

## General Chemistry II

RR # 10 Answer Key  
Summer 2022

1. Circle the best acid to combine with its sodium salt to make a solution buffered at pH 4.25. For the best choice, calculate the ratio of the conjugate base to the acid required to attain the desired pH

Chlorous acid $\text{HClO}_2$ $\text{pK}_a = 1.95$	<b>Formic acid</b> <b><math>\text{HCOOH}</math></b> <b><math>\text{pK}_a = 3.74</math></b>	Hypochlorous acid $\text{HClO}$ $\text{pK}_a = 7.54$
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It's best to choose the acid with the  $\text{pK}_a$  closest to the desired buffer pH.

To calculate the ratio of base to acid needed, use the Hendersen-Hasselbach equation

$$\text{pH} = \text{pka} + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

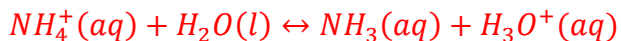
$$4.25 = 3.74 + \log(\text{base to acid ratio})$$

$$\log(\text{base to acid ratio}) = 4.25 - 3.74 = 0.51$$

$$10^{0.51} = 3.24$$

The ratio of base to acid should be 3.24 : 1

2. Calculate the pH of an aqueous buffer solution made from 0.15 M  $\text{NH}_4\text{Cl}$  and 0.100 M  $\text{NH}_3$ .  $K_a$  for  $\text{NH}_4^+ = 5.61 \times 10^{-10}$



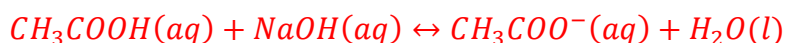
$$\begin{aligned}\text{pH} &= \text{pka} + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = -\log([5.61 \times 10^{-10}]) + \log\left(\frac{0.100 \text{ M}}{0.15 \text{ M}}\right) \\ &= 9.07\end{aligned}$$

3. A 1.0 L buffer solution contains 0.100 mol acetic acid ( $\text{CH}_3\text{COOH}$ ) and 0.100 mol sodium acetate ( $\text{CH}_3\text{COONa}$ ). Calculate the new pH after adding 0.010 mol of solid NaOH to the buffer. For comparison, calculate the pH after adding 0.010 mol of solid NaOH to 1.0 L pure water.  $K_a$  of acetic acid =  $1.8 \times 10^{-5}$ .

First, note that since we are adding solid NaOH to the existing buffer, changes to the volume of solution are negligible.

$$\frac{0.010 \text{ mol NaOH}}{1.0 \text{ L buffer}} = 0.010 \text{ M NaOH}$$

When adding NaOH, we expect that it will react with the acid component of the buffer,  $\text{CH}_3\text{COOH}$ .



	<b>[CH<sub>3</sub>COOH]</b>	<b>[NaOH]</b>	<b>[CH<sub>3</sub>COO<sup>-</sup>]</b>
<b>I</b>	0.100	0	0.100
<b>ADDITION of NaOH</b>	0	+ 0.010	0
<b>C</b>	0.100 – 0.010	- 0.010	0.100 + 0.010
<b>E</b>	0.09	0	0.110

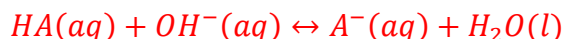
Now, use Henderson-Hasselbach.

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.110\text{M}}{.09\text{M}}\right) = \mathbf{4.83}$$

If you simply dropped 0.010 mol NaOH into 1.0 L pure water, you'd end up with 0.010 M NaOH solution.  $[\text{OH}^-]$  would be 0.010 M since NaOH is a strong base.  $\text{pOH}$  would be  $-\log(0.010) = 2$ , making pH **12**.

4. A chemist has synthesized a monoprotic weak acid and wants to determine its  $K_a$  value. To do so, she dissolves 2.00 millimoles of the solid acid in 100.0 mL of water. Assume negligible dissociation at this point. She titrates the resulting solution with 0.0500 M NaOH. After 20.0 mL NaOH has been added, the pH is 6.00. What is the  $K_a$  value for the acid?

Since we are told that the acid is weak, we know that titration with a strong base will result in the creation of a buffered solution.



Also, since the volume of the solution is changing, we should use moles instead of molarity for the ICE table for clarity's sake. It is ok to use moles for the Henderson-Hasselbach equation too, because all the molecules have ended up in the same solution, and would be divided by the same volume of solution anyway.

	HA	OH <sup>-</sup>	A <sup>-</sup>
I	0.002	0	0
ADDITION of NaOH	0	+ 0.001	0
C	- 0.001	- 0.001	+ 0.001
E	0.001	0	0.001

According to Henderson-Hasselbach,  $6 = pK_a + \log\left(\frac{0.001\text{ M}}{0.001\text{ M}}\right) = pK_a + 0$

$$pK_a = 6$$

$$K_a = 10^{-6}$$

5. A 20.0 mL sample of 0.115 M sulfurous acid ( $H_2SO_3$ ) solution is titrated with 0.1014 M KOH. At what added volume of base solution does each equivalence point occur?

At the first equivalence point, all the sulfurous acid should have been converted to  $HSO_3^-$ . This means having enough base to remove one of the protons per each sulfurous acid molecule.

$$0.020\text{ L} * \frac{0.115\text{ mol}}{\text{L}} = 2.3 * 10^{-3}\text{ mol } H_2SO_3, \text{ which requires the same moles of KOH}$$

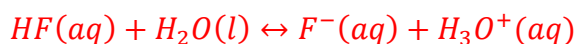
$$\frac{2.3 * 10^{-3}\text{ mol}}{0.1014\text{ M}} = 0.0227\text{ L} = \mathbf{22.7\text{ mL}}$$

To reach the second equivalence point, the remainder of the protons should have been removed from  $HSO_3^-$ , requiring another  $2.3 * 10^{-3}\text{ mol } OH^-$ . So,  $22.7\text{ mL} * 2 = 45.4\text{ mL}$  is needed.

6. Find the pH of each of the following points in the titration of 25.0 mL of 0.30 M HF with 0.30 M NaOH. The  $K_a$  of HF is  $7.2 \times 10^{-4}$

a. Before adding NaOH. "X" is negligible.

Before NaOH, there is only HF in solution. So, all we need to do is set up the ICE table for HF's acid/base reaction with water.



Molarity	[HF]	[F <sup>-</sup> ]	[H <sub>3</sub> O <sup>+</sup> ]
I	0.30	0	0
C	- x	+ x	+ x
E	0.30 - x	x	x

$$K_a = 7.2 \times 10^{-4} = \frac{[H_3O^+][F^-]}{[HF]} = \frac{x^2}{0.30 - x}$$

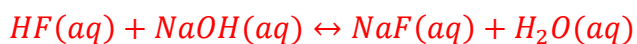
$$x^2 = 2.16 \times 10^{-4}$$

$$x = 0.0147 \text{ M } H_3O^+, \text{ so } pH = -\log(0.0147 \text{ M}) = 1.83$$

b. After adding 10.00 mL of NaOH

Since we're now changing the reaction system volume, let's change the ICE table values we're working with to moles.

Now, with NaOH present, some of the OH<sup>-</sup> will begin to react with the HF to create the conjugate base F<sup>-</sup>, causing us to enter the "buffer region."



Moles	[HF]	[OH <sup>-</sup> ]	[F <sup>-</sup> ]
I	0.0075	0	0
ADDITION of NaOH	0	+ 0.003	0
C	-0.003	0.003	+0.003
E	0.0045	0	0.003

$$pH = -\log(7.2 \times 10^{-4}) + \log\left(\frac{0.003}{0.0045}\right) = 2.97$$

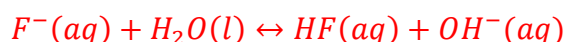
c. At the ½ equivalence point

At the ½ equivalence point,  $\text{pH} = \text{pK}_a$ .

$$\text{So, } \text{pH} = -\log(7.2 * 10^{-4}) = 3.14$$

d. At the equivalence point. "X" is negligible.

At the equivalence point, the NaOH will have fully reacted with all the HF to create the sodium fluoride salt. The only thing in solution will therefore be  $\text{Na}^+$ , a terrible acid,  $\text{H}_2\text{O}$ , and  $\text{F}^-$ , a passable base!  $\text{F}^-$  will react with water to produce  $\text{OH}^-$ , accounting for the pH.



There are  $0.0250 \text{ L} * 0.30 \text{ M} = 0.0075 \text{ mol}$  HF originally in the 25.0 mL solution, which requires the same amount of NaOH to neutralize.

$$\frac{0.0075 \text{ mol NaOH}}{0.300 \text{ M}} = 0.025 \text{ L NaOH solution}$$

This means that the total solution volume is now 50.0 mL, or 0.050 L. The molarity of  $\text{F}^-$  is therefore  $\frac{0.0075 \text{ mol F}^-}{0.050 \text{ L}} = 0.15 \text{ M}$ . Keep in mind that we need to go back to using molarity now because the Henderson-Hasselbach equation uses a ratio of base to acid, so units don't matter. But calculating pH via  $K_b$  **requires** concentration.

Molarity	[F <sup>-</sup> ]	[HF]	[OH <sup>-</sup> ]
I	0.15	0	0
C	- x	+ x	+ x
E	0.15 - x	x	x

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{7.2 * 10^{-4}} = 1.39 * 10^{-11} = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{x^2}{0.15 - x}$$

$$2.08 * 10^{-12} = x^2$$

$$x = 1.44 * 10^{-6} \text{ M OH}^-$$

$$\text{pH} = 14 - \text{pOH} = 14 - (-\log(1.44 * 10^{-6} \text{ M})) = \mathbf{8.16}$$

**e. After adding 28.00 mL of NaOH**

At this point, not only have we reacted with all of the HF, we're adding strong base to a solution that only had weak base F<sup>-</sup> in it. So, the huge amount of dissociation we with excess NaOH is going to completely obscure what little OH<sup>-</sup> is produced via F<sup>-</sup>'s reaction with water.

Since we know from the previous problem that 25.0 mL of NaOH is required to neutralize the HF, we know that we have 3.0 mL of 0.300 M NaOH solution that is in excess.

$$0.003 \text{ L NaOH} * 0.300 \text{ M NaOH} = 0.0009 \text{ mol NaOH}$$

What's the new molarity of this 0.0009 mol excess NaOH (and hence OH<sup>-</sup>) in solution?

$$28.0 \text{ mL} + 25.0 \text{ mL} = 53.0 \text{ mL} * \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0530 \text{ L}$$

$$\frac{0.0009 \text{ mol NaOH}}{0.0530 \text{ L}} = 1.70 * 10^{-2} \text{ M OH}^{-}$$

$$pH = 14 - (-\log([OH^{-}])) = 14 + \log(1.70 * 10^{-2} \text{ M}) = \mathbf{12.23}$$

**MCAT Style Question**

7.0 Researchers wish to mimic the conditions of the medial Golgi (pH  $\approx$  6.3. Which of these buffers would be best suited for this experiment?

- a. Acetic acid,  $K_a = 1.7 \times 10^{-5}$
- b. MES,  $K_a = 7.1 \times 10^{-7}$
- c. HEPES,  $K_a = 2.8 \times 10^{-8}$
- d. Tris,  $K_a = 6.3 \times 10^{-9}$

7.1 A buffer solution was prepared by adding 4.82 g of sodium acetate,  $\text{NaCH}_3\text{COO}$ , to  $2.50 \times 10^2 \text{ mL}$  of **0.160 M acetic acid,  $\text{CH}_3\text{COOH}$** . What is the pH of the buffer? The  $K_a$  of acetic acid is  $1.8 \times 10^{-5}$ . The volume of solution doesn't change.

Use H-H!  $\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$

Base:  $\left\{ \begin{array}{l} 4.82 \text{ g NaCH}_3\text{COO} \times \frac{1 \text{ mol}}{82.03 \text{ g}} = 0.0586 \text{ mol CH}_3\text{COO}^- \\ \frac{0.0586 \text{ mol CH}_3\text{COO}^-}{2.5 \times 10^{-1} \text{ L}} = \mathbf{0.2344 \text{ M CH}_3\text{COO}^-} \end{array} \right.$

$\text{pK}_a = -\log(K_a) = 4.7447$

$\text{pH} = 4.7447 + \log \frac{[0.2344 \text{ M}]}{[0.16 \text{ M}]} = 4.91$

### MCAT-Style Questions

8. Methanethiol,  $\text{CH}_3\text{SH}$ , has a  $\text{pK}_a$  of 10.3 and methanol,  $\text{CH}_3\text{OH}$ , has a  $\text{pK}_a$  of 15.5. Which is a stronger acid? Which is a stronger base,  $\text{CH}_3\text{S}^-$  or  $\text{CH}_3\text{O}^-$ ?

- Methanethiol is the stronger acid; its conjugate base is the stronger base
- Methanol is the stronger acid; its conjugate base is the stronger base
- Methanethiol is the stronger acid; methanol's conjugate base is the stronger base** A higher  $K_a$  results in a lower  $\text{pK}_a$ ; since methanethiol has a lower  $\text{pK}_a$  it is the stronger acid. However, this means that its conjugate base is comparatively weaker than methanethiol.
- Methanol is the stronger acid; methanethiol's conjugate base is the stronger base

9. Which of the following structural features may affect the  $\text{pK}_a$  of an acid?

- Electronegativity
- The length of the bond to the acidic hydrogen atom
- Inductive effects
- Resonance delocalization

- I only
- III only
- II and IV
- I, II, and IV
- I, II, III, and IV**

All of the above are true; the structure of a molecule is intimately related to its acidity and its propensity to gain or lose a  $\text{H}^+$ .

10. Based on the acid comparison in Table 1, which of the following organic acids will give a 0.10 M aqueous solution with the lowest pH?

Acid	Acid Formula (HA)	Conjugate Base (A <sup>-</sup> )	K <sub>a</sub>
Hydrochloric	HCl	Cl <sup>-</sup>	$1.3 \times 10^6$
Carbonic	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	$4.3 \times 10^{-7}$
Formic	HCO <sub>2</sub> H	CO <sub>2</sub> H <sup>-</sup>	$1.8 \times 10^{-4}$
Acetic	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	$1.8 \times 10^{-5}$
Lactic	H <sub>2</sub> C <sub>3</sub> H <sub>5</sub> O <sub>3</sub>	HC <sub>3</sub> H <sub>5</sub> O <sub>3</sub> <sup>-</sup>	$1.4 \times 10^{-4}$
Ascorbic	H <sub>2</sub> C <sub>6</sub> H <sub>6</sub> O <sub>6</sub>	HC <sub>6</sub> H <sub>6</sub> O <sub>6</sub> <sup>-</sup>	$7.9 \times 10^{-5}$
Citric	H <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	H <sub>2</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> <sup>-</sup>	$8.4 \times 10^{-4}$

- a. Acetic acid
- b. Carbonic acid
- c. Citric acid
- d. Lactic acid

Highest K<sub>a</sub> -> Lowest pK<sub>a</sub> -> Strongest acid -> most dissociation in water -> Highest [H<sub>3</sub>O<sup>+</sup>] -> lowest pH  
Remember, to be an organic acid we need carbon and oxygen!

11. Gastric acid has a pH of 1.0. How many millimoles of hydrogen ions are present in 10.0 mL of gastric acid? Assume gastric acid comprises solely HCl.

- a. 100 mmol
- b. 10 mmol
- c. 1.0 mmol
- d. 0.10 mmol

If pH is 1.0, then there are  $10^{-1}$  M of hydronium ions. If we have 10.0 mL solution (or 0.01 L of solution), we can use dimensional analysis to find moles of hydronium.  
( $10^{-1}$  mol/L) \* 0.01 L = 0.001 mol. Use conversion factor of 1000 mmol / mol and see that we have 1.0 mmol of hydronium.

12. In metal coordination complexes, the coordination number refers to:

- a. The number of ligands that form the complex
- b. The number of coordinate bonds formed
- c. The number of electrons involved in the coordinate bonding
- d. The oxidation number of the metal ion

This is the definition of coordination number, don't sweat this as Dr Watkins doesn't emphasize coordination at this point!