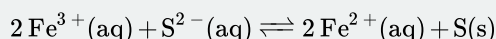


5.1: Separation of group III cations

Group II cations form sulfides that have very low solubility. After group II cations are removed under a low concentration of S^{2-} in an acidic medium, the solution is made alkaline. Remember that like sulfides, hydroxides are also insoluble according to insoluble ions rule#1 of solubility guidelines described in chapter 1 states “Hydroxide (OH^-) and sulfides (S^{2-}) are insoluble except when the cation is a heavy alkaline earth metal ion: Ca^{2+} , Ba^{2+} , and Sr^{2+} , alkali metal ions, and ammonium ion.”

Table 1 lists solubility product constants of hydroxides of group III & IV cations at 25 °C, maximum hydroxide (OH^-) concentration, and the maximum pH that can exist in a saturated solution containing 0.1M cation solutions that may be present in the test solution at this stage. It can be observed that the ions listed in table 1 will not precipitate as hydroxides during the precipitation of group II cations under the acidic pH range of 0.5 to 1.

Fe^{3+} forms the most insoluble hydroxide, but it is reduced to Fe^{2+} by H_2S during precipitation of group II cations:



Fe^{3+} may be present only if precipitation of group III starts from a fresh sample that has not been subjected to group II separation.

It can be observed from Table 1 that if the pH of the sample solution is increased to a range of 7 to 10, Fe^{3+} , Cr^{3+} , Ni^{2+} , and Fe^{2+} will precipitate as $Fe(OH)_3$ (s, rusty), $Cr(OH)_3$ (s, gray-green), $Ni(OH)_2$ (s, green), and $Fe(OH)_2$ (s, green), leaving behind in the solution rest of the ions that may still be present at this stage. Group III comprise of Fe^{3+} , Cr^{3+} , Ni^{2+} , and Fe^{2+} ions.

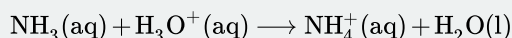
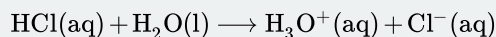
Table 1: Solubility product constants of hydroxides of group III & IV cations at 25 °C, maximum hydroxide (OH^-) concentration, and pH that can exist in a saturated 0.1M cation solution.*

Ion	Salt	K_{sp} at 25 °C	Minimum $[OH^-]$ and pH needed to precipitate
Fe^{3+}	$Fe(OH)_3$	$K_{sp} = [Fe^{3+}] [OH^-]^3 = 2.8 \times 10^{-39}$	$[OH^-] = 3.0 \times 10^{-13} M = pH 1.5$
Cr^{3+}	$Cr(OH)_3$	$K_{sp} = [Cr^{3+}] [OH^-]^3 = 1.0 \times 10^{-39}$	$[OH^-] = 2.2 \times 10^{-10} M = pH 4.3$
Ni^{2+}	$Ni(OH)_2$	$K_{sp} = [Ni^{2+}] [OH^-]^2 = 5.5 \times 10^{-16}$	$[OH^-] = 7.4 \times 10^{-9} M = pH 4.$
Fe^{2+}	$Fe(OH)_2$	$K_{sp} = [Fe^{2+}] [OH^-]^2 = 4.9 \times 10^{-15}$	$[OH^-] = 2.2 \times 10^{-9} M = pH 5.6$
Ca^{2+}	$Ca(OH)_2$	$K_{sp} = [Ca^{2+}] [OH^-]^2 = 5.0 \times 10^{-6}$	$[OH^-] = 7.1 \times 10^{-4} M = pH 10.9$
Ba^{2+}	$Ba(OH)_2$	$K_{sp} = [Ba^{2+}] [OH^-]^2 = 2.6 \times 10^{-6}$	$[OH^-] = 5.1 \times 10^{-3} M = pH 11.7$

- * Following cations that may be present in the initial solution are not listed in this table due to the reason: i) Pb^{2+} , Hg_2^{2+} , and Ag^+ are already removed as chloride precipitates of group I cations, ii) Sn^{4+} , Cd^{2+} , Cu^{2+} , and Bi^{3+} has been removed as group II sulfides under pH 0.5 to 1, iii) Na^+ and K^+ form soluble compounds with all anions according to rule#1 of solubility described in chapter 1. Source: Engineering ToolBox, (2017). Solubility product constants. [online] Available at: https://www.engineeringtoolbox.com/s...sp-d_1952.html [Accessed Feb. 5th, 2022]

Buffers, that resist change in pH are employed in such a situation where pH needs to be maintained in a narrow range. Buffers are a mixture of a weak acid and its conjugate base or a mixture of a weak base and its conjugate acid. Ammonia (NH_3), i.e., a weak base and ammonium ion (NH_4^+) is its conjugate acid.

The NH_3/NH_4^+ is a suitable buffer that can maintain pH of around 9. The buffer is prepared by adding 2 drops of 6M HCl into 15 drops of the sample and then adding 6M NH_3 drop by drop to neutralize the acid.



Then 5 drops more of 6M NH_3 are added after the HCl has been neutralized to make a mixture of NH_3 and NH_4^+ that maintains pH ~ 9 and OH^- at around $1 \times 10^{-5} \text{ M}$.

The group III cations precipitate at this stage as hydroxides, as shown in Figure 5.1.1, except Ni^{2+} :

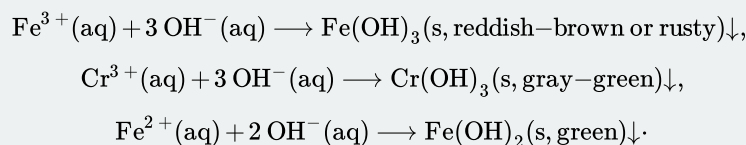


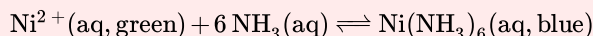
Figure 5.1.1: Precipitation of iron ions and chromium ions, as $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$, and $\text{Cr}(\text{OH})_3$ in the presence by OH^- at pH ~ 9 .

The concentration of Fe^{2+} , i.e., the most soluble hydroxide of group III cations, is reduced by more than 99.99%, i.e., from 0.1M to $4.9 \times 10^{-7} \text{ M}$ when pH is increased to 9 and OH^- concentration is increased to $1 \times 10^{-5} \text{ M}$:

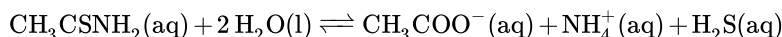
$$\text{Fe}^{2+} = \frac{K_{\text{sp}}}{[\text{OH}^{-}]^2} = \frac{4.9 \times 10^{-17}}{(1 \times 10^{-5})^2} = 4.9 \times 10^{-7} \text{ M}$$

Caution

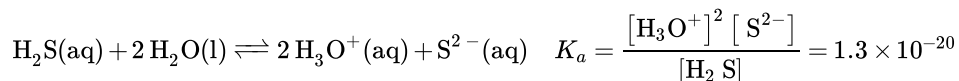
Nickel ion is not precipitated at this stage as it forms soluble coordination cation $[\text{Ni}(\text{NH}_3)_6]^{2+}$ with ammonia:



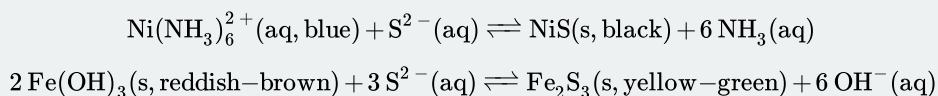
Therefore, S^{2-} is introduced by adding thioacetamide and heating the mixture in a boiling water bath. Decomposition of thioacetamide produces $\sim 0.01 \text{ M}$ H_2S :

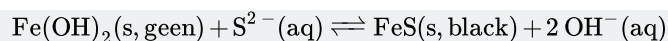


Nearly all of the H_2S dissociates to form $\sim 0.01 \text{ M}$ S^{2-} at pH ~ 9 :



The ammonia complex of nickel, i.e., $[\text{Ni}(\text{NH}_3)_6]^{2+}$ precipitates out as NiS , and, at the same time, $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ also convert to Fe_2S_3 and FeS :





Chromium remains as $\text{Cr}(\text{OH})_3$ precipitate because chromium sulfide is unstable in water.

Group III precipitates, i.e., $\text{Cr}(\text{OH})_3(\text{s, gray-green})$, $\text{NiS}(\text{s, black})$, $\text{Fe}_2\text{S}_3(\text{s, yellow-green})$, and $\text{FeS}(\text{s, black})$ in the mixture are separated as precipitates, and the rest of the ions, i.e. Ca^{2+} , Ba^{2+} , Na^{+} and K^{+} , etc. remain dissolved in the supernatant, as shown in Figure 5.1.2. The color of the precipitate does not give a clear indication of what ions are present at this stage as several species of different colors may be mixed at this stage.

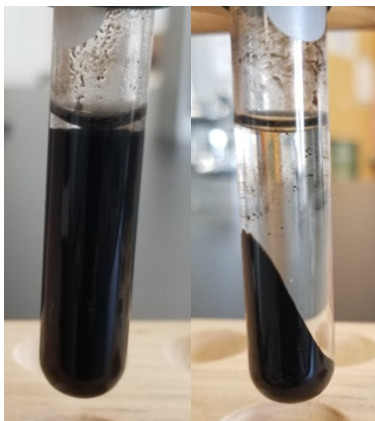


Figure 5.1.2: Group III precipitates, i.e., $\text{Cr}(\text{OH})_3(\text{s, gray-green})$, $\text{NiS}(\text{s, black})$, $\text{Fe}_2\text{S}_3(\text{s, yellow-green})$, and $\text{FeS}(\text{s, black})$ in the mixture before centrifuge (left) and separated as a pellet at the bottom of the test tube after centrifuge (right).

This page titled [5.1: Separation of group III cations](#) is shared under a [Public Domain](#) license and was authored, remixed, and/or curated by [Muhammad Arif Malik](#).