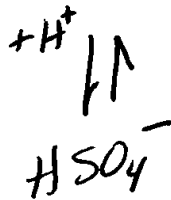
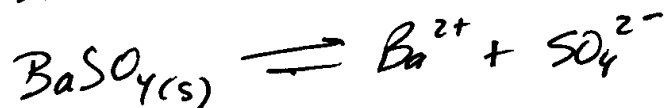


Homework. 10 (Solubility & Complexation).

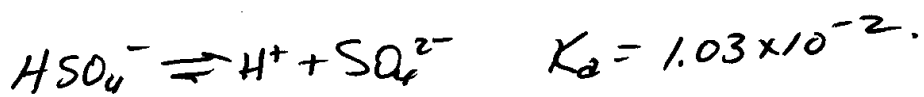
1. a) $K_{sp} = [Ba^{2+}][SO_4^{2-}]$ $S^0 = [Ba^{2+}] = [SO_4^{2-}]$

$$S^0 = \sqrt{K_{sp}} = 6.56 \times 10^{-6} \text{ M}$$

b) acidic: formation of HSO_4^- reduces $[SO_4^{2-}]$ causing more solid to dissolve.



c) $pH = 2.00$ $[H^+] = 10^{-2}$



since $K_a \sim [H^+]$ (or $pK_a \sim pH$), $[HSO_4^-] \approx [SO_4^{2-}]$

$$S = [Ba^{2+}] = [HSO_4^-] + [SO_4^{2-}] \quad \left\{ \begin{array}{l} [H_2SO_4] \approx 0 \\ \text{strong acid} \end{array} \right.$$

$$= 2[SO_4^{2-}] \quad \text{or} \quad [SO_4^{2-}] = \frac{S}{2}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = S \cdot \frac{S}{2}$$

$$S = \sqrt{2K_{sp}} = \underline{9.27 \times 10^{-6} \text{ M}}$$

2.

$$[\text{OH}^-] = \sqrt{\frac{K_{sp}}{[\text{Ni}^{2+}]}} = 7.75 \times 10^{-7}$$

$$\text{pH} = 7.89$$

3.

a) est of relative solubility:

	AgCl	K_{sp}
		1.8×10^{-10}
	PbCl_2	1.7×10^{-5}

$$\approx \sqrt[n]{K_{sp}} \quad n = \# \text{ ions}$$

$$\sqrt[2]{1.8 \times 10^{-10}} \ll \sqrt[3]{1.7 \times 10^{-5}} \Rightarrow \text{AgCl(s)} \text{ ppt. FIRST}$$

$$b) F_{\text{cl}} = \frac{6 \text{ g NaCl}}{58.5 \frac{\text{g NaCl}}{\text{mol NaCl}}} \cdot \frac{1 \text{ mol Cl}}{1 \text{ mol NaCl}} = 0.103 \text{ F}$$

1 L

Note: $F_{\text{cl}} \gg [\text{Ag}^+] = [\text{Pb}^{2+}]$ so we could do a good estimation if we assumed $[\text{Cl}^-] = F_{\text{cl}}$.

However, let's try a bit more exacting:

$$[\text{Cl}^-] = F_{\text{cl}} - \underbrace{(10^{-3} - [\text{Ag}^+])}_{\text{amount of Cl in precipitate}} - \underbrace{(2(10^{-3} - [\text{Pb}^{2+}]))}_{\text{amount of Cl in precipitate}}$$

Assume

Since AgCl and PbCl_2 are only slightly soluble.

$$[\text{Cl}^-] = 0.103 - 0.003 = 0.100 \text{ M}$$

$$[Ag^+] = \frac{K_{sp}}{\sum [Cl^-]} = 1.8 \times 10^{-9} M \quad \leftarrow \text{assumption good!}$$

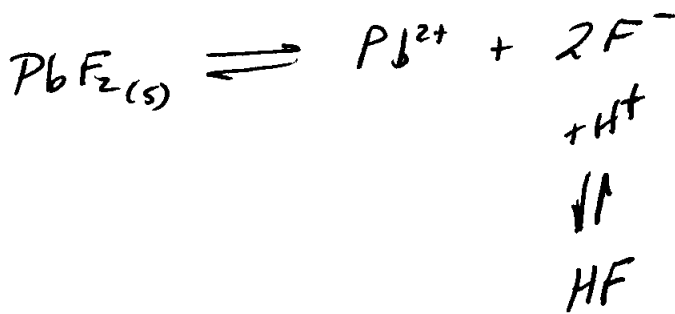
$$[Pb^{2+}] = \frac{K_{sp}}{\sum [Cl^-]^2} = 1.7 \times 10^{-3} M \quad \leftarrow \text{only started with } 1 \times 10^{-3} M \text{ } Pb^{2+}$$

So NO $PbCl_2$ precipitates!

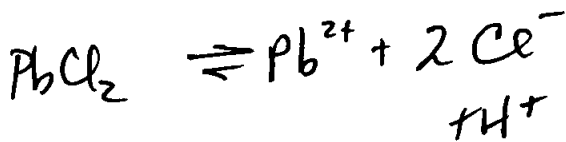
Recalculate: $[Cl^-] = F_{Cl} - (10^{-3} - [Ag^+]) = 0.102 M.$

$$[Ag^+] = 1.76 \times 10^{-9} \quad \langle \text{not significantly different} \rangle$$

4. a)



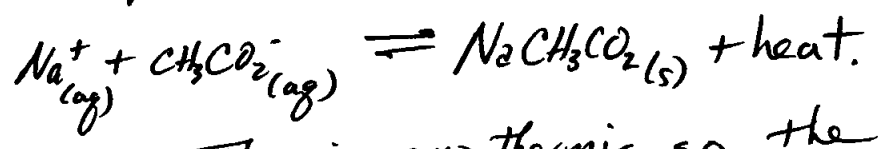
HF is a weak acid



HCl is a strong acid

b) Common ion effect!

5a From description.

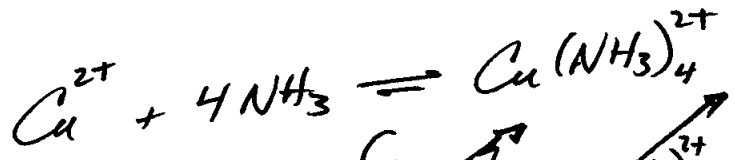


This is exothermic, so the reverse rxn (dissolution) - and the "heat of solution" - is endothermic: $\Delta H > 0$

b. heat it
 $\Delta H > 0$

6a. Big Picture: All K_s are large (favor the various complexes) and there is a large excess of NH_3 . So one might expect most of the copper to be fully coordinated by the NH_3 , i.e., $\text{Cu}(\text{NH}_3)_4^{2+}$ will dominate

ICE



$$\bullet \left[\text{Cu}(\text{NH}_3)_4^{2+} \right] = 10^{-3} - \left\{ \begin{array}{l} \cancel{[\text{Cu}^{2+}]} + \cancel{[\text{Cu}(\text{NH}_3)_3^{2+}]} + \cancel{[\text{Cu}(\text{NH}_3)_2^{2+}]} \\ + \text{Cu}(\text{NH}_3)_3^{2+} \end{array} \right\}$$

$$[\text{NH}_3] = 1.0 - (4 \cdot [\text{Cu}(\text{NH}_3)_4^{2+}])$$

$$\bullet [\text{Cu}^{2+}] = \frac{10^{-3}}{[\text{NH}_3]^4 K_f} \approx \frac{10^{-3}}{1.0^4 \cdot 1.1 \times 10^{15}} = 1.1 \times 10^{-15} \text{ M} \quad \text{OK}$$

• $Cu(NH_3)_3^{2+} = \frac{[Cu(NH_3)_4^{2+}]}{K_f [NH_3]} = 1.11 \times 10^{-5} M$

similarly for: $[Cu(NH_3)_2^{2+}] = 2.2 \times 10^{-8} M$

• $[Cu(NH_3)^{2+}] = 1.1 \times 10^{-11} M$

6b) If all the $CuCO_3(s)$ went into solution.

$[Cu^{2+}] = [CO_3^{2-}] = \frac{6.9}{(123.5g/mole) \cdot 1L} = 8.10 \times 10^{-3} M$

Since we're assuming no reaction of the CO_3^{2-} ; then if it dissolves...

$[CO_3^{2-}] = 8.1 \times 10^{-3}$ and...

$[Cu^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]} = 2.84 \times 10^{-8}$

Thus, the rest of the Cu^{2+} must be as $Cu(NH_3)_4^{2+}$!

$[Cu(NH_3)_4^{2+}] = 8.1 \times 10^{-3} - 2.84 \times 10^{-8} \approx 8.1 \times 10^{-3} M$

$[NH_3] = \frac{\{[Cu(NH_3)_4^{2+}]\}^{1/4}}{[Cu^{2+}] K_f} = 2.37 \times 10^{-2} M$

7a The title suggest that it has something to do with pH, H^+ , OH^- etc. Is $Pb(OH)_2$ relatively insoluble so an increase in OH^- would cause a drop in $[Pb^{2+}]_{aq}$? Yes!

6

7b. $[Pb^{2+}] = \frac{K_{sp}}{[OH^-]^2}$ in the case where $[OH^-]_1 = \frac{1}{10}[OH^-]_2$

more acidic \rightarrow

$$\frac{[Pb^{2+}]_1}{[Pb^{2+}]_2} = \frac{\frac{K_{sp}}{[OH^-]_1^2}}{\frac{K_{sp}}{[OH^-]_2^2}} = \frac{[OH^-]_2^2}{[OH^-]_1^2} = \frac{10^2 [OH^-]_2^2}{[OH^-]_2^2}$$

$$\frac{[Pb^{2+}]_1}{[Pb^{2+}]_2} = 100$$

8a.) $\Delta H > 0$

b). Keep $[Ca^{2+}]$ or $[CO_3^{2-}]$ low. Perhaps form complex with, as an example, Ca^{2+} . This would minimize or eliminate scale.
 OR... remove either Ca^{2+} or CO_3^{2-} from the water.