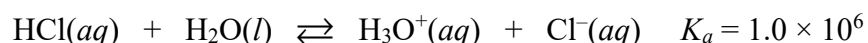


8.6 Molecular Structure of Acids and Bases

Essential knowledge statements from the AP Chemistry CED:

- The protons on a molecule that will participate in acid-base reactions, and the relative strength of these protons, can be inferred from the molecular structure.
 - Strong acids (such as HCl, HBr, HI, HClO₄, H₂SO₄, and HNO₃) have very weak conjugate bases that are stabilized by electronegativity, inductive effects, resonance, or some combination thereof.
 - Strong bases (such as group I and II hydroxides) have very weak conjugate acids.
 - Carboxylic acids are one common class of weak acid.
 - Common weak bases include nitrogenous bases such as ammonia as well as carboxylate ions.
 - Electronegative elements tend to stabilize the conjugate base relative to the conjugate acid, and so increase acid strength.
-



1. Hydrochloric acid ionizes in aqueous solution according to the equation shown above.



- (a) HCl and Cl⁻ represent a conjugate acid-base pair. Calculate the value of K_b for the reaction represented by the equation above.

- (b) Which of the following statements is true?

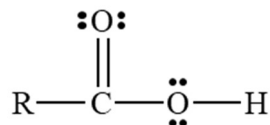
_____ The Cl⁻ ion is not likely to react with H₂O molecules to form OH⁻ ions.

_____ The Cl⁻ ion is very likely to react with H₂O molecules to form OH⁻ ions.

- (c) Justify your choice in part (b) in terms of the magnitude of the K_b value that you calculated in part (a).

Neutral Cations	Neutral Anions
Group I and Group II cations such as Na ⁺ , K ⁺ , Ca ²⁺ , and Sr ²⁺	Cl ⁻ , Br ⁻ , I ⁻ , ClO ₄ ⁻ , NO ₃ ⁻

The ions listed in the table above are neutral. They will not affect the pH of an aqueous solution.



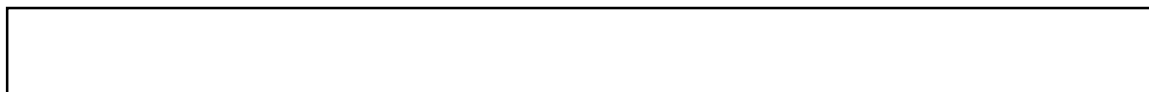
2. Carboxylic acids are one common class of weak acid. The general formula of a carboxylic acid is shown above, where the letter “R” refers to a group of atoms bonded to the $-\text{CO}_2\text{H}$ portion of the molecule. The “R” group consists of atoms that are mostly carbon and hydrogen.

(a) Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, is a weak acid found in household vinegar. It is one example of a carboxylic acid.

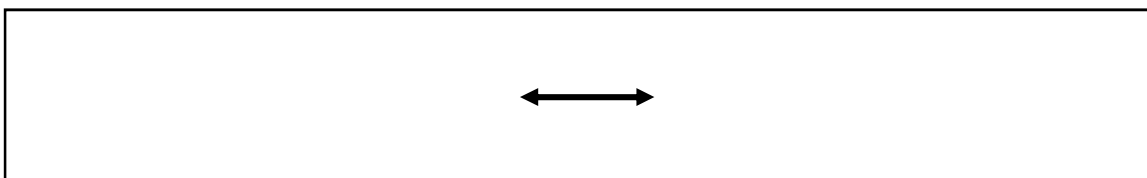
(i) In the box at right, draw the Lewis diagram for acetic acid.



(ii) Write the balanced chemical equation for the ionization of $\text{CH}_3\text{CO}_2\text{H}$ in aqueous solution.

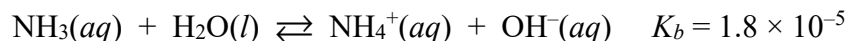


(iii) The acidic behavior of a carboxylic acid, RCO_2H , is supported by the fact that its conjugate base, RCO_2^- , is stabilized by resonance. Resonance helps to stabilize the conjugate base by delocalizing the negative charge over several atoms in the structure. Draw the Lewis diagrams for the two resonance forms of the acetate ion, CH_3CO_2^- .

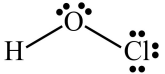
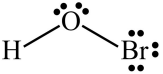
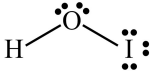
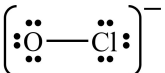

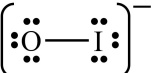


(b) For each structural formula in the table below, circle the H atom that is lost as a H^+ ion when the carboxylic acid molecule reacts as a H^+ donor.

Carboxylic Acid	Propanoic acid $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	Salicylic acid $\text{HC}_7\text{H}_5\text{O}_3$
Structural Formula	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{:O:} \\ \quad \quad \parallel \\ \text{H}-\text{C}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \quad \text{:}\ddot{\text{O}}-\text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H}-\text{C} \quad \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \quad \text{:}\ddot{\text{O}}-\text{H} \end{array}$
Conjugate base	Propanoate $\text{CH}_3\text{CH}_2\text{CO}_2^-$	Salicylate $\text{C}_7\text{H}_5\text{O}_3^-$

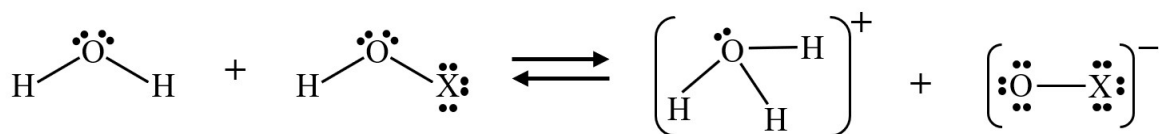


3. Ammonia, NH_3 , is one example of a weak base. The ionization of ammonia in aqueous solution is represented by the equation shown above. Ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$, is another example of a weak base that reacts with water in a similar way to NH_3 . Write the balanced chemical equation for the ionization of ethylamine in aqueous solution.

Acid	HOCl	HOBr	HOI
Structural Formula of Acid			
K_a of Acid	2.9×10^{-8}	2.4×10^{-9}	2.3×10^{-11}
Conjugate Base	ClO^-	BrO^-	IO^-
Structural Formula of Conjugate Base			

4. Information about three different acids is shown in the table above.

Which of these acids is the strongest acid? Justify your answer in terms of the K_a value.



The formula $\text{H}-\text{O}-\text{X}$ represents a weak acid in which $\text{X} = \text{Cl}, \text{Br}, \text{or I}$. As the electronegativity of X increases, the strength of the acid increases. There are two reasons why this occurs.

- As the electronegativity of X increases, electron density is drawn away from the $\text{H}-\text{O}$ bond. This causes the $\text{H}-\text{O}$ bond to become weaker and more polar, favoring the breaking of the $\text{H}-\text{O}$ bond in the acid molecule.
- As the electronegativity of X increases, this helps to stabilize the conjugate base by pulling electron density away from the oxygen atom that carries the negative charge. As the conjugate base becomes more stable, the strength of the acid increases.

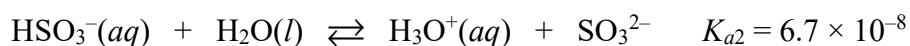
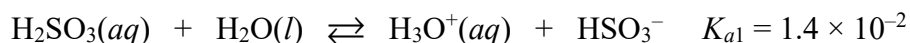
Acid	HOCl	HClO ₂	HClO ₃
Structural Formula of Acid			
K_a of Acid	2.9×10^{-8}	1.1×10^{-2}	5.0×10^2
Conjugate Base	ClO ⁻	ClO ₂ ⁻	ClO ₃ ⁻
Structural Formula of Conjugate Base			

5. Information about three different acids is shown in the table above.

Which of these acids is the strongest acid? Justify your answer in terms of the K_a value.

The acids shown in the table above are known as oxyacids. They contain a hydrogen atom bonded to an oxygen atom. Oxygen has a relatively high electronegativity. The presence of additional oxygen atoms bonded to the central atom increases the strength of the acid. There are two reasons why this occurs.

- (1) As the number of oxygen atoms increases, electron density is drawn away from the H–O bond. This causes the H–O bond to become weaker and more polar, favoring the breaking of the H–O bond in the acid molecule.
- (2) As the number of oxygen atoms increases, this helps to stabilize the conjugate base by allowing the negative charge to be delocalized or spread out over several oxygen atoms in the structure. As the conjugate base becomes more stable, the strength of the acid increases.



Sulfurous acid, H₂SO₃ is classified as a diprotic acid. The step-wise dissociation of the acid is represented by the equations above.

The value of K_{a1} is larger than the value of K_{a2} . This can be explained because of Coulomb's law and electrostatic attractions. It is easier to remove a positively charged H⁺ ion from a neutral H₂SO₃ molecule than it is to remove H⁺ from a negatively charged HSO₃⁻ ion.

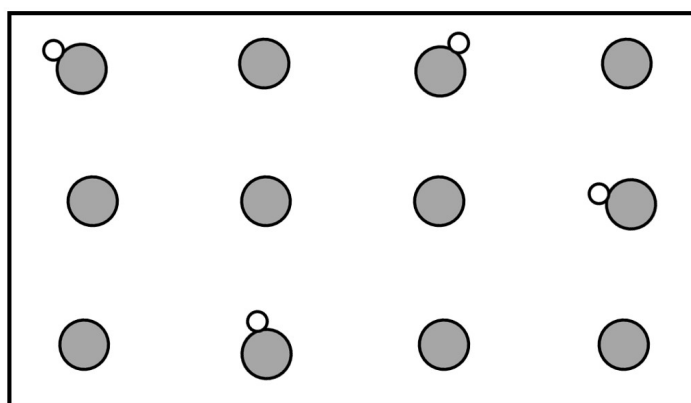
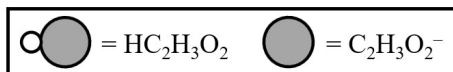
8.7 pH and pK_a

Essential knowledge statements from the AP Chemistry CED:

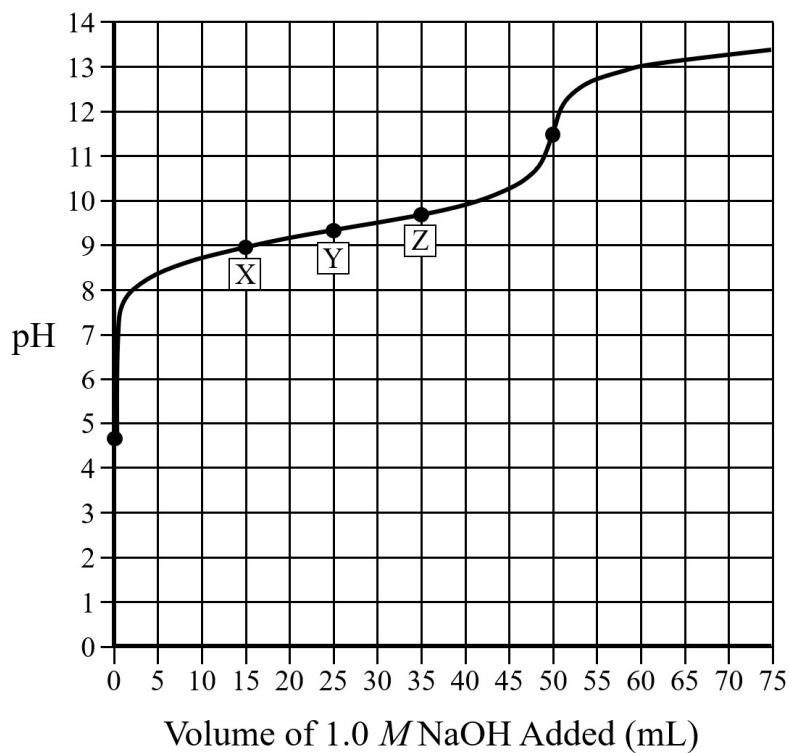
- The protonation state of an acid or base (i.e., the relative concentrations of HA and A^-) can be predicted by comparing the pH of a solution to the pK_a of the acid in that solution.
 - When solution $pH < acid\ pK_a$, the acid form has a higher concentration than the base form.
 - When solution $pH > acid\ pK_a$, the base form has a higher concentration than the acid form.
- Acid-base indicators are substances that exhibit different properties (such as color) in their protonated versus deprotonated state, making that property respond to the pH of a solution.

Acid	pK_a
$HC_2H_3O_2$	4.74
NH_4^+	9.26

6. The pK_a values of two different acids are listed in the table above. Use this information to answer the following questions.
- (a) A solution is prepared by combining samples of $HC_2H_3O_2(aq)$ and $NaOH(aq)$. The pH of the combined solution is equal to 4.00. Which substance, $HC_2H_3O_2$ or $C_2H_3O_2^-$, is present in a higher concentration in the combined solution? Justify your answer.
- (b) A solution is made by combining samples of $HC_2H_3O_2(aq)$ and $NaC_2H_3O_2(aq)$. A particulate representation of a small portion of this solution is shown below. Water molecules and Na^+ ions are not shown. Is the pH of the solution represented in the diagram less than, greater than, or equal to 4.74? Justify your answer.



6. (continued)

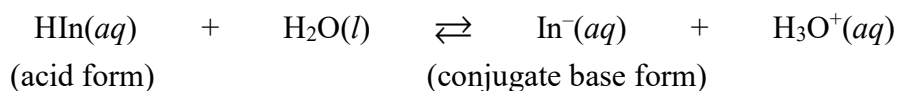


- (c) A student titrates 50.0 mL of 1.0 M $\text{NH}_4\text{Cl}(aq)$ with 1.0 M $\text{NaOH}(aq)$. The titration curve from the experiment is shown above. Three points on the titration curve are labeled as X, Y, and Z. Use the information from the titration curve to compare the relative concentrations of NH_4^+ and NH_3 at these three points.

Point	Circle the correct comparison of $[\text{NH}_4^+]$ and $[\text{NH}_3]$.		
X	$[\text{NH}_4^+] < [\text{NH}_3]$	$[\text{NH}_4^+] = [\text{NH}_3]$	$[\text{NH}_4^+] > [\text{NH}_3]$
Y	$[\text{NH}_4^+] < [\text{NH}_3]$	$[\text{NH}_4^+] = [\text{NH}_3]$	$[\text{NH}_4^+] > [\text{NH}_3]$
Z	$[\text{NH}_4^+] < [\text{NH}_3]$	$[\text{NH}_4^+] = [\text{NH}_3]$	$[\text{NH}_4^+] > [\text{NH}_3]$

Indicator	pK_a	Color of the Acid Form, HIn	Color of the Conjugate Base Form, In^-
Methyl Red	5.1	Red (below pH = 4)	Yellow (above pH = 6)
Bromothymol Blue	7.0	Yellow (below pH = 6)	Blue (above pH = 8)
Phenolphthalein	9.3	Colorless (below pH = 8)	Pink (above pH = 10)

Three examples of acid-base indicators are listed in the table above. An acid-base indicator is a substance that can exist in two different forms, each with a different color. The acid form of the indicator is represented as HIn, and the base form of the indicator is represented as In^- .



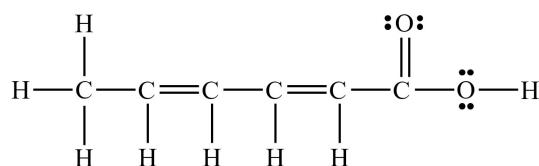
- If the pH of the solution is less than the pK_a of the indicator, the acid form (HIn) has a higher concentration than the conjugate base form (In^-).
- If the pH of the solution is greater than the pK_a of the indicator, the conjugate base form (In^-) has a higher concentration than the acid form (HIn).

7. Three solutions of bromothymol blue ($pK_a = 7.0$) were prepared with different pH values, as shown in the table below. Write the expected color for each solution.

pH of the solution	4.0	7.0	10.0
Expected Color			

Acid-base indicators can be used to signal the equivalence point in an acid-base titration. The **end point** of a titration marks the point at which a color change occurs in the indicator. The color change provides a signal to stop the titration and record the final volume on the buret.

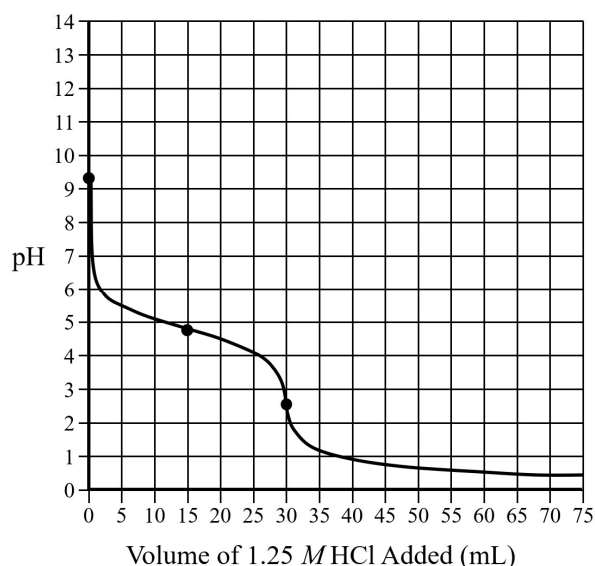
When selecting an acid-base indicator for a titration, it is important to choose an indicator that will change color at (or very near) the equivalence point. Therefore the best indicator to choose is the one with a pK_a value that is close to the pH of the solution at the equivalence point.



8. The structural formula of sorbic acid, $\text{HC}_6\text{H}_7\text{O}_2$, is shown above. Potassium sorbate, $\text{KC}_6\text{H}_7\text{O}_2$, is commonly added to diet soft drinks as a preservative. A student is given a stock solution of $\text{KC}_6\text{H}_7\text{O}_2(aq)$ of unknown concentration. The student titrates a sample of the stock solution with $\text{HCl}(aq)$, using both an indicator and a pH meter.

- (a) Write the net ionic equation for the reaction between $\text{KC}_6\text{H}_7\text{O}_2(aq)$ and $\text{HCl}(aq)$.

8. (continued)



(b) The student titrated a 50.0 mL sample of $\text{KC}_6\text{H}_7\text{O}_2(aq)$ with 1.25 M $\text{HCl}(aq)$. The titration curve is shown above. Use the information from the titration curve to answer the following questions.

(i) Calculate the value of $[\text{C}_6\text{H}_7\text{O}_2^-]$ in the stock solution.

(ii) Which of the indicators listed at right would be the best choice for determining the end point of the titration? Justify your answer.

Indicator	$\text{p}K_a$
Thymol Blue	2.0
Methyl Red	5.1
Bromothymol Blue	7.0
Phenolphthalein	9.3

(iii) Estimate the value of $\text{p}K_a$ for sorbic acid.

(c) The pH of a soft drink is 3.37 after the addition of a sample of $\text{KC}_6\text{H}_7\text{O}_2(aq)$. Which substance, $\text{HC}_6\text{H}_7\text{O}_2$ or $\text{C}_6\text{H}_7\text{O}_2^-$, has a higher concentration in the soft drink? Justify your answer.

8.8 Properties of Buffers

Essential knowledge statement from the AP Chemistry CED:

- A buffer solution contains a large concentration of both members in a conjugate acid-base pair. The conjugate acid reacts with added base and the conjugate base reacts with added acid. These reactions are responsible for the ability of a buffer to stabilize pH.

Examples of Conjugate Acid-Base Pairs			
Acid	pK_a	Base	pK_b
HClO ₂	1.96	ClO ₂ ⁻	12.04
HF	3.17	F ⁻	10.83
HNO ₂	3.40	NO ₂ ⁻	10.60
HCO ₂ H	3.74	HCO ₂ ⁻	10.26
C ₆ H ₅ NH ₃ ⁺	4.58	C ₆ H ₅ NH ₂	9.42
HC ₂ H ₃ O ₂	4.74	C ₂ H ₃ O ₂ ⁻	9.26
H ₂ S	7.04	HS ⁻	6.96
H ₂ PO ₄ ⁻	7.20	HPO ₄ ²⁻	6.80
HOCl	7.54	OCl ⁻	6.46
NH ₄ ⁺	9.26	NH ₃	4.74
CH ₃ NH ₃ ⁺	10.66	CH ₃ NH ₂	3.34

Several examples of weak acids and their corresponding conjugate bases are shown in the table above.

What are the components of a buffer solution?

A buffer solution contains approximately equimolar amounts of a conjugate acid-base pair.

- a weak acid and its conjugate base
- a weak base and its conjugate acid

What is the approximate pH of a buffer solution?

Consider the equilibrium constant expression for a weak acid.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad \frac{[\text{H}_3\text{O}^+][\text{B}]}{[\text{HB}^+]}$$

If a buffer solution is prepared that contains equimolar amounts of a weak acid and its conjugate base, then the following relationship is true.

$$[\text{H}_3\text{O}^+] = K_a \quad \text{and} \quad \text{pH} = \text{p}K_a$$

Therefore the pH of a buffer solution should be similar to the $\text{p}K_a$ of the weak acid that was used to create the buffer.

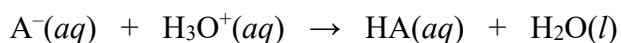
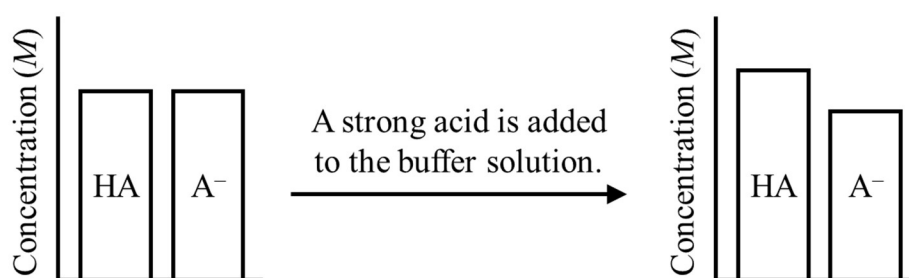
What are the properties of a buffer solution?

A buffer solution can maintain the pH at a fairly constant level when either a strong acid or a strong base is added to the solution.

- When a small amount of a strong acid is added to the buffer solution, the pH will decrease slightly.
- When a small amount of a strong base is added to the buffer solution, the pH will increase slightly.

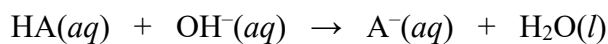
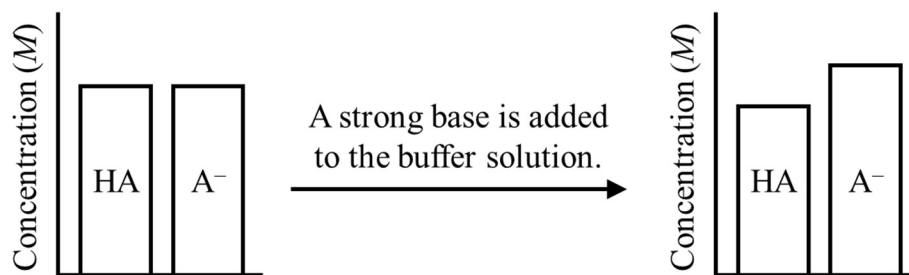
As long as the ratio of $\frac{[A^-]}{[HA]}$ or $\frac{[B]}{[HB^+]}$ remains fairly constant, the pH of the buffer solution will not change very much.

What happens when a strong acid is added to a buffer solution?



The value of $[A^-]$ decreases, the value of $[HA]$ increases, and the pH decreases slightly.

What happens when a strong base is added to a buffer solution?



The value of $[HA]$ decreases, the value of $[A^-]$ increases, and the pH increases slightly.

9. A buffer solution is prepared by combining 500.0 mL of 2.00 M $\text{HC}_2\text{H}_3\text{O}_2(aq)$ with 500.0 mL of 2.00 M $\text{NaC}_2\text{H}_3\text{O}_2(aq)$. The K_a for $\text{HC}_2\text{H}_3\text{O}_2$ is 1.8×10^{-5} .

(a) Calculate the pH of this buffer solution.

- (b) Write the net ionic equation for the reaction that occurs when $\text{HNO}_3(aq)$ (or any strong acid) is added to this buffer solution.

- (c) When a small amount of $\text{HNO}_3(aq)$ (or any strong acid) is added to this buffer solution, $[\text{HC}_2\text{H}_3\text{O}_2]$ will (decrease increase) and $[\text{C}_2\text{H}_3\text{O}_2^-]$ will (decrease increase)

- (d) Suppose that 4.0 mL of 10.0 M $\text{HNO}_3(aq)$ is added to 1.00 L of this buffer solution. Calculate the pH of the buffer solution after $\text{HNO}_3(aq)$ is added to it. A R-I-C-E table is shown below to guide you. Assume that the final volume of the solution remains constant, at 1.00 L.

R	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$	+	$\text{H}_3\text{O}^+(aq)$	\rightarrow	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	+	$\text{H}_2\text{O}(l)$
I	1.00 mol		mol		1.00 mol		N/A
C	mol		mol		mol		N/A
E	mol		mol		mol		N/A

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \text{_____} M$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = \text{_____} M$$

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$[\text{H}_3\text{O}^+] = \text{_____} M$$

$$\text{pH} = \text{_____}$$

- (e) Suppose that 4.0 mL of 10.0 M $\text{HNO}_3(aq)$ is added to 1.00 L of pure water. Calculate the pH of the solution after $\text{HNO}_3(aq)$ is added. Assume that the final volume of the solution remains constant, at 1.00 L.

9. (continued)

- (f) Write the net ionic equation for the reaction that occurs when $\text{KOH}(aq)$ (or any strong base) is added to this buffer solution.

- (g) When a small amount of $\text{KOH}(aq)$ (or any strong base) is added to this buffer solution, $[\text{HC}_2\text{H}_3\text{O}_2]$ will (decrease increase) and $[\text{C}_2\text{H}_3\text{O}_2^-]$ will (decrease increase)

- (h) Suppose that 4.0 mL of 10.0 M $\text{KOH}(aq)$ is added to 1.00 L of this buffer solution. Calculate the pH of the buffer solution after $\text{KOH}(aq)$ is added to it. A R-I-C-E table is shown below to guide you. Assume that the final volume of the solution remains constant, at 1.00 L.

R	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	+	$\text{OH}^-(aq)$	\rightarrow	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$	+	$\text{H}_2\text{O}(l)$
I	1.00 mol		mol		1.00 mol		N/A
C	mol		mol		mol		N/A
E	mol		mol		mol		N/A

$$[\text{HC}_2\text{H}_3\text{O}_2] = \text{_____} M$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \text{_____} M$$

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$[\text{H}_3\text{O}^+] = \text{_____} M$$

$$\text{pH} = \text{_____}$$

- (i) Suppose that 4.0 mL of 10.0 M $\text{KOH}(aq)$ is added to 1.00 L of pure water. Calculate the pH of the solution after $\text{KOH}(aq)$ is added. Assume that the final volume of the solution remains constant, at 1.00 L.

10. The pK_a of HNO_2 is 3.40. Select all of the following descriptions that would result in the formation of a buffer with a pH of 3.40.

_____ 100.0 mL of 1.0 M $\text{HNO}_2(aq)$ and 100.0 mL of 1.0 M $\text{KNO}_2(aq)$ are combined.

_____ 100.0 mL of 1.0 M $\text{HNO}_2(aq)$ and 100.0 mL of 1.0 M $\text{KOH}(aq)$ are combined.

_____ 100.0 mL of 1.0 M $\text{HNO}_2(aq)$ and 100.0 mL of 1.0 M $\text{HNO}_3(aq)$ are combined.

_____ 200.0 mL of 1.0 M $\text{HNO}_2(aq)$ and 100.0 mL 1.0 M $\text{KNO}_2(aq)$ are combined.

_____ 200.0 mL of 1.0 M $\text{HNO}_2(aq)$ and 100.0 mL 1.0 M $\text{KOH}(aq)$ are combined.

_____ 200.0 mL of 1.0 M $\text{HNO}_2(aq)$ and 100.0 mL 1.0 M $\text{HNO}_3(aq)$ are combined.

11. The pK_a of NH_4^+ is 9.26. Select all of the following descriptions that would result in the formation of a buffer with a pH of 9.26.

_____ 100.0 mL of 1.0 M $\text{NH}_3(aq)$ and 100.0 mL of 1.0 M $\text{NH}_4\text{NO}_3(aq)$ are combined.

_____ 100.0 mL of 1.0 M $\text{NH}_3(aq)$ and 100.0 mL of 1.0 M $\text{HNO}_3(aq)$ are combined.

_____ 100.0 mL of 1.0 M $\text{NH}_3(aq)$ and 100.0 mL of 1.0 M $\text{KOH}(aq)$ are combined.

_____ 200.0 mL of 1.0 M $\text{NH}_3(aq)$ and 100.0 mL 1.0 M $\text{NH}_4\text{NO}_3(aq)$ are combined.

_____ 200.0 mL of 1.0 M $\text{NH}_3(aq)$ and 100.0 mL 1.0 M $\text{HNO}_3(aq)$ are combined.

_____ 200.0 mL of 1.0 M $\text{NH}_3(aq)$ and 100.0 mL 1.0 M $\text{KOH}(aq)$ are combined.

There are four possible combinations that should result in the formation of a buffer solution.

HA = weak acid A^- = conjugate base B = weak base HB^+ = conjugate acid

Substances That Are Combined	Mole Ratio (approx.)	Components in the Buffer Solution
HA and A^-	moles of HA = moles of A^-	HA and A^-
HA and OH^-	moles of $\text{OH}^- = \frac{1}{2}$ (moles of HA) half-equivalence point	HA and A^-
B and HB^+	moles of B = moles of HB^+	B and HB^+
B and H_3O^+	moles of $\text{H}_3\text{O}^+ = \frac{1}{2}$ (moles of B) half-equivalence point	B and HB^+

8.9 Henderson-Hasselbalch Equation

Essential knowledge statement from the AP Chemistry CED:

- The pH of the buffer is related to the pK_a of the acid and the concentration ratio of the conjugate acid–base pair. This relation is a consequence of the equilibrium expression associated with the dissociation of a weak acid, and is described by the Henderson-Hasselbalch equation. Adding small amounts of acid or base to a buffered solution does not significantly change the ratio of $[A^-]/[HA]$ and thus does not significantly change the solution pH. The change in pH on addition of acid or base to a buffered solution is therefore much less than it would have been in the absence of the buffer.

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

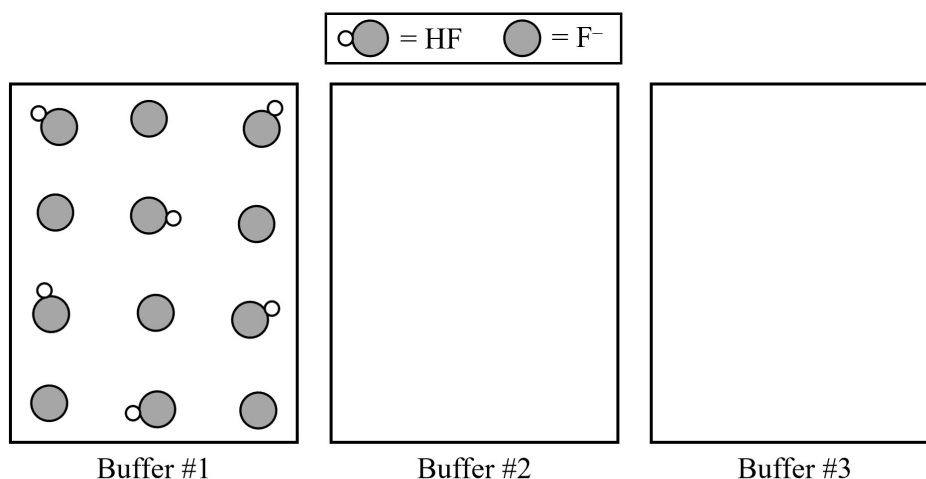
12. Three different buffer solutions are prepared by combining solutions of HF(aq) and NaF(aq) as described in the table below.

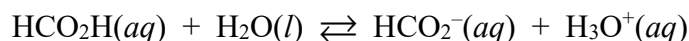
Buffer	Concentration of HF in the Buffer	Concentration of NaF in the Buffer	pH
#1	1.0 M	1.0 M	
#2	1.0 M	2.0 M	
#3	2.0 M	1.0 M	

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.8 \times 10^{-4}$$

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

- (a) Calculate the pH of each buffer solution in the table above by using the K_a expression for HF.
- (b) Calculate the pH of each buffer solution in the table above by using the Henderson-Hasselbalch equation.
- (c) A particulate representation of a small portion of buffer #1 is shown below. Water molecules and Na^+ ions are not shown. In the boxes below, draw diagrams to represent the components of buffer #2 and buffer #3. Represent HF molecules and F^- ions as indicated below.





$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} = 1.8 \times 10^{-4} \qquad \text{pH} = \text{p}K_a + \log \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$$

13. Formic acid, HCO_2H , ionizes in aqueous solution according to the chemical equation shown above. Use either the K_a expression for HCO_2H or the Henderson-Hasselbalch equation to fill in the missing information in the table below.

Solution	$[\text{HCO}_2\text{H}]$	$[\text{HCO}_2^-]$	$\frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$	pH
#1	1.00 M	1.00 M	1.00	3.74
#2	0.750 M	1.35 M		
#3		1.00 M		3.52
#4	1.00 M			3.82

8.10 Buffer Capacity

Essential knowledge statements from the AP Chemistry CED:

- Increasing the concentration of the buffer components (while keeping the ratio of these concentrations constant) keeps the pH of the buffer the same but increases the capacity of the buffer to neutralize added acid or base.
- When a buffer has more conjugate acid than base, it has a greater buffer capacity for addition of added base than acid.
- When a buffer has more conjugate base than acid, it has a greater buffer capacity for addition of added acid than base.

The term **buffer capacity** refers to amount of acid (or base) that a buffer can react with, without experiencing a significant change in pH. If the amount of acid (or base) that is added to a buffer exceeds the buffer capacity, then the buffer solution will experience a large change in pH.

14. Two different buffer solutions are prepared by combining solutions of $\text{HC}_2\text{H}_3\text{O}_2(aq)$ and $\text{NaC}_2\text{H}_3\text{O}_2(aq)$ as described in the table below. The K_a for $\text{HC}_2\text{H}_3\text{O}_2$ is 1.8×10^{-5} .

Buffer	Concentration of $\text{HC}_2\text{H}_3\text{O}_2$ in the Buffer	Concentration of $\text{NaC}_2\text{H}_3\text{O}_2$ in the Buffer	pH
#1	1.00 M	1.00 M	
#2	0.0500 M	0.0500 M	

- (a) Calculate the pH of each buffer solution in the table above.
- (b) A sample of 0.045 mol of $\text{HNO}_3(aq)$ is added to 1.00 L of buffer #1. Assume that the change in volume of the solution is negligible. Use the R-I-C-E table to help you calculate the pH of the solution after HNO_3 is added.

R	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$	+	$\text{H}_3\text{O}^+(aq)$	\rightleftharpoons	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	+	$\text{H}_2\text{O}(l)$
I	1.00 mol		0.045 mol		1.00 mol		N/A
C	mol		mol		mol		N/A
E	mol		mol		mol		N/A

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \text{_____} M$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = \text{_____} M$$

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$[\text{H}_3\text{O}^+] = \text{_____} M$$

$$\text{pH} = \text{_____}$$

- (c) A sample of 0.045 mol of $\text{HNO}_3(aq)$ is added to 1.00 L of buffer #2. Assume that the change in volume of the solution is negligible. Use the R-I-C-E table to help you calculate the pH of the solution after HNO_3 is added.

R	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$	+	$\text{H}_3\text{O}^+(aq)$	\rightleftharpoons	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	+	$\text{H}_2\text{O}(l)$
I	0.0500 mol		0.045 mol		0.0500 mol		N/A
C	mol		mol		mol		N/A
E	mol		mol		mol		N/A

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \text{_____} M$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = \text{_____} M$$

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$[\text{H}_3\text{O}^+] = \text{_____} M$$

$$\text{pH} = \text{_____}$$

- (d) Which buffer solution, #1 or #2, experienced a greater change in pH after the addition of 0.045 mol of HNO_3 ? _____
- (e) Which buffer solution, #1 or #2, has the greater buffer capacity? _____

15. Two different buffer solutions are prepared by combining solutions of $\text{NH}_3(aq)$ and $\text{NH}_4\text{NO}_3(aq)$. A sample of NaOH is added to each buffer solution. The solutions are mixed thoroughly and the pH is recorded. The data from the experiment are recorded in the table below.

Buffer	#1	#2
Buffer Components	NH_3 and NH_4^+	NH_3 and NH_4^+
Volume of Buffer	1.00 L	1.00 L
Initial pH of Buffer	9.26	9.26
Amount of NaOH added to the Buffer	0.10 mol	0.10 mol
Final pH of Buffer	9.35	9.96

Which buffer solution, #1 or #2, has the greater buffer capacity? Justify your answer in terms of the data in the table above.

16. Two different buffer solutions are prepared by combining solutions of $\text{HNO}_2(aq)$ and $\text{KNO}_2(aq)$ as described in the table below.

Buffer	Concentration of HNO_2 in the Buffer	Concentration of KNO_2 in the Buffer
#1	1.50 M	1.00 M
#2	1.00 M	1.50 M

- (a) Buffer #1 has a greater buffer capacity for the addition of added (acid base) because it contains a higher concentration of (HNO_2 NO_2^-).
- (b) Buffer #2 has a greater buffer capacity for the addition of added (acid base) because it contains a higher concentration of (HNO_2 NO_2^-).