1. The pH of a 0.10 M solution of NaH₂PO₄ is 4.5. Write a net ionic equation that accounts for this observation.

\[
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}
\]

2. HCN is a weak acid. The pH of a 0.10 M HCN solution is 5.2.

a. Calculate the molarity of H₃O⁺ in this solution.

\[
\text{pH} = -\log [\text{H}_3\text{O}^+] \Rightarrow [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.2} = 6.3 \times 10^{-6} \text{ M}
\]

(technically 1 sig fig)

b. Calculate the molarity of CN⁻ and HCN in this same solution.

\[
\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-\]

\[
\begin{array}{c|c|c|c|c}
\text{I(M)} & \text{0.10} & - & \text{X} & \text{0} \\
\text{C(M)} & \text{-X} & +X & +X & \text{X} \\
\text{E(M)} & \text{0.10-X} & \text{X} & \text{X} & \text{X} \\
\end{array}
\]

and \(X = 6.3 \times 10^{-6} \text{ M} = [\text{CN}^-] \Rightarrow [\text{HCN}] = (0.10 - 6.3 \times 10^{-6}) \text{ M} = 0.10 \text{ M}

\]

c. Use the above results to calculate a numerical value for \(K_a\) for HCN. Compare your value with that given in your text.

\[
K_a = \frac{[\text{H}_3\text{O}^+] [\text{CN}^-]}{[\text{HCN}]} = \frac{(6.3 \times 10^{-6})^2}{0.10} = 4 \times 10^{-10}
\]

vs. Silberberg p. 762 \(K_a = 6.2 \times 10^{-10}\)

so our estimate is \(\frac{(4-6.2) \times 10^{-10}}{6.2 \times 10^{-10}} \times 100 \% = 35 \% \text{ off}\)

(not bad!)
H$_3$O$^+$ (aq) + HCOO$^-$ (aq) $\rightarrow$ H$_2$O(l) + HCOOH (aq)

Moreover, since we still have a tiny bit of HCOO$^-$ in sol'n, we suppose (by Le Châtelier's principle) the run of HCOOH vs H$_2$O to (re-) generate H$_3$O$^+$.

Name **KEY**

**pH and Buffers ASA (cont.)**

3. A student is asked to use 0.10 M formic acid, HCOOH, and 0.10 M sodium formate, HCOONa to prepare a buffer solution having a pH of 3.40. $K_a$ for HCOOH is $1.8 \times 10^{-4}$.

$$\Rightarrow pK_a = -\log K_a = 3.745$$

a. Identify the weak acid and its conjugate weak base in this buffer system.

$$\text{HC}OO\text{H (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-\text{(aq)}$$

**weak acid**

**weak conjugate base**

b. Calculate the volumes of the two solutions that need to be mixed to make 1.00 liter of this buffer.

$$pH = pK_a + \log \frac{[\text{HCOO}^-]_0}{[\text{HCOOH}]_0}$$ (Henlema- Kabal batch - neglect the runs of both HCOOH + HCOO$^-$+ H$_2$O)

$$\log \frac{[\text{HCOO}^-]_0}{[\text{HCOOH}]_0} = pH - pK_a \Rightarrow \frac{[\text{HCOO}^-]_0}{[\text{HCOOH}]_0} = 10^{(pH - pK_a)}$$

$$= 10^{(3.40 - 3.745)} = 0.452$$ (only 2 sfg figs)

(continued...)

c. When 5 drops of 0.10 M HCl were added to 20 mL of this buffer, the pH went from 3.40 to 3.37. Write a net ionic equation that explains why the pH change was much smaller than it would have been if this volume of HCl were added to 20 mL of distilled water.

Let $V_a$ = vol of HCOOH sol'n used and $V_b$ = vol of HCOO-sol'n used

$$V_a + V_b = 1.00 \text{ L} \Rightarrow V_b = 1.00 \text{ L} - V_a$$

In buffer, $[\text{HCOOH}]_0 = \frac{(0.10M) V_a}{1.00 \text{ L}}$ and $[\text{HCOO}^-] = \frac{(0.10M) V_b}{1.00 \text{ L}}$

(i.e. the 2 individual sol'n get diluted when they're mixed)

$$\frac{[\text{HCOO}^-]_0}{[\text{HCOOH}]_0} = \frac{(0.10M) V_b}{1.00 \text{ L}} = \frac{V_b}{V_a} = \frac{1.00 \text{ L} - V_a}{V_a} = 0.452$$

$$1.00 \text{ L} - V_a = 0.452 V_a \Rightarrow 1.452 V_a = 1.00 \text{ L} \Rightarrow V_a = 0.69 \text{ L}$$

$V_b = 0.31 \text{ L}$