Chapter 8

Equilibria Containing Metal Ions

1. Explain why $Fe(H_2O)_6^{3+}$ is a stronger acid than $Fe(H_2O)_6^{2+}$.

The higher oxidation state on the Fe in $Fe(H_2O)_6^{3+}$ results in more electron density being withdrawn from the O-H bonds in H_2O, which makes the water a stronger acid.

3. Write the chemical equation that explains the acidity of an aqueous $CuSO_4$ solution and calculate the pH of a 0.20 M $CuSO_4$ solution.

$CuSO_4$ completely dissociates in water to form the copper hydrate, a weak acid. The K_a can be found in Table 8.1, and the reaction table for the reaction is

	$Cu(H_2O)_6^{2+}$	+	H_2O	$\rightleftharpoons$	$Cu(H_2O)_5OH^{1+}$	+	H_3O^+
Initial:	0.20		-		0		0
Δ	- x				+ x		+ x
Final:	0.20 –x				x		x

$$K_a = 3\times10^{-8} = \frac{[Cu(H_2O)_5OH^{1+}][H_3O^{1+}]}{[Cu(H_2O)_6OH^{2+}]} = \frac{(x)(x)}{0.20\text{-}x} = \frac{x^2}{0.20}$$

The above simplification is possible because K_a for the reaction is so small that *x* will be negligible relative to 0.20 M.

Therefore, $x = \sqrt{(3 \times 10^{-8})(0.20)} = 8 \times 10^{-5}$ M $\qquad$ $pH = -\log[H_3O^{1+}] = 4.1$

5. Write the chemical equation for the dissolution process and the K_{sp} expression in terms of the molar solubility for each of the following substances:

a) CoS	$CoS(s) \rightleftharpoons Co^{2+} + S^{2-}$	$K_{sp} = [Co^{2+}][S^{2-}]$
b) HgI_2	$HgI_2(s) \rightleftharpoons Hg^{2+} + 2I^{1-}$	$K_{sp} = [Hg^{2+}][I^{1-}]^2$
c) $Al(OH)_3$	$Al(OH)_3(s) \rightleftharpoons Al^{3+} + 3OH^{1-}$	$K_{sp} = [Al^{3+}][OH^{1-}]^3$

7. Express the K_{sp} expression of each of the compounds in Exercise 5 in terms of its molar solubility (x).

a) CoS	$K_{sp} = [Co^{2+}][S^{2-}] = (x)(x) = x^2$
b) HgI_2	$K_{sp} = [Hg^{2+}][I^{1-}]^2 = (x)(2x)^2 = 4x^3$
c) $Al(OH)_3$	$K_{sp} = [Al^{3+}][OH^{1-}]^3 = (x)(3x)^3 = 27x^4$

9. Write the chemical equations for the dissolution of each of the following substances and determine their molar solubilities.

a) AgI (a 1:1 salt)

$AgI(s) \rightleftharpoons Ag^{1+} + I^{1-}$ $\qquad$ $K_{sp} = 8.3 \times 10^{-17} = x^2$ $\qquad$ $x = \sqrt{K_{sp}} = \sqrt{8.3\times10^{-17}} = 9.1\times10^{-9}$ M

b) CaF_2 (a 1:2 salt)

$CaF_2(s) \rightleftharpoons Ca^{2+} + 2F^{1-}$ $\qquad$ $K_{sp} = 3.9 \times 10^{-11} = 4x^3$ $\qquad$ $x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{3.9\times10^{-11}}{4}} = 2.1\times10^{-4}$ M

11. The solubility of mercury(I) chloride is 0.0020 g/L. What is its K_{sp}? Note: mercury(I) exists as Hg_2^{2+} ions.

$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+} + 2Cl^{1-}$ $\qquad$ M_m (Hg_2Cl_2) = 472 g/mol

$$x = [Hg_2^{2+}] = \frac{0.0020\text{ g/L}}{472\text{ g/mol}} = 4.2\times10^{-6}\text{ M}$$

$$K_{sp} = [Hg_2^{2+}][Cl^{1-}] = (x)(2x)^2 = 4x^3 = 4(4.2\times10^{-6})^3 = 3.0\times10^{-16}$$

13. The gold ion concentration in a saturated solution of gold(III) chloride is 33 μM. What is the solubility-product constant of $AuCl_3$?

The dissolution reaction is $AuCl_3(s) \rightleftharpoons Au^{3+} + 3Cl^{1-}$.

$K_{sp} = [Au^{3+}][Cl^{1-}]^3 = (x)(3x)^3 = 27x^4$. $\qquad$ $x = [Au^{3+}] = 33 \times 10^{-6}$ M, so $K_{sp} = 27(33 \times 10^{-6})^4 = 3.2 \times 10^{-17}$

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15. What is the pH of saturated barium hydroxide?

Dissolution reaction: $Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^{1-}$ $K_{sp} = 5.0\times 10^{-3}$ from Appendix D

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{5.0\times10^{-3}}{4}} = 0.11\text{ M};\ [OH^{1-}] = 2x = 0.22\text{ M} \Rightarrow \text{pOH} = 0.67 \text{ and } \text{pH} = 14.00 - \text{pOH} = 13.33$$

17. A 386-mg sample of $PbCl_2$ is washed with 10.0 mL of 0.10 M HCl. What is the maximum fraction of $PbCl_2$ that can dissolve in the wash?

$PbCl_2(s) \rightleftharpoons Pb^{2+} + 2Cl^{1-}$, $K_{sp} = [Pb^{2+}][Cl^{1-}]^2$

We are given that the chloride ion concentration is 0.10 M, and asked to determine the solubility of the $PbCl_2$. This is a common ion solubility, so we solve for the lead(II) concentration: $[Pb^{2+}] = \frac{K_{sp}}{[Cl^{1-}]^2} = \frac{1.7\times10^{-5}}{(0.10)^2} = 1.7\times10^{-3}$ M

where we have assumed that the amount of chloride obtained by the dissolution is negligible compared to 0.10 M. The mass of $PbCl_2$ that must dissolve to produce that concentration is

$$10\text{ mL soln}\times\frac{1.7\times10^{-3}\text{ mmol }Pb^{2+}}{\text{mL soln}}\times\frac{1\text{ mmol }PbCl_2}{1\text{ mmol }Pb^{2+}}\times\frac{278.1\text{ mg }PbCl_2}{\text{mmol }PbCl_2} = 4.7\text{ mg }PbCl_2\text{ dissolve}$$

The fraction that dissolves expressed as percent is $\frac{4.7\text{ mg}}{386\text{ mg}}\times100\% = 1.2\%$

19. What is the molar solubility of lead(II) sulfate in:

a) water

$PbSO_4(s) \rightleftharpoons Pb^{2+} + SO_4^{2-}$

$K_{sp} = 1.7 \times 10^{-8} = [Pb^{2+}][SO_4^{2-}] = x^2$, so the molar solubility is $x = \sqrt{1.7\times10^{-8}} = 1.3 \times 10^{-4}$ M

b) 0.20 M MgSO4

The initial concentration of SO_4^{2-} is 0.20 M, so the $K_{sp} = 1.7 \times 10^{-8} = [Pb^{2+}][SO_4^{2-}] = (x)(0.20 +x)$

However, 0.20 M is much greater than the solubility of $PbSO_4$, so we can approximate 0.20 + x = x and simplify the expression to,

$K_{sp}(PbSO_4) = 1.7 \times 10^{-8} = (x)(0.20)$. Solving for x: $x = [Pb^{2+}] = \frac{1.7\times10^{-8}}{0.20} = 8.5\times10^{-8}$ M

c) 0.11 M $Pb(NO_3)_2$

The initial concentration of Pb^{2+} is 0.11 M, so $K_{sp} = 1.7 \times 10^{-8} = [Pb^{2+}][SO_4^{2-}] = (0.11+x)(x)$

0.11 is much greater than the solubility of $PbSO_4$, so we approximate that 0.11 + x = x and simplify the expression to,

$K_{sp}(PbSO_4) = 1.7 \times 10^{-8} = (0.11)(x)$. Solving for x: $x = [SO_4^{2-}] = \frac{1.7\times10^{-8}}{0.11} = 1.5\times10^{-7}$ M

21. Rank the following sulfides in order of decreasing solubility:

	CdS	**CoS**	**CuS**	**FeS**	**MnS**
K_{sp}	8×10^{-27}	4×10^{-21}	6×10^{-36}	6×10^{-18}	6×10^{-16}

All are 1:1 ion ratios, so the solubility decreases with the solubility product.
In terms of solubility, MnS > FeS > CoS > CdS > CuS

23. Would a precipitate form in a solution that contained the following concentrations?

a) 0.01 M NaCl and 0.02 M $Pb(NO_3)_2$

$PbCl_2(s) \rightleftharpoons Pb^{2+} + 2Cl^{1-}$ $K_{sp} = 1.7 \times 10^{-5}$

$Q_{ip} = [Pb^{2+}][Cl^{1+}]^2 = (0.02)(0.01)^2 = 2 \times 10^{-6}$ $Q_{ip} < K_{sp}$, so NO precipitate forms.

b) 1.0 mM $AgNO_3$ and 1 μM NaCl

$AgCl(s) \rightleftharpoons Ag^{1+} + Cl^{1-}$ $K_{sp} = 1.2 \times 10^{-10}$

$Q_{ip} = [Ag^{1+}][Cl^{1-}] = (1.0 \times 10^{-3})(1 \times 10^{-6}) = 1 \times 10^{-9}$ $Q_{ip} > K_{sp}$, so a precipitate does form.

c) 5.0 mM KI and 2.0 mM $Pb(NO_3)_2$

$PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^{1-}$ $\qquad K_{sp} = 6.5 \times 10^{-9}$

$Q_{ip} = [Pb^{2+}][I^{-}]^2 = (0.002)(5 \times 10^{-3})^2 = 5 \times 10^{-8}$ $\qquad Q_{ip} > K_{sp}$, so a precipitate does form.

b) What is the $[Cu^{2+}]$ after precipitation at this sulfide ion concentration?

$K_{sp} = [Cu^{2+}][S^{2-}] = 6.3 \times 10^{-36} = [Cu^{2+}](3 \times 10^{-19}) \quad \rightarrow [Cu^{2+}] = 2 \times 10^{-17}$ M

25. Construct the reaction table for mixing 20.0 mL of 0.124 M $Ca(NO_3)_2$ and 30.0 mL of 0.0852 M KF.

Checking Appendix D, we note that calcium fluoride is a slightly soluble salt with $K_{sp} = 3.9 \times 10^{-11}$
Initially, there are (20.0 mL)(0.124 mmol/mL) = 2.48 mmol Ca^{2+} ions, and
(30.0 mL)(0.0852 mmoL) = 2.56 mmol F^{1-}. The Reaction Table for the precipitation reaction is

	Ca^{2+}	+	$2F^{1-}$	→	$CaF_2(s)$	
In	2.48		2.56		0	mmol
Δ	-1.28		-2.56		+1.28	mmol
Final	1.20		~0		1.28	mmol

a) What mass of precipitate forms?

$$1.28 \text{ mmol } CaF_2 \times \frac{78.08 \text{ mg } CaF_2}{\text{mmol } CaF_2} = 99.9 \text{ mg } CaF_2 \text{ precipitates}$$

b) What is the concentration of the excess reactant at equilibrium?

$$[Ca^{2+}] = \frac{1.20 \text{ mmol}}{50.0 \text{ mL}} = 0.024 \text{ M}$$

c) What is the concentration of the limiting reactant at equilibrium?

$$[F^{1-}] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]}} = \sqrt{\frac{3.9\times10^{-11}}{0.024}} = 4.0\times10^{-5} \text{ M}$$

27. Construct the reaction table for mixing 35.0 mL of 0.175 M $AgNO_3$ and 25.0 mL of 0.200 M KI are mixed.

	Ag^{1+}	+	I^{1-}	→	AgI(s)	
In	6.13		5.00		0	mmol
Δ	-5.00		-5.00		+ 5.00	mmol
Fin	1.13		0		5.00	mmol

a) What mass of AgI should form?

$$5.00 \text{ mmol AgI} \times \frac{234.78 \text{ mg AgI}}{1 \text{ mmol AgI}} = 1.17 \times 10^{3} \text{ mg} = 1.17 \text{ g AgI}$$

b) What is the concentration of the excess reactant at equilibrium?

$$[Ag^{1+}] = \frac{1.13 \text{ mmol } Ag^{1+}}{35.0 \text{ mL} + 25.0 \text{ mL}} = 0.0188 \text{ M}$$

c) What is the concentration of the limiting reactant at equilibrium?

$K_{sp} = [Ag^{1+}][I^{1-}] = 8.3\text{x}10^{-17} = (0.0188 \text{ M})[I^{1-}] \qquad \rightarrow \qquad [I^{1-}] = 4.4\text{x}10^{-15}$ M

29. To what pH (to 0.1 pH unit) should a solution that is 0.030 M in Pb^{2+} and 0.030 M in Mg^{2+} be buffered in order to obtain maximum separation of the ions by precipitation of one of the hydroxides? What are the concentrations of the metal ions after the solution is buffered at this pH?

The K_{sp} values from Appendix D: $Pb(OH)_2 = 2.8 \times 10^{-16}$ M; and $Mg(OH)_2 = 1.8 \times 10^{-11}$
$Pb(OH)_2$ is less soluble, so it is the one that will precipitate. In order to minimize the concentration of Pb^{2+} in solution after precipitation, we make the pH as high as possible without precipitating $Mg(OH)_2$. The hydroxide ion required for precipitation of $Mg(OH)_2$ is $[OH^{1-}] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1.8\times10^{-11}}{0.030 \text{ M}}} = 2.4\times10^{-5}$ M , which is a pOH = 4.61 and a pH = 9.39.

Thus, we would adjust the pH to a value just under 9.39, which is pH = 9.3 or even 9.2 to be safe. At pH = 9.2, pOH = 4.8, and $[OH^{1-}] = 1.6 \times 10^{-5}$ M. The ion product form $Mg(OH)_2$ at this pH is $Q_{ip} = (0.030)(1.6 \times 10^{-5})^2 = 7.5 \times 10^{-12}$, which is well below the K_{sp} of $Mg(OH)_2$, so no magnesium ions precipitate. The concentration of Pb^{2+} ions remaining is

$$[Pb^{2+}] = \frac{K_{sp}}{[OH^{1-}]^2} = \frac{2.8\times10^{-16}}{(1.6\times10^{-5} \text{ M})^2} = 1.1\times10^{-6} \text{ M}$$

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31. Indicate whether or not a precipitate would form when the following solutions are mixed:

In this problem, we must identify the possible precipitate, determine the ion product from the given amounts, and compare the ion product to the K_{sp} of the possible precipitate. If $Q_{ip} > K_{sp}$, a precipitate forms. In each case, the two solutions have the same volume, so when they are mixed, the volume of each is doubled, which halves the concentrations of the ions.

a) 5.0 mL of 0.10 M HCl and 5.0 mL of 1.0 mM $Pb(NO_3)_2$

possible precipitate = $PbCl_2$ with $K_{sp} = 1.7 \times 10^{-5}$. $Q_{ip} = [Pb^{2+}][Cl^{1-}]^2 = (5.0 \times 10^{-4})(0.05)^2 = 1.3 \times 10^{-6}$

$Q_{ip} < K_{sp}$, so no precipitate.

b) 5.0 mL of 0.10 M KOH and 5.0 mL of 0.10 mM $Mn(NO_3)_2$

possible precipitate = $Mn(OH)_2$ with $K_{sp} = 1.9 \times 10^{-13}$. $Q_{ip} = [Mn^{2+}][OH^{1-}]^2 = (5.0 \times 10^{-5})(0.050)^2 = 1.3 \times 10^{-7}$

$Q_{ip} > K_{sp}$, so $Mn(OH)_2$ precipitates.

c) 5.0 mL of 0.10 M Na_2SO_4 and 5.0 mL of 0.10 mM $Ba(NO_3)_2$

possible precipitate = $BaSO_4$ with $K_{sp} = 1.1 \times 10^{-10}$. $Q_{ip} = [Ba^{2+}][SO_4^{2-}] = (5.0 \times 10^{-5})(0.050) = 2.5 \times 10^{-6}$

$Q_{ip} > K_{sp}$, so $BaSO_4$ precipitates.

33. Solid NaCl is added to a solution that is 0.10 M in Pb^{2+} and 0.10 M in Ag^{1+}.

a) Which compound precipitates first?

The solubility depends upon the value of K_{sp} and the compound stoichiometry (see Table 8.2). $K_{sp}(AgCl) = 1.8 \times 10^{-10}$, so $x = 1.3 \times 10^{-5}$ M. $K_{sp}(PbCl_2) = 1.7 \times 10^{-5}$, so x = 0.016 M. Therefore AgCl is less soluble and will precipitate first.

b) What is the concentration of the first ion precipitated when the second ion starts to precipitate?

To determine the $[Ag^{1+}]$ when Pb^{2+} begins to precipitate, we first calculate the chloride ion required to preciptate $PbCl_2$: $[Cl^{1-}] = \sqrt{\dfrac{K_{sp}}{[Pb^{2+}]}} = \sqrt{\dfrac{1.7\times10^{-5}}{0.10}} = 0.013$ M . We use this chloride ion concentration to determine the concentration of Ag^{1+} ion. $[Ag^{1+}] = \dfrac{K_{sp}}{[Cl^{1-}]} = \dfrac{1.8\times10^{-10}}{0.013} = 1.4\times10^{-8}$ M

35. What is $[Ni^{2+}]$ in a solution made by mixing 10.0 mL of 0.652 M $NiSO_4$ and 475 mL of 2.00 M NH_3?

Ni^{2+} reacts extensively with NH_3 to form $Ni(NH_3)_6^{2+}$, so the reaction table has the following form

	Ni^{2+}	+ $6NH_3(aq)$ $\rightleftharpoons$	$Ni(NH_3)_6^{2+}$	
In	6.52	950	0	mmol
Δ	-6.52	-39	+6.52	mmol
Eq	~0	911	6.52	mmol

The nickel ion concentration is very small, but it is not zero. The formation constant (5.6×10^8 from Table 8.3) and the concentrations of NH_3 and $Ni(NH_3)_6^{2+}$ are used to obtain $[Ni^{2+}]$. The concentrations are obtained by dividing the number of mmoles present at equilibrium by the total volume of 485 mL.

$$K_f = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6} \Rightarrow [Ni^{2+}] = \frac{[Ni(NH_3)_6^{2+}]}{K_f[NH_3]^6} = \frac{0.0134}{(5.6\times10^8)(1.88)^6} = 5.4\times10^{-13}\text{ M}$$

37. What is the free cyanide ion concentration in a 0.10 M $Fe(CN)_6^{3-}$ solution?

In this exercise, we need the dissociation constant of the complex ion. The dissociation constant is the reciprocal of the formation constant $K_d = (K_f)^{-1} = (1 \times 10^{42})^{-1} = 1 \times 10^{-42}$. K_d is small, so only a small fraction actually reacts.

	$Fe(CN)_6^{3+}$ $\rightleftharpoons$	Fe^{3+}	+ $6CN^{1-}$	$K = 1 \times 10^{-42}$
In	0.10	0	0	mmol
Δ	-x	+x	+6x	mmol
Eq	0.10 - x	x	6x	mmol

We assume that x is negligible and write the dissociation constant expression

$$K_d = 1\times10^{42} = \frac{[Fe^{3+}][CN^{1-}]^6}{[Fe(CN)_6^{3+}]} = \frac{(x)(6x)^6}{0.10 - x} \approx \frac{6^6x^7}{0.10}$$

$$x = [Fe^{3+}] = \sqrt[7]{\frac{(0.10)(1\times10^{-42})}{6^6}} = 2\times10^{-7}\text{ M} \qquad [CN^{1-}] = 6x = 1\times10^{-6}\text{ M}$$

39. Determine the equilibrium constants for the following reactions.

a) $Fe(OH)_2(s) + 6CN^{1-} \rightleftharpoons Fe(CN)_6^{4-} + 2OH^{1-}$

Combine the K_{sp} of $Fe(OH)_2$ with K_f of $Fe(CN)_6^{4-}$

$Fe(OH)_2(s) \rightleftharpoons Fe^{2+} + 2OH^{1-}$	$K_{sp} = 8.0 \times 10^{-16}$
$Fe^{2+} + 6CN^{1-} \rightleftharpoons Fe(CN)_6^{4-}$	$K_f = 1.0 \times 10^{35}$
$Fe(OH)_2(s) + 6CN^{1-} \rightleftharpoons Fe(CN)_6^{4-} + 2OH^{1-}$	$K = K_{sp} \times K_f = 8.0 \times 10^{19}$

b) $Ag_2S(s) + 4NH_3 \rightleftharpoons 2Ag(NH_3)_2^{1+} + S^{2-}$

Combine the K_{sp} of Ag_2S with K_f of $Ag(NH_3)_2^{1+}$. However, the formation reaction must be multiplied by two in order to obtain the desired reaction.

$Ag_2S(s) \rightleftharpoons 2Ag^{1+} + S^{2-}(aq)$	$K_{sp} = 6.3 \times 10^{-50}$
$2Ag^{1+} + 4NH_3 \rightleftharpoons 2Ag(NH_3)_2^{1+}$	$K = (K_f)^2 = (1.7 \times 10^7)^2$
$Ag_2S(s) + 4NH_3(aq) \rightleftharpoons 2Ag(NH_3)_2^{1+}(aq) + S^{2-}(aq)$	$K = K_{sp} \times (K_f)^2 = 1.8 \times 10^{-35}$

41. Consider the dissolution of $Al(OH)_3$ in hydrochloric acid.

a) Write the reaction for the dissolution.

$Al(OH)_3(s) + 3H_3O^{1+} \rightleftharpoons Al^{3+} + 6H_2O$

b) What is the equilibrium constant for the reaction?

This is the competition between hydronium and aluminum ions for hydroxided ions. The reaction is expressed as a combination of the K_{sp} reaction of $Al(OH)_3$ and the K_W reaction.

$Al(OH)_3(s) \rightleftharpoons 3OH^{1-} + Al^{3+}$	$K_1 = K_{sp} = 1.9 \times 10^{-33}$
$3H_3O^{1+} + 3OH^{1-} \rightleftharpoons 6H_2O$	$K_2 = K_W^{-3} = (1.0 \times 10^{-14})^{-3} = 1.0 \times 10^{+42}$
$3H_3O^{1+} + Al(OH)_3(s) \rightleftharpoons 6H_2O + Al^{3+}$	$K = K_1K_2 = 1.9 \times 10^{+9}$

Aluminum forms a very insoluble hydroxide that dissolves readily in strong acid.

43. At what pH should a solution be saturated with H_2S to separate 0.020 M Pb^{2+} and Zn^{2+}? What are the concentrations of the ions after separation?

The K_{sp}'s: PbS = 8.4×10^{-28} ZnS = 1.1×10^{-21} → PbS precipitates and Zn^{2+} stays in sol'n.

Determine $[S^{2-}]$ required to precipitate more soluble salt: $[S^{2-}] = \dfrac{K_{sp}}{[Zn^{2+}]} = \dfrac{1.1\times10^{-21}}{0.020} = 5.5\times10^{-20}$ M

Use K_{12} for H_2S to determine $[H_3O^{1+}]$: $[H_3O^{1+}] = \sqrt{\dfrac{K_{12}[H_2S]}{[S^{2-}]}} = \sqrt{\dfrac{(1.3\times10^{-20})(0.10)}{5.5\times10^{-20}}} = 0.15$ M ⇒ pH = 0.81

$[H_3O^{1+}]$ must be greater than 0.15 M, so we choose 0.16 M and pH = 0.80.

Use K_{12} to get $[S^{2-}]$ at this pH: $[S^{2-}] = \dfrac{K_{12}[H_2S]}{[H_3O^{1+}]^2} = \dfrac{(1.3\times10^{-20})(0.10)}{(0.16)^2} = 5.1\times10^{-20}$ M

$[S^{2-}]$ is less than required to precipitate ZnS, so $[Zn^{2+}] = 0.02$ M.

Determine $[Pb^{2+}]$ from K_{sp} and $[S^{2-}]$: $[Pb^{2+}] = \dfrac{8.4\times10^{-28}}{5.1\times10^{-20}} = 1.6\times10^{-8}$ M

45. Indicate whether each of the following salts produce an acidic, a neutral, or a basic solution in water?

$Fe(NO_3)_3$	$Fe(H_2O)_6^{2+}$ is a weak acid	acidic	**NH_4Cl**	NH_4^{1+} is a weak acid	acidic
$AlBr_3$	$Al(H_2O)_6^{3+}$ is a weak acid	acidic	**NaF**	NaF is a basic salt	basic
$ZnSO_4$	$Zn(H_2O)_6^{2+}$ is a weak acid	acidic	**KCl**	KCl is a neutral salt	neutral

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47. Use the following equilibrium: $PbI_2(s) + 3OH^{1-} \rightleftharpoons Pb(OH)_3^{1-} + 2I^{1-}$ and Le Châtelier's Principle to predict the effect on the solubility of PbI_2 of each of the following:

a) H^{1+} ions are added Adding H^{1+} will lower the pH, and therefore decrease the amount of OH^{1-} that is in solution, which lowers the solubility of PbI_2.

b) the concentration of I^{1-} is decreased As $[I^{1-}]$ is decreased, the equilibrium shifts to the right, increasing the solubility of PbI_2.

c) the amount of PbI_2 is increased Increasing the amount of PbI_2 has no effect on the solubility. (The activity of a solid is 1 and has no effect on the reaction quotient.)

d) the pH of the solution is increased As the solution pH increases, the $[OH^{1-}]$ also increases. This shifts the equilibrium to the right and increases the solubility of PbI_2.

49. In a foundry that produces brass plumbing fittings, the brass components are cleaned with nitric acid, which dissolves and oxidizes the copper and zinc of brass resulting in a solution of Cu^{2+} and Zn^{2+}. Given that K_{sp} of $Cu(OH)_2$ is $2.2\text{x}10^{-20}$ and K_{sp} of $Zn(OH)_2$ is 4.5×10^{-17}, determine the pH must to which the effluent must be adjusted to precipitate the copper and zinc hydroxides such that the levels of Cu and Zn in the water are below the federal clean water standards of 50. ppm? Are the solubilities of these two species sufficiently different such that the copper and zinc could be separated during this neutralization process? Assume the density of the water sample is 1.00 g/cm^3.

$Zn(OH)_2$ has a much higher K_{sp}, therefore, we must concentrate on getting $[Zn^{2+}]$ to 50 ppm.

$$\frac{50\text{ mg Zn}^{2+}}{1\text{ kg}}\times\frac{1\text{ g Zn}^{2+}}{1000\text{ mg}}\times\frac{1\text{ kg soln}}{1\text{ L soln}}\times\frac{1\text{ mol Zn}^{2+}}{65.39\text{ g}}=7.6\times10^{-4}\text{ M Zn}^{2+}$$

Using the expression for K_{sp},

$$[OH^{1-}] = \sqrt{\frac{K_{sp}}{[Zn^{2+}]}}=\sqrt{\frac{4.5\times10^{-17}}{7.654\times10^{-4}}}=2.4\times10^{-7}\text{ M, so pOH = - log}(2.4\text{ x }10^{-7}) = 6.62$$

pH ≤ 14.00 – 6.62 = 7.38. Doing the same procedure for $Cu(OH)_2$ after calculating the $[Cu^{2+}]$,

$$[OH^{1-}]=\sqrt{\frac{K_{sp}}{[Cu^{2+}]}}=\sqrt{\frac{2.2\times10^{-20}}{7.8\times10^{-4}}}=5.3\times10^{-9}\text{ M, so pOH = 8.3}$$

pH ≤ 14.0 – 8.3 ≤ 5.7

Yes, the solubility of these two cations differs enough to be separated.

51. Explain why the solubility of PbF_2 increases with the addition of HNO_3, but the solubility of $PbCl_2$ is unaffected?

The solubility of PbF_2 increases in a strong acid because F^{1-} is a weak base that reacts with H_3O^{1+} to produce HF. Thus, there is competing equilibria involving F^{1-}. All bases are more soluble in acid than in water for this reason. The solubility of $PbCl_2$ is not increased because Cl^{1-} is not a base in water, i.e., it is a weaker base than H_2O. Consequently, Cl^{1-} does not react with acid to produce HCl and there is no competing equilibria.

53. A sample of drinking water was found to contain 500 ppm of Fe^{3+}, which is well above clean water levels. How much phosphate, PO_4^{3-} must be added, per 1000. L, to the water supply to precipitate excess iron from the solution such that the final filtered supply has a concentration of less than 50. ppm? Assume the density of the water sample is 1.00 g/cm^3.

Setting up the equilibrium reaction: FePO4 $\rightleftharpoons$ Fe^{3+} + $PO4^{3-}$ $K_{sp} = 9.9\text{ x }10^{-29} = [Fe^{3+}]\,[PO_4^{3-}]$

The iron is 500 ppm $\left(\frac{500\text{ g Fe}}{10^6\text{ g sol'n}}\right)$, so $[Fe^{3+}] = \dfrac{\frac{500\text{ g Fe}}{55.85\text{ g/mol}}}{10^3\text{ L}} = 0.0090\text{ M}$.

$$10^3\text{ L}\times\frac{500\text{ g Fe}}{10^6\text{ g sol'n}}\times\frac{10^3\text{ g sol'n}}{\text{L sol'n}} = 500\text{ g Fe in the water supply \& }10^3\text{ L}\times\frac{50\text{ g Fe}}{10^6\text{ g sol'n}}\times\frac{10^3\text{ g sol'n}}{\text{L sol'n}} = 50\text{ g Fe desired}$$

So (500 – 50) = 450 g Fe^{3+} or $\dfrac{450\text{ g}}{55.85\text{ g/mol}} = 8.06\text{ mol Fe}^{3+}$ must be precipitated. There is a 1:1 stoichiometric ratio between Fe^{3+} and $PO4^{3-}$, so ~ 8.1 mol $PO4^{3-}$ should be added. Note that the K_{sp} of FePO4 is so small that any excess $PO4^{3-}$ remaining in solution can be ignored.