (NH_4)_3PO_4 \longrightarrow FePO_4 + 3NH_4Cl$$

Ferric acetate is also formed which changes to insoluble basic ferric acetate on boiling.

$$FeCl_3 + 3CH_3COONa \longrightarrow Fe(CH_3COO)_3 + 3NaCl$$

$$Fe(CH_3COO)_3 + 2H_2O \longrightarrow \underset{\text{Basic ferric acetate}}{Fe(OH)_2CH_3COO\downarrow} + 2CH_3COOH$$

Excess of ferric chloride should not be added as it peptises (dissolves) the ferric phosphate precipitate to almost a clear solution.

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CHAPTER
6
TESTS FOR BASIC RADICALS

Basic radicals can be tested by two types of tests :

(1) Dry Tests

(2) Wet Tests

Dry tests include the following :

(a) Dry heating test

(b) Charcoal cavity test

(c) Cobalt nitrate test

(d) Fusion test

(e) Flame test

(f) Borax bead test

Although these tests are limited for certain cations yet they provide valuable information and are carried out in the laboratory.

Generally bunsen burner is used as a source of heat in chemical laboratories. This burner gives luminous or non-luminous flame depending upon the amount of air supplied. The flame has following three parts.

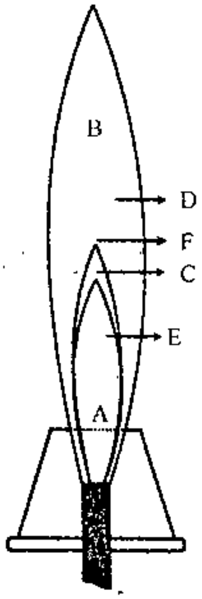

Fig. Bunsen burner-various regions of a flame

(i) The inner portion A which is blue. Practically no combustion takes place in this portion. It contains about 60% air and 40% combustible gases.

(ii) The flame mantle B in which the combustion of the mixed gases takes place. It is the hottest part of the flame.

(iii) The luminous portion C which is prominent only if insufficient air is supplied in the burner. D is the hottest part of the flame mantle B. It is used for volatilization, fusion and oxidation purposes. While E and F are the reducing part and used for reduction.

(a) Dry heating test : Take about 0.1 g of the given mixture in a dry test tube and heat it gently at first and strongly afterward over the Bunsen flame. Observe the changes taking place.

	Observation		**Inference**
(i)	Black infusible residue		Salts of Cu, Mn and Ni
(ii)	*Produces cracking* noise*		NaCl, KI, $Pb(NO_3)_2$ and $Ba(NO_3)_2$
(iii)	It sweels up		Borates, phosphates and alum
(iv)	It changes in colour		
	Hot	**Cold**	
	Yellow	white	ZnO
	Black	Brown or red	HgO
	Dark brown	Yellow	Fe_2O_3
	Yellow brown	Yellow	PbO
	Brown	Brown	SnO_2, Bi_2O_3
			CdO
(v)	It sublimes and colour of sublimate		
(a)	White		NH_4X, Hg_2Cl_2, $HgCl_2$, As_2O_3, Sb_2O_3
(b)	Yellow		HgI_2, As_2S_3
(c)	Black		Sulphides or iodides of As, Sb and Hg
(d)	Orange		Sb_2S_3
(vi)	*A gas is evolved*		
(a)	Colourless and odourless gas turning lime water milky		CO_2 from carbonates and oxalates
(b)	Colourless and odourless gas helps in burning		O_2 from nitrates
(c)	Colourless gas with a smell of burning sulphur		SO_2 from sulphites
(d)	Colourless gas with an ammonical odour		NH_3 from ammonium salts
(e)	Greenish gas		Cl_2 from chlorides
(f)	Brown gas		Oxides of nitrogen from nitrites and nitrates. Br_2 from some bromides
(g)	Violet gas		I_2 from some iodides

(ii) Charcoal cavity test

Principle : When mixture is heated in a charcoal cavity with Na_2CO_3 or $Na_2CO_3 + KNO_3$ in a reducing flame, metallic carbonate is formed which decomposes to metallic oxides. The metallic oxides reduce to metal with charcoal.

$$Pb(NO_3)_2 + Na_2CO_3 \longrightarrow PbCO_3 + 2NaNO_3$$
$$PbCO_3 \longrightarrow PbO + CO_2$$
$$PbO + C \longrightarrow Pb + CO$$

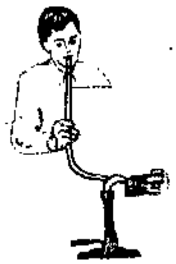

Fig. Charcoal Cavity test

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*In some crystals mother liquor remains. On heating such crystals it comes out from the crystal with cracking noise.

Experiment : Mix about 0.1 g mixture with about 0.2 g Na_2CO_3 or $Na_2CO_3 + KNO_3$ and heat it in a charcoal cavity in a reducing blow-pipe flame. Now observe the residue carefully.

	Observations	Inference
(i)	White shining bead without incrustation	Ag
(ii)	Grey metallic bead with yellow incrustation	Pb
(iii)	Red scales	Cu
(iv)	Red-brown incrustation	Cd
(v)	White bead with yellow incrustation	Bi
(vi)	White bead with bluish incrustation	Sb
(vii)	White bead	Sn
(viii)	Volatile white incrustation with garlic odour	As
(ix)	Incrustation which is yellow when hot and white when cold	Zn
(x)	Grey powder	Fe, Ni, Co and Mn

(iii) Cobalt nitrate test

Some metallic oxides (such as CaO, Al_2O_3, MgO and ZnO) do not reduce with carbon and remains as infusible residue in charcoal cavity test. When such oxides are heated with 1-2 drops of cobalt nitrate then residues of specific colour are obtained.

Principle : On heating, cobalt nitrate decomposes to cobalt oxide which produces double oxide of different colours with metallic oxides.

$$2Co(NO_3)_2 \longrightarrow 2CoO + 4NO_2 + O_2$$

$$CoO + ZnO \longrightarrow \underset{\text{Cobalt zincate (green)}}{CoO.ZnO \text{ or } CoZnO_2}$$

$$CoO + Al_2O_3 \longrightarrow \underset{\text{Cobalt aluminate (blue)}}{Co(AlO_2)_2}$$

Experiment : Mix about 0.1g mixture with about 0.2g Na_2CO_3 and heat it in a charcoal cavity in a reducing blow-pipe flame. If white residue is obtained, moisten it with 1-2 drops of $Co(NO_3)_2$ solution and heat it again in an oxidising blow pipe flame. Now observe the residue carefully.

	Observation	Inference
(i)	Bright green	Zn
(ii)	Blue (Infusible)	Al
(iii)	Blue (Fusible)	As, PO_4^{3-}, BO_3^{3-}
(iv)	Pink	Mg
(v)	Dirty green	Sn

(iv) Fusion test

Principle : The salt of chromium and manganese produce yellow and green salts respectively on fusion with solid KNO_3 and Na_2CO_3 or NaOH.

$$3KNO_3 + Cr_2(SO_4)_3 + 5Na_2CO_3 \longrightarrow \underset{\text{Yellow}}{2Na_2CrO_4} + 3KNO_2 + 3Na_2SO_4 + 5CO_2\uparrow$$

$$2KNO_3 + MnSO_4 + 2Na_2CO_3 \longrightarrow \underset{\text{Green}}{Na_2MnO_4} + 2KNO_2 + Na_2SO_4 + 2CO_2 \uparrow$$

Experiment : If mixture is not white, then fuse the mixture with about three times fusion mixture (KNO_3 and Na_2CO_3 or NaOH) in a porcelain crucible in the oxidising flame. Observe the colour developed.

(a) Green mass Mn

(b) Yellow mass Cr

If both Mn and Cr are present then green colour of Mn masks the yellow colour of Cr. In such case, the fused mass is dissolved water and add a few drops of alcohol, warm and filter. The filtrate is acidified with acetic acid and now add $AgNO_3$ solution. Red precipitate or colour indicates the presence of chromium.

$$Na_2CrO_4 + 2AgNO_3 \longrightarrow \underset{\text{Red}}{Ag_2CrO_4} + 2NaNO_3$$

(v) Flame test

Principle : Chlorides of metals when heated strongly are easily volatilized in the non-luminous flame of bunsen burner and their vapours become incandescent in the flame.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow$$
$$SrCO_3 + 2HCl \longrightarrow SrCl_2 + H_2O + CO_2 \uparrow$$
$$BaCO_3 + 2HCl \longrightarrow BaCl_2 + H_2O + CO_2 \uparrow$$

Experiment : Make a loop at the tip of the wira round the point of a pencil and clean by conc. HCl. Now pick up some substance or the group ppt. on it and hold it into the edge on a non-luminous bunsen flame. Observe the colour of flame with naked eye and then through blue glass.

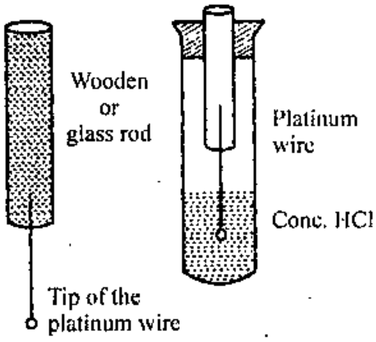


Fig. Platinum wire and its use

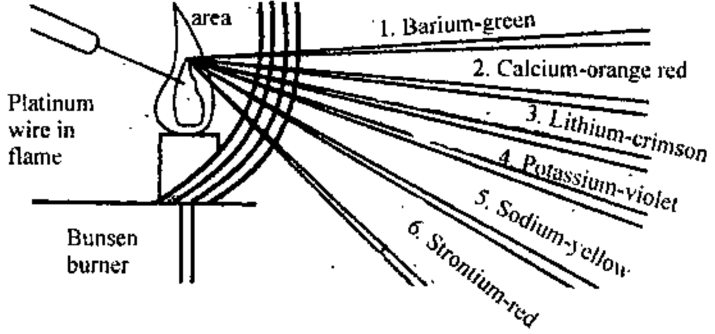
1. Clean the platinum wire needle in conc. HCl

2.Heat the platinum wire needle in flame.

3.Make paste of salt or mixture in conc. HCl with the help of a glass rod.

4. Put the platinum wire needle in paste.

5. Put the platinum wire needle again in the flame and note the colour of the flame.



Names of radicals	Colour with naked eye	Colour through blue glass
Sodium (Na)	Golden yellow	Nil
Potassium (K)	Violet	Pink or purple
Copper (Cu)	Bluish green	—

Calcium (Ca)	Brick red or dull red	Light green
Strontium (Sr)	Crimson red	Crimson red
Barium (Ba)	Apple Green	Bluish green

While performing this test one must have keen observation and bear patience.

(vi) Borax bead test

Principle : Borax ($Na_2B_4O_7.10H_2O$) on strong heating, first loses its water of crystallization and then shrinks forming a transparent glassy bead of sodium metaborate ($NaBO_2$) and boric anhydride (B_2O_3).

$$Na_2B_4O_7.10H_2O \longrightarrow Na_2B_2O_7 + 10H_2O$$

$$\underset{\text{Borax}}{Na_2B_4O_7} \longrightarrow \underbrace{2NaBO_2 + BO_3}_{\text{Transparent glassy bead}}$$

Boric anhydride, being non-volatile, displaces more volatile acidic oxides and combines with basic oxides present to form metaborates which are identified through their characteristic colours. The colour of the bead depends upon the flame in which it has been heated.

(i) Oxidising flame :

$$CuSO_4 \longrightarrow CuO + SO_3\uparrow$$

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$$

$$CuSO_4 + B_2O_3 \longrightarrow \underset{\text{(Green when hot blue when cold)}}{Cu(BO_2)_2 + SO_3\uparrow}$$

(ii) Reducing flame :

$$2Cu(BO_2)_2 + C \longrightarrow \underset{\text{Colourless}}{2CuBO_2} + B_2O_3 + CO\uparrow$$

$$2CuBO_2 + C \longrightarrow \underset{\text{Red}}{2Cu\downarrow} + B_2O_3 + CO\uparrow$$

This test is employed in the identification of coloured substances or some white substances which leave coloured residue on dry heating.

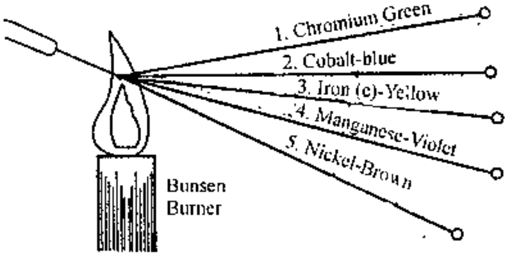
Experiment : Make a loop at the tip of the wire, heat in the flame and dip it into borax powder. Heat it strongly when borax loses its water of crystallization, swells up and is finally converted into a transparent glassy bead. Now this bead is touched with the group ppt. or the mixture under examination. Heat the bead strongly in non-luminous flame and then in luminous flame.

1 Dip the cleaned platinum wire needle in borax power.

2. Make borax bead in the flame

3. Dip borax bead in unknown salt or mixture.

4. Heat gently borax bead in the flame and observe the colour of the bead.



Observe the colour of the bead in the two cases :

Basic radicals	Oxidizing flame (Non-luminous)	Reducing flame (Luminous)
Cobalt (Co)	Deep blue	Deep blue
Nickel (Ni)	Light brown	Black
Manganese (Mn)	Amethyst violet	Colourless
Chromium (Cr)	Green	Green
Iron (Fe)	Yellow	Bottle green
Copper (Cu)	Light blue or green	Colourless or red

The bead can easily be removed by heating it in the flame and by jerking the bead. Subsequently the platinum wire may be cleaned by heating it with conc. HCl.

WET TESTS

They are most important tests because most of the radicals can only be confirmed by these tests.

Methods for the Preparation of Original Solution (O.S.)

The general procedure for preparing original solution is as follows :

(i) Boil a little mixture with water and shake well. If it does not dissolve then,

(ii) Warm the mixture with dil. HCl. Still if it does not dissolve then,

(iii) Boil 1g mixture with 5 ml. conc. HCl in 100 ml beaker for a couple of minutes then dilute with water and again boil. In most of the cases the mixture is dissolved in conc. HCl and the solution becomes transparent,

(iv) If the mixture is insoluble even in conc. HCl then solubility should be seen first in dil. HNO_3, then in conc. HNO_3,

(v) And in the last, attempt should be made with Aqua-Regia (3 parts HCl + 1 part HNO_3)

Note :

(i) The effect of the solvent on mixture should be seen for sufficient long period.

(ii) Solution, if made in HNO_3 or aqua-regia, should be evaporated to dryness and then this dry residue should be dissolved in dilute HCl or water after boiling. It is due to the fact that sulphur is precipitated on passing H_2S in the solution and thus interferes in the usual analysis.

$$2HNO_3 + H_2S \longrightarrow 2H_2O + 2NO_2\uparrow + S\downarrow$$

(iii) Least quantity of the acid should be used for the preparation of the original solution.

(iv) Sulphuric acid is never used as a solvent because it precipitates Ba, Sr, Ca and Pb as their sulphates and thus mixture containing these cations will never dissolve.

Separation of Basic Radicals into Groups

The basic radicals on the basis of solubility product and reagents are divided into the following six groups :

1. First Group : $Pb^{2+}, Ag^{+}, Hg_2^{2+}$ (ous)

2. Second Group : $Pb^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+}$ (ic)
As^{3+}, Sn^{2+} (ous), Sn^{4+} (ic) and Sb^{3+}.

3. Third Group : $Al^{3+}, Cr^{3+}, Fe^{3+}$

4. Fourth Group : $Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}$.

5. Fifth group : $Ca^{2+}, Sr^{2+}, Ba^{2+}$

6. Sixth Group : Mg^{2+}.

Other Radicals : NH_4^{+}, Na^{+}, K^{+}.

Group reagent is added to original solution one after another, till ppt. in any group is obtained. The ppt. shows the presence of any radical in that group. The complete precipitation of the radical in that group should be judged by adding sufficient amount of the group reagent otherwise it will create a great disturbance in the usual analysis of the subsequent group radicals.

It is absolutely necessary that there should be complete precipitation of metallic ions of a particular group by means of that group reagent before proceeding to the next group. If the volume of solution at any stage has become too large do not throw away a portion. Put it in a dish and evaporate it to a small volume.

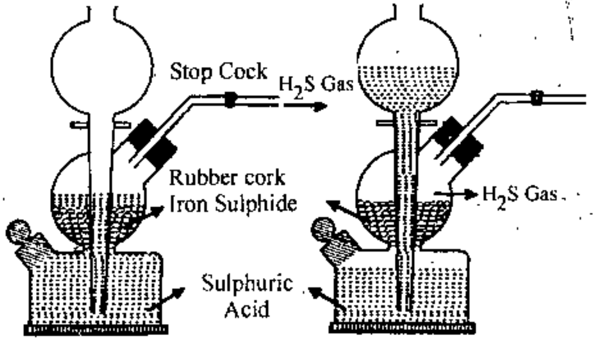
	Group	**Group Radicals**	**Group reagent**	**Salt Precipitated**	**Colour of the precipitate**
1.	First Group	Ag^+, Pb^{2+}, Hg_2^{2+} (ous)	Dil. HCl	(Chlorides) AgCl, $PbCl_2$, Hg_2Cl_2	White ppt.
2.	Second Group	Pb^{2+}, Hg^{2+} (ic), $Bi^{3+}, Cu^{2+}, Cd^{2+}$, Sb^{3+}, Sn^{2+} (ous), Sn^{4+} (ic), As^{3+}	Dil. HCl + H_2S	(Sulphides) HgS, CdS, Bi_2S_3, PbS, SnS CdS, SnS_2, As_2S_3 Sb_2S_3	Black ppt. (Sometimes red ppt.) Black or Brown ppt. Yellow ppt. Orange ppt.
3.	Third Group	$Al^{3+}, Cr^{3+}, Fe^{3+}$	After removing H_2S boil the solution with 0.5 c.c. of conc. HNO_3 and then add NH_4Cl and NH_4OH in excess.	(Hydroxides) $Al(OH)_3$ $Fe(OH)_3$ $Cr(OH)_3$	White ppt. Brown ppt. Blue or Green ppt.
4.	Fourth Group	Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}	IIIrd group filtrate + H_2S gas.	(Sulphides) ZnS MnS NiS, CoS	white or slate ppt. Chocolate-Pink ppt. Black ppt.
5.	Fifth Group	$Ba^{2+}, Sr^{2+}, Ca^{2+}$	Boil off H_2S and then add NH_4Cl + NH_4OH and $(NH_4)_2CO_3$ and shake well.	(Carbonates) $BaCO_3$, $SrCO_3$ $CaCO_3$	White ppt.
6.	Sixth Group	Mg^{2+}	Fifth group filtrate + Na_2HPO_4 solution.	(Phosphate) $MgNH_4PO_4$	White crystalline ppt.

There are Na^+, K^+ and NH_4^+ radicals also, among them Na^+ and K^+ are examined by flame test and for NH_4^+ radical special test is performed.

Hydrogen sulphide is a very important gas reagent for the precipitation of II and IV group radicals. It is preapred in the Kipp's apparatus by the action of dil. H_2SO_4 on ferrous sulphide. Through the Kipp's apparatus continuous supply of the gas is available.

Pb^{2+} (Lead), Ag^+ (Silver), Hg_2^{2+} (ous) [Mercurous*]

A white ppt. is obtained after the addition of dil. HCl to the original solution. It is filtered and washed with water and then boiled with 5-10 c.c. water. Filter and keep the filtrate for II group.



Stop Cock Open

Stop Cock Closed

Fig. 2. Kipps Apparatus

[**Note :** If solution is prepared in dil. HCl Ist group is considered to be absent.]

*Mercurous salts are partially oxidised to meruric salts and precipitated in second group as mercuric sulphide.

Filtrate : Obtained after dissolving the ppt. in hot water ($PbCl_2$). Divide the filtrate in three parts :	**Precipitate :** (Hg_2Cl_2, AgCl) Shake the ppt. with NH_4OH and filter.	
	Filtrate [$Ag(NH_3)_2Cl$] Divide this in three parts :	Precipitate (Hg + $HgNH_2Cl$)
(i) Cool first part under tap water White shining crystals ($PbCl_2$).	(i) To first part add dil. HNO_3 white ppt. of silver chloride.	(Black) Evaporate this ppt. with aqua-regia ($3HCl + HNO_3$) to dryness, then dilute with hot water and divide into two part :
(ii) Hot filtrate + $CH_3COOH + K_2CrO_4 \rightarrow$ yellow ppt. ($PbCrO_4$)	(ii) To the second part add K_2CrO_4 and $CH_3COOH \rightarrow$ Brick red ppt. (Ag_2CrO_4)	(i) To the first part add $SnCl_2 \rightarrow$ white or slate coloured ppt.
(iii) Hot filtrate + KI yellow ppt. (PbI_2)	(iii) To the third part add KI$\rightarrow$ yellow ppt. (AgI)	(ii) To the II part add Cu turnings. A white or slate coloured deposit on Cu turnings.
Pb^{2+} (Lead) confirmed.	*Ag^+ (silver) confirmed.*	*Hg^{2+} (Mercurous) confirmed.*

Note :

(1) If mixture contains *Sb, Bi* and *Sn* then white turbidity is obtained by the addition of dil HCl. But these are easily soluble in excess of HCl.

(2) Concentrated HCl should not be used because

(a) $PbCl_2$ forms H_2PbCl_4 which is soluble in water.

(b) Complete precipitation of Pb and Cd does not take place in group II.

(c) Barium of group V may precipitate as $BaCl_2$.

(d) Borates may yield boric acid which is also white crystalline precipitate and it is also soluble in water.

REACTIONS INVOLVED IN THE TESTS OF GROUP I RADICALS

Lead (Pb^{2+}) :

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 \downarrow + 2HNO_3$$

$$PbCl_2 + 2KI \longrightarrow \underset{\text{Yellow}}{PbI_2 \downarrow} + 2KCl$$

$$PbCl_2 + K_2CrO_4 \longrightarrow \underset{\text{Yellow}}{PbCrO_4 \downarrow} + 2KCl$$

$$PbCl_2 + H_2SO_4 \longrightarrow \underset{\text{White}}{PbSO_4 \downarrow} + 2HCl$$

Silver (Ag^+) :

$$AgNO_3 + HCl \longrightarrow \underset{\text{White}}{AgCl \downarrow} + HNO_3$$

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$$

$$[Ag(NH_3)_2]Cl + 2HNO_3 \longrightarrow \underset{\text{White}}{AgCl \downarrow} + 2NH_4NO_3$$

Mercurous (Hg_2^{2+}) :

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow \underset{\text{White}}{Hg_2Cl_2 \downarrow} + 2HNO_3$$

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Black}}{[HgNH_2Cl + Hg]} + NH_4Cl + 2H_2O$$

$$\underbrace{HNO_3 + 3HCl}_{\text{Aqua regia}} \longrightarrow 2H_2O + NOCl + 2Cl$$

$$Hg + 2Cl \longrightarrow HgCl_2$$

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White}}{Hg_2Cl_2 \downarrow} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey}}{2Hg \downarrow} + SnCl_4$$

ANALYSIS OF SECOND GROUP

This group is divided into two groups :

(i) II A Group (Copper group)

(ii) II B Group (Arsenic group)

Copper group consists of Pb^{2+}, Hg^{2+} **(ic),** Bi^{3+}, Cu^{2+} **and** Cd^{2+} **while arsenic group** contains Sb^{3+}, As^{3+}, Sn^{2+} (ous) and Sn^{4+} (ic).

In this group, H_2S is passed in a little portion of the Ist group filtrate. If precipitate does not appear, then it should be diluted with water, warmed and then H_2S is passed again in it for a period of at least 50 second. If ppt. does not come II group is taken to be absent. If ppt. appears H_2S is passed in the rest of the solution. It is filtered and washed well with water. The filtrate is kept for **III group.**

Different radicals give the following coloured precipitates.

HgS	Black (Sometimes red)	Cds	Yellow
PbS	Black (or Brown)	Ag_2S_3	Yellow
Bi_2S_3	Brown	SnS_2	Yellow
CuS	Black (or Brown)	Sb_2S_3	Orange
SnS	Black		

The washed precipitate is warmed with a little yellow ammonium sulphide* solution and filtered.

Residue	**Filtrate**
(II A Group)	(II B Group)
Hg (ic), Pb, Bi, Cu, Cd	As, Sb, Sn (ous), Sn ic)

II A Copper group—Residue is washed with water and then treated with 50% HNO_3, boiled, cooled and filtered.

<table>
<tr><td colspan="2">Black residue : It may be HgS. Dissolve it in aqua-regia and evaporate it to almost dryness. Add water and divide it into two parts :</td><td>Filtrate : It may Contain the nitrates of Pb, Bi, Cu, Cd, Take a little part of it, add dil. H_2SO_4. If a white ppt. appears then add alcohol and dil. H_2SO_4 to the whole filtrate and filter.</td></tr>
<tr><td></td><td>White residue : It may contain $PbSO_4$. Dissolve this residue in conc. solution of CH_3COONH_4 and add K_2CrO_4 → Yellow ppt.</td><td>Filtrate : It may contain Bi, Cu and Cd sulphates or nitrates. Add to it excess of NH_4OH and filter :</td></tr>
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*Yellow ammonium sulphide contains excess of sulphur dissolved in colourless ammonium sulphide solution and is expressed as $(NH_4)_2S_x$.

(i) To first part add $SnCl_2$ soln. → white or grey ppt.		**White residue :** It may be $Bi(OH)_3$ Dissolve the residue in the least quantity of conc. HCl. Divide it into two parts :	**Filtrate :** It may contain Cu and Cd. If it is blue, Cu is there, if it is colourless Cu is absent.
(ii) To second part add Cu turnings. Whitish deposit on Cu.	Pb^{2+} *(Lead confirmed).*	(i) To first part add excess of water → white ppt.	**First method :** (i) CH_3COOH in excess + $[K_4[Fe(CN)_6]$ → brown coloured ppt. Cu^{2+} (Copper) confirmed.
		(ii) To second part add sod. stannite soln.→black ppt.	
Hg^{2+} (ic) (Mercuric) confirmed.			(ii) To second part add KCN soln. till the filtrate becomes colourless. Now pass H_2S → yellow ppt. Cd^{2+} (Cadmium) confirmed.
		Bi^{3+} (Bismuth) confirmed.	
		Second Method : Add conc. HCl and pass H_2S and filter.	
		Black residue : Cu^{2+} (Copper) confirmed.	**Filtrate :** Dilute it and pass H_2S again → yellow ppt. Cd^{2+} (Cadmium) confirmed.
		Third method : Add 10 c.c. of conc. HCl and $FeSO_4$ soln. and filter.	
		Residue : Cu^{2+} (Copper confirmed)	Filtrate : Dilute it with water and pass H_2S gas → yellow ppt. Cd^{2+} (Cadmium) confirmed.

II B ARSENIC GROUP

Dilute the filtrate with water obtained aftet treating the second group ppt. with yellow ammonium sulphide and dil. HCl (in excess). A coloured ppt. indicates the presence of arsenic group radicals but if a white ppt. is obtained it shows the absence of arsenic group radicals and reject it. Filter the ppt. and boil it with conc. HCl and filter.

Yellow residue :	**Filtrate :**
It may be As_2S_3. Dissolve it in conc. HNO_3 and amm. molybdate solution and heat → yellow ppt.	It may contain chlorides of Sb and Sn. Sb and Sn may be confirmed by two different methods :

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[*] By the addition of NaOH in excess in $SnCl_2$ sodium stannite is obtained.

As^{3+} (Arsenic) confirmed.	**First method :** Make the filtrate just alkaline by adding NH_4OH soln. Add 1-2 g solid oxalic acid, boil and pass H_2S gas. Filter if a ppt. is obtained.	
	Orange residue : It may be Sb_2S_3. *Dissolve it in least quantity of conc.* HCl, dilute it with water → White ppt. or turbidity.	**Filtrate :** It may contain Sn. To it add NH_4OH to make it alkaline and pass H_2S gas → Dirty yellow ppt.
	Sb^{3+} (Antimony confirmed).	*Sn^{4+} (Stannic confirmed).*
	Second Method : To the filtrate add iron filings and heat for five minutes and filter.	
	Black residue : Sb^{3+} (Antimony confirmed).	**Filtrate :** It may contain $SnCl_2$. To it add $HgCl_2$ soln. → White or grey ppt. *Sn^{2+} (Stannous confirmed).*

Note :

(1) Original solution should not be prepared in HNO_3 because it oxidizes H_2S into S.

(2) H_2S gas should be passed slowly in hot solution to get crystalline precipitate.

(3) If mixture consists Hg^{2+} radical then first we get white ppt. ($HgCl_2 . HgS$) which changes to yellow, brown and at last black with increasing concentration of H_2S gas.

(4) For the separation of group II A and B sub groups colourless ammonium sulphide or NaOH solution *should not be used because SnS is insoluble in these solvents.*

(5) Sometimes the ppt. of As_2S_5 dissolves with difficulty in conc. HNO_3. In such case As_2S_5 should be dissolved in $KClO_3$ and 5% HCl. Now this solution should be evaporated and dissolve the residue in conc. HNO_3.

REACTIONS INVOLVED IN THE TEST OF GROUP II RADICALS

Sometimes in second group, white or a light yellow ppt. is observed which is due to sulpur precipitaed from H_2S by excess of HNO_3 or other oxidizing agents *e.g.* (NO_2^-, SO_3^{2-}, Fe^{3+}).

$$2HNO_3 + 3H_2S \longrightarrow 4H_2O + 2NO\uparrow + 3S\downarrow.$$

$$2NaNO_2 + 2HCl + H_2S \longrightarrow 2NaCl + 2NO\uparrow + 2H_2O + S\downarrow$$

$$Na_2SO_3 + 2HCl + 2H_2S \longrightarrow 2NaCl + 3H_2O + 3S\downarrow$$

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S\downarrow$$

(1) Mercuric (Hg^{2+}) :

$$HgCl_2 + H_2S \longrightarrow \underset{\text{Black}}{HgS\downarrow} + 2HCl$$

$$3HgS + 2HNO_3 + 6HCl \longrightarrow 3HgCl_2 + 2NO\uparrow + 3S\downarrow + 4H_2O$$

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White}}{HgCl_2\downarrow} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey}}{2Hg\downarrow} + SnCl_4$$

(2) Lead (Pb^{2+}) :

$$PbCl_2 + H_2S \longrightarrow \underset{\text{Black}}{PbS\downarrow} + 2HCl$$

$$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO\uparrow + 3S\downarrow + 4H_2O$$

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow \underset{\text{White}}{PbSO_4\downarrow} + 2HNO_3$$

$$2PbSO_4 + 2CH_3COONH_4 \longrightarrow (NH_4)_2Pb(SO_4)_2 + (CH_3COO)_2Pb$$

$$(CH_3COO)_2Pb + K_2CrO_4 \longrightarrow \underset{\text{Yellow}}{PbCrO_4\downarrow} + 2CH_3COOK$$

(3) Bismuth (Bi^{3+}) :

$$3BiCl_3 + 3H_2S \longrightarrow \underset{\text{Brown}}{Bi_2S_3\downarrow} + 6HCl$$

$$Bi_2S_3 + 8HNO_3 \longrightarrow 2Bi(NO_3)_3 + 2NO\uparrow + 3S\downarrow + 4H_2O$$

$$Bi(NO_3)_3 + 3NH_4OH \longrightarrow \underset{\text{White}}{Bi(OH)_3\downarrow} + 3NH_4NO_3$$

$$Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$$

$$BiCl_3 + H_2O \longrightarrow \underset{\text{Milky}}{BiOCl\downarrow} + 2HCl$$

$$2BiCl_3 + 3Na_2SnO_2 + 6NaOH \longrightarrow \underset{\text{Black}}{2Bi\downarrow} + 3Na_2SnO_3 + 6NaCl + 3H_2O$$

(4) Copper (Cu^{2+}) :

$$CuCl_2 + H_2S \longrightarrow \underset{\text{Black}}{CuS} + 2HCl$$

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 3S\downarrow + 4H_2O$$

$$Cu(NO_3)_2 + 4NH_4OH \longrightarrow \underset{\text{Blue}}{[Cu(NH_3)_4](NO_3)_2} + 4H_2O$$

$$[Cu(NH_3)_4](NO_3)_2 + 4CH_3COOH \longrightarrow Cu(NO_3)_2 + 4CH_3COONH_4$$

$$2Cu(NO_3)_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Chocolate}}{Cu_2[Fe(CN)_6]} + 4KNO_3$$

(5) Cadmium (Cd^{2+}) :

$$CdCl_2 + H_2S \longrightarrow \underset{\text{Yellow}}{CdS\downarrow} + 2HCl$$

$$CdS + 2HCl \longrightarrow CdCl_2 + H_2S\uparrow$$

$$CdCl_2 + 2NH_4OH \longrightarrow Cd(OH)_2\downarrow + 2NH_4Cl$$

$$Cd(OH)_2 + 2NH_4Cl + 2NH_4OH \longrightarrow [Cd(NH_3)_4]Cl_2 + 4H_2O$$

Separation of Copper (Cu^{2+}) and Cadmium (Cd^{++})

$$CuSO_4 + 2KCN \longrightarrow K_2SO_4 + Cu(CN)_2$$

$$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 + (CN)_2\uparrow$$

$$Cu_2(CN)_2 + 6KCN \longrightarrow 3K_2[Cu(CN)_4]$$

$$CdSO_4 + 2KCN \longrightarrow Cd(CN)_2 + K_2SO_4$$

$$Cd(CN)_2 + 2KCN \longrightarrow K_2[Cd(CN)_4]$$

The complexes of Cu^{2+} and Cd^{2+} ions ionise as :

Primary

$$K_2[Cu(CN)_4] \rightleftharpoons 3K^+ + [Cu(CN)_4]^{3-}$$

Secondary : $$[Cu(CN)_4]^{3-} \rightleftharpoons Cu^+ + 4CN^-$$

(less ionisation)

Primary : $$K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + [Cd(CN)_4]^{2-}$$

(less ionisation)

Secondary : $$[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^-$$

(more ionisation)

Thus when H_2S is passed through a solution containing these complexes, solubility product of CdS only is exceeded and therefore it gets precipitated.

Arsenic (As^{3+})

$$2AsCl_3 + 3H_2S \longrightarrow \underset{\text{Yellow}}{As_2S_3 \downarrow} + 6HCl$$

$$As_2S_3 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3AsS_3$$

$$2(NH_4)_3AsS_3 + 6HCl \longrightarrow \underset{\text{Yellow}}{As_2S_3 \downarrow} + 6NH_4Cl + 3H_2S\uparrow$$

As_2S_3 dissolves in nitric acid forming arsenic acid, H_3AsO_4.

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{Yellow}}{(NH_4)_3AsO_4.12MoO_3 \downarrow} + 21NH_4NO_3 + 12H_2O$$

Antimony (Sb^{3+})

$$2SbCl_3 + 3H_2S \longrightarrow \underset{\text{Orange}}{Sb_2S_3 \downarrow} + 6HCl$$

$$Sb_2S_3 + 3(NH_4)_2S \longrightarrow 2(NH_4.)_3SbS_3$$

$$Sb_2S_3 + 3(NH_4)_2S_2 \longrightarrow 2(NH_4)_3SbS_4 + S\downarrow$$

$$2(NH_4)_3SbS_3 + 6HCl \longrightarrow Sb_2S_3 \downarrow + 6NH_4Cl + 3H_2S\uparrow$$

$$2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb_2S_5 \downarrow + 6NH_4Cl + 3H_2S\uparrow$$

$$Sb_2S_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S\uparrow$$

$$Sb_2S_5 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S\uparrow + 2S\downarrow$$

$$SbCl_3 + H_2O \longrightarrow \underset{\text{Milky}}{SbOCl\downarrow} + 2HCl$$

$$2SbCl_3 + 3Fe \longrightarrow 3FeCl_2 + \underset{\text{Black}}{2Sb\downarrow}$$

Tin (Sn^{2+}, Sn^{4+})

$$SnCl_2 + H_2S \longrightarrow SnS\downarrow + 2HCl$$

$$SnCl_4 + 2H_2S \longrightarrow \underset{\text{Yellow}}{SnS_2 \downarrow} + 4HCl$$

SnS $\longrightarrow$ Insoluble in ordinary amm. sulphide but soluble in yellow amm. sulphide.

SnS_2 $\longrightarrow$ Soluble in ordinary amm. sulphide.

$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3$$

$$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2SnS_3$$

$$(NH_4)_2SnS_3 + 2HCl \longrightarrow \underset{\text{Yellow}}{SnS_2 \downarrow} + 2NH_4Cl + H_2S$$

$$SnS_2 + 4HCl \longrightarrow SnCl_4 + 2H_2S\uparrow$$

$$SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_2$$

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White}}{Hg_2Cl_2 \downarrow} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey}}{2Hg \downarrow} + SnCl_4$$

ANALYSIS OF THIRD GROUP (Fe^{3+}, Al^{3+}, Cr^{3+})

Boil off H_2S Completely (test with lead acetate paper for this) from filtrate of the second group and concentrate it. Boil it again with 1 ml of conc. HNO_3 as to convert all ferrous salt (if present) to ferric salt otherwise ferrous hydroxide will not be completely precipitated in this group and thus will interfere in IVth group giving a black precipitate of FeS. Then after cooling add NH_4Cl and NH_4OH in excess) till the solution distinctly gives smell of ammonia.

Filter and wash the precipitate with water and keep the filtrate for IV group. Dissolve the ppt. in 2 ml of H_2O_2, or in excess of Br_2 water + NaOH, boil* it and filter.

$Fe(OH)_3$—Brown ppt.

$Al(OH)_3$—White ppt.

$Cr(OH)_3$—Green or light bluish green ppt.

Residue : Brown ppt. It may contain $Fe(OH)_3$ and MnO(OH).	**Filtrate :** It may contain $NaAlO_2$ and Na_2CrO_4. If it is yellow Na_2CrO_4 will be there otherwise $NaAlO_2$ may be there. Divide it into three parts.	
Divide the precipitate into two parts :	(a) First part + CH_3COOH + $(CH_3COO)_2Pb$ → yellow ppt.	To this part add NH_4Cl and Boil → White gelatinous ppt.
(i) PPt. + conc. HNO_3 + PbO_2. Boil and cool by adding little water → Light pink, violet colour.	(b) Second part + $AgNO_3$ → Brick red ppt.	Al^{3+} (Aluminium) confirmed.
Mn^{2+} (Manganese) confirmed. (ii) Dissolve the precipitate in dil HNO_3 or dil. HCl and divide it into two parts :	*Cr^{3+} (Chromium) confirmed.*	
(a) To first part add $K_4[Fe(CN)_6]$ → deep blue colour or ppt.		
(b) To second part add ammonium sulphocyanide → Blood red colour		
Fe^{3+} (Ferric confirmed).		

Note :

(1) *H_2S should be completely removed before adding conc. HNO_3; otherwise it will be oxidised into H_2SO_4 and thus precipitates the V group radicals as sulphates.*

(2) *Sometimes Mn also precipitates as MnO.OH (Brown ppt.) in this group so its test becomes necessary.*

(3) *After boiling off H_2S addition of conc. HNO_3 is essential so as to convert all ferrous salts into ferrric salts.*

(4) *Addition of NH_4Cl before NH_4OH is absolutely essential otherwise the basic radicals of IV and V group precipitate out as hydroxide in this group.*

(5) *Interfering radicals should be removed before proceeding in this group.*

REACTIONS INVOLVED IN THE TEST OF GROUP III RADICALS

$$2FeCl_2 + 8HNO_3 \longrightarrow 2Fe(NO_3)_3 + 4HCl + 2NO_2\uparrow + 2H_2O$$

Iron (Fe^{3+})

$$FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{Brown}}{Fe(OH)_3\downarrow} + 3NH_4Cl$$

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

$$2FeCl_3 + 6NH_4CNS \longrightarrow \underset{\text{Blood red}}{2Fe(CNS)_3} + 6NH_4Cl$$

or

$$FeCl_3 + 6NH_4CNS \longrightarrow \underset{\text{Blood red}}{(NH_4)_3[Fe(CNS)_6]} + 3NH_4Cl$$

---

*Boiling at this stage is essential since this ensures the complete oxidation of Fe^{2+} to Fe^{3+}.

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Deep blue}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

Aluminium (Al^{3+}) :

$$AlCl_3 + 3NH_4OH \longrightarrow \underset{\text{White}}{Al(OH)_3} \downarrow + 3NH_4Cl$$

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow \underset{\text{White}}{Al(OH)_3} \downarrow + NH_3 \uparrow + NaCl$$

Chromium (Cr^{3+}) :

$$CrCl_3 + 3NH_4OH \longrightarrow \underset{\text{Green}}{Cr(OH)_3} \downarrow + 3NH_4Cl$$

$$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow \underset{\text{Yellow}}{2Na_2CrO_4} + 8H_2O$$

$$2NaOH + Br_2 \longrightarrow NaBr + NaOBr + H_2O$$

$$2Cr(OH)_3 + 4NaOH + 3NaOBr \longrightarrow 2Na_2CrO_4 + 5H_2O + 3NaBr$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\text{Yellow}}{PbCrO_4} \downarrow + 2CH_3COONa$$

ANALYSIS OF FOURTH GROUP (Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+})

Some of the characteristics of the basic radicals of fourth group are tabulated as follows :

	Forms of the salts	Nickel (Ni^{2+})	Cobalt (Co^{2+})	Zinc (Zn^{2+})	Manganese (Mn^{2+})
1.	Sulphide	Black (NiS)	Black (CoS)	White or Grey (ZnS)	Light Pink (MnS)
2.	Salts (Dry)	Green	Pink	White	White
3.	Salt solution in water	Green	Pink	Colourless	Colourless, Light pink, pink violet.

Pass H_2S continuously in the hot ammonical filtrate of III Group. Formation of the precipitate shows the presence of fourth group. Filter and wash the ppt. and keep the filtrate for fifth group.

Different radicals give the following coloured precipitates :

NiS	Black	ZnS	White or grey
CoS	Black	MnS	Light pink

Ppt. is treated with dil. HCl and filtered :

Residue : It may contain Nis and CoS. Dissolve it in aqua-regia ($3HCl + HNO_3$) and evaporate to dryness + water and divide it in a number of parts.		**Filtrate :** It may contain $MnCl_2$ and $ZnCl_2$. Boil off H_2S, and excess of NaOH and filter.	
To one part add NH_4OH (in excess) + dimethyl glyoxime → Scarlet red ppt.	(i) To one part add NH_4OH (in excess) + CH_3COOH (in excess) + KNO_2 Soln. → Yellow crystalline ppt.	Residue : White turning brown due to oxidation. (i) Dissolve the residue in conc. HNO_3 and add PbO_2. Boil for 2-3 minutes and dilute with water → Pink or violet colour.	Filtrate : It may contain zinc. Pass H_2S in the filtrate → A White grey ppt.

Ni^{++} (Nickel confirmed.)	(ii) To other part in a porcelain dish + $NaHCO_3$ solid (in excess) + Br_2 water. Shake for some time → Apple green colour (in cold)	(ii) Residue + oxidising fusion mixture (KNO_3 + Na_2CO_3) → heat strongly on a procelain dish → Green mass is obtained which dissolves to give pink solution.	*Zn^{2+} (Zinc) confirmed.*
	Co^{2+} (cobalt confirmed.	*Mn^{2+}* (Manganese confirmed)	
	Apple green colour in cold changing to black on heating →		
	Co^{2+} (cobalt and *Ni^{2+}* nickel both confirmed.)		

Note :

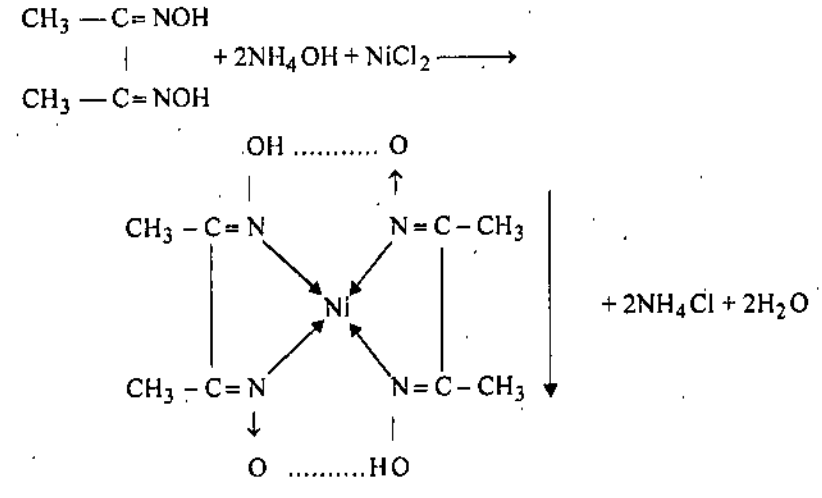
1. H_2S must be passed in hot solution otherwise ZnS and MnS will form colloidal solution.
2. H_2S should be not be passed for a very long time otherwise NiS and MnS will turn into colloidal solution.

Reactions Involved in the Test of Group IV Radicals

Nickel (Ni^{2+}) :

$$NiCl_2 + H_2S \longrightarrow \underset{\text{Black}}{NiS\downarrow} + 2HCl$$

$$3NiS + 2HNO_3 + 6HCl \longrightarrow 3NiCl_2 + 2NO\uparrow + 4H_2O + 3S\downarrow$$



Red

Cobalt (Co^{2+}) :

$$CoCl_2 + H_2S \longrightarrow \underset{\text{Black}}{CoS\downarrow} + 2HCl$$

$$3CoS + 2HNO_3 + 6HCl \longrightarrow 3CoCl_2 + 2NO\uparrow + 3S\downarrow + 4H_2O$$

$$COCl_2 + 2KNO_2 \longrightarrow Co(NO_2)_2 + 2KCl$$

$$CO(NO_2)_2 + 4KNO_2 \longrightarrow K_4[Co(NO_2)_6]$$

$$2K_4[Co(NO)_2)_6] + 2CH_3COOH + O \xrightarrow{\text{Air}} \underset{\text{Yellow}}{2K_3[Co(NO_2)_6]\downarrow} + 2CH_3COOK + H_2O$$

Test of Co and Ni with $NaHCO_3$—Br_2 water (Palit's Test) : When the solution of cobalt and nickel salts is treated with excess of sodium bicarbonate, cobalt forms a pink coloured complex sod.

cobalto-carbonate which on treatment with bromine water is oxidized to green coloured sodium-cobalti-carbonate. Nickel does not form a complex with $NaHCO_3$ but on heating with bromine water, it is oxidized to black nickelic oxide.

$$CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$$

$$Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4[Co(CO_3)_3] + 3H_2O + 3CO_2\uparrow$$

$$2Na_4[Co(CO_3)_3] + Br_2 \longrightarrow \underset{\text{Green}}{2Na_3[Co(CO_3)_3} + 2NaBr$$

$$Br_2 + H_2O \longrightarrow 2HBr + O$$

$$NiCl_2 + 2NaHCO_3 \longrightarrow NiCO_3 + 2NaCl + H_2O + CO_2\uparrow$$

$$2NiCO_3 + 3H_2O + O \longrightarrow 2Ni(OH)_3\downarrow + 2CO_2\uparrow$$

$$2Ni(OH)_3 \longrightarrow \underset{\text{Black}}{Ni_2O_3}\downarrow + 3H_2O$$

Manganese (Mn^{2+}) :

$$MnCl_2 + H_2S \longrightarrow \underset{\text{Buff}}{MnS}\downarrow + 2HCl$$

$$MnS + 2HCl \longrightarrow MnCl_2 + H_2S\uparrow$$

$$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2\downarrow + 2NaCl$$

$$2Mn(OH)_2 + O \longrightarrow \underset{\text{Brown}}{2MnO(OH)}\downarrow + H_2O$$

$$MnO.(OH) + 2PbO_2 + 4HNO_3 \longrightarrow \underset{\text{Pink}}{2Pb(NO_3)_2} + 2H_2O + HMnO_4$$

Zinck (Zn^{2+}) :

$$ZnCl_2 + H_2S \longrightarrow \underset{\text{White}}{ZnS}\downarrow + 2HCl$$

$$ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S\uparrow$$

$$ZnCl_2 + 2NaOH \longrightarrow \underset{\text{White}}{Zn(OH)_2}\downarrow + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$$

$$Na_2ZnO_2 + H_2S \longrightarrow \underset{\text{White}}{ZnS}\downarrow + 2NaOH$$

ANALYSIS OF FIFTH GROUP (Ba^{2+}, Sr^{2+}, Ca^{2+})

After boiling off H_2S, concentrate the fourth group filtrate of one-third of its original volume. Then add NH_4OH and $(NH_4)_2CO_3$ *(Never boil at this stage)*. Formation of white precipitate shows the presence of fifth group. Filter and wash the ppt. Keep the filtrate for the radical of sixth group.

Dissolve the precipitate in least quantity of acetic acid and boil for a few minutes. Take a small part of this soln. and add K_2CrO_4 soln. If a yellow ppt. appears, heat the whole solution with excess of K_2CrO_4 so as to precipitate barium completely. If no ppt. appears on adding K_2CrO_4 soln., then do not add K_2CrO_4 solution to the whole soln. Now proceed as follows :

Residue : Yellow ppt. $BaCrO_4$	**Filtrate :** It may contain $(CH_3COO)_2Sr$ and $(CH_3COO)_2Ca$. To it add $(NH_4)_2SO_4$ soln. in excess and boil and filter it.	
Ba^{++} (Barium confirmed.)	**Filtrate :** It may contain Ca. To it add $(NH_4)_2C_2O_4$ soln. White ppt.	**Residue :** White ppt. ($SrSO_4$)
	Ca^{2+} (Calcium confirmed)	*Sr^{2+}* (Strontium confirmed)

Note :

(1) It is better to use saturated solution of $(NH_4)_2SO_4$ to detect Sr^{2+} radical. After addition of the reagent, wait for a few minutes to see if a precipitate of $SrSO_4$ is obtained.

(2) Sometimes calcium does not precipitate in its group due to the formation of $Ca(HCO_3)_2$ on addition of $(NH_4)_2CO_3$ to the concentrated filtrate of IV group. As $Ca(HCO_3)_2$ is soluble and so it passes into the filtrate of V group. Hence filtrate of V group must be tested for calcium before proceeding to VI group.

(3) They are tested in the order BSC (Barium Strontium, Calcium).

REACTIONS INVOLVED IN THE TEST OF GROUP V RADICALS

Barium (Ba^{2+})

$$BaCl_2 + (NH_4)_2CO_3 \longrightarrow \underset{\text{White}}{BaCO_3} \downarrow + 2NH_4Cl$$

$$BaCO_3 + 2CH_3COOH \longrightarrow \underset{\text{Barium acetate}}{(CH_3COO)_2Ba} + H_2O + CO_2 \uparrow$$

$$(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow \underset{\text{Yellow}}{BaCrO_4} \downarrow + 2CH_3COOK$$

Strontium (Sr^{2+})

$$SrCl_2 + (NH_4)_2CO_3 \longrightarrow \underset{\text{White}}{SrCO_3} \downarrow + 2NH_4Cl$$

$$SrCO_3 + 2CH_3COOH \longrightarrow \underset{\text{Strontium acetate}}{(CH_3COO)_2Sr} + H_2O + CO_2 \uparrow$$

$$(CH_3COO)_2Sr + (NH_4)_2SO_4 \longrightarrow \underset{\text{White}}{SrSO_4} \downarrow + 2CH_3COONH_4$$

Calcium (Ca^{2+})

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow \underset{\text{White}}{CaCO_3} \downarrow + 2NH_4Cl$$

$$CaCO_3 + 2CH_3COOH \longrightarrow \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + H_2O + CO_2 \uparrow$$

$$(CH_3COO)_2CS + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{White}}{CaC_2O_4} \downarrow + 2CH_3COONH_4$$

ANALYSIS OF SIXTH GROUP (Mg^{2+})

Heat the fifth group filtrate with ammonium oxalate and discard the precipitate, if it comes. Add 2-3 c.c. of NH_4OH and excess of disodium hydrogen phosphate (Na_2HPO_4) to the filtrate. Shake the solution with a glass rod. After a few minutes a white crystalline precipitate results. Mg^{2+} is confirmed.

Magnesium (Mg^{2+})

$$Mg(NO_3)_2 + Na_2HPO_4 + NH_4OH \longrightarrow \underset{\text{White}}{Mg(NH_4)PO_4} \downarrow + 2NaNO_3 + H_2O$$

TEST FOR AMMONIUM (NH_4^+) RADICAL

(i) Heat a little mixture with 2-3 c.c. NaOH in a test-tube. A characteristic smell (NH_3) is obtained. On bringing a glass rod dipped in conc. HCl on the mouth of the test-tube, enormous white fumes are produced.

(ii) On adding *Nessler's reagent to the solution of the mixture → Brown colour or precipitate. The test is extremely sensitive and very characteristic.

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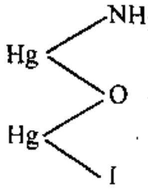
* Nessler's Reagent : Add KI in $HgCl_2$ solution until the red reprecipitate (HgI_2) formed, is dissolved (K_2HgI_4). Now shake it with NaOH. This is Nessler's reagent.

Ammonium (NH_4^+)

$$NH_4Cl + NaOH \longrightarrow NaCl + H_2O + NH_3\uparrow$$

$$NH_3 + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl\uparrow}$$

$$\underbrace{2K_2HgI_4 + 3NaOH}_{\text{Nessler's reagent}} + NH_4OH \longrightarrow .$$



$+ 4KI + 3NaI + 3H_2O$

Brown iodide of Million's base

TEST FOR Na^+ AND K^+.

No wet test to detect Na^+ and K^+ is there in B.Sc. course. Their detection is done by flame-test.

Golden flame—*Na^+ (Sodium) confirmed.*

Violet flame—*K^+ (Potassium) confirmed.*

Note : Detection of Na^+ and K^+ is rarely done in laboratories.

HOW TO WRITE IN PRACTICAL NOTE BOOK ?

Exercise : To analyse the given mixture* Dated .... No. ....

Experiment	Observation	Inference
Acid Radicals :		
(i) Mixture and dil. H_2SO_4	Colourless gas with brisk effervescence.	CO_3^{2-} possible.
(ii) Passed this coming gas into lime water	Lime water turned milky	CO_3^{2-} confirmed.
(iii) Mixture + conc. H_2SO_4 heated strongly.	A penetrating smell came out.	Cl^-, Br^-, NO_3^- possible.
(iv) On bringing the glass rod wet with NH_4OH over test-tube.	White fumes of NH_4Cl.	Cl^- may be there.
(v) Mixture + $K_2Cr_2O_7$ + conc. H_2SO_4 heated and passed the vapours into NaOH and then added acetic acid and lead acetate solution.	Yellow ppt.	Cl^- confirmed.
(vi) Mixture + dil. HCl + $BaCl_2$ solution	White ppt.	SO_4^{2-} may be there.
(vii) Filtered the precipitate and dissolved it in conc. HNO_3.	It is dissolved.	SO_4^{2-} confirmed.
Basic Radicals		
(i) Original solution + dil. HCl.	No ppt.	Ist group absent.
(ii) Passed H_2S in the above solution.	No ppt.	II group absent.
(iii) Removed H_2S after boiling then boiled it with 1 c.c. of HNO_3 (conc.) and added NH_4Cl and NH_4OH in excess.	No ppt.	III group absent.

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*The given mixture contains six radicals having at least two of the either kind (acidic or basic).

(iv) Passed H_2S in the above solution.	Grey ppt.	IV group present.
(v) Dissolved the ppt. in least amount of dil. HCl.	ppt. is dissolved.	Zn^{2+} may be there.
(vi) Boiled of H_2S. Add NaOH solution slowly in excess and then pass H_2S.	First a white ppt. is formed which is dissolved in excess and on passing H_2S white ppt. reappears.	Zn^{2+} confirmed.
(vii) Boiled off H_2S and added NH_4OH and $(NH_4)_2CO_3$ in excess and then pass H_2S.	No. ppt.	Vth group absent.
(viii) Boiled the fifth group filtrate with $(NH_4)_2C_2O_4$ and after filtration added disodium hydrogen phosphate and shook with a glass rod.	A white crystalline ppt.	Mg^{2+} confirmed.
(ix) Mixture + dil. NaOH and heated.	Ammonical smell.	NH_4^+ may be present.
(x) Bring a glass rod dipped in conc. HCl	White fumes.	NH_4^+ confirmed.

If some acidic or basic radical does not respond to confirmatory tets, it shoudl not be recorded since there is a negative marking for wrongly reported radicals.

Result : The given mixture contains the following radicals :

(i) CO_3^{2-}, (ii) Cl^-, (iii) SO_4^{2-} **—Acid Radicals.**

(ii) Zn^{2+}, (ii) Mg^{2+}, (iii) NH_4^+ **—Basic Radicals.**

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CHAPTER
7

QUICK APPROACH TO THE MIXTURE ANALYSIS

In some cases by performing the direct tests, observing the physical state of the mixture, one can analyse the mixture very quickly and can arrive at important conclusive results.

Physical Examination of the Mixture : It affords valuable information regarding the indentity of some of the basic and acid radicals. Inference may be drawn from the table given below :

	Observation	Inference
1.	**The substance is coloured :**	Cooper salts (Cu)
	(i) Blue	Salts and oxides of Chromium (Cr)
	(ii) Dark green	Salts of Fe, Ni, Cu, Cr
	(iii) Green	Salts of Fe
	(iv) Light yellow or brown	PbO_2. Bi_2S_3
	(v) Dark brown	Fe_2O_3
	(vi) Reddish Pink	Salts of Mn
	(vii) Light Pink	Salts of Cobalt
	(viii) Pink	Sb_2S_3
	(ix) orange red	HgO, HgI_2, Pb_3O_4
	(x) Red	*HgO (Freshly precipitated)*
	(xi) Yellow	CdS, As_2S_3, SnS_2
	(xii) Black	CuS, CuO, MnO_2, Sb_2S_3, FeS, CoO and sulphides of Ag, Hg, Pb, Bi, Ni, and Co
2.	The substance is wet.	$CaCl_2$, $ZnCl_2$, $MgCl_2$, $MnCl_2$ Nitrites, Nitrates of metals
3.	The substance is heavy.	Salts of Pb, Hg and Ba
4.	The substance is light.	Carbonates of Bi, Mg, Zn etc.
5.	The substance turns black or brown on exposure to laboratory atmosphere (H_2S gas)	Pb, Bi salts

Some substances yield characteristic colour in solution when dissolved in water or in dilute acids.

Colour	Solution of
Green	Nickel, ferrous and chromic salts
Blue	Copper (ic)
Pink	Mn and Co

Note the smell of the substance. If a characteristic smell is detected it may be due to the following salts.

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*One should not reach a definite conclusion regarding the identity of basic and acid radicals unless *they are confirmed by other* confirmative tests.

Smell	Salts
Ammonia (NH_3)	Ammonium salts
Vinegar (CH_3COOH)	An acetate
Burning sulphur (SO_2)	A sulphite
Hydrogen sulphide (H_2S)	A sulphide

WET TESTS

(1) Acetate (CH_3COO^-) : Rub a little of the given mixture with a few crystals of oxalic acid and 3-4 drops of water on your palm and smell it very carefully → **Vinegar smell (CH_3COOH).**

(2) Sulphite (SO_3^{2-}) : Rub a little of the given mixture with a few drops of dil. HCl on your palm and smell it very carefully → **Burning sulphur smell** (SO_2).

(3) *Sulphide (S^{2-}) : Rub a little of the given mixture with a few drops of dil. H_2SO_4 on your palm and smell it very carefully—**Rotten eggs smell (H_2S).**

(4) Ammonium (NH_4^+) : Rub a little of the given mixture with a few drops of NaOH soln. on your palm and smell it very carefully → **Ammonical smell (NH_3).**

(5) Copper (Cu^{2+}) : Original solution (O.S.) is blue. To it add NH_4OH deep blue colour will be developed. Now add CH_3COOH (in excess) + $K_4[Fe(CN)_6]$ → **Chocolate ppt.**

(6) Iron (Fe^{2+}) : O.S. + 1 drop of conc. HNO_3 boil it for a few minutes and divide it into two parts.

(i) Add K_4 $[Fe(CN)_6]$ → **Deep blue colour.**

(ii) Add NH_4CNS → **Blood red colour.**

(7) Nickel (Ni^{2+}) : (i) O.S. is **Greenish blue. O.S. + 1 drop of conc.** HNO_3 boil it for a few minutes and add excess of NH_4OH + dimethyl glyoxime → Red ppt.

(8) Cobalt (Co^{2+}) : O.S. is **pink.** O.S. + Excess of CH_3COOH + KNO_2 in excess → **Yellow ppt.**

If dark blue colour develops with conc. HCl which changes into pink on dilution then cobalt (Co^{2+}) is confirmed.

(9) Chromium (Cr^{3+}) : O.S. is green O.S. + NaOH + Br_2 water or H_2O_2 and boil it for five minutes. Filter it. Filtrate + CH_3COOH + $(CH_3COO)_2Pb$ → **Yellow ppt.**

(10) *Manganese (Mn^{2+}) : (i) Mixture + PbO_2 (Solid) + conc. HNO_3, boil it for five minutes. Cool and add water → **pink colouration.**

(ii) Take a dry test tube and in it take equal amounts of conc. HCl (1/2 c.c.) and conc. HNO_3 (1/2 c.c.). Now add a little amount of mixture. It turns black. Add a little water in it and shake. **The colour disappears.**

(11) **Barium (Ba^{2+}), **Strontium (Sr^{2+}), **Calcium (Ca^{2+}) : Take sodium carbonate extract residue and treat it with 10 ml. of acetic acid, boil it and filter. Now with this filtrate Ba, Sr, Ca, can be tested as usual.

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*To the mixture add dil. H_2SO_4 and a little lead carbonate, it turns black. Sulphide is confirmed.

*Manganese can only be tested directly by (i) method if cobalt is absent.

**These radicals can also be confirmed directly from the mixture by flame test.

(12) Bismuth, Antimony (Bi^{3+}, Sb^{3+}) : If original solution becomes trubid on dilution, then either Bismuth or Antimony may be there.

(13) Mercuric (Hg^{2+}) : (i) Rub the given mixture on copper coin → coin gets silver like shine.

(ii) O.S. + $SnCl_2$ sol → white greyish ppt.

Note :

If mixture contains SO_4^{2-} as the acid radical then Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+} cannot be there in that mixture.

(ii) If mixture is perfectly white then Cu^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+} cannot be there in that mixture.

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CHAPTER
8
ORGANIC ANALYSIS

The analysis of organic compounds is fundamentally different from that of the inorganic salts. The analysis of inorganic salts consists of the detection of acid and basic radicals which are relatively few in number and give quickly precipitates with the group reagents. The scheme of their analysis is, therefore, very systematic and concise. Organic compounds, on the other hand, give very slow and often indistinct reactions. Furthermore, the number of groups in organic compounds is too much large and their reactions vary from compound to compound, depending on the molecular structure. It is thus evident that organic analysis is highly complicated and no hard and fast rules can be laid down for the same.

Experiment 1 : Determine the melting point of the given organic compound.

Appratus : Flask (50 mL), test tube, thermometer, capillary tube, stand

Chemicals : Conc. H_2SO_4

Procedure :

Determination of melting point : It can be conveniently determined by the apparatus shown in the figure. In consists of 50 c.c. flask half filled with conc. sulphuric acid in which a loosely fitting test tube is so dipped that it remains about 1 cm above the bottom. This test tube also contains conc. H_2SO_4 sufficient to cover the bulb of thermometer inserted in it.

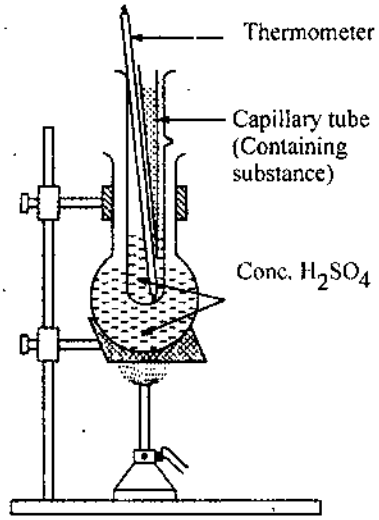


Fig. Determination of melting point

In actual practice, a small quantity of the organic substance is finely powdered between the pieces of filter paper and introduced in a glass capillary closed at one end. The material is picked by gently tapping the capillary on the table. This capillary is then dropped into the test tube of the bath, along the side of thermometer, with its sealed end down. The open end of the capillary should remain above the surface of sulphuric acid in this inner tube. The flask is gently heated and from time to time the burner is removed so that the slow steady rise of temperature is maintained. The temperature at which the substance melts and becomes almost transparent is noted. This is the melting point.

Traces of moisture of impurities considerably lower the melting point. The substance for the determination of the melting point should therefore, be dry and pure.

Result : The metling point of the given compound is ...°C

Note : The following compounds should be given for practice.

S.No.	Name	M.P. (°C)
1.	Acetanilide	113.5–114
2.	Aspirin	135
3.	Benzoic acid	121.5–122
4.	Cinnamic acid	132.5–133
5.	Dichlorobenzene	52
6.	*m*-dinitrobenzene	90
7.	Naphthalene	80–82
8.	Salicylic acid	157.5–158
9.	Succinic acid	184.5–185
10.	Urea	132.5–133

Calibration of Thermometer

Although the thermometers used by the students are calibrated, even then it may be checked by the determinatioon of the metling point or boiling point of pure substances. Accordingly we may modify the given values. For this purpose the following compounds may be used.

Naphthalene (80–82°C), Acetanilide (114.5–114°C),

Urea (132.5–133°C), Distilled water (100°C).

Experiment 2 : Determine the boiling point of the given organic compound.

Apparatus : Test tube, bend tube, thermometer, cork, stand.

Procedure :

Determination of Boiling Point : A simple apparatus for the determination of boiling point is shown in the figure. It consists of a hard glass test tube. It is fitted with a cork having two holes, one for the thermometer and the other for bend tube.

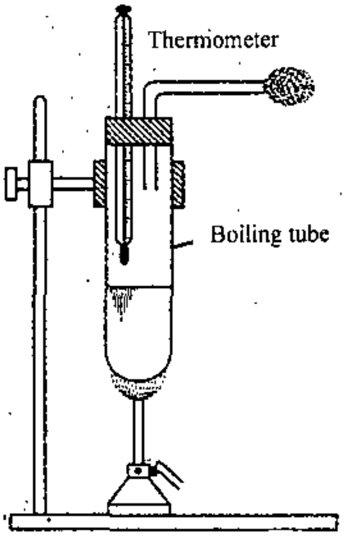


Fig. Determination of boiling point

The liquid, whose boiling point is to be determined, is taken in this tube and the bulb of thermometer is adjusted about one cm. above its surface. The tube is very gently heated. Heating must be very carefully regulated so that the temperature rises slowly and boiling takes place gently. A rapid stream of bubbles starts issuing in the liquid and the temperature in the thermometer ceases to increase and becomes constant. This temperature is the boiling point of the liquid.

To ensure a constant heating and to stop the bumping the glass chips may be added in the test tube.

Result : The boiling point of the given compound is ...°C.

Note : The following compounds should be given for practice.

S.No.	**Name**	**B.P. (°C)**
1.	Benzene	80
2.	Cyclohexane	81.4
3.	Ethanol	78
4.	Toluene	110.6

Experiment 3 : Determine the mixed melting point of the given mixture of organic compounds.

Apparatus : Flask (50 mL), test tube, thermometer, capillary tube, stand.

Chemicals : conc. H_2SO_4

Procedure : The mixed melting point is determined to establish the purity of known organic compound. A small amount of the mixture of compounds is taken. The melting point of such a mixture is determined in the usual manner (Ex. 1). If the value of the metling point of the mixture is the same as that of the pure compound then the compound under investigation is pure but if the value of melting point is lower than that of the pure compound then the compound under investigation is impure. Therefore, this technique not only helps in the identification of organic compound, but also in establishing the purity of known compound.

Result : The mixed melting point of the given mixture is ...°C.

Note : The mixture of urea-cinnamic acid of various composition (1 : 4, 1 : 1, 4 : 1) should be given for practice.

Experiment 4 : Crystallize the given organic compound.

Apparatus : Funnel,, Buchner funnel, suction pump, vacuum dessicator, filter papers, beakers and stand.

Chemicals : Solvent (water or alcohol)

Procedure : The given impure organic compound is powdered and mixed with a just sufficient quantity of the suitable solvent in a beaker. The mixture is heated on a water bath until the compound gets dissolved. The hot saturated solution obtained is then filtered through a filter paper placed in a glass funnel.

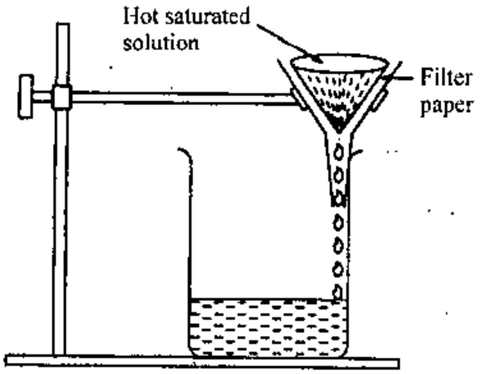


Fig. 3. Filtration with the help of ordinary funnel

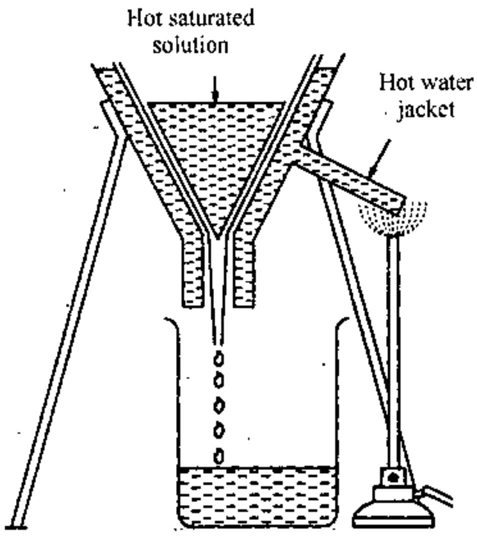


Fig. 4. Filtration with the help of hot water funnel

If the organic compound crystallises during filtration, a hot water funnel is used. This funnel is enclosed with a hot water jacket. The hot-water keeps the solution hot and prevents crystallisation during filtration. The insoluble and suspended impurities remain on the filter paper and a clear solution is collected in the beaker placed below the funnel.

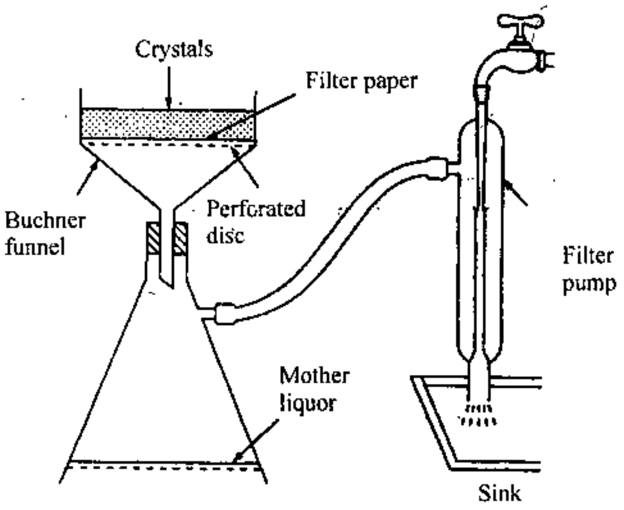


Fig. 5. Filtration with a Buchner funnel using a suction pump

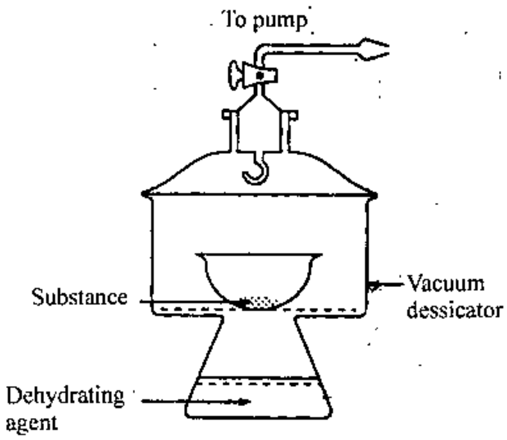


Fig. 6. Drying crystals in a vacuum dessicator

The hot filtrate is now allowed to cool undisturbed in a beaker. After sometime, crystals of the substance are obtained in the beaker. Now the crystals are separated from the mother liquor by filtration with the help of a *Buchner funnel* and a *suction pump.* (as shown in figure). When whole of the mother liquor has been drained into the filtration flask, crystals present in the Buchner funnels are washed two or three times with small quantities of the pure solvent to remove the impurities if adhered on their surface.

The crystals are now dried by pressing between folds of filter paper. The crystals are finally dried over anhydrous calcium chloride in a vacuum dessicator.

Result : The colourless shining crystals of the given compound are obtained and shown to your Professor concerned.

Note : The following compounds should be given for practice :

S.No.	Name	Solvent
1.	Benzoic acid	Water
2.	Phthalic acid	Hot water
3.	Acetanilide	Boiling water
4.	Naphthalene	Ethanol

Experiment 5. Decolourise and crystallize using charcoal of given organic compound.

Apparatus : Funnel, Buchner funnel, suction pump, vacuum dessicator, filter papers, beakers and stand.

Chemicals : Solvent (water or alcohol), charcoal.

Procedure : Sometimes, the crystals obtained are slightly coloured due to the presence of traces of impurities in them. In such a case, the crystals are redissolved in a small quantity of the solvent and the solution is boiled with a small quantity of animal charcoal. The suspension is filtered and crystallised as described in Ex. 4 to get the colourless crystals.

Result : The colourless crystals of the given compound are obtained and shown to your Professor concerned.

Note : The following compounds should be given for decolourisation and crystallisation.

S.No.	Name
1.	Brown sugar (sucrose)
2.	Impure napthalene (100 g napthalene mixed with 0.3 g of congo red) from ethanol.

Experiment 6 : Purify the given compound by sublimation.

Apparatus : Sand bath, burner, china dish, perforated filter paper, funnel, glass wool.

Procedure : Sublimation is the process in which a substance, when heated, passes directly from the solid to the vapour state without melting, and the vapour when cooled, gives back the solid substance.

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Vapour}$$

Evidently, this process has limited applications as only a few substances sublimate *e.g.* benzoic acid, camphor, naphthalene, anthracene etc.

In this method the impure substance is gently heated in a china dish over a sand bath. The china dish is covered with a perforated filter paper over which an inverted funnel is placed (figure 7).

The stem of the funnel is plugged with glass wool to prevent the escape of vapours. The vapour rising from the solid pass through the holes in filter paper and get deposited as solid on the walls of the funnel. The filter paper used for covering the porcelain dish prevents the sublimated substance to drop back into the dish and keeps the funnel cool by cutting off the direct heat from the dish. Thus, we get pure substance as sublimate.

Result : Show the pure sublimate to your Professor concerned.

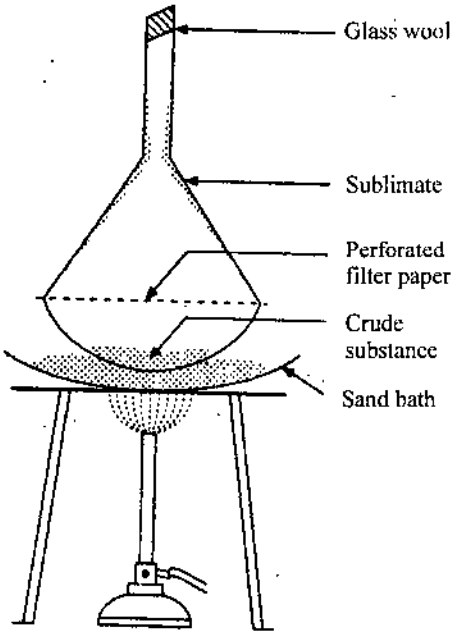


Fig. 7. Sublimation

Note : The following compounds should be given for practice :

(i) Camphor

(ii) Naphthalene.

Experiment 7 : Purify the given impure organic liquid by simple distillation method.

Apparatus : Distillation assembly, thermometer.

Procedure : The apparatus used consists of a distillation flask having a side tube connected with a Liebig condenser or an air condenser (if the boiling point of the liquid is above 110°C). In a Liebig condenser, water is continuously circulated in the outer jacket. The mouth of the flask is closed with a cork through which passes a thermometer. The bulb of the thermometer is kept just below the opening of the side tube. A suitable vessel is attached to the lower end of the condenser through an adopter.

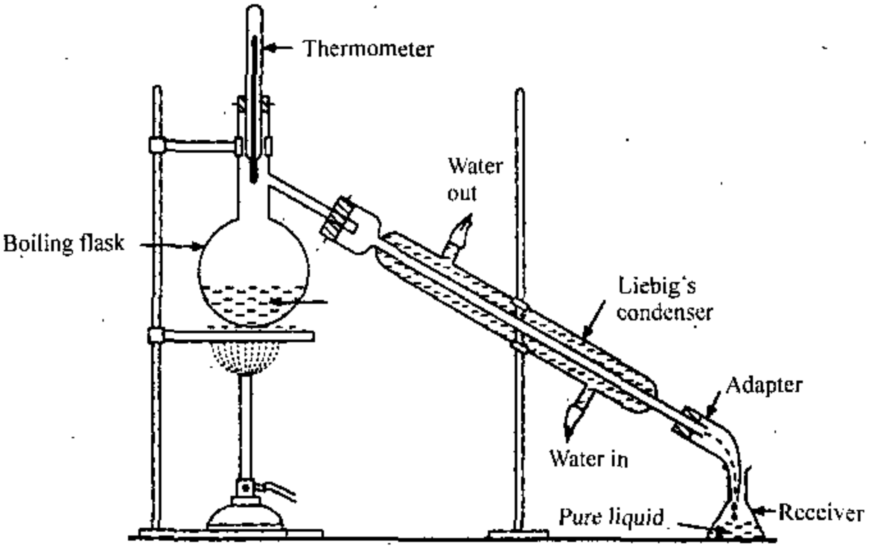


Fig. 8. Simple distillation

The liquid to be purified is taken in the distillation flask along with a few small pieces of porcelain to prevent bumping. The flask is heated on a water bath or a sand bath. As the heating is continued, thermometer first records a rise in temperature. Soon the temperature becomes constant. At this temperature (which corresponds to the B.P. of pure liquid), most of the liquid passes over in the form of vapour which passes through the condenser and gets condensed. The condensed liquid collects in a receiver. The distillate thus obtained is pure liquid.

Result : The pure liquid is obtained by distillation and shown to the Professor concerned.

Note : The following organic liuqids should be given for practice.

1. Ethanol-water mixture using water condenser.

2. Nitrobenzene and aniline using air condenser.

Experiment 8 : Detect nitrogen, sulphur and halogen in the given organic compounds.

Apparatus : Ignition tube, tongs, porcelain dish, beakers, funnel, burner, filter papers.

Chemicals : Sodium piece, ferrous sulphate, ferric chloride, hydrochloric acid, silver nitrate, chlorine water, carbon tetrachloride or chloroform, sodium nitroprusside, lead acetate.

Procedure :

Detection of Elements (Nigrogen, Sulphur and Halogens) In an organic compound the most commonly occurring elements are nitrogen, sulphur and halogens along with carbon, hydrogen and oxygen. The organic compound is subjected to the detection of these elements before the functional groups are to be looked for. In order to identify these elements in organic compounds, they are converted into ionisable inorganic substances. This may be accomplished by fusing the susbtance with metallic sodium, thus converting nitrogen, sulphur and halogens into ionisable sodium cyanide, sulphide and halides respectively. This process is knwon as **Lassaigne's test.**

Lessaigne's Test

Dry a piece of metallic sodium between a piece of filter paper. Introduce it into a clean ignition tube and then cover it with the given substance and heat gently in the flame holding the tube by means of a pair of tongs. Take the ignition tube away from flame, again heat and repeat this process, three to four times when reaction begins. Wait for some time and heat strongly until the bottom of the tube becomes red hot. Then plunge the tube while hot, into a small beaker or porcelain dish containing 15 mL of distilled water. Stir the contents and allow the remaining sodium to react with water. Boil the mixture for five minutes and filter. This filtrate known as **Sodium extract** (lessaigne's solution) should be, clear, colourless and transparent, if not, repeat the fusion using a larger piece of sodium.

$$\mathrm{Na + C + N \longrightarrow NaCN \rightleftharpoons Na^{2} + + CN^{-}}$$

$$\mathrm{2Na + S \longrightarrow Na_2S \rightleftharpoons 2Na^{+} + S^{2-}}$$

$$\mathrm{2Na + X_2 \longrightarrow 2NaX \rightleftharpoons 2Na^{+} + 2X^{-}} \quad \text{(where, x = Cl, Br, I)}$$

Detection of Nitrogen

Treat 2 mL of sodium extract with 2-3 drops of fresh and saturated solution of $FeSO_4$ followed by 2 drops of NaOH. Boil the contents for 1-2 minutes. Cool it and add 1 mL conc. HCl or 2 mL dil. H_2SO_4 to dissolve the precipitate of ferrous hydroxide and make the solution acidic. Then add 2 drops of $FeCl_3$. Formation of a **prussan blue or greenish blue** precipitate or colouration indicates the presence of nitrogen.

$$\mathrm{FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 \downarrow + Na_2SO_4}$$

$$\mathrm{Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH}$$

$$\mathrm{2Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl}$$

In the presence of sulphur and nitrogen both, it gives blood red colour with the drops of $FeCl_3$.

$$\mathrm{Na + C + N + S \longrightarrow NaCNS}$$

$$\mathrm{3NaCNS + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric sulphocyanide}\\ \text{(Blood ed)}}}{Fe(CNS)_3} + 3NaCl}$$

Detection of Sulphur

(i) Add 2-3 mL of freshly prepared sodium nitroprusside (colourless) to 1 mL of sodium extract. **A violet or purple** colouration confirms the presence of sulphur.

$$\mathrm{Na_2S + Na_2[Fe((CN)_5.NO] \longrightarrow \underset{\text{Violet colour}}{Na_4[Fe(CN)_5.NOS]}}$$

(ii) Alternately add lead acetate to the sodium extract acidifed with acetic acid. **A black** precipitate indicates the presence of sulphur.

$$\mathrm{Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COONa}$$

(iii) Treat sodium extract (1 c.c.) with 1 or 2 drops of sodium plum-bite. Formation of a black colour or precipitate confirms sulphur.

$$\mathrm{Na_2S + \underset{\text{Sod. plumbite}}{Na_2PbO_2} + 2H_2O \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + 4NaOH}$$

Detection of Halogens

(a) **Silver nitrate text :** Boil 2 mL of sodium extract with 1 mL conc. HNO_3 and then add $AgNO_3$. Note that :

(i) **White curdy** precipitate soluble in NH_4OH — **Cl Present.**

(ii) **Pale yellow** precipitate partially soluble in NH_4OH — **Br Present.**

(iii) **Yellow** precipitate insoluble in NH_4OH — **I Present.**

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl\downarrow} + NaNO_3$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

$$NaBr + AgNO_3 \longrightarrow \underset{\text{Pale yellow}}{AgBr\downarrow} + NaNO_3$$

$$AgBr + 2NH_4OH \longrightarrow \underset{\text{Partially soluble}}{[Ag(NH_3)_2]Br} + 2H_2O$$

$$NaI + AgNO_3 \longrightarrow \underset{\text{Yellow ppt.}}{AgI\downarrow} + NaNO_3$$

(b) Chloroform test : Acidify the sodium extract with dil. HNO_3, add 2 drops of chloroform (or CS_2 or CCl_4) and shake vigorously with chlorine water. If chloroform layer turns **pale-brown, Bromine** is present; but if it turns violet then **Iodine** is present.

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$$

$$Br_2 + CHCl_3 \longrightarrow \text{Pale-brown colour}$$

$$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$$

$$I_2 + CHCl_3 \longrightarrow \text{Violet colour}$$

(c) Beilstein's test for halogens : This test. is of course, very sensitive for detecting even the traces of halogens. Heat a copper wire at one end in a non-luminous flame till it ceases to impart green colour to the flame. Take a little substance to be tested on the copper wire. Again heat, a green or **blusih green** flame indicates the presence of halogen.

This test should not be applied in the presence of urea or thiourea, as they also give green colouration on heating with flame.

Note :

The following facts should be known that :

(a) If aliphatic solid does not contain strong characteristic smell-Halogen absent. And if it does not evolve NH_3 on heating with NaOH

—**Nitrogen absent.**

(b) Aliphatic liquids never contain **Nitrogen :** If they give sweet smell and are immiscible and heavier than water.

—**Halogen definitely present.**

(c) If aromatic compounds are soluble in cold water

—**Nitrogen and halogen absent.**

Experiment 9. Identify the presence of different functional groups in the given organic compounds.

Presence of Functional Groups

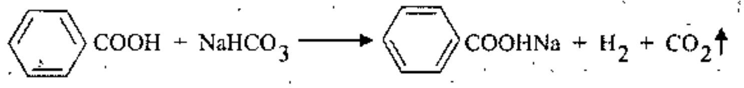
Organic compounds may be regarded as the derivatives of hydrocarbons having different functional groups in place of one or more of hydrogen atoms. Their characteristic properties and reactions are largely due to the functional groups present in their molecules. Correct detection of functional groups present in an organic compound leads to a very reasonable and accurate identification of that compound.

Now we describe different tests for some important functional groups.

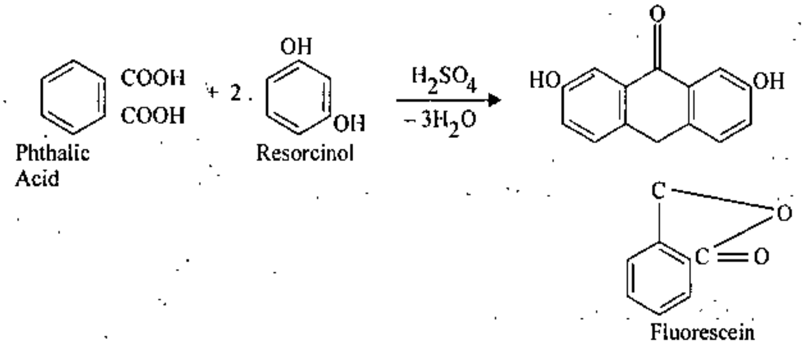
(1) CARBOXYLIC ACID (— COOH)

(i) Sodium bicarbonate test : Add a small amount of the compound of 3 mL of saturated sodium bicarbonate solution. Formation of brisk effervescence shows the presence of —COOH group.

(ii) Litmus paper test : Add the litmus paper or solution to the aqueous solution or suspension of the compound. It turns red.



(iii) Fluorescence test : Heat gently 0.2 gm of organic compound with 0.5 gm of resorcinol and a few drops of conc. H_2SO_4 in a hard test tube for two minutes. Cool and pour the contents into a beaker containing NaOH diluted largely with water. Formation of intense green fluorescence indicates the presence of 1, 2 or *ortho*-dicarboxylic groups (*i.e.*, phthalic acid).



(iv) Ester formation : Heat a small quantity of the substance with ethyl alcohol and a little conc. H_2SO_4. Cool the solution and pour into a tube containing water. A **fruity** smell due to the formation of an ester, indicates the presence of carboxylic groups.

(v) Ferric chloride test : Neutralise 0.5 gm of the acid with excess of ammonia in a boiling test tube. Boil the solution to remove excess of ammonia. Cool and add a few drops of neutral $FeCl_3$ solution. Note the colour produced.

Observation	**Inference**
Yellow ppt.	Cinnamic acid
Reddish brown ppt.	Aliphatic Carboxylic acid
Buff ppt.	Aromatic acids and certain dibasic acids
Yellow colour	α-Hydroxy acids
Red brown colour	*m*- or *p*-Hydroxy benzoic acids
violet colour	Aromatic hydroxy acids.

Note : Phenols and α-Naphthyl amine also produce characteristic colour with $FeCl_3$.

(vi) Iodate-Iodide test : This is very sensitive test for the detection of even weak carboxylic acids.

To a small quantity of the compound add two drops of 5% KI solution and two drops of 5% KIO_3 solution. Cork the tube and place it in a boiling water bath for two minutes. Cool the contents and add a few drops of freshly prepared starch solution. Appearance of a blue colour shows the presence of carboxylic acid.

$$6RCOOH + 5KI + 3KIO_3 \longrightarrow 6RCOOK + 3H_2O + \underset{\text{gives blue colour with starch}}{3I_2}$$

Note : Phenols, some aromatic amines and certain other compounds which are readily oxidised to coloured compounds, also give a green to brown ppt. with the reagent.

Quick Guess

(i) Aliphatic Solid : Heat with conc. H_2SO_4

(a) turns black-Tartaric acid.

(b) turns brown after sometime—Citric acid.

(c) nothing taking place —Oxalic or succinic acid.

(ii) Aliphatic Liquid : Warm with conc. H_2SO_4 and burn the gas evolving out.

(a) blue flame—Formic acid.

(b) does not burn—Acetic acid.

(iii) Aromatic Solid : Add 2 drops of $FeCl_3$ to the aqueous solution or suspension.

(a) Violet colour-Salicylic acid.

(b) No change in colour-Benzoic acid and phthalic acid

Phthalic acid can be confirmed by performing fluorescence test.

(2) ALCOHOL (—OH)

(i) Ceric Ammonium Nitrate Test : Treat 2 drops of the organic substance with 0.5 mL of ceric ammonium nitrate solution and dilute it with 2 mL of water. A red colouration indicates alcoholic hydroxy group.

(ii) Sodium test : Take about 2 mL of the given liquid in a test tube and add a piece of anhydrous $CaCl_2$ to absorb any water if present. Transfer the clear liquid (free from water) to another dry test tube and add a dry piece of sodium. Effervescence indicates the liquid to be an alcohol.

$$2ROH + 2Na \longrightarrow 2RONa + H_2\uparrow$$

(iii) Iodoform Test : To the ethyl alcohol add double of iodine solution followed by dilute sodium hydroxide until the colour is pale yellow and warm gently. Formation of yellow precipitate indicates the presence of simple alcohol.

(iv) Evolution of HCl and H_2 : In a completely dry test tube take about 2 mL of the compound and add a small amount of anhydrous $CaSO_4$. Filter the solution in another dry test tube and divide the filtrate into two parts. To first part add 2 drops of acetyl chloride very carefully and expose a moist blue litmus paper at the mouth of the test tube. If the compound contains an alcoholic group, the paper becomes red.

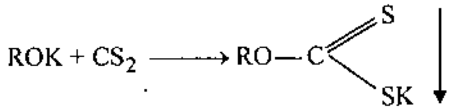
$$CH_3COCl + ROH \longrightarrow CH_3COOH + RCl$$

To second part, add a small piece of dry sodium. Effervescence indicates the compound to be an alcohol.

$$2ROH + 2Na \longrightarrow 2RONa + H_2\uparrow$$

(v) Xanthate test : To one ml of the conc. aq solution of the original compound add 2 pellets of KOH. Heat and cool. Then add 1 mL of the ether followed by the addition of 2-3 drops of carbon disulphide. Formation of a yellow ppt. indicates the prsesence of alcoholic groups.

$$ROH + KOH \longrightarrow ROK + H_2O$$



$$ROK + CS_2 \longrightarrow RO-C(=S)SK\downarrow$$

Yellow

Filter the above solution and to 1 mL of the filtrate add 0.5 mL of ammonium molydate solution and excess of dil. HCl. Formation of a red or blue colour confirms the presence of alcoholic group in the original substance.

Distinction among Primary, Secondary and Tertiary Alcohols

Treat 2 mL of the compound with about 8 mL of Lucas reagent (Dissolve 32 g of anhydrous $ZnCl_2$ in 20 mL of conc. HCl) and shake. Note the following observations. Separation of an insoluble layer at once Tertiary alcohol; Appearance of cloudiness within 4-5 minutes Secondary alochol, solution remains clear Primary alcohol.

Quick Guess :

(a) If liquid burns in flame—Methyl alcohol, ethyl alcohol, *n*-propyl alcohol.

(b) If liquid does not burn in flame, shake it with water.

(i) Soluble—Glycol.

(ii) Floating on water—*n*Butyl alcohol.

(iii) Forming layer below water-Benzyl alcohol.

(3) PHENOL* (—OH)

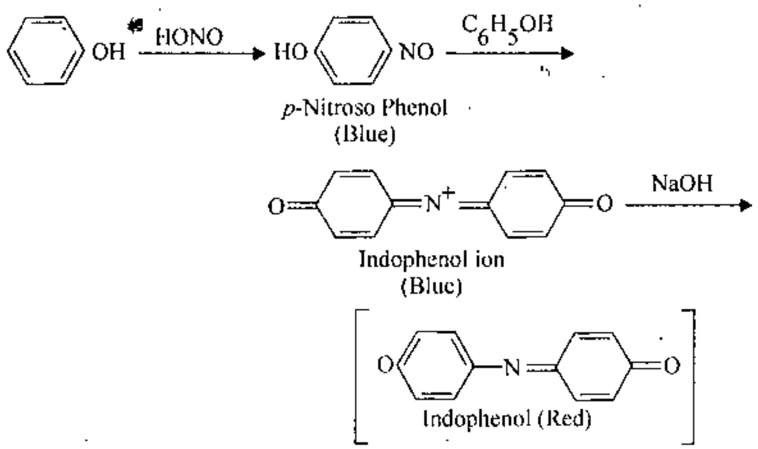
(i) Ferric chloride test : Add 2 drops of ferric chloride to 2 c.c. of aqueous or alcoholic solution of the compound. Formation of green blue or violet colour shows the presence of phenols.

Violet	—Phenol, *o*-Cresols, Salicyclic acid, Aspirin
Green colour	—Catechol
Blue changing to red	—Hydroquinone, Pyrogallo
White opalescence	—β-Napthol
If on boiling with water blue-violet colour appears	—*m*-and *p*-Nitrophenol
White ppt.	—α-Naphthol
Bluish violet colour in alc. solution	—α-Naphthol
Green colour in alc. solution	—β-Naphthol; *o, m, p*-Cresols; Resorcinol

(***Exceptions :*** α-Napthylamine gives blue colour and benzoic acid gives buff. ppt. with $FeCl_3$).

$$6C_6H_5OH + FECl_3 \longrightarrow 3H^+ + \underset{\text{Violet}}{[Fe(OC_6H_5)_6]^{3-}} + 3HCl$$

(ii) Liebermann's reaction : Fuse a little amount of the compound with a crystal of sodium nitrite in a tube. Cool the mixture and add 1 c.c. conc. sulphuric acid. A deep green to blue solution is formed which turns red when poured in large excess of water. This red aqueous solution becomes again deep green or blue if made alkaline with NaOH. It indicates the presence of phenol. (Nitrophenols do not respond to this test).



(iii) Azo-dye formation : Treat a drop of aniline in a test tube with 0.5 mL conc. HCl, dilute it with water and cool in a freezing bath and add dilute $NaNO_3$ solution while shaking. Pour this diazotised solution

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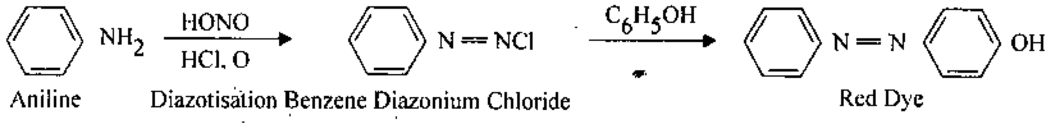
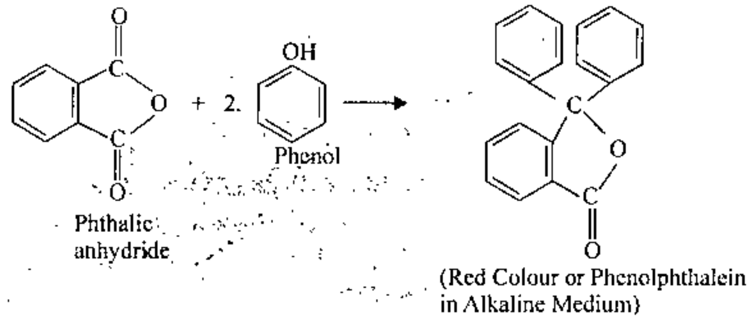
*Almost all phenols on exposure to air and light acquire darker colours. Some phenols even become dark-brown or black in colour. Hence the colour of phenols should not be given any importance when identifying them.

into that of phenol in excess of 2N—NaOH solution. Formation of a dye or orange or red colour indicates the presence of phenolic group.



(iv) Phthalein test : Heat 0.5 gm of compound with 1 gm. phthalic anhydride and a drop of conc. H_2SO_4 for one minute. Cool and make it alkaline liquid with dil. NaOH solution. Pour a few drops of the alkaline liquid into 20 mL of water. Characteristic colour shows the presence of phenol.



Red colour — Phenol, o-Cresol.

Blue colour — Catechol, *m-Cresol.*

Fluorescent green — Resorcinol.

No coloration — *p*-Cresol.

Deep blue — Hydroquinone.

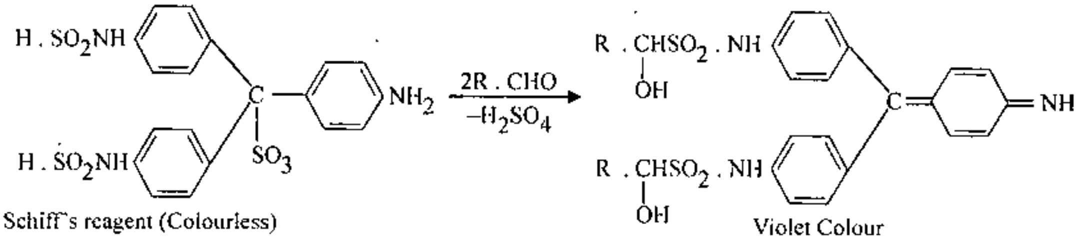
Green — α-Naphthol

Light — β-Naphthol.

(v) Ceric ammonium nitrate reagent : Add 3-4 drops of the subtance or its concentrated solution in water to 0.2 mL of the reagent, dilute with 2 mL of distilled water and shake. A brown to green precipitate is obtained in case of phenol.

(4) ALDEHYDE (—CHO)

(i) Schiff's reagent : Add 5-6 drops of liquid or 0.1 gm of solid compound to 2 mL of the reagent, shake vigorously and wait for 1-2 minutes. A deep red or violet colour indicates the presence of an aldehydic group. It is not to be heated here.



(ii) Tollen's Reagent : Add 0.1 gm. of solid or 0.1 mL of liquid compound to 2 mL to Tollen's reagent, warm and allow the contents to stand for 2-3 minutes. The formation of silver mirror or a grey ppt. (if the test tube is not clean) confirms the presence of aldehyde.

$$2Ag(NH_3)_2OH + R.CHO \longrightarrow \underset{\substack{\text{Sivler mirr}\\ \text{or grey precipitate}}}{2Ag\downarrow} + RCOONH_4 + 3NH_3 + H_2O$$

(iii) Fehling's Solution : Add 0.1 gm of solid or 0.2 mL of liquid compound to 5 mL of Fehling's solution and boil the mixture. Formation of red ppt. shows the presence of aldehyde.

$$2CuO + R.CHO \longrightarrow \underset{\text{Red ppt.}}{Cu_2O\downarrow} + R.COOH$$

(iv) Benedict's Solution : Boil 0.1 gm of the compound with 2-3 mL of Benedict's solution for a few minutes. Appearance of a red yellow precipitate confirms its presence.

Quick Guess :

(a) Smell of bitter almonds—Benzaldehyde.

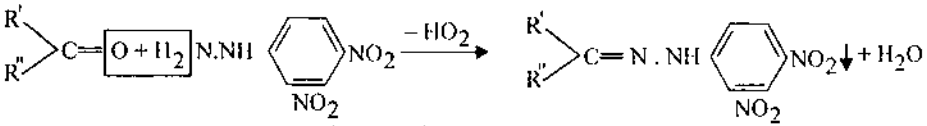
(b) If bad pungent odour, add NaOH to the liquid compound and shake—

(i) brown resin formed—Acetaldehyde.

(ii) no such change—Formaldehyde.

(5) KETONE (>C = O)

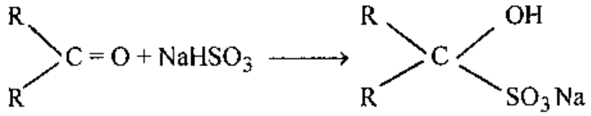
(i) 2 : 4-Dinitro phenyl hydrazine test : Add 1 or 2 drops (0.05 gm) of the substance to about 2 mL of the reagent solution. Shake vigorously and heat, if necessary. A yellow or organe red precipitate separates out in case of ketone.



2 : 4-Dinitrophenyl hydrazine

Yellow or Orange Red Coloured Crystalline Derivative of 2 : 4 Dinitrophenyl Hydrazine of Carbonyl Compound

(ii) Sodium bisulphite test : Add 0.2 gm (0.3 mL) of the compound to 1 mL of saturated sodium bisulphite solution and shake vigorously. Formation of white precipitate shows the presence of ketone.



Crystalline ppt. of sodium bisulphite derivative of carbonyl compound.

(iii) Sodium nitroprusside test : Add 0.1 gm of solid or 0.2 mL of liquid compound to 2 mL of 0.5 aq. sodium nitroprusside solution and then make it alkaline with 2-3 drops of sodium hydroxide. A red or purpole colour indicates the presence of ketone (benzophenone does not give this test.)

Note : The first two tests are given by aldehydes. Therefore to differentiate between aldehydes and ketones it should be known that ketones do not give any test with Tollen's reagent, Schiff's solution, Fehling's solution and Benedict's solution.

Quick Guess :

(a) All the ketones are sweet smelling.

(b) Burns with smoky flame—Acetophenoe.

(6) ESTER (RCOOR)

(i) Smell : All the esters possess fruity smell.

(ii) Phenolphthalein test : To 3 mL of the compound add 2-3 drops of very dilute NaOH solution followed by a drop of phenolphthalein and heat gently. The pink colour is gradually discharged in case of ester.

It is due to the hydrolysis of ester.

$$CH_3COOC_2H_5 + H.OH \longrightarrow CH_3COOH + C_2H_5OH$$

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

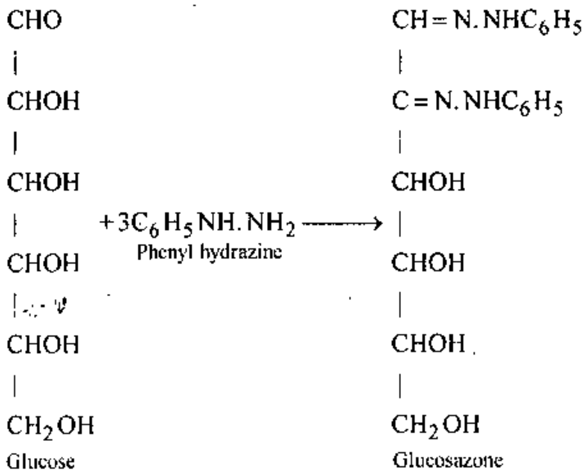
(iii) Feigl test : To 0.5 mL of a normal solution of hydroxylamine hydrochloride in methanol, add one drop or a small crystal of the compound followed by 0.5 mL of 2N-KOH solution in methanol. Boil for one minute, cool and just acidify the solution with dil. HCl. Now add 1-2 drops of $FeCl_3$. The appearance of red-violet coloration indicates the presence of an ester group.

$$CH_3COOC_2H_5 + NH_4OH \longrightarrow CH_3COONH_4 + C_2H_5OH$$

(7) CARBOHYDRATE*

(i) Molisch's test : Add 2 drops of 10% alcoholic solution of α-naphthol in 1 mL aqueous suspension of compound and shake well. Now add carefully 2 mL of conc. H_2SO_4 along the side of test tube. Formation of a reddish violet ring at the junction of two layers indicates the presence of carbohydrate.

(ii) Osazone formation : Add 0.5 g of phenyl hydrazine hydrochloride to a 3% aq. sodium acetate and shake well till a clear solution is obtained. Now add 0.3 gm of the compound followed by 1 mL alcohol and heat the contents for about 10 minutes. On concentrating the solution, yellow crystalline osazone separates out. It clearly shows the presence of sugar.



$$\begin{array}{lcl} CHO & & CH=N.NHC_6H_5 \\ | & & | \\ CHOH & & C=N.NHC_6H_5 \\ | & & | \\ CHOH & & CHOH \\ | & +\underset{\text{Phenyl hydrazine}}{3C_6H_5NH.NH_2} \longrightarrow & | \\ CHOH & & CHOH \\ | & & | \\ CHOH & & CHOH \\ | & & | \\ CH_2OH & & CH_2OH \\ \text{Glucose} & & \text{Glucosazone} \end{array}$$

(iii) Sulphuric acid test : Treat a small amount of the powdered compound with 1 c.c. cold conc. H_2SO_4. Formation of colour varying between yellow, brown and black indicates carbohydrates.

(iv) Fehling's solution test : Boil the mixture of 1 mL of solution of the compound and 2 mL of Fehling's solution for two minutes. Formation of red preciptate clearly indicates the presence of reducing sugar.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + 2CuO \longrightarrow \underset{\text{Red ppt.}}{Cu_2O\downarrow} + \underset{\text{Gluconic acid}}{C_6H_{12}O_7}$$

(v) Benedict's solution test : Boil 1 mL of the aqueous solution of the compound with 2 mL of Benedict's solution for two minutes. It gives a red ppt. which shows the presence of reducing sugar.

If the mixture, in the above case, remains blue and only slightly yellowish turbidity appears then sucrose is confirmed.

(vi) Tollen's reagent test : Add 0.1 gm of the compound to 2 mL of Tollen's reagent and heat gently. A silver mirror is obtained inside the wall of the vessel in case of carbohydrates.

(vii) Furfural test : In the Molisch test add 8 ml. conc. HCl instead of conc. H_2SO_4 and boil the solution. Production of a violet colour immediately after the boiling starts shows the compound to be fructose or sucrose. Glucose produces this colour only after 1-2 minutes continuous shaking.

(viii) Barfoed's reagent test : This test is applied for differentiating mono saccharide from oligosaccharides. Take a little quantity of the compound in a test tube and add 2 ml. of the freshly prepared Barfoed's reagent. Shake and heat the contents for 2-3 minutes. Allow to stand. Formation of a yellow or orange red ppt. indicates the presence of a monosaccharide (Glucose, fructose or galactose). On the other hand if a red ppt. is formed only after a prolonged heating, this indicates the presence of an oligosaccharide (sucrose or insulin).

Quick Guess :

(a) Soluble in cold water—Glucose, sucrose.

(b) Insoluble in cold water—Starch (gives blue colour with iodine).

(c) Blue coloration with Benedict's solution—Sucrose.

(8) AMIDE (—$CONH_2$)

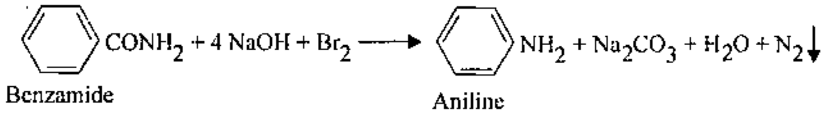
(i) Sodium hydroxide test : Heat 0.2 gm. of the substance, with 4 mL aq. NaOH. Evolution of ammonia indicates the presence of amino group.

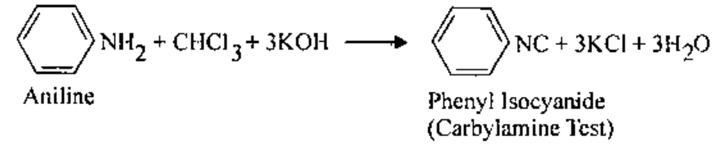
$$R.CONH_2 + NaOH \longrightarrow RCOONa + NH_3$$

(ii) Nitrous acid test : To 0.2 gm. of substance, add 2 mL of dil. HCl followed by 2 mL of 2% aq. $NaNO_2$ and shake. Brisk effervescence due to the evolution of nitrogen indicates an acid amide.

$$RCONH_2 + HNO_2 \longrightarrow RCOOH + H_2O + N_2\uparrow$$

(iii) Hofmann's test : Dissolve a few drops of liquid bromine in an ice cold solution of caustic soda and shake it with 0.5 gm of the substance. Cool with stirring for a few minutes. Now add a piece of solid caustic soda and stir for a few minutes. An ammoniacal smell is obtained due to the evolution of an amine. This ammoniacal smell turns into a very offensive smell of carbylamine on addition of chloroform in case of aromatic compounds.

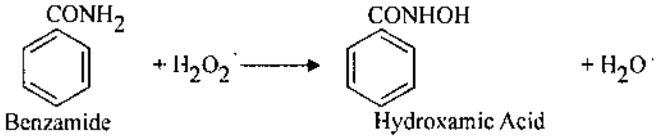




(iv) Hydroxylamine hydrochloride test : In a test tube take 0.2 gm. of the compound, 0.2 gm. of hydroxylamine HCl and 2 mL ehtyl alcohol. Boil for five minutes. Cool and add a few drops of $FeCl_3$. Formation of a blue-red colour indicates the presence of aliphatic amide.

$$RCONH_2 + NH_3OH.HCl \longrightarrow RCONHOH + NH_4Cl$$

(v) To the aqueous solution of the compound add about 7-8 drops of 6% H_2O_2 and heat the contents to nearly boiling. Cool and add 1-2 drops of 5% $FeCl_3$ solution. Formation of bluish red colour in cold within 2 minutes or a brown colour on warming shows the presence of an aromatic amide.



(Note—The result should not be applied in presence of phenolic group)

Quick Guess :

(a) All amides are solid.

(b) Dissolve the compound in water by heating, cool and add 1 mL conc. HNO_3 :

(i) Crystalline ppt. —Urea.

(ii) No ppt. —Acetamide (burns with non-smoky flame).

—Benzamide (burns with smoky flame).

(9) ANILIDE (—NHCOR)

(i) Dye test : Boil 0.1 gm. of the susbtance with 5 mL dil. HCl cool and filter. Treat the filtrate with 4 mL aq. $NaNO_2$ and pour all this content into a beaker containing 10% alkaline β-naphthol. Formation of a bright orange red dye shows the presence of anilide.

(ii) Carbylamine test : Boil 0.1 gm. of the substance with 3 mL alc. KOH, cool and add a few drops of $CHCl_3$. On boiling this mixture, offensive va;pours of intolerable smell are obtained.

(iii) Tafel's test : Add 4 mL conc. H_2SO_4 to about 0.5 gm. of the compound in a dry test tube, shake and then add a little of powdered potassium dichromate. Red or violet colour changing to green on heating confirms acetanilide.

(10) AMINE (– NH_2, NH, → N)

(A) Primary Amine

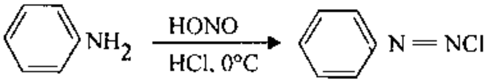
(i) Carbylamine test : Boil a mixture of 2 drops of the compound, 2 drops of chloroform and 2 mL of alcoholic caustic potash. An intolerable offensive odour of carbylamine indicates the presence of a primary amine.

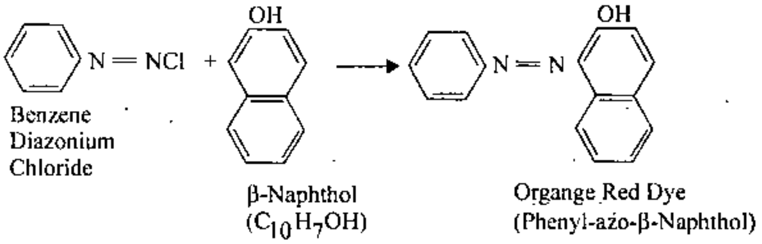
$$R.NH_2 + CHCl_2 + 3KOH \longrightarrow \underset{\text{Carbylamine}}{R.NC\uparrow} + 3KCl + 3H_2O\uparrow$$

(ii) Nitrous acid test : Dissolve about 0.2 gm of the compound in 10 c.c. dil. HCl and cool. Now add 10% aq. $NaNO_2$. Formation of brisk effervescence indicatres the presence of **aliphatic** primary amine.

$$R.NH_2 + HNO_2 \longrightarrow R.OH + H_2O + N_2\uparrow$$

(iii) Diazotisation test : Dissolve about 0.2 gm. of the compound in dil. HCl, and cool. Now add 10% aq. $NaNO_2$. Pour all this content into a beaker containing 10% alkaline β-naphthol. The apperance of a bright orange red dye indicates the presence of aromatic primary amine.





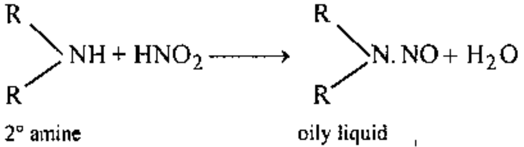
(iv) Rimini test : To about 0.3 gm of the compound taken in a test tube add 5 mL of water, 1 mL acetone and a few drops of sodium nitropruside. Allow to stand for 2 minutes. Formation of a violet red colour shows the presence of aliphatic primary amine.

(v) Hinsberg's test : To about 0.2 gm. of the compound add 1 mL of 5% NaOH and 3 ml pyridine. Shake well and add a few drops of benzene sulphonyl chloride with continuous shaking. Formation of a yellow colour indicates the presence of a primary amine.

(**Note**—Naphthylamines do not respond to this test. Diamines give characteristic colour with $FeCl_3$)

(B) Secondary Amine

(i) Nitrous acid test : Prepare a solution of nitrous acid by adding ice cold dil. HCl to a solution of 1% aq. $NaNO_2$. Add gradually this solution of 0.2 gm. of the compound in di. HCl (10 mL). An oily dark coloured liquid or low melting solid indicates the presence of aliphatic or aromatic secondary amine.



$$\underset{\text{2° amine}}{R_2NH} + HNO_2 \longrightarrow \underset{\text{oily liquid}}{R_2N.NO} + H_2O$$

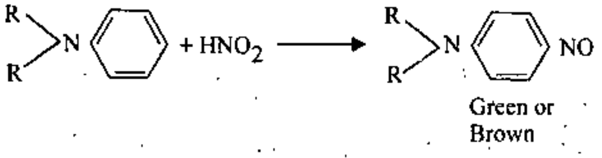
(ii) Libermann's nitroso reaction : The nitroso compound formed as in above reactions, is treated cautiously with 1 mL conc. H_2SO_4. A blue colouration which changes to red on dilution with water and blue or green with aqueous alkali confirms the presence of secondary amine strongly.

(iii) Hinsberg test : Repeat as above ⟶ Orange red colour.

(C) Tertiary Amine

(i) Nitrous acid test : Prepare a solution of nitrous acid by adding ice cold dil. HCl to 1% aq. $NaNO_2$. Add gradually this solution to 0.2 gm of the compound in dil. HCl (10 mL)

No reaction indicates aliphatic tertiary amine.



Production of green or brown coloured salt indicates aromatic tertiary amine.

(ii) Hinsberg test : Proceed as in the Hinsberg's test for primary amines -Red or purple colour.

(ii) Ohkuma test : Add asbout 5-6 drops of the citric acid and acetic anhydride reagent to the alcoholic solution of the compound, shake and heat in a boiling water bath. Development of a red or purple colour within 2-3 minutes, indicates the presence of tertiary amine.

Quick Guess :

(a) Aromatic solid—Naphthlamines, *p*-Toluidine.

(b) Aromatic liquid, shake with water in a test tube,

(i) Floats on water-*m*-Toluidine, Dimethylamine.

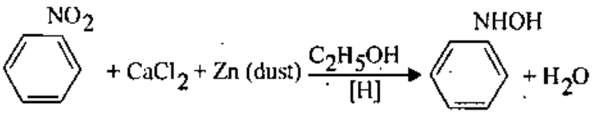
(ii) Forms layer below water-*o*-toluidine, Aniline.

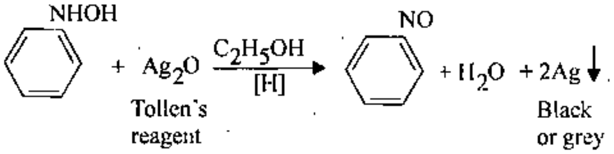
(11) NITRO COMPOUND (—NO_2)

(i) Colour : Almost all nitro compounds are light yellow or yellow in colour.

(ii) Sodium hydroxide test : Shake a small quantity of the compound with 2 c.c. of NaOH solution. Proudction to yellow, intense yellow or orange colour shows the presence of a nitro group.

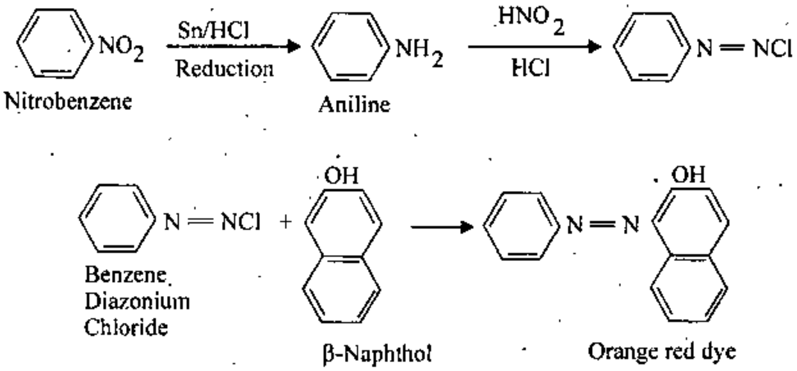
(iii) Mulliken test : Dissolve 0.1 gm. of the compound in 3 mL alcohol and then add a few drops of 10% $CaCl_2$ solution followed by a pinch of zinc dust. Boil the mixture and set aside for five minutes to cool and filter directly in 2 mL of Tollen's reagent. On warming this content a grey or black precipitate is obtained which confirms the presence of a nitro group.





(iv) Zinc-ammonium chloride test : Boil a small amount of the substance with 5 mL of 5% alcohol, 0.2 gm. each of NH_4Cl and zinc dust. Cool, filter and add 2 mL of Tollen's reagent to the filtrate. On heating, the formation of a black grey precipitate shows the presence of nitro group.

(v) Azo dye formtion : Heat 0.1 gm of the substance with 0.5 mL of conc. HCl and 2-3 small pieces of metallic tin for 3-4 minutes. Filter, cool and add 3 mL aqueous solution of $NaNO_2$. Pour this content into a beaker containing alkaline β-naphthol. Formation of an orange red dye identifies the presence of nitro group.



Quick Guess :

(a) Solid if soluble in hot water—Nitro phenols.

(b) Solid if insoluble in hot water—Nitro naphthalene, *m*-dinitro benzene, *p*-nitro toluene (bitter almond smell).

(c) Liquid with smell of bitter almond—Nitro benzene.

□□□

CHAPTER
9
CHEMICAL KINETICS

✥ INTRODUCTION

A study of features of chemical reaction such as its rate, condition for maintaining or improving such a rate and the reaction mechanism, constitute the chemical kinetics of the reaction.

Velocity of Reaction : Speed in the process of chemical change has been a very important factor. Some reactions are instantaneous while others proceed slowly. The velocity of reaction is defined as

"The rate of change of the concentration of the reactants with time."

$$\text{Velocity of reaction} = -\frac{dx}{dt}$$

where dx is the amount of the substance changed and dt is a very small interval of time. During this small interval, the velocity is assumed to be constant. The negative sign indicates that the velocity goes on decreasing with time.

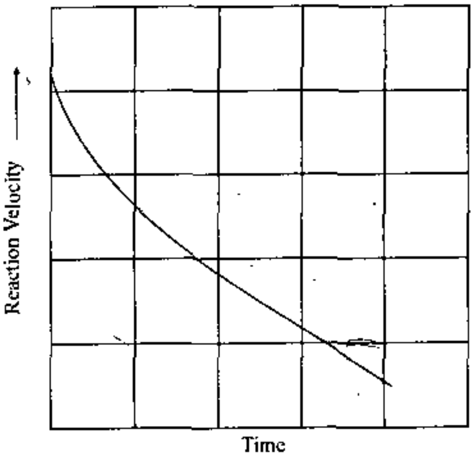


Fig. 1. Reaction velocity with time

Consider a simple change,

$$\begin{array}{lll} A \longrightarrow B & & \\ a \qquad\quad 0 & & \text{(Initial Concentration)} \\ a-x \qquad x & & \text{(Concentration after time } t.) \end{array}$$

Let us start with 'a' moles of substance A and let x moles undergo change in time t, then

$$\text{Velocity of reaction, } \frac{dx}{dt} \propto (a-x)$$

or $$\frac{dx}{dt} = k\,(a-x)$$

where k is proportionality factor known as the velocity constant or velocity coefficient or specific reaction rate. It is equal to the reaction velocity at a constant temperature only when the molecular concentration is unity.

$$\begin{array}{ll} A \longrightarrow B & \\ a \qquad\quad 0 \;\ldots\ldots & \\ (a-x) \qquad x \;\ldots\ldots\; t & \end{array}$$

$$\frac{dx}{dt} = k \qquad \left[\frac{dx}{dt} = \right]$$

Order of Reaction : The rate of chemical reaction depends upon the concentration of the reactants and it alters as the reaction proceeds.

The number of reacting molecules whose concentration alters as a result of chemical change is called the **"Order of Reaction".**

$$mA + nB \rightarrow pC + D$$

Consider that the concentration of the reactants A and B alters during the reaction.

At any instant, the velocity $\frac{dx}{dt}$ will, therefore, be given by the equation.

$$\frac{dx}{dt} = k\,[A]^m\;[B]^n$$

and the order of the reaction will be $(m+n)$.

Thus a reaction may be zero, first, second or third order according as the value of $(m+n)$ comes out to be zero, one, two or three respectively.

The hydrolysis of methyl acetate catalysed by H^+ ions is an example of **first order reaction.**

$$\underset{\text{Methyl acetate}}{CH_3COOCH_3} + H_2O \rightleftharpoons \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

Experiment 1 : To determine the velocity constant of the hydrolysis of methyl acetate catalysed by 0.5N - HCl.

Apparatus and Chemicals : A constant temperature bath, conical flask, burette, stop watch, methyl acetate, 0.5N HCl, 0.1N NaOH, phenolphthalein etc.

Method : Let freshly distilled methyl acetate and N/2 – HCl stand in separate bottles in a thermostat for half an hour, when they have acquired the temperature of the bath, mix 5 ml of methyl acetate and 10 ml of N/2 – HCl. Immediately withdraw 5 ml of the reaction mixture with the help of a pipette and add a few pieces of ice to freeze the equilibrium. Now titrate the solution by adding N/10 solution of NaOH from the burette using phenolphthalein as an indicator. Similarly, again pipette out 5 ml of the reaction mixture after five minutes and repeat the procedure. Repeat the above procedure by withdrawing 5 ml of the reaction mixture after 10, 15, 20, 30, 45 minutes. These readings give the value of V_t at different timings. The V_∞ reading indicates the reading when hydrolysis is complete. Hence to obtain this reading either the whole or remaining mixture is kept for 20 hrs. and then titration should be performed with NaOH of the remaining mixture which is heated at 50°C for about an hour to complete the reaction and then V_∞ is determined by titration with NaOH.

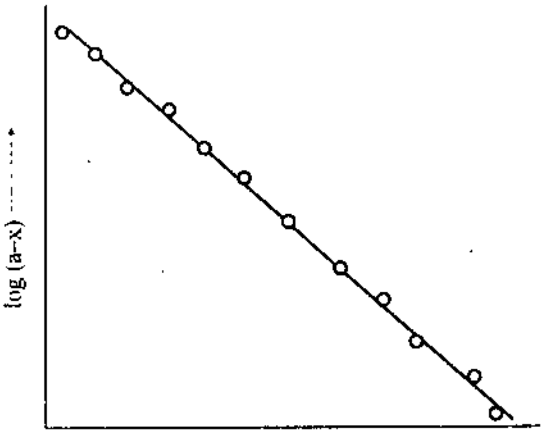


Fig. 2.

Observations :

S.No.	**Time in minutes**	**Volume of alkali ml**	$(a-x)$	$\log \frac{a}{(a-x)}$	$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$
1.	0	V_0	$V_\infty - V_0 = a$	—	
2.	10	V_{10}	$V_\infty - V_{10}$	—	
3.	15	V_{15}	$V_\infty - V_{15}$	—	
4.	20	V_{20}	$V_\infty - V_{20}$	—	
5.	30	V_{30}	$V_\infty - V_{30}$	—	
6.	45	V_{45}	$V_\infty - V_{45}$	—	
7.	∞	V_∞	—	—	

Calculations :

$$V_\infty - V_0 = a$$
$$V_\infty - V_t = (a-x)$$

$$\therefore \qquad K = \frac{2.303}{t} \log 10 \frac{V_\infty - V_0}{V_\infty - V_t}$$

Result : If the values of K are constant, then the hydrolysis of CH_3COOCH_3 is a first order reaction.

Precautions :

(i) The reactan's are allowed to attain the temperature of the thermostat or water bath.

(ii) The zero time should only be noted when ice is added to the first 5 ml of the reaction mixture.

(iii) Titration should be performed immediately when the reaction mixture has been taken out.

Experiment 2 : To study the effect of acid strength on the hydrolysis of methyl acetate.

Apparatus and chemicals : As experimental no. 1. Take 0.1 N, 0.2 N, 0.3 N, 0.4 N and 0.5 N HCl solutions.

Procedure : Proceed as Exp. 1 using 0.1 N HCl and calculate the value of rate constant K. Now determine the values of K using different concentrations of HCl (*e.g.*, 0.2 N, 0.3 N, 0.4 N and 0.5 N) and observe the effect of acid strength on the hydrolysis of methyl acetate.

Experiment 3 : To compare the strengths of HCl and H_2SO_4 by studying the kinetics of *hydrolysis of ethyl acetate.*

Apparatus and chemicals: As experimental no. 1. Take equinormal (0.5 N) solution of HCl and H_2SO_4.

Procedure : Proceed as in experiment 1. Take 0.5 N HCl and 0.5 N H_2SO_4 turn by turn and determine the velocity constant K as usual. Thus the strength of HCl : strength of $H_2SO_4 = K_{HCl} : K_{H_2SO_4}$.

Experiment 4 : To study kinetically the reaction rate of decomposition of iodide by H_2O_2.

Apparatus : As experiment no. 1.

Chemicals : H_2O_2, KI, $Na_2S_2O_3$, starch and H_2SO_4.

Theory : Consider the reaction of hydrogen peroxide with a solution of potassium iodide containing starch and a low concentration of sodium thiosulphate. The H_2O_2 oxidises iodide ion (I^-) to iodine (I_2) in *preference to oxidising thisosulphate ion* ($S_2O_3^=$)

(i) $$H_2O_2 + 2H^+ + 2I^- \longrightarrow 2H_2O + I_2 \text{ (slow)}$$

The liberated iodine cannot colour starch solution blue as it reacts instantaneously with the thiosulphate ions.

(ii) $$I_2 + 2S_2O_3^= \longrightarrow S_4O_6^= + 2I^- \text{ (fast)}$$

This goes on till thiosulphate is completely consumed and then the solution at once turns blue due to the action of iodine and starch.

(iii) I_2 + Colourless starch $\longrightarrow$ Blue starch iodide.

The (i), (ii) and (iii) reactions are known as main reaction, monitor reaction and indicator reaction respectively.

The time for the appearance of blue colour depends upon the following two factors :

(i) Initial rate of formation of I_2, which, in turn, depends upon the concentration of iodide and H_2O_2.

(ii) Amount of sodium thiosulphate present.

For any specific condition of concentration and temperature, the time for the appearance of blue colour has a clock like accuracy. This is the reason why the combination of the above three reactions are called ***clock reactions.*** *The blue colour discharge, by adding a quantity of thiosulphate, and it re-appears after* some time. This can be repeated a number of times by adding more quantities of monitor, till all H_2O_2 is consumed. Addition of monitor can be compared to rewinding the chemical clock. The subsequent time intervals will be larger even when thiosulphate additions are equal as the concentration of H_2O_2 goes on decreasing and the main reaction becomes slower.

Procedure : Take about 140 mL of distilled water in a conical flask and add about 20 mL of 1 M KI solution, 10 mL of 2 M H_2SO_4 and 1 mL of starch solution into it. Add to it exactly 5 mL of 0.025 M $Na_2S_2O_3$ solution. Keep the flask as well as 0.1 M H_2O_2 solution in the water bath.

Now add 5 mL of 0.1 M H_2O_2 solution with a pipette and start the stop watch half way through the addition. Shake the flask and keep it in a water bath. Note the time for the appearance of the blue colour without stopping the stop watch. Now add further 5 mL of 0.025 M $Na_2S_2O_3$ from the burette and shake well. Again note the time of disappearance of the blue colour. Repeat this procedure by adding 5 mL of 0.025 M $Na_2S_2O_3$ solution 4–5 times. Calculate the value of concentrations of H_2O_2 *i.e.* $(a-x)$ at the measured time interval after taking into account increase in volume of solution due to $Na_2S_2O_3$ addition. The concentrations of H^+ and I^- ions change, but since the initial concentrations are high, the change is small and may be neglected.

Initial concentration of H_2O_2 can be calculated in terms of equivalent volume of $Na_2S_2O_3$ solution. For this purpose, measure 10 mL of H_2O_2 solution and add slowly 10 mL of conc. H_2SO_4 and 8 g of KI dissolved in minimum quantity of water. The liberated iodine is then titrated against 0.025 M $Na_2S_2O_3$ solution.

Observations :

Time, t (secs)	....	t_s
Volume (mL) V_t of 0.025 M $Na_2S_2O_3$	....	V_s

Calculations :

$$V_s \propto [H_2O_2]0$$

$$V_s - V_t \propto [H_2O_2]t$$

Plot a graph between values of V_t and time, t. Slopes of tangents to this curve at various times, t, represent rate of reaction at that time.

□□□

CHAPTER
10
DISTRIBUTION LAW

◆ INTRODUCTION

This distribution law or partition law can be stated as follows: "**A mathematically constant ratio exists between the concentration of a given molecular species in any two phases in contact with each other at a constant temperature.**"

Suppose the two phases A and B have the concentration C_A and C_B of a given molecular species, then

$$\frac{C_A}{C_B} = K \qquad \text{(At constant temperature)}$$

This constant K is called **Partition coefficient or Distribution coefficient.** The partition of solute between two immiscible solvents is governed by the following law :

(i) In case, when solute undergoing partition has a molecular weight in organic solvent n times higher than water at equilibrium, we have

$$K = \frac{C_{aq.}}{{C_{org}}^{1/n}} = \frac{C_{sq}}{\sqrt[n]{C_{org}}}$$

where C_{aq} = Concentration of solute in aqueous phase.

and C_{org} = Concentration of solute in organic phase.

(ii) In second case, when solute undergoing partition has some molecular weight in both the solvents at equilibrium then

$$K = \frac{C_{aq.}}{C_{org}}$$

The study of these relationships has assumed wide importance because they provide means for determining the state of association of substance in solution.

At equilibrium, $$K = \frac{C_{\text{water}}}{C_{\text{carbonic}}}$$

where C_{water} = Concentration of the solution in aquous solvent

C_{carbonic} = Concentration of the solete in organic solvent

Experiment 1 : To determine the partition coefficient of benzoic acid between water and benzene at room temperature.

Apparatus : 4 Bottles with stoppers, separating funnel, pipette etc.

Method :

(i) In this experiment four bottles of capacity 50 ml are taken. In each bottle 10 ml of distilled water and 10 ml of liquid is added. Now add 0.25 g, 0.5 g. 0.75 g and 1.00 g of benzoic acid respectively.

(ii) Shake all the four bottles time to time for about 50-60 minutes.

(iii) Allow the mixture to separate into two distinct clear layers. the upper layer will be of benzene and lower that of water.

(iv) Separate the layers from pipette, titrate them with standard solution of NaOH using phenolpthalein as indicator.

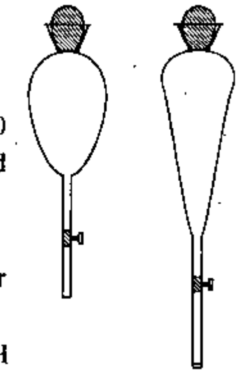


Fig. 3. Separating funnels

(v) Now separate upper layer from aqueous layer by separating funnel and titrating the definite amount of aqueous layer by pipette with standard solution of NaOH *using phenolphthalein as indicator.*

Observation Table :

S. No.	Amount of Benzoic acid	Volume with benzene layer	Volume used with aqueous layer	Normality of NaOH (From water)	Normality of NaOH (with liquid)	$\frac{C_1}{\sqrt{C_2}}$
1.	0.25gm	—	—	—	—	—
2.	0.50 gm	—	—	—	—	—
3.	0.75 gm	—	—	—	—	—
4.	1.00 gm	—	—	—	—	—

Calculations :

$$K_1 = \frac{\text{Normality of NaOH used with water layer}}{\text{Normality of NaOH used with benzene layer}} \times \frac{\text{Reading with water layer}}{\text{Reading with benzene layer}}$$

$$= x_1 \text{ (suppose)}$$

$$K_2 = x_2, K_3 = x_3, K_4 = x_4$$

Hence $$K = \frac{x_1 + x_2 + x_3 + x_4}{4}$$

Result : The distribution coefficient of benzoic acid between benzene and water at room temperature is ....

Precautions :

(i) Observations should be performed at constant temperature.

(ii) The separation of layer should be done very accurately.

(iii) Before taking the observations the mixture should be shaken well for about an hour.

Experiment 2 : To determine the distribution coefficient of iodine between carbon tetrachloride and water.

Apparatus : 4 Bottles, separating funnel, pipette, beaker etc.

Method :

(i) Prepare, first of all, a standard solution of iodine in carbon tetrachloride.

(ii) Take 10 ml, 20 ml, 30 ml. and 40 ml of this solution in different bottles.

(iii) Now add 40 ml, 30 ml, 20 ml, and 10 ml, CCl_4 in each bottle, respectively.

(iv) Add 50 ml of water in each bottle and shake them thoroughly for about 40 minutes.

(v) After shaking, separate layer with the help of separating funnel. Take out 10 ml with pipette, of each of the two layers separately and titrate with standard hypo solution.

Observations Table

S. No.	Percentage	Volume with H_2O layer	Volume with CCl_4 layer	Normality of hypo (with H_2O layer)	Normality of hypo (with CCl_4 layer)	$\frac{C_1}{C_2}$
1.	10%	0.2	0.4	*N*/100	*N*/20	—
2.	20%	—	—	—	—	—
3.	30%	—	—	—	—	—
4.	40%	—	—	—	—	—

Calculations :

The partition coefficient

$$K_1 = \frac{C_1}{C_2} = \frac{\text{Concentration of layer in } CCl_4}{\text{Concentration of layer in water}}$$

$$K = \frac{C_1}{C_2} = CCl_4$$

(i) For 10%

$$K_1 = \frac{\text{Reading with water layer}}{\text{Reading with } CCl_4 \text{ layer}} \times \frac{\text{Normality of hypo with water}}{\text{Normality of hypo with } CCl_4}$$

(ii) For 20%, $K_2 = ...$
(iii) For 30%, $K_3 = ...$
(iv) For 40%, $K_4 = ...$

Hence, $K = \dfrac{K_1 + K_2 + K_3 + K_4}{4} = ...$

Result : The value of distribution coefficient of iodine between CCl_4 and water is ...

Experiment 3 : To Study the distribution of benzoic acid between benzene and water.

Apparatus : Reagent bottles, burette, pipette, conical flask, separating funnel etc.

Theory : If the solute has the same molecular weight in both the immiscible solvents *i.e,* it is in the same molecular state, then its partition coefficient K, between the two layers will be given by

$$K = \frac{C_A}{C_B}$$

where C_A and C_B are the respective concentration of the solute in the two solvents.

Suppose in one solvent, say in solvent A, the solute has the normal molecular weight while in the second solvent B, it is associated as follows :

$$XY_n \rightleftharpoons n\,XY$$

In such a case the ratio $\frac{C_A}{C_B}$ will not be constant. The value of partition coefficient can now be calculated as follows :

Consider C_1 be the concentration of the solute XY in phase I (Solvent A) and C_2 be its concentration in phase II (second solvent B) (See fig.). Applying the law of mass action to the equilibrium (i), we get

$$KC = \frac{[XY]^n}{[(XY)_n]}$$

$$\therefore \quad [XY] = [K_c \times (XY)_n]^{1/n} = \text{constant X } [XY_n]^{1/n} \qquad ...(ii)$$

If the solute exists largely as associated molecules, which is generally true except at large dilutions, the concentration of the associated molecule $[(XY)_n]$, may be taken as equal to C_2, the total concentration, *i.e.,*

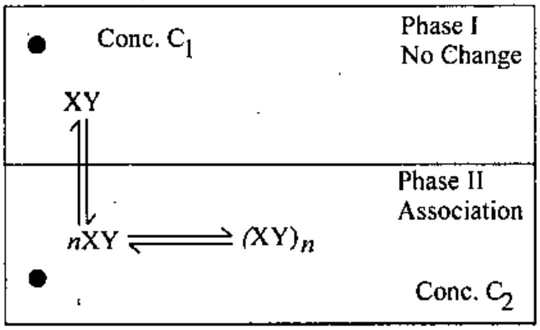
$$[(XY)_n] = C_2$$

From equation (ii), we have

$$[XY] = \text{constant} \times n\sqrt{C_2}$$

As the distribution law is valid only when concentration of similar molecular species in the two solvents is taken into consideration, therefore,

$$\frac{C_1}{[XY]} = \text{constant}$$



or $$\frac{C_1}{\sqrt[n]{C_2}} = \text{constant} = K$$

$$= (\text{partition coefficient})$$

In case of benzoic acid, which generally exists as dimer in aprotic solvents, the value of $n = 2$.

Procedure :

Dissolve about 30 g of benzoic acid in about 200 ml benzene. Now take three reagent bottles and make the following mixtures in each of them.

Bottle number	Volume of benzoic acid solution in C_6H_6 (ml)	Volume of pure C_6H_6 (ml)	Volume of distilled water (ml)
1	60	40	100
2	50	50	100
3	40	60	100

Stopper the bottles properly and shake all the bottles for about 30-45 minutes. Now allow the mixture to separate into two layers -- the lower layer will be the aqueous layer while the upper layer will be the benzene layer. Now separate each layer of each bottle by means of a separating funnel.

Now take 10 ml of the benzene layer by means of a pipette in a conical flask and add a few drops of phenolphthalein. Titrate it against $N/10$ NaOH solution. Repeat the process till you get two concordant readings. Similarly, titrate the benzene layer of each bottle by pipetting out 10 ml of the solution and titrating it against $N/10$ NaOH solution.

Pipette out 10 ml of the aqueous layer of the first bottle and titrate is against $N/50$ NaOH solution, using phenolphthalein as an indicator. Repeat the process for the other three bottles also.

Observations : Room temperature = t°C.

Bottle number	Titration with aqueous layer				Titration with benzene layer			
	Volume taken (ml)	Initial burette reading (ml)	Final burette reading (ml)	Volume of alkali used (ml)	Volume taken (ml)	Initial burette reading (ml)	Final burette reading (ml)	Volume of alkali used (ml)
	10				10			
1				V_2 (say)				V_3 (say)
	10				10			
	10				10			
2				...				...
	10				10			
	10				10			
3				...				...
	10				10			

Calculations :

Bottle I. (a) **For water layer :** $$N_1V_1 = N_2V_2$$

or $$N_1 \times 10 = \frac{N}{50} \times V_2$$

∴ $$N_1 = \frac{N \times V_2}{50 \times 10}$$

(b) For benzene layer : $$N_1V_1 = N_3V_3$$

or $$N_1 \times 10 = \frac{N}{10} \times V_3$$

$\therefore$ $$N_1 = \frac{N \times V_3}{10 \times 10}$$

$\therefore$ Concentration (C_2) of benzoic acid in benzene layer $= \dfrac{122 \times V_3}{10 \times 10}$

Similarly, the values of C_1 and C_2 for the remaining bottles can be calculated. Then for each bottle, the value of partition coefficient K, is calculated as follows, which comes out to be constant.

$$K = \frac{C_1}{(C_2)^{1/2}}$$

The mean of all the values of K is taken as the partition coefficient.

Result : The partition coefficient of benzoic acid between water and benzene = ...

Precautions : The solute should be thoroughly mixed with the immiscible solvents. The mixing should be continuously done for at least 30–45 minutes.

❑❑❑

CHAPTER
11
VISCOSITY

◆ INTRODUCTION

Flowing in one of the characteristic properties of liquids. Some liquids flow more readily than others. Thus ether will move over a glass plate much more quickly than glycerol. The rate of flow depends on the nature of the liquid and on the force which produces the flow. When a liquid flows between two plates or in a cylindrical tube – one layer slides past another and a frictional force exists along the surface in contact between any two layers. Thus a force opposes the relative motion between the two layers and this is called the viscous force.

Let us consider a stream of liquid flowing over a fixed horizontal surface. Each layer of liquid moves with different velocity. The layer in contact with the fixed surface is at rest while the velocity of other layers increases with distance from the fixed surface and is maximum for the uppermost layer. If we consider any two thin layers, the lower (slower) layer exerts a viscous force on the upper tending to drag backward. Conversely, the upper (faster) layer exerts an equal viscous force on the lower layer but tends to destroy the relative motion between the layers. Hence, if the flow of the liquid is to be maintained, some external force has to be applied. In the absence of any external force the viscous force would soon bring the liquid to rest.

"The property of a liquid owing to which it resists the relative motion of its parts is called viscosity."

When the flow of the liquid becomes steady, there will be a constant difference in the velocity between two different layers (*i.e.*, **Velocity gradient**). Newton deduced that the internal friction of viscosity would produce retarding forces proportional to the velocity gradient (dV/dx) (normal to the direction of the flow) and to the area of contact (A) between the moving sheets of liquid, *i.e.*,

$$F \propto A \cdot \frac{dV}{dx}$$

or

$$F = \eta \cdot A \cdot \frac{dV}{dx}$$

where η is constant and is known as **Coefficient of viscosity** which may be defined as :

"Tangential viscous or dragging force per unit area acting between layers of liquid in which unit velocity gradient is maintained in a direction normal to the layer."

The coefficient of viscosity, or simply known as viscosity has the dimension, $ML^{-1}T$, and is measured in C.G.S. units, *i.e.*, poise (dynes per square centimetre). Common liquids range in viscosity from 0.02 poise (ether) to 8 poise (glycerol) that of the water being about 0.01 poise. The reciprocal of the coefficient of viscosity is called **Fluidity.**

$$\text{Fluidity } (\phi) = \frac{1}{\text{Viscosity } (\eta)}$$

The determination of absolute viscosity is not always convenient. But it is easier to compare the viscosities of two liquids and if the viscosity of one of them is known, that of the other can be determined. The simple apparatus used for determining the relating flow is known as **Ostwald's Viscometer.**

Experiment 1. To determine the viscosity of the given liquid with the help of Ostwald's viscometer.

Apparatus and Chemicals : Ostwald's viscometer, pyknometer, pure given liquid, distilled water, chemical balance, stop watch etc.

Description : ***Ostwald's viscometer*** fig. (4) is a very convenient apparatus for determination of viscosity at higher temperature as it can be easily suspended in thermostat. It consists of a fine capillary tube BDconnected at its upper part with a bulb B' and its lower part with a wider U-tube provided with bulb C'. On the right hand, this capillary tube bears two marks, one above the bulb (A), and the other below it (B). A certain volume of liquid is introduced into C ', through E which is then sucked at C into the right limb and liquid rises above the mark A. This whole apparatus should be well polished.

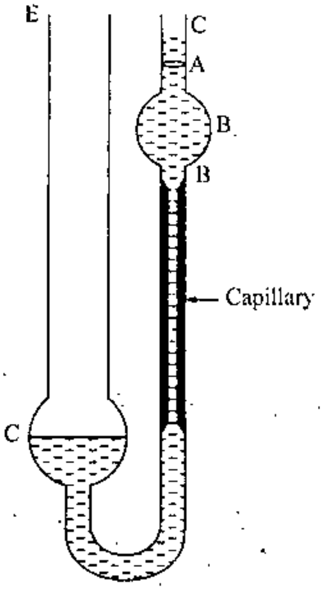


Fig. 4 Viscometer

Pyknometer is an apparatus for measuring the density or specific gravity of a liquid. It consists of a very fine capillary U-tube having a bulb on one side. It bears two marks *A* and *B*.

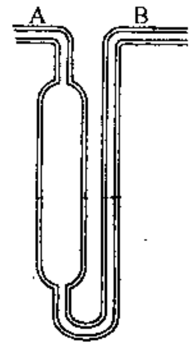


Fig. 5. Pyknometer

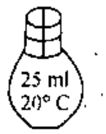


Fig. 6. Specific gravity bottle

Specific gravity bottle (Fig. 6) is also an apparatus used for measuring the density or specific gravity of a liquid. Usually its capacity is 25 c.c. at 20°C.

Theory : Let l be the length of the capillary tube BD and r its radius, then the volume of liquid (V) flowing through the capillary tube for a difference of pressure P is given by the formula :

$$V = \frac{\pi P r^4}{8\eta l}$$

where η is the viscosity of the liquid taken in viscometer.

For the first liquid $$V_1 = \frac{\eta P 1 r^4}{8\eta_1 l} \quad \text{...(i)}$$

For the second liquid $$V_2 = \frac{\eta P_2 r^4}{8\eta_2 l} \quad \text{...(ii)}$$

i.e., $$\frac{V_1}{V_2} = \frac{P_1}{P_2} \times \frac{\eta_2}{\eta_1} \quad \text{... (iii)}$$

Now pressure of the liquid, $P = h\rho g$.

Since h and g are the same for the two liquids.

Hence $P \propto \rho$

i.e., pressure of the liquid in each case is proportional to the density of liquid, therefore

$P_1 \propto \rho_1$ and $P_2 \propto \rho_2$

So, $$\frac{P_1}{P_2} = \frac{\rho_1}{\rho_2} \quad \text{...(iv)}$$

Let Q be the volume of each liquid flowing through the capillary tube in time t_1 and t_2 second, then

$$V_1 = \frac{Q}{t_1} \text{ and } V_2 = \frac{Q}{t_2}$$

$\therefore$ $$\frac{V_1}{V_2} = \frac{t_2}{t_1} \quad \text{... (v)}$$

Substituting the value of $\frac{P_1}{P_2}$ from equation (iv) and of $\frac{V_1}{V_2}$ from equation (v), in equation (iii), we get

$$\frac{t_2}{t_1} = \frac{\rho_1}{\rho_2} \times \frac{\eta_2}{\eta_1}$$

or, $$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \times \frac{\rho_1}{\rho_2}$$

Thus the comparison of viscosities is made by knowing the time for corresponding flow and the densities of the liquids.

Method : The viscometer is thoroughly rinsed with chromic acid and finally four or five times with distilled water. It is then rinsed with alcohol, ether and then dried in hot air or in electric oven.

About 10 ml of distilled water is introduced in the bulb through *E*. Now a piece of clean rubber tube is attached at the end of *C* and through it the water is sucked until is rises 1–2 cm. above the mark *A*. The viscometer is strictly kept vertical and water is allowed to reflow under its own weight. When the liquid is just at *A*, the stop watch is started and stopped immediately just when the liquid passes the point *B*. This is the time of flow of water. The experiment is repeated five to six times and the mean value is calculated.

The viscometer is dried up and the same procedure is repeated with liquid of which the viscosity is to be determined. Its time of flow is also recorded. Now to determine the density of the liquid, the pyknometer or specific gravity bottle is thoroughly cleaned first with chromic acid (solid $K_2Cr_2O_7$ + conc. H_2SO_4) and then successively with distilled water and alcohol. It is then dried in hot air or in electric oven. It is then weighed empty on a pan (in case of specific gravity). The pyknometer or bottle is then filled with distilled water upto the mark and is weighed again. It is then emptied, dried with a cloth and filled with given liquid and carefully weighed again. All the observations are recorded in the table.

Observations :

(a) Table of measurement of flow time (t_1 and t_2).

S.No.	Water		Liquid	
	Flow time between A and B	**Mean**	**Flow time between A and B**	**Mean**
1.	...		...	
2.	...		...	
3.	...		...	
4.	...	t_1	...	t_2
5.	...		...	

(b) Table for measurement of density (ρ2) :

Weight of empty pyknometer = x g

Weight of pyknometer + water = y g

Weight of pyknometer + liquid = z g

∴ Weight of water filled = $(y-x)$ g

and Weight of liquid filled = $(z-x)$ g

∴ Density of liquid $= \dfrac{(z-x)}{(y-x)} = \rho 2$ (say);

(c) Room temperature = 20°C

(d) Density of water at 20°C (ρ1) = 1.00

(e) Viscosity of water at 20°C = 0.0101 poise

Calculations :

The viscosity of liquid is calculated by the following formula assuming η_1 and ρ_1 for water 0.0101 and 1.000 respectively at 20°C.

$$\frac{\eta 1}{\eta 2} = \frac{t_1}{t_2} \times \frac{\rho 1}{\rho 2}$$

∴ Viscosity of given liquid

$$= \frac{(\text{Time } \times \text{density}) \text{ for liquid}}{(\text{Time } \times \text{density}) \text{ for water}} \times \text{Viscosity of water.}$$

Result :

Viscosity of liquid at 20°C = ... poise

Standard values at 20°C (Room temperature)

Acetic acid : 2.30; Acetone : 0.325; Aniline : 4.40; Carbon disulphide 0.363; Carbon tetra chloride : 0.969; Ethyl alcohol 1.2000; Benzene : 0.652 poise

Precautions :

1. The flow time of a liquid filled in viscometer should be between 1 to 10 minutes.
2. The viscometer and pyknometer should be thorough by cleaned.
3. The viscometer should be adjusted in an accurately vertical position.
4. The temperature should be controlled within ± 0.1°C.
5. Five or six observations should be recorded in each case.

Experiment 2. To determine the percentage composition of the given solution say, acetic acid by Ostwald Viscometer.

Apparatus : Viscometer, fractional pipette, stop watch and the given solution.

Theory : Similar to experiment 1. Note that the viscosity of any solution may be given as :

$$\frac{1}{\eta}=\frac{x}{\eta 1}-\frac{y}{\eta 2}$$

where x and y are the volume fractions of water and acetic acid, respectively, η1 and η2 are the viscosities of water and acetic acid respectively and η is the viscosity of the solution.

$$\frac{1}{\eta}=\frac{x}{\eta 1}-\frac{y}{\eta 2}$$

Method : First of all a known solution, say acetic acid is taken and its solutions of 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% are prepared. The time of flow for each solution for a definite range is noted by Ostwald viscometer. Now we take an unknown solution and again note the time of flow for the same definite range. A graph is then plotted between time in second as abscissa and percentage composition as ordinate. From this graph the percentage composition of unknown solution is calculated by drawing a perpendicular or the ordinate from known time reading as shown in figure. Suppose the time of flow in case of unknown solution is 110 seconds, then the perpendicular is drawn on the curve and from the point of curve. Another perpendicular is drawn on the ordinate and percentage composition is calculated.

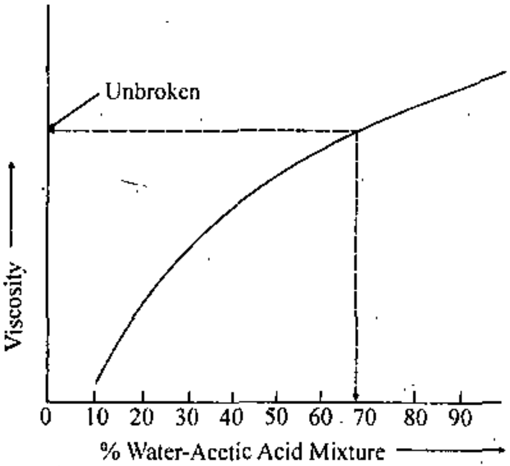


Fig. 7

Observations :

S.No.	Percentage of glacial acetic acid	Time in second
1.	10%	...
2.	20%	...
3.	30%	...
4.	40%	...
5.	50%	...
6.	60%	...
7.	70%	...
8.	80%	...
1.	Unknown solution	...

Calculation : The percentage composition of the unknown solution is calculated with the help of the graph shown above.

Result : The percentage of unknown solution = ... %.

CHAPTER
12
SURFACE TENSION

INTRODUCTION

A molecule such as *B*, in the body of the liquid experiences equal attraction from all sides so that the resultant force on it is zero. But molecule, such as *A*, on the surface layer experiences an unbalanced force because it is attracted by molecules in the bulk of the solution. There is downward pull only and not the upward pull due to the absence of molecules above them to attract. Because of this downward pull the molecules at the surface, tend to go down as if the surface were a stretched membrane. The force on the surface of the liquid is known as Surface tension and may be defined as :

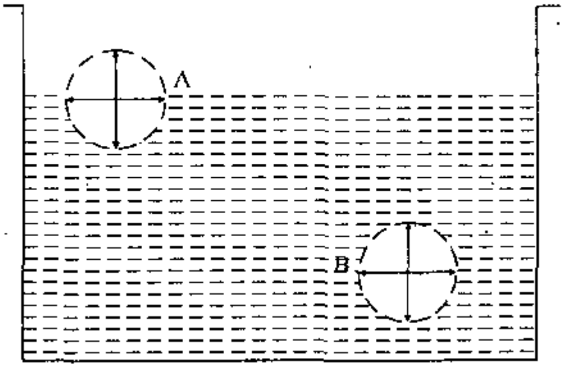


Fig. 8. Representation of surface tension

"***The force per unit length of a line drawn on the surface and acting at right angle to the line is tending to pull the surface apart along the line.***"

The dimension of the surface tension is MT^{-2}. *It is expressed in dynes per centimetre.*

Experiment 1. To determine the surface tension of liquid by drop weight method (Traube's method).

Apparatus & Chemicals : Stalagmometer, pyknometer, specific gravity bottle, beaker, water and thermometer.

Description : The apparatus used for determination of surface tension by the drop weight method is known as stalagmometer Fig (9). It consists of a dropping tube with a capillary tube, the end of which is flattened. This flattened end helps to give a larger dropping surface. This surface is already ground, flat and polished. The other end of the capillary is sealed on to a tube of wide bore containing a bulb. There are two marks etched on this stem, one above and the other below the bulb.

Pyknometer and specific gravity bottle : Pyknometer is an apparatus for measuring the density of specific gravity of a liquid. It consists of a very fine capillary U-tube having a bulb on one side. It is etched with two marks *A* and *B*.

Specific gravity bottle is also an apparatus used for measuring the density or specific gravity of a liquid. Usually its capacity is of 25 ml at 20°C.

Theory : It is based upon the fact that when a liquid is allowed to flow through capillary tube then at the end, a small drop of the liquid remains sticking at the end of the tube due to the force of tension acting along the circumference of the capillary tube and it falls down when its weight becomes just equal to surface tension force. In short, a drop just held at a surface or just dropped from the surface balances the two forces.

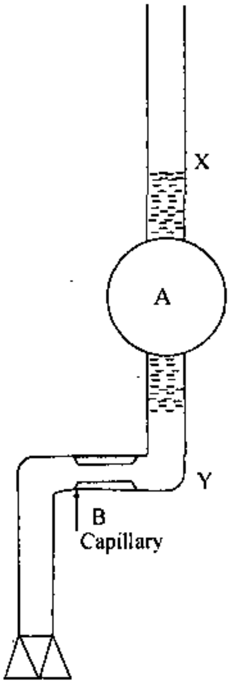


Fig. 9. Stalagmometer

(i) The gravity force exerted on the drop given by $V.d.g.$ where V is the volume of drop, d its density and g gravity, and

(ii) The force tending to uphold the drop, is given by $2\pi r\gamma$, where $2\pi r$ is the circumference of the circular surface of radius r and γ is surface tension.

When the two forces are balanced, then

The equation may be arranged as

$$2\pi r\gamma = V.d.g \qquad ...(i)$$

But if there are n number of drops counted in a volume V of the liquid of density d, then the weight of each drop is $\frac{Vd}{n}$.

$$2\pi r\gamma = \frac{Vd}{n}.g \qquad ...(ii)$$

If there are two liquids of densities d_1 and d_2 having the volume V and with surface tension γ_1 and γ_2, and the number of drops is counted be $n1$ and $n2$ respectively in the same volume, then,

$$2\pi r\gamma_1 = \frac{Vd_1}{n_1}.g$$

and $$2\pi r\gamma_2 = \frac{Vd_2}{n_2}.g \qquad \text{(For liquid 2)}$$

Therefore $$\frac{\gamma_1}{\gamma_2} = \frac{d_1}{d_2} \times \frac{n_2}{n_1}$$

Thus, if the densities of both the liquids and the number of drops in case of each liquid are known .and the surface tension of any one liquid is also known then the surface tension of the other may be calculated.

Method : The stalagmometer is cleaned first with chromic acid and finally with distilled water four or five times so as to remove any greasiness. The stalagmometer is then immersed in beaker of distilled water and it is sucked till the water rises 2–3 cm above the mark A. The stalagmometer is kept strictly vertical and water is allowed to fall till level reaches at A. Now the stop watch is started when at A, and the number of drops are counted till the water level reaches the lower mark B. It gives the drop number* n_1 of water.

The stalagmometer is then dried in hot air or in electric oven and filled with liquid upto the upper mark. The number of drops of liquid is determined exactly in the same manner .The density of liquid is then determined with the help of density bottle or pyknometer. The surface tension of liquid may be easily calculated from the above formula. It is to be noted that the density and surface tension of water are 1.0 and 72.6 dynes/cm. respectively at 20°C.

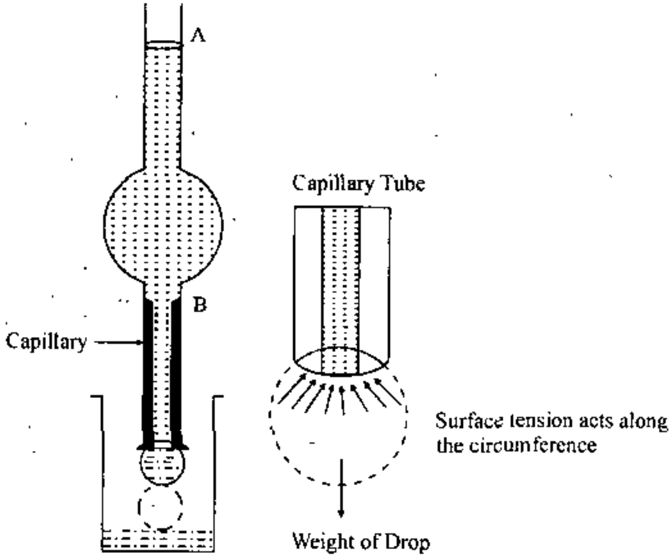


Fig. 10. Stalagmometer

The rate of dropping in this experiment should bot exceed 20 drops per minute. If the rate of formation of drops is high it can be decreased by attaching a piece of rubber tubing with a screw pinch cock to the open and adjusting the pressure till the rate becomes

Observations :

(a) Table for the number of drops (n_1 & n_2)

S.No.	Water		Liquid	
	Number of drops between A and B	*Mean* (n_1)	*Number of drops* between A and B	*Mean* (n_2)
1.	...		...	
2.	...		...	
3.	...		...	
4.	...		...	
5.	...		...	

(b) Table for measurement of density (d_2) :

Weight of empty pyknometer $= x$ g

Weight of pyknometer + water $= y$ g

Weight of pyknometer + liquid $= z$ g

∴ Weight of water filled $= (y - x)$ g

and Weight of liquid filled $= (z - x)$ g

$$\therefore \quad \text{Density of liquid} = \frac{(z-x)}{(y-x)} = \rho 2 \text{ (say)}$$

(c) Room temperature $= 20°\text{C}$

(d) Density of water at 20°C (d_1) $= 1.00$

(e) Surface tension of water at 20°C (γ_1) = 7.26 dynes/cm

Calculations : From the formula

$$\frac{\gamma_1}{\gamma_2} = \frac{n_1}{n_2} \cdot \frac{d_1}{d_2}$$

$$\gamma_2 = \frac{\gamma_1 \times n_1 \times d_2}{n_2 \times d_1}$$

or, Surface tension of liquid

$$= \frac{\text{No. of drops of water}}{\text{No. of drops of liquid}} \times \frac{\text{Density of liquid}}{\text{Density of water}} \times \text{Surface tension of water}$$

Substituting all the values, γ_2, the surface tension of liquid may be calculated.

Result : The surface tension of liquid at 20°C = ... dynes/cm.

Standard values at 20°C. (Room temperature)

Acetic acid 27.8; Acetone 23.10: Aniline 42.9; Methyl alcohol 22.61; Ethyl alcohol 23; Benzene 29.2 dynes/cm.

Precautions :

(1) Stalagmometer, pyknometer etc. all should be thoroughly cleaned and dried.

(2) The rate of flow of the liquid *i.e.* number of drops should lie between 20–25 drops per minute.

(3) *At least five or six readings should be taken with stalagmometer.*

(4) The tip of stalagmometer should be quite from free any greasy matter.

Experiment 2. To determine the percentage composition of the given mixture of two liquids Acetone and Ethyl methyl ketone, by stalagmometer.

Apparatus and chemicals : Stalagmometer, pyknometer or specific gravity bottle, thermometer, water, given solutions.

Method : First of all known solutions of (Acetone and Ethyl methyl ketone) say (10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%) are prepared. The surface tension of these solutions is determined buy stalagmometer in the usual way. Now the sample solution (of Acetone and Ethyl methyl ketone) is taken in stalagmometer and its surface tension is determined .A graph is plotted between percentage composition (abscissa) and surface tension (as ordinate) and from this graph the percentage composition of sample solution is determined with the help of its surface tension.

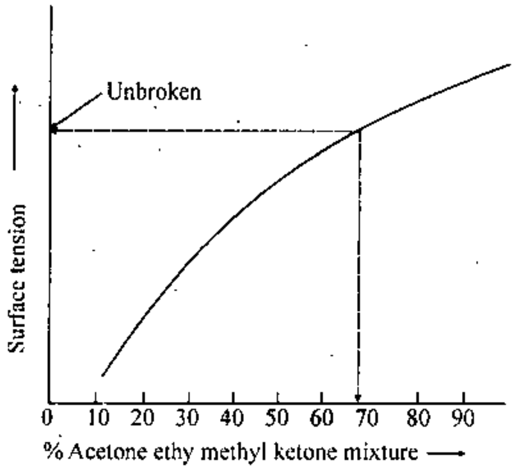


Fig. 11

Liquid	No. of drops				Average	Sepcific gravity (gmL^{-1})	Sruface tension (dyne/cm)
	I	II	III	IV			
Acetone-ethyl methyl ketone mixture.	—	—	—	—	—	—	—
10%	—	—	—	—	—	—	—
20%	—	—	—	—	—	—	—
30%	—	—	—	—	—	—	—
40%	—	—	—	—	—	—	—
50%	—	—	—	—	—	—	—
60%	—	—	—	—	—	—	—
70%	—	—	—	—	—	—	—
80%	—	—	—	—	—	—	—
Unknown solution	—	—	—	—	—	—	—

Calculations : Surface tension of the given solutions is calculated as given in experiment 1.

Result : The percentage composition of the given unknown solution is ...

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CHAPTER
13
SURFACE TENSION

✧ INTRODUCTION

Thomas Graham classified the soluble substances into two categories (i) **Crystalloids** and (ii) **Colloids.**

Crystalloids were those substances which could be obtained in crystalline form and solutions of which could pass through an animal membrane. On the other hand, colloids were those substances which were amorphous in nature and solutions of which could not pass through the membrane, Modern work has shown that crystalloids and colloids are not different kinds of matter but rather different states of matter depending upon the size of the particles.

Collodial solutions are heterogeneous system and have the size of dispersed particles lying between 10 Å – 1000 Å $(10^{-7}$ cm -10^{-4} cm). These particles can be seen with the help of an ultramicroscope.

Thus we conclude that a colloidal system is a hetergeneous system of two phases. The substance which is distributed in a medium is known as **disperse phase** and the medium in which the particles are distributed is known as **dispersion medium.** For example, in a colloidal solution of arsenious sulphide in water, the *former is a disperse phase and the* latter is the dispersion medium.

Colloidal systems can be classified into following two categories – (i) Lyophilic sols and (ii) Lyophobic sols.

The substances which mixed with a suitable liquid (dispersion medium) readily form colloidal solutions are called *lyophilic colloids, e.g., gelatin, starch, albumin etc. The substances which do not possess* much affinity for the dispersion medium and do not readily pass into the sol state when mixed with medium are called lyophobic colloids. *e.g.,* metals, precipitates etc.

Purification of Colloidal Solutions : The collodial solutions obtained any method may contain some impurities, both in the dissolved as well as suspended state. The latter can be easily removed by simple filtration method. The dissolved impurities can be removed by **dialysis.** The process of separating the impurity particles of true solution dimensions (crystalloids) from an impure sol by means of diffusion through a suitable membrane is called dialysis and the apparatus used in this method is called dialyser. It consists of a bag made of parchment paper and filled with impure colloidal solution and suspended in a tank through which pure water is circulated. The impurities of electrolytes present in the colloidal solution diffuse out of the bag leaving behind pure sol in the bag.

Coagulation : The phenomenon involving the precipitation of a colloidal solution on addition of an electrolyte is called coagulation. This is due to neutralisation of charge on colloidal particles by electrolyte, due to the fact that the neutral particles come nearer and grow in size. When the particles become sufficiently large they get precipitated or coagulated.

The coagulation capacity of an electrolyte depends upon the valence of ion responsible for causing coagulation. According to Hardy and Schulze, the greater is the valency of the oppositely charged ion of the electrolyte added to a colloidal solution, the faster is the coagulation of the colloidal solution.

Experiment 1. To prepare arsenious sulphide sol and compare the precipitation power of mono-, *bi- and trivalent cation (NaCl, $BaCl_2$ and $AlCl_3$).*

Apparatus and chemicals : Kipp's apparatus, dialyser, burette, beakers, 0.2 M solution of NaCl (11.7 g/L), 0.001 M $BaCl_2 . 2H_2O$ (0.2443 g/L) and 0.001 M $AlCl_3$ (0.1336g / L).

Procedure : Boil about 1 gram of As_2O_3 with 500 mL of distilled water until sufficiently dissolved. Cool the solution and filter. Pass through it a current of H_2S gas until it is saturated with the gas. Remove the excess of H_2S gas by bubbling through the sol a slow current of hydrogen gas. Filter the sol and dialyse if further purification be necessary.

First determine the coagulating concentrations with NaCl and then with other electrolytes. An approximate value of the coagulating concentrations may be obtained by running solutions of the electrolytes from a burette into a given volume, say 5 mL of the solution.

Now take dry and clean test tubes and arrange them in two rows (one behind the other) in the test tube stand. In the front row take 5 mL colloidal sol of As_2O_3 in each test tube. In the back row, take 1, 2, 3, 4, and 5 mL of NaCl solution; add to these solutions 4, 3, 2, 1 and 0 mL distilled water to get total volume of 5 mL in each test tube. Now mix each of the test tube contents with the corresponding As_2S_3 sol and allow the sol to stand for 30 minutes. Ascertain in which case the coagulation has occurred after this period. Say, the value lies between 3 and 4 mL.

Arrange again another set similarly and narrow down the limit of accuracy to 0.1 mL

Proceed similarly with other electrolytes. Allow the same time for coagulation.

Calculation : If the strength of the electrolyte be *x*M and if the quantity required to coagulate a given solution in a particular time be *v* mL when the total volume kept constant is 10 mL, the coagulating concentration is

$$\frac{x.v.1000}{10} \text{ millimoles L}^{-1}$$

The reciprocals of these values represent the coagulating power of Na^+, Ba^{2+} and Al^{3+} ions.

Result : The order of coagulation power of mono-, bi- and trivalent cations (Na^+, Ba^{2+} and Al^{3+}) is as follows :

$$Na^+ < Ba^{2+} < Al^{3+}$$

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APPENDIX

Table 1: Molecular Weights and Equivalent Weights

Substance	Mol. wt.	Eq. wt.	Substance	Mol. wt.	Eq. wt.
Sodium carbonate	106.00	53.00	Iodine	253.82	126.91
Sodium oxalate	134.00	67.00	Potassium hydroxide	56.00	56.00
Silver nitrate	169.89	169.89	Potassium nitrate	101.10	101.10
Oxalic acid	126.06	63.03	Sodium chloride	58.52	58.52
Benzoic acid	122.13	122.13	Copper sulphate	249.71	249.71
Ferrous ammonium sulphate	392.16	392.16	Sodium thiosulphate	248.2	248.2
Potassium ferrocyanide	422.41	422.41	Lead sulphate	303.27	303.27
Potassium dischromate	294.92	49.03			
Potassium permanganate	158.03	31.60	Sodium bicarbonate	84.00	84.00
Potassium chloride	74.56	74.56	Borax	381.44	190.72

Table 2: Atomic Number and Atomic weight of Elements

Name	Symbol	At. No.	At. Wt.
Aluminium	Al	13	26.9815
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9246
Barium	Ba	56	137.34
Beryllium	Be	4	9.0122
Bismuth	Bi	83	208.98
Boron	B	5	10.811
Bromine	Br	35	79.909
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.80
Carbon	C	6	12.01115
Cerium	Ce	58	140.12
Chlroine	Cl	17	35.513
Chromium	Cr	24	51.996

Cobalt	Co	27	58.932
Copper	Cu	29	63.57
Fluorine	F	9	18.9984
Gallium	Ga	31	67.72
Germanium	Ge	32	72.58
Gold	Au	79	196.9757
Hafnium	Hf	72	176.49
Helium	He	2	4.0026
Hydrogen	H	1	1.00797
Indium	In	49	114.82
Iodine	I	53	126.9044
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.847
Lanthanum	La	57	138.31
Lead	Pb	82	207.19
Lithium	Li	3	6.39
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.9380
Mercury	Hg	80	200.39
Molybdenum	Mo	42	95.93
Neon	Ne	10	20.183
Nickel	Ni	28	58.71
Nitrogen	N	7	14.0067
Niobium	Nb	41	92.906
Osmium	Os	76	199.2
Oxygen	O	8	15.994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Potassium	K	19	39.102
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2

Rhodium	Rh	45	102.905
Rubedium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Selenium	Se	34	78.97
Silicon	Si	14	20.086
Silver	Ag	47	107.870
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulphur	S	16	32.064
Tantalum	Ta	73	180.94
Tellurium	Te	52	127.60
Thallium	Tl	81	204.37
Thorium	Th	90	232.038
Tin	Sn	50	118.68
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.03
Vanadium	V	23	150.942
Xenon	Xe	54	131.30
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

Table 3. Physical Constant of Water at Different Temperatures :

Temperature	Density per cu. cm	Viscosity (poise)	Surface Tension (Dyne/cm)
20	0.9981	0.010087	72.75
21	0.9980	—	72.59
22	0.9978	—	72.44
23	0.9975	—	72.28
24	0.9973	—	72.13
25	0.9970	0.008973	71.97
26	0.9968	0.008737	71.82
27	0.9965	0.00855	71.66
28	0.9962	0.00836	71.50

29	0.9959	0.00818	71.35
30	0.9956	0.00800	71.18
31	0.9953	0.00784	71.02
32	0.9950	0.00768	70.86
33	0.9947	0.00762	70.71
34	0.9944	0.00737	70.54
35	0.9940	0.00722	70.38

Table 4 ; Viscosity of Liquids

Liquid	Viscosity (centipoise)	Liquid	Viscosity (centipoise)
Acetaldehyde	0.255 (10°)	Chlorobenzene	0.719 (20°)
	0.22 (20°)		0.631 (40°)
Acetic acid	1.31 (5°)	Chloroform	0.58 (20°)
	1.155 (25°)		0.542 (25°)
	1.04 (30°)		0.514 (30°)
Acetone	0.337 (15°)	Cyclohexane	1.02 (17°)
	0.316 (25°)		
	0.295 (30°)	Ethyl acetate	0.455 (20°)
Aniline	3.71 (25°)		0.441 (25°)
	3.16 (30°)		0.400 (30°)
Benzene	0.652 (20°)	Ethyl alcohol	1.200 (20°)
	0.564 (30°)		1.003 (30°)
	0.503 (40°)		0.834 (40°)
Benzaldehyde	1.39 (25°)	*Ethylene glycol*	19.9 (20°)
			9.13 (40°)
n-Buty alcohol	2.948 (20°)	Formic acid	1.804 (20°)
	2.30 (30°)		1.465 (30°)
	1.782 (40°)		1.219(40°)
Carbon tetrachloride	0.969 (20°)	Glycerine	1.490 (20°)
	0.843 (30°)		954 (25°)
	0.739 (40°)		692 (30°)
Heptane	0.409 (20°)	Methyl acetate	0.381 (20°)
	0.386 (25°)		0.320 (40°)
	0.341 (40°)	Nitrobenzen	2.03(20°)

Hexane	0.326 (20°)		
	0.294 (25°)		
iso-Butyl alcohol	4.703 (15°)	Toluene	0.590 (20°)
			0.526 (30°)
			0.471 (40°)
iso-Propyl	2.86 (15°)	Turpentine	1.487 (20°)
alcohol	1.77 (30°)		1.272 (30°)
			1.070 (40°)
Methyl alcohol	0.597 (20°)		
	0.547 (25°)		
	0.510 (30°)		
	0.456 (40°)		

Liquid	**0°C**	**10°C**	**15°C**	**20°C**	**25°C**	**30°C**	**100°C**
Formic acid	...	2.226	...	1.804	....	1:69	0.594
Glycerol	12.110	...	2.330	1.490	0.954	0.625	...
Methyl acetate	0.454	...	...	0.320	...	...	...
Methyl alcohol	0.82	...	0.623	0.597	5.547	0.510	...
Nitro benzene	...	2.48	2.24	2.03	...	...	...
Arandy oil	...	2.420	...	9.86	...	451.0	16.9
Cotton seed oil	...	...	...	70.4	...	...	...
Linseed oil (light)	...	...	...	...	...	33.1	...
Machine oil	...	...	113.80	...	...	...	4.9
Jaitun oil	...	1.38	...	84.0	...	...	...
Phenol	...	...	...	12.7	...	...	...
Propanoic acid	...	1.289	1.18	1.102	...	...	...
Propyl alcohol	3.883	...	2.52	2.256	...	1.72	...
Pyridine	...	...	...	0.974	...	...	....
Sulphuric acid	48.8	...	32.8	25.4	...	...	....
Toluene	0.772	...	0.61	0.59	...	0.526	...

Table 5. Surface Tension of Liquids

Substance	°C	Surface tension	°C	Surface tension
Acetic acid	20	27.6	50	24.7
Acetone	20	23.7	50	18.6
Benzene	20	28.88	50	25.6
Carbon tetrachloride	20	26.8	50	23.1
Chlorobenzene	20	33.2	50	29.6
Chloroform	20	27.1	60	21.7
Cycohexane	20	25.3	...	...
Ethyl acetate	20	23.9	50	20.2
Ethyl alcohol	20	22.3	50	19.8
Formic acid	20	18.4	40	16.3
n- Hexane	20	22.6	50	20.1
Methyl alcohol	20	28.4	50	25.0
Toluene	20	37.6	50	35.1

Table 6: Viscosity of Sugar Solutions of Different Concentrations

Sugar solution	15°C	20°C	125°C
0%	—	1.000	—
1%	—	1.026	—
2%	—	1.053	—
3%	—	1.082	—
4%	—	1.112	—
5%	—	1.144	—
6%	—	1.177	—
7%	—	1.213	—
8%	—	1.251	—
9%	—	1.291	—
10%	—	1.336	—
15%	—	1.589	—
20%	2.254	1.941	1.695
25%	2.859	2.442	2.118
30%	3.757	3.181	2.735
35%	5.154	4.314	3.670
40%	7.463	6.15	5.164
45%	11.59	9.36	7.710
50%	19.53	15.0	12.40
55%	36.65	28.02	21.93

60%	79.46	58.37	40.03
65%	211.3	149.9	105.4
70%	749.1	480.6	321.4
75%	403.9	222.3	140.5

Table 7 : Viscosity of Glycerine Solutions of Different Concentrations

Percentage of glycerene solution by (weight)	0°C	10°C	20°C	30°C	100°C
10	2.44	1.74	1.31	1.03	0.2838
20	3.44	2.41	1.76	1.36	—
30	5.14	3.49	2.50	1.87	—
40	8.25	5.37	3.72	2.72	0.668
50	14.6	9.10	6.00	4.21	0.910
60	29.9	17.4	10.8	7.19	1.28
70	76.0	38.8	22.5	14.1	1.93
80	225	116	60.1	33.9	3.18
90	1310	468	219	109	6.00
100	12070	3900	1412	612	14.8

Table 8 : Concentration of Acids

Acid	Specific Gravity	Percent by Weight	Approximate Normality
HCl (conc.)	1.19	37.89	11 N
HCl (dil.)	—	—	5 N
H_2SO_4 (conc.)	1.84	96.01	36 N
H_2SO_4 (dil)	—	—	5 N
HNO_3 (conc.)	1.41	69.80	16 N
HNO_3 (dil.)	—	—	5 N
CH_3COOH (conc.)	1.06	99.51	17 N
CH_3COOH (dil.)	—	—	5 N

Table 9 : Physical Constants of Liquids at 20°C

Liquid	Molecular Weight	Index of Refraction for D–Solution Line	Density (g/ml)
Acetic acid	60.05	1.3721	1.040
Aniline	93.12	1.5863	1.622
Acetone	58.08	1.3588	0.792
Benzene	78.11	1.5011	0.879

Carbon tetrachloride	153.84	1.4620 (15°)	1.595
Chloroform	119.39	1.4465(18°)	1.4984 (15°)
Ethyl alcohol	46.07	1.3611	0.785 (25°)
n- Heptane	100.20	1.3876	0.6837
n- Hexane	86.19	1.3749	0.6603
Methyl alcohol	32.04	1.3288	0.7917
Toluene	92.13	1.4969	0.8669

Table 10 : Solubility Product

Substance	Solubility product at given temperature	Substance	Solubility product at given temperature
Barium	7.0×10^{-9} (16°)	Lithium	1.7×10^{-3} (25°)
carbonate	8.1×10^{-9} (25°)	carbonate	
Barium	1.6×10^{10} (18°)	Magnesium carbonate	2.6×10^{-5} (12°)
chromate	2.4×10^{-10} (28°)		
Barium oxalate ($BaC_2O_4.2H_2O$)	1.2×10^{-7} (18°)	Magnesium oxalate	8.57×10^{-5} (18°)
Barium sulphate	0.87×10^{-10} (18°)	Mercuric sulphide	4×10^{-53} to
			2×10^{-18} (25°)
	1.08×10^{-10} (25°)	Mercurous chloride	2×10^{-18} (25°)
	1.98×10^{-10} (50°)		
Cadium sulphide	3.6×10^{-29} (18°)	Silver bromide	4.1×10^{-13} (18°)
			7.7×10^{-13} (25°)
Calcium sulphate	6.11×10^{-5} (10°)	Silver chloride	1.50×10^{-10} (25°)
			13.2×10^{-10} (50°)
Cuprous chloride	1.02×10^{-6} (18°)	Silver chromate	1.2×10^{-16} (15°)
			9×10^{-12} (25°)
Lead carbonate	3.3×10^{-14} (18°)	Silver iodide	1.5×10^{-16} (15°)
Lead chromate	1.77×10^{-14} (18°)	Strontium carbonate	1.6×10^{-8} (25°)
Lead iodide	7.47×10^{-9} (15°)	Zinc oxalate	1.35×10^{-9} (18°)
	1.39×10^{-8} (25°)		

Table 11 : Approximate pH values

Substance	pH	Substance	pH	Substance	pH
Hydrochloric acid, N	0.1	Citric acid, 0.1 N	2.2	Sodium hydroxide, 0.01N	12.0
Hydrochloric acid, 0.1 N	1.1	acetic acid N	2.4	Sodium carbonate, 0.1N	11.6

Hydrochloric acid, 0.01N	2.0	Acetic acid, 0.1 N	2.9	Ammonia, N	11.6
Sulphuric acid, N	0.3	Acetic acid, 0.01 N	3.4	Ammonia, 0.1 N	11.1
Sulphuric acid, acid, 0.01 N	1.2	Benzoic acid, 0.01 N	3.1	Ammonia, 0.01 N	10.6
Sulphuric acid, 0.01 N	2.1	Boric acid, 0.1N	3.1	Borax, 0.1 N	9.2
Oxalic acid, 0.1 N	1.6	Sodium hydroxide, N	14.0	Sodium bicarbonate, 0.1N	8.4
Tartaric acid, 0.1 N	2.2	Sodium hydroxide. 0.1 N	13.0		

Table 12 : Solubility Chart

Substance	10°	20°	30°	40°	50°	60°	80°	100°
AgCl	8.9×10^{-4}	8.9×10^{-4}	—	—	5.23×10^{-4}	—	—	2.1×10^{-3}
AgI	—	—	3.0×10^{-7}	—	—	3.0×10^{-6}	—	—
$AgNO_3$	170	222	300	376	455	526	669	952
$BaCl_2$	33.3	35.7	38.2	40.7	43.6	46.4	52.4	58.8
$Ba(NO_3)_2$	7.0	9.2	11.6	14.2	17.1	20.3	27.0	34.2
$Ca(NO_3)_2.4H_2O$	53.5	56.39	60.41	66.21	—	—	—	—
$CaCl_2.6H_2O$	65.0	74.5	102	—	—	—	—	—
$CoSO_4$	30.55	36.21	46.26	48.85	55.2	60.4	70.0	83.0
$CuSO_4.5H_2O$	17.4	20.7	25.0	28.5	33.3	40.0	55.0	75.4
$CuCl_2$	42.45	43.5	44.55	45.6	46.65	47.7	49.8	51.9
$HgCl_2$	4.6	6.1	7.7	9.3	—	14	23.1	38
I_2	—	2.9×10^{-2}	4.0×10^{-2}	5.6×10^{-2}	7.8×10^{-2}	—	—	—
KBr	59.5	65.2	70.6	75.5	80.2	85.5	95.0	105.0
KCl	31.0	34.0	37.0	40.0	42.6	45.5	51.1	56.7
$K_2Cr_2O_7$	8.5	13.1	—	29.2	—	50.5	73.0	102.0
K_2CrO_4	60.0	61.7	63.4	65.2	66.8	68.6	72.1	75.61
KI	136	144	152	160	168	176	192	208
$KMnO_4$	4.4	6.4	9.0	12.56	16.89	22.2	—	—
KNO_3	20.9	31.6	45.8	63.9	85.5	110.0	169	246
$KOH.2H_2O$	112	126	—	—	—	—	—	—
K_2SO_4	9.22	11.11	12.97	14.76	16.50	18.17	21 4	24.1
$K_2SO_4.Al(SO_4)_3.24H_2O$	4.0	5.9	8.39	11.70	17.0	24.75	71.0	—
$MgSO_4.7H_2O$	23.6	26.2	29.0	31.3	—	—	—	—
$MnCl_2.4H_2O$	68.1	73.9	80.71	88.59	98.15	—	—	—
NH_4Cl	33.3	37.2	41.4	45.8	50.4	55.2	65.6	77.3
$NaBr.2H_2O$	—	47.5	49.4	51.4	53.7	—	—	—
NaCl	35.8	36.0	36.3	36.6	37.0	37.3	38.4	39.8
$Na_2B_4O_7.10H_2O$	1.6	2.7	3.9	—	10.5	20.3	—	—
$Na_2CO_3.10H_2O$	12.5	21.5	38.8	—	—	—	—	—
$NaHCO_3$	8.15	9.6	11.1	12.7	14.45	16.4	—	—

$NaOH.H_2O$	—	1.09	119	129	145	174	—	—
$NaI.2H_2O$	168.65	178.7	190.3	205.0	227.8	256.8	—	—
$NaNO_3$	80	88	96	104	114	124	148	180
$Pb(C_2H_3O_2)_2$	—	55.04	—	—	—	—	—	—
$Pb(NO_3)_2$	48.3	56.5	66	75	85	95	115	138.8
$SrCl_2.6H_2O$	47.7	52.9	58.7	65.3	72.4	81.8	—	—
$ZnSO_4.7H_2O$	47	54.4	—	—	—	—	—	—

Table 13 : Buffer Solutions.

(a) Acetic acid – Sodium Acetic Buffer

(0.2 *M acetic* acid ; 0.2 *M* sodium acetate)

pH	Acetic acid (ml)	Sodium acetate (ml)	pH	Acetic acid (ml)	Sodium acetate (ml)
3.5	94	6	5.2	20	80
4.0	82	18	5.5	12	88
4.5	56	44	5.6	10	90
5.0	30	70	...	...	...

(*b*) *Phosphate Buffer*

(*M*/15 potassium dihydrogen phosphate; *M*/15 disodium hydrogen phosphate).

pH	KH_2PO_2 (ml)	Na_2PHO_2 (ml)	pH	KH_2PO_2 (ml)	Na_2HPO_4 (ml)
5.5	96	4	6.8	50	50
6.0	88	12	7.0	38	62
6.4	72	28	7.5	15	85
6.5	69	31	7.9	7	93
6.6	63	37	8.0	6	94

(c) *Borate Buffer*

(d) 0.05 *M* borax ; 0.2 *M boric acid*)

pH	Borax (ml)	Boric acid (ml)	
7.0	6.0	94.0	
8.0	27.5	72.5	
9.0	80.0	20.0	pH of 0.1 M borax solution is 9.2
10.0	97.5	2.5	
11.0	98.4	1.6	

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