Answers - Additional Probs - Ch. 17 pt 2

1. a. overall $Cu(OH)_2 + 2H_3O^+ \rightleftharpoons Cu^{2+} + 4H_2O$

use:

$$Cu(OH)_{2(s)} \rightleftharpoons Cu^{2+} + 2OH^- \quad K_{sp} = 1.1\times10^{-15}$$

$$2H_3O^+ + 2OH^- \rightleftharpoons 4H_2O \quad K = \left(\frac{1}{K_w}\right)^2$$

$$Cu(OH)_2 + 2H_3O^+ \rightleftharpoons Cu^{2+} + 4H_2O \quad K = \frac{1.1\times10^{-15}}{(1.0\times10^{-14})^2} = 1.1\times10^{13}$$

K is huge. Goes to completion.
$Cu(OH)_2$ is very soluble in acid.

b. $CaF_2 + 2H_3O^+ \rightleftharpoons Ca^{2+} + 2HF + 2H_2O$

use

$$CaF_{2(s)} \rightleftharpoons Ca^{2+} + 2F^- \quad K_{sp} = 3.45\times10^{-11}$$

$$2H_3O^+ + 2F^- \rightleftharpoons 2HF + 2H_2O \quad K = \frac{1}{K_{a\,HF}^2} = \frac{1}{(6.3\times10^{-4})^2}$$

$$CaF_2 + 2H_3O^+ \rightleftharpoons Ca^{2+} + 2HF + 2H_2O \quad K = \frac{3.45\times10^{-11}}{(6.3\times10^{-4})^2}$$

$K = 8.7\times10^{-5}$ not very large, but larger than 3.45×10^{-11}. CaF_2 is more soluble in acid than in water, because F^- is a weak base.

c. $Ba_3(PO_4)_{2(s)} + 6H_3O^+ \rightleftharpoons 3Ba^{2+} + 2H_3PO_4 + 6H_2O$

use:

$$Ba_3(PO_4)_{2(s)} \rightleftharpoons 3Ba^{2+} + 2PO_4^{3-} \quad K_{sp} = 3.4\times10^{-23}$$

$$2PO_4^{3-} + 2H_3O^+ \rightleftharpoons 2HPO_4^{2-} + 2H_2O \quad K = \left(\frac{1}{K_{a\,HPO_4^{2-}}}\right)^2 = \left(\frac{1}{4.8\times10^{-13}}\right)^2$$

$$2HPO_4^{2-} + 2H_3O^+ \rightleftharpoons 2H_2PO_4^- + 2H_2O \quad K = \left(\frac{1}{K_{a\,H_2PO_4^-}}\right)^2 = \left(\frac{1}{6.2\times10^{-8}}\right)^2$$

$$2H_2PO_4^- + 2H_3O^+ \rightleftharpoons 2H_3PO_4 + 2H_2O \quad K = \left(\frac{1}{K_a\,H_3PO_4}\right)^2 = \left(\frac{1}{6.9\times10^{-3}}\right)^2$$

overall:

$$Ba_3PO_4 + 6H_3O^+ \rightleftharpoons 2H_3PO_4 + 6H_2O \quad K = \frac{3.4\times10^{-23}}{(4.8\times10^{-13})^2(6.2\times10^{-8})^2(6.9\times10^{-3})^2}$$

$K = 8.1\times10^{20}$ huge

Ba_3PO_4 is very soluble in acid.

2. $K_{sp}\ Al(OH)_3 = 4.6\times10^{-33}$ $\quad K_{sp} = [Al^{3+}][OH^-]^3$

$K_{sp}\ Cd(OH)_2 = 7.2\times10^{-15}$ $\quad K_{sp} = [Cd^{2+}][OH^-]^2$

Al^{3+} will start to ppt when $Q = K_{sp}$

$$[OH^-]^3 = \frac{K_{sp}}{[Al^{3+}]} \qquad [OH^-] = \sqrt[3]{\frac{K_{sp}}{[Al^{3+}]}} = \sqrt[3]{\frac{4.6\times10^{-33}}{0.0020}} = 1.32\times10^{-10}\,M$$

~~Al~~ OH^- needed for $Al(OH)_3$ to start to ppt.

Cd^{2+} will start to ppt when $Q = K_{sp}$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Cd^{2+}]}} = \sqrt{\frac{7.2\times10^{-15}}{0.0020}} = 1.9\times10^{-6}\,M\ OH^-$$

needed for $Cd(OH)_2$ to start to ppt.

$Al(OH)_3$ ppts first $\quad [OH^-] = 1.3\times10^{-10}\,M$ at this point.

b. when Cd^{2+} starts to ppt, $[OH^-] = 1.9\times10^{-6}\,M$.
what is $[Al^{3+}]$ at this point?

$$K_{sp} = [Al^{3+}][OH^-]^3 \qquad [Al^{3+}] = \frac{K_{sp}}{[OH^-]^3} = \frac{4.6\times10^{-33}}{(1.9\times10^{-6})^3}$$

$$[Al^{3+}] = 6.7\times10^{-16}\,M$$

$$\frac{6.7\times10^{-16}\,M}{0.0020\,M}\times100 = 3.4\times10^{-11}\,\%\ \text{remains}$$

yes! very complete.

very little of the original remains.

$K_{sp} = 3.4\times10^{-23}$

3. $\frac{(0.0200\,L)(0.10\,mol/L)}{0.0600\,L} = 0.03\bar{3}\bar{3}\,M\ Na_3PO_4$ after mixing, before rxn.

$= 0.10\,M\ Na^+,\ 0.03\bar{3}\bar{3}\,M\ PO_4^{3-}$

$M_2 = \frac{M_1V_1}{V_2} = \frac{(0.10\,M)(40.0\,mL)}{60.0\,mL} = 0.06\bar{6}7\,M\ Ba(NO_3)_2$

$0.06\bar{6}7\,M\ Ba^{2+}$

$0.1\bar{3}3\,M\ NO_3^-$

Na^+ and NO_3^- are spectator ions.

	$3Ba^{2+}$	+ $2PO_4^{3-}$	$\longrightarrow Ba_3(PO_4)_{2(s)}$
i	$0.06\bar{6}7\,M$	$0.03\bar{3}\bar{3}\,M$	0
Δ	$-3x$	$-2x$	$+x$
end	$(0.06\bar{6}7-3x)$	$(0.03\bar{3}\bar{3}-2x)$	

$K = \frac{1}{K_{sp}}$ huge! goes to completion.

Need: $\frac{3Ba^{2+}}{2PO_4^{3-}} = \frac{1.5\ Ba^{2+}}{1\ PO_4^{3-}}$

have $\frac{0.0667}{0.0333} = \frac{2\ Ba^{2+}}{1\ PO_4^{3-}}$

plenty of Ba^{2+}: PO_4^{3-} is LR

LR so = 0

$0.0333-2x=0$

$\frac{0.0333}{2}=\frac{2x}{2}$

$x = 0.01\bar{6}7\,M$

$0.0667-3(0.0167)$

$= 0.01\bar{6}7\,M$ 0

goes to equilibrium

	$Ba_3(PO_4)_{2(s)}$	$\rightleftharpoons 3Ba^{2+}$	+ $2PO_4^{3-}$
i	some	$0.01\bar{6}7\,M$	0
Δ	$-x$	$+3x$	$+2x$
eq	some $-x$	$0.01\bar{6}7+3x$	$2x$

$K_{sp} = 3.4\times10^{-23} = (0.01\bar{6}7+3x)^3(2x)^2 \approx (0.01\bar{6}7)^3(4x^2)$

↑ neglect ($3x$)

$x = \sqrt{\frac{3.4\times10^{-23}}{4(0.0167)^3}} = 1.35\times10^{-9}\,M$

$2x = 2.7\times10^{-9}\,M$

$[Na^+] = 0.10\,M$ $[Ba^{2+}] = 0.017\,M$

$[NO_3^-] = 0.13\,M$ $[PO_4^{3-}] = 2.7\times10^{-9}\,M$

4. a. $CuCl_{(s)} \rightleftharpoons Cu^+ + Cl^-$ $K_{sp} = 1.9 \times 10^{-7}$

$Cu^+ + 2CN^- \rightleftharpoons Cu(CN)_2^-$ $K_f = 1.0 \times 10^{16}$

$CuCl_{(s)} + 2CN^- \rightleftharpoons Cu(CN)_2^- + Cl^-$ $K = K_{sp}K_f = 1.9 \times 10^9$ huge.

goes to completion!

i	some	1.5 M	0	0
Δ	−x	−2x	+x	+x
eq.	some − x	1.5 − 2x	x	x

LR = 0

$1.5 - 2x = 0$

$1.5 = 2x$

$x = \frac{1.5}{2} = 0.75$ M

x = amt that dissolves

So 0.75 M CuCl will dissolve.

$\left(\frac{0.75 \text{ mol CuCl}}{L}\right)\left(\frac{99.00 g}{1 \text{ mol}}\right) = 74$ g/L will dissolve!

* More dissolves in presence of a ligand *

b. In 1.5 M NaCl · contains Cl^-, a common ion.

	$CuCl_{(s)}$	$\rightleftharpoons$	Cu^+	+	Cl^-
i	some		0		1.5 M
Δ	−x		+x		+x
eq.	some − x		x		1.5 + x

$K_{sp} = 1.9 \times 10^{-7} = (x)(1.5 + x)$ ↑ neglect

$x = \frac{K_{sp}}{1.5} = \frac{1.9 \times 10^{-7}}{1.5}$

$x = 1.2\bar{7} \times 10^{-7}$ M = amt CuCl that dissolves.

$\left(\frac{1.2\bar{7} \times 10^{-7} \text{ mol}}{L}\right)\left(\frac{99.00 g}{1 \text{ mol}}\right) = 1.3 \times 10^{-5}$ g/L dissolves

* Less dissolves in the presence of a common ion *

5. Find conc. after mixing, before rxn.

$M_2 = \frac{M_1 V_1}{V_2} = \frac{(10.0\text{ mL})(0.20\text{ M})}{90.0\text{ mL}} = 0.02\bar{2}\bar{2}\text{ M } Cu^{2+}$

$M_2 = \frac{(80.0\text{ mL})(2.0\text{ M})}{(90.0\text{ mL})} = 1.\bar{7}8\text{ M } NH_3$

① goes to completion

	Cu^{2+}	+ $4\,NH_3$	⇌	$Cu(NH_3)_4^{2+}$
i	$0.02\bar{2}2$	$1.\bar{7}8$		0
Δ	$-x$	$-4x$		$+x$
eqd	$0.02\bar{2}2-x$	$1.\bar{7}8-4x$		x
	LR = 0			
	$x = 0.0222$	$1.\bar{7}8-4(0.0222)$ 1.69 M		$0.022\bar{2}$

② equilibrium

	$Cu(NH_3)_4^{2+}$	⇌	Cu^{2+}	+ $4\,NH_3$
i	$0.02\bar{2}\bar{2}$ M		0	$1.\bar{6}9$ M
Δ	$-x$		$+x$	$+4x$
eq.	$0.0222-x$		x	$1.69+4x$

$K = K_d = \frac{1}{K_f} = \frac{1}{6.8\times10^{12}} = 1.\bar{4}7\times10^{-13} = \frac{(x)(1.\bar{6}9+4x)^4}{(0.0222-x)}$

neglect x's

$K_d = \frac{(x)(1.\bar{6}9)^4}{0.02\bar{2}2}$

$x = \frac{K_d\,(0.02\bar{2}2)}{(1.\bar{6}9)^4} = 4.0\times10^{-16}\text{ M } Cu^{2+}$ remains

6. $AgSCN_{(s)} \rightleftharpoons Ag^+ + SCN^-$ $K_{sp} = 1.0 \times 10^{-12}$

$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$ $K_f = 1.6 \times 10^7$

$AgSCN_{(s)} + 2NH_{3\,(aq)} \rightleftharpoons SCN^-_{(aq)} + Ag(NH_3)_2^+{}_{(aq)}$ $K = K_{sp}K_f = 1.6 \times 10^{-5}$

i	some	2.5 M	0	0
A	−x	−2x	+x	+x
eq.	some − x	(2.5−2x) M	x	x M

$K = \frac{x^2}{(2.5-2x)^2} = 1.6 \times 10^{-5}$ $\sqrt{}$ both sides

$\frac{x}{2.5-2x} = \sqrt{1.6 \times 10^{-5}} = 0.0040$

$x = 0.0040(2.5-2x)$

$x = 0.010 - 0.008x$

$+0.008x \qquad +0.008x$

$\frac{1.008x}{1.008} = \frac{0.010}{1.008}$

$x = 0.00992$ = amt ~~AgSN~~ AgSCN that dissolved. (in M)

$\left(\frac{0.00992 \text{ mol AgSCN}}{L}\right)\left(\frac{165.99 \text{ g AgSCN}}{1 \text{ mol AgSCN}}\right) =$ 1.64646 g/L ⇒ 1.6 g/L