

4.1: Precipitation of group II cations

The bases of Group II cations separation

The solubility guideline#1 of insoluble ions states “Hydroxide (OH^-) and sulfides (S^{2-}) are insoluble except when the cation is alkali metal, ammonia, or a heavy alkaline earth metal ion, i.e., Ca^{2+} , Ba^{2+} , and Sr^{2+} ”. The sulfide of Cr^{3+} is also in the exceptions list as its sulfide is unstable in water. It is obvious that the number of insoluble sulfides and hydroxides is large. The solution is made acidic to decrease $[\text{OH}^-]$ to below the level that can cause precipitation of any ion. The $[\text{S}^{2-}]$ also remains low due to the common ion effect of H_3O^+ in the acidic medium as explained in the next section. Therefore among the insoluble sulfides, only those that have very low solubility limits are selectively precipitated. These include Bi^{3+} , Cd^{2+} , Cu^{2+} , and Sn^{4+} among the cations selected in this study that are left in the solution after group I cations have been separated. Group II comprise of Bi^{3+} , Cd^{2+} , Cu^{2+} , and Sn^{4+} .

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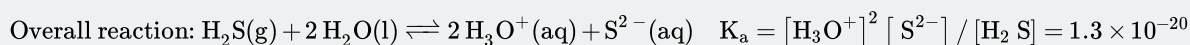
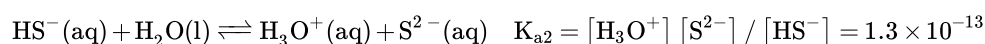
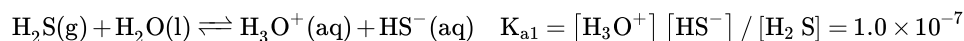
Among the ions in the initial solution after removal of group I cations, the following ions form insoluble sulfides: Bi^{3+} , Cd^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , and Sn^{4+} . Among these, Bi^{3+} , Cd^{2+} , Cu^{2+} , and Sn^{4+} are in group II that form very insoluble sulfides, and Cr^{3+} , Fe^{2+} , Fe^{3+} , and Ni^{2+} are in group III form insoluble hydroxides and sulfides in basic medium, as reflected by their solubility product constants (K_{sp}) listed in Table 1. The minimum concentration of S^{2-} needed to start precipitation of the cation can be calculated from the K_{sp} expressions as shown in Table 1. It can be observed from Table 1 that there is a huge difference in the minimum S^{2-} concentration ($1.8 \times 10^{-20}\text{M}$) needed to precipitate Ni^{2+} -the least soluble sulfide of group III and Cd^{2+} (7.8×10^{-26}) -the most soluble sulfide of group II. If the S^{2-} is kept more than $1.8 \times 10^{-20}\text{M}$ but less than $7.8 \times 10^{-26}\text{M}$ group II cations will selectively precipitate while group III cations and the rest of the cations will remain dissolved.

Table 1: Solubility product constants of insoluble sulfides of group II, and group III and minimum sulfide ion concentration needed to start precipitation from 0.1M cation solution*.

Ion	Sulfide	K_{sp} at 25 °C	Minimum $[\text{S}^{2-}]$ needed to precipitate
Fe^{2+}	FeS	$K_{\text{sp}} = [\text{Fe}^{2+}] [\text{S}^{2-}] = 4.9 \times 10^{-18}$	$[\text{S}^{2-}] = K_{\text{sp}} / [\text{Fe}^{2+}] = 4.9 \times 10^{-17}$
Ni^{2+}	NiS	$K_{\text{sp}} = [\text{Ni}^{2+}] [\text{S}^{2-}] = 1.8 \times 10^{-21}$	$[\text{S}^{2-}] = K_{\text{sp}} / [\text{Ni}^{2+}] = 1.8 \times 10^{-20}$
Cd^{2+}	NiS	$K_{\text{sp}} = [\text{Cd}^{2+}] [\text{S}^{2-}] = 7.8 \times 10^{-27}$	$[\text{S}^{2-}] = K_{\text{sp}} / [\text{Cd}^{2+}] = 7.8 \times 10^{-26}$
Bi^{3+}	Ba_2S_3	$K_{\text{sp}} = [\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3 = 6.8 \times 10^{-87}$	$[\text{S}^{2-}] = \sqrt[3]{K_{\text{sp}} / [\text{Bi}^{3+}]^2} = 4.1 \times 10^{-30}$
Sn^{4+}	SnS_2	$K_{\text{sp}} = [\text{Sn}^{4+}] [\text{S}^{2-}]^2 = 1.0 \times 10^{-26}$	$[\text{S}^{2-}] = \sqrt{K_{\text{sp}} / [\text{Sn}^{4+}]} = 3.2 \times 10^{-14}$
Cu^{2+}	CuS	$K_{\text{sp}} = [\text{Cu}^{2+}] [\text{S}^{2-}] = 8.7 \times 10^{-36}$	$[\text{S}^{2-}] = K_{\text{sp}} / [\text{Cu}^{2+}] = 8.7 \times 10^{-35}$

- * Following cations that may be present the initial solution are not listed in this table due to the following reasons: i) group I cations, i.e., Pb^{2+} , Hg_2^{2+} , and Ag^+ are already removed, ii) Ca^{2+} and Ba^{2+} for soluble sulfides, iii) sulfide of Cr^{3+} is not stable in water, and iv) Fe^{3+} is reduced to Fe^{2+} by H_2S in acidic medium: $2\text{Fe}^{3+}(\text{aq}) + \text{S}^{2-} \rightleftharpoons 2\text{Fe}^{2+}(\text{aq}) + \text{S}(\text{s})$. Source of K_{sp} values: chem 202 lab manual, 2008, by Michael Stranz, cengage learning, ISBN 13: 978-0-534-66904-1

Source of S^{2-} is H_2S gas -a weak diprotic acid that dissociated in water by the following equilibrium reactions:



Extent of H_2S dissociation, and, consequently, the concentration of S^{2-} produced is dependent on H_3O^+ :

$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]} \quad \text{rearranges to:} \quad [\text{S}^{2-}] = \frac{K_{\text{a}} [\text{H}_2\text{S}]}{[\text{H}_3\text{O}^+]^2}$$

It is obvious from the above formula that $[S^{2-}]$ is dependent on $[H_3O^+]$, which is related to pH ($pH = \text{Log} \frac{1}{[H_3O^+]} = -\text{Log}[H_3O^+]$). Therefore, $[S^{2-}]$ can be controlled by adjusting the pH.

H_2S is a toxic gas. To minimize the exposure, H_2S is produced in-situ by decomposition of thioacetamide (CH_3CSNH_2) in water:



The decomposition of thioacetamide is an endothermic reaction, which, according to Le Chatelier's principle, moves in the forward direction upon heating. An aqueous solution of thioacetamide is heated in a boiling water bath in a fume hood producing $\sim 0.01M$ H_2S solution.

Rearranging acid dissociation constant of H_2S and plugging in $0.01M$ H_2S in the rearranged formula allows calculating S^{2-} concentration at various concentrations of H_3O^+ , i.e., at various pH values:

$$[S^{2-}] = \frac{K_a[H_2S]}{[H_3O^+]^2} = \frac{1.3 \times 10^{-20} \times 0.01}{[H_3O^+]^2} = \frac{1.3 \times 10^{-22}}{[H_3O^+]^2}$$

It shows that S^{2-} concentration can be varied by $[H_3O^+]$, i.e., by varying pH. At pH 1 and 0, H_3O^+ is $0.10 M$ and $1.0 M$, respectively, that produces $[S^{2-}]$ in the range of $1.3 \times 10^{-20} M$ S^{2-} and $1.3 \times 10^{-22} M$ S^{2-} :

$$[S^{2-}] = \frac{1.3 \times 10^{-22}}{(0.10)^2} = 1.3 \times 10^{-20} M \quad \text{and} \quad [S^{2-}] = \frac{1.3 \times 10^{-22}}{(1.0)^2} = 1.3 \times 10^{-22} M$$

This range of $[S^{2-}]$ is less than the solubility limit of Ni^{2+} -the least soluble cation of group III but more than the solubility limit of Cd^{2+} -the most soluble cation of group II. If pH of the test solution is maintained between 0 and 1, group II cations will precipitate and group III and higher group cations will remain dissolved. At pH 0.5, S^{2-} is $5.2 \times 10^{-22} M$ that will precipitate more than 99.99% Cd^{2+} :

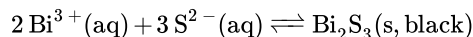
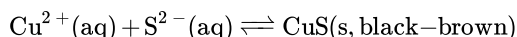
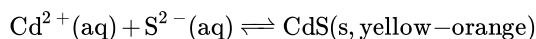
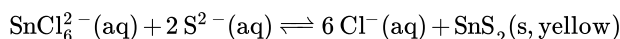
$$K_{sp} = [Cd^{2+}][S^{2-}] = 7.8 \times 10^{-27} \quad \text{gives:} \quad [Cd^{2+}] = \frac{7.8 \times 10^{-27}}{[S^{2-}]} = \frac{7.8 \times 10^{-27}}{5.2 \times 10^{-22}} = 1.5 \times 10^{-5} M$$

, which is 0.0002% of the initial $[Cd^{2+}]$.

The supernatant after removal of group I chlorides is usually within the pH range of 0.5 ± 0.3 , which is the appropriate pH for precipitation of group II cations under the conditions of this study. If the pH of the test sample is outside this range, the pH can be increased to ~ 0.5 by adding $0.5M$ $NH_3(aq)$ drop by drop under stirring. Determine pH by using a pH paper after each drop of $0.5M$ $NH_3(aq)$ is added and thoroughly mixed. Keep in mind that NH_3 solution in water is also labeled as NH_4OH . Similarly, the pH can be decreased to ~ 0.5 by adding $0.5M$ $HCl(aq)$ drop by drop under stirring. Determine pH by using a pH paper after each drop of $0.5M$ $HCl(aq)$ is added and thoroughly mixed.

Thioacetamide reagent is added to the test solution at pH ~ 0.5 and heated in a boiling water bath to precipitate out group II cations.

The precipitates include SnS_2 (yellow), CdS (yellow-orange), CuS (Black-brown), Bi_2S_3 (black), formed by the following precipitation reactions:



The overall color of the combined precipitate may vary depending on its composition. Black color dominates, i.e., if all precipitates are present, the color of the mixture will be black as shown in Figure 4.1.1.



Figure 4.1.1: Mixture of Group II precipitates, i.e., SnS_2 (yellow), CdS (yellow-orange), CuS (Black-brown), and Bi_2S_3 (black).

The solution is cooled to room temperature by using a room temperature water bath. Cooling helps precipitation of CdS . A drop of 0.5 M $\text{NH}_3(\text{aq})$ is added while stirring, which promotes precipitation of CdS and CuS , as both tend to stay dissolved in a supersaturated solution. The mixture is centrifuged and decanted to separate the supernatant that is used for the analysis of group III and higher group cations. The precipitate is washed with 0.1M NH_4Cl solution and the washed precipitate is used to separate and confirm individual cations of group II.

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