

# Cation Group II: The Acid-Insoluble Sulfides

## Introduction

The ions of analytical cation Group II are called the acid-insoluble sulfide group because they can be precipitated as sulfides from a saturated solution of  $\text{H}_2\text{S}$  that is also  $0.3\text{ M HCl}$ .

As your text shows, in a saturated  $\text{H}_2\text{S}$  solution with  $[\text{H}^+]$  being controlled, one has

$$K_i = [\text{H}^+][\text{S}^{2-}] = K_{a_1}K_{a_2}[\text{H}_2\text{S}] = (1.1 \times 10^{-7})(1.3 \times 10^{-13})(0.10) \quad (\text{EQ 12.1})$$

$$K_i = [\text{H}^+]^2[\text{S}^{2-}] = 1.4 \times 10^{-21}$$

So when  $[\text{H}^+]$  is kept at  $0.1\text{ M}$  to  $0.3\text{ M}$ , the  $[\text{S}^{2-}]$  is high enough to precipitate the metal sulfides that are in Group II, but is too low to precipitate the cations that are in Group III. Table 12.1 gives  $K_{\text{sp}}$  values.

The common cations in this acid-insoluble sulfide group are  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Hg(II)}$  as  $\text{HgCl}_4^{2-}$ ,  $\text{As(III)}$  as  $\text{H}_3\text{AsO}_3$ ,  $\text{As(V)}$  as  $\text{H}_3\text{AsO}_4$ ,  $\text{Sb(III)}$  as  $\text{SbCl}_4^-$ ,  $\text{Sb(V)}$  as  $\text{SbCl}_6^-$ ,  $\text{Sn(II)}$  as  $\text{SnCl}_4^{2-}$ , and  $\text{Sn(IV)}$  as  $\text{SnCl}_6^{2-}$ . We will do an abbreviated analysis of Group II, looking at copper (II), bismuth (III), cadmium (II), mercury (II), and tin (IV).

**TABLE 12.1 Solubility Products of Group II & Group III Sulfides**

Acid-Insoluble Sulfides		Basic-Insoluble Sulfides	
Salt	$K_{\text{sp}}$	Salt	$K_{\text{sp}}$
CuS	$8.5 \times 10^{-36}$	ZnS	$1.1 \times 10^{-21}$
$\text{Bi}_2\text{S}_3$	$2.9 \times 10^{-70}$	CoS	$5.9 \times 10^{-21}$
CdS	$3.6 \times 10^{-29}$	NiS	$2.0 \times 10^{-21}$
HgS	$1.6 \times 10^{-54}$	FeS	$4.9 \times 10^{-18}$
$\text{SnS}_2$	$1 \times 10^{-70}$	MnS	$7 \times 10^{-16}$

TABLE 12.1 Solubility Products of Group II &amp; Group III Sulfides

Acid-Insoluble Sulfides		Basic-Insoluble Sulfides	
Salt	$K_{sp}$	Salt	$K_{sp}$
PbS	$7 \times 10^{-27}$		
Sb <sub>2</sub> S <sub>3</sub>	$1.6 \times 10^{-93}$		

### Precipitation of the Group

We will use thioacetamide as a source of H<sub>2</sub>S, a poisonous gas. Thioacetamide hydrolyzes in hot solutions to produce H<sub>2</sub>S and ammonium acetate. By generating the H<sub>2</sub>S in the solution containing the cations it reacts with, we minimize the amount of H<sub>2</sub>S released into the laboratory. The reaction is

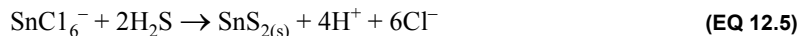
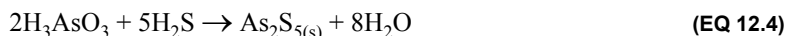


Whenever directions call for adding thioacetamide and heating, you are adding H<sub>2</sub>S to your reaction mixture.

The following equation shows the reaction of simple cations with H<sub>2</sub>S.



Molecular substances or complex ions are converted to insoluble sulfides.

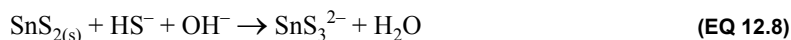
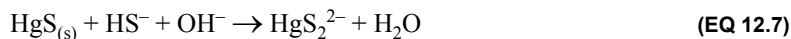


### Subdivision of the Group

The basis for the separation of Group IIA, copper, bismuth, and cadmium from Group IIB, mercury and tin is the ability of Group IIB cations to form sulfide complexes. Formation of sulfide complexes requires a high sulfide ion concentration in solution. This is achieved by adding NaHS and NaOH resulting in the reaction:



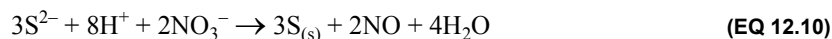
The dissolution of the metal sulfides occurs as the net reactions:



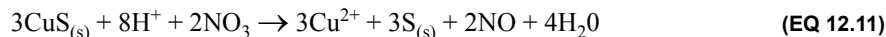
### Analysis of Group IIA

**Dissolving the Metal Sulfides.** The Group IIA sulfides are dissolved by reaction with hot dilute nitric acid which oxidizes the sulfide ions to elemental sulfur. This decreases the sulfide concentration in solution, causing the metal sulfides to dissolve to replace it.

The two reactions involved for copper are



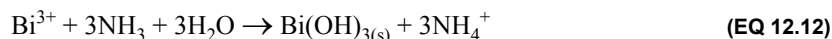
The net reaction is the sum of these two or



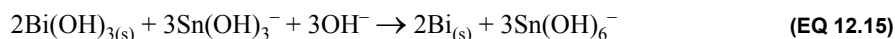
Similar reactions occur for CdS and Bi<sub>2</sub>S<sub>3</sub>.

### Separation and Identification of Bismuth.

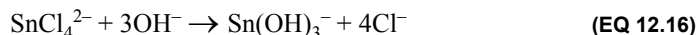
The basis of the separation of Bi<sup>3+</sup> from Cu<sup>2+</sup> and Cd<sup>2+</sup> is the formation of insoluble Bi(OH)<sub>3</sub> in excess NH<sub>3</sub>. Copper and cadmium form NH<sub>3</sub> complexes.



Identification of bismuth is achieved by addition of stannite solution which reduces the Bi(OH)<sub>3</sub> to black metallic bismuth.

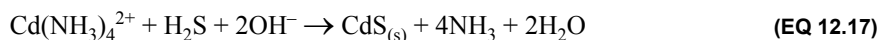


**NOTE:** Stannite solution is a strong reducing agent that reacts with O<sub>2</sub> in the air. It must therefore be made just prior to use by treating a solution of SnCl<sub>2</sub> in HCl with NaOH. The net reaction is:

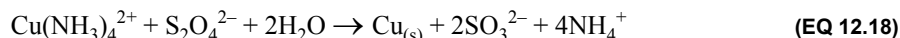


**Identification of Copper.** The intense blue color of Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> is a confirmation of copper.

**Identification of Cadmium.** Cadmium is identified by precipitation of cadmium with H<sub>2</sub>S to form yellow CdS.



However, if the copper ions are present, they precipitate as CuS which is black and prevent the yellow CdS from being seen. Thus, copper must be removed before running the final cadmium test. This is done by addition of sodium dithionite, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, which reduces the copper (II) to metallic copper but does not react with the cadmium in solution.

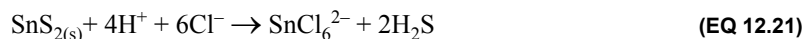


### Analysis of Group II B

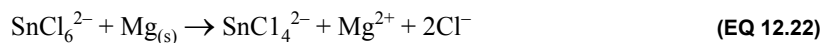
**Reprecipitation of the Metal Sulfides.** Acidification of the basic solution of the sulfide complexes causes the metal sulfides to reprecipitate.



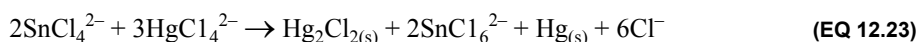
**Separation of Mercury From Tin.**  $\text{SnS}_2$  is soluble in concentrated HCl while HgS is not.



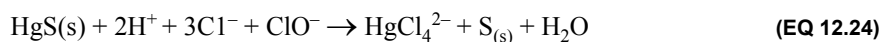
**Identification of Tin.** The tin (IV) is first reduced to the tin (II) state using metallic Mg in HCl solution.



Addition of  $\text{HgCl}_2$  in HCl solution to tin (II) results in a reduction of the mercury (II) to elemental Hg (black) and insoluble  $\text{Hg}_2\text{Cl}_2$  (white) for an observed grey precipitate.



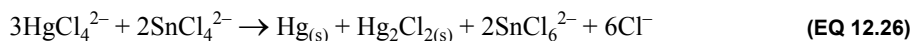
**Identification of Mercury.** HgS is one of the most insoluble inorganic compounds and requires addition of HCl + NaOCl which oxidizes the sulfide ion to sulfur and complexes the mercury (II) ion.



This solution must be heated for several minutes to destroy any excess hypochlorite ions, i.e.,



Mercury is confirmed by adding  $\text{SnCl}_2$  in HCl solution which reduces the Hg(II) to Hg and  $\text{Hg}_2\text{Cl}_2$  as in the tin test above, producing a grey precipitate.




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## Procedure

Test a known solution **simultaneously with your unknown**. Do Steps 2, 3, 4, 8 and 9 on hot plate in the hood. The flow chart is Figure 12.1 on page 78.

**STEP 1: pH Adjustment.** To 10 drops of solution to be analyzed add 6M  $\text{NH}_3$  until just basic to litmus (count the drops of  $\text{NH}_3$  added). Add sufficient  $\text{H}_2\text{O}$  to make 1 mL of solution; then add exactly 2 drops 6 M HCl. (This results in a pH of about 0.5.)

**STEP 2: Precipitation with  $\text{H}_2\text{S}$ .** Add 8 - 10 drops of thioacetamide (TA) solution, stir, and heat in a boiling water bath for 5 minutes. Stir several times while heating. Add 6-8 drops TA; heat another 5 minutes. Cfg. (If the resulting solution is not clear, add 2 drops 1 M  $\text{NH}_4\text{Cl}$  and heat for 3 - 5 min. Cfg.) Treat the ppt (P3) as in step 3. Discard the supernatant.

**STEP 3: Separation of Subgroups.** Wash ppt P3 with 10 drops  $\text{H}_2\text{O}$ . Cfg. Discard the washings. To the ppt add 5 drops 6 M NaOH and 3 drops 2 M NaHS. Heat for 3-5 min, stirring occasionally. Cfg. Decant the solution (S4) from the ppt (P4). Repeat the extraction with NaOH and NaHS on the ppt and combine the two extraction solutions (S4). Treat P4 as in Step 4. Treat S4 as in Step 8.

**STEP 4: Dissolving Cu Subgroups (CuS, Bi<sub>2</sub>S<sub>3</sub>, CdS).** Wash ppt P4 with 10 drops H<sub>2</sub>O. Discard the washings. To ppt P4 add 5 drops 6 M HNO<sub>3</sub> and 5 drops H<sub>2</sub>O. Heat for 5 minutes to dissolve the ppt. Cfg and discard any sulfur formed. (If considerable black ppt remains, treat it with a second HNO<sub>3</sub> + H<sub>2</sub>O portion and combine both solutions.) Treat the solution (S5) as in Step 5.

**STEP 5: Precipitation of Bismuth.** Cu Test: To solution S5 add 15 M NH<sub>3</sub> until it is distinctly basic plus 1 drop. The development of a deep blue solution of Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> confirms copper. Cfg. Formation of a white gelatinous ppt (P5) indicates Bi(OH)<sub>3</sub>. Test P5 as in Step 6. Test the solution (S6) as in Step 7.

**STEP 6: Bismuth Test.** Make a fresh solution of sodium stannite, NaSn(OH)<sub>3</sub>, by putting 3 drops of 0.1 M SnCl<sub>2</sub> in a test tube and adding 6 M NaOH dropwise until the white ppt that initially forms redissolves. Add this solution to ppt P5. Formation of black elemental Bi confirms bismuth.

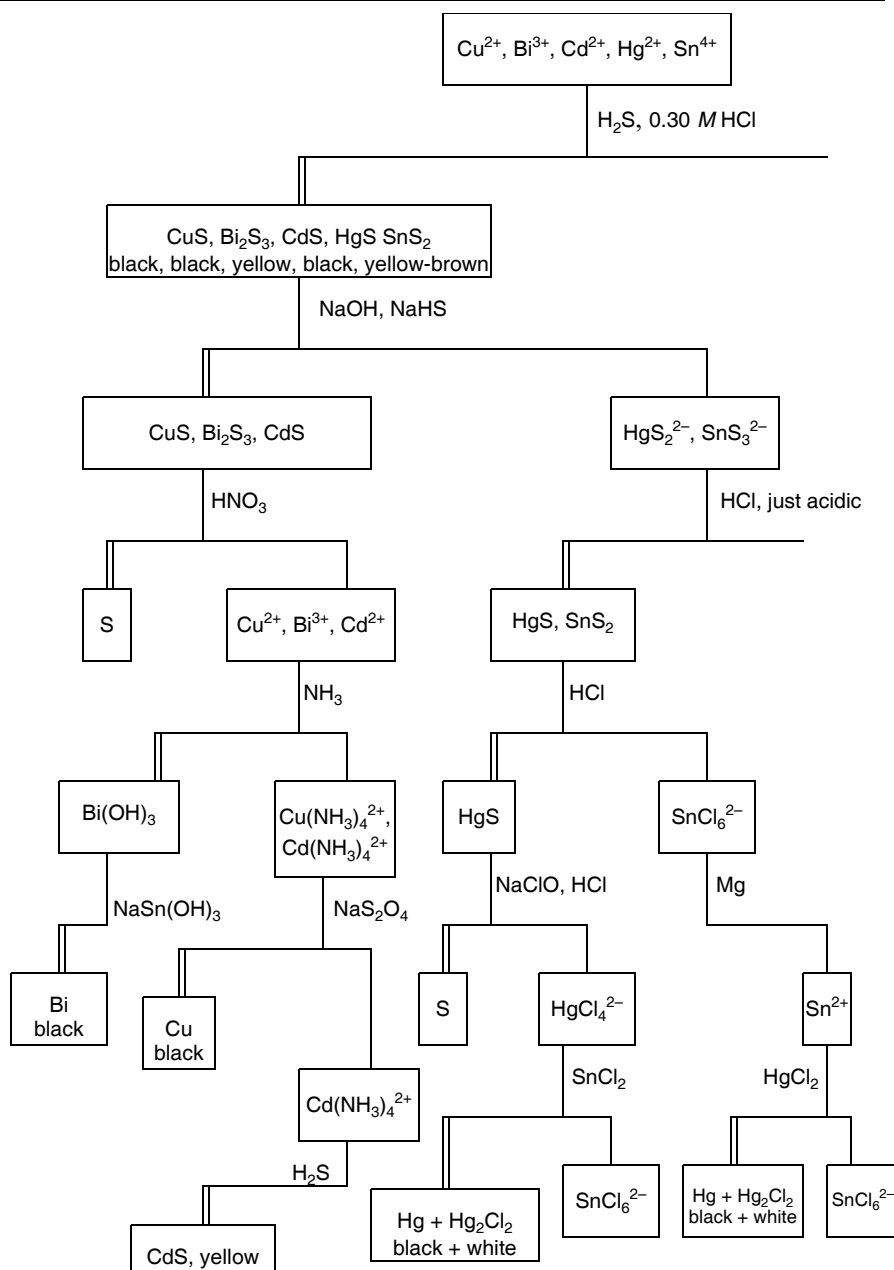
**STEP 7: Cadmium Test.** If Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> is present in S6 (blue solution) add a small amount of solid Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (sodium dithionite) about the size of half a pea. Stir well and heat for 3 - 5 min. The solution should become colorless and copper metal should precipitate. Cfg while warm and decant the colorless solution (S7) into another test tube. (If the solution is not colorless or if copper metal has not precipitated, treat again with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>.) To the colorless solution S7 (or colorless S6 if Cu was absent), add 5 drops thioacetamide and heat 3 - 5 min. Formation of a yellow ppt of CdS confirms cadmium.

**STEP 8: Precipitation of Hg Subgroup (Hg<sub>2</sub><sup>2+</sup>, SnS<sub>3</sub><sup>2-</sup>).** To S4 from Step 3, add 6 M HCl with stirring until just acidic to litmus. Heat for 3 - 5 min. Cfg and discard the liquid. Treat the ppt (P6) as in step 9. (If you obtain only small amounts of a nearly white ppt, you have only elemental sulfur.)

**STEP 9: Separation of HgS from SnS<sub>2</sub>.** To ppt P6 add 1 mL 6 M HCl, stir and heat for 3 min. Cfg. Separate the solution (S8) from the ppt (P7). Treat the remaining ppt P7 with another 10 drops HCl, heat, Cfg, and combine the solutions. Test P7 as in Step 11 and S8 as in Step 10.

**STEP 10: Test for Tin.** To solution S8 add a 1 cm piece of Mg ribbon and heat to reduce the SnCl<sub>6</sub><sup>2-</sup> to Sn<sup>2+</sup>. Cfg to remove any solid formed. To the clear solution add 5 drops of 0.1 M HgCl<sub>2</sub>. Formation of a silky grey-white ppt of Hg<sub>2</sub>Cl<sub>2</sub> + Hg confirms tin.

**STEP 11: Dissolving HgS.** To ppt P7 add 6 drops 5% NaClO and 2 drops 6 M HCl. Stir to dissolve the black HgS. Heat 3 - 5 min to decompose any remaining NaClO. Cfg and decant the clear solution into a clean test tube. To the clear solution add 3 - 4 drops 0.1 M SnCl<sub>2</sub>. Formation of a silky grey-white ppt of Hg<sub>2</sub>Cl<sub>2</sub> + Hg confirms mercury.

FIGURE 12.1 Analytical Group II The H<sub>2</sub>S Acid Group

### Questions

- Write net-ionic equations for & the reactions occurring for each cation in the group.
  - copper
  - bismuth
  - cadmium
  - mercury
  - tin

2. Give the formula for a reagent which will:
  - a. dissolve  $\text{SnS}_2$  but not  $\text{HgS}$
  - b. dissolve  $\text{Cu}(\text{OH})_2$  but not  $\text{Bi}(\text{OH})_3$
  - c. form a precipitate with  $\text{Cu}^{2+}$  but not with  $\text{Cd}^{2+}$
  - d. form a precipitate with  $\text{Bi}^{3+}$  but not with  $\text{Cd}^{2+}$
  - e. form a precipitate with  $\text{HgCl}_2$  but not with  $\text{SnCl}_2$
3. Give the formula of a site reagent (or combination of reagents if a single reagent is insufficient) which would enable you to distinguish between the following pairs of compounds contained in separate test tubes. Tell what would happen in each case to let you make the distinction.
  - a.  $\text{Cu}(\text{OH})_2$  and  $\text{Bi}(\text{OH})_3$  (solids)
  - b.  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  (solutions)
  - c.  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  (solutions)
4.  $\text{CuS}$  ( $K_{\text{sp}} = 8.7 \times 10^{-36}$ ) is the least soluble of the Group II sulfides while  $\text{PbS}$  ( $K_{\text{sp}} = 8.4 \times 10^{-28}$ ) is much more soluble. Consider a solution saturated in  $\text{H}_2\text{S}$  (0.10 M) and 0.3 M HCl (the conditions for pptn of Group II cations).
  - a. Calculate the  $[\text{S}^{2-}]$  present.
  - b. Calculate the concentrations of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions that remain in solution (unprecipitated) at these conditions.

