Chapter 7: End−of−Chapter Solutions

1.
(a) $KMnO_4(s)$: Mn(VII) in a covalent oxyanion, MnO_4^-.

(b) $MnCl_6^{3-}(aq)$: Mn(III), Cl has a −1 oxidation state, and the overall complex charge is −3.

(c) $Mn(H_2O)_6^{2+}(aq)$: Mn(II), water is neutral, and the overall charge of this ion is +2.

(d) $Mn(H_2O)_6^{7+}(aq)$: Mn(VII), this complex as written does not exist, the charge of a Mn(VII) ion is so high that it will react with water to form an oxyanion.

(e) $MnO_2(s)$: Mn(IV), O has the usual −2 oxidation state, and there is no charge to this neutral solid material.

2.
Ligands have unbonded electrons (usually pairs) and metal ions have empty orbitals. Coordinate covalent bonds form between the electron pairs on the ligands and the empty orbitals of the metal ions. The bonding between a base and a proton is analogous. The base has unbonded pairs of electrons and the proton has the 1s orbital empty.

3.
When using the indicator, the indicator remains uncomplexed until reaching the endpoint. At the endpoint where all EDTA is complexed, metal ion will bind to the indicator. If we assume that the indicator binds either the Ca^{2+} analyte or the Pb^{2+} titrant equally, then the indicator will still change color at the endpoint.

When using a Pb^{2+}-sensitive electrode, Pb^{2+} titrant that displaces Ca^{2+} from $Ca(edta)^{2-}$ will cause an overshoot of the endpoint. The measurement of the excess EDTA will be erroneously high. Calculation of the Ca^{2+} concentration will then be erroneously low.

4.
The Cl^- is a strong electrolyte and has no direct effect on $p[H_3O^+]$. The pK_a and the conversion to K_a for each cation is listed in the table. For 1.0 mM ionic strength, I assume $pK_a' = pK_a$. The calculation is the same as for any weak acid as done in Chapter 5:

$$K_a' = \frac{[H_3O^+]^2}{0.001\ M - [H_3O^+]}$$

and the results are tabulated in the last column of the table. The calculation for Li^+ and Ca^{2+} gives a result higher than 7.0, so these two ions have no effect on $p[H_3O^+]$.

	pK_a	K_a	$p[H_3O^+]$
Li^+	13.8	1.6×10^{-14}	7.0 (no effect)
Ca^{2+}	12.6	2.5×10^{-13}	7.0 (no effect)
Cu^{2+}	7.5	3.2×10^{-8}	5.2

5.

In this question we find the concentration of the metal ion that produces $p[H_3O^+] = 6.5$ or: $[H_3O^+] = 10^{-6.5} = 3.2 \times 10^{-7}$ M

Setting up the K_a' expression and solving for c:

$$K_a' = \frac{[H_3O^+]^2}{[Ca^{2+}] - [H_3O^+]}$$

$$2.5 \times 10^{-13} = \frac{(3.2 \times 10^{-7})^2}{[Ca^{2+}] - 3.2 \times 10^{-7}}$$

$$[Ca^{2+}] = 0.4 \text{ M}$$

$$3.2 \times 10^{-8} = \frac{(3.2 \times 10^{-7})^2}{[Cu^{2+}] - 3.2 \times 10^{-7}}$$

$$[Cu^{2+}] = 3.2 \times 10^{-6} \text{ M}$$

6.

(a) $Mn(edta)^{2-}$: at high pH the Mn^{2+} can form hydroxide complexes and at low pH the EDTA can be protonated, either extreme will reduce the $Mn(edta)^{2-}$ concentration.

(b) $Mn(H_2O)_6^{2+}$(aq): at high pH the Mn^{2+} can form hydroxide complexes to reduce the $Mn(H_2O)_6^{2+}$ concentration. At low pH there is no effect.

(c) $Cu(NH_3)_4^{2+}$(aq): at high pH the Cu^{2+} can form hydroxide complexes and at low pH the NH_3 can be protonated, either extreme will reduce the $Cu(NH_3)_4^{2+}$ concentration.

7.

Common interferences in EDTA titrations are copper or iron. They can interfere by appearing as analyte, giving erroneously high results, or by interfering with the complexometric indicator. These metals have very large formation constants with cyanide. Adding cyanide to a test portion will mask these metals so they do not complex with the EDTA titrant.

8.

(a) These pH values correspond to pOH values of 9 and 13. Using Figure 7.5 we see that at pOH = 9 we have significant fractions of $Fe(OH)_3$, $Fe(OH)_2^+$, and $FeOH^{2+}$. At pOH = 13 there is $FeOH^{2+}$ and Fe^{3+}.

(b) The concentration is found by multiplying the total concentration by the alpha fraction. At pOH = 9 we can get the Fe^{3+} alpha from Figure 7.6 and it is 0.001. The concentration is then $(1.0 \times 10^{-3} \text{ M})(0.001) = 1.0 \times 10^{-6}$ M.

The alpha at pOH = 13 is 0.92, and the concentration is $(1.0 \times 10^{-3} \text{ M})(0.92) = 9.2 \times 10^{-4}$ M

(c) You are starting with 0.10 M NH_4^+ and 0.10 M Cl^- from the buffer and 0.005 M Fe^{3+} and 0.015 M Cl^- from the $FeCl_3$. At pH = 9.2 (pOH = 4.8), all of the iron is in the form of $Fe(OH)_3$, which has no charge. To reach that form it has reacted with water to form H_3O^+. The NH_3 of the buffer system neutralizes this H_3O^+ to produce 0.015 mol of NH_4^+. After the solution reaches equilibrium, it is now 0.115 M NH_4^+ and 0.115 M Cl^-. The ionic strength is thus:

$$I_c = 0.5\{(-1)^2(0.115 \text{ M}) + (+1)^2(0.115 \text{ M})\}$$
$$I_c = 0.115 \text{ M}$$

9.

The log cumulative formation constants for Ag^+ and Br^- are 4.38, 7.33, 8.00, and 8.73.

(a) The stepwise formation constants are
$$10^{4.38} = 2.4 \times 10^4$$
$$10^{7.33-4.38} = 10^{2.95} = 8.9 \times 10^2$$
$$10^{8.00-7.33} = 10^{0.67} = 4.7$$
$$10^{8.73-8.00} = 10^{0.73} = 5.4$$

(b) The 1,10−phenanthroline has larger formation constant values for Ag^+ than does Br^-, so for comparable concentrations, it will displace Br^- to complex with the Ag^+.

10.

At the end point of a titration, there will either be complete depletion of a metal being titrated or the presence of a metal from the titrant. Complexometric indicators have different colors when a metal is bound or unbound. Taking the case of EDTA titrant and a metal ion as analyte, at the end point the EDTA complexes all of the metal ion, removing metal from a metal−indicator complex. (Suitable indicators have K_f' values lower than for the metal ion and EDTA.) Electronically, binding of the metal changes the distribution of electrons in the complex compared to the electron distribution in the absence of the metal. This change in electron distribution can shift the electronic energy levels. We see the shift in wavelength of the absorbed light as a color change.

11.

Less than the maximum number of ligands might be stable in solution if the stepwise formation values are well separated. The alpha plots show that the different complexes appear to be separable for Cu^{2+} and Fe^{3+} oxalate but not for Al^{3+} oxalate.

12.

$$\beta_{eff}' = \alpha_M \, \alpha_L \, \beta_1$$

		pH = 5				pH = 6	
	β_1'	α_M	α_L	β_{eff}'	α_M	α_L	β_{eff}'
Ca^{2+}	1×10^{11}		3.54×10^{-7}			2.25×10^{-5}	
Pb^{2+}	2×10^{18}		3.54×10^{-7}			2.25×10^{-5}	
Zn^{2+}	3×10^{16}		3.54×10^{-7}			2.25×10^{-5}	

13.
equilibria

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

14.
(a) The $Cu_3(PO_4)_2$ is insoluble and the precipitation equilibrium is:
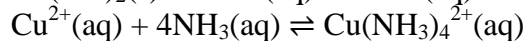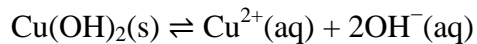$$Cu_3(PO_4)_2(s) \rightleftharpoons 3Cu^{2+}(aq) + 2PO_4^{3-}(aq)$$
The NH_3 can complex with copper so you also have:
$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$
There will also be the base hydrolysis equilibria for the ammonia and PO_4^{3-} to form the protonated form of each.
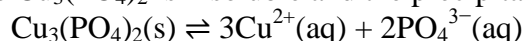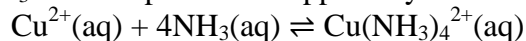
(b) Mixing these two soluble salts will form a $Cu(OH)_2$ precipitate and the copper ammine complex:
$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$
$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$
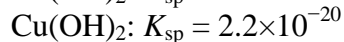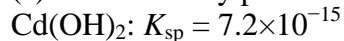There will also be the acid−base equilibrium for the NH_4^+.

15.
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:

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

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

So, $AlPO_4$ will precipitate first.

16.
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) $Ca(C_2O_4)\cdot H_2O$: $s = [Ca^{2+}] = [C_2O_4^{2-}]$
(the waters of hydration in the solid have no effect)

17.
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

18.

Calculate Q, the reaction quotient, and compare it to K_{sp}' (since we are neglecting activity effects we will use $K_{sp}' = K_{sp} = 5.3\times10^{-9}$). If Q exceeds K_{sp}', the concentrations have exceeded the solubility limit and a precipitate will form.

$$Q = [Ca^{2+}][F^-]^2$$
$$Q = (0.00010 \text{ M})(0.00010 \text{ M})^2 = 1.0\times10^{-12} \text{ M}$$
$$Q < K_{sp}'$$

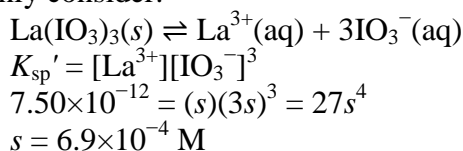So the concentrations are below the level at which a precipitate will form.

19.

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.

20.

Neglecting ionic strength effects, $K_{sp}' = K_{sp} = 7.50\times10^{-12}$. Neglecting competing equilibria, we need only consider:

$$La(IO_3)_3(s) \rightleftharpoons La^{3+}(aq) + 3IO_3^-(aq)$$
$$K_{sp}' = [La^{3+}][IO_3^-]^3$$
$$7.50\times10^{-12} = (s)(3s)^3 = 27s^4$$
$$s = 6.9\times10^{-4} \text{ M}$$

21.

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:

$$\gamma_{La} = 0.44 \text{ and } \gamma_{IO3} = 0.90$$
$$K_{sp}' = \frac{7.50\times10^{-12}}{(0.44)(0.90)^3} = 1.9\times10^{-11}$$

Setting up the equilibrium problem
$$K_{sp}' = [La^{3+}][IO_3^-]^3 = 1.9\times10^{-11}$$

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
$$K_{sp}' = (s)(0.010 \text{ M} + 3s)^3 = 1.9\times10^{-11}$$

Try neglecting $3s$ compared to 0.010 M
$$K_{sp}' = (s)(0.010 \text{ M})^3 = 1.9\times10^{-11}$$
$$s = 1.9\times10^{-5} \text{ M}$$
Checking our assumption:
$$3(1.9\times10^{-5}) << 0.010 \text{ M}$$
The approximation in the calculation is reasonable and our answer is 1.9×10^{-5} M.

22.
(a) $Cd(OH)_2$ $K_{sp} = 4.5\times10^{-15}$

(b) $Mg(OH)_2$ $K_{sp} = 7.1\times10^{-12}$
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) $Pb(OH)_2$ $K_{sp} = 1.2\times10^{-15}$

(d) $Zn(OH)_2$ $K_{sp} = 1\times10^{-17}$
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.

23.
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.

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