# Systematic Approach to pH, Equilibrium, and Titrimetry

Use any tools you wish to perform these calculations. Some of these problems can best be solved by using mathematical or technological aids (successive approximations, quadratic formula, calculator solver, etc.). Computer use is recommended wherever appropriate and possible.

Buffer Systems

9. What is the pH of a mixture of 10 mL of 0.2 M sodium pyruvate and 10 mL of 0.3 M pyruvic acid?

$$HOpyr + H_2O \rightleftharpoons Opyr^- + H_3O^+$$
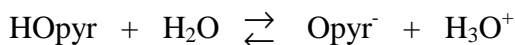
$$n_{Opyr^-} = 10mL \times 0.2M = 2 \text{ mmol } Opyr^-$$
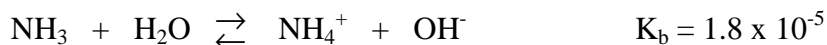
$$n_{HOpyr} = 10mL \times 0.3M = 3 \text{ mmol } HOpyr$$

$$3.2 \times 10^{-3} = [H_3O^+] \times \frac{2 \text{ mmol}}{3 \text{ mmol}}$$

$$[H_3O^+] = 0.0048 \text{ M}$$

$$pH = 2.32$$

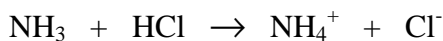10. Calculate the approximate pH of the buffer solution which is 0.30 M in NH_4Cl dissolved 0.1 M NH_3.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} = [OH^-] \times \frac{0.3 \text{ M}}{0.1 \text{ M}}$$

$$[OH^-] = 6.0 \times 10^{-6} \text{ M}$$

$$pH = 8.78$$

11. What would the pH be if 1.0 mL of 0.5 M HCl were added to 200.0 mL of the buffer solution above? Does the solution buffer pH?

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$

$$\text{new } C_{NH_3} = \frac{200.0 \text{ mL}(0.1 \text{ M NH}_3) - 1.0 \text{ mL}(0.5 \text{ M HCl})(\frac{1\,NH_3}{1\,HCl})}{201.0 \text{ mL}} = 0.097 \text{ M NH}_3$$
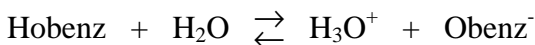
$$\text{new } C_{NH_4^+} = \frac{200 \text{ mL}(0.3 \text{ M NH}_4^+) + 1.0 \text{ mL}(0.5 \text{ M HCl})(\frac{1\,NH_4^+}{1\,HCl})}{201.0 \text{ mL}} = 0.301 \text{ M NH}_4^+$$

$$[OH^-] = 1.8 \times 10^{-5} \times \frac{0.097 \text{ M}}{0.301 \text{ M}} = 5.8 \times 10^{-6} \text{ M OH}^-$$

$$pH = 8.76$$

12. What mass of sodium benzoate should be added to 500.0 mL of 0.01 M benzoic acid to make a buffer of pH 4.0?

Benzoic acid (HObenz), 144.1 g/mol $K_a = 6.3 \times 10^{-5}$

$$\text{Hobenz} + H_2O \rightleftharpoons H_3O^+ + \text{Obenz}^-$$

$$n_{HObenz} = 500.0 \text{ mL} \times 0.01 \text{ M} = 5.0 \text{ mmol HObenz}$$

$$K_a = [H_3O^+] \frac{C_{Obenz^-}}{C_{HObenz^-}} = [H_3O^+] \frac{n_{Obenz^-}}{n_{HObenz^-}}$$

$$[H_3O] = 10^{-4.0} = 1.0 \times 10^{-4} \text{ M}$$

$$n_{Obenz^-} = \frac{(6.3 \times 10^{-5}) \times (5.0 \text{ mmol})}{1.0 \times 10^{-4} \text{ M}} = 3.15 \text{ mmol NaObenz}$$

$$m_{NaObenz} = 3.15 \text{ mmol} \times 144.1 \text{g}/_{mol}$$
$$m_{NaObenz} = 454 \text{ mg NaObenz}$$

13. Try this for fun. What is the approximate pH of the solution which is 0.1 M acetic acid in 0.1 M ammonia?

14. Calculate the pH of the solution at each of the volumes shown during the titration of 25 mL of 0.10 M sulfanilic acid (K_a = 5.9 x 10^{-4}) with 0.10 M NaOH.

a. 0 mL

$$K_a = \frac{[H_3O^+]^2}{0.10-[H_3O^+]} \approx \frac{[H_3O^+]^2}{0.10}$$

$$[H_3O^+]=\sqrt{5.9\times10^{-5}} = 7.68\times10^{-3} \text{ M}$$

pH=2.11

b. 15 mL

$n_{HOsulf \text{ available}}$ = 25 mL×0.10 M = 2.5 mmol

$n_{HOsulf \text{ reacted}}$ =15 mL×0.10 M ×$\frac{1 \text{ HOsulf}}{1 \text{ NaOH}}$ =1.5 mmol

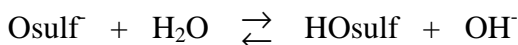$n_{HOsulf \text{ remaining}}$ = 2.5 mmol−1.5 mmol =1.0 mmol

$n_{Osulf^- \text{ produced}}$ =1.5 mmol

$$5.9\times10^{-4} =[H_3O^+]\frac{1.5 \text{ mmol}}{1.0 \text{ mmol}}$$

$$[H_3O^+]=3.93\times10^{-4} \text{ M}$$

pH=3.41

c. 25 mL

EQUIVALENCE POINT: All sulfanilic acid converted to sulfanilate

$$Osulf^- + H_2O \rightleftarrows HOsulf + OH^-$$

n_{NaOH} = 40 mL×0.10 M=4.0 mmol NaOH

n_{HOsulf} = 2.5 mmol = $n_{NaOH \text{ reacted}}$

$n_{NaOH \text{ remaining}}$ = 4 mmol-2.5 mmol=1.5 mmol

$$C_{NaOH} = \frac{1.5 \text{ mmol}}{65 \text{ mL}} = 0.0231 \text{ M NaOH}$$

pOH=1.6
pH=12.4

d. 40 mL

Excess strong base

$$n_{Osulf^-} = 25 \text{ mL} \times 0.10 \text{ M} = 2.5 \text{ mmol}$$

$$C_{Osulf^-} = \frac{2.5 \text{ mmol}}{50.0 \text{ mL}} = 0.050 \text{ M}$$

$$K_b = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-4}} = 1.69 \times 10^{-11}$$

$$K_b = \frac{[OH^-]^2}{0.05 - [OH^-]} \approx \frac{[OH^-]^2}{0.05}$$

$$[OH^-] = 9.2 \times 10^{-7} \text{ M}$$

pH=7.96

15. Use a spreadsheet program and determine the entire titration curve for question 14 from 0-50 mL added base. Use only as many points as you feel necessary to adequately define the curve.