



*Shree H. N. Shukla Group of colleges
(Affiliated to Saurashtra University & Gujarat Technological University)*

**B. Sc. Chemistry (CBCS) C-603
Semester-6 – Chapter 7
Basic Principal Of Qualitative analysis**

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✚ Introduction

There are mainly two types of analysis for the study of substance or mixture of substances Quantitative and Qualitative analysis.

❖ Quantitative Analysis

The method used to find out the amount of components present in the substance is known as quantitative analysis. This type of analysis is performed by volumetric and Gravimetric analysis.

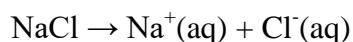
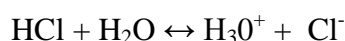
❖ Qualitative Analysis

Qualitative analysis is used for the detection and identification of constituents present in the substance or mixture of substances. If testing sample is organic than organic qualitative analysis term is used where as for Inorganic components Inorganic qualitative analysis term is used. Inorganic qualitative analysis is concerned with the detection and identification of ions present in inorganic salt. Inorganic salts are made up of positive and negative ions. Which are the results of a neutralization process 'between an acid and a base. So, each inorganic salt consists of two parts. The part contributed by an acid is called acidic radical or anion (negative ion), and the part contributed by a base is called basic radical or cation (positive ion). eg. Sodium chloride (NaCl) is a salt obtained by the neutralization of base NaOH with acid HCl. Here, Na^+ is the basic radical or cation and Cl^- is the acidic radical or anion.

So, the method of analysis of the inorganic salt or detection of the radicals present in an inorganic mixture is known as inorganic qualitative analysis.

Principle In qualitative analysis “an electrolyte (inorganic salt) reacts with the solvent and dissociate into ions — positive and negative ions”.

- ✓ The process of formation of ions by dissociation of electrolyte is called ionization.
- ✓ Acid — base or salt interact with water and dissociate into ions.
- ✓ The proportion of ions depends on the strength of the electrolyte.
- ✓ Strong electrolyte dissociates almost completely while weak electrolyte undergoes partial ionization,



- ✓ Here, ions of the inorganic components react with ions of the reagent. As a result precipitates are formed or specific colouration is observed.

✚ Some basic terms used in qualitative analysis

1) Precipitate (ppt):

Precipitate is the insoluble substance resulting from a reaction of homogeneous solution of salt with another reagent. The precipitation occurs when the value of solubility product is reached.

2) Solubility:

The maximum amount of salt dissolved in a definite volume of solution is known as its solubility.

3) Saturated solution:



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A solution in which no more solute can be dissolved is known as saturated solution. The concentration of a salt in the saturated solution of a definite temperature is known as the solubility of the salt.

It can be expressed in terms of gms/litre, mg/litre, %w/v and mole/litre.

4) Soluble salt:

If the concentration of the saturated solution is 0.1 M or more at room temperature then the salt is known as a soluble salt.

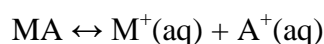
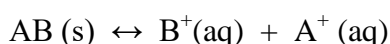
5) Sparingly soluble salt:

If the concentration of the salt is less than 0.1 M then the salt is known as a sparingly soluble salt.

6) Common ion effect:

When an electrolyte having one common ion is added to an aqueous solution of the sparingly soluble salt, the solubility of the sparingly soluble salt decreases. This effect is known as the common ion effect.

i.e



Now if an electrolyte is added to the aqueous solution of BA the equilibrium in BA shifts to left according to Lechatelier's principle and BA gets precipitates because solubility of BA decreases.

Separation of Cl^- , Br^- and I^-

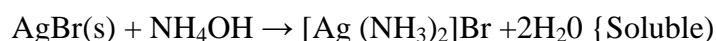
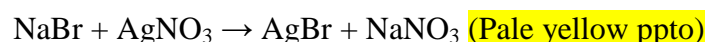
Separation of Br^- and I^- is important in qualitative analysis. Generally chlorides, bromides and iodides are soluble except those of Ag^+ (silver), Mercurous (Hg^+), lead (Pb^{+2}) and cuprous Cu^{+2} i.e in Group I. Silver chloride, bromide and iodide are insoluble in dilute or concentrated HCl, but halides of mercury, cuprous and lead are soluble in dil HCl or Conc. HCl.

■ Mixture of Cl^- , Br^- , I^- is separated by different methods as follows:

Chloride Cl^- salts react with $AgNO_3$ to form a curdy white precipitates (Ppts) which is insoluble in HNO_3 but soluble in NH_4OH solution.



Bromide (Br^-) salt react with $AgNO_3$ to form a pale yellow precipitate which is insoluble in HNO_3 but soluble in excess.



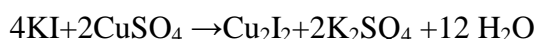
Iodide (I^-) salts react with $AgNO_3$ to form a pale yellow precipitate which is insoluble in dilute HNO_3 and NH_4OH both.



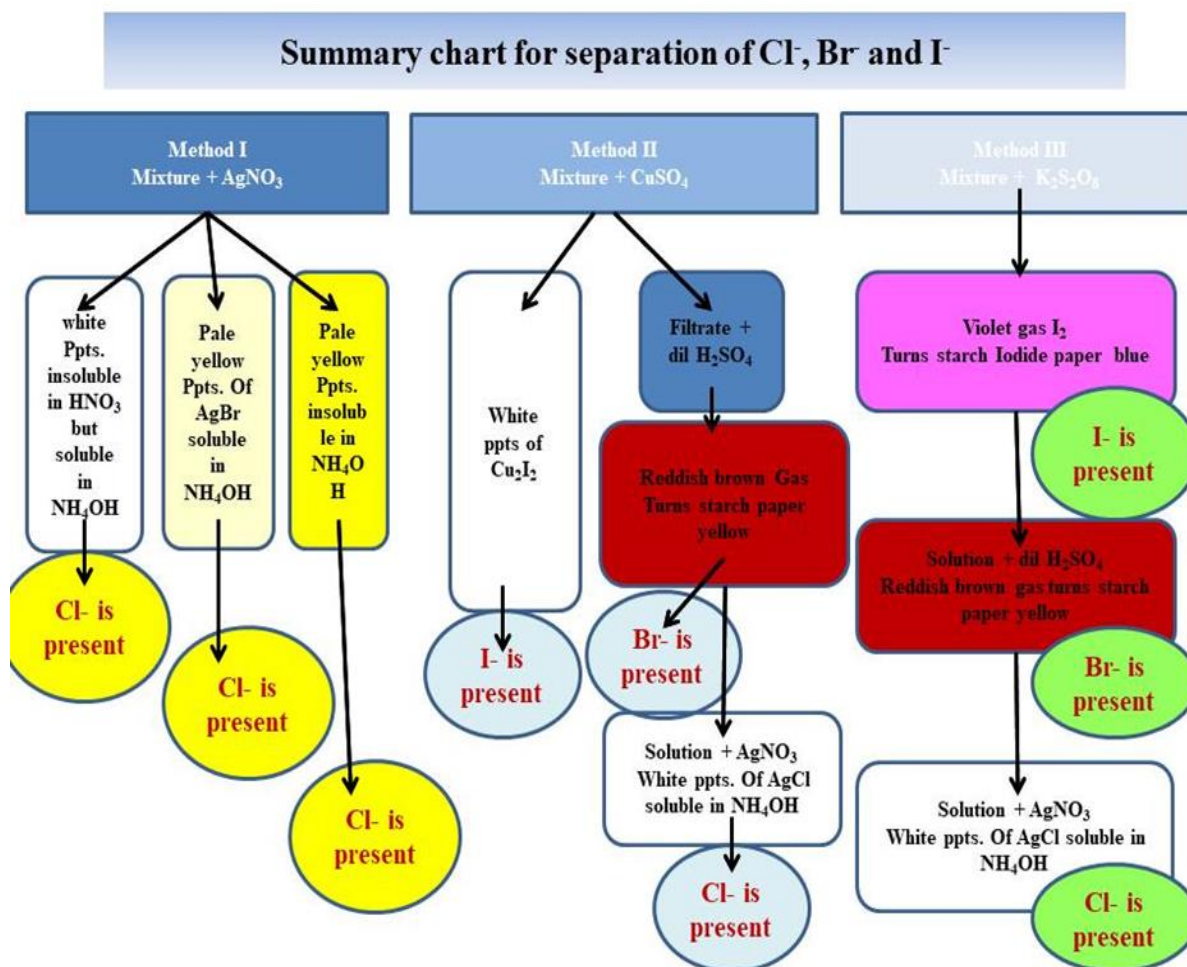
Thus on the basis of colour of silver halides and their solubility in HNO_3 and NH_4OH the halides Cl^- , Br^- , I^- can be identified.

■ Cl^- , Br^- , and I^- can be identified by the following method also;

To an aqueous solution of a mixture of a^- , Br^- , and r^- when $CuSO_4$ solution is added first precipitates of Cu_2I_2 are formed.



Filter the precipitate and add dilute H_2SO_4 to the filtrate and boil. If Br^- is present reddish brown bromine gas is evolved. Boil till all Br_2 gas is evolved. To the solution now add $AgNO_3$ for the test of which will give curdy white precipitates of Cl^- and soluble in NH_4OH .



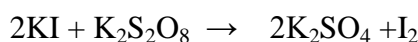


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■ Mixture of Cl^- , Br^- , I^- can be also separated by following method

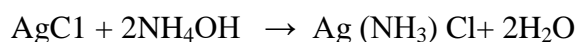
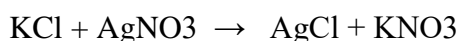
In an evaporating dish take mixture and add potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$) as per required amount. First, I^- is oxidized in I_2 (Iodine) gas and violet gas of I_2 will be evolved. Which turns starch paper blue.



After complete removal of I_2 gas, add dilute H_2SO_4 to the solution and reddish brown gas of Br_2 will be evolved which converts starch paper yellow. It shows presence of Br^- .



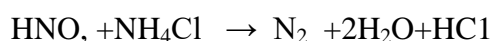
After complete removal of Br_2 as reddish brown gas, to the solution AgNO_3 is added white ppt of AgCl is formed which is soluble in NH_4OH , It shows presence of Cl^- .



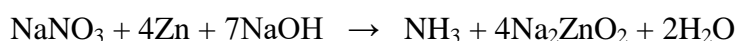
✚ Separation of NO_2^- , NO_3^- , Br^-

In the mixture of ions (sodium salts of NO_2^- , NO_3^- , Br^-) dilute HCl is added and heated, brown coloured gas of Nitrous acid is evolved, which turns starch iodide paper blue-black in colour. Shows NO_2^- is present.

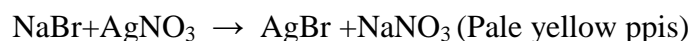
OR The aqueous solution of mixture is heated with ammonium chloride (solid), hence NO_2^- (nitrite) is converted to N_2 therefore NO_2^- is present.



After separating NO_2^- from the mixture, now the filtrate contains NO_3^- (nitrate) and bromide (Br^-). To the solution zinc (Zn) powder is added and heated after adding NaOH solution therefore ammonia gas is evolved which indicates the presence of NO_3^- ; If NH_4^+ is already present in the mixture then first it is removed by adding NaOH which converts NH_4^+ to NH_3 gas. Then the solution is cooled, add Zn powder and NaOH , so NO_3^- gets converted to NH_3 gas which indicates the presence of NO_3^- . NH_3 gas is confirmed from its smell or test with turmeric paper which turns red.

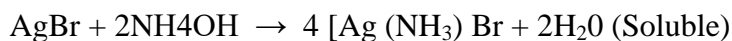


Strong smell turns red litmus blue after complete conversion of NO_3^- to NH_3 gas the filtrate is cooled which contains only Br^- . This can be detected by adding AgNO_3 , which gives pale yellow precipitates of AgBr .

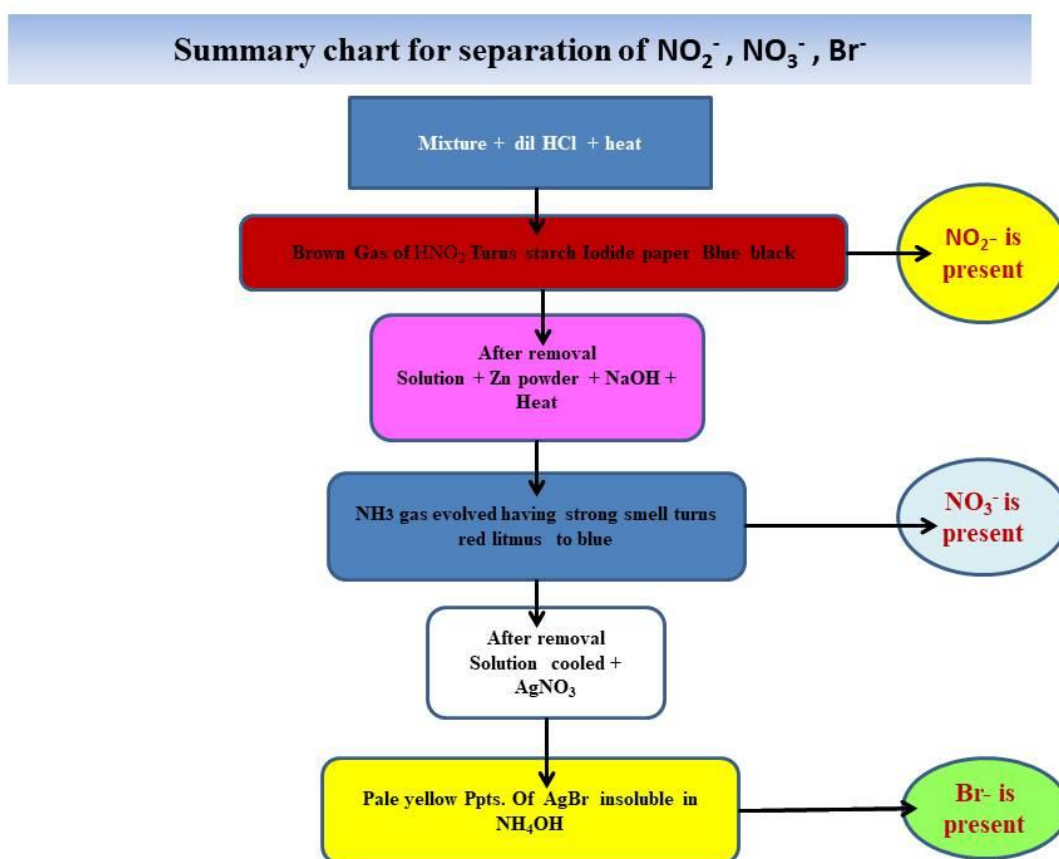




AgBr precipitates are insoluble in HNO₃ but soluble in excess NH₄OH.

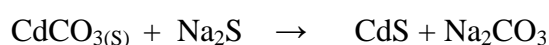


If in the mixture NH₄ is already present as cation then first it is removed by adding NaOH, which converts NH₄ to NH₃ gas. Then solution is cooled, add Zn powder and NaOH.



✚ Separation of S⁻², SO₃⁻², SO₄⁻²

The aqueous solution containing a mixture of S⁻², SO₃⁻², SO₄⁻² is first neutralized and then CdCO₃ is added and shaken vigorously so that S⁻² present will precipitate as cadmium sulphide.



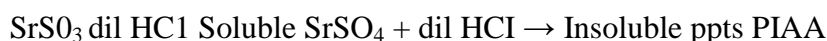
Cadmium sulphide yellow ppts



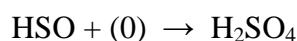
It shows presence of S^{2-} . The solution is then filtered. If excess $CdCO_3$ is present along with yellow precipitates of cadmium sulphide will dissolve in acetic acid so that only yellow cadmium sulphide precipitates will be obtained.

A slight excess $Sr(NO_3)_2$ is then added to the filtrate with constant stirring so that SO_3^{2-} and SO_4^{2-} precipitates as white $SrSO_3$ and $SrSO_4$ respectively. The precipitates are then heated with dilute HCl in which $SrSO_3$ will be soluble while $SrSO_4$ will remain as white precipitate in the solution.

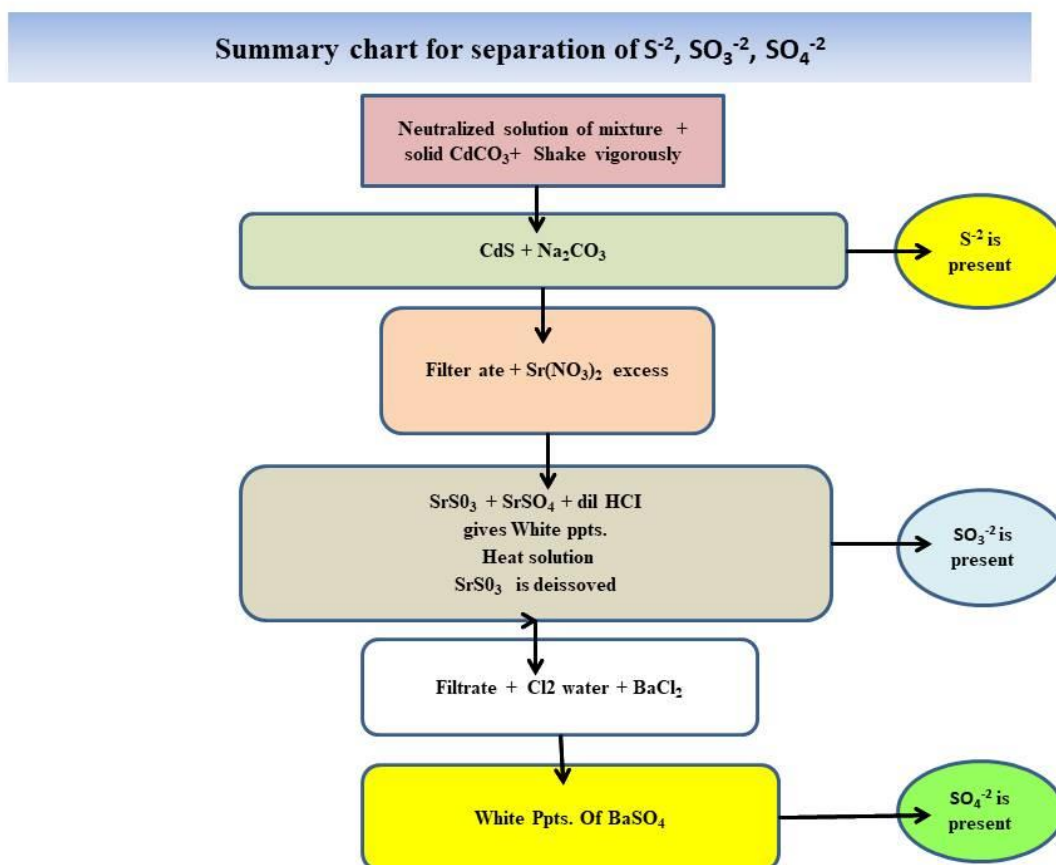
Filter precipitate of $SrSO_4$.



It shows presence of SO_4^{2-} . The filtrate now contains dissolved $SrSO_3$ on addition of chlorine water the sulphite is oxidized to sulphate. Addition of $BaCl_2$ to the solution will precipitate $BaSO_4$. In this way SO_4^{2-} can be detected.



It shows presence of SO_4^{2-}



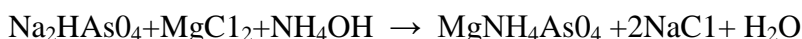
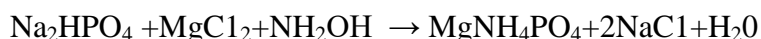


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✚ Separation Of PO_4^{-3} , AsO_4^{-3} , AsO_3^{-3}

To the neutral solution of the mixture, add Magnesia mixture ($\text{MgCl}_2 + \text{NH}_4\text{OH} \rightarrow$ white ppts.) than dissolve precipitates in NH_4Cl .



Now scratch the sides of test-tube with glass rod, wait for some time, white precipitates are formed of MgNH_4PO_4 and $\text{MgNH}_4\text{AsO}_4$. Centrifuge it. Centrifuge contains AsO_3^{-3} which does not react with magnesia mixture. Now AsO_3^{-3} present in filtrate can be detected.

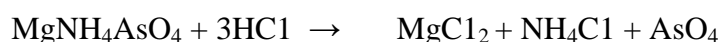
a) Filtrate + dilute HCl so that the medium becomes acidic. Then pass H_2S gas hence yellow precipitates of As_2S_3 will be formed confirming the presence of AsO_3^{-3}



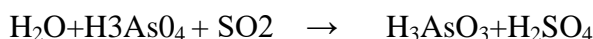
b) Filtrate + AgNO_3 gives yellow precipitates Ag_3AsO_3 indicating the presence of AsO_3^{-3}



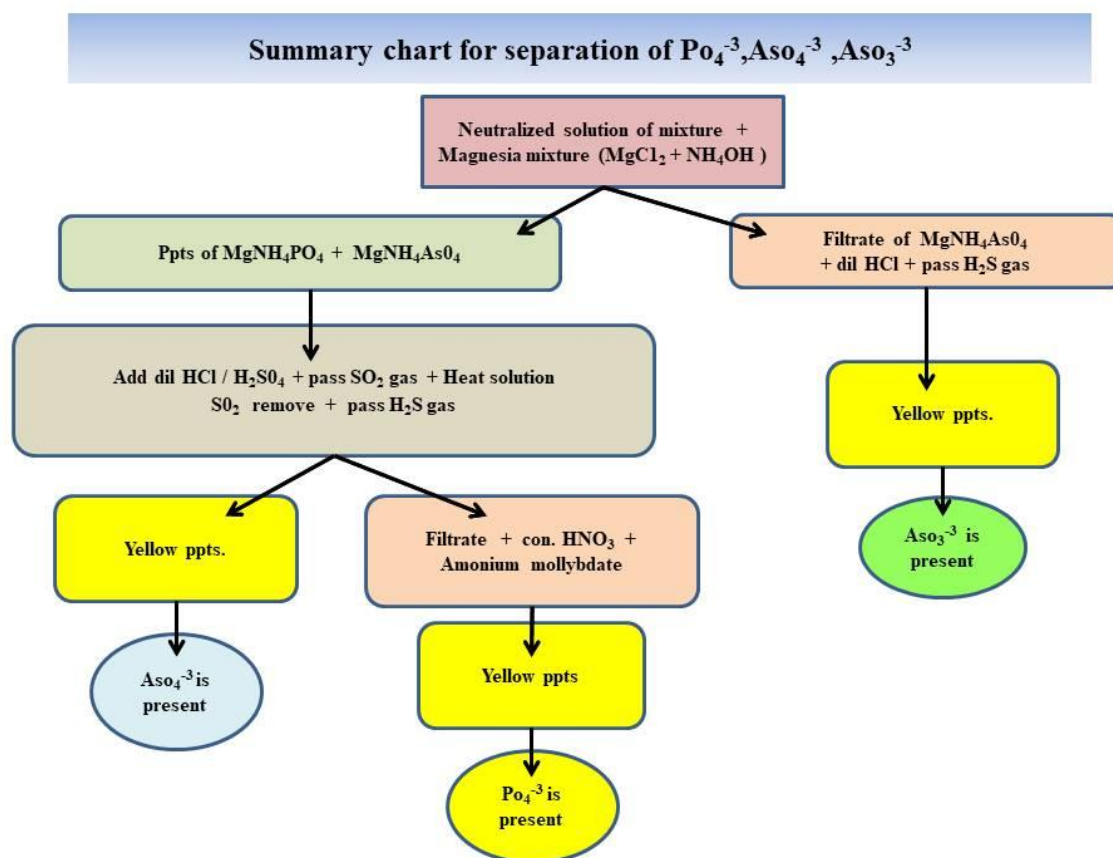
Now the white precipitates of MgNH_4PO_4 and $\text{MgNH}_4\text{AsO}_4$ are Dissolved in dilute HCl or H_2SO_4 then add SO_2 water. Boil till SO_2 gas is removed. Then pass H_2S gas-yellow precipitates are formed which indicates the presence of AsO_4^{-3} .



SO_2 gas passed and then H_2S gas.

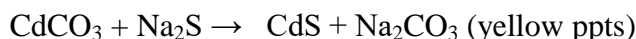


Now the filtrate contains PO_4^{-3} which can be detected by adding concentrated HNO_3 and ammonium molybdate which gives yellow precipitates of Ammonium phosphomolybdenum. Hence PO_4^{-3} is present.



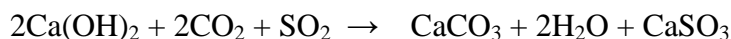
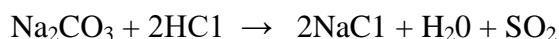
✚ Separation Of CO_3^{-2} , SO_3^{-2} , S^{-2}

To the aqueous solution of a mixture of CO_3^{-2} , SO_3^{-2} , S^{-2} sodium nitroprusside is added which gives red precipitates. To this, boiled CdCO_3 is added hence S^{-2} precipitates as yellow precipitates of cadmium sulphide. Filter ppts. of CdS .
Sodium salt of CO_3^{-2} , S^{-2} and SO_3^{-2} + CdCO_3



It shows presence of S^{-2} .

Filtrate contains CO_3^{-2} and SO_3^{-2} . Adding dilute HCl to this mixture, SO_2 and CO_2 gas is obtained which gives white precipitates with lime water.

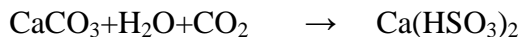
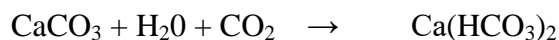


If excess of SO_2 and CO_2 gas is passed bicarbonates and bisulphate formed which are soluble.

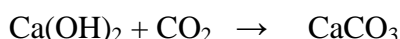


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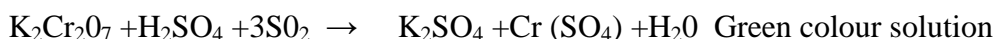
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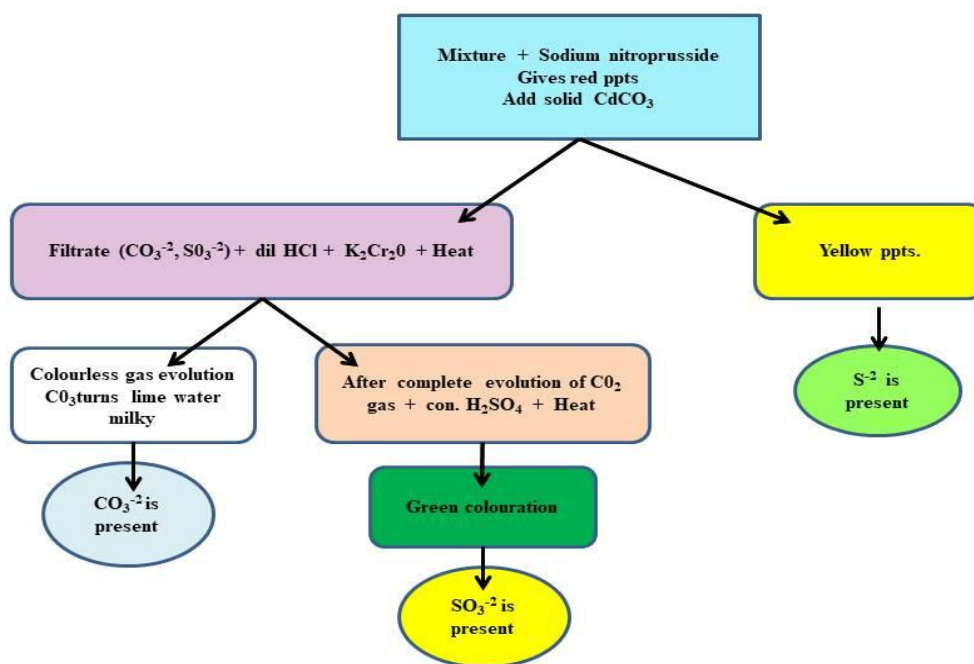
Now on adding $\text{K}_2\text{Cr}_2\text{O}_7$ to this mixture only CO_2 gas is evolved which turns lime water milky. Hence CO_3^{2-} is present.



After complete evolution of CO_2 gas, dilute H_2SO_4 is added. Due to reduction of $\text{Cr}_2\text{O}_7^{2-}$ solution becomes green in colour shows the presence of SO_3^{2-}



Summary chart for separation of CO_3^{2-} , SO_3^{2-} , S^{2-}



✚ Separation Of Cu^{+2} And Cd^{+2}

Before separating (II) group ions like Cu^{+2} and Cd^{+2} , (I) group radicals are precipitating in the acidic medium and filter ppts. Then H_2S gas is passed through the solution to precipitates the radicals of the second group. Cu^{+2} ion will precipitates as black CuS while Cd^{+2} ion will precipitates as yellow ppts of CdS . It is difficult to separate each one in presence of the other. Particularly Cd^{+2} in presence of Cu^{+2} .



Therefore Cu^{+2} is converted to a complex by addition of KCN in the basic medium (i.e by masking). Thus even when H_2S gas is passed CuS does not precipitates. For this first NH_4OH is added to a dilute solution containing Cu^{+2} and Cd^{+2} , as a result light blue precipitates of $\text{Cu}(\text{OH})_2$ is obtained. Now $\text{Cu}(\text{OH})_2$ is soluble in excess NH_4OH due to formation of $[\text{Cu}(\text{NH}_3)_4]^{+2}$.

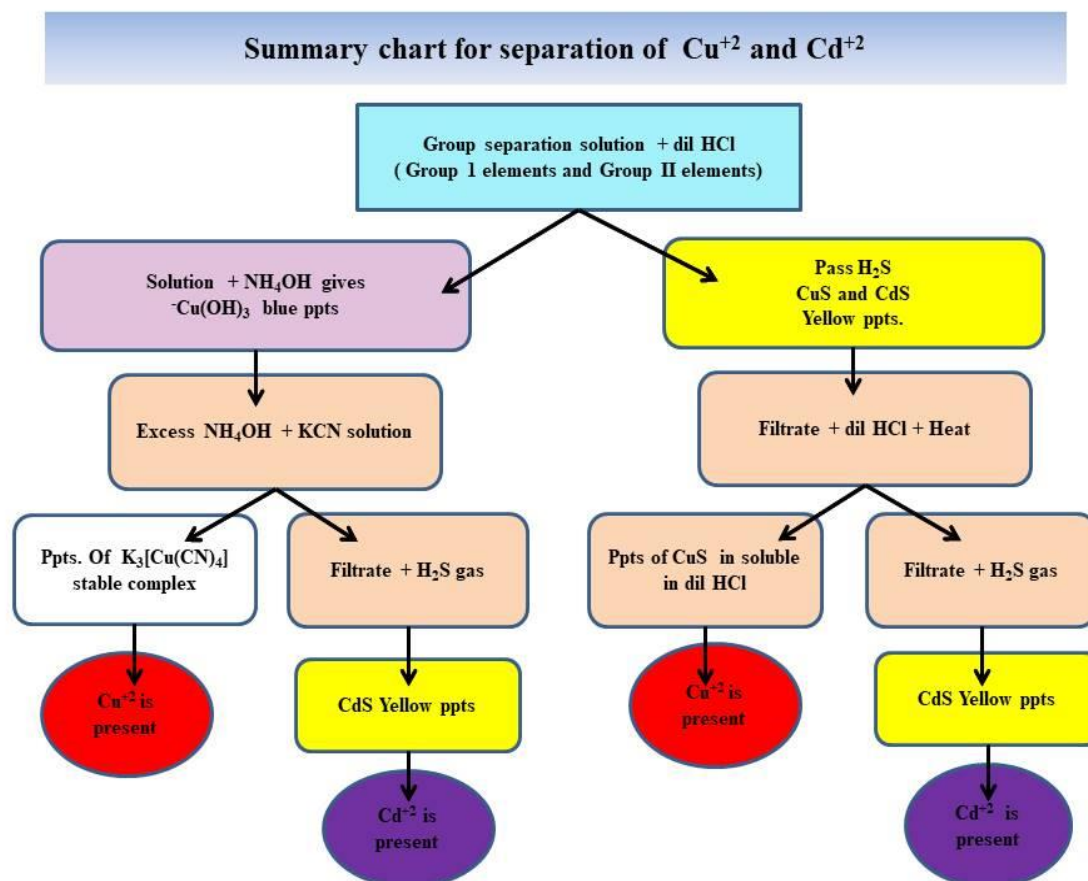
Now add dilute KCN solution till the blue colour is completely discharged.



Thus a stable potassiumcuprocyanide complex is formed which is not affected by H_2S and CuS is not precipitated. Now by passing H_2S gas through this dilute solution only cadmium sulphide can be precipitated.

OR

The solubility of sulphides of Cu_{+2} and Cd_{+2} in HCl is different. Using this difference in solubility Cu_{+2} and Cd_{+2} also can be separated CuS is insoluble in dilute HCl while CdS is soluble in boiling dilute HCl . For this the freshly obtained precipitate of sulphide is washed thoroughly with water and boiled with dilute HCl . This solution is then filtered. The filtrate is diluted with water and then H_2S gas is passed so that sulphide will precipitate. Both the precipitates separated can be dissolved in appropriate solvents and can be used for confirmatory test.





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✚ Questionary

- 1) Explain the separation of Cl^- ; Br^- , I^- with the help of any one method
- 2) Explain How to separate NO_3^- , NO_2^- , and Br^- by any one method
- 3) Explain how to separate S^{2-} , $\text{S}_2\text{O}_3^{2-}$ and SO_3^{2-} , present in a mixture.
- 4) Explain how to separate Pb^{2+} , As_2S_3 and As_2S_5 by any one method.
- 5) Explain how to separate CO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ and S^{2-} present in a mixture.
- 6) How to separate Cu^{2+} and Cd^{2+} by any one method