1. Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$ is a weak diprotic acid with $K_{a1} = 5.9 \times 10^{-2}$ and $K_{a2} = 6.4 \times 10^{-5}$ at 25°C.

a) Write these two acid dissociation reactions for oxalic acid.

\[
\begin{align*}
\text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{H}_2\text{O}(\ell) & \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4^- (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq}) \\
\text{acid} & \quad \text{base} & \quad \text{conj base} & \quad \text{conj acid} \\
\text{HC}_2\text{O}_4^- (\text{aq}) + \text{H}_2\text{O}(\ell) & \rightleftharpoons \text{C}_2\text{O}_4^{2-} (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq}) \\
\text{acid} & \quad \text{base} & \quad \text{conj base} & \quad \text{conj acid}
\end{align*}
\]

b) Which is the stronger acid, $\text{H}_2\text{C}_2\text{O}_4$ or $\text{HC}_2\text{O}_4$? $K_{a1} > K_{a2}$.

c) Determine $K_b$ for $\text{HC}_2\text{O}_4$:

\[
K_w = K_a K_b
\]

\[
10^{-\text{pH}} = (6.4 \times 10^{-5}) K_b
\]

\[
K_b = 1.7 \times 10^{-13}
\]

2. If water is heated and placed under pressure is has a pH of 6.6. Find the $K_w$ of the water under these conditions. Determine whether it is acidic, basic, or neutral.

\[
K_w = [\text{H}^+][\text{OH}^-]
\]

In pure water, $[\text{H}^+] = [\text{OH}^-]$

Therefore the solution is \text{neutral}.

\[
K_w = [\text{H}^+]^2 = (10^{-6.6})^2 = 6.3 \times 10^{-14}
\]

3. Consider the two weak acids $\text{HX}$ (molar mass = 180 g/mol) and $\text{HY}$ (molar mass = 78 g/mol). If a solution of 16.9 g/L of $\text{HX}$ has the same pH as one containing 9.05 g/L of $\text{HY}$, which is the stronger acid?

\[
\begin{align*}
\text{HX:} & \quad \frac{16.9 \text{ g}}{180 \text{ g}} \text{ mol} \text{ L}^{-1} = 0.094 \text{ mol L}^{-1} \\
\text{HY:} & \quad \frac{9.05 \text{ g}}{78 \text{ g}} \text{ mol L}^{-1} = 0.116 \text{ mol L}^{-1}
\end{align*}
\]

$[\text{HX}] < [\text{HY}]$

$[\text{HX}]$ is the stronger acid, it takes less $\text{HX}$ to produce more $\text{H}^+$ ions.
4. Find the pH of the mixture of 0.100M in CH₃COOH ($K_a = 1.8 \times 10^{-5}$) and 0.050M in HCN ($K_a = 4.9 \times 10^{-10}$). $K_a,\text{CH}_3\text{COOH} \gg K_a,\text{HCN}$, use CH₃COOH only.

$$\text{CH}_3\text{C}_2\text{O}_2\text{H} + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{C}_2\text{O}_2^- + \text{H}_3\text{O}^+$$

Initial:
- I C E
- .1 O 0
- -x +x +x
- .1-x x x

% ionization = $\frac{[\text{CH}_3\text{C}_2\text{O}_2^-]_{eq}}{[\text{CH}_3\text{C}_2\text{O}_2\text{H}]} \times 100\% = 1.34\%$

$1.34 \times 10^{-3} = \frac{x^2}{1-x}$, weak acid approx

pH = $-\log[\text{H}_3\text{O}^+]_{eq} = 2.87$

5. Determine if each salt will form a solution that is acidic, basic, or pH-neutral.

a) (NH₄)₂SO₄: acidic
b) Na₃PO₄: basic
c) KCl: neutral
d) RbI: neutral
e) Al(NO₃)₃: acidic
f) K₂CO₃: basic
g) BaCl₂: neutral

6. Calculate the pH of a solution that is 0.00115M in HCl and 0.0100M in HClO₂ ($K_a = 1.1 \times 10^{-2}$).

$$\text{HClO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}_2^-(aq)$$

Initial:
- I C E
- .01 0 0
- -x +x +x
- .01-x 0 0

$K_a = 1.1 \times 10^{-2} = \frac{(0.0115+x)(x)}{(0.01-x)}$, weak acid approx

$1x^2 + 1.1 \times 10^{-2}x - 1.1 \times 10^{-4} = 0$

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$x = \frac{[6.34 \times 10^{-3}] \text{ or } -0.174}{2}$
7. We are dealing with a diprotic acid, which means 2 moles of H⁺ ions will react with 1 mole of ion.

\[
\text{Moles KOH} = \frac{11.1 \text{ mL} \times 1.00 \text{ mmol/L}}{\text{L}} \times \frac{1}{1000 \text{ mL}}
\]
\[
= 1.11 \times 10^{-4} \text{ moles}
\]

\[
\text{Moles of acid} = \frac{1.11 \times 10^{-4} \text{ moles}}{2}
\]
\[
= 5.55 \times 10^{-5} \text{ moles}
\]

\[
\text{H}_2\text{A} \rightarrow 2\text{H}^+ + \text{A}^{2-}
\]

Each mole of diprotic acid releases 2 moles of H⁺.

*Neutalizing an acid or a base is to add enough OH⁻ or H⁺ ions that the molar quantities are equal.*

To find the # of moles of acid in 250mL, just multiply by 10 (25mL x 10 = 250mL).

\[
\text{Moles of acid in 250mL} = 5.55 \times 10^{-3} \times 10 = 5.55 \times 10^{-2} \text{ moles}
\]

\[
\text{Molar mass Acid} = \frac{5.009}{5.55 \times 10^{-2} \text{ moles}} = 90.1 \text{ g/mol}
\]

8. Equivalence point is where the moles of H⁺ are equal to base.

Finding moles of NaOH:

\[
\text{Moles NaOH} = [\text{NaOH}] \times \text{Volume Titrated}
\]
\[
= 0.0633 \text{ M} \times (18.4 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}})
\]
\[
= 1.16 \times 10^{-3} \text{ moles}
\]

Since the acid is monoprotic, there is a 1:1 ratio; meaning the moles of acid should be the same as the equivalence point.

\[
\text{Moles of HA} = 1.16 \times 10^{-3} \text{ moles NaOH} \frac{1 \text{ mole HA}}{1 \text{ mole NaOH}} = 1.16 \times 10^{-3} \text{ moles}
\]
Since we used 0.1276g of acid,
\[
\text{molar mass } HA = \frac{0.1276g}{1.16 \times 10^{-3}\text{moles}} = 110.2 \text{ mol}^{-1}
\]

b. We can find the moles of NaOH added by multiplying the concentration by the volume.
\[
\text{moles } NaOH = (0.0633M) \times (100\text{mL} \cdot \frac{1\text{L}}{1000\text{mL}}) = 6.33 \times 10^{-4}\text{ moles } NaOH
\]
NaOH will dissociate equimolarly into Na⁺ and OH⁻. Some OH⁻ will react with the H⁺ in solution.

\[
\text{HA} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{A}^- \\
\]
\[
\begin{align*}
\text{I:} & \quad 116 \times 10^{-3}\text{mol} & 6.33 \times 10^{-4}\text{mol} & 0 \\
\text{C:} & \quad -6.33 \times 10^{-4} & -6.33 \times 10^{-4} & +6.33 \times 10^{-4} \\
\text{E:} & \quad 5.27 \times 10^{-4} & 0 & 6.33 \times 10^{-4}
\end{align*}
\]

\[
K_A = \frac{[\text{H}^+][\text{A}^-]_{eq}}{[\text{HA}]_{eq}} = \frac{(1.35 \times 10^{-4}\text{m})(0.018\text{m})}{(0.015\text{m})}
\]
\[
K_A = 1.61 \times 10^{-6}
\]

9. \(\text{CH}_3\text{NH}_3\text{Cl}\) will dissociate into \(\text{CH}_3\text{NH}_3^+\) and \(\text{Cl}^-\). Initially, it will further dissociate into \(\text{CH}_3\text{NH}_2\) and \(\text{H}^+\).

\[
K_w = K_a K_b
\]
\[
K_A = \frac{10^{-14}}{4.4 \times 10^{-4}} = 2.27 \times 10^{-11}
\]
Set up ICE Chart:

\[
\begin{align*}
\text{CH}_3\text{NH}_3^+ & \rightleftharpoons \text{H}^+ & + & \text{CH}_3\text{NH}_2 \\
\text{I:} & \quad 0.35\text{m} & 0 & 0 \\
\text{C:} & \quad -x & +x & +x \\
\text{E:} & \quad 0.35 - x & x & x
\end{align*}
\]
\[ K_A = \frac{[H^+][H_2NH_2]}{[H_2NH_3^+]} = \frac{x^2}{0.35 - x} = 2.27 \times 10^{-11} \]

*\( K_A \) value is very small, assume weak acid approximation.*

\[ \frac{x^2}{0.35} = 2.27 \times 10^{-11} \]

\[ x = 2.82 \times 10^{-6} \text{ M} = [H^+] \]

\[ pH = -\log([H^+]) = -\log(2.82 \times 10^{-6}) \]

\[ pH = 5.55 \]

\[ \frac{[H_2NH_2]}{[H_2NH_3^+]} = 2.82 \times 10^{-6} \text{ M} \]

10a. Invalid. *\( K_{sp} \) is an equilibrium value that depends on the products of solubility in a solvent.*

In \( AgNO_3 \):

\[ H_2O(l) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq) \]

\[ K_{sp} = [Ag^{+}] [Cl^{-}] = 5.5 = s^2 = (2.5 \times 10^{-3})^2 \]
\[ K_{sp} = 6.25 \times 10^{-15} \text{M} \]

b. Invalid. \( K_{sp} \) is different for each solvent. In the case for \( AgNO_3 \), we should expect \( K_{sp} \) to be lower due to its contribution of \( Ag \) solubility and different intermolecular forces.

c. Invalid. Due to the common ion effect, \( AgCl \) solubility is severely hindered.

d. Valid. \( K_{sp} \) value is low, therefore \( AgCl \) will tend to precipitate.

e. Invalid. Same reason as part c. Common ion effect is present in \( AgNO_3 \), thus lowering solubility.

IIa. In pure water:

\[ PbBr_2(s) \rightarrow Pb^{2+}(aq) + 2Br^- \]

\[ K_{sp} = [Pb^{2+}][Br^-]^2 \]

Set \( S = [Pb^{2+}] \)

and since \( [Br^-] = 2[Pb^{2+}] \), \( [Br^-] = 2S \)

\[ K_{sp} = S(2S)^2 = 4S^3 = 8.9 \times 10^{-6} \]

\[ S = 1.7 \times 10^{-2} \text{M} \]

b. In 0.20 M KBr solution:

Same thing as part a., but KBr contributes to 0.20 M of \( Br^- \). We must add this to the final \( [Br^-] \).

\[ [Br^-] = 0.20 + 2S \]

\[ K_{sp} = 5(0.20 + 2S)^2 = 8.9 \times 10^{-6} \]

We can assume 0.20 M >> 2S since \( K_{sp} \) is small.

\[ 8.9 \times 10^{-6} = 5(0.20)^2 \]

\[ S = 2.2 \times 10^{-4} \text{M} \]

c. Same method as above:

\[ [Pb^{2+}] = 0.2 + 5 \text{ due to contribution of } Pb(NO_3)_2 \]

\[ K_{sp} = 8.9 \times 10^{-6} = (0.2 + 5)(2S)^2 \]
Assume $0.2 > S$:

$$8.9 \times 10^{-6} = 0.2(2s)^2$$

$$S = 3.3 \times 10^{-2} \text{M}$$

12. We use the Henderson-Hasselbalch equation for buffer.

$$pOH = pK_b + \log \left( \frac{\text{base}}{\text{conjugate acid}} \right)$$

$K_b$ of $NH_3 = 1.8 \times 10^{-5}$

$$pOH = -\log(1.8 \times 10^{-5}) + \log \left( \frac{0.10}{0.10} \right)$$

$pOH = 4.74$

$PH = 14 - 4.74 = 9.26$

Now if we add HCl, some of the $H^+$ ions will react with $NH_3$ to form $NH_4^+$.

Before adding HCl:

moles $NH_3 = 0.1\, M \times (0.125\, L) = 0.0125\, \text{moles}$