R = 0.08206 L amt/mol K = 8.314 J/mol K

1. Consider a 1.00-L buffer made by adding 0.110 mol formic acid, HCO₂H, and 0.100 mol sodium formate, NaHCO₂, to sufficient water. Calculate the pH of the buffer (a) before any acid or base is added; (b) after the addition of 0.015 mol of HNO₃; (c) after the addition of 0.015 mol of KOH. \(K_a(HCO₂H) = 1.8 \times 10^{-4}\). (12 pt)

\[
\text{HA} \rightleftharpoons H^+ + A^- \\
K_a = \frac{[H^+][A^-]}{[HA]} \\
[H^+] = \frac{K_a[A^-]}{[HA]} \\
pH = -\log \left( \frac{K_a[A^-]}{[HA]} \right)
\]

(a) \(pH = -\log \left( 1.8 \times 10^{-4} \times \frac{0.110}{0.100} \right) = 3.70\)

(b) \(pH = -\log \left( \frac{K_a \text{ mol HA + mol H}^+ \text{ added}}{\text{mol HA} - \text{mol H}^+ \text{ added}} \right) = -\log \left( \frac{1.8 \times 10^{-4} \times (0.110 + 0.015)}{0.100 - 0.015} \right) = 3.58\)

(c) \(pH = -\log \left( \frac{K_a \text{ mol HA} - \text{mol OH}^- \text{ added}}{A^- + \text{mol OH}^- \text{ added}} \right) = -\log \left( \frac{1.8 \times 10^{-4} \times 0.110 - 0.015}{0.100 + 0.015} \right) = 3.83\)
2. If a 0.10 M solution of a weak acid has a pH of 3.8, what is the $K_a$ of the acid? (8 pt)

\[ \text{pH} = 3.8 \quad [H^+] = 10^{-3.8} = 1.58 \times 10^{-4} \]

\[ HN \rightleftharpoons H^+ + A^- \quad [HA] = 0.10 \text{ M} \]

\[ K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(1.58 \times 10^{-4})(1.58 \times 10^{-4})}{0.10} = 2.5 \times 10^{-7} \]

3. Calculate the pH of a 0.2 M solution of NH₄Cl. $K_b$ of NH₃ is $1.8 \times 10^{-5}$. (12 pt)

\[ \text{NH}_4^+ \rightleftharpoons H^+ + \text{NH}_3 \quad [H^+] = [\text{NH}_3] = x \]

\[ K_a = \frac{[\text{NH}_3][H^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \]

\[ x^2 = K_a [\text{NH}_4^+] \]

\[ x = [H^+] = \sqrt{K_a [\text{NH}_4^+]} = \sqrt{(5.6 \times 10^{-10})(0.2)} = 1.1 \times 10^{-5} \]

\[ \text{pH} = -\log (1.1 \times 10^{-5}) = 4.98 \]
4. For the titration curve below, describe (a) what is in the flask, what is it being titrated with; (b) what is the pH be at the equivalence point (<7, 7, >7) (6 pt.)

(a) weak acid 
(b) strong base 
(c) pH > 7

5. Calculate the molar solubility of silver carbonate, Ag$_2$CO$_3$, given that the solubility product constant, K$_{sp}$, of silver carbonate is $8.1 \times 10^{-12}$. (8 pt)

$$K_{sp} = [Ag^{+}]^2[CO_3^{2-}]$$

$$= (2x)^2(x)$$

$$8.1 \times 10^{-12} = 4x^3$$

$$x^3 = 2.0 \times 10^{-12}$$

$$x = 1.3 \times 10^{-4}$$

Molar solubility of Ag$_2$CO$_3$ is $1.3 \times 10^{-4}$ M.
6. Will a precipitate form when 0.150 L of 0.10 M Pb(NO₃)₂ and 0.100 L of 0.20 M NaCl are mixed together? For PbCl₂, Ksp = 1.7 x 10⁻⁵. (13 pt)

\[
\begin{align*}
0.150 \text{ L} \times 0.10 \text{ M} \ P b^{2+} &= 0.0150 \text{ mol} \ P b^{2+} \\
0.100 \text{ L} \times 0.20 \text{ M} \ Cl^- &= 0.0200 \text{ mol} \ Cl^- \\

\text{New volume} &= 0.250 \text{ L} \\
\left[ P b^{2+} \right] &= \frac{0.0150}{0.250} = 0.060 \text{ M} \\
\left[ Cl^- \right] &= \frac{0.0200}{0.250} = 0.080 \text{ M} \\
\end{align*}
\]

\[
\begin{align*}
Q &= \left[ P b^{2+} \right] \left[ Cl^- \right]^2 \\
&= (0.060)(0.080)^2 = 3.8 \times 10^{-4} \text{ M} \\

Q &> K \\
3.8 \times 10^{-4} &> 1.7 \times 10^{-5} \\
\end{align*}
\]

Since \( Q > K \), \( \text{PbCl}_2 \) will form.
7. Which of the following will be more soluble in acidic solution than in pure water? Give a brief reason why you think it is more soluble or not. (7.5 pt)

- **(a)** Mg(OH)₂ \(\text{OH}^-\) reacts with \(\text{H}^+\) → H₂O

- **(b)** BaF₂ \(\text{F}^-\) reacts with \(\text{H}^+\) → H₂F

- **(c)** PbCl₂ NO REACTION

- **(d)** CuS \(\text{S}^{2-}\) reacts with \(\text{H}^+\) → H₂S

- **(e)** CuI NO REACTION

8. Indicate whether you think there is an increase, decrease, or no change in entropy? Give a brief reason for your choice. (7.5 pt)

- **(a)** \(2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)\) Decrease, more mols of gas on left

- **(b)** \(\text{CaO}(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s)\) Decrease, gas on left, none on right

- **(c)** \(2 \text{NH}_3(g) \rightarrow \text{N}_2(g) + 3 \text{H}_2(g)\) Increase, more mols on right

- **(d)** \(2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)\) Decrease, few mols on right

- **(e)** \(\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2 \text{HCl}\) Relatively no change
9. Calculate the equilibrium constant, $K$, for the following reaction at 25°C and 1000°C. Also indicate the value of $\Delta G$ and whether the reaction is spontaneous or not at that temperature. (26 pt)

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

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$(g)</td>
<td>-395.2</td>
<td>256.2</td>
</tr>
<tr>
<td>SO$_2$(g)</td>
<td>-269.9</td>
<td>248.5</td>
</tr>
<tr>
<td>O$_2$(g)</td>
<td>0</td>
<td>205.0</td>
</tr>
</tbody>
</table>

$$\Delta H_{1000}^\circ = (2(-269.9) + 0) - (2(-395.2)) = +250.6 \text{ kJ}$$

$$\Delta S_{1000}^\circ = (2(248.5) + 205.0) - (2(256.2)) = 189.6 \frac{\text{J}}{\text{K}}$$

$$\Delta G = \Delta H - T \Delta S = +250.6 \text{ kJ} - (298 \text{ K})(189.6 \frac{\text{J}}{\text{K}})(\frac{1000 \text{ J}}{1000 \text{ J}})$$

$$= 194.1 \text{ kJ} \quad \text{NOT SPONTANEOUS}$$

$$\Delta G_{298}^\circ = +250.6 \text{ kJ} - (298 \text{ K})(189.6 \frac{\text{J}}{\text{K}})(\frac{1000 \text{ J}}{1000 \text{ J}})$$

$$= 194.1 \text{ kJ} - 28.7 \text{ kJ} \quad \text{SPONTANEOUS}$$

$$K_{298} = \frac{9.47 \times 10^{-3}}{8.71 \times 298}$$

$$\frac{K_{1000}}{1000} = \frac{9.47}{10.4}$$