ACIDS & BASES

- Many common substances in our daily lives are **acids and bases**. **Oranges, lemons and vinegar** are examples of **acids**. In addition, our stomachs contain acids that help digest foods. **Antacid** tablets taken for heartburn and **ammonia** cleaning solutions are examples of **bases**.

- General properties associated with acids include the following:

  - sour taste
  - change color of litmus from blue to red
  - react with metals to produce H_2 gas
  - react with bases to produce salt and water

- General properties associated with bases include the following:

  - bitter taste
  - slippery soapy feeling
  - change color of litmus from red to blue
  - react with acids to produce salt and water

- The most common definition of acids and bases was formulated by the Swedish chemist Svante **Arrhenius** in 1884.

- According to the **Arrhenius** definition,

Acids are substances that produce hydronium ion (H_3O^+) in aqueous solution

$$HCl\ (g) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

Commonly written as

$$\underset{\text{polar covalent}}{HCl\ (g)} \xrightarrow{H_2O} H^+\ (aq) + Cl^-\ (aq)$$

Bases are substances that produce hydroxide ion (OH^-) in aqueous solution

$$\underset{\text{ionic compound}}{NaOH\ (s)} \xrightarrow{H_2O} Na^+\ (aq) + OH^-\ (aq)$$

$$NH_3\ (aq) + H_2O\ (l) \longrightarrow NH_4^+\ (aq) + OH^-\ (aq)$$

ACID & BASE STRENGTH

- According to the **Arrhenius** definition, the **strength** of acids and bases is based on the amount of their **ionization** in water.

- **Strong** acids and bases are those that **ionize completely** in water.
- Strong acids and bases are **strong electrolytes**.

$$HCl\ (aq) \longrightarrow H^+\ (aq) + Cl^-\ (aq)$$

$$NaOH\ (s) \xrightarrow{H_2O} Na^+\ (aq) + OH^-\ (aq)$$

- **Weak** acids and bases are those that **ionize partially** in water.
- Weak acids and bases are **weak electrolytes**.

$$HC_2H_3O_2 \xrightleftharpoons{H_2O} H^+\ (aq) + C_2H_3O_2^-\ (aq)$$

$$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

COMMON STRONG ACIDS & BASES

HCl	Hydrochloric acid	LiOH	Lithium hydroxide
HBr	Hydrobromic acid	NaOH	Sodium hydroxide
HI	Hydroiodic acid	KOH	Potassium hydroxide
HNO_3	Nitric acid	$Ba(OH)_2$	Barium hydroxide
H_2SO_4	Sulfuric acid		

COMMON WEAK ACIDS & BASES

$HC_2H_3O_2$	Acetic acid	NH_3	Ammonia
H_2CO_3	Carbonic acid	$CO(NH_2)_2$	Urea
HF	Hydrofluoric acid		
HCN	Hydrocyanic acid		
H_2S	Hydrosulfuric acid		

BRØNSTED-LOWRY ACIDS & BASES

- The **Arrhenius** definition of acids and bases is **limited to aqueous solutions**.

- A broader definition of acids and bases was developed by **Brønsted and Lowry** in the early 20th century.

- According to **Brønsted-Lowry** definition, an **acid** is a **proton donor**, and a **base is a proton acceptor**.

$$\begin{array}{lllll} \mathrm{HCl\ (g)\ +} & \mathrm{H_2O\ (l)} & \longrightarrow & \mathrm{H_3O^+\ (aq)\ +} & \mathrm{Cl^-\ (aq)} \\ \text{(Acid)} & \text{(Base)} & & & \end{array}$$

$$\begin{array}{lllll} \mathrm{NH_3\ (aq)\ +} & \mathrm{H_2O\ (l)} & \longrightarrow & \mathrm{NH_4^+\ (aq)\ +} & \mathrm{OH^-\ (aq)} \\ \text{(Base)} & \text{(Acid)} & & & \end{array}$$

- A substance that can act as a **Brønsted-Lowry acid and base** (such as **water**) is called **amphiprotic**.

- In Brønsted-Lowry definition, any pair of molecules or ions that can be **interconverted by transfer of a proton** is called **conjugate acid-base pair**.

$$\begin{array}{lllll} \mathrm{HCl\ (g)\ +} & \mathrm{H_2O\ (l)} & \longrightarrow & \mathrm{H_3O^+\ (aq)\ +} & \mathrm{Cl^-\ (aq)} \\ \text{(Acid)} & \text{(Base)} & & \text{(Conjugate} & \text{(Conjugate} \\ & & & \text{acid of water)} & \text{base of HCl)} \end{array}$$

$$\begin{array}{lllll} \mathrm{NH_3\ (aq)\ +} & \mathrm{H_2O\ (l)} & \longrightarrow & \mathrm{NH_4^+\ (aq)\ +} & \mathrm{OH^-\ (aq)} \\ \text{(Base)} & \text{(Acid)} & & \text{(Conjugate} & \text{(Conjugate} \\ & & & \text{acid of } \mathrm{NH_3}\text{)} & \text{base of water)} \end{array}$$

BRØNSTED-LOWRY ACIDS & BASES

Examples:

1. Identify the conjugate acid-base pairs for each reaction shown below:

$$H_2O + Cl^- \rightarrow HCl + OH^-$$

$$C_6H_5OH + C_2H_5O^- \rightarrow C_6H_5O^- + C_2H_5OH$$

2. Write the formula for the conjugate acid for each base shown:

HS^-

NH_3

CO_3^{2-}

3. Write the formula for the conjugate base for each acid shown:

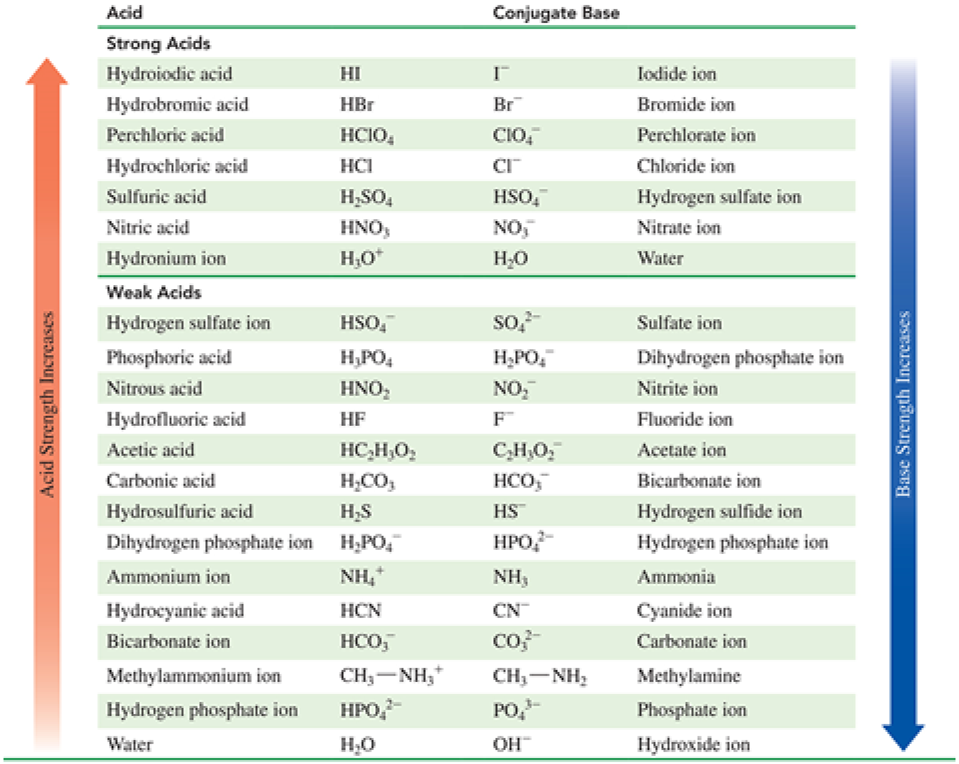
HI

CH_3OH

HNO_3

ACID & BASE STRENGTH

- The strength of acids and bases and their conjugates can be tabulated as shown below:



Acid		Conjugate Base	
Strong Acids			
Hydroiodic acid	HI	I^-	Iodide ion
Hydrobromic acid	HBr	Br^-	Bromide ion
Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion
Hydrochloric acid	HCl	Cl^-	Chloride ion
Sulfuric acid	H_2SO_4	HSO_4^-	Hydrogen sulfate ion
Nitric acid	HNO_3	NO_3^-	Nitrate ion
Hydronium ion	H_3O^+	H_2O	Water
Weak Acids			
Hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	Sulfate ion
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion
Nitrous acid	HNO_2	NO_2^-	Nitrite ion
Hydrofluoric acid	HF	F^-	Fluoride ion
Acetic acid	$HC_2H_3O_2$	$C_2H_3O_2^-$	Acetate ion
Carbonic acid	H_2CO_3	HCO_3^-	Bicarbonate ion
Hydrosulfuric acid	H_2S	HS^-	Hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	HPO_4^{2-}	Hydrogen phosphate ion
Ammonium ion	NH_4^+	NH_3	Ammonia
Hydrocyanic acid	HCN	CN^-	Cyanide ion
Bicarbonate ion	HCO_3^-	CO_3^{2-}	Carbonate ion
Methylammonium ion	$CH_3{-}NH_3^+$	$CH_3{-}NH_2$	Methylamine
Hydrogen phosphate ion	HPO_4^{2-}	PO_4^{3-}	Phosphate ion
Water	H_2O	OH^-	Hydroxide ion

- Note that strong acids have weak conjugate bases, and weak acids have strong conjugate bases.

- In an acid-base reaction, there are two acids and two bases. Using the table above, the relative strength of the two acids and bases can be determined in the reaction. As a result, the reaction proceeds in the direction of the weaker acid and weaker base to reach equilibrium.

- For example, in the reaction of H_2SO_4 and H_2O (shown below), the reaction proceeds in the forward direction since H_3O^+ and HSO_4^- are the weaker acid and base in the reaction:

$$\begin{array}{ccccccc} H_2SO_4\ (aq) & + & H_2O\ (l) & \longrightarrow & H_3O^+\ (aq) & + & HSO_4^-\ (aq) \\ \text{stronger} & & \text{stronger} & & \text{weaker} & & \text{weaker} \\ \text{acid} & & \text{base} & & \text{acid} & & \text{base} \end{array}$$

Mostly products

- And in the reaction of CO_3^{2-} and H_2O (shown below), the reaction proceeds in the reverse direction since H_2O and CO_3^{2-} are the weaker acid and base in the reaction:

$$CO_2^{2-}\ (aq)\ +\ H_2O\ (l) \rightleftharpoons HCO_3^-\ (aq)\ +\ OH^-\ (aq)$$

weaker	weaker	weaker	weaker	**Mostly reactants**
base	acid	acid	base	

Examples:

1. Is the forward or reverse direction favored in the reaction shown below:

$$HF\ (aq)\ +\ H_2O\ (l) \longrightarrow H_3O^+\ (aq)\ +\ F^-\ (aq)$$

2. Predict whether each of the following reactions contains mostly reactants or products at equilibrium:

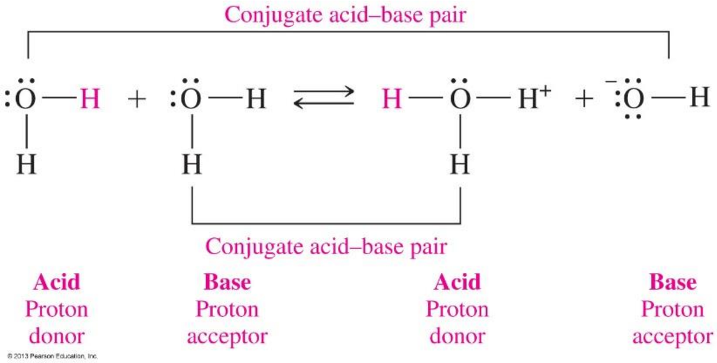
a) $NH_4^+\ (aq)\ +\ H_2O\ (l) \rightleftharpoons NH_3\ (aq)\ +\ H_3O^+\ (aq)$

b) $HNO_2\ (aq)\ +\ NH_3\ (aq) \rightleftharpoons NO_2^-\ (aq)\ +\ NH_4^+\ (aq)$

IONIZATION OF WATER

- As noted previously, **water** can act both as an **acid and a base**.

- In pure water, one **water** molecule **donates a proton** to another water molecule to produce **ions**.



- In pure water, the **transfer of protons** between water molecules produces **equal numbers of H_3O^+ and $OH^–$ ions**. However, the number of ions produced in pure water is very small, as indicated below:

Pure water $[H_3O^+] = [OH^–] = 1.0 \times 10^{–7}$ M

- When the **concentrations of H_3O^+ and $OH^–$ are multiplied** together, the **ion-product constant (K_w)** is formed.

$$K_w = [H_3O^+] \times [OH^–]$$

$$= (1.0 \times 10^{–7} \text{ M}) \times (1.0 \times 10^{–7} \text{ M}) = 1.0 \times 10^{–14}$$

- All aqueous solutions have **H_3O^+ and $OH^–$ ions**. An **increase in the concentration** of one of the ions will cause an equilibrium shift that causes a **decrease in the other one**.

ACIDIC & BASIC SOLUTIONS

- When **[H_3O^+]** and **[OH^-] are equal** in a solution, it is **neutral**.
- When **[H_3O^+]** is **greater** than **[OH^-]** in a solution, it is **acidic**.

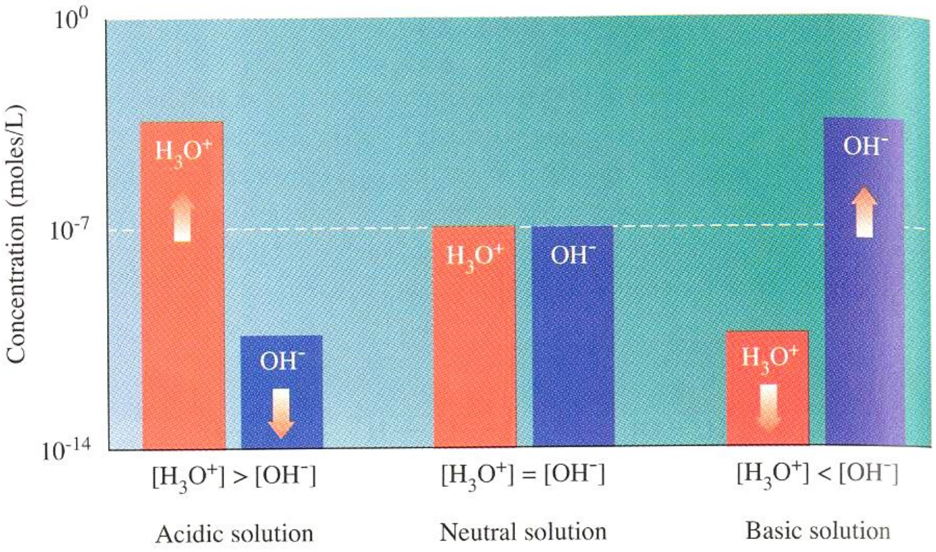
For example, if [H_3O^+] is 1.0 x 10^{-4} M, then [OH^-] would be 1.0 x 10^{-10} M.

$$\left[OH^-\right]=\frac{K_w}{\left[H_3O^+\right]}=\frac{1.0 \text{ x } 10^{-14}}{1.0 \text{ x } 10^{-4}}=1.0 \text{ x } 10^{-10} \text{ M}$$

- When **[OH^-]** is **greater** than **[H_3O^+]** in a solution, it is **basic**.

For example, if [OH^-] is 1.0 x 10^{-6} M, then [H_3O^+] would be 1.0 x 10^{-8} M.

$$\left[H_3O^+\right]=\frac{K_w}{\left[OH^-\right]}=\frac{1.0 \text{ x } 10^{-14}}{1.0 \text{ x } 10^{-6}}=1.0 \text{ x } 10^{-8} \text{ M}$$



ACIDIC & BASIC SOLUTIONS

Examples:

1. Calculate the $[OH^-]$ in a solution with $[H_3O^+] = 2.3 \times 10^{-4}$ M. Classify the solution as acid or basic.

$$\left[OH^-\right] = \frac{K_w}{\left[H_3O^+\right]} =$$

2. Calculate the $[H_3O^+]$ in a solution with $[OH^-] = 2.3 \times 10^{-4}$ M. Classify the solution as acid or basic.

$$\left[H_3O^+\right] = \frac{K_w}{\left[OH^-\right]} =$$

3. Calculate the $[OH^-]$ in a solution with $[H_3O^+] = 5.8 \times 10^{-8}$ M. Classify the solution as acid or basic.

4. Calculate the $[H_3O^+]$ in a solution with $[OH^-] = 1.3 \times 10^{-2}$ M. Classify the solution as acid or basic.

THE pH SCALE

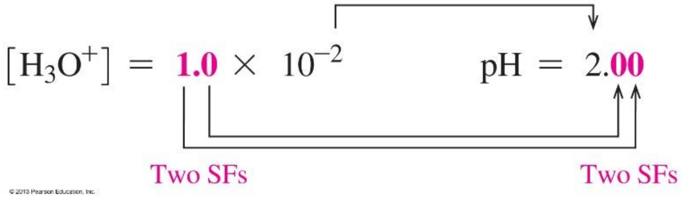
- The **acidity** of a solution is commonly measured on a **pH scale**.

$$\mathbf{pH = -\log [H_3O^+]}$$

- The **pH scale** ranges from **0-14**, where **acidic** solutions are **less than 7** and **basic** solutions are **greater than 7**.

Acidic solutions	**pH < 7**	**$[H_3O^+] > 1.0 \times 10^{-7}$**
Neutral solutions	**pH = 7**	**$[H_3O^+] = 1.0 \times 10^{-7}$**
Basic solutions	**pH > 7**	**$[H_3O^+] < 1.0 \times 10^{-7}$**

- When calculating pH, note that the number of decimal places in the pH value is the same as the number of significant figures in the $[H_3O^+]$. For example:



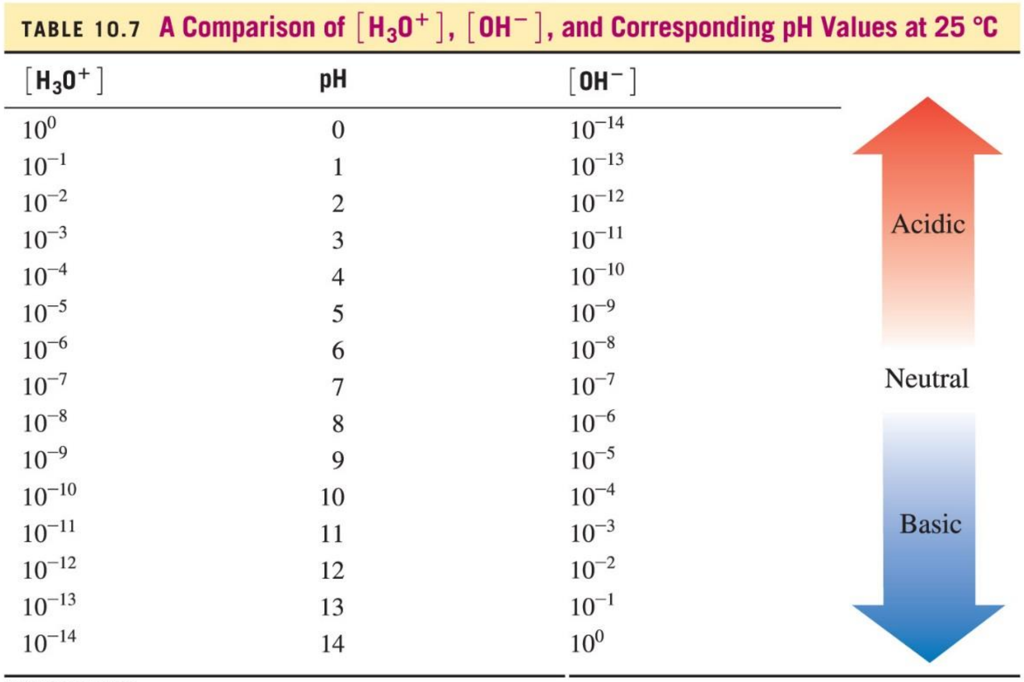


TABLE 10.7 A Comparison of $[H_3O^+]$, $[OH^-]$, and Corresponding pH Values at 25 °C

$[H_3O^+]$	pH	$[OH^-]$
10^{0}	0	10^{-14}
10^{-1}	1	10^{-13}
10^{-2}	2	10^{-12}
10^{-3}	3	10^{-11}
10^{-4}	4	10^{-10}
10^{-5}	5	10^{-9}
10^{-6}	6	10^{-8}
10^{-7}	7	10^{-7}
10^{-8}	8	10^{-6}
10^{-9}	9	10^{-5}
10^{-10}	10	10^{-4}
10^{-11}	11	10^{-3}
10^{-12}	12	10^{-2}
10^{-13}	13	10^{-1}
10^{-14}	14	10^{0}

THE pH SCALE

Examples:

1. The $[H_3O^+]$ of a liquid detergent is 1.4×10^{-9} M. Calculate its pH.

$$pH = -\log [H_3O^+] = -\log [1.4 \times 10^{-9}] = -(-8.85) = 8.85$$

2. The pH of black coffee is 5.3. Calculate its $[H_3O^+]$.

$$[H_3O^+] = \text{antilog}(-pH) = 10^{-pH} = 10^{-5.3} = 5 \times 10^{-6}$$

3. The $[H_3O^+]$ of a solution is 3.5×10^{-3} M. Calculate its pH.

4. The $[OH^-]$ of a cleaning solution is 1.0×10^{-5} M. What is the pH of this solution?

$[H_3O^+] =$ pH=

5. What is the pH of a solution prepared by dissolving 2.5 g of HCl in water to make 425 mL of solution?

REACTIONS OF ACIDS & BASES

- The most important reaction of acids and bases is called **neutralization**. In these reactions an acid combines with a base to form a **salt and water**. For example:

$$\mathbf{HCl\ (aq) + NaOH\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l)}$$

acid **base** **salt** **water**

- Acids also react with **carbonates and bicarbonates** to produce **salt, carbon dioxide gas and water**. For example:

$$\mathbf{2\ HCl\ (aq) + Na_2CO_3\ (aq) \longrightarrow 2\ NaCl\ (aq) + CO_2\ (g) + H_2O\ (l)}$$

$$\mathbf{HCl\ (aq) + NaHCO_3\ (aq) \longrightarrow NaCl\ (aq) + CO_2\ (g) + H_2O\ (l)}$$

- Acids also react with **active metals** to produce a **salt and hydrogen gas**. For example:

$$\mathbf{Mg\ (s) + 2\ HCl\ (aq) \longrightarrow MgCl_2\ (aq) + H_2\ (g)}$$

Examples:

Complete and balance each of the following equations:

1. $ZnCO_3$ (aq) + HCl (aq) →

2. HNO_3 (aq) + $Mg(OH)_2$ (aq) →

3. Al (s) + HCl (aq) →

TITRATION

- Determination of concentration of an acid or base from the known concentration of the other is called **titration**.

HCl	+	NaOH	→	NaCl	+	H_2O
acid		**base**		salt		
known conc.		**unknown conc.**				

- In a titration, a measured volume of the acid in a flask and add a few drops of an indicator, such as phenolphtalein. (Solution is clear)
- Next, a solution of NaOH with a known molarity is added to the acid dropwise, using a buret.
- When neutralization is complete, the indicator changes color to pink. This is called ***endpoint.***
- Based on the measured volume of the NaOH solution added and its molarity, the concentration of the acid can be calculated.

TITRATION

- When solving titration problems,
  1. Write a balanced equation.
  2. Determine moles of known from concentration and volume.
  3. Determine moles of unknown based on reaction stoichiometry.
  4. Determine the concentration of unknown from moles and volume titrated.

Examples:

1. If 32.6 mL of 1.85 M NaOH is required to titrate 25.0 mL of an HCl solution to the end point, what is the molarity of HCl?

Bal. Eq.	$HCl + NaOH \rightarrow NaCl + H_2O$
Vol (mL)	
Conc. (M)	
mol NaOH	
mol HCl	
Conc. HCl	

Examples:

2. How many mL of 2.15 M KOH are required to titrate 25.0 mL of 0.300 M $HC_2H_3O_2$?

Bal. Eq.	
Vol (mL)	
Conc. (M)	
mol HAc	
mol NaOH	
Vol NaOH (mL)	

3. If 50.0 mL of 0.300 M NaOH solution is required to titrate 20.0 mL of sulfuric acid, what is the molarity of the acid?

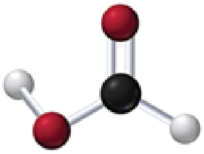
Bal. Eq.	
Vol (mL)	
Conc. (M)	
mol NaOH	
mol H_2SO_4	
Conc. H_2SO_4	

ACID DISSOCIATION CONSTANT

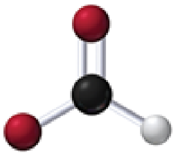
- As discussed earlier, the strength of an acid depends on how much it dissociates in water. Because strong acids dissociate completely in water, the reaction is not considered reversible.

- However, because weak acids dissociate partially in water, the ion products reach an equilibrium with the undissociated weak acid molecules. For example, formic acid ($HCHO_2$) is a weak acid that dissociates to form H_3O^+ and formate ion (CHO_2^-).

$$HCHO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CHO_2^-(aq)$$



$HCHO_2$



CHO_2^-

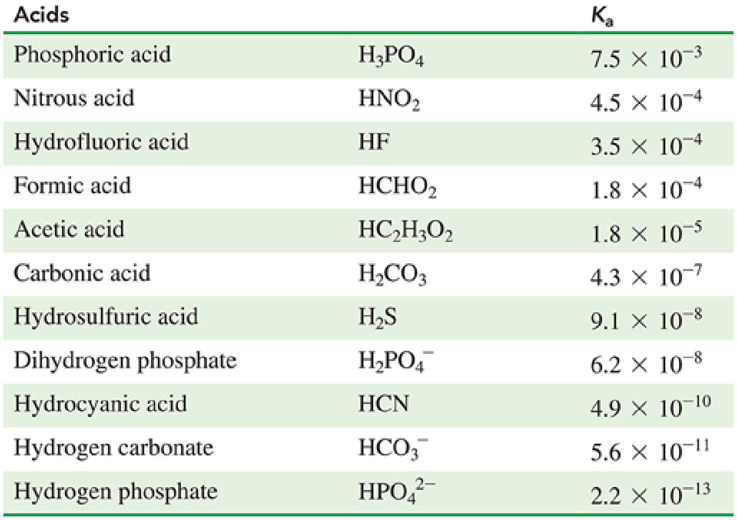
- The dissociation of weak acids can be quantified with the ***acid dissociation constant (K_a),*** as shown below:

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = 1.8x10^{-4}$$

- The acid dissociation constant for formic acid has been experimentally determined to be $1.8x10^{-4}$ at 25°C. This value is relatively small, which confirms that the equilibrium mixture of this acid in water contains mostly reactants and small amount of products.

- The magnitude of the acid dissociation constant (K_a) is a measure of the degree of ionization of the acid. In general, weak acids have small K_a values, while strong acids that are completely dissociated have large K_a values.

- The table on the right lists K_a values for some common weak acids. The greater the K_a value, the stronger the acid.



Acids		K_a
Phosphoric acid	H_3PO_4	7.5×10^{-3}
Nitrous acid	HNO_2	4.5×10^{-4}
Hydrofluoric acid	HF	3.5×10^{-4}
Formic acid	$HCHO_2$	1.8×10^{-4}
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}
Carbonic acid	H_2CO_3	4.3×10^{-7}
Hydrosulfuric acid	H_2S	9.1×10^{-8}
Dihydrogen phosphate	$H_2PO_4^-$	6.2×10^{-8}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrogen carbonate	HCO_3^-	5.6×10^{-11}
Hydrogen phosphate	HPO_4^{2-}	2.2×10^{-13}

ACID DISSOCIATION CONSTANT

Examples:

1. Write the expression of the acid dissociation constant for nitrous acid (HNO_2), a weak acid.

2. Consider the following acids and their dissociation constants:

   H_2SO_3 (aq) + H_2O (l) $\rightleftharpoons$ H_3O^+ (aq) + HSO_3^- (aq) $K_a = 1.2\text{x}10^{-2}$
   HS^- (aq) + H_2O (aq) $\rightleftharpoons$ H_3O^+ (aq) + S^{2-} (aq) $K_a = 1.3\text{x}10^{-19}$

   a) Which is the strongest acid, H_2SO_3 or HS^-?

   b) Identify the two conjugate bases for these two acids?

   c) Which is the weaker and which is the stronger conjugate base? Explain.

3. For each of the following acids: 1) H_2S; 2) H_3PO_4

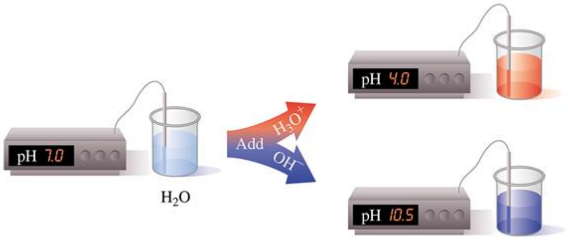
   a) Write the formula for the conjugate base.

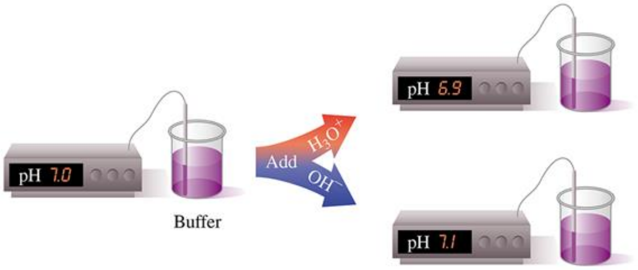
   b) Write the K_a expression

   c) Which is the weaker acid?

BUFFERS

- The pH of water and most solutions changes dramatically when a small amount of acid or base is added. However, if a small amount of acid or base is added to a ***buffer solution***, there is little change in the pH. Many biological systems, such as blood, use buffers to maintain a narrow pH range for proper functioning.





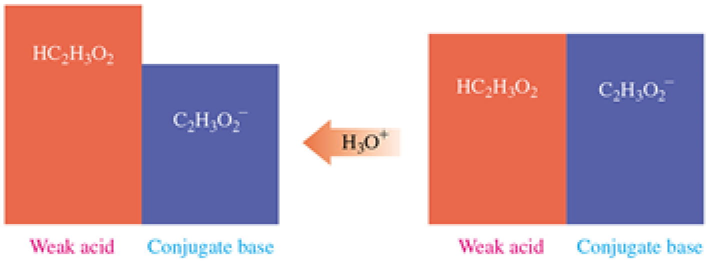
- In a buffer, an acid must be present to react with any added OH^-, and a base must be added to react with any added H_3O^-. However, the acid and base must not neutralize each other. Therefore, a combination of an acid-base conjugate pair is used as buffers.

- For example, a common buffer can be made from the weak acid acetic acid ($HC_2H_3O_2$) and its salt, sodium acetate ($NaC_2H_3O_2$). Acetic acid dissociates in water to form H_3O^+ and a small amount of $C_2H_3O_2^-$. The addition of sodium acetate provides a much larger concentration of acetate ion ($C_2H_3O_2^-$) that is necessary for good buffering capability.

$$\underset{\text{Large amount}}{HC_2H_3O_2\,(aq)} \quad + \quad H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) \quad + \quad \underset{\text{Large amount}}{C_2H_3O_2^-\,(aq)}$$

- When a small amount of acid is added to this buffer, the added H_3O^+ reacts with the acetate ion present in solution causing the equilibrium to shift towards the reactants. As a result, $C_2H_3O_2^-$ concentration decreases slightly and $HC_2H_3O_2$ increases slightly, but the pH is maintained.

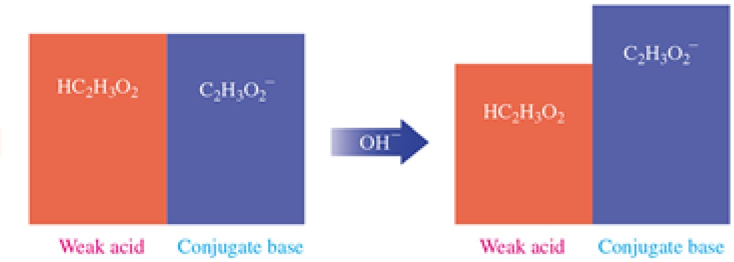
$$HC_2H_3O_2\,(aq) \quad + \quad H_2O\,(l) \longleftarrow H_3O^+\,(aq) \quad + \quad C_2H_3O_2^-\,(aq)$$



BUFFERS

- When a small amount of base is added to this buffer, the added OH^- reacts with the acetic acid present in solution causing the equilibrium to shift towards the products. As a result, $C_2H_3O_2^-$ concentration increases slightly and $HC_2H_3O_2$ decreases slightly, but the pH is maintained.

$$HC_2H_3O_2\ (aq) \quad + \quad OH^-\ (aq) \quad \longrightarrow H_2O\ (l) \quad + \quad C_2H_3O_2^-\ (aq)$$



- To calculate the pH of a buffer solution, follow the guide below. For example, in the acetic acid/acetate buffer discussed previously, K_a expression can be rearranged to find the $[H_3O^+]$:

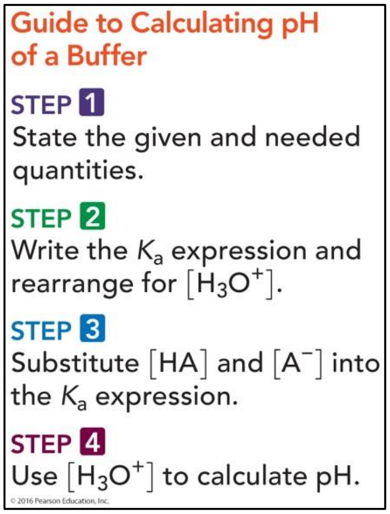
$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$[H_3O^+] = K_a \times \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]}$$

Weak acid

Conjugate base

- The $[H_3O^+]$ thus calculated can then be used to calculate the pH of the buffer.



Guide to Calculating pH of a Buffer

STEP 1
State the given and needed quantities.

STEP 2
Write the K_a expression and rearrange for $[H_3O^+]$.

STEP 3
Substitute [HA] and $[A^-]$ into the K_a expression.

STEP 4
Use $[H_3O^+]$ to calculate pH.

Examples:

1. Which of the following represents a buffer system? Explain

   a) NaOH and NaCl

   b) HF and KF

   c) H_2CO_3 and $NaHCO_3$

   d) KCl and NaCl

Examples (cont'd):

2. Consider the buffer system shown below:

$$HNO_2\ (aq) \quad + \quad H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) \quad + \quad NO_2^-\ (aq)$$

a) Write an equation to describe the reaction that takes place when small amount of acid is added to this buffer.

b) Write an equation to describe the reaction that takes place when small amount of base is added to this buffer.

c) Nitrous acid (HNO_2) has a $K_a = 4.5x10^{-4}$. Calculate the pH of a buffer containing 0.10 M HNO_2 and 0.12 M NO_2^-.

3. In blood, a buffer system utilizing carbonic acid (H_2CO_3) and sodium bicarbonate ($NaHCO_3$) is used to regulate the pH. A typical blood buffer contains $1.2x10^{-3}$M carbonic acid and $2.4x10^{-2}$ M sodium bicarbonate. The K_a for carbonic acid is $7.9x10^{-7}$.

    a) Calculate the pH of this buffer system.

    b) Write equations for the reactions that occur when small amounts of acid and base are added to this buffer.