1) We can get a good start here by writing the balanced equation for the dissolving of the (presumably) insoluble salt:

\[ M_3X_2 \leftrightarrow 3 M^{2+} + 2 X^{3-} \]

thus, we can see that we have an 5 particles, which will give us an apparent molarity 5 times the actual molarity. The osmotic pressure data helps us find this apparent molarity:

\[
M = \frac{\Pi}{RT} = \frac{20.1 \text{mmHg}}{760 \text{mmHg/atm}} \times \frac{1}{(0.08206 \text{L \cdot atm/K \cdot mol})(298.15 \text{K})} = 1.08 \times 10^{-3} \text{ M.}
\]

Remember, this is the apparent molarity; the actual molarity is one-fifth of this, or \(2.16 \times 10^{-4}\).

As in the calcium phosphate example in class, this molarity represents the molarity (or moles/L) of the initial salt; therefore, \([M^{2+}] = \) three times this value, and the \([X^{3-}] = \) twice this value. Letting the molarity we just found be represented by ‘x’, we get

\[
K_{sp} = (3x)^3(2x)^2 = 108x^5 = 108(2.16 \times 10^{-4})^5 = 5.1 \times 10^{-17},
\]

which is a perfectly fine value for a \(K_{sp}\).

2a) We are given \(\text{Fe(OH)}_3\), and its \(K_{sp}\) value. We also know the [OH\(^-\)] in pure water = 10\(^{-7}\) M. Given our \(K_{sp}\) value, we can calculate the [OH\(^-\)] assuming no contribution from water. Done in this manner, we get:

\[
K_{sp} = 4 \times 10^{-38} = \text{[Fe}^{3+}]\text{[OH}^-\] = (x)(3x) = 27x^4,
\]

which leads to \(x = 1.96 \times 10^{-10} \text{ M and [OH}^-\] = 5.89 \times 10^{-10} \text{ in the absence of any contribution from water. But we know water contributes 10}^{-7} \text{ M OH}\(^-\), so our molar solubility of \(\text{Fe(OH)}_3\) in pure water is

\[
[\text{Fe}^{3+}] = \text{molar solubility} = \frac{K_{sp}}{[\text{OH}^-]^3} = \frac{4 \times 10^{-38}}{(10^{-7})^3} = 4 \times 10^{-17} \text{ M}.
\]

b) Here we are buffered at pH = 5 (meaning pOH = 9) so we know our [OH\(^-\)] = 1 \times 10^{-9} M. Substituting this value, we get

\[
[\text{Fe}^{3+}] = \text{molar solubility} = \frac{K_{sp}}{[\text{OH}^-]^3} = \frac{4 \times 10^{-38}}{(10^{-9})^3} = 4 \times 10^{-11} \text{ M}.
\]
c) Here we are buffered at pH = 11 (meaning pOH = 3) so we know our [OH⁻] = 1 x 10⁻³ M. Substituting this value, we get [Fe³⁺] = molar solubility = \( \frac{K_{sp}}{[OH^-]^3} = \frac{4 \times 10^{-38}}{(10^{-3})^3} = 4 \times 10^{-29} \) M.

3a) In this group, the only salt that is formed from a weak acid is AgF, so this is going to be the one which is most affected by a change in pH. The supporting equation is:

\[ \text{AgF}(s) + \text{H}^+(aq) \leftrightarrow \text{Ag}^+(aq) + \text{HF}(aq) \]

b) Here we have a metal hydroxide, which should clearly be the one to be most affected by pH changes. That is, the Pb(OH)₂. The supporting equation is:

\[ \text{Pb(OH)}_2(s) + 2\text{H}^+(aq) \leftrightarrow \text{Pb}^{2+}(aq) + 2\text{H}_2\text{O}(l) \]

\( \text{(Pb(OH)}_2(s) + 2\text{OH}^-(aq) \leftrightarrow \text{Pb(OH)}_4^{2-}(aq) \text{ works also}) \)

c) In this grouping, we are contrasting a nitrate and a nitrite. Recall that nitrates come from nitric acid (a strong acid) and nitrites come from nitrous acid (a weak acid). Thus, our answer is Sr(NO₂)₂. The supporting equation is:

\[ \text{Sr(NO}_2)_2(s) + 2\text{H}^+(aq) \leftrightarrow \text{Sr}^{2+}(aq) + 2\text{HNO}_2(aq) \]

d) In this group, we have nitrate vs. cyanide. As said above, nitric acid (from whence we get nitrates) is a strong acid, whereas hydrocyanic acid (from whence we get cyanides) is a weak acid. Again, this analysis answers our question: Ni(CN)₂. The supporting equation is:

\[ \text{Ni(CN)}_2(s) + 2\text{H}^+(aq) \leftrightarrow \text{Ni}^{2+}(aq) + 2\text{HCN}(aq) \]

4) We need to take the hint given in the problem. The equilibrium we need to examine closely is:

\[ \text{SrF}_2(s) + 2\text{H}^+(aq) \leftrightarrow \text{Sr}^{2+}(aq) + 2\text{HF}(aq) \]

This equilibrium is composed of the solubility equilibrium for SrF₂ and the reverse of twice the \( K_a \) expression for HF, so the equilibrium constant, \( K \), for this reaction is: \( K = \frac{K_{sp}}{K_a^2} = \frac{7.9 \times 10^{-10}}{(6.8 \times 10^{-4})^2} = 1.71 \times 10^{-3} = \left[ \frac{\text{Sr}^{2+}(aq)\text{HF}(aq)}{\text{H}^+(aq)} \right]^2 \). From the buffer solution we are given (0.50 M NaHSO₄ and 0.55 M Na₂SO₄; \( K_a = 1.02 \times 10^{-2} \)) we can get the pH and thereby the \([\text{H}^+]\): pH = \( pK_a + \log\left(\frac{[SO_4^{2-}]}{[HSO_4^-]}\right) = 1.99 + \log\left(\frac{0.55}{0.50}\right) = 1.99 + 0.04 = 2.03 \) which leads
to \([H^+] = 10^{-2.03} = 9.33 \times 10^{-3}\). Now comes the important part to realize. If we let \(x = [Sr^{2+}]\), we need to find an expression for \([HF]\) (It is not simply \(2x\)!) The part here that is deeper is that, even in the above equilibrium, there is a measurable concentration of \(F^-\), so \(2x = [HF] + [F^-]\). From the \(K_a\) expression (and value) for HF, and using the pH above, we can get how \([F^-]\) relates to \([HF]\) and thereby get an expression for \([HF]\) which we can use.

\[
K_a = \left(\frac{H^+ [F^-]}{[HF]}\right) = 6.8 \times 10^{-4} = \left(9.33 \times 10^{-3}\right)^2 \frac{[F^-]}{[HF]} \text{ which leads to } 0.0728 = \frac{[F^-]}{[HF]} \text{ or } 0.0729[HF] = [F^-] \text{ and } 2x = 1.0729[HF] \text{ so } [HF] = \frac{2x}{1.0729} \text{. Substituting it all into } 1.71 \times 10^{-3} = \frac{[Sr^{2+}] [HF]^2}{[H^+]} \text{, we get: } 1.71 \times 10^{-3} = \frac{(x)(1.864x)^2}{(9.33 \times 10^{-3})^2} \text{, which simplifies to: } 1.49 \times 10^{-7} = 3.47x^3 \text{ or } x = [Sr^{2+}] = 3.50 \times 10^{-3} \text{ } M = \text{ molar solubility of } SrF_2 \text{ in this buffer. (This is one of the toughest problem, I believe, to date; tougher even than the buffer problem last chapter.) (It is interesting to note that if one ignores the contribution from HF to the } F^- \text{ concentration, one arrives at an answer which is within 5% of the answer given above!)}

5) Both silver bromide and silver chloride are 1:1 salts \(i.e.\) there is one cation and one anion per formula unit; therefore, \(K_{sp} = x^2\), where \(x = [Ag^+] = [X^-] = \text{ molar solubility of the salt.}\) In the case of silver chromate \((Ag_2CrO_4)\), letting \(x = [CrO_4^-] = \text{ the molar solubility of the salt, we get the } K_{sp} = 4x^3 \text{ i.e. the extra “x” could lower the } K_{sp} \text{ of a more soluble salt below that of a less soluble salt. For example, using } AgCl \text{ and } Ag_2CrO_4 \text{ } (K_{sp} = 1.8 \times 10^{-10} \text{ and } 1.1 \times 10^{-12} \text{ respectively), we get the molar solubility of } AgCl = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5} \text{ } M \text{ as compared to the molar solubility of } Ag_2CrO_4 = \sqrt[3]{\frac{1.1 \times 10^{-12}}{4}} = 6.5 \times 10^{-5} \text{ } M \text{. Thus, we see that although the } K_{sp} \text{ for } Ag_2CrO_4 < K_{sp} \text{ for } AgCl, the reverse is true for the molar solubilities } i.e. M_{AgCl} < M_{Ag_2CrO_4}. \text{ (Note two things: (1) you could have chosen a different example to illustrate the idea; (2) you didn’t need necessarily to use an example, so long as your math/algebra was sufficiently clear that you communicated the concept.)}