EXPERIMENT 13

Cation Group III: The Basic Insoluble Sulfides

Background

The cations of this analytical group are those that form insoluble sulfides or hydroxides in a buffered ammonia solution saturated with H_2S. The common cations we will look at from this group are nickel (II), iron (III), cobalt (II), chromium (III), and zinc (II).

A combination of NH_3, NH_4C1, and thioacetamide is used to precipitate this group. The sulfides of this group have large enough solubilities that they do not precipitate under the 0.3 *M* HCl plus thioacetamide used to precipitate Cation Group II. Under these conditions, the Fe (III) and Cr (III) precipitate as hydroxides and the Co (II), Ni (II), and Zn (II) precipitate as sulfides. Table 13.1 on page 81 gives solubility product values for these salts

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TABLE 13.1 **K_{sp} Values for Group III Precipitates**

Salt	**K_{sp}**
CoS	5.9×10^{-21}
NiS	3.0×10^{-21}
ZnS	1.1×10^{-21}
$Cr(OH)_3$	6.7×10^{-31}
$Fe(OH)_3$	6.3×10^{-38}

Precipitation of the Group

Under the basic condition that H_2S is being generated, it rapidly converts to sulfide ion by reacting with the ammonia present.

$$2NH_3 + H_2S \rightarrow 2NH_4^+ + S^{2-} \qquad \textbf{(EQ 13.1)}$$

It is sulfide ion that is the precipitating agent for the insoluble sulfides. For example,

$$Co^{2+} + S^{2-} \rightarrow CoS_{(s)} \qquad \textbf{(EQ 13.2)}$$

The Fe (III) and Cr (III) react with the aqueous ammonia and precipitate as hydroxides. For example,

$$Fe^{3+} + 3NH_3 + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3NH_4^+ \qquad \textbf{(EQ 13.3)}$$

Separation of the Nickel and Iron Subgroups

Separation of Ni and Co from Fe, Cr, and Zn is based on the fact that NiS and CoS are very slowly soluble in dilute HCl, whereas the ZnS, $Cr(OH)_3$, and $Fe(OH)_3$ dissolve rapidly. In doing this step, it is important that the NiS and CoS not remain in contact with the HCl very long. Typical reactions for dissolving the iron-subgroup are:

$$ZnS + 2H^+ \rightarrow Zn^{2+} + H_2S \qquad \textbf{(EQ 13.4)}$$

$$Fe(OH)_{3(s)} + 3H^+ \rightarrow Fe^{3+} + 3H_2O \qquad \textbf{(EQ 13.5)}$$

Analysis of the Nickel Subgroup

CoS and NiS readily dissolve in **aqua regia**, a mixture of HCl and HNO_3 that is a strong oxidizing agent. It readily oxidizes sulfide ion to elemental sulfur, causing the metal sulfides to dissolve.

$$CoS_{(s)} + 4H^+ + Cl^- + NO_3^- \rightarrow Co^{2+} + S_{(s)} + NOCl + 2H_2O \qquad \textbf{(EQ 13.6)}$$

The tests for Co and Ni can be made in the presence of each other so further separation is unnecessary. Simply divide the solution in half. To test for Ni, the solution is made basic with NH_3, forming the ammine complex.

$$Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_6^{2+} \qquad \textbf{(EQ 13.7)}$$

Dimethylglyoxime is an organic compound that forms a bright red insoluble complex with Ni(II).

$$Ni(NH_3)_6^{2+} + 2H_2C_4H_6N_2O_2 \rightarrow Ni(HC_4H_6N_2O_2)_{2(s)} + 2NH_4^+ + 4NH_3 \qquad \textbf{(EQ 13.8)}$$

Cobalt (II) also forms a complex with dimethylglyoxime but it is brown in color and is soluble, so it does not interfere with the formation of the red precipitate with Ni.

The test for Co involves its reaction with thiocyanate, SCN^-, to form a soluble complex-ion which is a distinctive blue-green in 1:1 H_2O:acetone solution.

$$Co^{2+} + 4SCN^- \rightarrow Co(SCN)_4^{2-} \qquad \textbf{(EQ 13.9)}$$

If the separation of the Ni-subgroup from the Fe-subgroup is incomplete, any Fe (III) ions present will interfere with this test. Iron (III) reacts with thiocyanate to form a deep-red soluble complex

$$Fe^{3+} + SCN^- \rightarrow Fe(SCN)^{2+} \qquad \textbf{(EQ 13.10)}$$

This interference can be removed by addition of fluoride ions which form a more stable and colorless complex-ion with iron.

$$Fe(SCN)^{2+} + 6F^- \rightarrow FeF_6^{3-} + SCN^- \qquad \textbf{(EQ 13.11)}$$

Separation and Identification of Iron

The separation of Fe (III) from the solution containing Fe (III), Cr (III), and Zn (II) is based on the amphoteric nature of the Cr (III) and Zn (II). Addition of excess NaOH results in precipitation of $Fe(OH)_{3(s)}$ and formation of hydroxo-complex ions with Cr (III) and Zn (II).

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3(s) \qquad \textbf{(EQ 13.12)}$$

$$Cr^{3+} + 4OH^{-} \rightarrow Cr(OH)_4^{-} \qquad \textbf{(EQ 13.13)}$$

$$Zn^{2+} + 4OH^{-} \rightarrow Zn(OH)_4^{2-} \qquad \textbf{(EQ 13.14)}$$

Hydrogen peroxide is also added at this step to oxidize the chromium complex to the yellow chromate ion, CrO_4^{2-}

$$2Cr(OH)_4^{-} + 3H_2O_2 + 2OH^{-} \rightarrow 2CrO_4^{2-} + 8H_2O \qquad \textbf{(EQ 13.15)}$$

The $Fe(OH)_3$ formed above is dissolved, using HCl.

$$Fe(OH)_3(s) + 3H^{+} \rightarrow Fe^{3+} + 3H_2O \qquad \textbf{(EQ 13.16)}$$

The presence of the iron ion is confirmed by reaction with KSCN which forms a deep-red soluble iron-thiocyanate complex ion.

$$Fe^{3+} + SCN^{-} \rightarrow Fe(SCN)^{2+} \qquad \textbf{(EQ 13.17)}$$

Identification of Chromium and Zinc

Chromate and zinc can be tested for in the presence of each other, so the solution to be tested for these is divided in half.

The solution to be tested for chromate is acidified with acetic acid and chromate is then precipitated as lead chromate, a yellow precipitate, by adding lead acetate solution. Lead acetate, $Pb(C_2H_3O_2)_2$, is one of the few covalent salts in solution.

$$CrO_4^{2-} + Pb(C_2H_3O_2)_2 \rightarrow PbCrO_4(s) + 2C_2H_3O_2^{-} \qquad \textbf{(EQ 13.18)}$$

The solution to be tested for zinc is acidified with HNO_3 which destroys the tetrahydroxozincate ion.

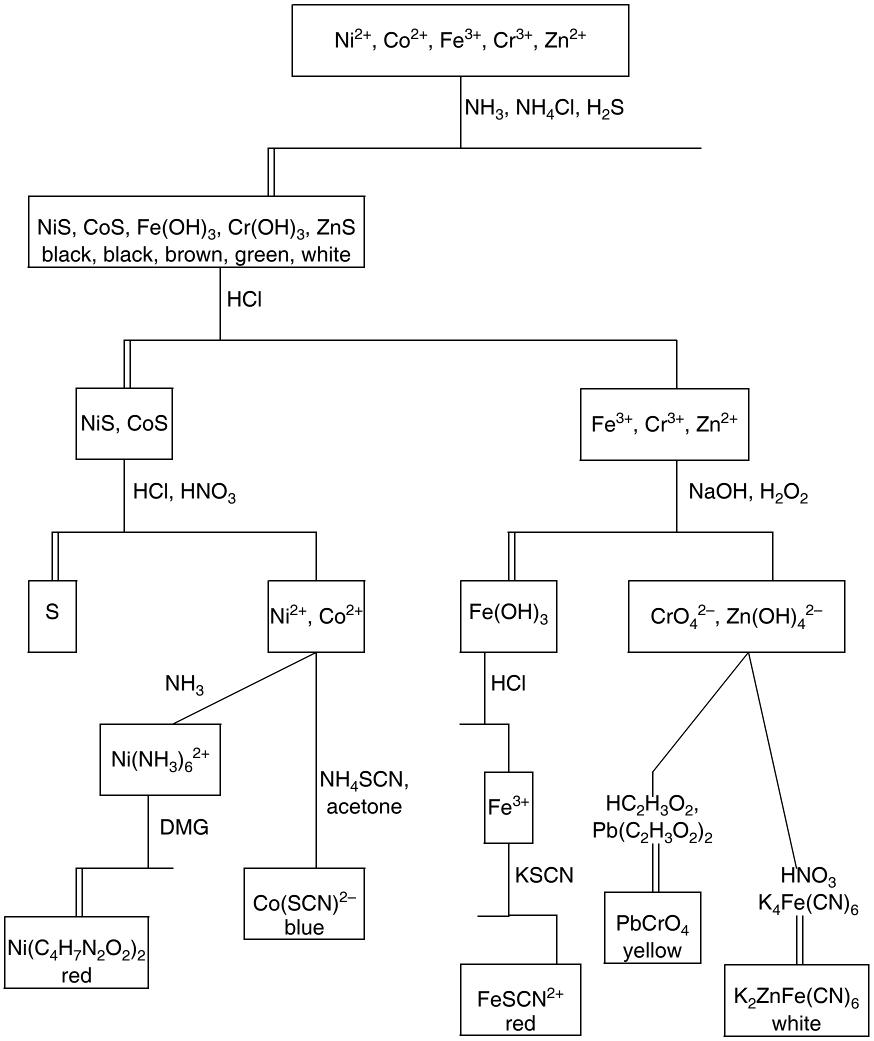
$$Zn(OH)_4^{2-} + 4H^{+} \rightarrow Zn^{2+} + 4H_2O \qquad \textbf{(EQ 13.19)}$$

Addition of $K_4Fe(CN)_6$ then precipitates the zinc as a mixed complex salt, a pale yellow precipitate.

$$Zn^{2+} + 2K^{+} + Fe(CN)_6^{4-} \rightarrow K_2ZnFe(CN)(s) \qquad \textbf{(EQ 13.20)}$$

Procedure

FIGURE 13.1 **Analytical Group III: The H_2s Basic Group**



NOTE: We are doing an abbreviated form of Group III. The complete Group III also includes $A1^{3+}$ and Mn^{2+}. Time considerations require a shortened form of this group

Test a known solution simultaneously with your unknown. Do Steps 1, 2 and 6 in hood.

STEP 1: Precipitation of Group III . To 10 drops of the solution to be analyzed, add 10 drops H_2O, then 3 drops 1 *M* NH_4Cl. Add 6 *M* NH_3 until just basic to litmus. Add 2 drops 15 *M* NH_3. Add 8 drops thioacetamide and heat 5 min in a water bath, stirring occasionally. Cfg and test the ppt (P7) as in step 2.

STEP 2: Separation of Subgroups. Wash ppt P7 with 15 drops H_2O plus 1 drop 1 *M* NH_4Cl. Cfg and discard the washings. To the ppt add 10 drops 1 *M* HCI, stir thoroughly. Cfg immediately and separate the solid (P8) from the solution (S8). Treat the ppt P8 with 4 more drops 1 *M* HCl, stir, cfg, and add the solution to S8. Treat P8 according to Step 6 and S8 according to Step 3.

STEP 3 Separation of Fe from Cr and Zn. To solution S8 add 6 *M* NaOH until basic, then 4 drops more. Add 6-8 drops 3% H_2O_2. Heat 5 min in a water bath, stir occasionally. Cfg. Decant the solution (S9) into another test tube. Formation of a red brown ppt indicates iron. Treat the ppt (P9) according to Step 4 and the solution S9 according to Step 5.

STEP 4: Test for Iron. To ppt P9 add 10 drops $H_2O$and 5 drops 6 *M* HCl, stir to dissolve. To the solution add 2 drops 0.2 *M* KSCN. Formation of a deep red solution confirms iron.

STEP 5: Tests for chromium and zinc. Divide solution S9 into two parts. (A yellow solution indicates chromium). To one part add 6 *M* $HC_2H_3O_2$ until acidic, then add 2 drops 0.1 *M* $Pb(C_2H_3O_2)_2$. Formation of a yellow ppt of $PbCrO_4$ proves chromium. To the second portion of S9 add 6 *M* HNO_3 until acidic, then add 5 drops 0.1 *M* $K_4Fe(CN)_6$. Formation of an off-white ppt of $K_2ZnFe(CN)_6$ proves zinc.

STEP 6: Dissolving NiS and CoS. Wash ppt P8 from step 2 with 10 drops H_2O, cfg and discard washings. Now add 3 drops 12 *M* HCl and 1 drop 15 *M* HNO_3, heat in water bath to dissolve the NiS and CoS. Add 5 drops H_2O. Cfg and discard any ppt. Divide the solution (S 10) in half, treating one half as in Step 7 and the other half as in Step 8.

STEP 7: Nickel Test. To one half of S 10 add 6 *M* NH_3 until basic, then add 1 more drop. Add 3 drops 1% dimethylglyoxime. Formation of a bright red ppt of $Ni(C_4H_7N_2O_2)_2$ proves nickel.

STEP 8: Cobalt Test. To one half of S 10 add 6 *M* NH_3 until basic, then add 1 drop 6 *M* HCl. Add a few crystals of NH_4SCN. Now add an equal volume of acetone and stir. The development of a blue-green color proves cobalt. (If the solution becomes red, iron (III) is present. Add 1 drop 1 *M* NaF to the solution to remove the iron. If the resulting solution is blue to green, cobalt is present.)

Questions

1. Write the net-ionic equations for the reactions occurring for each cation in the group.

- **a.** nickel
- **b.** cobalt
- **c.** iron
- **d.** chromium
- **e.** zinc

2. Give the formula of a single reagent that will separate the following pairs in one step.

- **a.** ZnS and CoS (solids)
- **b.** Ni^{2+} and Fe^{3+} (solutions)
- **c.** $Fe(OH)_3$ and $Zn(OH)_2$ (solids)
- **d.** $AgNO_3$ and $Ni(NO_3)_2$ (solutions)

3. What color is each of the following?

- **a.** $Fe(OH)_3$ solid
- **b.** $PbCrO_4$ solid
- **c.** $Co(SCN)_4^{2-}$ solution
- **d.** $Ni(NO_3)_2$ solution

4. A 0.050 *M* $Co(NO_3)_2$ is saturated with H_2S (0.10*M*). Using $K_{spa} = 3$ for CoS, what $[H_3O^+]$ is required to precipitate CoS from the 0.050 *M* $Co(NO_3)_2$ solution? See Section 16.14 in your textbook for a discussion of K_{spa}.