

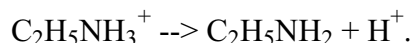
CHEM131 HOMEWORK #12 KEY

7-76. a. KCl comes from mixing HCl and KOH, which are completely dissociated and are a strong acid and base respectively. The solution is neutral.

b. Same as a.

c.  $\text{HNO}_2$  is a weak acid while NaOH is a strong base, so the solution is basic.  $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$ .

d. HI is a strong acid while ethyl ammine is a weak base, so the solution is acidic.



e. Ammonia and HCN are both weak, but  $\text{NH}_3$  is a stronger base than HCN is an acid:  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$  is much larger than  $K_a(\text{HCN}) = 6.2 \times 10^{-10}$  so the solution will be basic. Both ions have equilibria expressions:

$\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$  and  $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$  but the  $\text{CN}^-$  equilibrium lies much further to the right than the  $\text{NH}_4^+$  equilibrium. Remember the fact that HCN is a very weak acid means that its conjugate base,  $\text{CN}^-$ , is a good base.

f. Same as c.  $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^-$ .

g. This one is a ringer because both ions derive from a weak acid/base pair, but  $K_a$  just happens to equal  $K_b$  so the solution is still neutral. The  $\text{H}^+$  ions generated by the dissociation of  $\text{NH}_4^+$  are just neutralized by the  $\text{OH}^-$  ions generated by acetate ions reacting with water to make undissociated acetic acid and  $\text{OH}^-$ .

h. Same as c.  $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$ .

7-89. Let's do this the "normal" way: Here we have the dissociation of a weak acid. Write down standard ICE relations. Note that HCN is VERY weak and I have a feeling we will need to consider water here....

	$\text{HCN}$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{CN}^-$
Initial	0.0005		0		0
Change	-x		+x		+x
Equil.	$0.0005 - x$		x		x

$K_a = (x^2)/(0.0005 - x) = 6.2 \times 10^{-10}$ ; assume  $x \ll 0.0005$  and drop the x in the denominator.

$x^2 = 3.1 * 10^{-13}$ , which means  $x = 5.57 * 10^{-7}$ . Not good – this is  $< 10^{-6}$  so we have to consider the exact expression.

Note that we know  $x$  will be  $< 6.6 * 10^{-7}$ , which is  $\ll [\text{HCN}]_0$ . So, using the simplified form found on page 266:  $[\text{H}^+] = (\text{K}_a[\text{HCN}]_0 + \text{K}_w)^{1/2}$ .

Plugging in:  $[\text{H}^+] = (6.2 * 10^{-10} * 0.0005 + 1.0 * 10^{-14})^{1/2} = 5.66 * 10^{-7}$ .  $\text{pH} = -\log(5.66 * 10^{-7}) = 6.24$

7-101. We are given three acids all with roughly the same order of magnitude concentrations.  $\text{K}_a$  for HA is  $\gg \gg \text{K}_a$  for HB which is  $\gg \text{K}_a$  for HC  $\gg \text{K}_w$ . Effectively, the  $[\text{H}^+]$  is going to be determined by

	HA	$\rightleftharpoons$	H <sup>+</sup>	+	A <sup>-</sup>
Initial	0.5		0		0
Change	-x		+x		+x
Equil.	0.5 - x		x		x

$\text{K}_a = (x^2)/(0.5 - x) = 1.0 * 10^{-3}$ ; assume  $x \ll 0.5$  and drop the  $x$  in the denominator.  $x^2 = 5.0 * 10^{-4}$ , which means  $x = 0.022 \text{ M} = [\text{H}^+]$ . 5% rule check:  $.022/.5 = .044 = 4.4\%$  - we just make it.

8-17. The capacity of a buffer is the amount of acid or base it can absorb without exhibiting a significant change in pH. Each of the solutions have the same pH but quite different capacities. In most cases the pH of a solution containing equal concentrations of a weak acid(base) and its salt is just the  $\text{pK}_a$ . This is seen by considering a solution made by adding  $N$  moles of HA and  $N$  moles of A<sup>-</sup> to a given volume of water, such that the initial concentration of each is  $[C] \text{ M}$ . When HA dissociates to arrive at equilibrium we have

$$\text{K}_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+](C + x)}{(C - x)}$$

As long as  $x \ll C$ , we can drop the  $x$ 's, cancel the  $C$ 's and  $[\text{H}^+] = \text{K}_a$ ,  $\text{pH} = \text{pK}_a = -\log(1.8 * 10^{-5}) = 4.74$ .

To consider the capacities of the three solutions, consider adding 0.1 M of NaOH to each. For solution a. the acetic acid is completely neutralized, giving 0.2 M of A<sup>-</sup> (0.1 M from the original solution and 0.1 from the neutralized acid) and 0.09 M OH<sup>-</sup> remains in solution. Solution a. is strongly basic.

For solution b. we first think of the stoichiometric reaction and then allow the components to come to equilibrium. The added base is just enough to neutralize all of the acid, giving 0.2 M of A<sup>-</sup>. The acetate ion reacts with water to form a weakly basic solution. Calling  $[\text{OH}^-] = x$ , we have:

$K_b = x^2 / (0.2 - x) = K_w / K_a = 5.6 \times 10^{-10}$ . Ignoring the  $x$  in the denominator gives  $[\text{OH}] = (0.2 \times 5.6 \times 10^{-10})^{1/2} = 1.06 \times 10^{-5}$ .  $\text{pOH} = -\log(1.06 \times 10^{-5}) = 4.98$ .  $\text{pH} = 14 - \text{pOH} = 9.02$ .

For solution c. we again do the stoichiometric reaction followed by equilibration. Before equilibrium is established we have 0.9 M HA and 1.1 M  $\text{A}^-$ . At equilibrium  $x$  mole of HA dissociates, giving:

$K_a = x(1.1 + x) / (0.9 - x)$ . Ignoring the  $x$ 's in the parentheses gives  $x = [\text{H}^+] = (0.9/1.1)K_a = 1.5 \times 10^{-5}$  and  $\text{pH} = 4.83$ , just slightly different from the solution before the base was added. Clearly the pH of the buffer depends on the ratio,  $[\text{HA}]/[\text{A}^-]$ , while the capacity depends of the quantities of HA and  $\text{A}^-$ .

8-19. Label propionic acid HA and sodium propionate  $\text{Na}^+ \text{A}^-$



Init.      .100                      0              0

Change   -x                              x              x

Equilib.   .100-x                      x              x

$1.3 \times 10^{-5} = x^2 / (.100 - x) \approx x^2 / .100$ ;  $x = [\text{H}^+] = 1.1 \times 10^{-3}$ ;  $\text{pH} = 2.96$ ; assumption good to within 5%.

b. Think of this as a weak base problem:



Init.      .100                              0              0

Change   -x                                      x              x

Equilib.   .100-x                              x              x

$7.7 \times 10^{-10} = x^2 / (.100 - x) \approx x^2 / .100$ ;  $x = [\text{OH}^-] = 8.8 \times 10^{-6}$ ;  $\text{pOH} = 5.06$ ;  $\text{pH} = 8.94$ ; assumption valid.

c.  $\text{pH} = 7.0$

d. This is a buffer solution

$$HA \rightleftharpoons H^+ + A^- \quad K_a = 1.3 \cdot 10^{-5}$$

Init.	.100	0	.100
Change	-x	x	x
Equilib.	.100-x	x	.100+x

$1.3 \cdot 10^{-5} = (.100+x)x / (.100-x) \approx .100x / .100$ ;  $x = [H^+] = 1.3 \cdot 10^{-5}$ ; pH = 4.89; assumption good

Note the Henderson-Hasselbalch eq. gives the same result.

- 8-27.  $C_5H_5N$ , pyridine, is a weak base having  $K_b = 1.7 \cdot 10^{-9}$ . Its conjugate acid is  $C_5H_5NH^+$ . For this problem, use the Henderson-Hasselbalch equation,  $pH = pK_a + \log \{ [base] / [acid] \}$ .  $K_a = K_w / K_b = 5.9 \cdot 10^{-6}$ .  $pK_a = 5.23$ .

a.  $4.50 = 5.23 + \log \{ [C_5H_5N] / [C_5H_5NH^+] \}$ ;  $\log \{ [C_5H_5N] / [C_5H_5NH^+] \} = -0.73$ ;  
 $[C_5H_5N] / [C_5H_5NH^+] = 10^{-0.73} = 0.19$ .

Parts b through d are exactly the same, and the answers are :  
 b) 0.59, c) 1.0, d) 1.9

Next H.W. Ch 8: 47, 55, 68