UNIT 5 DETECTION OF THE CATIONS - I

Structure

5.1 INTRODUCTION

In Unit 4 you studied the detection of the anions present in a mixture. Therein you have learnt that the anions are classified into groups. For carrying out the detection of anions, group tests are first performed to find out the presence or absence of a group of anions. Individual anions of a group are then identified by performing specific tests for anions.

In this unit and in the following unit you will learn the scheme of analysis of the cations present in any mixture. You may be required to detect the presence of three or four cations in a mixture.

The scheme of analysis of cations also, which you will study in this course, involves separation of cations into several groups and then identification of individual cations. This scheme of analysis is based upon the concepts of solubility, solubility product, common ion effect and complex formation. In this unit you will study these concepts and their application in qualitative analysis. In the following unit you will study the actual scheme of analysis and the tests and reactions involved in the scheme.

Objectives

- After studying this unit, you should be able to:
- define solubility, solubility product and explain the relation between them,
- calculate solubility product from solubility data and vice-versa,
- explain the application of solubility product data in classification and analysis of cations,
- explain the common ion effect,
- describe the effect of complex formation on the solubility of a salt,

- describe the conditions for selective precipitation of a salt from solution, and
- explain how to adjust the concentration of an ion in solution.

5.2 CLASSIFICATION OF CATIONS INTO ANALYTICAL GROUPS

In this course you may be required to detect the presence of three or four cations in a mixture out of the following 26 cations:

Ag^+, Hg_2^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+},Sn^{4+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, K^+, and NH_4^+.

If we had separate specific tests for each of these ions and each such test was applicable to an individual ion even in presence of others, then we could apply them one by one and thus detect different ions present in any mixture, although it would be a cumbersome process. But, we do not have such tests which will be applicable only to individual cations and will not be interfered by other cations.

Therefore, a systematic scheme of identification of cations in any mixture has been developed. In this scheme cations are first separated into seven small groups and then cations of each group are identified individually by applying specific tests.

The separation of cations into groups is based on similar chemical properties. For example, formation of a precipitate on reaction with some common reagent. Thus, when dilute hydrochloric acid (0.2 M) is added to a solution of various cations, only Ag^+, Hg_2^{2+} and Pb^{2+} form a white precipitate (which can be filtered) whereas all the other cations remain in solution. Ag^+, Hg_2^{2+} and Pb^{2+} constitute analytical Group I of the scheme and dilute hydrochloric acid is the group reagent of Group I. Classification of cations along with group reagents and the formulae of precipitates formed is given in Table 5.1.

Table 5.1 :Classification of Cations into Analytical Groups

Analytical group	Cations	Group reagent	Precipitate
I	Ag^+, Hg_2^{2+}, Pb^{2+}	0.2 M HCl	AgCl, Hg_2Cl_2, $PbCl_2$
II	Pb^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+}, Bi^{3+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+}	H_2S in presence of 0.3 M HCl	PbS, HgS, CdS, CuS, Bi_2S_3, As_2S_3, As_2S_5,, Sb_2S_3, Sb_2S_5, SnS and SnS_2
III	Al^{3+}, Cr^{3+}, Fe^{3+}	0.1 M NH_4OH in presence of 1.5 M NH_4Cl	$Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$
IV	Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}	H_2S in presence of NH_4Cl and NH_4OH	ZnS, MnS, CoS, NiS
V	Ca^{2+}, Sr^{2+}, Ba^{2+}	$(NH_4)_2CO_3$ in presence of NH_4Cl and NH_4OH	$CaCO_3$, $SrCO_3$, $BaCO_3$
VI	Mg^{2+}	$(NH_4)_2HPO_4$ in presence of NH_4Cl and NH4OH	$Mg(NH_4)PO_4$
Zero	K^+, NH_4^+	No common group reagent	

You should realise that an analytical group number in the above table does not refer to a group number in the periodic table.

Classification of cations into analytical groups as shown in Table 5.1 is based on whether or not a cation forms an insoluble salt on reacting with a group reagent under specified conditions. Thus, all cations which form an insoluble salt on reacting with a group reagent fall in one analytical group. Whether a salt will be soluble or insoluble in a solution, depends on the solubility and the solubility product of the salt which you will study in the next section. But before that you may like to try the following SAQ.

SAQ 1

Both Cu^{2+} and Co^{2+} form a precipitate on reaction with H_2S, then why do they belong to two different analytical groups? Explain in one or two sentences.

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5.3 SOLUBILITY AND SOLUBILITY PRODUCT

When a solid is added to a given amount of solvent, the solid has a tendency to pass into solution. If we go on adding the solid to the solution at a given temperature, a state is reached when some of the solid remains undissolved. The solution is then said to be **saturated. The amount of solute that can be dissolved in a specified amount of solvent at a specified temperature to give a saturated solution is called its solubility**. Solubility is generally expressed in the units of moles per cubic decimeter ($mol\ dm^{-3}$) or in grams per cubic decimeter ($g\ dm^{-3}$). Solubility when expressed in moles per cubic decimeter is called **molar solubility** and when expressed in grams per cubic decimeter is called **gram solubility**.

Nearly all compounds dissolve in water to some extent, their solubility varying over a very wide range. Compounds that dissolve in water to give a solution with a concentration of about 0.02 moles per cubic decimeter at room temperature are usually considered as soluble compounds. If the concentration of the solution of a compound is less than $0.02\ mol\ dm^{-3}$ at room temperature, the compound is classified as sparingly soluble.

Silver chloride with a solubility of $1.37 \times 10^{-5}\ mol\ dm^{-3}$ in water indeed is a sparingly soluble salt. As a result when silver chloride is placed in water, only a very small amount of it dissolves in water to give a saturated solution. As you know that all the sparingly soluble salts are strong electrolytes, the AgCl that dissolves will be completely dissociated into Ag^+ and Cl^- ions. Thus there will be an equilibrium between undissolved AgCl and its ions in solution:

$$AgCl(s) \xrightleftharpoons{H_2O} AgCl(aq) \xrightleftharpoons{H_2O} Ag^+(aq) + Cl^-(aq)$$

The equilibrium constant for the above reaction can be written as:

$$K_c = \frac{[Ag^+]\,[Cl^-]}{[AgCl(s)]} \qquad \text{(Eq. 5.1)}$$

Water is not included in the above expression because it is neither consumed nor produced in the reaction. The terms $[Ag^+]$ and $[Cl^-]$ in the above expression represent the concentrations of Ag^+ and Cl^- ions in moles per cubic decimeter when the reaction is at equilibrium and the solution is saturated with AgCl. The term $[AgCl(s)]$ represents the concentration of solid AgCl i.e., the number of moles of AgCl in one cubic decimeter of solid AgCl, which can be calculated from the density and molecular weight of AgCl. Thus,

$$[AgCl(s)] = \frac{\text{Volume} \times \text{density}}{\text{molecular weight}} = \frac{1000 \times 5.56}{143.34}$$

$$= 38.8 \text{ mol/dm}^3 = \text{constant}$$

Hence, from equation 5.1, you will get,

$K_c \times [AgCl(s)] = [Ag^+][Cl^-]$

Since, the product of K_c and [AgCl(s)] will be constant, we can introduce a new constant K_{sp} in place of $K_c \times [AgCl(s)]$. Hence,

$$K_c \times [AgCl(s)] = K_{sp} = [Ag^+][Cl^-] \qquad \text{(Eq. 5.2)}$$

Here, K_{sp} is known as **solubility product constant** or simply **solubility product.** In general, for any sparingly soluble salt like A_xB_y which may dissociate as following:

$$A_xB_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

The equilibrium constant $K_c = \dfrac{[A^{y+}]^x . [B^{x-}]^y}{[A_xB_y(s)]}$

or $$K_c \times [A_xB_y(s)] = K_{sp} = [A^{y+}]^x[B^{x-}]^y \qquad \text{(Eq. 5.3)}$$

Expressed in words the **solubility product constant of a sparingly soluble salt is equal to the product of concentrations of ions in its saturated solution with each concentration raised to the power equal to the number of ions in one formula unit of the compound**. Solubility product constants of some common inorganic salts are listed in Table 5.2.

Table 5.2 : Solubility Product Constants at 25° C

Name of Solid	Formula	K_{sp}
Aluminium hydroxide	$Al(OH)_3$	1.9×10^{-33}
Aluminium phosphate	$AlPO_4$	1.3×10^{-20}
Antimony sulphide	Sb_2S_3	2.0×10^{-93}
Barium carbonate	$BaCO_3$	8.1×10^{-9}
Barium hydroxide	$Ba(OH)_2$	5.0×10^{-3}
Barium sulphate	$BaSO_4$	1.1×10^{-10}
Bismuth sulphide	Bi_2S_3	2.0×10^{-72}
Cadmium sulphide	CdS	4.0×10^{-29}
Calcium carbonate	$CaCO_3$	4.8×10^{-9}
Calcium hydroxide	$Ca(OH)_2$	7.9×10^{-6}
Cobalt sulphide (α)	CoS(α)	6.0×10^{-21}
Copper(II) sulphide	CuS	8.7×10^{-36}
Iron(II) hydroxide	$Fe(OH)_2$	8.0×10^{-15}
Iron(III) hydroxide	$Fe(OH)_3$	6.3×10^{-38}
Iron(II) sulphide	FeS	5.0×10^{-18}
Iron(III) sulphide	Fe_2S_3	1.0×10^{-88}
Lead chloride	$PbCl_2$	1.6×10^{-5}

Lead sulphide	PbS	8.0×10^{-28}
Magnesium carbonate	$MgCO_3$	4.0×10^{-5}
Magnesium hydroxide	$Mg(OH)_2$	1.5×10^{-11}
Manganese(II) hydroxide	$Mn(OH)_2$	2.0×10^{-13}
Manganese(II) sulphide	MnS	5.0×10^{-15}
Mercury(I) chloride	Hg_2Cl_2	1.1×10^{-18}
Mercury(II) sulphide	HgS	3.0×10^{-53}
Nickel hydroxide	$Ni(OH)_2$	2.0×10^{-15}
Nickel sulphide (α)	$NiS(\alpha)$	3.0×10^{-21}
Silver bromide	$AgBr$	5.0×10^{-13}
Silver chloride	$AgCl$	1.8×10^{-10}
Silver iodide	AgI	1.5×10^{-16}
Silver sulphide	Ag_2S	7.0×10^{-50}
Strontium carbonate	$SrCO_3$	9.4×10^{-10}
Strontium hydroxide	$Sr(OH)_2$	3.2×10^{-4}
Strontium sulphate	$SrSO_4$	2.8×10^{-7}
Tin(II) sulphide	SnS	8.0×10^{-29}
Zinc hydroxide	$Zn(OH)_2$	4.5×10^{-17}
Zinc sulphide	ZnS	1.1×10^{-21}

* When freshly precipitated from basic solution, the more soluble alpha (α) forms of CoS and NiS are formed.

Before we discuss the relation between solubility and solubility product, you may like to attempt SAQ 2 on solubility product constant.

SAQ 2

Write solubility product expressions for saturated solutions of Ag_2CO_3 and Bi_2S_3

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5.3.1 Relation Between Solubility and Solubility Product

You have studied the concepts of solubility and solubility product. We will now establish a relation between the two so that you could find out the one if you know the other.

Let S mol dm^{-3} be the solubility of the sparingly soluble salt A_xB_y, then the corresponding concentrations of cations and anions in its saturated solution will be xS mol dm^{-3} and yS mol dm^{-3}, respectively:

$$A_xB_y(s) \xrightleftharpoons{H_2O} \underset{S}{A_xB_y(aq)} \xrightleftharpoons{H_2O} \underset{xS}{xA^{y+}(aq)} + \underset{yS}{yB^{x-}(aq)}$$

Substituting the values of [A^{y+}] and [B^{x-}] in Eq. 5.3, we get,

$$K_{sp} = [xS]^x [yS]^y$$

or $$K_{sp} = x^x \cdot y^y . S^{x+y} \qquad \text{(Eq. 5.4)}$$

Can you apply Eq. 5.4 to find out the relation between the solubility and the solubility product constant for AgCl, CaF_2 and As_2S_3 ?

In case of AgCl, x = 1, y = 1, hence from Eq. 5.4

$$K_{sp}(AgCl) = S^{1+1} = S^2$$

Since the solubility of AgCl at 25° C is 1.37×10^{-5} mol dm^{-3},

$$K_{sp}(AgCl) = (1.37 \times 10^{-5})^2 = 1.88 \times 10^{-10}$$

In case of CaF_2, we have x = 1, y = 3, hence from Eq. 5.4,

$$K_{sp}(CaF_2) = 1^1 \cdot 2^2 \cdot S^{1+2} = 4S^3$$

In case of As_2S_3, we have x = 2, y = 3, hence from Eq. 5.4,

$$K_{sp}(As_2S_3) = 2^2 \cdot 3^3 \cdot S^{2+3} = 4 \times 27\, S^5 = 108\, S^5$$

Thus, if you know the solubility of a sparingly soluble salt, its solubility product constant can be easily calculated and vice-versa.

SAQ 3

Solubility product constant of CaF_2 is 4.0×10^{-11}, can you calculate the solubility of CaF_2 in water?

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5.3.2 Use of Solubility Products in Comparing Relative Solubilities of Salts

The value of dissociation constant, K_a, of an acid, HA, is directly proportional to the concentration of H_3O^+ ions furnished by the acid in solution:

$$HA + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

You can see that the value of K_a is directly proportional to the concentration of H_3O^+ in solution or in otherwords to the strength of the acid. Thus, by looking at the following K_a values, you can immediately conclude that formic acid is a stronger acid than acetic acid:

Formic acid (HCOOH), $K_a = 1.8 \times 10^{-4}$

Acetic acid (CH_3COOH), $K_a = 1.8 \times 10^{-5}$

Similarly the value of dissociation constant, K_b, of a base B, is directly proportional to the concentration of OH^- ions furnished by the base in solution:

$$B + H_2O \rightleftharpoons HB^+(aq) + OH^-(aq)$$

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

By comparing the dissociation constants of methylamine ($K_b = 4.8 \times 10^{-4}$) and ammonia ($K_b = 1.8 \times 10^{-5}$), you can immediately say that the former is a stronger base than the latter.

Now the question arises, can we in the same manner use the solubility product data to compare the relative solubilities of salts in solution?

Answer is yes, if the salts produce the same number of cations and anions in solution. For example, CuS and NiS produce the same number of cations and anions in solution and their solubility products are 8.7×10^{-36} and 3.0×10^{-21}, respectively. For these salts $K_{sp} = S^2$, therefore you can immediately conclude that the solubility of NiS is higher than that of CuS in water.

But, if the salts produce different number of cations and anions on dissolution in water, you cannot predict their relative solubilities so easily from their solubility product data. Although the solubility product of $CaCO_3$ (4.8×10^{-9}) is larger than that of Ag_2CO_3 (8.1×10^{-12}), it will be erroneous to conclude that $CaCO_3$ is more soluble than Ag_2CO_3 in water because they do not produce the same number of ions in solution. In fact $CaCO_3$ is less soluble (6.9×10^{-5} mol dm^{-3}) than Ag_2CO_3 (1.3×10^{-4} mol dm^{-3}) in water.

5.4 THE COMMON ION EFFECT

In preceding section, you studied the relation between solubility and solubility product of a sparingly soluble salt. In this section, you will study the common ion effect which in fact means the effect of common ions on the solubility of a sparingly soluble salt.

By a common ion we mean an ion that is common to two substances in the same solution/mixture. For example, the common ion in a solution of a mixture of AgCl and $AgNO_3$ is the Ag^+ ion. Similarly the common ion in a solution of a mixture of AgCl and NaCl is the Cl^- ion. We will try to find out what will happen to the solubility of AgCl, if it is dissolved in a solution containing $AgNO_3$ or NaCl i.e., containing a common ion.

A qualitative answer to this question can be easily found on the basis of Le Chatelier principle. According to this principle, when the concentration of either Ag^+ or Cl^- ions is increased, the solubility equilibrium should shift towards left forming more of solid AgCl in order to oppose the effect of the increase in concentration of either Ag^+ or Cl^- ions.

$$AgCl(s) \xrightleftharpoons{H_2O} Ag^+(aq) + Cl^-(aq)$$

This means, there will be a decrease in the solubility of AgCl in presence of a common ion such as Ag^+ or Cl^- as compared to that in pure water. Now let us derive an expression that will be useful in calculating the solubility of sparingly soluble salts in presence of common ions.

Solubility of Silver Chloride in Presence of Silver Nitrate

Let us assume that silver chloride is dissolved in a solution containing C mol dm^{-3} of $AgNO_3$. In solution, then, there will be Ag^+, Cl^- and NO_3^- ions present. The Cl^- and NO_3^- ions are provided by the dissolution of AgCl and $AgNO_3$ in water, respectively. However, there are two sources of Ag^+ ions in solution. One is from dissolution of $AgNO_3$ and the other from dissolution of AgCl in water. A solution of $AgNO_3$ of concentration C mol dm^{-3} will furnish C mol dm^{-3} of Ag^+ ion (and C mol dm^{-3} of NO_3^- ions) in solution. If S mol dm^{-3} is the solubility of AgCl at equilibrium in presence of $AgNO_3$, then AgCl will furnish S mol dm^{-3} of Ag^+ ions (and S mol dm^{-3} of Cl^- ions) in solution. This phenomenon can be represented as given below:

$$AgCl(s) \xrightleftharpoons{H_2O} Ag^+(aq) + Cl^-(aq)$$

Initial concentration	C M	0M
Equilibrium concentration	(C+S)M	SM
	(from $AgNO_3$)	(from AgCl)

Substituting the values of $[Ag^+(aq)]$ and $[Cl^-(aq)]$ in solubility product expression of AgCl, we get

$$K_{sp}\,(AgCl) = [Ag^+]\,[Cl^-]$$
$$= (C + S)\,(S)$$

or $$S = \frac{K_{sp}}{C + S}$$

In pure water, the solubility of AgCl is 1.37×10^{-5} mol dm^{-3}. In a solution of $AgNO_3$, we expect it to be even smaller. It is, therefore, quite reasonable to expect that the Ag^+ ion concentration from dissolution of AgCl, S, will be much smaller as compared to the Ag^+ ion concentration from dissolution of $AgNO_3$ i.e., C>>S. Hence,

$$S = \frac{K_{sp}}{C}$$

The K_{sp} of AgCl is 1.88×10^{-10} and if the concentration of $AgNO_3$ solution, C, is 1.0 mol dm^{-3}, then the solubility of AgCl, S, at equilibrium in this solution will be

$$S = \frac{K_{sp}}{C} = \frac{1.88 \times 10^{-10}}{1.0} = 1.88 \times 10^{-10} \text{ mol dm}^{-3}$$

If you compare the solubility of AgCl in 1.0 mol dm^{-3} solution of $AgNO_3$ with that of AgCl in pure water, you will find that the solubility of AgCl in former is roughly 100,000 times less than that in the latter.

$$\frac{\text{Solubility of AgCl in 1.0 mol dm}^{-3}\text{ AgNO}_3\text{ solution}}{\text{Solubility of AgCl in pure water}}$$
$$= \frac{1.88 \times 10^{-10}\text{ mol dm}^{-3}}{1.37 \times 10^{-5}\text{ mol dm}^{-3}}$$
$$= 1.37 \times 10^{-5}.$$

This decrease in the solubility of AgCl in a solution of $AgNO_3$ is due to the common ion effect. We can similarly show that the solubility of AgCl, S, in a solution containing C mol dm^{-3} of NaCl will be as follows:

$$S = \frac{K_{sp}}{C} = \frac{1.88 \times 10^{-10}}{C} \text{ mol dm}^{-3}.$$

Thus, we can say that the **solubility of sparingly soluble salts such as AgCl is further decreased due to the common ion effect.**

We derived an expression for the solubility of AgCl in a solution of $AgNO_3$ and NaCl of concentration C mol dm^{-3}. Can you now find out the solubility of CaF_2 in i) pure water and ii) 0.10 mol dm^{-3} NaF ?. The K_{sp} of CaF_2 is 4.0×10^{-11}.

i) Let us assume that the solubility of CaF_2 in pure water is S. According to Eq. 5.4,

$$K_{sp} = x^x \cdot y^y \cdot S^{x+y}$$

For CaF_2, $x = 1$ and $y = 2$

Hence, $K_{sp} = 1^1 . 2^2 . S^{1+2} = 4S^3$

or $4.0 \times 10^{-11} = 4S^3$

$$\therefore S^3 = \frac{4.0 \times 10^{-11}}{4}$$

$$\therefore S = (1.0 \times 10^{-11})^{1/3}$$

$$= 2.2 \times 10^{-4} \text{ mol dm}^{-3}.$$

ii) Let S be the solubility of CaF_2 at equilibrium in a solution of NaF of concentration 0.10 mol dm^{-3}. According to the solubility equilibrium expression,

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

Initial concentration	0M	0.10 M (from NaF)
Equilibrium concentration	SM	(2S + 0.10) M
	(from CaF2)	(from NaF)

$$K_{sp} \text{ of } CaF_2 = [Ca^{2+}][F^-]^2$$

$$\text{or } 4.0 \times 10^{-11} = (S)(2S + 0.10)^2$$

Since S is very small in comparison to 0.10, hence

$$4.0 \times 10^{-11} = S(0 + 0.10)^2$$

or $$S = \frac{4.0 \times 10^{-11}}{(0.10)^2} = 4.0 \times 10^{-9} \text{ mol dm}^{-3}.$$

You can again see that the solubility of CaF_2in a solution of 0.10 M NaF is 5.5×10^4 times smaller than that in pure water.

Now that we have seen how the presence of common ion affects the equilibrium of sparingly soluble salt, we come to the following conclusions:

- In a saturated solution, the solubility product, K_{sp}, is equal to the product of the concentrations of the constituent ions raised to suitable powers, i.e., the ionic product, Q.
  $K_{sp} = Q$.
- When the ionic product is less than the solubility product, i.e., $Q < K_{sp}$, the solution is unsaturated and the concentration of the ions can be increased by dissolving more of the salt.

Ionic product of a compound is equal to the product of the concentrations of the constituent ions, each raised to the power that corresponds to the number of ions in one formula unit of the compound.

- When the concentration of either of the two ions of a sparingly soluble salt in solution is increased by the addition of a soluble salt containing a common ion, the ionic product increases i.e., $Q > K_{sp}$. The equilibrium responds in such a way that the value of K_{sp} is preserved. As a result, the solubility of sparingly soluble salt decreases and it precipitates out from the solution.

5.5 COMPLEX FORMATION

In the preceding section you studied the concept of common ion effect and its effect on the solubility of sparingly soluble salts. In this section you will study the concept of complex formation which finds extensive application in qualitative analysis.

You might have studied in the CHE-02 course that an ion or a compound, in which a central metal ion/atom is attached to a group of ions and/or molecules such that the normal valency of the metal is exceeded, is known as a complex ion or a complex compound. $[Ag(NH_3)_2]^+$, $[Cu(NH_3)_4]^{2+}$, $[Cd(CN)_4]^{2-}$ and $[HgCl_4]^{2-}$ are some of the examples of complex ions. In complex ions/compounds, the ions/molecules attached to the central metal ion/atom are called as ligands. NH_3, CN^- and Cl^- are the examples of ligands. Each ligand is bonded to the central metal ion/atom by donation of atleast one pair of electrons.

When the Cu^{2+} ion combines with the ammonia molecules in aqueous solution, a deep blue complex ion, $[Cu(NH_3)_4]^{2+}$, is formed:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

To deal with the complex ion equilibria quantitatively, we use the equilibrium constant for the complexation reaction. The equilibrium constant for the complexation reaction is known as the **formation constant**, K_f. The formation constant for the above complexation reaction can be represented as follows:

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}]\,[NH_3]^4}$$

Formation constants of some complex ions are listed in Table 5.5. The higher is the value of the formation constant, the greater is the stability of the complex ion in solution.

Table 5.5 : Formation Constants of Some Complex Ions

Complex ion	Equilibrium reaction	K_f
$[AgCl_2]^-$	$Ag^+ + 2Cl^- \rightleftharpoons [AgCl_2]^-$	1.1×10^5
$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.6×10^7
$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	5.6×10^{18}
$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	1.7×10^{13}
$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.1×10^{13}
$[Cu(CN)_3]^{2-}$	$Cu^+ + 3CN^- \rightleftharpoons [Cu(CN)_3]^{2-}$	2.0×10^{27}
$[CdCl_4]^{2-}$	$Cd^{2+} + 4Cl^- \rightleftharpoons [CdCl_4]^{2-}$	6.3×10^2
$[Cd(CN)_4]^{2-}$	$Cd^{2+} + 4CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	7.1×10^{18}
$[Co(NH_3)_6]^{2+}$	$Co^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	1.3×10^5

Complex ion	Equilibrium reaction	K_f
$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^{8}
$[Zn(NH_3)_4]^{2+}$	$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$	2.9×10^{9}
$[Fe(CN)_6]^{4-}$	$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1.0×10^{37}
$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1.0×10^{42}
$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
$[PbCl_4]^{2-}$	$Pb^{2+} + 4Cl^- \rightleftharpoons [PbCl_4]^{2-}$	40

Sometimes complex ion equilibria are written for the dissociation of a complex ion that is, the reverse of the formation reaction. In this case, the equilibrium constant is called the **dissociation constant**, K_d, or **instability constant**, K_i. Thus for the reaction

$$[Cu(NH_3)_4]^{2+}(aq) \rightleftharpoons Cu^{2+}(aq) + 4NH_3(aq)$$

$$K_d = K_i = \frac{[Cu^{2+}]\,[NH_3]^4}{[[Cu(NH_3)_4]^{2+}]} = 1/K_f$$

Effect of Complex Formation on Solubility

In the preceding unit, you studied that a white precipitate of silver chloride dissolves when a moderately concentrate solution of ammonia is added to the precipitate:

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

The Ag^+ ions from AgCl combine with NH_3 to form the complex ion $[Ag(NH_3)_2]^+$. As the complex compound $[Ag(NH_3)_2]$ Cl is soluble in water, AgCl dissolves in water in presence of NH_3 molecules. The dissolution of AgCl in aqueous NH_3 can be better explained, if we consider that the above complexation reaction involves two equilibria simultaneously:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq),\ K_{sp} = 1.8 \times 10^{-10} \qquad (I)$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq),\ K_f = 1.6 \times 10^{7} \qquad (II)$$

The value of the formation constant, K_f, of $[Ag(NH_3)_2]^+$ is quite large, it suggests that the equilibrium in complexation reaction is shifted far to the right. The equilibrium concentration of $Ag^+(aq)$ becomes so low that the ionic product $[Ag^+]\,[Cl^-]$ does not exceed the solubility product of AgCl and it dissolves. To appreciate the effect of complex formation on solubility, let us now calculate the solubility of AgCl in aqueous 1 M NH_3 solution.

As you know from the above, the overall reaction for the dissolution of AgCl in aqueous ammonia can be written as following; the equilibrium constant, K, for the overall reaction is the product of K_{sp} for AgCl and K_f for $[Ag(NH_3)_2]^+$.

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq),\ K = 2.9 \times 10^{-3}.$$

If the solubility of AgCl is x mol dm^{-3}, according to the above equation the concentration of $[Ag(NH_3)_2]^+$ and Cl^- ions are also expected to be x mol dm^{-3}.

$$AgCl(s) + 2NH_3\,(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

Initial concentration	1.0 M	0 M	0 M
Equilibrium concentration	(1 – 2x) M	x M	x M

$$K = \frac{[[Ag(NH_3)_2]^+]\,[Cl^-]}{[NH_3]^2}$$

or $$2.9 \times 10^{-3} = \frac{x \cdot x}{(1-2x)^2}$$

on taking square root of both sides, we get,

$$5.4 \times 10^{-2} = \frac{x}{1-2x}$$

or $$5.4 \times 10^{-2}(1-2x) = x$$

or $$5.4 \times 10^{-2} - 0.108x = x$$

or $$5.4 \times 10^{-2} = 1.108x$$

Hence, $$x = \frac{5.4 \times 10^{-2}}{1.108} = 4.9 \times 10^{-2}\ M.$$

Thus the solubility of AgCl in aqueous 1 M NH_3 is 4.9×10^{-2} mol dm^{-3}, which is much greater than that in pure water.

Advantage of this higher solubility of AgCl in aqueous ammonia solution is taken in the separation of AgCl(s) from Hg_2Cl_2(s) in the analysis of the cations of analytical Group I. As^{3+}/As^{5+}, Sb^{3+}/Sb^{5+} and Sn^{2+}/Sn^{4+} form soluble complexes on reaction with disulphide ion, S_2^{2-}. This fact is utilised in the separation of the cations of analytical Group IIA from those of Group IIB. In the following sections and in Unit 6, you will learn more about the application of complex formation in qualitative analysis.

5.6 THE SEPARATION OF CATIONS INTO ANALYTICAL GROUPS

In the preceding two sections you learnt the concepts of the solubility product, common ion effect and complex formation. Let us now discuss the scheme of separation of cations into analytical groups, which is based mainly on these concepts.

5.6.1 Precipitation of Cations of Analytical Group I

Solubility products of AgCl, Hg_2Cl_2 and $PbCl_2$ are very small in comparison to those of the other metal chlorides. To a solution containing various cations, if enough hydrochloric acid is added to raise the Cl^- concentration to 0.2 M, the solubility products of only AgCl, Hg_2Cl_2 and $PbCl_2$ are exceeded. As a result most of the Ag^+, Hg_2^{2+} and Pb^{2+} ions precipitate from the solution as their chlorides whereas all other cations remain in solution.

Let us calculate the residual Ag^+ ion concentration in a solution when the Cl^- ion concentration is 0.20 M. This we can do with the help of solubility product expression.

We know that the K_{sp} of AgCl is 1.8×10^{-10}.

$$K_{sp} = [Ag^+]\,[Cl^-] = 1.8 \times 10^{-10}$$

If we substitute the value of $[Cl^-]$ in this expression we get,

$$[Ag^+](0.2) = 1.8 \times 10^{-10}$$

Hence, $$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.2} = 9.0 \times 10^{-10}\ M$$

Thus the residual Ag^+ ion concentration in a solution of Cl^- ions of concentration 0.2 M is extremely small and we can say that Ag^+ ions are completely precipitated from the solution. If you calculate you will find that the residual Hg_2^{2+} ion concentration is even smaller than that of Ag^+ ion.

The residual Pb^{2+} ion concentration in a solution of Cl^- ions of concentration 0.2 M is 4×10^{-4} M as shown below:

$$K_{sp}(PbCl_2) = [Pb^{2+}][Cl^-]^2 = 1.6 \times 10^{-5}$$

Hence, $$[Pb^{2+}] = \frac{1.6 \times 10^{-5}}{[Cl^-]^2} = \frac{1.6 \times 10^{-5}}{0.2 \times 0.2} = 4.0 \times 10^{-4}\ M$$

You can see that the residual lead ion concentration is inversely proportional to the square of chloride ion concentration. Theoretically the residual Pb^{2+} ion concentration should decrease on increasing the Cl^- ion concentration by adding concentrated HCl. But if we increase the Cl^- ion concentration too much, precipitate of $PbCl_2$ and AgCl starts redissolving due to the formation of soluble complex ions with the Cl^- ions:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq),\ K_{sp} = 1.6 \times 10^{-5}$$

$$Pb^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [PbCl_4]^{2-}(aq),\ K_f = 40$$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq),\ K_{sp} = 1.8 \times 10^{-10}$$

$$Ag^+(aq) + 2Cl^-(aq) \rightleftharpoons [AgCl_2]^-(aq),\ K_f = 1.1 \times 10^5$$

One consequence of chloro complex formation is that the Ag^+ and Pb^{2+} ions remain in solution and do not precipitate as their chlorides. Another consequence of addition of too much Cl^- ions is that stable chloro complexes of other cations also, e.g., Cd^{2+} and Bi^{3+} may be formed:

$$Cd^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CdCl_4]^{2-}(aq),\ K_f = 6.3 \times 10^2$$

$$Bi^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [BiCl_4]^-(aq),\ K_f = 4 \times 10^5$$

Due to the formation of stable chloro complexes, the concentration of $Cd^{2+}(aq)$ and $Bi^{3+}(aq)$ is reduced and these ions then may not precipitate on passing H_2S gas. The qualitative analysis scheme thus represents a delicate balance between many such competing processes. You should follow it carefully to avoid errors in analysis.

5.6.2 The Separation of Group II Cations from Group IV Cations

Cations of both Group II (Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Sb^{3+}, Sb^{5+}, As^{3+}, As^{5+}, Sn^{2+}, Sn^{4+}) and Group IV (Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) precipitate as their sulphides on passing H_2S gas in their solution. The cations of Group II precipitate on passing H_2S gas in their solution in HCl medium. The cations of Group IV on the other hand precipitate when H_2S is passed in their solution in the presence of NH_4OH. The key to separate the cations of Group II from those of Group IV is the large difference between the solubility product constants of their sulphides listed in Table 5.5.

Table 5.5 : Solubility Product Constants and Molar Solubilities of Sulphides of Group II and Group IV at 25 ° C

	Group II			Group IV	
Sulphide	K_{sp}	Molar solubility	Sulphide	K_{sp}	Molar solubility
Sb_2S_3	2.0×10^{-93}	1.1×20^{-19} M	ZnS	1.1×10^{-21}	3.3×10^{-11} M
Bi_2S_3	2.0×10^{-72}	1.8×10^{-15} M	NiS	3.0×10^{-21}	5.5×10^{-11} M
HgS	3.0×10^{-53}	5.5×10^{-27} M	CoS	6.0×10^{-21}	7.8×10^{-11} M
CuS	8.7×10^{-36}	3.0×10^{-18} M	MnS	5.0×10^{-15}	7.1×10^{-8} M
CdS	4.0×10^{-29}	6.3×10^{-15} M			
SnS	8.0×10^{-29}	8.9×10^{-15} M			
PbS	8.0×10^{-28}	2.8×10^{-14} M			

You can see from the data in Table 5.5 that PbS is the most soluble of the Group II sulphides and ZnS is the least soluble of the Group IV sulphides. If we could separate PbS from ZnS, then we would have no difficulty in separating the other cations of Group II from those of Group IV. This is because the differences in solubilities in case of other sulphides are even larger than that of PbS and ZnS.

You know that a sparingly soluble salt precipitates out from its solution on addition of common ion so that the solubility product of the salt is exceeded. If we could find out the sulphide ion concentration such that the solubility product of only PbS is exceeded, in that case only PbS will precipitate from the solution whereas ZnS will remain in solution and we will be able to separate PbS from ZnS.

Let us calculate the S^{2-} ion concentration to separate Pb^{2+} from Zn^{2+} if both cations have a concentration of 0.02 M.

We calculate the S^{2-} ion concentration at which ZnS just starts to precipitate from a 0.02 M solution of Zn^{2+} ions. We know that

$$K_{sp}(ZnS) = [Zn^{2+}]\,[S^{2-}]$$

Substituting the value of K_{sp} and Zn^{2+} in the above expression we can get the concentration of S^{2-} ions at which ZnS just starts to precipitate.

$$1.1 \times 10^{-21} = 0.02 \times [S^{2-}]$$

Hence, $$[S^{2-}] = \frac{1.1 \times 10^{-21}}{0.02} = 5.5 \times 10^{-20}\ \text{M}$$

Thus at a S^{2-} ion concentration of 5.5×10^{-20} M, ZnS just begins to precipitate. If we keep the sulphide ion concentration below 5.5×10^{-20} M, no ZnS precipitates.

Now we find out what happens to Pb^{2+} ions when the S^{2-} concentration is 5.5×10^{-20} M. The ionic product of PbS under these conditions

$$\begin{aligned} Q &= [Pb^{2+}]\,[S^{2-}] \\ &= 0.02 \times 5.5 \times 10^{-20} = 1.1 \times 10^{-21} \end{aligned}$$

Hence, $Q > K_{sp}$

As the ionic product of PbS is greater than the solubility product of PbS, which is 8.0×10^{-28}, PbS will precipitate from the solution.

Let us now calculate what fraction of the Pb^{2+} ions will remain in solution when the

S^{2-} ion concentration is maintained at 5.5×10^{-20} M. We know

$$K_{sp}\,(PbS) = [Pb^{2+}]\,[S^{2-}]$$

Substituting the values of K_{sp} and S^{2-}, we get,

$$8.0 \times 10^{-28} = [Pb^{2+}] \times 5.5 \times 10^{-20}$$

Hence,
$$[Pb^{2+}] = \frac{8.0 \times 10^{-28}}{5.5 \times 10^{-20}} = 1.4 \times 10^{-8}\text{ M}$$

You can see that out of 0.02 M Pb^{2+} ions, only 1.4×10^{-8} M Pb^{2+} ions remain in solution, rest of the Pb^{2+} ions precipitate as PbS. We can also say that only

$$\frac{1.4 \times 10^{-8}\text{ M}}{0.02\text{ M}} \times 100\% = 0.00007\%$$ Pb^{2+} ions remain in solution, i.e., the precipitation of PbS is nearly complete. Thus we can conclude that if the S^{2-} ion concentration is maintained at 5.5×10^{-20} M, we can separate the cations of the Group II from those of the Group IV by precipitation as their sulphides.

Adjusting the Concentration of Sulphide Ions in Solution

We have calculated that if the sulphide ion concentration is kept below 5.5×10^{-20} M, Pb^{2+} ions can be separated from Zn^{2+} ions in solution containing 0.02 M of each cation. Now two questions arise:

Q1. What is the concentration of S^{2-} ions in a saturated solution of H_2S ?

Q2. How to adjust the concentration of S^{2-} ions to a given value?

Let us first find out the answer to the question 1. A saturated solution of H_2S has a concentration of 0.1 M. Hydrogen sulphide is a weak dibasic acid as is indicated by the values of K_1 (1.0×10^{-7}) and K_2 (1.3×10^{-13}).

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-(aq),\ K_1 = 1.0 \times 10^{-7}$$

$$H_2S + H_2O \rightleftharpoons H_3O^+ + S^{2-}(aq),\ K_2 = 1.3 \times 10^{-13}$$

Let x mol dm^{-3} of H_2S ionise in the first step. Hence the concentration of unionised H_2S in solution will be (0.1 – x) mol dm^{-3} as depicted below:

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-(aq),\ K_1 = 1.0 \times 10^{-7}$$

Initial concentration	0.1 M	0M	0M
After first ionisation	(0.1 – x) M	xM	xM

$$K_1 = \frac{[H_3O^+]\,[HS^-]}{[H_2S]}$$

or
$$1.0 \times 10^{-7} = \frac{x \cdot x}{0.1 - x}$$

As H_2S is a very weak acid, the amount of H_2S that ionises in the first step, x M, will be very small and can be disregarded in the denominator of the above expression.

Hence,
$$1.0 \times 10^{-7} = \frac{x^2}{0.1 - 0}$$

or
$$x^2 = 1.0 \times 10^{-8}$$

or
$$x = 1.0 \times 10^{-4}\text{ M}$$

Hence, $[H_3O^+] = 1.0 \times 10^{-4}\,M = [HS^-]$

In the second step, HS^- produced in the first step ionises to give H_3O^+ and S^{2-}. Let y mol dm^{-3} be the concentration of HS^- which ionises in this step to give y mol dm^{-3} of H_3O^+ and S^{2-} each:

$$HS^-(aq) + H_2O \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)$$

Initial concentration	1.0×10^{-4} M	1.0×10^{-4} M	0M
After second ionisation	$(1.0 \times 10^{-4} - y)$ M	$(1.0 \times 10^{-4} - y)$ M	yM

$$K_2 = \frac{[H_3O^+][S^{2-}]}{[HS^-]}$$

or
$$1.3 \times 10^{-13} = \frac{(1.0 \times 10^{-4} + y) \times y}{1.0 \times 10^{-4} - y}$$

Value of K_2 (1.3×10^{-13}) is small which suggests that the value of y will be very small. Hence we can assume that $1.0 \times 10^{-4} + y = 1.0 \times 10^{-4}$ and $1.0 \times 10^{-4} - y = 1.0 \times 10^{-4}$. Therefore, the above expression changes to

$$1.3 \times 10^{-13} = \frac{1.0 \times 10^{-4}\, y}{1.0 \times 10^{-4}}$$

or
$$y = 1.3 \times 10^{-13}\,M = S^{2-} \text{ ion concentration}$$

Thus our assumption that y is very small is correct. But it does give us the equilibrium concentration of S^{2-} ions in solution. The concentration of different species present in a saturated solution of H_2S will be as following:

$$[H_2S] = (0.1 - x)\,M = 0.1 - 1.0 \times 10^{-4}\,M \approx 0.1\,M$$

$$[S^{2-}] = y = 1.3 \times 10^{-13}\,M$$

$$[HS^-] = 1.0 \times 10^{-4} - y = 1.0 \times 10^{-4} - 1.3 \times 10^{-13} \approx 1.0 \times 10^{-4}\,M$$

$$[H_3O^+] = 1.0 \times 10^{-4} + y = 1.0 \times 10^{-4} + 1.3 \times 10^{-13} \approx 1.0 \times 10^{-4}\,M$$

In the preceding section we learnt that PbS (and obviously the other sulphides of Group II) is completely precipitated and ZnS just begins to precipitate at S^{2-} ion concentration of 5.5×10^{-20} M. Thus in a saturated solution of H_2S, though the S^{2-} ion concentration is small, but it is large enough to precipitate the sulphides of cations of both Group II and Group IV. Hence to effect separation of the cations of the Group II from those of the Group IV, we need to adjust the concentration of the S^{2-} ions.

Now we shall try to find out the answer to second question i.e., how to adjust the concentration of S^{2-} ions in a saturated solution of H_2S.

As discussed above, a saturated solution of H_2S in water has a concentration of 0.1 M, in which the concentration of S^{2-} ions is 1.3×10^{-13} M. In aqueous solution, H_2S dissociates in a stepwise manner as shown below:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq),\ K_1 = 1.0 \times 10^{-7}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq),\ K_2 = 1.3 \times 10^{-13}$$

By adding the above two equations, we get the equation for the overall dissociation of H_2S into S^{2-} ions:

$$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq)$$

The equilibrium constant expression for the overall reaction is equal to the product of the equilibrium constant expressions for the individual steps:

$$K = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = \frac{[H_3O^+][HS^-]}{[H_2S]} \times \frac{[H_3O^+][S^{2-}]}{[HS^-]}$$

or $$K = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = K_1 \times K_2$$

or $$K = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = 1.0 \times 10^{-7} \times 1.3 \times 10^{-13} = 1.3 \times 10^{-20}$$

Hence, $$[S^{2-}] = \frac{1.3 \times 10^{-20}[H_2S]}{[H_3O^+]^2}$$

A saturated solution of H_2S has an initial concentration of 0.1 M. As H_2S is a very weak acid, we can safely assume that the concentration of H_2S at equilibrium is approximately equal to its initial concentration.

Hence, $$[S^{2-}] = \frac{1.3 \times 10^{-20} \times 0.1}{[H_3O^+]^2}$$

or $$[S^{2-}] = \frac{1.3 \times 10^{-21}}{[H_3O^+]^2}$$

Thus in a saturated aqueous solution of H_2S, the concentration of S^{2-} ions is inversely proportional to the square of hydrogen ion concentration. By adjusting the hydrogen ion concentration of a solution of H_2S, the concentration of S^{2-} ions can be suitably adjusted. The variation of the S^{2-} ion concentration in a saturated solution of H_2S with the pH of the solution is given in Table 5.6.

Table 5.6 : Variation of the S^{2-} ion concentration in a saturated solution of H_2S with the pH of the solution

pH	$[S^{2-}]$ mol dm^{-3}
1	1.3×10^{-19}
3	1.3×10^{-15}
5	1.3×10^{-11}
7	1.3×10^{-7}
10	0.13

In the preceding sub-section, we concluded that if the S^{2-} ion concentration is maintained at 5.5×10^{-20} M, it is possible to separate the cations of the Group II from those of the Group IV by precipitation as their sulphides. Let us calculate the hydrogen ion concentration necessary to adjust the S^{2-} ion concentration to this value.

$$[H_3O^+]^2 = \frac{1.3 \times 10^{-21}}{[S^{2-}]}$$

$$= \frac{1.3 \times 10^{-21}}{5.5 \times 10^{-20}}$$

$$= 2.4 \times 10^{-2}$$

Hence, $[H_3O^+] = 0.15$ M

Thus, the concentration of H_3O^+ must be at least 0.15 M to prevent the precipitation of ZnS with the Group II sulphides. The concentration of H_3O^+ is maintained at 0.3 M to provide some margin of safety. However, when H_2S gas is passed into a solution of cations of Group IV, which has been buffered with aqueous NH_3 and NH_4Cl, a very high concentration of sulphide ions is provided. This is because the acid (H_2S) and the base (NH_3) react to form a salt $(NH_4)_2S$.

$$2NH_3(aq) + H_2S(aq) \rightarrow 2NH_4^+(aq) + S^{2-}(aq)$$

The sulphide ion concentration is sufficiently large so that the solubility products of ZnS, NiS, CoS and MnS are exceeded and these sulphides precipitate from the solution.

5.6.3 The Precipitation of Group III Cations

Group III consists of Al^{3+}, Fe^{3+} and Cr^{3+}. The precipitating reagent for these cations is ammonium hydroxide in the presence of a high concentration of ammonium chloride. To explain why only Al^{3+}, Fe^{3+} and Cr^{3+} precipitate as their hydroxides on addition of the group reagent, let us consider the solubility product constants of the hydroxides of the cations of Group III, IV, V and VI, which are given in Table 5.7.

Table 5.7 : Solubility Product Constants of the Hydroxides of Cations of Group III, IV, V and VI at 25° C

Formula	K_{sp}
$Fe(OH)_3$	6.3×10^{-38}
$Al(OH)_3$	1.9×10^{-33}
$Cr(OH)_3$	7.0×10^{-31}
$Zn(OH)_2$	4.5×10^{-7}
$Co(OH)_2$	2.0×10^{-16}
$Ni(OH)_2$	2.0×10^{-15}
$Mn(OH)_2$	2.0×10^{-13}
$Mg(OH)_2$	1.5×10^{-11}
$Ca(OH)_2$	7.9×10^{-6}
$Sr(OH)_2$	3.2×10^{-4}
$Ba(OH)_2$	5.0×10^{-3}

In the presence of a high concentration of ammonium chloride, the dissociation of the ammonium hydroxide is suppressed. As a result the concentration of hydroxide ions is reduced so much that the solubility products of only less soluble $Al(OH)_3$, $Cr(OH)_3$ and $Fe(OH)_3$ are exceeded and they are precipitated from the solution. In the first place, the above seems to be a plausible explanation. But the following discussion shows that this is not the whole truth, and some other factors as well must be at work to prevent the precipitation of $Ni(OH)_2$, $Co(OH)_2$ and $Zn(OH)_2$. Let us consider that the initial concentration of ammonium hydroxide is

0.1 M and x mol dm^{-3} of it dissociates into NH_4^+ and OH^- ions at equilibrium:

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

Initial concentration	0.1 M	0	0
At equilibrium	0.1 – x M	x M	x M

From the Law of Mass Action, $\frac{[NH_4^+]\,[OH^-]}{[NH_4OH]} = K(NH_4OH) = 1.8 \times 10^{-5}$

Substituting the values in the above expression, we get,

$$\frac{x\,.\,x}{0.1 - x} = 1.8 \times 10^{-5}$$

As NH_4OH is a very weak electrolyte, value of x will be very small and it can be ignored in the denominator. Hence,

$$\frac{x^2}{0.1} = 1.8 \times 10^{-5}$$

or $$x^2 = 1.8 \times 10^{-6}$$

or $$x = 1.34 \times 10^{-3}\ M$$

Thus the concentration of OH^- ions in a solution of 0.1 M NH_4OH is 1.34×10^{-3} M.

As you know that the ionic products of divalent and trivalent metal hydroxides can be written as

$$[M^{2+}]\,[OH^-]^2 = Q \text{ for } M(OH)_2 \text{ and}$$

$$[M^{3+}]\,[OH^-]^3 = Q \text{ for } M(OH)_3.$$

Assuming that the concentration of metal ions, $[M^{2+}]$ or $[M^{3+}]$, is 0.1 M, the ionic products, Q, of $M(OH)_2$ and $M(OH)_3$ in presence of 0.1 M NH_4OH will be

$$(0.1) \times (1.34 \times 10^{-3})^2 = 1.79 \times 10^{-7} \text{ for } M(OH)_2 \text{ and}$$

$$(0.1) \times (1.34 \times 10^{-3})^3 = 2.4 \times 10^{-10} \text{ for } M(OH)_3.$$

As you can see that the ionic products of $Zn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Mn(OH)_2$, $Mg(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ are higher than their solubility products. Hence, all the above should precipitate from the solution. The ionic products of $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ are lower than their solubility products and therefore, these should remain in solution. These will require a higher OH^- ion concentration for their precipitation.

Let us now find out, what happens to OH^- ion concentration and ionic products of $M(OH)_2$ and $M(OH)_3$ in a solution of 0.1 M NH_4OH in the presence of a high concentration of ammonium chloride.

In the presence of a high concentration of ammonium chloride the concentration of the NH_4^+ ion is raised to about 1.5 M, since NH_4Cl is a strong electrolyte and is completely dissociated into ions in solution:

$$NH_4Cl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$$

$$1.5\ M \quad \rightleftharpoons \quad 1.5\ M \qquad 1.5\ M$$

Hence, $[NH_4^+] = 1.5$ M, since the NH_4^+ ions from the ammonium hydroxide can be neglected as compared with those from the strong electrolyte NH_4Cl. But

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

$$\text{or} \quad \frac{1.5 \times [OH^-]}{0.1} = 1.8 \times 10^{-5}$$

Hence, $[OH^-] = 1.2 \times 10^{-6}$ mol dm^{-3}.

Thus, in the presence of a high concentration of NH_4Cl, the concentration of OH^- ions in a solution of NH_4OH of concentration of 0.1 M is reduced to 1.2×10^{-6} M. Assuming that the concentration of metal ions, $[M^{2+}]$ or $[M^{3+}]$ is 0.1 M, the ionic products, Q, of $M(OH)_2$ and $M(OH)_3$ in presence of 0.1 M NH_4OH and 1.5 M NH_4Cl will be

$$(0.1) \times (1.2 \times 10^{-6})^2 = 1.4 \times 10^{-13} \text{ for } M(OH)_2 \text{ and}$$

$$(0.1) \times (1.2 \times 10^{-6})^3 = 1.7 \times 10^{-19} \text{ for } M(OH)_3$$

You can see from the above that even in the presence of a high concentration of NH_4Cl, the ionic products of $Zn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ are higher than their solubility products. Hence, all these should precipitate from the solution even in the presence of 1.5 M NH_4Cl. Then why only $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ precipitate from the solution, whereas $Zn(OH)_2$, $Co(OH)_2$ and $Ni(OH)_2$ remain in the solution?

The answer to this conflict between experimental fact (that only $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ are precipitated) and theoretical prediction based upon the solubility product concept almost certainly lies in the formation of soluble complex ions with ammonia molecules. Ammonia molecules are in plenty in ammonium hydroxide solution. Actually the concentration of free ammonia molecules in ammonia solution far exceeds the concentration of ammonium hydroxide molecules.

$$Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Zn(NH_3)_4]^{2+}(aq),\ K_f = 2.9 \times 10^9$$

$$Co^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{2+}(aq),\ K_f = 1.3 \times 10^5$$

$$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq),\ K_f = 5.5 \times 10^8$$

As a result of the formation of soluble complex ions, the concentration of metal cations, i.e., Zn^{2+}, Co^{2+}, and Ni^{2+} is so reduced that the solubility products of their hydroxides are not exceeded in the presence of ammonium chloride and they remain in solution. However, the solubility products of ZnS, CoS, NiS and also MnS are much lower than those of their hydroxides and are easily exceeded on passing H_2S gas in presence of NH_4OH. Therefore, ZnS, CoS, NiS and MnS precipitate from the solution and constitute Group IV of the scheme of qualitative analysis.

5.6.4 The Precipitation of Group V Cations

Ba^{2+}, Sr^{2+} and Ca^{2+} constitute the analytical Group V. These are referred to as the insoluble carbonate group because they are precipitated as carbonates from a buffered solution of aqueous ammonia by the addition of ammonium carbonate.

It is important to note that these cations are derived from the metals of the same group of the periodic table, their properties are similar. Therefore, separations of individual ions are more difficult than most separations in the earlier groups of cations. Mg^{2+} ions are not precipitated in the group because $MgCO_3$ has a much higher solubility product than those of $BaCO_3$, $SrCO_3$ and $CaCO_3$ (Table 5.8) and the aqueous ammonia solution is buffered to prevent the precipitation of $Mg(OH)_2$.

Table 5.8 : Solubility Products and Molar Solubilities of Group V Carbonates and $MgCO_3$

Compound	K_{sp}	Molar Solubility
$MgCO_3$	4.0×10^{-5}	6.6×10^{-3} M
$BaCO_3$	8.1×10^{-9}	9.0×10^{-5} M
$CaCO_3$	4.8×10^{-9}	6.9×10^{-5} M
$SrCO_3$	9.4×10^{-9}	3.1×10^{-5} M

The precipitating reagent of Group V, 1 M ammonium carbonate, contains the cation of a weak base and the anion of a weak dibasic acid. Both these hydrolyse in aqueous solution, but carbonate ion hydrolyses to a much greater extent than the ammonium ion as their dissociation constants show:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq),\ K_a = 5.6 \times 10^{-10}$$

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq),\ K_b = 2.1 \times 10^{-4}$$

Therefore, solutions of $(NH_4)_2CO_3$ do not contain sufficiently high concentrations of CO_3^{2-} ions to precipitate the Group V carbonates completely. Precipitation of the cations of Group V is, therefore, carried out in a buffered aqueous ammonia (ammonium hydroxide) solution:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$NH_4Cl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$$

The OH^- ions from aqueous ammonia suppress the hydrolysis of CO_3^{2-} ions. Thus, there are enough CO_3^{2-} ions to precipitate Ca^{2+}, Sr^{2+} and Ba^{2+}. The reactions by which the Group V cations are precipitated can be represented as following:

$$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

$$Sr^{2+}(aq) + CO_3^{2-}(aq) \rightarrow SrCO_3(s)$$

These carbonates precipitate as white, dense, crystalline compounds, so there appears to be relatively less amount of the precipitate.

5.7 THE DISSOLUTION OF PRECIPITATES

After precipitation of cations of an analytical group, the next step in the analysis is the separation of individual cations. Separation of cations is achieved by selective dissolution of the precipitate. Dissolution of a precipitates is accomplished by reducing the concentrations of the constituent ions so that K_{sp} is no longer exceeded, i.e., $Q < K_{sp}$. The dissolution of precipitates is based upon the following type of reactions.

5.7.1 By Converting Anion into a Weak Electrolyte

When anion part of the precipitate is converted into a weak electrolyte, the ionic product becomes lesser than the solubility product of the compound resulting into the dissolution of the precipitate. A few typical examples are:

a) Acidification of insoluble $Al(OH)_3$ in contact with its saturated solution converts OH^- ions to the weak electrolyte water. This shifts the solubility equilibrium to the right until $[Al^{3+}]\,[OH^-]^3 < K_{sp}$, and dissolution occurs:

$$\begin{array}{l} Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq) \\ 3OH^-(aq) + 3H^+(aq) \rightarrow 3H_2O(l) \\ \hline Al(OH)_3(aq) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l) \end{array}$$

b) Treatment of $Mg(OH)_2$ with NH_4^+ ions from a salt, such as NH_4Cl, converts OH^- ions (from saturated solution of $Mg(OH)_2$) to the weak electrolytes, NH_3 and H_2O. As a result, $[Mg^{2+}]\,[OH^-]^2 < K_{sp}$ and $Mg(OH)_2$ dissolves.

$$\begin{array}{l} Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \\ 2OH^-(aq) + 2NH_4^+(aq) \rightarrow 2NH_3(aq) + 2H_2O(l) \\ \hline Mg(OH)_2(s) + 2NH_4^+(aq) \rightarrow Mg^{2+}(aq) + 2NH_3(aq) + 2H_2O(l) \end{array}$$

c) Acidification of some metal sulphides such as ZnS and MnS, converts S^{2-} ions (from saturated solution of MS) into H_2S, a weak electrolyte. As a result, $[M^{2+}]\,[S^{2-}] < K_{sp}$ and the sulphide dissolves.

$$\begin{array}{l} MS(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq) \\ S^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(g) \\ \hline MS(s) + 2H^+(aq) \rightarrow M^{2+}(aq) + H_2S(g) \end{array}$$

Highly insoluble sulphides, such as CuS, CdS, PbS, CoS, NiS, etc., do not produce sufficiently high concentrations of S^{2-} ions in their saturated solutions to react with even the strongest non-oxidising acids. They require oxidation of S^{2-} ions for their dissolution.

5.7.2 By Converting Anion into Another Species by Redox Reaction

Highly insoluble metal sulphides, such as those mentioned above, can be dissolved in hot nitric acid because the NO_3^- ions oxidise the S^{2-} ions to elemental sulphur, thereby removing S^{2-} ions from solution:

$$\begin{array}{l} CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)] \times 3 \\ 3S^{2-}(aq) + 2NO_3(aq) + 8H^+(aq) \rightarrow 3S(s) + 2NO(g) + 4H_2O(l) \\ \hline 3CuS(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 3S(s) + 2NO(g) + 4H_2O(l) \end{array}$$

5.7.3 By Complex Ion Formation

Many insoluble compounds can be dissolved by converting them into soluble complex ions. For example, when a precipitate of AgCl and Hg_2Cl_2 is treated with aqueous ammonia solution, AgCl passes into solution due to the formation of the complex ion, $[Ag(NH_3)_2]^+$:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$Ag^+(aq) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq)$$

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

When a mixture of sulphides of Group II cations is treated with a solution of yellow ammonium sulphide, As_2S_3, Sb_2S_3 and SnS_2 dissolve due to the formation of soluble complex ions leaving behind a residue of other metal sulphides:

$$(NH_4)_2S_2(aq) \rightleftharpoons 2NH_4^+(aq) + S_2^{2-}(aq)$$

$$As_2S_3(s) + 4S_2^{2-}(aq) \rightarrow 2[AsS_4]^{3-}(aq) + S_3^{2-}(aq)$$

Tetrathioarsenate(V) ion

$$SnS_2(s) + S_2^{2-}(aq) \rightarrow [SnS_3]^{2-}(aq) + S(s)$$

Trithiostannate(IV) ion

5.8 SUMMARY

In this unit you studied solubility, solubility product constant and the relation between the two. You also studied the common ion effect, complex formation and the classification of cations into analytical groups. You studied how the cations of an analytical group are separated from those of the other analytical groups by selective precipitation. The cations of an analytical group are then separated from each other by selective dissolution of their precipitate.

5.9 ANSWERS

To Self-Assessment Questions

1. Cu^{2+} and Co^{2+} are precipitated as their sulphides on reaction with H_2S in acidic and basic medium, respectively. Therefore, they belong to two different analytical groups.

2. $$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

   $$K_{sp}(Ag_2CO_3) = [Ag^+]^2 [CO_3^{2-}]$$

   $$Bi_2S_3(aq) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$$

   $$K_{sp}(Bi_2S_3) = [Bi^{3+}]^2 [S^{2-}]^3.$$

3. For a salt of A_xB_y type, the solubility product $K_{sp} = x^x . y^y . S^{x+y}$, where S is solubility of the salt.

   For CaF_2, $x = 1$ and $y = 2$

   Hence, $K_{sp} = 1^1 . 2^2 . S^{1+2}$

   or $4.0 \times 10^{-11} = 4S^3$

   or $S^3 = \dfrac{4.0 \times 10^{-11}}{4} = 1.0 \times 10^{-11}$

Hence, $S = (1.0 \times 10^{-11})^{1/3} = 2.15 \times 10^{-4}$ mol dm^{-3}

Hence, solubility of CaF_2 is 2.15×10^{-4} mol dm^{-3}.