HW Assignment 2 CHEM 311

8.2

a) HBr is a strong acid

$HBr + H_2O \rightarrow Br^- + H_3O^+$

So $[H_3O^+] = 1.0*10^{-3}$ M

$pH = -\log[H_3O^+] = 3.00$

Two sig figs in $[H_3O^+]$, so keep to sig figs after the decimal place in the pH (log rule, see chapter 3)

b) KOH is a strong base

$KOH(aq) \rightarrow K^+ + OH^-$

So $[OH^-] = 1.0*10^{-2}$ M

$[H_3O^+] = Kw/[OH^-] = 10^{-14}/1.0*10^{-2} = 1.0*10^{-12}$ M

$pH = -\log[H_3O^+] = 12.00$

Two sig figs in $[H_3O^+]$, so keep to sig figs after the decimal place in the pH (log rule, see chapter 3)

8.3

$HClO_4$ is a very dilute strong acid

$HClO_4 + H_2O \rightarrow ClO_4^- + H_3O^+$

So $[H_3O^+] = 5.0*10^{-8}$ M + (what ever comes from the dissociation of water)

	$[OH^-]$	$[H_3O^+]$
initial	$1.0*10^{-7}$ M	$1.5*10^{-7}$ M
equilibrium	$1.0*10^{-7} - x$	$1.5*10^{-7} - x$

$Kw = [OH-][H_3O^+] = 10^{-14} = (1.0*10^{-7} – x)(1.5*10^{-7} – x)$

Use quadratic equation to solve for x or use the method of successive approximations with Excel to arrive at the answer.

$x = 2.19*10^{-8}$ M

$[H_3O^+] = 1.5*10^{-7} – x = 1.3*10^{-7}$ M
pH = $-\log[H_3O^+] = 6.89$

What fraction of H_3O^+ comes from the dissociation of water?

$H_20 + H_2O \leftrightarrow OH^- + H_3O^+$

Although, for this problem the water dissociation reaction is only one of the sources of H_3O^+, it is the only source of OH^-, and for every mole of OH^- that is formed in the reaction, a mol of H_3O^+ is also produced. Therefore,

$[OH^-] = [H_3O^+]_{\text{water dis}} = Kw/[H_3O^+] = 10^{-14}/(1.3*10^{-7}) =$
$7.81*10^{-8}$ M

$\alpha_{(H+diss)} = (7.81*10^{-8})/(1.3*10^{-7}) = 0.61$

8-6

$Ka = 1.00*10^{-5} = [H_3O^+][A^-] / [HA]$
Assume $[H_3O^+] = [A^-]$, and let $[A^-] = x$
Assume $F_{HA} \cong [HA]$, then

$1.00*10^{-5} = x^2/(0.100)$
$x = [H_3O^+] = 1.00*10^{-3}$ M
pH = 3.000 (3 sig fig)

check assumptions
$[OH-]/[A-] = 1*10^{-8} <<< .01$
$[A-]/F_{HA} = 0.01$
assumptions are OK!!!

$\alpha_{(diss)} = (1.00*10^{-3})/(0.100) = 0.0100 \rightarrow 1.00$ %

8.8

$(CH_3)_3NHCl \rightarrow (CH_3)_3NH^+ + Cl^-$

$(CH_3)_3NH^+ + H_2O \leftrightarrow (CH_3)_3N + H_3O^+$

Ka $= 1.58*10^{-10}$

$= [(CH_3)_3N][H_3O^+] / [(CH_3)_3NH^+]$

Assume $[H_3O^+] = [(CH_3)_3N]$, and let $[(CH_3)_3N] = x$

Assume $F_{(CH3)3NH+} \cong [(CH_3)_3NH^+]$, then

$1.58*10^{-10} = x^2/(0.060)$

$x = [H_3O^+] = 3.1*10^{-6}$ M

pH = 5.51 (3 sig fig)

check assumptions

$[OH-]/[A-] = 3.2*10^{-9}/3.1*10^{-6} \sim 10^{-3} < .01$

$[A-]/F_{HA} = 3.1*10^{-6}/.060 <<< .01$

assumptions are OK!!!

$[(CH_3)_3N] = 3.1*10^{-6}$ M

$[(CH_3)_3NH^+] = 0.060$ M

8-15

$Cr^{+3} + H_2O \leftrightarrow Cr(OH)^{+2} + H_3O^+$

Ka $= 1.58*10^{-10}$

$= [Cr(OH)^{+2}][H_3O^+] / [Cr^{+3}]$

Assume $[H_3O^+] = [Cr(OH)^{+2}]$, and let $[Cr(OH)^{+2}] = x$

Assume $F_{Cr(OH)+2} = 0.010 \cong [Cr(OH)^{+2}]$, then

$1.58*10^{-4} = x^2/(0.010)$

$x = [H_3O^+] = 1.26*10^{-3}$ M

check assumptions

$[OH-]/[A-] = 1*10^{-11}/1.3*10^{-3} <<<<<< .01$

$[A-]/F_{HA} = 1.3*10^{-3}/.010 = 0.13 \rightarrow 13\ \%$

assumption # 2 is not justified!!!!

Solve without making assumption

$1.58*10^{-4} = x^2/(0.010-x)$

Use quadratic equation to solve for x or use the method of successive approximations with Excel to arrive at the answer. If you use quadratic

$1.58*10^{-4}(0.010-x) = x^2$

$1.58*10^{-4}(0.010-x) = x^2 + 1.58*10^{-4}x - 1.58*10^{-3}$

$x = 1.18*10^{-3}$ M $= [H_3O^+] = [Cr(OH)^{+2}]$

$pH = -\log(1.18*10^{-3}) = 2.93$

$\alpha_{(diss)} = (1.18*10^{-3})/(0.010) = 0.1200 \rightarrow 12.0\ \%$

8-20

$(CH_3)_3N + H_2O \leftrightarrow (CH_3)_3NH^+ + OH^-$

$Kb(CH_3)_3N) = Kw/Ka((CH_3)_3NH^+) = 10^{-14}/1.58*10^{-10}$

$= 6.33*10^{-5}$

$6.33*10^{-5} = [(CH_3)_3NH^+][OH^-] / [(CH_3)_3N]$

Assume $[OH^-] = [(CH_3)_3NH^+]$, and let $[(CH_3)_3NH^+] = x$

Assume $F_{(CH3)3N} \cong [(CH_3)_3N]$, then

$6.33*10^{-5} = x^2/(0.060)$

$x = [OH^-] = 1.95*10^{-3}$ M

$[H_3O^+] = 10^{-14}/[OH]- = 5.13*10^{-12}$ M

pH = 11.29 (3 sig fig)

check assumptions

$[H_3O^+]/[(CH_3)_3NH^+] = 5.13*10^{-12}/1.95*10^{-3} <<<< .01$

$[(CH_3)_3NH^+] /F_{HA} = 1.95*10^{-3}/.060 = .03 \rightarrow 3\%$

assumptions are OK!!!

$[(CH_3)_3NH^+] = 1.95*10-3$ M

$[(CH_3)_3N] = 0.06 – 1.95*10^{-3} = 0.058$ M

8-23

$B + H_2O \leftrightarrow BH^+ + OH^-$

$Kb = [BH^+][OH^-]/ (F_B - [BH^+])$

Assume $[BH^+] = [OH^-]$, and you can write

$Kb = [OH^-]^2/ (0.1 - [OH^-])$

$pH = -\log[H_3O^+] = 9.28$

$[H_3O^+] = 5.2*10^{-10}$ M

$[OH^-] = Kw/[H_3O^+] = 10^{-14}/5.2*10^{-10} = 1.9*10^{-5}$ M

$Kb = (1.9*10^{-5})^2/ (0.1 - 1.9*10^{-5}) = 3.6*10^{-9}$

8.24

$B + H_2O \leftrightarrow BH^+ + OH^-$

$Kb = [BH^+][OH^-]/ [B]$

2% hydrolyzed means →

$[BH+]/F_B = [BH^+] / ([BH^+] + [B]) = 0.02$

$F_B = [B] + [BH^+] = 0.1$ M,

If

$$[BH^+] / ([BH^+] + [B]) = 0.02$$

and

$$[B] + [BH^+] = 0.1$$

then

$$[BH]^+/0.1 = 0.02$$

and

$$[BH^+] = 0.002 \text{ M and } [B] = 0.098 \text{ M}$$

$$Kb = (.002)^2/(0.098) = 4.1*10^{-5}$$

8.27

$pH = pKa + \log ([A^-]/[HA])$

The pH of a buffer is nearly independent of concentration because the log term is the quotient of concentrations of two species in the same solution. Let's do a unit analysis!!!

$$\log ([A^-]/[HA]) = \log \{(\text{moles of } A^-/\text{volume})/\text{mol of HA/volume})\}$$
$$= \log (\text{moles of } A^- / \text{mol of HA})$$

The volume terms cancel because the two species are in the same solution. So, the pH is really only dependent on the relative molar ratios of the acid and conjugate base.

8.28

Buffer capacity is the ability of a buffer to react with a strong acid or base without making a large change in the $[A^-]/[HA]$ ratio. The greater the concentration of each component, the less the relative change in pH brought about by small additions of strong acids and bases.

8.33

$Ka = 1.00*10^{-5}$

pKa = 5.000 (3 sig fig, log rule)

pH = 5.000 + log [A-]/[HA]
= 5.000 + log(0.050/.100)
= 4.699

8.38

pKa = 4.34

B = 2,2-bipyridine and BH+ is its conjugate acid

pH = 10.626 + log([B] / [BH^+]) =
10.626 + log[(mmol B) / (mmol BH^+)]

initially:

(213 mL/1)*(6.66 mmol/1000mL) = 1.42 mmol B

Final

$CH_3CH_2NH_2 + H^+ \rightarrow CH_3CH_2NH_3^+$

For every mmol H^+ added, one mmol of B is converted to its conjugate acid.

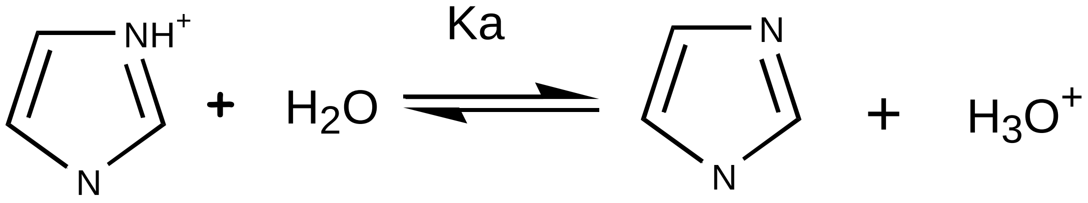
mmol B = 1.42 – x
mmol BH^+ = x
where x = mmol of acid added

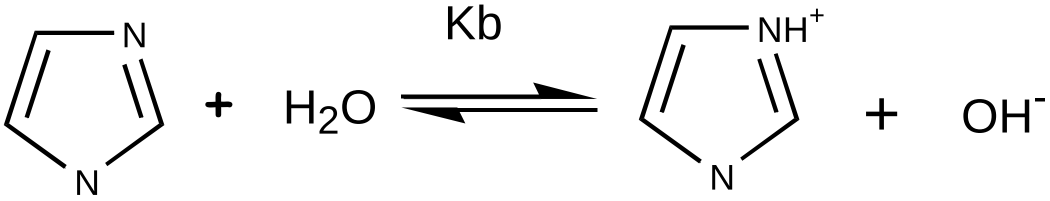
4.32 = 4.19 + log[1.42 – x)/x]
antilog(4.32-4.19) = (1.42 - x) / x
1.35 = (1.42 – x) / x
1.35x = 1.42 – x
2.35x = 1.42
x = 0.605 mmol H^+ added

$(0.605 \text{ mmol H}^+ / 1) * (\text{mL} / 0.246 \text{ mmol HNO}_3) = 2.46 \text{ mL HNO}_3$

8.39

a)





b)

$(1.00 \text{ g Imid}/1)*(1\text{mol}/68.079 \text{ g Imid}) =$
$1.47*10^{-2} \text{ mol} = 14.7 \text{ mmol Imid}$

$(1.00 \text{ g ImidH}^+/1)*(1\text{mol}/104.54 \text{ g ImidH}^+)$
$= 9.57*10^{-3} \text{ mol} = 9.57 \text{ mmol ImidH}^+$

$\text{pH} = \text{pKa} + \log([\text{Imid}]/[\text{ImidH}^+])$
$= 6.993 + \log(14.7/9.57)$
$= 7.179$

c)

$(2.30 mL/1)*(1.07 mmol/ml) = 2.46 mmol H^+$

pH = 6.993 + log[(14.7-2.46)/(9.57+2.46)]
7.000

d)

pH = 6.993 + log[(14.7-x)/x]
6.993 = 6.993 + log[(14.7-x)/x]
0 = log[(14.7-x)/x]
1 = (14.7-x)/x
14.7 = 2x
x = 7.35 mmol H^+

(7.35 mmol H^+/1)*(1 ml/1.07 mmol) = 6.90 mL $HClO_4$

8.40
a. pH = 2.865 + log (.0400/.0800) = 2.564

b.
The pKa is so low that this might have to be solved systematically. In other words, what you mix might not be what you get.

$[HA] = F_{HA} - [H^+]$

$[A^-] = F_{A-} - [H^+]$

Let’s find $[H^+]$!!!

Ka $= 1.365*10^{-3} = [A^-][H^+]/[HA]$

$= ((F_{A-} + [H^+])[H^+]) / (F_{HA} - [H^+])$

let $[H^+] = x$

$= (F_{A-} + x)x / (F_{HA} - x)$

$= (4.00*10^{-2} – x)x / (8.00*10^{-2} – x)$

Use quadratic equation to solve for x or use the method of successive approximations with Excel to arrive at the answer. If you use quadratic

$x = 0.002488$ M

$[HA] = 0.0800 – x = 0.0775$ M

$[A^-] = 0.0400 + x = 0.0425$ M

pH = 2.604

c)

in head: pH = pKa, because the strong acid neutralized half of the strong base, and the excess strong base reacts with the conjugate acid to make conjugate base. The final result gives 0.100 mol of HA and A-.

solving systematically (as in part b) gives

pKa = 2.876

8.42

A buffer that has a concentration in this low range might have to be treated systematically.

pKa of acetic acid is 4.757. So, an acetic acid/acetate buffer will have an acidic pH. Therefore,

$[HA] = F_{HA} - [H^+]$

$[A^-] = F_{A-} + [H^+]$

Let's find $[H^+]$!!!

Ka $= 1.75*10^{-5} = [A^-][H^+]/[HA]$

$= ((F_{A-} + [H^+])[H^+]) / (F_{HA} - [H^+])$

let $[H^+] = x$

$= (F_{A-} + x)x / (F_{HA} - x)$

$= (4.00*10^{-3} + x)x / (2.00*10^{-3} – x)$

Use quadratic equation to solve for x or use the method of successive approximations with Excel to arrive at the answer. If you use quadratic

$(1.75*10^{-5})*(2.00*10^{-3} – x) = 4.00*10^{-3}x + x^2$

x = 8.73E-6 M

pH = 5.059

$[HA] = 2.00*10^{-3} – 8.73E-6 = 1.99*10^{-3}$ M

$[A^-] = 4.00*10^{-3} + 8.73E-6 = 4.01*10^{-3}$ M

pH = 5.058, without assumption