Equilibrium V: Acid-Base Buffers and Titrimetry

1. Calculate the pH of the solution which is prepared to be 0.10 M in nitrous acid and 0.15 M sodium nitrite.

$$HNO_2 + H_2O \rightleftarrows H_3O^+ + NO_2^- \qquad K_a = 4.5\times10^{-4}$$

Recall that for a typical acid-base buffer of relatively high concentration, the equilibrium concentrations of the acid and conjugate base differ very little from their analytical concentrations

$$K_a = 4.5\times10^{-4} = \frac{[H_3O^+](0.15\text{ M})}{(0.10\text{ M})}$$

$$[H_3O^+] = 3.0\times10^{-4}\text{ M} \qquad \text{pH} = 3.5$$

2. What is the calculated pH of the buffer solution formed by dissolving 4.2 g of acetic acid and 9.0 g of sodium acetate in water and diluting to 500.0 mL?

$$C_{HOAc} = \frac{4.2\text{ g }CH_3COOH / 60.05\frac{g}{mol}}{0.5000\text{ L}} = 0.140\text{ M} \qquad C_{OAc^-} = \frac{9.0\text{ g }NaCH_3COO / 82.04\frac{g}{mol}}{0.5000\text{ L}} = 0.22\text{ M}$$

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \cong \frac{C_{CH_3COO^-}}{C_{CH_3COOH}}[H_3O^+]$$

$$[H_3O^+] = \frac{C_{CH_3COOH}}{C_{CH_3COO^-}}(1.75\times10^{-5}) = \frac{0.14}{0.22}(1.75\times10^{-5}) = 1.11\times10^{-5}\text{ M}$$

$$p\text{H} = 4.95$$

3. A 10.0 mL quantity of 0.1 M HCl is mixed with 95 mL of 0.15 M sodium nitrite. What is the pH of the new solution?

$$n_{NO_2^-} = 95 \text{ mL} \times 0.15 \text{ M} = 14.25 \text{ mmol } NO_2^- \qquad n_{HCl} = 10.0 \text{ mL} \times 0.1 \text{ M} = 1.0 \text{ mmol HCl}$$

$$HCl \quad + \quad NO_2^- \quad \rightleftarrows \quad HNO_2 \quad + \quad Cl^-$$

$$n_{HNO_2,\text{formed}} = 1.0 \text{ mmol HCl} \times \tfrac{1 \text{ mmol } HNO_2}{1 \text{ mmol HCl}} = 1.0 \text{ mmol } HNO_2 \qquad C_{HNO_2} = \frac{1.0 \text{ mmol } HNO_2}{105 \text{ mL}} = 9.52 \times 10^{-3} \text{ M}$$

$$n_{NO_2^-,\text{remaining}} = 14.25 \text{ mmol } NO_2^- - 1.0 \text{ mmol HCl} \times \tfrac{1 \text{ mmol } NO_2^-}{1 \text{ mmol HCl}} = 13.25 \text{ mmol } NO_2^-$$

$$C_{NO_2^-} = \frac{13.25 \text{ mmol } NO_2^-}{105 \text{ mL}} = 0.126 \text{ M}$$

$$HNO_2 \quad + \quad H_2O \quad \rightleftarrows \quad H_3O^+ \quad + \quad NO_2^-$$

$$4.5 \times 10^{-4} = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$[H_3O^+] = \frac{9.52 \times 10^{-3} \text{ M}}{0.126 \text{ M}}(4.5 \times 10^{-4}) = 3.39 \times 10^{-5} \text{ M} \qquad pH = 4.47$$

4. What is the calculated pH of the solution formed by mixing 10.0 mL of 0.15 M NaOH with 85 mL of 0.10 M benzoic acid?

This problem starts as simple stoichiometry problema dn ends as a buffer problem.
Start with the acid-base neutralization:

$$NaOH \quad + \quad C_6H_5COOH \quad \rightarrow \quad NaO_2CC_6H_5 \quad + \quad H_2O$$

$$n^{\text{initial}}_{C_6H_5COOH} = 0.085 \text{ L} \times 0.10 \text{ M } C_6H_5COOH = 0.0085 \text{ mol } C_6H_5COOH$$

$$n^{\text{added}}_{NaOH} = 0.0100 \text{ L} \times 0.15 \text{ M NaOH} = 0.0015 \text{ mol NaOH}$$

$$n^{\text{remaining}}_{C_6H_5COOH} = 0.0085 \text{ mol } C_6H_5COOH - 0.0015 \text{ mol NaOH} \times \left(\frac{1 \text{ mol } C_6H_5COOH}{1 \text{ mol NaOH}}\right) = 0.0070 \text{ mol } C_6H_5COOH$$

$$n^{\text{made}}_{C_6H_5CO_2^-} = 0.0015 \text{ mol NaOH} \times \left(\frac{1 \text{ mol } C_6H_5CO_2^-}{1 \text{ mol NaOH}}\right) = 0.0015 \text{ mol } C_6H_5CO_2^-$$

Now, work out the equilibrium. This is a buffer solution so dividing each of the quantities by volume is convenient but not necessary.

$$C_6H_5COOH \quad + \quad H_2O \quad \rightleftarrows \quad C_6H_5CO_2^- \quad + \quad H_3O^+$$

$$K_a = \frac{[H_3O^+][C_6H_5CO_2^-]}{[C_6H_5COOH]} = \frac{[H_3O^+](0.0015 \text{ mol})}{0.0070 \text{ mol}} = 6.3 \times 10^{-5}$$

$$[H_3O^+] = 2.94 \times 10^{-4} \text{ M} \qquad pH = 3.53$$