1. Which of the following acids would you expect to be the stronger. Explain your choice (provide a reason why it would be stronger - don’t just say you know it is).

\[ \text{H}_2\text{S} \quad \text{vs} \quad \text{H}_2\text{O} \]

\[ \text{H}_2\text{S} \text{ since bond strength decreases down a group we expect the H-S bond to be more easily broken than the H-O bond. This trend should NOT be confused with the change in EN experienced across a period.} \]

2. Which of the following acids would you expect to be the stronger. Explain your choice (provide a reason why it would be stronger - don’t just say you know it is).

\[ \text{HNO}_3 \quad \text{vs} \quad \text{HNO}_2 \]

\[ \text{HNO}_3 \text{ has three oxygen atoms attached to the central N in the structure. One of these oxygen atoms has the acidic H attached to it. The presence of the two other oxygen atoms help explain the acidic nature HNO}_3\text{ in two ways related to the high EN of oxygen. First, we can say that the O-H bond has electron density pulled away by the other two oxygen atoms (thereby weakening the bond). Second we can state that the NO}_3^- \text{ ion should be more stable than the NO}_2^- \text{ ion (since there are three oxygen atoms to carry the minus one charge on the ion vs. two oxygen atoms in the NO}_2^- \text{).} \]

3. An aqueous solution of two basic species is prepared. The first base is NaOH and it is present at a concentration of 0.20 M. The second base is a weak base, ammonia with a \( K_b = 1.8 \times 10^{-5} \), and it is present at a concentration of 0.222 M.

In the space below write the relevant reactions . . AND find the following concentrations: \([\text{OH}^-]\), \([\text{Na}^+]\), \([\text{NH}_3]\), \([\text{NH}_4^+]\), pH, pOH, and \([\text{H}_3\text{O}^+]\) when equilibrium is established.

\[
\begin{align*}
\text{NaOH}_{(aq)} & \rightarrow \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)} \\
\text{I} & \quad 0.20 \text{ M} \quad 0 \quad \sim 0 \\
\text{C} & \quad -0.20 \text{ M} \quad +0.20 \text{ M} \quad +0.20 \text{ M} \\
\text{E} & \quad \sim 0 \text{ M} \quad 0.20 \text{ M} \quad 0.20 \text{ M} \\
\text{NH}_3_{(aq)} & + \text{H}_2\text{O}_(l) \leftrightarrow \text{NH}_4^+_{(aq)} + \text{OH}^-_{(aq)} \quad \text{K}_b = 1.8 \times 10^{-5} \\
\text{I} & \quad 0.222 \text{ M} \quad 0 \quad 0.20 \text{ M} \\
\text{C} & \quad -x \text{ M} \quad +x \text{ M} \quad +x \text{ M} \\
\text{E} & \quad 0.222-x \text{ M} \quad x \text{ M} \quad 0.20 + x \text{ M} \\
\end{align*}
\]

\[
\text{K}_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3]} = \frac{x [0.20 + x]}{0.222 - x} = \frac{x [0.20]}{0.222}
\]

\[
\begin{align*}
[\text{Na}^+] &= 0.20 \text{ M} \\
[\text{NH}_4^+] &= x = 2.0 \times 10^{-5} \text{ M} \\
[\text{OH}^-] &= \sim 0.20 \text{ M} \\
[\text{NH}_3] &= 0.222-x = \sim 0.222 \text{ M} \\
p\text{OH} = & -\log [\text{OH}^-] = -\log (0.20) = 0.68_9 \\
p\text{H} = & 14.00 - p\text{OH} = 13.30_1 \\
[\text{H}_3\text{O}^+] &= 10^{-p\text{H}} = 10^{-13.30} = 5.0 \times 10^{-14} \text{ M}
\end{align*}
\]
(10 points)

4. a. For PbCrO$_4$, $K_{sp} = 2.8 \times 10^{-13}$. What is the molar solubility of PbSO$_4$ in pure water?

$$\text{PbCrO}_4 (s) \leftrightharpoons \text{Pb}^{2+} (aq) + \text{CrO}_4^{2-} (aq)$$

$$K_{sp} = 2.8 \times 10^{-13} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}]$$

$$S = [\text{Pb}^{2+}] = [\text{CrO}_4^{2-}] = 5.3 \times 10^{-7} \text{ M}$$

b. For PbCrO$_4$, $K_{sp} = 2.8 \times 10^{-13}$. What is the molar solubility of PbSO$_4$ in a 0.010 M solution of K$_2$CrO$_4$.

$$\text{PbCrO}_4 (s) \leftrightharpoons \text{Pb}^{2+} (aq) + \text{CrO}_4^{2-} (aq)$$

$$K_{sp} = 2.8 \times 10^{-13} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}]$$

$$I = 0 \quad 0.010 \text{ M}$$

<table>
<thead>
<tr>
<th>C</th>
<th>S</th>
<th>+S</th>
<th>+S</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>S</td>
<td>0.010</td>
<td>+S</td>
<td></td>
</tr>
</tbody>
</table>

$$S = [\text{Pb}^{2+}] = S = 2.8 \times 10^{-11} \text{ M}$$

(4 points)

5. In which of the following 1.0 M solutions would you expect cadmium sulfide, CdS, to be the least soluble? Explain your choice in the open space below the possible answers!

a. NaCl  

b. HCl  

c. NaOH  

d. C$_2$H$_5$OH (ethanol)

Sulfide ions are basic. We expect bases to dissolve less well in basic solutions (relates to common ion effect).

(4 points)

6. Which of the following solid salts is LESS soluble in 1.0 M HCl than in pure water? Explain your choice in the open space below the possible answers!

a. NaBr  

b. KNO$_3$  

c. Fe(NO$_3$)$_2$  

d. AgCl  

e. KNO$_3$

HCl contains a common ion for AgCl.

(10 points)

7. a. What is the pH of a buffer with [conj. base] = 1.00 M and [weak acid] = 0.80 M if the Ka of the weak acid is $1.25 \times 10^{-5}$?

$$pK_a = -\log K_a = -\log (1.25 \times 10^{-5}) = 4.90$$

$$pH = pK_a + \log \left[ \frac{[\text{base}]}{[\text{acid}]} \right] = 4.90 + \log \left[ \frac{1.00}{0.80} \right] = 5.00$$

b. If 0.200 mole of H$^+$ is added to 2.00 L of the buffer in part “a”, what will the new pH of the buffer be?

$$[\text{H}^+]_{\text{added}} = \frac{0.200 \text{ mole}}{2.00 \text{ L}} = 0.100 \text{ M}$$

The rxn that takes place is \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+

$$pH = pK_a + \log \left[ \frac{[\text{base}]}{[\text{acid}]} \right] = 4.90 + \log \left[ \frac{1.00 - 0.100}{0.80 + 0.100} \right] = 4.90 + \log \left[ \frac{0.90}{0.90} \right] = 4.90$$

It is reasonable for the pH to decrease since we have added a source of H$^+$ to the buffer.
8. (25 pts.) NOTE: I have calculated more in part (b) than I would expect from an average student.

(a) In the space below, sketch a titration curve for the titration of 25.00 mL 0.100 M HNO₃(aq) with 0.100 M NaOH(aq). Be sure to include the starting pH, equiv. pt, pH, and mL of base needed to reach the equiv. pt.

\[ \text{NaOH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NaNO}_3 \]

Show any calculations you do in this space:

HNO₃ is a strong acid – it dissociates 100%

**Initial pH** = -\log [H⁺] = -\log (0.100) = 1.000

The volume of base needed to reach the equivalence point will contain a number of moles of OH⁻ equivalent to number of moles of H⁺ in the 25.00 mL of 0.100 M HNO₃.

\[(25.00 \text{ mL})(0.100 \text{ M}) = 2.50 \text{ mmole H}^+ \]

2.50 mmole H⁺ = 2.50 mmole OH⁻

\[(x \text{ mL})(0.100 \text{ M}) = 2.50 \text{ mmole OH}^- \]

\[x \text{ mL} = 25.0 \text{ mL of the NaOH solution} \]

NaNO₃ is the salt produced and it is made up of spectator ions (Na⁺ and NO₃⁻) so the pH at the equivalence point is 7.00

After the equivalence point the pH will approach the pH of the 0.100 M NaOH (pH = 13.00).

(b) On the same set of axes, sketch a titration curve for the titration of 25.00 mL of a 0.100 M weak acid solution with \( K_a = 1.0 \times 10^{-7} \) titrated with 0.100 M NaOH(aq). Indicate significant differences from the curve in part (a). Try to impress the instructor with your knowledge of titration curves.

\[ \text{NaOH} + \text{HA} \rightarrow \text{H}_2\text{O} + \text{NaA} \]

Show any calculations you need to do in this space:

**Initial pH** found by solving weak acid equilibrium.

\[ K_a \sim x^2/0.100 \], giving \( x = [H^+] = 1.0 \times 10^{-4} \text{ M} \)

**So the initial pH = 4.00**

Volume of base needed = 25.00 mL [same logic as shown in part (a)]

At the ½ equivalence volume (12.50 mL) the [HA] = [NaA] so we find that \( pH = pK_a = 7.00 \)

At the equivalence point a solution of NaA is created and \([A^-] = \frac{(25.00 \text{ mL})(0.100 \text{ M})}{(50.00 \text{ mL})} \)

Equiv. pt. pH found by solving weak base equil.

\[ K_b = Kw/Ka = 1.0 \times 10^{-7} \]

\[ K_b \sim y^2/0.050 \], giving \( y = [OH^-] = 7.1 \times 10^{-5} \text{ M} \)

So the equiv. pt. pH = 14.00 – 4.15 = 9.85
9. Predict whether the change listed next to each set of equations will increase or decrease the solubility of the underlined salts. **Explain your reasoning AND** if no change should occur, so indicate.

<table>
<thead>
<tr>
<th>REACTION</th>
<th>CHANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg(OH)}_2 \overset{(s)}{\rightleftharpoons} \text{Mg}^{2+} + 2 \text{OH}^- )</td>
<td>( K_{sp} = 1.8 \times 10^{-11} ) add ( \text{H}_3\text{O}^+ )</td>
</tr>
</tbody>
</table>

*Increase the solubility of Mg(OH)$_2$ (s) due to the very favorable conversion of OH$^-$ into H$_2$O.*

| CaSO$_4$ |  |
| Ca$^{2+}$ + SO$_4^{2-}$ | \( K_{sp} = 9.1 \times 10^{-6} \) add CaSO$_4$(s) |

**NO CHANGE IN SOLUBILITY** – CaSO$_4$(s) is the same solid not a “Common Ion” source. **If the solid added was Na$_2$SO$_4$(s) the solubility of CaSO$_4$(s) would decrease due to common ion effect.**

Treat the next pair of reactions as one unit . . . i.e. the reactions are coupled!

| AgI |  |
| Ag$^+$ + I$^-$ | \( K_{sp} = 8.5 \times 10^{-17} \) |

| Ag$^+$ + 2 CN$^-$ | \([\text{Ag(CN)}_2^-]^+ \) | \( K_f = 5.6 \times 10^{18} \) add \( \text{H}_3\text{O}^+ \) |

*Decrease the solubility of AgI (s) due to conversion of CN$^-$ into HCN. This frees up Ag$^+$ ions from the complex \([\text{Ag(CN)}_2^-]^+\) and shifts the first reaction to the left.*

(12 points)

10. For \([\text{Ag(NH}_3)_2]^+ \) \( K_f = 1.6 \times 10^7 \) and for AgI \( K_{sp} = 8.5 \times 10^{-17} \). What is the molar solubility of AgI in a solution that is 2.00 M in NH$_3$? See the last set of reactions in #9 for some useful info.

| AgI |  |
| Ag$^+$ + I$^-$ | \( K_{sp} = 8.5 \times 10^{-17} \) |

| Ag$^+$ + 2 NH$_3$ | \([\text{Ag(NH}_3)_2]^+ \) | \( K_f = 1.6 \times 10^7 \) |

\[
\begin{align*}
\text{AgI} & \rightarrow \text{Ag}^+ + \text{I}^- \\
& \text{Ag}^+ + 2 \text{NH}_3 \rightarrow [\text{Ag(NH}_3)_2]^+ \\
\text{I} & \text{2.00 M} \\
\text{C} & -2x \text{ M} \\
\text{E} & 2.00-2x \\
\text{K} & = (K_{sp})(K_f) = 1.4 \times 10^{-9} \\
\text{K} & = 1.4 \times 10^{-9} = \frac{[\text{Ag(NH}_3)_2]^+][\text{I}^-]}{[\text{NH}_3]^2} = \frac{[x][x]}{[2.00-2x]^2} \\
\text{Take the square root of both sides and solve for } x = 7.5 \times 10^{-5} \text{ M} = [\text{Ag(NH}_3)_2]^+ = [\text{I}^-]
\end{align*}
\]
BONUS (for up to 8 points complete the following)

Most ordinary soaps are water-soluble sodium or potassium salts of long-chain fatty acids. However, salts formed by fatty acids with divalent cations (like \( \text{Ca}^{2+} \)) are only slightly soluble and are often seen in the common soap scum formed in hard water. A handbook lists the solubility of a typical calcium soap salt, calcium palmitate, \( \text{Ca}[\text{CH}_3(\text{CH}_2)_{14}\text{COO}]_2 \), as 0.0030 grams / 100 mL of water at 25°C. The molar mass of calcium palmitate is 550.93 g per mole.

(a) What is the numerical value of \( \text{K}_{sp} \) for calcium palmitate?

\[
\begin{align*}
S &= \frac{1\text{mole}}{550.93\text{g}} \times \frac{0.0030\text{g}}{100\text{mL}} \times \frac{1000\text{mL}}{1\text{L}} = 5.45 \times 10^{-5} \text{M} \\
\text{Ca}[\text{CH}_3(\text{CH}_2)_{14}\text{COO}]_2(s) &\rightleftharpoons \text{Ca}^{2+} + 2 \text{CH}_3(\text{CH}_2)_{14}\text{COO}^- \\
\text{K}_{sp} &= (S)(2S)^2 = 4S^3 = 4(5.45 \times 10^{-5})^3 = 6.46 \times 10^{-13}
\end{align*}
\]

(b) If sufficient sodium soap is used to produce a concentration of palmitate ions equal to 0.10 M in water having 25 ppm \( \text{Ca}^{2+} \), would you expect any soap scum to form?

\[
\begin{align*}
25 \text{ppm} \text{Ca}^{2+} &= \frac{25\text{mg}}{1\text{L}} \times \frac{1\text{g}}{1000\text{mg}} \times \frac{1\text{mole}}{40.08\text{g}} = 6.24 \times 10^{-4} \text{M} \\
\text{Ca}[\text{CH}_3(\text{CH}_2)_{14}\text{COO}]_2(s) &\rightleftharpoons \text{Ca}^{2+} + 2 \text{CH}_3(\text{CH}_2)_{14}\text{COO}^- \\
\text{Q} &= (\text{Ca}^{2+})(\text{CH}_3(\text{CH}_2)_{14}\text{COO}^-)^2 = 6.24 \times 10^{-6} \\
\text{Q} > \text{K}_{sp} \Rightarrow \text{so, yes ppt. (soap scum will definitely be expected to form)}
\end{align*}
\]

(c) If any soap scum does form under the conditions described in part “B”, how many grams of calcium palmitate would precipitate in a bowl containing 6.5 L of water?

\[
\begin{align*}
\text{Ca}^{2+} + 2 \text{CH}_3(\text{CH}_2)_{14}\text{COO}^- &\rightleftharpoons \text{Ca}[\text{CH}_3(\text{CH}_2)_{14}\text{COO}]_2(s) \\
6.24 \times 10^{-4} \text{M} &\text{0.10 M}
\end{align*}
\]

The reverse of the dissolution reaction is very favorable. We can assume \( \sim 100\% \) reaction until the limiting reactant (the calcium ions) are essentially completely consumed.

\[
(6.5 \text{ L}) \times (6.24 \times 10^{-4} \text{ mole/L of water}) \times (1 \text{ mole soap scum/mole Ca}^{2+}) \times (550.93 \text{g/mole}) = 2.23 \text{ g soap scum}
\]

Note: the key to this exam appears on the following pages. A second “make-up” exam 3 was also given in Sp 2003 due to a low class performance on the first exam 3. The make-up exam 3 and the key for that exam are also included in this study guide. The make-up exam was comprised of problems assigned from the text and I also included the bonus from exam 3 as a regular question on the make-up. Scores did not improve dramatically.

Do NOT rely on your instructor being generous again this year. Study hard and pass the regular exam. There may very well NOT be a make-up exam.