1) Make sure your exam copy contains 6 questions, an extra credit question, 2 sheets of scratch paper and a periodic table.
2) You have until 10:45 (1 hr. 15 min.) to finish the exam.

Potentially useful information:

\[ pH = pK_a + \log \left( \frac{[\text{Conjugate Base}]}{[\text{Acid}]} \right) \]

\[ S = k \ln W \]

\[ \Delta S = (q_{\text{rev}}) / T \]

\[ \Delta S^0 = \left[ \sum v_p S^0 (\text{products}) - \sum v_r S^0 (\text{reactants}) \right] \]
1) (25 pts.) Question 1 has 5 parts, each being worth 5 points. Circle or write the correct answer in the space provided.

a. Which of the following combinations cannot behave as a buffer?
   
   A) HNO₂/NaNO₂
   
   B) HCN/NaCN
   
   C) (NH₄)₂SO₄/NH₃
   
   D) HClO₄/NaClO₄
   
   E) None of the above
   
   D) HClO₄/NaClO₄
   
   St. Acid

b. What is the pH of a buffer solution containing 0.30 M HClO and 0.15 M NaClO? (Kₐ = 3.0 x 10⁻⁸)
   
   A) 7.22
   
   B) 7.82
   
   C) 7.52
   
   D) 7.35
   
   E) 7.00
   
   A) 7.22
   
   pH = \[ \log \left( \frac{0.15 \text{M}}{0.3 \text{M}} \right) \]

   \[ \rho \text{H} = 7.22 \]

   c. Considering the chart on the first page of the test, which of the following acid/base indicators would be most appropriate for determination of the endpoint for a titration of a weak acid with a strong base?
   
   A) Bromphenol Blue
   
   B) Bromresol Green
   
   C) Methyl Red
   
   D) Thymol Blue (base range)
   
   E) Thymol Blue (acid range)
   
   F) None of these indicators are appropriate
   
   D) Thymol Blue (base range)
d. For which of the following would we expect an increase in entropy?

A) $\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (s)}$

B) $\text{C}_{12}\text{H}_{22}\text{O}_{11} \text{(aq)} \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11} \text{(s)}$

C) $2 \text{NH}_4\text{NO}_3 \text{(s)} \rightarrow 2 \text{N}_2 \text{(g)} + 4 \text{H}_2\text{O(g)} + \text{O}_2 \text{(g)}$

D) $2 \text{SO}_2 \text{(g)} + \text{O}_2 \text{(g)} \rightarrow 2 \text{SO}_3 \text{(g)}$

E) None of these processes

e. For which of the following substances will solubility NOT depend on pH?

A) $\text{AgCH}_3\text{COO}$

B) $\text{PbF}$

C) $\text{Mg(OH)}_2$

D) $\text{AgF}$

E) None of the above

2) (15 pts) Question 2 has 2 parts.

a. (8 pts) Sketch titration curves for 1) a titration of a strong monoprotic acid with a strong base, 2) a titration of a weak monoprotic acid with a strong base and label the following points on each curve: equivalence points, and any regions of the curves which correspond to a buffer solution. Also be sure to label the axis properly.
b. (7 pts.) Calculate the standard molar entropy change for the following reaction:

\[
\text{CO (g) + H}_2\text{O (g) } \rightarrow \text{CO}_2 (g) + \text{H}_2 (g)
\]

\[
\begin{align*}
S^0_{\text{CO}_2(g)} &= 213.7 \\
S^0_{\text{CO}(g)} &= 197.7 \\
S^0_{\text{H}_2\text{O}(g)} &= 188.8 \\
S^0_{\text{H}_2(g)} &= 130.7
\end{align*}
\]

\[
\Delta S^0_{\text{reaction}} = \left( 1(13.7) + 1(130.7) \right) - \left( 1(188.8) + 1(197.7) \right)
\]

\[
\Delta S^0_{\text{reaction}} = -42.1 \text{ J mol}^{-1} \text{ K}^{-1}
\]
3) (15 pts.) A handbook lists the $K_{sp}$ of silver carbonate ($\text{Ag}_2\text{CO}_3$) as $8.5 \times 10^{-12}$. If 0.5 g of silver carbonate is added to a 1 L flask containing 0.5 M Na$_2$CO$_3$ (aq), what will be the concentration of Ag$^+$ ions in a solution?

$$K_{sp} = [\text{Ag}^+] [\text{CO}_3^{2-}] = 8.5 \times 10^{-12}$$

$$\text{Ag}_2\text{CO}_3 (s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{CO}_3^{2-}(aq)$$

**Initial**
\begin{align*}
\text{Ag}_2\text{CO}_3 &\quad 0 \\
\text{Na}_2\text{CO}_3 &\quad 0.5 \text{M}
\end{align*}

**Change:**
\begin{align*}
+ 2x &\quad + x \\
\text{Ag}_2\text{CO}_3 &\quad \text{Equl.} \\
\text{Na}_2\text{CO}_3 &\quad 0.5 + x
\end{align*}

$$K_{sp} = [2x]^2 [0.5 + x] = 8.5 \times 10^{-12}$$

\[\text{make assumption } x \ll 0.5\]

$$4x^2 \cdot 0.5 = 8.5 \times 10^{-12}$$

$$2x^3 = 8.5 \times 10^{-12}$$

$$x = 2.06 \times 10^{-6} \rightarrow \text{Ass. is valid}$$

$$[\text{Ag}^+] = (2x) = 4.12 \times 10^{-6} \text{ M}$$
4) (15 pts) You are presented with a solution that is 0.001 M in Al\(^{3+}\), Ba\(^{2+}\) and Co\(^{3+}\) that you wish to selectively precipitate with the hydroxide anion (OH\(^-\)) according to the following equations.

\[
\begin{align*}
\text{Al(OH)}_3 & \leftrightarrow \text{Al}^{3+} + 3 \text{OH}^- \\
\text{Ba(OH)}_2 & \leftrightarrow \text{Ba}^{2+} + 2 \text{OH}^- \\
\text{Co(OH)}_3 & \leftrightarrow \text{Co}^{3+} + 3 \text{OH}^-
\end{align*}
\]

\[K_{sp} = 1.3 \times 10^{-33}\]
\[K_{sp} = 5 \times 10^{-3}\]
\[K_{sp} = 1.6 \times 10^{-44}\]

Find the minimum concentrations of OH\(^-\) that is required to begin precipitation of each cation. In which order will they precipitate as [OH\(^-\)] is increased? Is it possible to reduce each cation’s concentration in solution to below 1% of its initial concentration before the next cation begins to precipitate? Show all work to receive full credit.

\[
\text{For Al(OH)}_3, \quad Q_{sp} = \frac{[\text{Al}^{3+}][\text{OH}^-]^3}{[\text{OH}^-]^3} = 1.3 \times 10^{-33}
\]
\[[\text{OH}^-] > 1.09 \times 10^{-10} \text{ M}\]

\[
\text{For Ba(OH)}_2, \quad Q_{sp} = \frac{[\text{Ba}^{2+}][\text{OH}^-]^2}{[\text{OH}^-]^2} = 5 \times 10^{-3}
\]
\[[\text{OH}^-] > 2.23 \text{ M}\]

\[
\text{For Co(OH)}_3, \quad Q_{sp} = \frac{[\text{Co}^{3+}][\text{OH}^-]^3}{[\text{OH}^-]^3} = 1.6 \times 10^{-44}
\]
\[[\text{OH}^-] > 2.51 \times 10^{-44} \text{ M}\]
Order of precipitation:

1) Co(OH)$_3$
2) Al(OH)$_3$
3) Ba(OH)$_2$

The Al(OH)$_3$ begins to precipitate at $1.09 \times 10^{-10}$ M $\text{OH}^-$

At this $[\text{OH}^-]$ we solve for conc. of Co$^{3+}$ ions.

$$K_{sp} = 1.6 \times 10^{-44} = [\text{Co}^{3+}][1.09 \times 10^{-10}]^3$$

$$[\text{Co}^{3+}] = 1.24 \times 10^{-14} \text{M}$$

Since this is less than 1% of the original conc. it is possible to separate the cobalt + the aluminum ions.

Similarly at 2.23 M Ba(OH)$_2$ begins to precipitate

So $K_{sp} = [\text{Al}^{3+}][2.23]^3 = 1.3 \times 10^{-33}$

$$[\text{Al}^{3+}] = 1.2 \times 10^{-34} \text{M}$$

So again the separation is possible.
5) (15 pts.) Calculate the pH at each of the following points on a titration curve of 25.00 mL of 0.5 M acetic acid (CH₃COOH) with 0.5 M NaOH. (Kₐ = 1.8 x 10⁻⁵)

a. Before addition of any NaOH
b. After the addition of 12.50 mL of NaOH
c. After the addition of 25.00 mL of NaOH
d. After the addition of 40.00 mL of NaOH

a) Before

\[ \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \]

\[ K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.5-x} \]

Assume \( x \ll 0.5 \)

\[ x = 0.003 \]

\[ \text{pH} = 3.52 \text{ also solve quadratic} \]

b) 12.50 mL of NaOH

\[ \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]

\[ (0.0125 L)(0.5 \text{ M NaOH}) = 0.00625 \text{ moles NaOH} \text{ lim. React.} \]

\[ (0.035 L)(0.5 \text{ M CH}_3\text{COOH}) = 0.0175 \text{ moles CH}_3\text{COOH} \]

- So after reaction we have \( 0.0125 - 0.00625 = 0.00625 \text{ moles of CH}_3\text{COOH left. This is a conc. of } \frac{0.00625}{0.0375} = 0.166 \text{ M} \)

- The neutralization reaction has also produced 0.00625 moles of CH₃COO⁻ which corresponds to a concentration of 0.166 M CH₃COO⁻.

Since we have a buffer:

\[ \text{pH} = pK_a + \log \left( \frac{[\text{Base}]}{[\text{Acid}]} \right) \]

\[ \text{pH} = 4.74 \]
After we add 25 ml NaOH we are at the equimolar point. The hydrolysis of acetate controls the pH.

\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \]

In solution we have \( n \) moles \( \text{CH}_3\text{COO}^- \) in 50 mL.

\[
\begin{align*}
\text{Initial} & : \\
\text{CH}_3\text{COO}^- & : 0.005 \\
\text{H}_2\text{O} & : 0.0502
\end{align*}
\]

At equilibrium:

\[
\begin{align*}
\text{CH}_3\text{COO}^- & : (0.005 - x) \\
\text{H}_2\text{O} & : 0.0502 + x \\
\text{CH}_3\text{COOH} & : x \\
\text{OH}^- & : x
\end{align*}
\]

The equilibrium constant is:

\[
K = \frac{x^2}{0.05 - x}
\]

\[
\text{Assume } x \ll 0.05
\]

\[
x^2 = \left(5.55 \times 10^{-10}\right) \times (0.05)
\]

\[
x = 1.17 \times 10^{-5} = [\text{OH}^-]
\]

\[p[OH^-] = 14 - 4.92 = 9.08\]

\[
\text{pH} = 14 - 4.92 = 9.08
\]
After 40.00 mL NaOH

- we are way past the endpoint, so pH will be determined by extra OH⁻ added!!!

we have added \((0.040 \text{ L})(0.5 \text{ M NaOH}) = 0.020 \text{ moles NaOH}\)

and \((0.025 \text{ L})(0.5 \text{ M CH₃COOH}) = 0.0125 \text{ moles CH}_3\text{COOH}\)

we can see the acid is titrated away and we are left with \(0.020 - 0.0125 = 0.0075 \text{ moles of NaOH}\). So the \([\text{OH}^-] \text{ is:}\)

\[
\frac{0.0075 \text{ moles OH}^-}{0.065 \text{ L}} = 0.1154 \text{ M OH}^-
\]

\[
\rho[\text{OH}^-] = 0.93285
\]

\[
\rho \text{ pH} = 13.06
\]
6) (15 pts) Answer the three questions below.
   a. Over what pH range would the butyric acid/butyrate pair be an effective buffer? The $K_a$ of butyric acid is $1.5 \times 10^{-5}$.
   b. How many moles of butyrate ($C_4H_7O_2^-$) need to be added to a 1 L flask containing 0.75 M butyric acid to produce a buffer solution with a pH of 5.10? Assume no volume change when the butyrate is added.
   c. If 0.1 mol of $H_3O^+$ is added to the buffer prepared in b what will the new pH be?

a) An effective buffer will result if pH unit of the acids $pK_a$ so $pK_a(1.5 \times 10^{-5}) = 4.82$ an effective buffer range between $pH = 3.82 - 5.82$ is expected.

b) $5.1 = 4.82 + \log \left( \frac{[\text{butyrate}]}{[0.75]} \right)$

$[\text{butyrate}] = 1.42 \text{ M}$ so $1.42 \text{ mol}$

$c)$ If we add 0.1 mol $H_3O^+$ it will react with the butyrate ion to form butyric acid

$H_3O^+ + C_4H_7O_2^- \rightarrow C_4H_7O_2H + H_2O$

$[C_4H_7O_2^-] = 1.42 \text{ M} - 0.1 \text{ M} = 1.32 \text{ M}$

$[C_4H_7O_2H] = 0.75 \text{ M} + 0.1 \text{ M} = 0.85 \text{ M}$

$pH = 4.82 + \log \left( \frac{[1.32]}{[0.85]} \right) \therefore pH = 5.01$
**Extra Credit:** (5 pts.) The Thursday before spring break we worked a problem at the end of the class involving solubility product constants (Ksp). Briefly describe the nature of the problem and did the patient die? You must answer both correct to receive any points.

The problem involved determining whether or not a patient would die after drinking a barium solution commonly used in x-rays of the abdominal track.

- The patient would not have died.