Chapter 7: End−of−Chapter Solutions

1.
(a) $KMnO_4(s)$: Mn(VII) in a covalent oxyanion, MnO_4^-, with overall charge of −1.

(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^+] = $10^{-6.5}$ = 3.2×10^{-7} M
Setting up the K_a' expression and solving for c:

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

$$2.5\times10^{-13} = \frac{(3.2\times10^{-7})^2}{[Ca^{2+}] - 3.2\times10^{-7}}$$

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

$$3.2\times10^{-8} = \frac{(3.2\times10^{-7})^2}{[Cu^{2+}] - 3.2\times10^{-7}}$$

$[Cu^{2+}] = 3.2\times10^{-6}$ 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 $(1.0\times10^{-3}$ M$)(0.001) = 1.0\times10^{-6}$ M.

The alpha at pOH = 13 is 0.92, and the concentration is $(1.0\times10^{-3}$ M$)(0.92) = 9.2\times10^{-4}$ 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

$$10^{4.38} = 2.4\times10^4$$
$$10^{7.33-4.38} = 10^{2.95} = 8.9\times10^2$$
$$10^{8.00-7.33} = 10^{0.67} = 4.7$$
$$10^{8.73-8.00} = 10^{0.73} = 5.4$$

(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 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.

The expressions are:

$$K_{a1}' = \frac{[HA^-][H_3O^+]}{[H_2A]}$$

$$K_{a2}' = \frac{[A^{2-}][H_3O^+]}{[HA^-]}$$

$$K_b' = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

$$\beta_4' = \frac{[ML_4^{2-}]}{[M^{2+}][L^-]^4}$$

$$K_{sp}' = [M^{3+}]^2[X^{2-}]^3$$

All these expressions follow the general rules for writing an equilibria constant. The difference is that each type of equilibrium has a convention for the direction in which the reaction is written.

14.

The control line is included to check that the test works as designed. Lateral flow tests are usually packaged in a sealed foil wrapper to protect them from moisture. If the reagent pad becomes wet, the reagents can disperse and not be available for binding when a test sample solution is applied to the device. A physical break between the sample and reagent pads or along the flow path will cause a test to fail. Excessive heat can also destroy the SARS and control reporters. Failure due to any of these problems will be evident because the control line will not appear when a test is run.

15.

Lateral flow tests include at-home pregnancy tests (first introduced in 1988) and COVID tests. Point-of-care testing, i.e., in a medical facility, is available or in-development for HIV, dengue, malaria, influenza A and B, and other disease vectors.

Other lateral flow tests include detecting food pathogens such as Salmonella and Listeria or pesticides and toxins.

Depending on the target analyte, home and point-of-care sampling can be blood, urine, saliva, or mucous. For food pathogens, the agricultural product is the sample.

The antigen is generally a unique protein or a nucleic acid strand that is taken from or occurs on the surface of a pathogen. For toxins, the antigen is the molecule of interest.