

HW #16-3: p. 722# 10, 11*, 14*, 17*, 19, 20 Some hints are given below:

*For #11 and 14: First, determine the identity of the weak acid and the weak base in the buffer. Second, write the equilibrium acid ionization equation, use an ICE chart and K_a expression to solve for pH.

*For #17, When HCl is added, write the neutralization reaction and use an ICF chart. Write equilibrium acid ionization reaction, set up an ICE chart and transfer "final" values into ICE chart. Use K_a expression. (This is very similar to #15 on Buffer POGIL.)

16.10 Which of the following solutions can act as a buffer?

- (a) **KCN/HCN:** HCN is a weak acid, and its conjugate base, CN^- , is a weak base. Therefore, this is a buffer system.
- (b) **$\text{Na}_2\text{SO}_4/\text{NaHSO}_4$:** HSO_4^- is a weak acid, and its conjugate base, SO_4^{2-} is a weak base (see Table 15.5 of the text). Therefore, this is a buffer system.
- (c) **$\text{NH}_3/\text{NH}_4\text{NO}_3$:** NH_3 (ammonia) is a weak base, and its conjugate acid, NH_4^+ is a weak acid. Therefore, this is a buffer system.
- (d) **NaI/HI:** Because HI is a strong acid, its conjugate base, I^- , is an extremely weak base. This means that the I^- ion will not combine with a H^+ ion in solution to form HI. Thus, this system cannot act as a buffer system.

16.11 Calculate the pH of the buffer system made up of 0.15 M NH_3 / 0.35 M NH_4Cl .

- Solution consists of NH_3 (weak base), NH_4^+ (weak acid) and Cl^- (neutral ion).
- There is nothing "strong" (no strong acid or strong base). Thus, there is no neutralization reaction that would go to completion (stoichiometry). Thus, just do equilibrium. (ICE chart!)
- Show the acid ionization reaction of weak acid in water: (You could also do the reaction of the weak base in water, but when there is a weak acid and a weak base most people do the reaction of the weak acid in water.)

	$\text{NH}_4^+(aq)$	$+\text{H}_2\text{O}$	\rightleftharpoons	$\text{NH}_3(aq)$	$+$	$\text{H}_3\text{O}^+(aq)$
I	0.35 M			0.15 M		0
C	-x			+x		+x
E	0.35 - x			0.15 + x		x

Look up: K_b of $\text{NH}_3 = 1.8 \times 10^{-5}$
 Thus, K_a of $\text{NH}_4^+ = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \Rightarrow [\text{H}_3\text{O}^+] = K_a \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$[\text{H}_3\text{O}^+] = 5.6 \times 10^{-10} \frac{[0.35 - x]}{[0.15 + x]} \approx 5.6 \times 10^{-10} \frac{[0.35]}{[0.15]}$$

$$[\text{H}_3\text{O}^+] = 1.3 \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log(1.3 \times 10^{-9} \text{ M}) = \boxed{8.88}$$

Another option is to use the Henderson-Hasselback equation:

$$\text{p}K_a = -\log(5.6 \times 10^{-10}) = 9.25$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.25 + \log \frac{0.15 \text{ M}}{0.35 \text{ M}} = \mathbf{8.88}$$

16.14 What is the pH of the buffer 0.10 M Na₂HPO₄/0.15 M KH₂PO₄?

- Solution consists of Na⁺ (neutral ion), HPO₄²⁻ (weak base) and H₂PO₄⁻ (weak acid).
(Yes, both HPO₄²⁻ and H₂PO₄⁻ are amphoteric. However, one has to be the weak acid and the other the weak base. Thus, choose the one that is the strongest base to be the weak base. The strongest acid will be the weak acid.)
- Just like #11, there is nothing “strong” (no strong acid or strong base). Thus, there is no neutralization reaction that would go to completion (stoichiometry). Thus, just do equilibrium. (ICE chart!)
- Show the acid ionization reaction of weak acid in water: (You could also do the reaction of the weak base in water, but when there is a weak acid and a weak base most people do the reaction of the weak acid in water.)

	$\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$
Initial (M):	0.15 0 0.10
Change (M):	-x +x +x
Equilibrium (M):	0.15 - x x 0.10 + x

Look up the K_a of dihydrogen phosphate in Table 15.5 of your text. $K_a = 6.2 \times 10^{-8}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]}$$

$$[\text{H}_3\text{O}^+] = 6.2 \times 10^{-8} \frac{(0.15 - x)}{(0.10 + x)} \approx 6.2 \times 10^{-8} \frac{(0.15)}{(0.10)}$$

$$x = [\text{H}_3\text{O}^+] = 9.3 \times 10^{-8} \text{ M};$$

$$\text{pH} = -\log[\text{H}^+] = -\log(9.3 \times 10^{-8}) = \mathbf{7.03}$$

Alternately, you can use HH to determine pH:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$= -\log(6.2 \times 10^{-8}) + \log \frac{0.10 \text{ M}}{0.15 \text{ M}}$$

$$= 7.21 + (-0.18) = \mathbf{7.03}$$

16.17 Calculate the pH of the 0.20 M NH₃/0.20M NH₄Cl buffer (1st part of question):

NH₃ is the weak base and NH₄⁺ is the weak acid.

Show the acid ionization reaction of weak acid in water, fill in ICE chart, use K_a and solve for pH.

	$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$	
I	0.20 M	0.20 M 0
C	-x	+x +x
E	0.20-x	0.20+x x

Look up: K_b of NH₃ = 1.8×10^{-5}

$$\text{Thus, } K_a \text{ of } \text{NH}_4^+ = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \text{ M}} = 5.6 \times 10^{-10}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \Rightarrow [\text{H}_3\text{O}^+] = K_a \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$[\text{H}_3\text{O}^+] = 5.6 \times 10^{-10} \frac{[0.20 - x]}{[0.20 + x]} \approx 5.6 \times 10^{-10} \frac{[0.20]}{[0.20]}$$

$$[\text{H}_3\text{O}^+] = 5.6 \times 10^{-10} \text{ M}$$

$$\text{pH} = -\log(5.6 \times 10^{-10} \text{ M}) = \mathbf{9.25}$$

Simpler method: Since you know it is a buffer—we can use initial concentrations of the weak acid and weak base. And since you know the concentrations of the weak acid is equal to the weak base, you know that the pH = pK_a

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{NH}_4^+]}{[\text{NH}_3]}; \text{ so } [\text{H}_3\text{O}^+] = K_a; \text{ pH} = \text{p}K_a$$

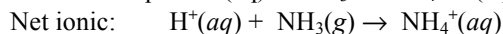
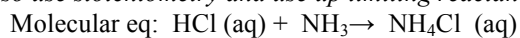
Thus, just do $pH = pK_a = -\log K_a = -\log(5.6 \times 10^{-10} M) = 9.25$

The Henderson–Hasselbalch equation is the same logic.

$$pH = -\log(5.6 \times 10^{-10}) + \log \frac{(0.20 M)}{(0.20 M)} = 9.25$$

What is the pH of the buffer after the addition of 10.0 mL of 0.10 M HCl to 65.0 mL of the buffer? (2nd part)

Since the HCl is a strong acid, HCl will react with the weak base in the buffer and the acid–base (neutralization) reaction will occur (100% completion—so use stoichiometry and use up limiting reactant.)



	H^+	+	NH_3	\rightarrow	NH_4^+
I	0.0133 M		0.173 M		0.173 M
C	-0.0133 M		-0.0133 M		+0.0133 M
F	0 M		0.160 M		0.187 M

To fill in the ICF chart with molarities, one has to take dilution into consideration. Then, enter into the ICF table. (It is also possible to just use moles in the table. I will show this at end of this question.)

$$[\text{H}^+] = \frac{(0.0100\text{L})(0.10\text{M})}{(0.0750\text{L})} = 0.0133\text{M} \quad [\text{NH}_3] = [\text{NH}_4^+] = \frac{(0.0650\text{L})(0.20\text{M})}{(0.0750\text{L})} = 0.173\text{M}$$

Now, let the solution come to equilibrium. Fill in the ICE chart below and use K_a expression

	$\text{NH}_4^+(\text{aq})$	$+\text{H}_2\text{O} \rightleftharpoons$	$\text{NH}_3(\text{aq})$	$+$	H_3O^+
I	0.1887M		0.160 M		0
C	-x		+x		+x
E	0.187-x		0.160 +x		x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \Rightarrow [\text{H}_3\text{O}^+] = K_a \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$[\text{H}_3\text{O}^+] \approx 5.6 \times 10^{-10} \frac{[.187\text{M}]}{[.160\text{M}]}$$

$$[\text{H}_3\text{O}^+] = 6.55 \times 10^{-10} M$$

$$pH = -\log(6.55 \times 10^{-10} M) = \boxed{9.18}$$

Alternative method is to just use mole values in the ICF chart instead of molarities.

$$10.0 \text{ mL} \times \frac{0.10 \text{ mol HCl}}{1000 \text{ mL soln}} = 0.0010 \text{ mol HCl}$$

$$\text{Moles of NH}_3 = \text{moles of NH}_4^+ = 65.0 \text{ mL} \times \frac{0.20 \text{ mol}}{1000 \text{ mL soln}} = 0.013 \text{ mol}$$

	$\text{NH}_3(\text{aq})$	$+$	$\text{H}^+(\text{aq})$	\rightarrow	$\text{NH}_4^+(\text{aq})$
Initial (mol):	0.013		0.0010		0.013
Change (mol):	-0.0010		-0.0010		+0.0010
Final (mol):	0.012		0		0.014

Now, since it is a buffer, you can again just use initial amounts. As long as you are solving for H_3O^+ you can even use MOLE values instead of concentrations because the units on the acid/base ratio cancel out!!!

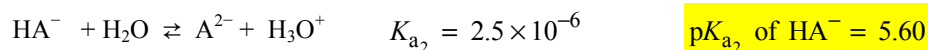
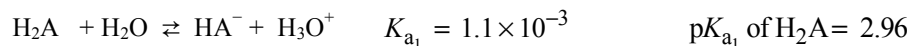
$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 5.6 \times 10^{-10} \frac{[0.014 \text{ moles NH}_4^+ / 0.075\text{L}]}{[0.012 \text{ moles NH}_3 / 0.075\text{L}]}$$

$$[\text{H}_3\text{O}^+] = 6.5 \times 10^{-10} M$$

$$pH = -\log(6.5 \times 10^{-10} M) = \boxed{9.18}$$

Or—use Henderson-Hasselback (really the same calculation): $pH = 9.25 + \log \frac{(0.012)}{(0.014)} = 9.18$

16.19 A diprotic acid, H_2A , has the following ionization constants: $K_{a1} = 1.1 \times 10^{-3}$ and $K_{a2} = 2.5 \times 10^{-6}$. In order to make up a buffer solution of $pH = 5.80$, which combination would you choose?



In order for the buffer solution to behave effectively, the pK_a of the acid component must be close to the desired pH. Therefore, the proper buffer system is **$Na_2A/NaHA$** .

16.20 A student is asked to prepare a buffer solution at $pH=8.60$ using one of the following weak acids: HA ($K_a = 2.7 \times 10^{-3}$), HB ($K_a = 4.4 \times 10^{-6}$), or HC ($K_a = 2.6 \times 10^{-9}$). Which acid should she choose? Why?

For a buffer to function effectively, the concentration of the acid component must be roughly equal to the conjugate base component. According to Equation (16.4) of the text, when the desired pH is close to the pK_a of the acid, that is, when $pH \approx pK_a$,

Solution: To prepare a solution of a desired pH, we should choose a weak acid with a pK_a value close to the desired pH. Calculating the pK_a for each acid:

$$\text{For HA, } pK_a = -\log(2.7 \times 10^{-3}) = 2.57$$

$$\text{For HB, } pK_a = -\log(4.4 \times 10^{-6}) = 5.36$$

$$\text{For HC, } pK_a = -\log(2.6 \times 10^{-9}) = 8.59$$

The buffer solution with a pK_a closest to the desired pH is HC. Thus, **HC** is the best choice to prepare a buffer solution with $pH = 8.60$.