QUALITATIVE ANALYSIS OF METAL CATIONS

In the last post we studied the solubility product of salts and leant how we can manipulate the solubility of any salt by applying the common ion effect. In the coming posts we will study the practical aspects of these two phenomenons.

The common metal cations are classified into five groups for systematic qualitative analysis. This classification is based on the differences of their behaviour against some reagents and solubilities of their chlorides, sulphides and carbonates. Each group of cations reacts with a particular reagent and forms precipitates. This particular reagent is known as the group reagent of corresponding group.

Let's see what are these groups and their characteristics, and which metal ion falls in which group.

Group I: Cations of this group are lead(II) Pb^{2+}, mercury(I) Hg^{+} and silver(I) Ag^{+}. **Group reagent** of this group is dilute Hydrochloric acid. These cations form chloride precipitates with dilute HCl. Solubility product of Chlorides of lead, mercury and silver are lowest so they are precipitated first.

Group II: Cations of this group are divided in to two groups IIA and IIB on the basis of their solubility in ammonium polysulphide $(NH_4)_2S_x$. IIA group consists of mercury(II) Hg^{2+}, lead(II) Pb^{2+}, bismuth(III) Bi^{3+}, copper(II) Cu^{2+}, cadmium(II) Cd^{2+} and they are insoluble in ammonium polysulphide. IIB group consists of arsenic(III) As^{3+}, arsenic(V) As^{5+}, antimony(III) Sb^{3+}, antimony(V) Sb^{5+}, tin(II) Sn^{2+} and tin(IV) Sn^{4+} and these are soluble in ammonium polysulphide.

Group reagent: Hydrogen sulphide (gas or saturated aqueous solution). Cations of this group form precipitate in the form of sulphides on reacting with H_2S.
Did you notice? Lead(II) is common among two groups. That is because when lead reacts with 1st group reagent dil HCl it forms lead chloride, while other cations get precipitated as chloride, it doesn't precipitate completely because its chloride is more soluble than others. Its complete precipitation can be done as sulphide in 2nd group.

Group III: cations of this group are cobalt(II) Co^{2+}, Nickel(II) Ni^{2+}, iron(II) Fe^{2+}, iron(III) Fe^{3+}, chromium(III) Cr^{3+}, aluminium(III) Al^{3+}, zinc(II) Zn^{2+}, manganese(II) Mn^{2+}, manganese(VII) Mn^{7+},
Group reagent: ammonium sulphide solution or hydrogen sulphide gas in the presence of ammonia and ammonium chloride. Cations of this group don't react with group reagents of 1st or 2nd group. They all precipitate with ammonium sulphide in the form of sulphides.

Group IV: calcium(II) Ca^{2+}, strontium(II) Sr^{2+} and barium(II) Ba^{2+}
Group reagent: 1M solution of ammonium carbonate in neutral or alkaline medium. Cations of this group don't react with previous three group reagents; they give precipitate with ammonium carbonate in the form of carbonates.

Group V: Magnesium(II) Mg^{2+}, sodium(I) Na^{+}, potassium(I) K^{+} and ammonium ion NH_4^{+}. You might be surprised here to see ammonium with metal cations. It has similar characteristics to alkali metals. Its general properties are similar to that of potassium as the sizes of both ions are identical.
Group reagent: this group has no group reagent.
These groups are arranged in increasing order of solubility of chloride, sulphides and carbonates of cations. For example, chlorides of Ist group cations have lowest solubility

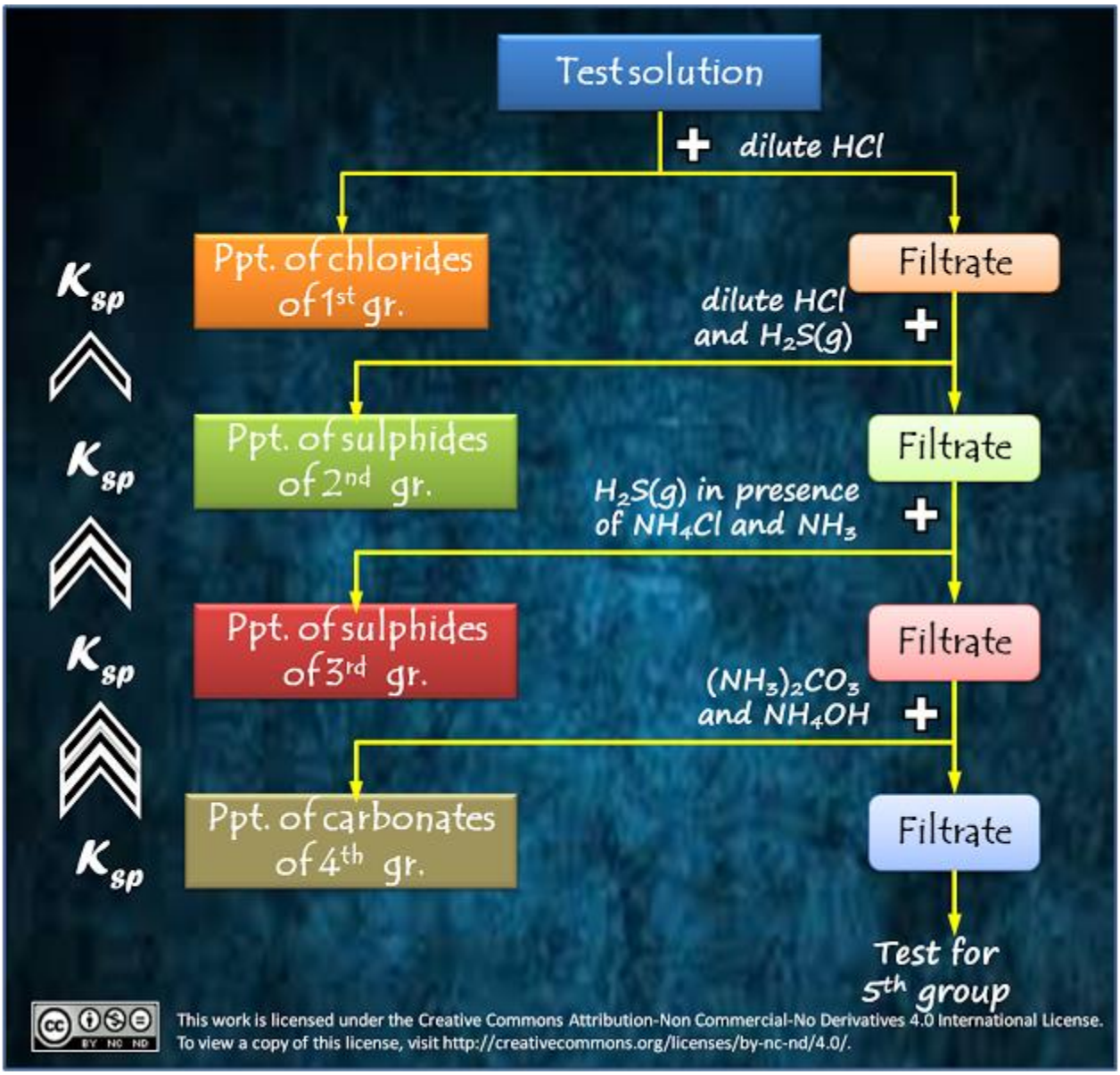
so they precipitate prior to others. Cations of any one group don't react with group reagent of any other group. Let's see how we can detect which metal cation is present in a given mixture.

On the basis of above information we can develop a strategy to find out which group of cations are present and then we can perform particular tests to detect that particular cation. First of all we have to dissolve the given mixture and prepare a clear solution. Take a small quantity of powdered mixture and check its solubility in different solvents to see which solvent dissolves it completely.

Water is the universal solvent so first we will try to dissolve the mixture in cold water, if it doesn't dissolve then try hot water. If it doesn't dissolve in water then try following solvents:

a. 6M hydrochloric acid HCl
b. Concentrated hydrochloric acid HCl
c. 8M nitric acid HNO_3
d. Concentrated nitric acid HNO_3
e. Auqa regia (3 part conc. HCl and 1 part conc. HNO_3)

Always check solubility in cold solvent then on warming. Once you have found the suitable solvent take 0.5-1g powdered mixture and prepare a solution for analysis. If mixture has been dissolved in conc. HCl, evaporate most of the acid. Then dilute it with water and make it up to 20-50 ml. If HNO_3 or aqua regia has been used for dissolution then evaporate almost all acid then add small amount of HCl and again evaporate it to a small amount then dilute it with water. The volume of final solution must be 20-50 ml for analysis.



We have prepared a solution for analysis, now we will try to find out which group cations are present in it.

Step 1: Add excess of dilute HCl (group reagent for group I) to the solution. If a white precipitate is obtained, it may contain Istgroup cations. If there is no change on adding dilute HCl then proceed to second step.

Step 2: To the above acidified solution pass H_2S gas (group reagent of IInd group) in excess. If precipitate is obtained, it may contain IIA or IIB group cations. Filter the precipitate and wash it with dilute HCl then check the solubility of precipitate in ammonium polysulphide, if it is soluble then it may contain IIB cations otherwise IIA cations may be present. If no precipitate is formed on passing H_2S gas then follow step 3.

Step 3: Neutralize the above solution with ammonia NH_3 and add ammonium polysulphide $(NH_4)_2S_x$ (group reagent for IIIrdgroup). If precipitate is obtained, it may contain group III cations. If you notice no changes then proceed to step 4.

Step 4: Add ammonium carbonate $(NH_4)_2CO_3$ (group reagent for IVth group) in excess. If precipitate is obtained, it may contain group IV cations. If no changes occur then follow step 5.

Step 5: Add disodium hydrogen phosphate Na_2HPO_4 solution in excess. If precipitate formed, it may contain Mg^{2+} cation. If no precipitate is formed then test for Na^+ and K^+.

Now you are able to detect groups of cations in a given mixture. In the coming posts we will discuss each group separately and learn how to perform confirmatory tests for particular cations.

Source : http://chemistrynotmystery.blogspot.in/2015/05/qualitative-analysis-of-metal-cations.html