Chapter 8: End−of−Chapter Solutions
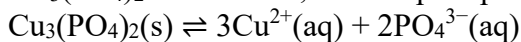
1.
(a) The $Cu_3(PO_4)_2$ is insoluble, and the precipitation equilibrium is:

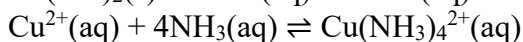$$Cu_3(PO_4)_2(s) \rightleftharpoons 3Cu^{2+}(aq) + 2PO_4^{3-}(aq)$$

The NH_3 can complex with copper so you also have:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$
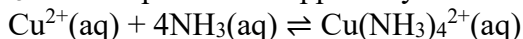
There will also be the base hydrolysis equilibria for the ammonia and PO_4^{3-} to form the protonated form of each.

(b) Mixing these two soluble salts will form a $Cu(OH)_2$ precipitate and the copper ammine complex:

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$
$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$
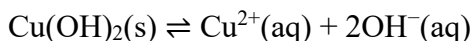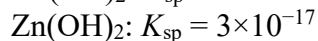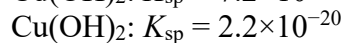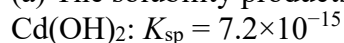
There will also be the acid−base equilibrium for the NH_4^+.

2.
Predict the precipitation order for the following solutions
(a) The solubility products for these precipitates are
$Cd(OH)_2$: $K_{sp} = 7.2\times10^{-15}$
$Cu(OH)_2$: $K_{sp} = 2.2\times10^{-20}$
$Zn(OH)_2$: $K_{sp} = 3\times10^{-17}$
Since the stoichiometry is the same for all of these precipitates, we can predict the precipitation order to be $Cu(OH)_2$ first, $Zn(OH)_2$ second, and $Cd(OH)_2$ last.

(b) adding PO_4^{3-} to a solution that is 0.1 mM each of Cu^{2+} and Al^{3+}. The K_{sp} values are $Cu_3(PO_4)_2$: 1.40×10^{-37} and $AlPO_4$: 9.84×10^{-21}. The PO_4^{3-} concentration at which each precipitate forms is:

$K_{sp} = [Cu^{2+}]^3[PO_4^{3-}]^2$
$1.40\times10^{-37} = (1\times10^{-4})^3[PO_4^{3-}]^2$
$[PO_4^{3-}] = 3.7\times10^{-13}$ M

$K_{sp} = [Al^{3+}][PO_4^{3-}]$
$9.84\times10^{-21} = (1\times10^{-4})[PO_4^{3-}]$
$[PO_4^{3-}] = 9.8\times10^{-17}$ M

So, $AlPO_4$ will precipitate first.

3.
Neglecting competing equilibria:
(a) $BaCO_3$: $s = [Ba^{2+}] = [CO_3^{2-}]$

(b) $Ba(OH)_2$: $s = [Ba^{2+}] = 0.5[OH^-]$
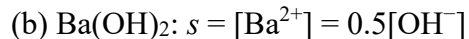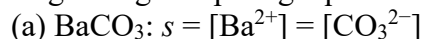
(c) $Pb_3(PO_4)_2$: $s = 0.333[Pb^{2+}] = 0.5[PO_4^{3-}]$

(d) ZnF_2: $s = [Zn^{2+}] = 0.5[F^-]$

(e) $Ca(C_2O_4)·H_2O$: $s = [Ca^{2+}] = [C_2O_4^{2-}]$
(the waters of hydration in the solid have no effect)

4.
pH effects:
(a) $BaCO_3$: Ba^{2+} is a strong electrolyte so there is no effect at high pH, at low pH the CO_3^{2-} is protonated and solubility increases.

(b) $Ba(OH)_2$: Ba^{2+} is a strong electrolyte so there is no effect at high pH, at low pH the OH^- is neutralized so more $Ba(OH)_2$ dissolves.

(c) $Pb_3(PO_4)_2$: High pH will increase solubility due to formation of lead hydroxide complexes and low pH will increase solubility due to protonation of PO_4^{3-}.

(d) ZnF_2: High pH will increase solubility due to formation of zinc hydroxide complexes and low pH will increase solubility due to protonation of F^- to form HF.

(e) $Ca(C_2O_4)·H_2O$: Ca^{2+} is usually treated as a strong electrolyte so there is little effect at high pH. Low pH will increase solubility due to protonation of $C_2O_4^{2-}$ to form $H_2C_2O_4$.

5.
Calculate Q, the reaction quotient, and compare it to K_{sp}' (since we are neglecting activity effects we will use $K_{sp}' = K_{sp} = 5.3 \times 10^{-9}$). If Q exceeds K_{sp}', the concentrations have exceeded the solubility limit and a precipitate will form.
$$Q = [Ca^{2+}][F^-]^2$$
$$Q = (0.00010 \text{ M})(0.00010 \text{ M})^2 = 1.0 \times 10^{-12} \text{ M}$$
$$Q < K_{sp}'$$
So the concentrations are below the level at which a precipitate will form.

6.
There are different ways to think qualitatively about the effect of ionic strength on ionic equilibria. One way is to think of the high ion concentration as "screening" the electrostatic attraction of oppositely charged ions that are involved in an equilibrium. Thus, increasing the ionic strength of an aqueous solution will reduce the tendency of ions to recombine. The result is higher ion concentrations relative to neutral species, such as precipitates, in higher ionic strength environments.
If some amount of an ion involved in a precipitation equilibrium is present or added from an additional source other than the precipitate, the concentration of this \common" ion will have a

direct effect on solubility. This direct effect will decrease solubility and will usually be much larger than the indirect effect caused by ionic strength affecting equilibrium constants.

7.
Neglecting ionic strength effects, $K_{sp}' = K_{sp} = 7.50 \times 10^{-12}$. Neglecting competing equilibria, we need only consider:

$$La(IO_3)_3(s) \rightleftharpoons La^{3+}(aq) + 3IO_3^-(aq)$$
$$K_{sp}' = [La^{3+}][IO_3^-]^3$$
$$7.50 \times 10^{-12} = (s)(3s)^3 = 27s^4$$
$$s = 6.9 \times 10^{-4} \text{ M}$$
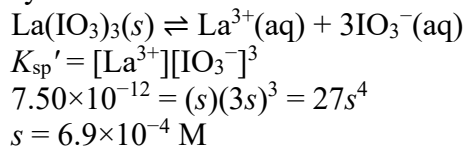
8.
We will neglect competing equilibria, such as lanthanum hydroxide complexes, but we will correct K_{sp} for activity effects.

$$K_{sp} = (a_{La})(a_{IO3})^3$$
$$K_{sp} = (\gamma_{La})[La^{3+}](\gamma_{IO3})^3[IO_3^-]^3$$
$$K_{sp} = (\gamma_{La})[La^{3+}](\gamma_{IO3})^3 K_{sp}'$$
$$K_{sp}' = \frac{K_{sp}}{(\gamma_{La})(\gamma_{IO3})^3}$$

The ionic strength is 0.010 M (neglecting the concentrations of La^{3+} and IO_3^- ions from the lanthanum iodate), and activity coefficients from the Debye-Hückel equation are:

$$\gamma_{La} = 0.44 \text{ and } \gamma_{IO3} = 0.90$$
$$K_{sp}' = \frac{7.50 \times 10^{-12}}{(0.44)(0.90)^3} = 1.9 \times 10^{-11}$$

Setting up the equilibrium problem
$$K_{sp}' = [La^{3+}][IO_3^-]^3 = 1.9 \times 10^{-11}$$

The equilibrium concentration of IO_3^- is the total that comes from both the sodium iodate and the lanthanum iodate.
$$[IO_3^-] = 0.010 \text{ M} + 3s$$
Thus
$$K_{sp}' = (s)(0.010 \text{ M} + 3s)^3 = 1.9 \times 10^{-11}$$

Try neglecting $3s$ compared to 0.010 M
$$K_{sp}' = (s)(0.010 \text{ M})^3 = 1.9 \times 10^{-11}$$
$$s = 1.9 \times 10^{-5} \text{ M}$$
Checking our assumption:
$$3(1.9 \times 10^{-5}) \ll 0.010 \text{ M}$$
The approximation in the calculation is reasonable and our answer is 1.9×10^{-5} M.

9.

(a) $Cd(OH)_2$ $K_{sp} = 4.5 \times 10^{-15}$

(b) $Mg(OH)_2$ $K_{sp} = 7.1 \times 10^{-12}$
Since this metal hydroxide has the highest K_{sp}, it is predicted to be the most soluble and will dissolve first as a basic solution is made more acidic.

(c) $Pb(OH)_2$ $K_{sp} = 1.2 \times 10^{-15}$

(d) $Zn(OH)_2$ $K_{sp} = 1 \times 10^{-17}$
Since this metal hydroxide has the smallest K_{sp}, it is predicted to be the least soluble and will precipitate first as an acidic solution is made more basic.

10.
Since CO_3^{2-} has the largest K_b' of these anions, it will react with water to the greatest extent. Thus for the listed insoluble Ba salts, the solubility of $BaCO_3$ will be affected the most by a competing equilibrium.

$$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$$
$$+$$
$$H_2O$$
$$\updownarrow$$
$$HCO_3^-(aq)$$
$$+$$
$$OH^-(aq)$$

11.
A search page for public water systems in the US is at:
US EPA, Consumer Confidence Reports (CCR),
https://ordspub.epa.gov/ords/safewater/f?p=ccr_wyl:102.
It is uncommon for contaminants to exceed the EPA action level. Typical results from my hometown include:

Contaminant	Maximum Contaminant Level (MCL)	Amount Detected
barium	2 ppm	0.023 ppm
fluoride	4 ppm	0.60 ppm
Haloacetic acids	60 ppb	5 – 39 ppb
nitrate	10 ppm	0.85 ppm
trihalomethanes	80 ppb	14 – 57 ppb
Copper	1.3 ppm	0.053 ppm
Lead	15 ppb	Not detected
Cryptosporidium		0.005 oocysts per liter

12.

The EPA drinking water standards monitor the following types of contaminants. Typical analytical methods for these contaminants are listed in the second column of the table. There are numerous methods depending on the specific analyte being determined. The brief description omits many steps in the method procedures. You can find lists of approved methods at: https://www.epa.gov/dwanalyticalmethods/approved-drinking-water-analytical-methods

Contaminant	Analytical Method
Microorganisms	Various microbial culture methods
Disinfectants	Test strips or colorimetry for chlorine, ion chromatography for anions
Disinfection Byproducts	GC-MS using a nitrogen purge gas
Inorganic Chemicals	ICP atomic emission spectrometry for metals, ion chromatography for anions
Organic Chemicals	GC-MS using a nitrogen purge gas
Radionuclides	Coprecipitation followed by scintillation counting

13.

The EPA secondary drinking water standards monitor physical characteristics and contaminants that can affect the "aesthetic qualities" of the water. Typical analytical methods for these contaminants are the same as listed in question 12. Atomic spectrometry is used for metals and ion chromatography is used for anions. Precipitation (turbidity) and titration are also common for contaminants at greater than trace concentrations.

14.

I'm not copying an image here to avoid copyright violations. On searching for "arsenic well water map" I found numerous maps of the US and individual states. Minnesota and Wisconsin have extensive maps and data about the prevalence of arsenic in ground water.