Solubility and Complex Equilibria

1. Determine the solubility in (i) in mol/L, and (ii) in gram/L of each of the following salts:
   (a) AgCl, $K_{sp} = 1.6 \times 10^{-10}$
   (b) AgBr, $K_{sp} = 5.0 \times 10^{-13}$
   (c) Ag$_2$CrO$_4$, $K_{sp} = 9.0 \times 10^{-12}$

2. The solubility of calcium hydroxide, Ca(OH)$_2$, in water at 25°C is 0.51 g/L. Determine the solubility product constant ($K_{sp}$) for calcium hydroxide.

3. A saturated solution of magnesium hydroxide, Mg(OH)$_2$, has a pH = 10.42. What is the solubility of Mg(OH)$_2$ in mol/L? Determine the $K_{sp}$ of magnesium hydroxide.

4. Calcium phosphate, Ca$_3$(PO$_4$)$_2$, has solubility product, $K_{sp} = 1.3 \times 10^{-32}$. (a) What are the concentrations of Ca$^{2+}$ and PO$_4^{3-}$, respectively, in a saturated solution of Ca$_3$(PO$_4$)$_2$. (b) If a hard water contains 75 ppm (75 mg/L) of Ca$^{2+}$, at what concentration of PO$_4^{3-}$ would a precipitate of Ca$_3$(PO$_4$)$_2$ begin to appear?

5. A solution containing 0.010 M AgNO$_3$ and 0.050 M Pb(NO$_3$)$_2$ is titrated with 0.050 M NaCl solution. (a) At what concentration of Cl$^-$ (i) AgCl begins to precipitate; (ii) PbCl$_2$ begins to precipitate? (b) Determine the concentration Ag$^+$ in solution when the precipitation of PbCl$_2$ begins.

6. Determine the solubility of AgCl ($K_{sp} = 1.6 \times 10^{-10}$) in 0.010 M NaCl solution.

7. (a) Will precipitate of PbCl$_2$ form when a 30.0-mL solution of 0.20 M NaCl is added 20.0 mL of 0.20 M Pb(NO$_3$)$_2$ solution? (b) If precipitate is formed, what are the concentrations of Pb$^{2+}$ and Cl$^-$, respectively, in the saturated solution of PbCl$_2$? (c) Determine if a precipitate will form if the initial concentrations of Pb(NO$_3$)$_2$ and NaCl were each 0.020 M? ($K_{sp} = 1.6 \times 10^{-5}$).
8. Which of the following compounds the solubility is influenced by the pH of the solution? Write chemical equations that show how pH will increase (or decrease) their solubility.

(a) PbCl$_2$

(b) PbCO$_3$

(c) CaF$_2$

(d) Ag$_3$PO$_4$

(e) AgBr

9. Calculate the solubility (in mol/L) of magnesium hydroxide (Mg(OH)$_2$; $K_{sp} = 8.9 \times 10^{-12}$) in a solution buffered at pH 10.00?

10. What is the solubility of silver chloride ($K_{sp} = 1.6 \times 10^{-10}$) in water and in 3.0 $M$ NH$_3$ solution, respectively? [Ag$^+$ (aq) + 2NH$_3$(aq) $\rightleftharpoons$ Ag(NH$_3$)$_2^+$ (aq), $K_f = 1.7 \times 10^7$]

11. Certain transition metal cations have the ability to form complex ions with ammonia (NH$_3$) and hydroxide ion (OH$^-\$). The formation of complex ions significantly increases the solubility of slightly soluble compounds containing these cations. Identify compounds from the following list which solubility will significantly increase: (i) in excess NH$_3$, and (ii) in excess NaOH solution.

(a) Cr(OH)$_3$

(b) Fe(OH)$_3$

(c) Cu(OH)$_2$

(d) Zn(OH)$_2$

(e) AgOH

(f) Pb(OH)$_2$

12. A solution contains Ag$^+$ and Ba$^{2+}$ ions. What reagents would you use to separate and extract the two cations from the mixture? Explain your choice of the reagents and the process involved.
13. In a qualitative experiment, you are given a solution that contains a mixture of the following cations: \( \text{Ag}^+ \), \( \text{Ba}^{2+} \), \( \text{Cr}^{3+} \), \( \text{Fe}^{3+} \), and \( \text{Cu}^{2+} \). Create a flow chart to show how these cations are separated. Indicate specific reagents used in each separation step. (Available reagents are 0.1 M NaCl, 0.1 M Na\(_2\)SO\(_4\), 6 M HNO\(_3\), 6 M NaOH, and 6 M NH\(_3\))

14. Given the following equilibria:

\[
\begin{align*}
\text{AgBr(s)} & \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq); & K_{sp} &= 5.0 \times 10^{-13} \\
\text{Ag}^+(aq) + \text{S}_2\text{O}_3^{2-}(aq) & \rightleftharpoons \text{Ag(S}_2\text{O}_3)^{\text{aq}}; & K_{\text{f1}} &= 7.4 \times 10^8 \\
\text{Ag(S}_2\text{O}_3)^{\text{aq}} + \text{S}_2\text{O}_3^{2-}(aq) & \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{3-}(aq); & K_{\text{f2}} &= 3.9 \times 10^4 \\
\end{align*}
\]

(a) What is the equilibrium constant \( K_c \) for the following equilibrium?

\[
\text{AgBr(s)} + 2\text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag(S}_2\text{O}_3)_2^{3-}(aq) + \text{Br}^-(aq)
\]

(b) Calculate the solubility of AgBr (in mol/L) in 0.50 M Na\(_2\)S\(_2\)O\(_3\) solution.

(c) How many grams of AgBr will dissolve in 100 mL of 0.50 M Na\(_2\)S\(_2\)O\(_3\)?

15. Given the following equilibria:

\[
\begin{align*}
\text{AgCl(s)} & \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq); & K_{sp} &= 1.6 \times 10^{-10} \\
\text{Ag}^+(aq) + 2\text{NH}_3(aq) & \rightleftharpoons \text{Ag(NH}_3)_2^+(aq); & K_{\text{f}} &= 1.7 \times 10^7 \\
\end{align*}
\]

(a) Calculate the equilibrium constant, \( K_c \), for the following equilibrium:

\[
\text{AgCl(s)} + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) + \text{Cl}^-(aq)
\]

(b) Predict whether precipitates of AgCl will form when each of the following solutions are mixed.

(i) 5.0 mL of 0.10 M AgNO\(_3\)(aq) + 5.0 mL of 0.20 M NaCl(aq) + 10.0 mL of 1.0 M NH\(_3\)(aq);

(ii) 5.0 mL of 0.10 M AgNO\(_3\)(aq) + 5.0 mL of 0.20 M NaCl(aq) + 10.0 mL of 2.0 M NH\(_3\)(aq);

16. What are the equilibrium concentrations of Na\(^+\), NO\(_3\)\(^-\), Pb\(^{2+}\), and Br\(^-\), respectively, in an equilibrium obtained by mixing equal volumes of 0.10 M Pb(NO\(_3\))\(_2\) and 0.20 M NaBr? (PbBr\(_2\) has \( K_{sp} = 4.6 \times 10^{-6} \))

17. Explain how you would separate the cations in each of the following mixtures using only one reagent. (For each mixture, find specific reagents that would cause the precipitation of one of the cations, but not the other. (Hint: use solubility rules and \( K_{sp} \) values.)

(a) Al\(^{3+}\) from Mg\(^{2+}\); (b) Fe\(^{3+}\) from Cu\(^{2+}\); (c) Ag\(^+\) from Pb\(^{2+}\); (d) Cu\(^{2+}\) from Zn\(^{2+}\);
Answers:

1. (a) (i) $1.3 \times 10^{-5}$ mol/L; (ii) $1.8 \times 10^{-3}$ g/L; (b) (i) $7.1 \times 10^{-7}$ mol/L; (ii) $8.2 \times 10^{-5}$ g/L; (c) (i) $1.3 \times 10^{-4}$ mol/L; (ii) $4.3 \times 10^{-7}$ g/L

2. Solubility = $6.9 \times 10^{-3}$ mol/L; $K_{sp} = 1.3 \times 10^{-6}$

3. Solubility = $1.3 \times 10^{-4}$ mol/L; $K_{sp} = 9.1 \times 10^{-12}$

4. (a) $[\text{Ca}^{2+}] = 4.9 \times 10^{-7}$ M; $[\text{PO}_4^{3-}] = 3.2 \times 10^{-7}$ M; (b) $[\text{PO}_4^{3-}] = 2.6 \times 10^{-12}$ M

5. (a) If $[\text{Cl}^{-}] = 1.6 \times 10^{-8}$ M AgCl begins to ppt; (ii) $[\text{Cl}^{-}] = 1.8 \times 10^{-2}$ M, PbCl$_2$ begins to ppt; (b) If $[\text{Cl}^{-}] = 1.8 \times 10^{-2}$ M, $[\text{Ag}^{+}] = 8.9 \times 10^{-9}$ M

6. Solubility = $1.6 \times 10^{-8}$ mol/L

7. (a) $Q_{sp} = 1.2 \times 10^{-3} > K_{sp} \rightarrow$ precipitate will form; (b) $[\text{Pb}^{2+}] = 0.031$ M; $[\text{Cl}^{-}] = 0.023$ M; (solved using iteration method) (c) $Q_{sp} = 1.2 \times 10^{-6} < K_{sp} \rightarrow$ precipitate will NOT form.

8. (b) PbCO$_3$(s) $\rightleftharpoons$ Pb$^{2+}$(aq) + CO$_3^{2-}$(aq); CO$_3^{2-}$(aq) + 2H$^+$(aq) $\rightleftharpoons$ H$_2$O + CO$_2$(g) Acid reacts with CO$_3^{2-}$, HCO$_3^-$ or H$_2$O and CO$_2$; more solids dissolve to maintain equilibrium; (c) CaF$_2$(s) $\rightleftharpoons$ Ca$^{2+}$(aq) + F$^-$(aq); F$^-$(aq) + H$^+$(aq) $\rightleftharpoons$ HF(aq) Acid reacts with F$^-$; more solid CaF$_2$ dissolves to compensate loss of F and maintain equilibrium; (d) Ag$_3$PO$_4$(s) $\rightarrow$ 3Ag$^+$(aq) + PO$_4^{3-}$(aq); PO$_4^{3-}$(aq) + H$^+$(aq) $\rightleftharpoons$ HPO$_4^{2-}$(aq); Acid converts PO$_4^{3-}$ to HPO$_4^{2-}$; [PO$_4^{3-}$]$_{eq}$ decreases; more solid to dissolve to maintain equilibrium.

9. Solubility = $8.9 \times 10^{-4}$ mol/L

10. Solubility of AgCl = $1.3 \times 10^{-5}$ mol/L in water; and 0.14 mol/L in 3.0 $M$ NH$_3$;

11. Compounds soluble in NH$_3$: (c) Cu(OH)$_2$(s) + 4NH$_3$(aq) $\rightleftharpoons$ Cu(NH$_3$)$_4^{2+}$(aq) + 2 OH (aq); (e) AgOH(s) + 2NH$_3$(aq) $\rightleftharpoons$ Ag(NH$_3$)$_2^+$(aq) + OH$^-$ (aq);

Compounds soluble in excess NaOH: (a) Cr(OH)$_3$(s) + OH (aq) $\rightleftharpoons$ Cr(OH)$_4$^−(aq); (d) Zn(OH)$_2$ + 2OH$^-$ (aq) $\rightleftharpoons$ Zn(OH)$_4^{2-}$(aq); (f) Pb(OH)$_2$(s) + 2OH (aq) $\rightleftharpoons$ Pb(OH)$_4^{2-}$(aq).

12. Add HCl or NaCl; AgCl will form ppt and Ba$^{2+}$ remains in solution – BaCl$_2$m is soluble; Ba$^{2+}$ can be extracted using Na$_2$SO$_4$ to form BaSO$_4$ ppt.

13. Mixture-#1: (Ag$^+$ + Ba$^{2+}$ + Cr$^{3+}$ + Fe$^{3+}$ + Cu$^{2+}$) + NaCl(aq) $\rightarrow$ precipitate AgCl(s); Centrifuge; Mixture-#2: (Ba$^{2+}$ + Cr$^{3+}$ + Fe$^{3+}$ + Cu$^{2+}$) + Na$_2$SO$_4$(aq) $\rightarrow$ precipitate BaSO$_4$(s); Centrifuge; Mixture-#3: (Cr$^{3+}$ + Fe$^{3+}$ + Cu$^{2+}$) + excess NH$_3$ $\rightarrow$ Cr(OH)$_3$(s) + Fe(OH)$_3$(s) + Cu(NH$_3$)$_4^{2+}$(aq); Centrifuge;

Mixture-#4: (Cr(OH)$_3$(s) + Fe(OH)$_3$(s) + excess NaOH(aq) $\rightarrow$ Cr(OH)$_4$^−(aq) + Fe(OH)$_3$(s); Centrifuge

14. (a) $K_c = 14$; (b) solubility = 0.22 mol/L; (c) 4.1 g

15. $K_c = 2.7 \times 10^{-3}$; (a) $Q_c = 5.0 \times 10^{-3} > K_c \rightarrow$ ppt forms; (b) $Q_c = 1.3 \times 10^{-3} < K_c \rightarrow$ no ppt

16. $[\text{Pb}^{2+}] = 0.010$ M; $[\text{Br}^-] = 0.021$ M; $[\text{Na}^+] = 0.10$ M; $[\text{NO}_3^-] = 0.10$ M

17. (a) Add buffered NH$_3$:NH$_4$Cl; pH=9.5; precipitate of Al(OH)$_3$(s) is formed; Mg$^{2+}$ remains in solution; (b) Add excess NH$_3$; Fe(OH)$_3$(s) is formed, Cu(NH$_3$)$_4^{2+}$ remains in solution; (c) Add NaCl and heat mixture; PbCl$_2$(s) dissolves when heated, AgCl(s) remains as precipitate; (d) Add excess NaOH(aq); Cu(OH)$_2$(s) is formed; Zn(OH)$_2$ is soluble in excess OH-(aq)