TOPIC : ORGANOMETALLIC CHEMISTRY_ CATION AND ANION ANALYSIS TESTS

Qualitative Analysis of Cations

Preliminary Tests

Some preliminary tests needs to be done before doing the analysis of cations.

(a) Physical Appearance: Colour and Smell

The physical examination of the unknown salt involves the study of colour, smell and density. The test is not much reliable, but certainly helpful in identifying some coloured cations. Characteristic smell helps to identify some ions like ammonium ion.

(b) Charcoal Cavity Test

This test is based on the fact that metallic carbonates when heated in a charcoal cavity decomposes to give corresponding oxides. The oxides appear as coloured incrustation or residue in the cavity. In certain cases, the oxides formed partially undergo reduction to the metallic state producing metallic beads or scales.

Examples:

a) $ZnSO_4 + Na_2CO_3 \rightarrow ZnCO_3 + Na_2SO_4$

$ZnCO_3 \rightarrow \underset{\text{Yellow when hot, white when cold}}{ZnO} + CO_2\uparrow$

b) $Pb(NO_3)_2 + Na_2CO_3 \rightarrow PbCO_3 + 2NaNO_3$

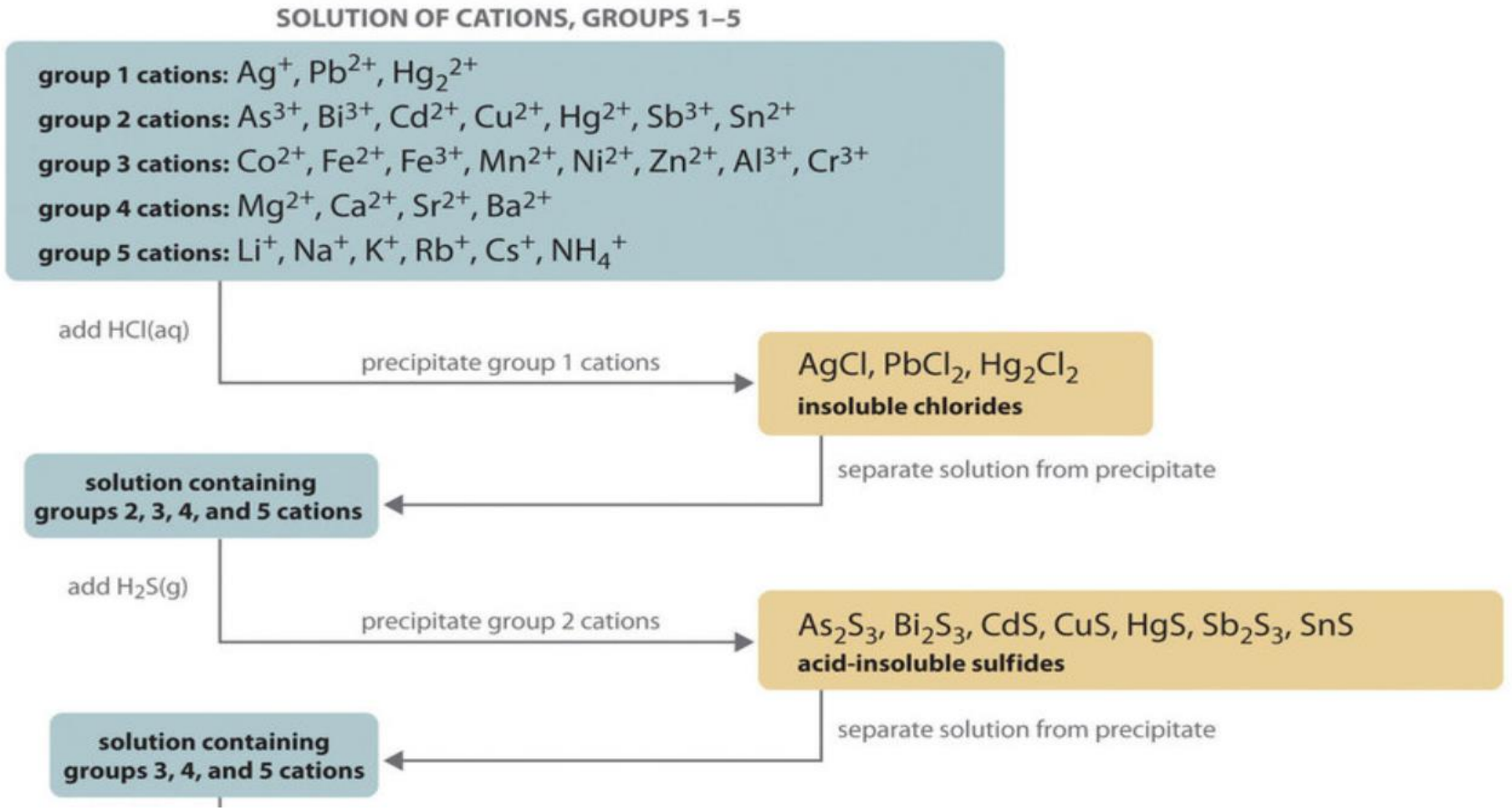
$PbCO_3 \rightarrow PbO + CO_2\uparrow$

$PbO + C \rightarrow \underset{\text{Bead}}{Pb} + CO$

c) $CuSO_4 + Na_2CO_3 \rightarrow CuCO_3 + Na_2SO_4$

$CuCO_3 \rightarrow CuO + CO_2\uparrow$

$CuO + C \rightarrow \underset{\text{(Reddish scales)}}{Cu} + CO$


SOLUTION OF CATIONS, GROUPS 1–5
group 1 cations: Ag^+, Pb^{2+}, Hg_2^{2+}
group 2 cations: As^{3+}, Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Sb^{3+}, Sn^{2+}
group 3 cations: Co^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}
group 4 cations: Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}
group 5 cations: Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+
add HCl(aq)
precipitate group 1 cations
$AgCl$, $PbCl_2$, Hg_2Cl_2
insoluble chlorides
separate solution from precipitate
solution containing groups 2, 3, 4, and 5 cations
add H_2S(g)
precipitate group 2 cations
As_2S_3, Bi_2S_3, CdS, CuS, HgS, Sb_2S_3, SnS
acid-insoluble sulfides
separate solution from precipitate
solution containing groups 3, 4, and 5 cations

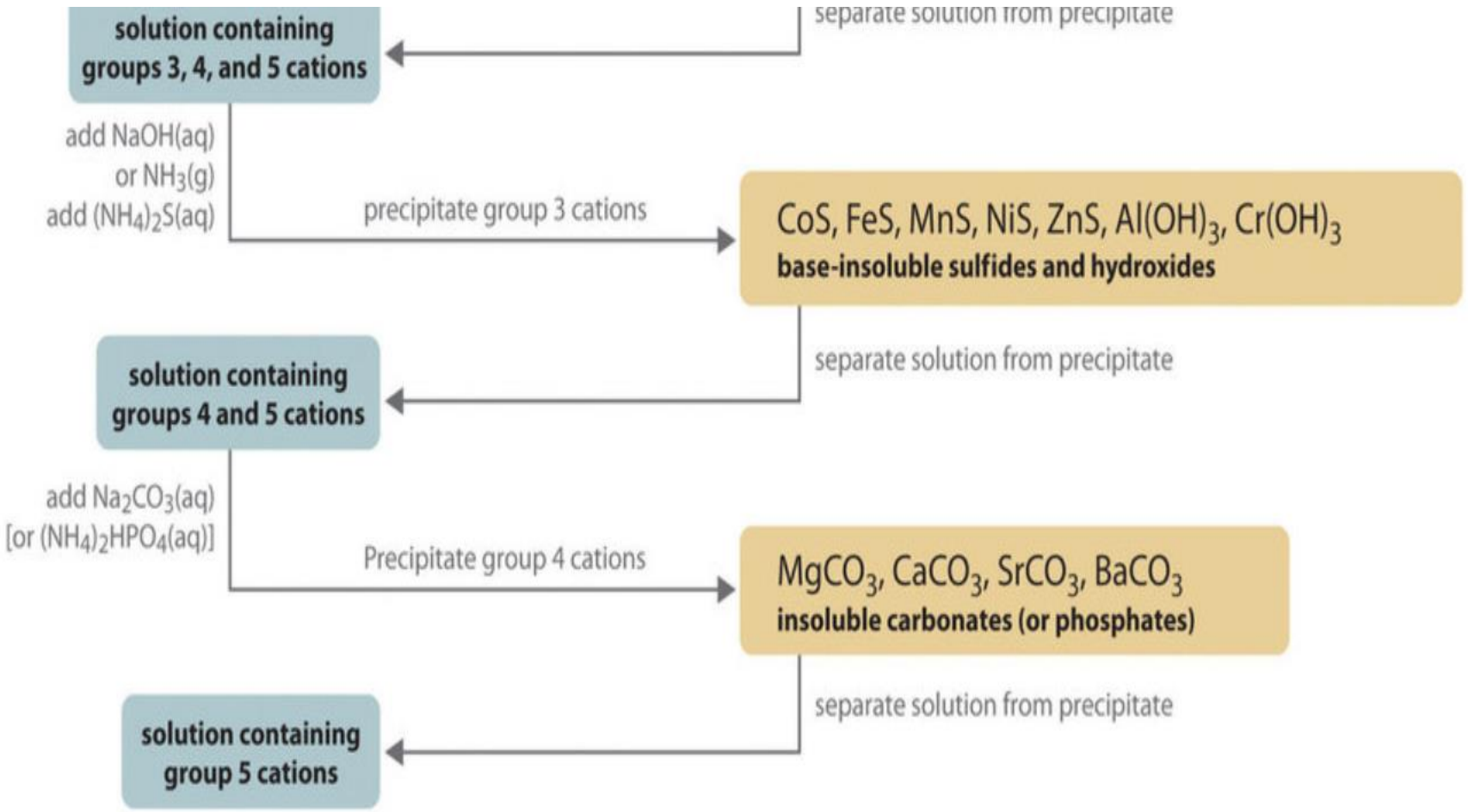


Figure 18.9.1: Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

Observations	Inference	
	Gas Evolved	Possible Anion
A colourless, odourless gas is evolved with brisk effervescence, which turns lime water milky.	CO_2	Carbonate (CO_3^{2-})
Colourless gas with the smell of rotten eggs is evolved which turns lead acetate paper black.	H_2S	Sulphide (S^{2-})
Colourless gas with a pungent smell, like burning sulphur which turns acidified potassium dichromate solution green.	SO_2	Sulphite (SO_3^{2-})
Brown fumes which turn acidified potassium iodide solution containing starch solution blue.	NO_2	Nitrite (NO_2^-)
Colourless vapours with smell of vinegar. Vapours turn blue litmus red.	CH_3COOH vapours	Acetate, (CH_3COO^-)

Confirmatory tests for CO3 2- S 2–, SO3 2-, NO2 – and CH3COO– Confirmatory (wet) tests for anions are performed by using water extract when salt is soluble in water and by using sodium carbonate extract when salt is insoluble in water. Confirmation of CO3 2– is done by using aqueous solution of the salt or by using solid salt as such because sodium carbonate extract contains carbonate ions. Water extract is made by dissolving salt in water.

Anion	Confirmatory Test
Carbonate (CO_3^{2-})	Take 0.1 g of salt in a test tube, add dilute sulphuric acid. CO_2 gas is evolved with brisk effervescence which turns lime water milky. On passing the gas for some more time, milkiness disappears.
Sulphide (S^{2-})	Take 1 mL of water extract and make it alkaline by adding ammonium hydroxide or sodium carbonate extract. Add a drop of sodium nitroprusside solution. Purple or violet colouration appears.
*Sulphite (SO_3^{2-})	(a) Take 1 mL of water extract or sodium carbonate extract in a test tube and add barium chloride solution. A white precipitate is formed which dissolves in dilute hydrochloric acid and sulphur dioxide gas is also evolved. (b) Take the precipitate of step (a) in a test tube and add a few drops of potassium permanganate solution acidified with dil. H_2SO_4. Colour of potassium permanganate solution gets discharged.
Nitrite (NO_2^-)	(a) Take 1 mL of water extract in a test tube. Add a few drops of potassium iodide solution and a few drops of starch solution, acidify with acetic acid. Blue colour appears. (b) Acidify 1 mL of water extract with acetic acid. Add 2-3 drops of sulphanilic acid solution followed by 2-3 drops of 1-naphthylamine reagent. Appearance of red colour indicates the presence of nitrite ion.

Summary

In qualitative analysis, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

Chemistry of Confirmatory Tests 1. Test for Carbonate ion [CO2 3 –]
If there is effervescence with the evolution of a colourless and odourless gas on adding dil. H2SO4 to the solid salt, this indicates the presence of carbonate ion. The gas turns lime water milky due to the formation of CaCO3

Na2CO3 + H2SO4 Na2SO4 + H2O +CO2 Ca(OH)2 + CO2 CaCO3 + H2O

If CO2 gas is passed in excess through lime water, the milkiness produced disappears due to the formation of calcium hydrogen carbonate which is soluble in water. CaCO3 + CO2 + H2O Ca (HCO3)2

2. Test for Sulphide ion [S2–] (a) With warm dilute H2SO4 a sulphide gives hydrogen sulphide gas which smells like rotten eggs. A piece of filter paper dipped in lead acetate solution turns black on exposure to the gas due to the formation of lead sulphide which is black in colour.

Na2S + H2SO4 Na2SO4 + H2S (CH3COO)2Pb + H2S PbS + 2CH3COOH

3. Test for Sulphite ion [SO2 3 –]

(a) On treating sulphite with warm dil. H2SO4 , SO2 gas is evolved which is suffocating with the smell of burning sulphur.

Na2SO3 + H2SO4 Na2SO4 + H2O + SO2

The gas turns potassium dichromate paper acidified with dil. H2SO4 , green.

K2Cr2O7 + H2SO4 + 3SO2 K2SO4 + Cr2 (SO4)3 + H2O Chromium sulphate (green)

(b) An aqueous solution or sodium carbonate extract of the salt produces a white precipitate of barium sulphite on addition of barium chloride solution.

Na2SO3 + BaCl2 2NaCl + BaSO3

This precipitate gives following tests. (i) This precipitate on treatment with dilute HCl, dissolves due to decomposition of sulphite by dilute HCl. Evolved SO2 gas can be tested.

BaSO3 + 2HCl BaCl2 + H2O + SO2

$NO_2^- + CH_3COOH \rightarrow HNO_2 + CH_3COO^-$ $2HNO_2 + 2KI + 2CH_3COOH \rightarrow 2CH_3COOK + 2H_2O + 2NO + I_2$ I_2 + Starch → Blue complex

(b) Sulphanilic acid — 1-naphthylamine reagent test (Griss-Ilosvay test)

On adding sulphanilic acid and 1-naphthylamine reagent to the water extract or acidified with acetic acid, sulphanilic acid is diazotised in the reaction by nitrous acid formed.

Diazotised acid couples with 1-naphthylamine to form a red azo-dye. $NO_2^- + CH_3COOH \rightarrow HNO_2 + CH_3COO^-$

Test for Acetate ion [CH_3COO^-]

(a) If the salt smells like vinegar on treatment with dil. H_2SO_4 , this indicates the presence of acetate ions. Take 0.1 g of salt in a china dish and add 1 mL of ethanol. Then add about 0.2 mL of conc. H_2SO_4 and heat. Fruity odour of ethyl acetate indicates the presence of CH_3COO^- ion.

(b) $2\,CH_3COONa + H_2SO_4 \rightarrow Na_2SO_4 + 2\,CH_3COOH$ $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$ Ethylacetate (Fruity odour)

Step-II : Preliminary Test with Concentrated Suphuric Acid.

If no positive result is obtained from dil.

Observe the change in the reaction mixture in cold and then warm it.

Observations	Inference	
	Gas/Vapours Evolved	Possible Anions
A colourless gas with pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.	HCl	Chloride, (Cl^-)
Reddish brown gas with a pungent odour is evolved. Intensity of reddish gas increases on heating the reaction mixture after addition of solid MnO_2 to the reaction mixture. Solution also acquires red colour.	Br_2 vapours	Bromide, (Br^-)
Violet vapours, which turn starch paper blue and a layer of violet sublimate is formed on the sides of the tube. Fumes become dense on adding MnO_2 to the reaction mixture.	I_2 vapours	Iodide, (I^-)
Brown fumes evolve which become dense upon heating the reaction mixture after addition of copper turnings and the solution acquires blue colour.	NO_2	Nitrate, (NO_3^-)
Colourless, odourless gas is evolved which turns lime water milky and the gas coming out of lime water burns with a blue flame, if ignited.	CO and CO_2	Oxalate, ($C_2O_4^{2-}$)

Borax Bead Test This test is employed only for coloured salts because borax reacts with metal salts to form metal borates or metals, which have characteristic colours.

(i) To perform this test make a loop at the end of the platinum wire and heat it in a flame till it is red hot.

(ii) Dip the hot loop into borax powder and heat it again until borax forms a colourless transparent bead on the loop. Before dipping the borax bead in the test salt or mixture, confirm that the bead is transparent and colourless. If it is coloured this means that, the platinum wire is not clean. Then make a fresh bead after cleaning the wire.

(iii) Dip the bead in a small quantity of the dry salt and again hold it in the flame.

(iv) Observe the colour imparted to the bead in the non - luminous flame as well as in the luminous flame while it is hot and when it is cold.

(v) To remove the bead from the platinum wire, heat it to redness and tap the platinum wire with your finger.

On heating, borax loses its water of crystallisation and decomposes to give sodium metaborate and boric anhydride.

Na2B4O7 .10H2O Na2B4O7 + 10H2O Borax Na2B4O7 2NaBO2 + B2O3

Sodium metaborate Boric anhydride On treatment with metal salt, boric anhydride forms metaborate of the metal which gives different colours in oxidising and reducing flame. For example, in the case of copper sulphate, following reactions occur.

CuSO4 + B2O3 Non-luminous flame Cu(BO2)2 + SO3

Cupric metaborate Blue-green Two reactions may take place in the reducing flame: (i) The blue Cu (BO2)2 is reduced to colourless cuprous metaborate as follows: 2 2 2 2 Luminous flame

2Cu(BO) + 2NaBO + C 2CuBO + Na B O + CO 2 4 7 or
(ii) Cupric metaborate may be reduced to metallic copper and the bead appears red and opaque. 2 2 2 2 4 7
Luminous flame 2Cu(BO) + 4NaBO + 2C 2Cu + 2Na B O + 2CO

Wet Tests for Identification of Cations

The cations indicated by the preliminary tests given above are confirmed by systematic analysis given below. The first essential step is to prepare a clear and transparent solution of the salt. This is called original solution.

It is prepared as follows: Preparation of Original Solution (O.S.)

To prepare the original solution, following steps are followed one after the other in a systematic order. In case the salt does not dissolve in a particular solvent even on heating, try the next solvent. The following solvents are tried:

1.

Take a little amount of the salt in a clean boiling tube and add a few mL of distilled water and shake it. If the salt does not dissolved, heat the content of the boiling tube till the salt completely dissolves. 2.

If the salt is insoluble in water as detailed above, take fresh salt in a clean boiling tube and add a few mL of dil HCl to it. If the salt is insoluble in cold, heat the boiling tube till the salt is completely dissolved.

3. If the salt does not dissolve either in water or in dilute HCl even on heating, try to dissolve it in a few mL of conc. HCl by heating. 4. If salt does not dissolve in conc. HCl, then dissolve it in dilute nitric acid. 5. If salt does not dissolve even in nitric acid then a mixture of conc. HCl and conc. HNO3 in the ratio 3:1 is tried.

Reference Books:

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