1. What is the pH of the solutions:
   a. 0.0150 M nitric acid
   b. 0.0150 M nitrous acid
   c. 0.0150 M ammonia
   d. 0.0150 M sodium hydroxide

Answer: **Part a:** Because this is a strong, monoprotic acid, the concentration of the hydrogen ion can be determined from the concentration of the strong acid:

$$\text{HNO}_3(\text{aq}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{NO}_3^-(\text{aq}) \quad K \gg 1$$

The vast majority of the species are products such that:

$$[\text{HNO}_3]_0 = [\text{H}^+]$$ so $$[\text{H}^+] = 0.0150 \text{ M}$$

$$pH = -\log[\text{H}^+] = -\log(0.0150 \text{ M}) = 1.824$$

**Part b:** Because this is a weak acid, we will need to consider the equilibrium (where now $$K_a < 1$$), so the majority of the species at equilibrium are water and unionized acid (HNO$_2$):

$$\text{HNO}_2(\text{aq}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{NO}_2^-(\text{aq})$$

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x^2}{0.0150 - x}$$

$$[\text{HNO}_2]_0 = 0.015 \text{ M}$$

$$x = \frac{-K_a + \sqrt{K_a^2 + 4(0.0150 \text{ M})(K_a)}}{2} = 0.00238 \text{ M}$$

$$pH = -\log(0.00238) = 2.623$$

**Part c:** Because this is a weak base, we will need to consider the equilibrium (where $$K_b < 1$$), so the majority of the species at equilibrium are water and unionized base (NH$_3$):

$$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^- (\text{aq}) + \text{NH}_4^+ (\text{aq})$$

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = \frac{x^2}{0.0150 - x}$$

$$[\text{NH}_3]_0 = 0.015 \text{ M}$$

$$x \approx \sqrt{K_b(0.0150 \text{ M})} = 0.000520 \text{ M}$$

$$pOH = 14 - pH = 14 - \log(0.000520) = 10.716$$
Part d: Because this is a strong base, the concentration of the hydroxide ion can be determined from the concentration of the strong base:

\[ \text{NaOH(aq)} \rightleftharpoons \text{Na}^+(aq) + \text{OH}^-(aq) \quad K \gg 1 \]

The vast majority of the species are products such that:

\[ [\text{NaOH}]_0 = [\text{OH}^-] \quad \text{so} \quad [\text{OH}^-] = 0.0150 \text{ M} \]

\[ \text{pH} = 14 - \text{pOH} = 14 - \log[\text{OH}^-] = 14 - \log(0.0150 \text{ M}) = 12.176 \]

2. Calculate the molar concentration of the hydrogen ion in 0.100 M carbonic acid. Why can the pH of carbonic acid be calculated by only considering the first ionization \((K_{a1})\)?

Answer: Carbonic acid is diprotic, so there are two ionizable hydrogens and is also weak. This means that the concentration of the hydrogen ion (and therefore, the pH) will be affected by two equilibria:

\[
\text{H}_2\text{CO}_3(aq) \rightleftharpoons H^+(aq) + \text{HCO}_3^-(aq) \quad K_{a1} = \frac{[H^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{0.100 - x}
\]

\[
\text{HCO}_3^-(aq) \rightleftharpoons H^+(aq) + \text{CO}_3^{2-}(aq) \quad K_{a2} = \frac{[H^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(0.000205 + x)x}{0.000205 - x}
\]

\[ x \cong \sqrt{K_{a1}(0.100 \text{ M})} = 0.000205 \text{ M} = [H^+] \quad \text{H}_2\text{CO}_3, \text{ first ionization} \]

There will not be a contribution to \([H^+]\) from the second ionization (adding \(4.8 \times 10^{-11}\) to \(2.05 \times 10^{-4}\) doesn’t change the concentration of \(2.05 \times 10^{-4} \text{ M}\)). Therefore,

\[ \text{pH} = -\log[H^+] = -\log(0.000205) = 3.688 \]

3. What is the pH of the solutions:
   a. 0.100 M sodium bromide
   b. 0.100 M sodium formate
   c. 0.100 M ammonium bromide
   d. 0.100 M ammonium formate

Will adding lead(II) nitrate affect the pH of solutions a or c?

Answer: To determine the acidity of a salt, you will need to consider the role of the anion separate from the cation in the acid/base chemistry of the solution. Namely is the anion and/or the cation a conjugate species of a weak acid or base. If it is, it will affect the pH of the solution. Therefore, our procedure will be to first separate into
ions, then consider the chemistry of the ion in water and any resulting weak species (and the corresponding equilibrium).

**Part a:** Sodium bromide dissociates into sodium ions (Na⁺) and bromide ions (Br⁻).
First, considering the cation: \( \text{Na}^+ (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NaOH}(aq) + \text{H}^+ (aq) \). Because sodium hydroxide is a strong base (and the equilibrium constant for the process is very large), sodium ions (the conjugate “acid”) will not react with water (the equilibrium constant for the process is so very small, it is essentially zero). Therefore, sodium ions in solution do not contribute to the pH.
Second, considering the cation: \( \text{Br}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HBr}(aq) + \text{OH}^- (aq) \). Because hydrobromic acid is a strong acid (and the equilibrium constant for the process is very large), bromide ions (the conjugate “base”) will not react with water (the equilibrium constant for the process is so very small, it is essentially zero). Therefore, bromide ions in solution do not contribute to the pH.

The pH of the solution overall is 7.

**Part b:** Sodium formate dissociates into sodium ions and formate ions (HCOO⁻).
Using the same discussion above, sodium ions do not contribute to the pH.
Considering the anion: \( \text{HCOO}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCOOH}(aq) + \text{OH}^- (aq) \). Because formic acid is a weak acid (and the equilibrium constant for the process less than 1 – 1.7×10⁻⁴), formate ions (the conjugate base) will react with water (the equilibrium constant for the process, \( K_b \), can be calculated using \( K_a \)). Therefore, formate ions in solution do contribute to the pH and we will calculate that based on the equilibrium:

\[
\begin{align*}
\text{HCOO}^- (aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{HCOOH}(aq) + \text{OH}^- (aq) \\
I & 0.100 \text{ M} \quad 0 \quad 0 \\
C & -x \quad x \quad x \\
E & 0.100 - x \quad x \quad x \\
\end{align*}
\]
\[
x \approx \sqrt{K_b(0.100 \text{ M})} = 2.4 \times 10^{-6} \text{ M} = [\text{OH}^-] \quad \text{pH} = 14 - \log[\text{H}^+] = 14 - \log(2.4 \times 10^{-6}) = 8.39
\]

**Part c:** Ammonium bromide dissociates into ammonium ions (NH₄⁺) and bromide ions.
Considering the cation: \( \text{NH}_4^+ (aq) \rightleftharpoons \text{NH}_3(aq) + \text{H}^+ (aq) \). Because ammonia is a weak base (and the equilibrium constant for the process less than 1 at 1.8×10⁻⁵), ammonium ions (the conjugate acid) will react with water (the equilibrium constant
for the process, $K_a$, can be calculated using $K_b$. Therefore, ammonium ions in solution do contribute to the pH and we will calculate that based on the equilibrium:

\[
\begin{align*}
\text{NH}_4^+ (aq) & \rightleftharpoons \text{NH}_3 (aq) + \text{H}^+ (aq) \\
K_a &= \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}
\end{align*}
\]

For this discussion, we need to consider this equilibrium as well. We will consider the equilibrium constant for the weak acid (ammonium) and weak base (formate):

\[
\begin{align*}
K_a (\text{NH}_4^+) &= 5.6 \times 10^{-10} \\
K_b (\text{HCOO}^-) &= 5.9 \times 10^{-11}
\end{align*}
\]

Because the equilibrium constant for ammonium ($K_a$) is higher than for formate ($K_b$), the solution will be acidic (however slight).

The final question was will adding Pb(NO$_3$)$_2$ affect the pH when adding to solutions a or c (or those solutions containing bromide ions)? Lead(II) ions will react with bromide ions forming the precipitate, PbBr$_2$. Removing bromide ions from solution will not affect any equilibrium that would affect the pH.