Classical qualitative analysis. 1A. Solubility product, factors affecting solubility

In the case of the sparingly soluble compound part of the compound that has been dissolved, is in solution virtually completely dissociated into ions. Between the precipitate (solid) and its aqueous solution exists dynamic equilibrium, this means that the rates of dissolution and precipitation are equal to one another, e.g.

$AgCl\downarrow \leftrightarrow Ag^+ + Cl^-$

This is a reversible reaction, and thus the thermodynamic equilibrium expression is:

$$K_{rozp} = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

Since this is a solid phase, the [AgCl] is constant and then K_{eg} $[AgCl]$ = K_{sp} that is, $K_{sp} = [Ag^+]\ [Cl^-]$.

K_{sp} is called the solubility product of sparingly soluble compound.

In the saturated solution of sparingly soluble electrolyte (compound) the product of the numerical values of the concentrations of the ions, to which the electrolyte (compound) dissociates, is constant at given temperature and is called the solubility product.

If $[Ag^+][Cl^-] < K_{sp,}$ no precipitate is form . If $[Ag^+][Cl^-] > K_{sp,}$ a precipitate is form.

A measure of the solubility of a substance is its concentration in the saturated solution (at a given temperature).

Factors affecting the solubility of the precipitate:

1) temperature – temperature increase generally increases the solubility.
2) common ion effect e.g.: $K_{sp} = [Ba^{2+}][SO_4^{2-}]$ = const. Increasing the concentration of one of the ions Ba^{2+} or SO_4^{2-}, decreases the solubility.
3) salt effect.
4) pH effect
5) hydrolysis of precipitate .
6) complex formation reactions.

The values of solubility products for barium and calcium salts at 25°C:

	SO_4^{2-}	CrO_4^{2-}
Ba^{2+}	$1 \cdot 10^{-10}$	$2 \cdot 10^{-10}$
Ca^{2+}	$6 \cdot 10^{-5}$	-

Experimental procedure:

I.

1. Pour approximately 1 cm^3 a) of Ba^{2+} ions solution b) Ca^{2+} ions solution into two glass test tubes.
2. Into each of these tubes pour approximately 0.5 cm^3 1 M/L H_2SO_4 solution.
3. Only in the tube a) the white precipitate of $BaSO_4$ is form: $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$ (white). Explain why the precipitate is formed.

II.

1. Pour approximately 1 cm^3 a) of Ba^{2+} ions solution b) Ca^{2+} ions solutions into two glass test tube.
2. Into each of these tubes pour approximately 1 M/L $K_2Cr_2O_7$ (pay attention to the color of the solution).
3. Only in the tube a) the yellow precipitate of $BaCrO_4$ is form: $2Ba^{2+} + Cr_2O_7^{2-} + 3H_2O \leftrightarrow 2BaCrO_4\downarrow + 2H_3O^+$.

Explain why a yellow and not an orange precipitate is formed, taking into account the equilibrium:

$Cr_2O_7^{2-} + 3H_2O \leftrightarrow 2CrO_4^{2-} + 2H_3O^+$.

III.

Each student receives two test tubes with Ba^{2+} ions solution or Ca^{2+} ions solution, or with H_2O. Identify which of the two ions is in the test tube. Describe the identification of ions with appropriate reaction equations.

Classical qualitative analysis. 1B. Identification reactions – precipitation reactions, complex formation reactions, oxidation-reduction reactions

Analytical reagents for the detection of ions can be divided into:
I) selective - with a limited group of ions give a similar reaction, e.g. $BaCl_2$ solution with CO_3^{2-}, SO_3^{2-}, PO_4^{3-} ions**;**
II) specific - which uniquely react with only one specified ion, e.g. in certain conditions, dimethylglyoxime with Ni^{2+} ion - **it is the identification reaction**

1. **Precipitation reaction** is a type of reaction involving the precipitation (sparingly soluble substance) with aqueous solutions of readily soluble substances.
2. **Complex formation reactions** are reactions of formation of the complex compounds. The complex formation reaction equilibrium constant is called the stability constant and the opposing reaction constant (i.e. dissociation or decomposition of the complex) is defined as the instability constant of the complex. The complex formation reactions are affected by the presence of other (beyond the ligands of the complex) substance and the value of pH of solution. Complex compounds (complexes, coordination compounds) – compounds containing one or more central atoms, surrounded by other atoms or groups of atoms called ligands, wherein at least one bond between the central atom and the ligand is a coordination bond. Atoms or ions coordinating molecules is called central atom. Groups or ions bounded with it are known as ligands. The total number of full single bonds of the central atom with the ligands' atoms (coordinating atoms) is called the coordination number (CN).
3. **Oxidation-reduction (redox) reactions** are reactions involving electron transfer between the reactants, what lead to a change in oxidation state of the elements contained in these reagents. In oxidation process electrons are lost and oxidation number increases. In reduction process electrons are accepted and oxidation number decreases. Both oxidation and reduction processes proceed simultaneously and the number of electron lost and gained by reactants must be equal. This reactant, which reduces the second reactant (being itself oxidized), is called **reducer,** whereas this one, which oxidizes the other reactant (being s itself reduced) is called **oxidant**.

Experimental procedure:

1. **Precipitation reactions:**

a) **identification of Zn^{2+} ions**
Pour approximately 1 cm^{3+} of Zn2+ ions solution into glass test tube. Using indicator paper check the pH of the solution. If it is not neutral, adjust it. Add formate buffer (HCOOH/HCOONa), so that the value of pH will be about 1.5. Next pour into the tube water solution of H_2S, heat for about 10 min in water bath under the hood, and closed with the tube cap with the pipe. White precipitate of ZnS should be formed:
$Zn^{2+} + H_2S + 2H_2O \rightarrow ZnS\downarrow + 2H_3O^+$ (white)

b) **identification of Cd^{2+} ions**
Pour approximately 1 cm^3 of Cd^{2+} ions solution into glass test tube. Using indicator paper check the pH of the solution. If the solution is acid, adjust it using $NH_3 \cdot H_2O$ until a turbidity (not dissapearing during shaking) appeared, which next dissolve in 2-3 drops of dilute (2 M/L) HCl and add 2 M/L HCl to its concentration 0.3 M/l. Then the pH value is 0.5. Next pour into the tube H_2S aqueous solution, heat for about 10 min in water bath under the hood, closing the tube with the tube cap with pipe. Yellow precipitate of CdS should be formed: $Cd^{2+} + H_2S + 2H_2O \rightarrow CdS\downarrow + 2H_3O^+$ (yellow)
If sulphide does not precipitate and the pH of the solution is too acidic, dilute the solution with water and repeat the precipitation at pH 0.5.

c) **identification of Ag^+ ions**
Pour approximately 1 cm^3 of Ag^+ ions solution into glass test tube. Add a dilute solution of HCl. White precipitate of silver chloride(I), AgCl should be formed. $Ag^+ + Cl^- \rightarrow AgCl\downarrow$
Note: AgCl precipitate can dissolve in an excess of Cl^-: $AgCl + Cl^- \leftrightarrow AgCl_2^-$

After prolonged standing in the light precipitate turns gray as a result of the forming of metallic silver in photochemical reaction: $2AgCl \rightarrow 2Ag + Cl_2$

2.Complex formation reactions:

a) **identification of Fe^{3+} ions**

Pour approximately 0.5 cm^3 of Fe^{3+} ions solution into glass test tube. Using indicator paper check the reaction of the solution, it should be neutral or weakly acid. Add few drops of dilute solution of KSCN. In the presence of Fe^{3+} the solution should stain on dark red color as the result of complex ion formation $[Fe(SCN)_6]^{3-}$. Complex formation reaction proceeds gradually and is very sensitive.:

$Fe^{3+} + SCN^- \leftrightarrow [Fe(SCN)]^{2+}$ ...... (the last step): $Fe^{3+} + 6SCN^- \leftrightarrow [Fe(SCN)_6]^{3-}$

b**) identification of Cu^{2+} ions**

Pour approximately 0.5 cm^3 of Cu^{2+} ions solution (e.g. dilute solution of $CuSO_4$) into glass test tube. Next carefully add ammonia solution: $NH_3{\cdot}H_2O$. Bluish-green precipitate of basic Cu(II) salt [e.g. $(CuOH)_2SO_4$] should be formed according to the reaction equation:

$2Cu^{2+} + 2NH_3{\cdot}H_2O \rightarrow (CuOH)_2^{2+} + 2NH_4^+$

Upon addition of axcess of $NH_3{\cdot}H_2O$ precipitate dissolves. Cu^{2+} complex ion (with a characteristic, strongly blue colour) is formed, in accordance with the equation:

$(CuOH)_2^{2+} + 2NH_4^+ + 6NH_3{\cdot}H_2O \leftrightarrow 2[Cu(NH_3)_4]^{2+} + 8H_2O$

Reaction is very sensitive, what allows for detection of Cu^{2+} ions at a dilution of 1 : 25 000.

3. Redox reactions:

a) identification of Bi^{3+} ions

Pour approximately 0.5 cm^3 of dilute Sn^{2+} ions solution into glass test tube. Add dropwise dilute NaOH solution. White precipitate of tin(II) hydroxide is formed, which will dissolve in axcess of NaOH (amphoteric properties): $Sn^{2+} + 2OH^- \rightarrow Sn(OH)_{2\downarrow}$ $Sn(OH)_{2\downarrow} + OH^- \rightarrow Sn(OH)_3^-$

Next pour the solution containing Bi^{3+} ions, as a result black precipitate of metallic bismuth will appear. This is redox reaction for identification of Bi^{3+} ions. Sn^{2+} ions are oxidized, whilst Bi^{3+} ions are reduced to metallic Bi:

$Sn(OH)_3^- + 3OH^- \rightarrow Sn(OH)_6^{2-} + 2e$ / x3 oxidation reaction

$Bi^{3+} + 3e \rightarrow Bi^0_{\downarrow(\text{ black})}$ /x2 reduction reaction

$2Bi^{3+} + 3Sn(OH)_3^- + 9OH^- \rightarrow 2Bi^0_{\downarrow(\text{ black})} + 3Sn(OH)_6^{2-}$

b) identification of Sn^{2+} ions

Pour approximately 0.5 cm^3 of saturated solution of $HgCl_2$ and carefully add dropwise the solution containing Sn^{2+} ions. White Hg_2Cl_2 (calomel) precipitate is formed. This is redox reaction: Sn^{2+} ions are oxidized, and Hg(II) ions are reduced to Hg(I) ions to forming a sparingly soluble precipitation of mercury(I) chloride.:

$Sn^{2+} + 2Hg^{2+} + 8Cl^- \rightarrow SnCl_6^{2-} + Hg_2Cl_{2\downarrow(\text{white})}$

When the excess of $SnCl_2$ is added, a black metallic mercury may precipitate, according to the reaction:

$Sn^{2+} + HgCl_2 + 4Cl^- \rightarrow SnCl_6^{2-} + Hg_{\downarrow(\text{black})}$