Chem 220

Practice Problem Set Seven

You should memorize the buffer formulas. They look like the K_a definition but have added restrictions.

$$K_a = \frac{[H^+]M_{NaA}}{M_{HA}} \qquad \text{if } [H^+] \text{ and } [OH^-] << M_{NaA} \text{ and } M_{HA}$$

$$K_a = \frac{[H^+]M_{B}}{M_{BHCl}} \qquad \text{if } [H^+] \text{ and } [OH^-] << M_{B} \text{ and } M_{BHCl}$$

The problems on Rain page 81-82 demonstrate the properties of a buffer.

- pH is unchanged by dilution (as long as the restrictions hold.)
- pH change due to added strong acid or base is resisted (since strong acids or bases are exchanged for weak acids and bases.)

Part 1. Try problems 4C-6, 4C-7, and 4C-8 that use the buffer equation.

Part 2. Try problems 4C-9, 4C-10, 4C-11, 4C-12, and 4C-13

Part 3. Use the titrations on the web site (move the slider bar to change variables) to review the answers to 4D-1, 4D-2, 4D-3, 4D-4, and 4D-5, and then try problems 4D-8, 4D-9, and 4D-10.

You should memorize the buffer formulas. They look like the K_a definition but have added restrictions.

$$K_a = \frac{[H^+]M_{NaA}}{M_{HA}} \quad \text{if } [H^+] \text{ and } [OH^-] << M_{NaA} \text{ and } M_{HA}$$

$$K_a = \frac{[H^+]M_{B}}{M_{BHCl}} \quad \text{if } [H^+] \text{ and } [OH^-] << M_{B} \text{ and } M_{BHCl}$$

Many of these problems demonstrate the properties of a buffer.

- pH is unchanged by dilution (as long as the restrictions hold.)
- pH change due to added strong acid or base is resisted (since strong acids or bases are exchanged for weak acids and bases.)

4C-6 pH of a solution containing 0.75 M lactic acid and 0.25 M sodium lactate.
Use the buffer formula:

$$1.4\times10^{-4} = \frac{[H^+]M_{NaA}}{M_{HA}} = \frac{[H^+](0.25)}{0.75} \text{ if } [H^+] \text{ and } [OH^-] << .25 \text{ and } .75$$

$[H^+] = 4.20\times10^{-4}$; pH = 3.38 *Yes*, 10^{-4} and 10^{-11} << 0.25 and 0.75

4C-7 pH of a solution containing 0.25 M NH_3 and 0.40 M NH_4Cl.
Use the buffer formula:

$$5.70\times10^{-10} = \frac{[H^+]M_{B}}{M_{BHCl}} = \frac{[H^+](0.25)}{0.40} \text{ if } [H^+] \text{ and } [OH^-] << .25 \text{ and } .40$$

$[H^+] = 9.12\times10^{-10}$; pH = 9.04 *Yes*, 10^{-10} and 10^{-5} << 0.25 and 0.40

4C-8 Calculate the ratio of sodium benzoate to benzoic acid that will produce a pH 4.30 buffer. Use the buffer formula:

$$6.28\times10^{-5} = \frac{[H^+]M_{NaA}}{M_{HA}} = \frac{(10^{-4.30})M_{NaA}}{M_{HA}}; \quad \frac{M_{NaA}}{M_{HA}} = 1.25$$

4C-9 What is the pH of 70 g NH_4Cl and 600 mL concentrated aqueous NH_3 (14.5 M) diluted to 1.0 L ?

$$\frac{70 \text{ g } NH_4Cl}{L}\,\frac{\text{mol } NH_4Cl}{53.49 \text{ g } NH_4Cl} = 1.31 \text{ M } NH_4Cl \qquad \frac{600 \text{ mL}}{1000 \text{ mL}}\,14.5 \text{ M } NH_3 = 8.70 \text{ M } NH_3$$

Buffer! $10^{-9.244} = \frac{[H^+](8.70)}{1.31}$; pH = **10.066** *Yes*, 10^{-4} and 10^{-10} << 1.31 and 8.70

What happens to pH if dilute 5 mL buffer to 500 mL using water?

$10^{-9.244} = \frac{[H^+](8.70/100)}{1.31/100}$; pH = **10.066** *Yes*, 10^{-4} and 10^{-10} << 0.0131 and 0.0870

The pH remains unchanged as long as the assumptions hold.
(Using the K, charge, and mass balance method shows diluting to 5 L gives pH = 10.03, diluting to 20 L gives pH = 9.94)

4C-10 How does the pH of 400 mL of water change when

a. 100 mL 0.0500 M NaOH is added?

Dilution! $\frac{100}{100+400}$ 0.0500 M NaOH = 0.0100 M NaOH; pH = **12.000**

pH 12 is a 5 order increase from pH 7 so $[H^+]$ changes by 10^5

b. 100 mL 0.0500 M HCl is added?

Dilution! $\frac{100}{100+400}$ 0.0500 M HCl = 0.0100 M HCl; pH = **2.000**

pH 2 is a 5 order decrease from pH 7 so $[H^+]$ changes by 10^5

4C-11 How does pH of 400 mL of 0.200 M NH_3 and 0.300 M NH_4Cl change when

$10^{-9.244} = \frac{[H^+]0.200}{0.300}$; pH = **9.068** *Yes*, 10^{-9} and 10^{-5} << 0.200 and 0.300

a. 100 mL of 0.0500 M NaOH is added?

Dilution! $\frac{400}{400+100}$ 0.300 M NH_4^+ = 0.240 M NH_4^+

$\frac{400}{400+100}$ 0.200 M NH_3 = 0.160 M NH_3

$\frac{100}{400+100}$ 0.050 M NaOH = 0.010 M NaOH

Reaction! Strong base NaOH will convert NH_4^+ to NH_3. Calculate new M.
(M are just the recipe, this is an equivalent, easier, recipe.)

$$0.240\text{ M }NH_4^+ - 0.010\text{ M NaOH}\frac{1\text{ mol }NH_4^+}{1\text{ mol NaOH}} = 0.230\text{ M }NH_4^+$$

$$0.160\text{ M }NH_3 + 0.010\text{ M NaOH}\frac{1\text{ mol }NH_3}{1\text{ mol NaOH}} = 0.170\text{ M }NH_3.$$

Buffer! $10^{-9.244} = \frac{[H^+]0.170}{0.230}$; pH = **9.113**

Yes, 10^{-9} and 10^{-5} << 0.170 and 0.230

pH changes from 9.068 to 9.113, much less than from pH 7 to 12 in 4C-10a!

b. 100 mL of 0.0500 M HCl is added?

Dilution! $\frac{400}{400+100}$ 0.300 M NH_4^+ = 0.240 M NH_4^+

$\frac{400}{400+100}$ 0.200 M NH_3 = 0.160 M NH_3

$\frac{100}{400+100}$ 0.050 M HCl = 0.010 M HCl

Reaction! Strong acid HCl will convert NH_3 to NH_4^+. Calculate new M.

$$0.160\text{ M }NH_3 - 0.010\text{ M HCl}\frac{1\text{ mol }NH_3}{1\text{ mol HCl}} = 0.150\text{ M }NH_3$$

$$0.240\text{ M } NH_4^+ + 0.010\text{ M HCl}\frac{1\text{ mol } NH_4^+}{1\text{ mol HCl}} = 0.250\text{ M } NH_4^+$$

Buffer! $10^{-9.244} = \frac{[H^+]0.150}{0.250}$; pH = **9.022**

Yes, 10^{-9} and 10^{-5} << 0.150 and 0.250

pH changes from 9.068 to 9.022, much less than from pH 7 to 2 in 4C-10b!

4C-12 What is the pH of 20.00 mL of 0.0800 M NH_3 added to

a. 40.00 mL of water?

Dilution! $\frac{20.00}{20.00+40.00}0.0800\text{ M } NH_3 = 0.02667\text{ M } NH_3$

$K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = 10^{-9.244}$; $[H^+][OH^-] = 10^{-14}$

charge: $[H^+] + [NH_4^+] = [OH^-]$

mass: $0.02667 = [NH_3] + [NH_4^+]$

solve: $[H^+] = 1.481\times10^{-11}$; pH = **10.829**

b. 40.00 mL of 0.0300 M HCl?

Dilution! $\frac{20.00}{20.00+40.00}0.0800\text{ M } NH_3 = 0.02667\text{ M } NH_3$

$\frac{40.00}{20.00+40.00}0.0300\text{ M HCl} = 0.0200\text{ M HCl}$

Reaction! Strong acid HCl will convert NH_3 to NH_4^+. Calculate new M.

$$0.026667\text{ M } NH_3 - 0.0200\text{ M HCl}\frac{1\text{ mol } NH_3}{1\text{ mol HCl}} = .006667\text{ M } NH_3$$

$$0.0200\text{ M HCl}\frac{1\text{ mol } NH_4Cl}{1\text{ mol HCl}} = 0.0200\text{ M } NH_4Cl$$

Buffer! $K_a = \frac{[H^+]0.006667}{0.0200} = 10^{-9.244}$; $[H^+] = 1.710\times10^{-9}$; pH = **8.767**

Yes, 10^{-9} and 10^{-5} << 0.006667 and 0.0200

c. 40.00 mL of 0.0300 M NH_4Cl?

Dilution! $\frac{20.00}{20.00+40.00}0.0800\text{ M } NH_3 = 0.02667\text{ M } NH_3$

$\frac{40.00}{20.00+40.00}0.0300\text{ M } NH_4Cl = 0.0200\text{ M } NH_4Cl$

Buffer! $K_a = \frac{[H^+]0.026667}{0.0200} = 10^{-9.244}$; $[H^+] = 4.276\times10^{-10}$; pH = **9.369**

Yes, 4×10^{-10} and 2×10^{-5} << 0.026667 and 0.0200

d. 40.00 mL of 0.0400 M HCl?

Dilution! $\frac{20.00}{20.00+40.00}$ 0.0800 M NH_3 = 0.02667 M NH_3

$\frac{40.00}{20.00+40.00}$ 0.0400 M HCl = 0.02667 M HCl

Reaction! Strong acid HCl will convert NH_3 to NH_4^+. Calculate new M.

$$0.026667 \text{ M NH}_3 - 0.026667 \text{ M HCl}\frac{1 \text{ mol NH}_3}{1 \text{ mol HCl}} = .00000 \text{ M NH}_3$$

$$0.026667 \text{ M HCl}\frac{1 \text{ mol NH}_4\text{Cl}}{1 \text{ mol HCl}} = 0.02667 \text{ M NH}_4\text{Cl}$$

$K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = 10^{-9.244}$; $[H^+][OH^-] = 10^{-14}$

charge: $[H^+] + [NH_4^+] = [OH^-] + [Cl^-]$

mass: $0.026667 = [NH_3] + [NH_4^+]$; $0.026667 = [Cl^-]$

solve: $[H^+] = 3.903\times10^{-6}$; pH = **5.409**

e. 40.00 mL of 0.0400 M NH_4Cl?

Dilution! $\frac{20.00}{20.00+40.00}$ 0.0800 M NH_3 = 0.02667 M NH_3

$\frac{40.00}{20.00+40.00}$ 0.0400 M NH_4Cl = 0.02667 M NH_4Cl

Buffer! $K_a = \frac{[H^+]0.026667}{0.02667} = 10^{-9.244}$; $[H^+] = 5.702\times10^{-10}$; pH = **9.244**

Yes, 6×10^{-10} and 2×10^{-5} << 0.026667 and 0.026667

f. 40.00 mL of 0.0400 M NaOH?

Dilution! $\frac{20.00}{20.00+40.00}$ 0.0800 M NH_3 = 0.02667 M NH_3

$\frac{40.00}{20.00+40.00}$ 0.0400 M NaOH = 0.02667 M NaOH

mass balance on hydroxide: $0.02667 + [NH_4^+] + [H^+] = [OH^-]$ but we expect $[NH_4^+] + [H^+]$ << .02667; $[OH^-] = 0.02667$; pH = 14 – pOH = **12.426**

Weak base is irrelevant in the presence of a strong base. (Le Chatelier)

4C-13 0.10 M NaOH added to a 25.0 mL sample of 0.10 M acetic acid.

a. 0 mL added

$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75\times10^{-5}$ A solution of acetic acid.

charge: $[H^+] = [OH^-] + [CH_3COO^-]$

mass: $0.100 = [CH_3COOH] + [CH_3COO^-]$

solve: $[H^+] = 0.0013$; pH = 2.88

b. 5.0 mL added

Dilution! $\frac{25}{25+5}$ 0.100 M CH_3COOH = 0.08333 M CH_3COOH

$\frac{5}{25+5}$ 0.100 M NaOH = 0.01667 M NaOH

Reaction! Strong base NaOH will convert CH_3COOH to CH_3COONa.

$$0.08333 \text{ M } CH_3COOH - 0.01667 \text{ M NaOH} \frac{1 \text{ mol } CH_3COOH}{1 \text{ mol NaOH}} = 0.06667 \text{ M } CH_3COOH$$

$$0.01667 \text{ M NaOH} \frac{1 \text{ mol } CH_3COONa}{1 \text{ mol NaOH}} = 0.01667 \text{ M } CH_3COONa.$$

Buffer! $K_a = \frac{[H^+]0.01667}{0.06667}$; $[H^+] = 7.02\times10^{-5}$; pH = 4.15

Yes, 0.00007 and 1.4×10^{-10} << 0.01667 and 0.06667

c. 10.0 mL added

Dilution! $\frac{25}{25+10}$ 0.100 M CH_3COOH = 0.07143 M CH_3COOH

$\frac{10}{25+10}$ 0.100 M NaOH = 0.02857 M NaOH

Reaction! Strong base NaOH will convert CH_3COOH to CH_3COONa.

$$0.07143 \text{ M } CH_3COOH - 0.02857 \text{ M NaOH} \frac{1 \text{ mol } CH_3COOH}{1 \text{ mol NaOH}} = 0.04286 \text{ M } CH_3COOH$$

$$0.02857 \text{ M NaOH} \frac{1 \text{ mol } CH_3COONa}{1 \text{ mol NaOH}} = 0.028577 \text{ M } CH_3COONa.$$

Buffer! $K_a = \frac{[H^+]0.02857}{0.04286}$; $[H^+] = 2.63\times10^{-5}$; pH = 4.58

Yes, 0.00003 and 3.8×10^{-10} << 0.02857 and .04286

d. 15.0 mL added

Dilution! $\frac{25}{25+15}$ 0.100 M CH_3COOH = 0.06250 M CH_3COOH

$\frac{15}{25+15}$ 0.100 M NaOH = 0.03750 M NaOH

Reaction! Strong base NaOH will convert CH_3COOH to CH_3COONa.

$$0.06250 \text{ M } CH_3COOH - 0.03750 \text{ M NaOH} \frac{1 \text{ mol } CH_3COOH}{1 \text{ mol NaOH}} = 0.02500 \text{ M } CH_3COOH$$

$$0.03750 \text{ M NaOH} \frac{1 \text{ mol } CH_3COONa}{1 \text{ mol NaOH}} = 0.03750 \text{ M } CH_3COONa.$$

Buffer! $K_a = \frac{[H^+]0.03750}{0.02500}$; $[H^+] = 1.17\times10^{-5}$; pH = 4.93

Yes, 0.00001 and 8.6×10^{-10} << 0.03750 and 0.02500

e. 20.0 mL added

Dilution! $\frac{25}{25+20}$ 0.100 M CH_3COOH = 0.05556 M CH_3COOH

$\frac{20}{25+20}$ 0.100 M NaOH = 0.04444 M NaOH

Reaction! Strong base NaOH will convert CH_3COOH to CH_3COONa.

$$0.05556\text{ M }CH_3COOH - 0.04444\text{ M NaOH}\frac{1\text{ mol }CH_3COOH}{1\text{ mol NaOH}} = 0.01112\text{ M }CH_3COOH$$

$$0.04444\text{ M NaOH}\frac{1\text{ mol }CH_3COONa}{1\text{ mol NaOH}} = 0.04444\text{ M }CH_3COONa.$$

Buffer! $K_a = \frac{[H^+]0.04444}{0.01111}$; $[H^+] = 4.38\times10^{-6}$; pH = 5.36

Yes, 0.000004 and 2.3×10^{-9} << 0.04444 and 0.01111

f. 25.0 mL added

Dilution! $\frac{25}{25+25}$ 0.100 M CH_3COOH = 0.05000 M CH_3COOH

$\frac{25}{25+25}$ 0.100 M NaOH = 0.05000 M NaOH

Reaction! Strong base NaOH will convert CH_3COOH to CH_3COONa.

$$0.05000\text{ M }CH_3COOH - 0.05000\text{ M NaOH}\frac{1\text{ mol }CH_3COOH}{1\text{ mol NaOH}} = 0.0000\text{ M }CH_3COOH$$

$$0.05000\text{ M NaOH}\frac{1\text{ mol }CH_3COONa}{1\text{ mol NaOH}} = 0.05000\text{ M }CH_3COONa.$$

$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75\times10^{-5}$ A solution of sodium acetate.

charge: $[Na^+] + [H^+] = [OH^-] + [CH_3COO^-]$

mass: $0.05000 = [CH_3COOH] + [CH_3COO^-]$

$0.05000 = [Na^+]$

solve: $[H^+] = 1.87\times10^{-9}$; pH = 8.73

g. 30.0 mL added

Dilution! $\frac{25}{25+30}$ 0.100 M CH_3COOH = 0.04545 M CH_3COOH

$\frac{30}{25+30}$ 0.100 M NaOH = 0.05454 M NaOH

Reaction! Strong base NaOH will convert CH_3COOH to CH_3COONa.

$$0.05454\text{ M NaOH} - 0.04545\text{ M }CH_3COOH\frac{1\text{ mol NaOH}}{1\text{ mol }CH_3COOH} = 0.009091\text{ M NaOH}$$

$$0.04545\text{ M }CH_3COOH\frac{1\text{ mol }CH_3COONa}{1\text{ mol }CH_3COOH} = 0.04545\text{ M }CH_3COONa.$$

Mass balance on hydroxide: $0.009091 + [CH_3COOH] + [H^+] = [OH^-]$ but we expect $[CH_3COOH] + [H^+]$ << .009091; $[OH^-] = 0.009091$; pH = 14 – pOH = 11.96

h. 35.0 mL added

Dilution! $\frac{25}{25+35}$ 0.100 M CH_3COOH = 0.041667 M CH_3COOH

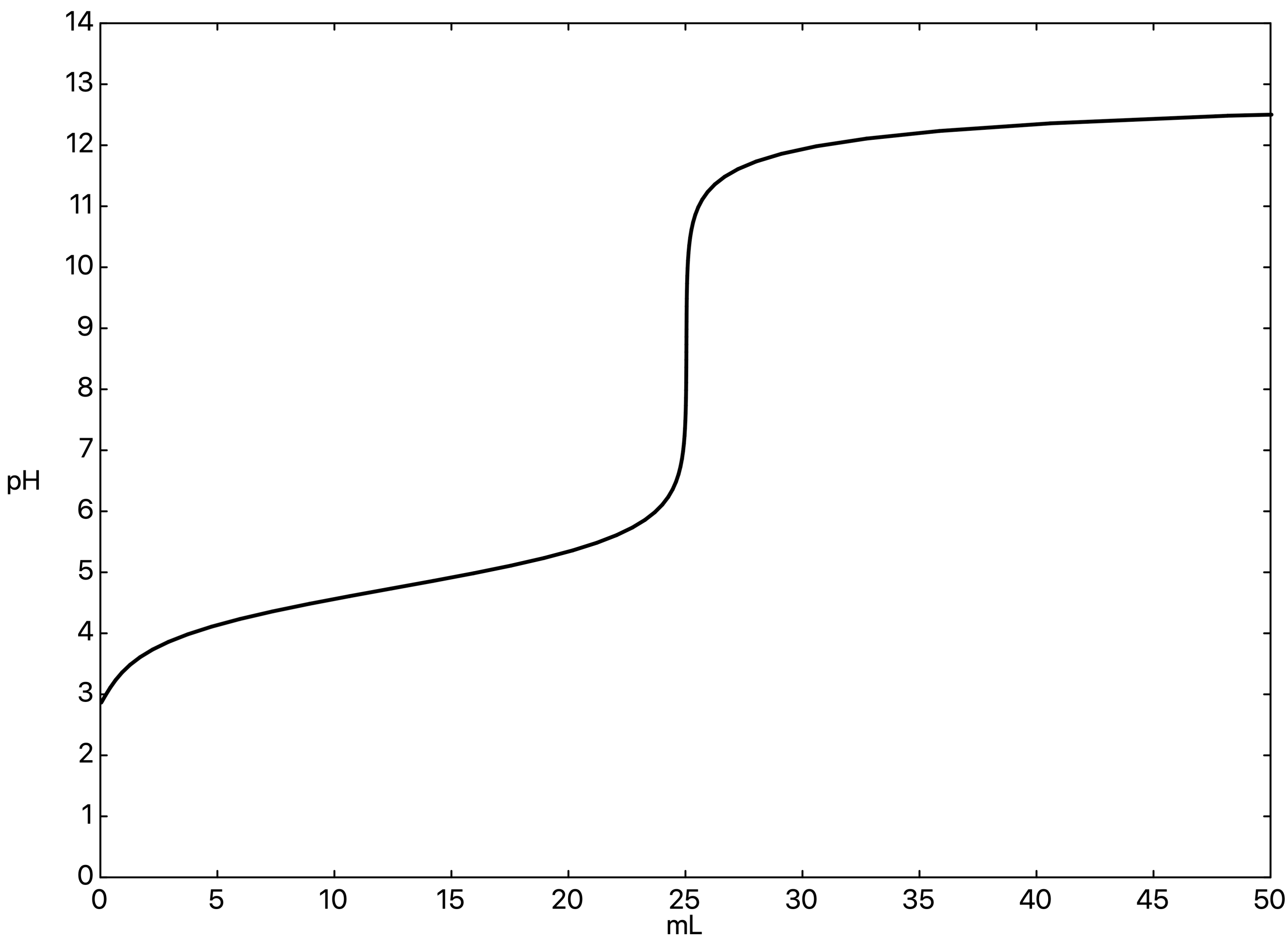
$\frac{35}{25+35}$ 0.100 M NaOH = 0.058333 M NaOH

Reaction! Strong base NaOH will convert CH_3COOH to CH_3COONa.

$$0.058333 \text{ M NaOH} - 0.041667 \text{ M CH}_3\text{COOH}\frac{1 \text{ mol NaOH}}{1 \text{ mol CH}_3\text{COOH}} = 0.01667 \text{ M NaOH}$$

$$0.041667 \text{ M CH}_3\text{COOH}\frac{1 \text{ mol CH}_3\text{COONa}}{1 \text{ mol CH}_3\text{COOH}} = 0.041667 \text{ M CH}_3\text{COONa}.$$

Mass balance on hydroxide: 0.01667 + $[CH_3COOH]$ + $[H^+]$ = $[OH^-]$ but we expect $[CH_3COOH] + [H^+] << .01667$; $[OH^-] = 0.01667$; pH = 14 – pOH = 12.22



Results from Problem 4C-13

Answers to titration Problems 4D-1, 4D-2, 4D-3, 4D-4, 4D-5 can be found on the module web site, http://chemistry.beloit.edu/Rain/pages/titr.html