

Chapter 8 Lecture Notes: Acids, Bases, and pH

Educational Goals

1. Given a chemical equation, write the **law of mass action**.
2. Given the **equilibrium constant** (K_{eq}) for a reaction, predict whether the reactants or products are predominant.
3. Use **Le Châtelier's Principle** to explain how a chemical reaction at equilibrium responds when a change is made to the concentration of reactant or product.
4. Know the definitions of Bronsted-Lowry acids and bases.
5. Given the **acid form** or the **base form** of a **conjugate pair**, identify its conjugate.
6. List the properties of **acidic** and **basic solutions**.
7. Understand the term "**acid strength**," and know how acid strength is related to the **acidity constant** (K_a) value.
8. Given the $[H_3O^+]$, be able to calculate the $[OH^-]$ (and vice versa).
9. Given the $[H_3O^+]$, be able to calculate the pH (and vice versa).
10. Given the $[H_3O^+]$, $[OH^-]$, or pH, be able to characterize a solution as being **acidic**, **basic**, or **neutral**.
11. Given the reactants, predict the products of a **neutralization reaction**.
12. Given the pH of a solution and the pK_a for a particular acid, determine whether the acid or base form of a conjugate pair is predominant.
13. Define a **buffer**, and describe how a buffer solution is made.

In this chapter, you will learn what is meant by the terms **acid**, **base**, **acidic**, **basic**, and **pH**.

You will learn about the chemical system called a "**buffer**" that is used in nature to control the pH in plants and animals.

In order for you to adequately understand acids, bases, pH, and buffers, I must begin this chapter by discussing a concept called _____.

Chemical Equilibrium

In chapter 6, you learned about **chemical reactions**.

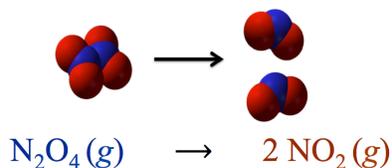
You learned that in chemical reactions, new chemical bonds are made and/or existing chemical bonds are broken, and in doing so, **reactants** are converted to new substances that we called **products**.

You learned to represent chemical reactions with **chemical equations** by writing the formulas of the reactants, then an arrow, followed by the formulas of the products.

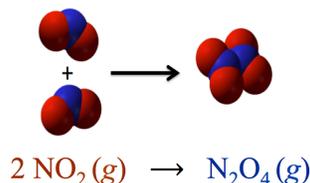
What I did not tell you in chapter 6 is that the **products** can be converted _____ into **reactants**!

Example:

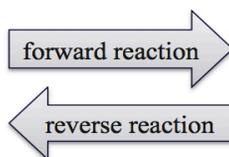
Dinitrogen tetroxide (N_2O_4) can undergo a decomposition reaction to produce two nitrogen dioxide (NO_2) molecules:



The *reaction* is _____; two NO_2 molecules can collide then bond with each other to form N_2O_4 :

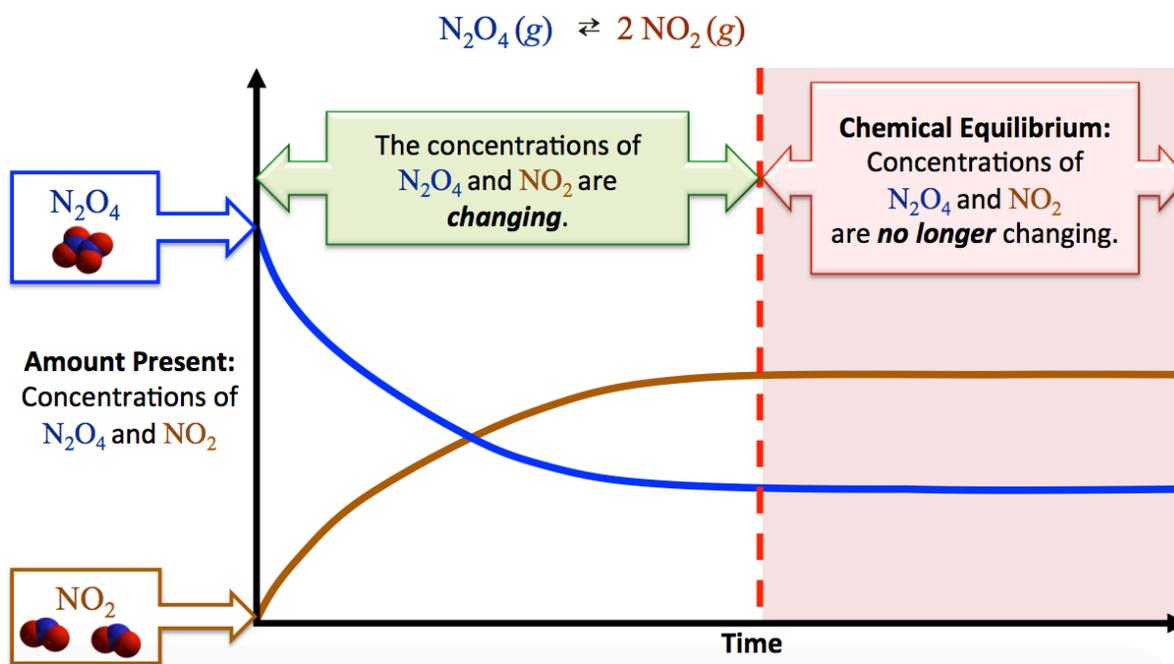


We use “double arrows” in *reversible* chemical reaction equations. For our example reaction, we write:



Even though reversible reactions proceed in both *forward* **and** *reverse* directions, we use the convention of calling the substances on the left-hand side of the reaction arrows “reactants,” and those on the right-hand side “products.”

We call the process that occurs in the left-to-right direction (reactants to products) the “_____ *reaction*,” and the process that occurs in the right-to-left direction (products to reactants) the “_____ *reaction*.”



Chemical equilibrium is defined as the state in which the **rate** of the *forward reaction* is _____ to the rate of the *reverse reaction* and _____ of the reactants and products **do not change**.

Some chemical reactions reach equilibrium in a few seconds or less, others can take days (or longer).

Once chemical equilibrium has been reached, the concentrations of reactants and products remain constant unless a change is made to the system, such as adding or removing some products or reactants or changing the temperature.

If $\text{N}_2\text{O}_4(g)$ and $\text{NO}_2(g)$ are allowed to reach equilibrium and the equilibrium concentrations of each are measured, then the following will always be true:

$$K_{eq} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

Law of Mass Action

For any chemical reaction *at equilibrium*:



where a , b , c , and d are the *stoichiometric coefficients* for substances A, B, C, and D respectively, the concentrations of reactants and products must satisfy the *law of* _____:

$$K_{eq} = \frac{[\text{C}]^c [\text{D}]^d \leftarrow \text{products}}{[\text{A}]^a [\text{B}]^b \leftarrow \text{reactants}}$$

The square brackets, [], indicate concentration in _____, for example, “[A]” means “**molarity of substance A.**”

The *law of mass action* is written by multiplying the concentration of the **products** (raised to their stoichiometric coefficient powers) in the _____, and multiplying the concentration of the **reactants** (raised to their stoichiometric coefficient powers) in the _____.

K_{eq} is called the _____.

Each chemical reaction has its *own* equilibrium constant value.

- K_{eq} values for particular reactions are determined *experimentally* and are often tabulated in reference books or online.
- The value of the equilibrium constant for any particular reaction depends on temperature. Tabulated equilibrium constants usually indicate the temperature at which they were measured. The equilibrium constants used in the remainder of the book and videos are for reactions at (or close to) room temperature (25 °C).

The *law of mass action* is also referred to as the *equilibrium expression*.

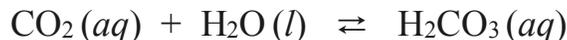
IMPORTANT NOTE FOR EQUILIBRIUM EXPRESSIONS:

When solids (s) or liquids (l) are present as reactants and/or products, they are _____ *from the equilibrium expression*.

- The only substances that appear in the equilibrium expression are gases (g), aqueous (aq) solutes (or solutes dissolved in non aqueous solutions).

- **Example:**

Write the *equilibrium expression* for the reaction of dissolved carbon dioxide and water:



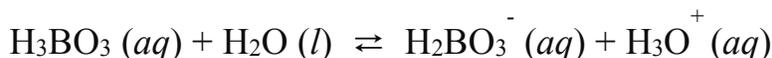
NOTE: When solids (*s*) or liquids (*l*) are present as reactants and/or products, they are *omitted from the equilibrium expression*.

$$K_{eq} = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]}$$

Understanding Check: Write the *equilibrium expression* for the following reaction:



Equilibrium constants have been measured experimentally for many reactions. For example, in the reaction of boric acid (H_3BO_3) and water,



the equilibrium expression and the measured value of the equilibrium constant (K_{eq}) is:

$$K_{eq} = \frac{[\text{H}_2\text{BO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{BO}_3]} = 5.75 \times 10^{-10} \text{ M}$$

The _____ of the equilibrium constant allows us to know the *relative* _____ of products vs. reactants that are present *at equilibrium* for a particular reaction.

If K_{eq} is *much greater* than **1**, then there are many more product species than reactant species present at equilibrium.

- In this case, we say that *the products are* _____ *at equilibrium*.

Conversely, if K_{eq} is *much less* than **1**, then there are many more reactant species than product species present at equilibrium.

- In this case, we say that *the reactants are predominant at equilibrium*.

Value of K_{eq}	Predominant Species
$K_{eq} \gg 1$	Products
$K_{eq} \ll 1$	Reactants

Understanding Check: For the reaction shown below, predict whether *the reactants or the products are predominant at equilibrium*.



Le Châtelier's Principle

If a reaction is at equilibrium, and then *more* of one of the reactants is **added**, the system is *no longer in equilibrium*. Consider the general reaction:



- When a reaction is *at equilibrium*, the forward rate *is equal to* the reverse rate, and the concentrations of reactants and products **are not changing**.
- If the concentration of reactant **A** or **B** is increased by *adding* more of substance **A** or **B**, this causes an increase in the rate of the *forward reaction* because there is now a greater probability of **A** colliding with **B** and then reacting.
- Upon the addition of substance **A** or **B**, substances **A** and **B** are converted to **C** and **D** at a faster forward rate than the reverse rate.
- This will continue to occur until enough of **C** and **D** are produced so that the reverse rate is once again equal to the forward rate and *equilibrium is reestablished*.
- A similar situation occurs if the concentration of one of the products (**C** or **D**) is increased; the reaction will then proceed faster in the reverse direction until enough **A** and **B** are formed so that the forward rate once again equals the reverse rate.

The *opposite* situation occurs if one of the reactants or products is **removed** from the system.

Reactants (or products) can be removed from the system if they are consumed by another chemical reaction, form a solid, or form a gas that is bubbled or evaporated from a liquid-phase reaction.

Consider the general reaction *at equilibrium*: $A + B \rightleftharpoons C + D$

- If some of substance **A** or **B** is *removed*, this causes a significant decrease in the rate of the forward reaction relative to the reverse reaction simply because there is now a lower probability of **A** colliding with **B** and reacting.
- Substance **C** and **D** continue to be converted to **A** and **B** at a faster rate than the rate of the forward direction until enough of **A** and **B** are produced so that the forward rate is once again equal to the reverse rate and *equilibrium is reestablished*.
- An equivalent situation occurs if *products are removed*; the reaction will proceed faster in the forward direction until enough products are formed so that the reverse rate is equal to the forward rate and equilibrium is reestablished.

What I have just described is part of a law known as **Le Châtelier's Principle**.

- Predictions based on Le Châtelier's Principle of responses to changes in concentration of reactants or products for a reaction at equilibrium are summarized in the table below.

Change Made to a Reaction that was at Equilibrium:	Response:
Increase the concentration of a <i>reactant</i> .	Rate of the forward reaction becomes greater than the rate of the reverse reaction until equilibrium is reestablished.
Increase the concentration of a <i>product</i> .	Rate of the reverse reaction becomes greater than the rate of the forward reaction until equilibrium is reestablished.
Decrease the concentration of a <i>reactant</i> .	Rate of the forward reaction becomes less than the rate of the reverse reaction until equilibrium is reestablished.
Decrease the concentration of a <i>product</i> .	Rate of the reverse reaction becomes less than the rate of the forward reaction until equilibrium is reestablished.

Understanding Check: If the reaction below is initially at equilibrium, and then each of the following changes are made, predict which direction the reaction rate will be *fastest* until equilibrium is once again established: **forward or reverse**.



a) adding PCl_5

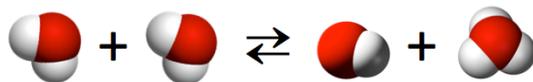
b) removing Cl_2

c) removing PCl_3

d) adding Cl_2

The Ionization of Water

A reversible reaction that is very important in understanding the chemical behavior of biological solutions is the _____ of water.



- The reactants are *two* water molecules.
- One water molecule transfers a hydrogen ion (H^+) to the other water molecule to produce a hydroxide ion (OH^-) and a _____ ion (H_3O^+).

The reason that this reaction is important in biological systems is that: (1) cells are filled with and surrounded by water, (2) hydronium and hydroxide ions are involved in many biological reactions and effect many biological processes. This reaction occurs wherever water is present, regardless of what other substance(s) may be present.

Ionization of water obeys the **law of mass action**, just like _____ other chemical reaction.

The **equilibrium expression** for this reaction is:

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} \text{M}^2$$

$\text{H}_2\text{O}(\text{l})$ does not appear in the equilibrium expression because *it is a* _____.

This equilibrium expression is so commonly used, that the symbol “ K_w ” is used for equilibrium constant (instead of K_{eq}).

- The value of the equilibrium constant has been measured experimentally for this reaction.
- The unit for K_w is M^2 because we are multiplying two molarity concentrations ($\text{M} \cdot \text{M} = \text{M}^2$).

I want to draw your attention to a few things about this equilibrium expression:

- 1) The **mathematical product** of the hydroxide ion concentration $[\text{OH}^-]$ and hydronium ion concentration $[\text{H}_3\text{O}^+]$ is always equal to $1.0 \times 10^{-14} \text{M}^2$; this is true whether the system is pure water *or* an aqueous solution containing one or more solutes.

$$K_w = \overbrace{[\text{OH}^-][\text{H}_3\text{O}^+]}^{\text{mathematical product}} = 1.0 \times 10^{-14} \text{M}^2$$

- 2) The value of K_w is much less than 1. There is always much **more water molecules present** (reactants) than hydroxide ions and hydronium ions (products).
- 3) In solutions (not pure water), there may be *other sources of hydroxide ions and hydronium ions*; therefore the hydroxide ion concentration **is not necessarily equal to** the hydronium ion concentration.

The Concentration of Hydroxide and Hydronium Ions in *Pure Water*

In pure water, the **only** source of hydroxide ions and hydronium ions is from the ionization of water reaction:



Every time this reaction proceeds in the forward direction **exactly** one hydroxide and one hydronium ion are formed. Therefore, **in pure water** the hydroxide ion concentration is always equal to the hydronium ion concentration.

If we solve the equilibrium expression to find which number multiplied by itself is equal to K_w ($1.0 \times 10^{-14} \text{ M}^2$), we can find the concentration of the hydroxide and hydronium ions in *pure water*:

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} \text{ M}^2$$
$$(1.0 \times 10^{-7} \text{ M}) \times (1.0 \times 10^{-7} \text{ M}) = 1.0 \times 10^{-14} \text{ M}^2$$

In *pure water*, the **hydroxide ion** concentration **and** the **hydronium ion** concentration are both equal to $1.0 \times 10^{-7} \text{ M}$.

The concentration of hydroxide and hydronium in aqueous solutions containing *other* solutes.

In aqueous *solutions* (not pure water), there may be *other sources of hydroxide ions and hydronium ions*; therefore the hydroxide ion concentration **is not necessarily equal to** the hydronium ion concentration.

- For example, a sodium hydroxide (NaOH) solution contains more hydroxide than pure water.
- In aqueous solutions, K_w does not give us enough information to determine the hydroxide ion (OH^-) and hydronium ion (H_3O^+) concentrations individually; we only know that their mathematical product, $[\text{OH}^-] \cdot [\text{H}_3\text{O}^+]$, is always equal to $1.0 \times 10^{-14} \text{ M}^2$.

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} \text{ M}^2$$

We know the equilibrium constant for *the ionization of water*.

That means whenever we know $[\text{OH}^-]$, we can calculate the concentration of _____.

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} \text{ M}^2$$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[\text{OH}^-]}$$

Also, whenever we know $[\text{H}_3\text{O}^+]$ we can calculate the concentration of _____.

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} \text{ M}^2$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[\text{H}_3\text{O}^+]}$$

Example:

What is the concentration of $[\text{OH}^-]$ in an aqueous solution when $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-3} \text{ M}$?

Strategy: $K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} \text{ M}^2$
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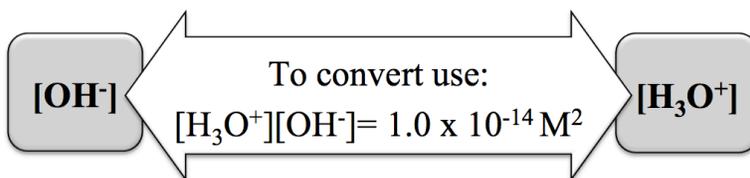
$$[\text{OH}^-] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14} \text{ M}^2}{1.0 \times 10^{-3} \text{ M}} = \mathbf{1.0 \times 10^{-11} \text{ M}}$$

Understanding Check

What is the concentration of $[\text{H}_3\text{O}^+]$ in an aqueous solution when $[\text{OH}^-] = 5.0 \times 10^{-11} \text{ M}$?

Summary of the Ionization of Water

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} \text{ M}^2$$



The ionization of water is a very important reaction in the chemical behavior of biological organisms and environments because hydronium and hydroxide ions are products or reactants in many biological reactions.

As described by Le Châtelier's Principle, changes in the hydronium or hydroxide ions can therefore affect the amounts of other products and/or reactants present in biological reactions such as the citric acid cycle and photosynthesis.

Acids and Bases

A compound can be classified as an “**acid**” or a “**base**” depending on its ability to _____ or _____ a hydrogen ion (H^+) *in a chemical reaction*.

We will use the definitions of acids and bases popularized and published by Johannes Brønsted and Thomas Lowry.

- An **acid** _____ an H^+ *in a chemical reaction*.
- A **base** _____ an H^+ *in a chemical reaction*.

Reactions in which an H^+ is transferred are called **acid-base reactions**.

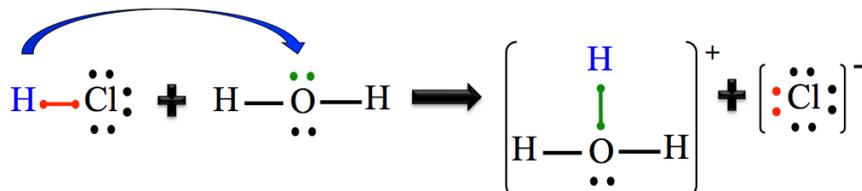
If you are given a specific *acid-base reaction*, you can **only** determine which reactant is the *acid* and which reactant is the *base* by inspection of the products *and* reactants.

Let's consider the chemical reaction of aqueous hydrogen chloride and water:



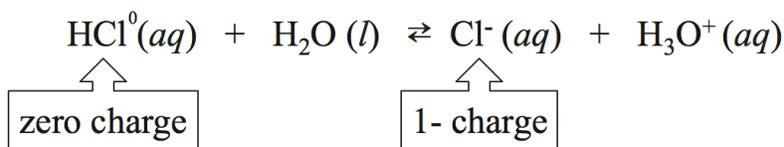
When discussing which reactant is the **acid** and which reactant is the **base**, we consider the reaction in the _____ **direction**.

- In the forward direction of this reaction, HCl is the **acid** because it _____ an H^+ .
- The **water** molecule is the **base** in this reaction because it _____ an H^+ .



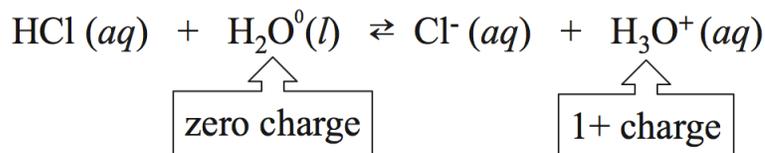
When a reactant molecule **donates** an H^+ , its charge _____ by one charge unit.

- For example, the HCl in the reaction had *zero charge* as a reactant, however after donating the H^+ , it is converted to Cl^- ; the charge **decreased** by one charge unit.



Conversely, when a reactant molecule **accepts** an H^+ in a reaction, its charge **increases** by one charge unit.

- For example, the H_2O in the reaction had *zero charge* as a reactant, however after accepting the H^+ and becoming H_3O^+ , its charge **increased** by one charge unit.



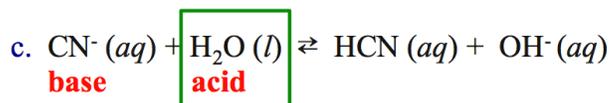
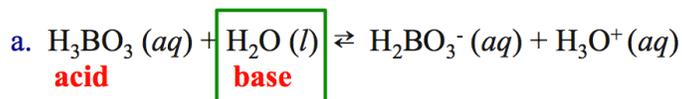
Understanding Check

Determine which reactant is the acid and which reactant is the base in each of the following reactions.

- $\text{H}_3\text{BO}_3 (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_2\text{BO}_3^- (aq) + \text{H}_3\text{O}^+ (aq)$
- $\text{HSO}_4^- (aq) + \text{HNO}_3 (aq) \rightleftharpoons \text{H}_2\text{SO}_4 (aq) + \text{NO}_3^- (aq)$
- $\text{CN}^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{HCN} (aq) + \text{OH}^- (aq)$

Amphoteric Compounds

Did you notice that water acted as a **base** in problem (a) from the previous understanding check and as an **acid** in problem (c):



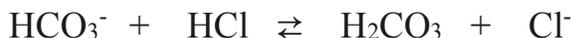
Compounds that can act as acids *or* as bases are called _____ compounds.

An example of another **amphoteric compound** is the bicarbonate ion (HCO_3^-).

Bicarbonate acts as an **acid** in this reaction:



Bicarbonate acts as a **base** in this reaction:

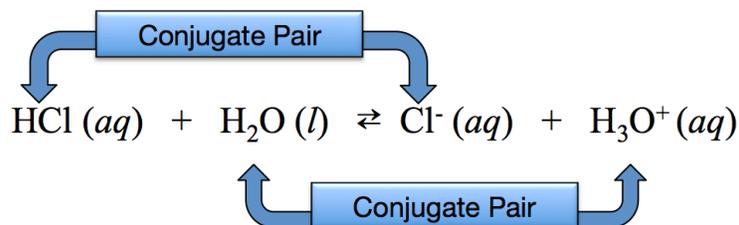


Conjugates

Pairs of chemical species, such as HCN and CN^- *or* H_3BO_3 and H_2BO_3^- , which differ only in the presence or absence of an H^+ are called _____.

For each conjugate pair, the species that **contains the extra hydrogen** is called the “_____” or the “**conjugate acid**,” and the species **with one fewer hydrogen** is called the “_____” or the “**conjugate base**.”

Consider the chemical reaction of aqueous hydrogen chloride and water:



There are _____ conjugate pairs in every acid-base reaction.

For the HCl/Cl^- conjugate pair, HCl is the **acid form** and Cl^- is the **base form**.

Understanding Check

For the $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ conjugate pair, label the **acid form** and the **base form**.

$$\text{HCl} (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{Cl}^- (aq) + \text{H}_3\text{O}^+ (aq)$$

Understanding Check

Identify the *acid form* and the *base form* in each of the conjugate pairs:

- H_3BO_3 and H_2BO_3^-
- H_2O and OH^-
- HSO_4^- and H_2SO_4
- HNO_3 and NO_3^-

Note that because the “*acid form*” in a conjugate pair has one more H^+ , it will have **one unit greater charge** than the “*base form*.”

pH

There are many applications, in both nature and laboratory settings, when it is important to measure and know the hydronium ion concentration. Since hydronium is a product or reactant in many chemical reactions, its concentration affects the amounts of other products and/or reactants involved in these reactions. An excess or deficiency of hydronium ions will hinder the ability of biological enzymes to catalyze crucial chemical reactions. The concentration of hydronium ions both affects, and is affected by, cellular metabolic activity. If the concentration of hydronium ions is too large or too small, irreversible damage to cells will occur. For these and many other reasons, much work has gone into enabling the experimental measurement of hydronium ion concentration.

The concentration of hydronium ions is determined experimentally and assigned a numeric value using the _____.

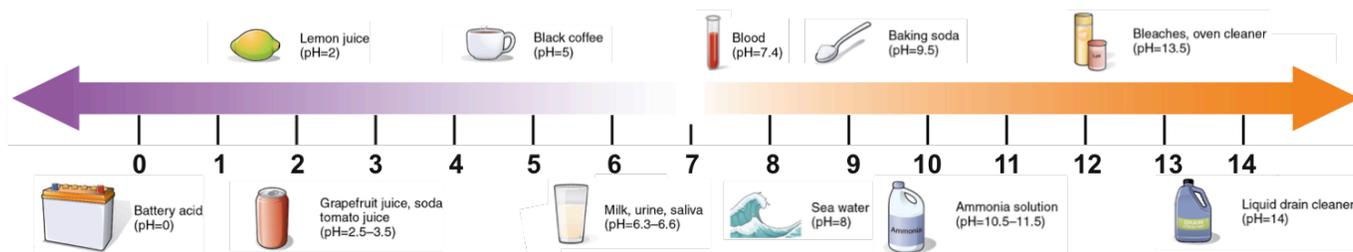


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pH is most commonly defined as the “**negative logarithm of the hydronium ion concentration.**”

- This definition can be written as a mathematical equation:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

- pH* is simply another way to express the _____ of _____ ions in a solution.

Logarithms

If a value (number) changes by a factor of 10, then its logarithm changes by 1.

You may be familiar with the **Richter scale** used in describing the magnitude of earthquakes.

- The Richter scale is a logarithm scale. An earthquake that has a magnitude of 7 on the Richter scale is *ten times stronger* than an earthquake with a Richter scale value of 6. An earthquake with a Richter scale value of 8 is *one hundred times stronger* than a quake with a Richter scale value of 6.

A Quick Review of Logarithms

The $\log(10)$ is 1 because $10^1 = 10$

The $\log(100)$ is 2 because $10^2 = 100$

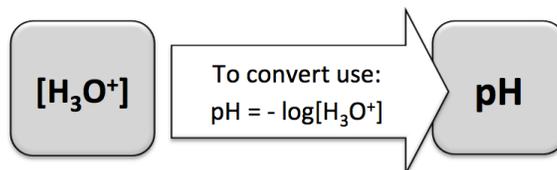
The $\log(1000)$ is 3 because $10^3 = 1000$

The $\log(.1)$ is -1 because $10^{-1} = .1$

The $\log(.01)$ is -2 because $10^{-2} = .01$

The $\log(3.4)$ is .53 because $10^{(.53)} = 3.4$ (We need to use a calculator for this one.)

Calculating the pH from the $[\text{H}_3\text{O}^+]$



Example:

What is the pH of an aqueous solution with $[\text{H}_3\text{O}^+] = 6.3 \times 10^{-1}\text{M}$?

Strategy: $\text{pH} = -\log[\text{H}_3\text{O}^+]$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log [6.3 \times 10^{-1}] = -(-0.20) = \mathbf{0.20}$$

NOTE: pH is a _____ value.

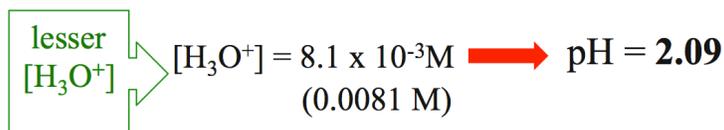
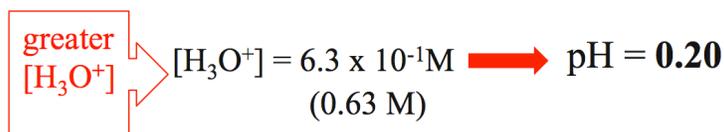
Understanding Check: What is the pH of an aqueous solution with $[\text{H}_3\text{O}^+] = 8.1 \times 10^{-3}\text{M}$?

The rule for significant figures in pH values:

Numbers to the _____ of the *decimal point* are _____ significant in pH values.

- *Be careful*, only apply this rule to the **pH** value and not to $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$.

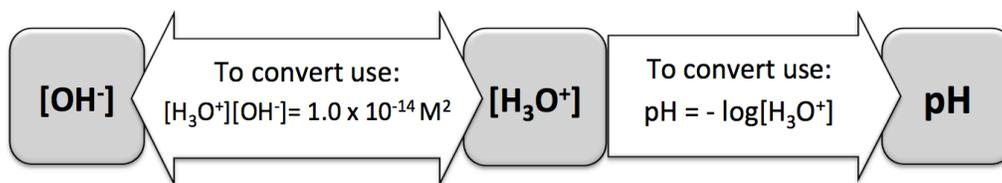
$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$



Because of the **negative sign** in our definition of pH, the _____ the **hydronium ion concentration**, the _____ the pH value.

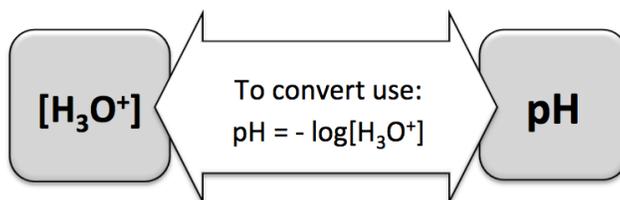
Understanding Check: What is the pH of an aqueous solution with $[\text{OH}^-] = 6.3 \times 10^{-14} \text{ M}$?

Strategy:



Calculating the $[\text{H}_3\text{O}^+]$ from the pH

We calculated the pH from the $[\text{H}_3\text{O}^+]$ in the previous example and review problems. Since there are many devices that are used to experimentally measure pH, many applications require that the $[\text{H}_3\text{O}^+]$ be calculated from the measured pH value. In this case we must employ a mathematical operation called the *antilog*.



Example: What is the $[\text{H}_3\text{O}^+]$ of an aqueous solution with $\text{pH} = 5.3$?

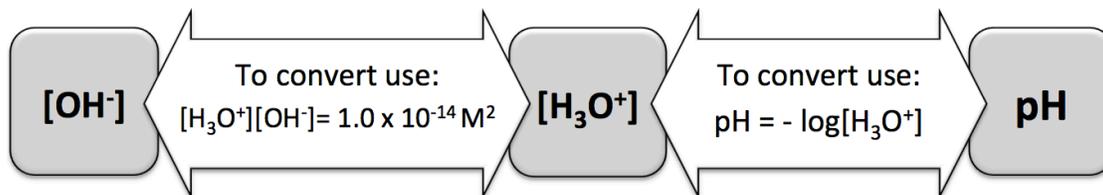
Start with the definition of pH:

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ 5.3 &= -\log[\text{H}_3\text{O}^+] && \leftarrow \text{Multiply both sides by } (-1) \\ -5.3 &= \log[\text{H}_3\text{O}^+] \\ 10^{(-5.3)} &= [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 5 \times 10^{-6} \text{ M} \end{aligned}$$

Take the antilog of both sides

Understanding Check: What is the $[\text{H}_3\text{O}^+]$ of an aqueous solution with $\text{pH} = 3.25$?

Now that you know how to convert between the hydronium ion concentration and the hydroxide ion concentration, **and** convert between the $[\text{H}_3\text{O}^+]$ and the pH, if you are given *any one of these three quantities*, $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, or pH, you should be able to *calculate the other two*.



Understanding Check: Complete each row of the table:

$[\text{OH}^-]$	$[\text{H}_3\text{O}^+]$	pH
	$1.1 \times 10^{-3} \text{ M}$	
	$1.0 \times 10^{-7} \text{ M}$	
$1.2 \times 10^{-14} \text{ M}$		
$1.4 \times 10^{-3} \text{ M}$		
		1.0
		7.00
		9.3
		12.00

Acidic and Basic Solutions

_____ are characterized as **acids** or **bases** depending on whether they donate or accept H^+ in a *particular acid-base reaction*.

_____ are characterized as **acidic**, **basic**, or **neutral** by the relative amounts of H_3O^+ and OH^- that are present.

- Solutions that contain more H_3O^+ than OH^- are called _____ **solutions**.
- Solutions that contain more OH^- than H_3O^+ are called _____ **solutions**.
- Solutions that contain equal concentrations of H_3O^+ and OH^- are called _____ **solutions**.

Let's do an example problem to find the **pH** of a **neutral solution**:

By definition, in neutral solutions, the $[\text{H}_3\text{O}^+] = [\text{OH}^-]$.

$$[\text{OH}^-][\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} \text{ M}^2$$

$$(1.0 \times 10^{-7} \text{ M}) \times (1.0 \times 10^{-7} \text{ M}) = 1.0 \times 10^{-14} \text{ M}^2$$

In neutral solutions, the $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, therefore they are both equal to $1.0 \times 10^{-7} \text{ M}$.

Once the $[\text{H}_3\text{O}^+]$ is calculated, it can be used to calculate the pH:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0 \times 10^{-7} \text{ M}) = -(-7.00) = \mathbf{7.00}$$

The pH of a **neutral solution** equals _____.

Next, let's think about the pH range of **acidic** or **basic solutions**.

In **acidic solutions**, $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, therefore $[\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} \text{ M}$.

- When the hydronium ion concentration is **greater** than $1.0 \times 10^{-7} \text{ M}$, then the pH is **less than 7.00**.
- Note that as the *hydronium ion* concentration **increases**, the pH **decreases**; this is because of the *negative sign* in the definition of pH.

In **basic solutions**, $[\text{OH}^-] > [\text{H}_3\text{O}^+]$, therefore $[\text{H}_3\text{O}^+] < 1.0 \times 10^{-7} \text{ M}$.

- When the hydronium ion concentration is **less** than $1.0 \times 10^{-7} \text{ M}$, then the pH is **greater than 7.00**.
- Note that as the *hydronium ion* concentration **decreases**, the pH **increases**.

Solution Characterization	pH	$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$
Acidic	less than 7.00	greater than $1.0 \times 10^{-7} \text{ M}$	less than $1.0 \times 10^{-7} \text{ M}$
Neutral	7.00	$1.0 \times 10^{-7} \text{ M}$	$1.0 \times 10^{-7} \text{ M}$
Basic	greater than 7.00	less than $1.0 \times 10^{-7} \text{ M}$	greater than $1.0 \times 10^{-7} \text{ M}$

Understanding Check:

For each of the following, write whether it describes an acidic, basic, or neutral solution.

- | | | |
|--|---|---|
| a) pH = 8.9 | e) $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ | i) pH = 0.06 |
| b) $[\text{H}_3\text{O}^+] = 1 \times 10^{-9} \text{ M}$ | f) pH = 1.7 | j) $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ |
| c) $[\text{H}_3\text{O}^+] = 1 \times 10^{-7} \text{ M}$ | g) pH = 12.0 | k) pH = 7.00 |
| d) $[\text{OH}^-] > [\text{H}_3\text{O}^+]$ | h) $[\text{OH}^-] = 6.8 \times 10^{-2} \text{ M}$ | l) $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ |

Properties of Acidic Solutions

Acidic solutions will turn a plant pigment molecule (in blue litmus) from blue to red.

Molecules such as litmus are often used as pH indicators.

- The color of the pH indicator, after being placed in contact with the test solution, indicates that the solution is in a certain pH range.

A more precise way to measure the pH of a solution is to use a pH meter.

- A pH meter is an electronic device with an electrode that is sensitive to the *hydronium ion concentration*.

Acidic solutions taste **sour**.

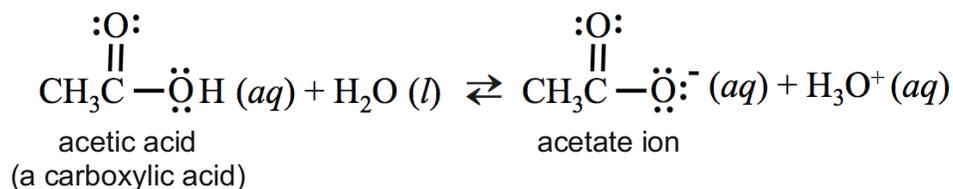
- The juice from lemons has a relatively high concentration of citric acid, (about 5%(w/v),) which gives lemons their sour taste.
- Many solutions are so acidic (pH much less than 7.00) that they will damage your mouth and digestive tract, and can result in death if enough is ingested.

Some molecules contain the word “*acid*” in their name based on the fact that they act as acids when they react with water.

Carboxylic *acids* are examples of this.

An **acidic solution** can be prepared by the addition into water of a compound that acts as an acid when reacting with the water.

- For example, when acetic acid (a carboxylic *acid*) is added to pure water, a reaction occurs and an equilibrium is established:



Before the acetic acid was added to pure water, the $[\text{H}_3\text{O}^+]$ was equal to the $[\text{OH}^-]$. When the acetic acid was added, *more* H_3O^+ was produced and the $[\text{H}_3\text{O}^+]$ increased.

The resulting acetic acid solution is **acidic** ($\text{pH} < 7$) because $[\text{H}_3\text{O}^+] > [\text{OH}^-]$.

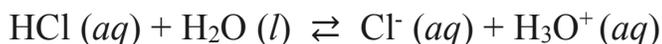
The pH of a solution that is prepared by adding an **acid** into pure water is determined by two factors:

- The _____ of the compound that was added.
- The extent to which the compound _____ (donates H^+ and thereby produces its **base form** and H_3O^+).

The extent to which an acid dissociates when reacting with water is referred to as “**acid strength**.”

When a “_____” is placed in water and reacts with it, there is very little of the **acid form** present and much more of the **base form** present **at equilibrium**.

- An example of a **strong acid** is HCl (often referred to as hydrochloric acid).
- When hydrogen chloride is in water, it dissociates as shown in the chemical equation below:



Recall that the value of the equilibrium constant (K_{eq}) for a reaction indicates the relative amounts of products and reactants that exist at equilibrium.

If K_{eq} is much greater than 1, then, at equilibrium, the concentrations of the products are much greater than those of the reactants.

- In this case we say *the products are predominant at equilibrium*.

Conversely, if K_{eq} is much less than 1, at equilibrium, the concentrations of the reactants are much greater than those of the products.

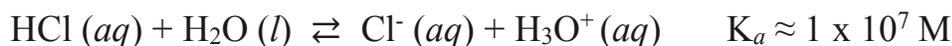
- In this case we say *the reactants are predominant at equilibrium*.

When writing the equilibrium constant for the reaction of an acid with water, we use the symbol _____ instead of K_{eq} .

K_a is referred to as the **acidity constant** or the **acid dissociation constant**.

- Keep in mind that it is just the **equilibrium constant** for the reaction of the acid with water.

K_a for the reaction of HCl and water is about 1×10^7 M.



The equilibrium expression for this reaction is:

$$K_a = \frac{[\text{Cl}^-][\text{H}_3\text{O}^+]}{[\text{HCl}]} \approx 1 \times 10^7 \text{ M}$$

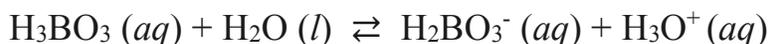
Because K_a is approximately 1×10^7 M, at equilibrium there are about about **ten million** Cl^- ions and **ten million** H_3O^+ ions for every **one HCl** molecule.

- Almost all of the HCl that is added to pure water is converted to Cl^- and H_3O^+ .

When a “_____” is placed in water and reacts with it, at equilibrium, there is very little of its **base form** and much more of the **acid form** present.

An example of a **weak acid** is boric acid (H_3BO_3).

- When boric acid is in water, it dissociates as shown in the chemical equation below:



K_a for the reaction of H_3BO_3 and water is 5.75×10^{-10} M.

The equilibrium expression for this reaction is:

$$K_{eq} = \frac{[\text{H}_2\text{BO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{BO}_3]} = 5.75 \times 10^{-10} \text{ M}$$

K_a for this reaction is much less than 1, and *the reactant* (H_3BO_3) *is predominant at equilibrium*.

- At equilibrium, there are about about 25000 H_3BO_3 molecules for every *one* H_2BO_3^- or H_3O^+ ion present.

Summary of Acid Strength

Strong acids have K_a values **much** _____ than 1.

- When **strong acids** are placed in pure water, they react with water and an equilibrium is establish in which there is much more of the **base form** and H_3O^+ than the **acid form** present.

Weak acids have K_a values **much** _____ than 1.

- When **weak acids** are placed in pure water, they react with water and an equilibrium is establish in which there is much more of the **acid form** than the **base form** and H_3O^+ present.

The greater the K_a , the stronger the acid.

Acid Name	Acid Formula	K_a
Perchloric acid	HClO_4	1×10^9 M (estimated)
Hydrochloric acid	HCl	1×10^7 M (estimated)
Chloric acid	HClO_3	1×10^3 M (estimated)
Phosphoric acid	H_3PO_4	7.5×10^{-3} M
Hydrofluoric acid	HF	6.6×10^{-4} M
Acetic acid	$\text{CH}_3\text{CO}_2\text{H}$	1.8×10^{-5} M
Carbonic acid	H_2CO_3	4.4×10^{-7} M
Dihydrogen phosphate ion	H_2PO_4^-	6.2×10^{-8} M
Boric acid	H_3BO_3	5.7×10^{-10} M
Ammonium ion	NH_4^+	5.6×10^{-10} M
Hydrocyanic acid	HCN	4.9×10^{-10} M
Bicarbonate ion	HCO_3^-	5.6×10^{-11} M
Methylammonium ion	CH_3NH_3^+	2.4×10^{-11} M
Hydrogen phosphate ion	HPO_4^-	4.2×10^{-13} M

Understanding Check: Use the table (on the previous page) to determine which is a stronger acid, *phosphoric acid* or *acetic acid*.

Properties of Basic Solutions

Basic solutions *feel slippery*, have a *bitter* taste, and will turn litmus pH indicator from red to blue.

Basic solutions can be prepared by dissolving an ionic compound that contains hydroxide in water.

For example, the addition of sodium hydroxide to pure water will result in dissociation of the sodium hydroxide crystals to produce sodium ions and hydroxide ions:



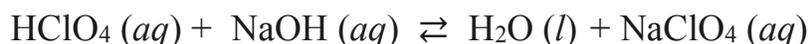
When the NaOH was added, the $[\text{OH}^-]$ increased.

The resulting NaOH solution is *basic* ($\text{pH} > 7$) because $[\text{OH}^-] > [\text{H}_3\text{O}^+]$.

Neutralization Reactions

An *acid* will react with a *hydroxide-containing base* compound to produce _____ and an _____ *compound* in a reaction called _____.

An example of a *neutralization reaction* is the reaction of perchloric acid and sodium hydroxide:



In *neutralization reactions*, the H^+ from the *acid* bonds to the OH^- to produce H_2O .

The (anionic) *base form* of the acid (ClO_4^- in this case) combines with the cationic part of the base (Na^+ in this case) to make an *ionic compound* called a _____.

- Although sodium chloride is commonly called “salt,” the chemical definition of salt states that a *salt* is an ionic compound *formed in a neutralization reaction*.

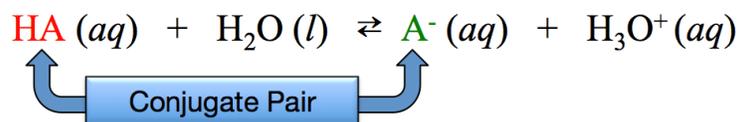
Understanding Check: Predict the products of the following *neutralization reactions*:



The Henderson-Hasselbalch Relationship

There is a unique relationship between the **pH** of a solution and the relative amounts of *acid* and *base forms* of a conjugate pair that is present in the solution.

The **general form** of a chemical equation for an acid reacting with water to produce its base form and hydronium can be written as:

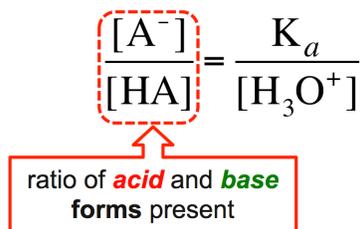


HA represents the *acid form*, and **A⁻** represents the *base form* of any **conjugate pair**.

The equilibrium expression for this general reaction is:

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

We can rearrange this equation to get the ratio of the equilibrium concentration of the acid and base form of a conjugate pair.

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


The important thing to see here is that the relative amounts (ratio) of the *base form* and *acid form* of a conjugate pair at equilibrium depends on the K_a value for the particular acid *and* $[\text{H}_3\text{O}^+]$.

Since pH is used as a measure of $[\text{H}_3\text{O}^+]$, it is more practical to use pH instead of $[\text{H}_3\text{O}^+]$.

- The $[\text{H}_3\text{O}^+]$ in equation can be replaced with **pH** by taking the *negative logarithm* of both sides of the equation and doing some other algebraic steps.

$$\text{pH} = -\log(K_a) + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

The “ $-\log(K_a)$ ” term in this equation above is written as “ $\text{p}K_a$.”

Doing so yields what is known as the **Henderson-Hasselbalch Equation**:

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

For a particular conjugate pair, the **Henderson-Hasselbalch Equation** gives the relationship between the relative amounts of the *acid and base forms* present at equilibrium and the **pH** of the solution.

Henderson-Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

The Henderson-Hasselbalch Equation is used so often that K_a values for acids are sometimes tabulated as pK_a s.

Do not be confused by the use of pK_a ; it is simply the $-\log(K_a)$.

Acid Name	Acid Formula	K_a	pK_a $\text{pK}_a = -\log(K_a)$
Perchloric acid	HClO_4	$1 \times 10^9 \text{ M}$ (estimated)	-9.0 (estimated)
Hydrochloric acid	HCl	$1 \times 10^7 \text{ M}$ (estimated)	-7.0 (estimated)
Chloric acid	HClO_3	$1 \times 10^3 \text{ M}$ (estimated)	-3.0 (estimated)
Phosphoric acid	H_3PO_4	$7.5 \times 10^{-3} \text{ M}$	2.12
Hydrofluoric acid	HF	$6.6 \times 10^{-4} \text{ M}$	3.18
Acetic acid	$\text{CH}_3\text{CO}_2\text{H}$	$1.8 \times 10^{-5} \text{ M}$	4.74
Carbonic acid	H_2CO_3	$4.4 \times 10^{-7} \text{ M}$	6.36
Dihydrogen phosphate ion	H_2PO_4^-	$6.2 \times 10^{-8} \text{ M}$	7.21
Boric acid	H_3BO_3	$5.7 \times 10^{-10} \text{ M}$	9.24
Ammonium ion	NH_4^+	$5.6 \times 10^{-10} \text{ M}$	9.25
Hydrocyanic acid	HCN	$4.9 \times 10^{-10} \text{ M}$	9.31
Bicarbonate ion	HCO_3^-	$5.6 \times 10^{-11} \text{ M}$	10.25
Methylammonium ion	CH_3NH_3^+	$2.4 \times 10^{-11} \text{ M}$	10.62
Hydrogen phosphate ion	HPO_4^{2-}	$4.2 \times 10^{-13} \text{ M}$	12.38

We will not use the Henderson-Hasselbalch Equation to do calculations; but we will take advantage of its *implications* in order to _____ whether the **acid form** or the **base form** of a **particular conjugate pair** is **predominant** at equilibrium.

A solution containing a conjugate pair can be at **any** pH; other species that are in the solution (or might be added) can affect the pH. However, the K_a , and therefore pK_a , for a particular conjugate pair *does not change*.

In order to solve problems in this course, you should know and understand the following three statements that are **implied** by the **Henderson-Hasselbalch Equation**.

- When the **pH** of a solution is _____ than the **pK_a** of an acid, then the concentration of the **acid form**, [HA], is **greater than** the concentration of the **base form**, [A⁻].
 - In this case, we say that **the acid form is predominant**.
- When the **pH** of a solution is _____ than the **pK_a** of an acid, then the concentration of the **base form**, [A⁻], is **greater than** the concentration of the **acid form**, [HA].
 - In this case, we say that **the base form is predominant**.
- When the **pH** of a solution is _____ **to** the **pK_a** of an acid, then the concentration of the **acid form**, [HA], is **equal to** the concentration of the **base form**, [A⁻].

Solution Condition	Relative Amounts of Acid and Base Forms
$\text{pH} < \text{pK}_a$	$[\text{HA}] > [\text{A}^-]$
$\text{pH} > \text{pK}_a$	$[\text{A}^-] > [\text{HA}]$
$\text{pH} = \text{pK}_a$	$[\text{HA}] = [\text{A}^-]$

Understanding Check: For each of the following conjugate pairs, predict whether the *acid form* or the *base form* is predominant at the given pH.

a. HF/F⁻ at pH = 2.7

b. H₂PO₄⁻/HPO₄²⁻ at pH = 8.5

c. NH₄⁺/NH₃ at pH = 7.0

Buffer Solutions

Predicting, measuring, and controlling the pH of a solution or biological environment are important.

Nature and certain laboratory applications employ a chemical system, called a _____, that helps to *maintain a narrow pH range* in bodily fluids or other aqueous solutions.

A _____ is a solution that resists changes in pH when *small amounts* of acid or base are added.

A buffer solution contains fairly high concentrations of the *acid and base forms of a conjugate pair*.

Solution Condition	Relative Amounts of Acid and Base Forms
pH < pK _a	[HA] > [A ⁻]
pH > pK _a	[A ⁻] > [HA]
pH = pK _a	[HA] = [A ⁻]

A high concentration of *both* the *acid and base form* of the conjugate pair is needed; this occurs when the pH is equal to, or very close to, the pK_a.

How does a buffer work? Example of a Buffer Solution: Blood Plasma.

The pH of your blood normally ranges between 7.35 and 7.45.

A blood pH below the normal range is called *acidosis*, while a blood pH above this range is called *alkalosis*, either one of which is potentially fatal.

Blood is kept in this narrow range (pH = 7.35 – 7.45) with the help of buffers.

Adding Acid to a Buffer Solution

If acid (hydronium ions) is added to the carbonic acid (H₂CO₃)/bicarbonate (HCO₃⁻) *buffer in blood*, the excess hydronium ions would cause an *increase in the reverse reaction rate of the buffer conjugate pair equilibrium*, shown below, as predicted by Le Chatalier's Principle.



The excess hydronium ions that are added and bicarbonate (HCO₃⁻) are converted to carbonic acid (H₂CO₃) + H₂O (l) in the reverse direction of the reaction, and therefore there is **not** a significant change in the pH.

The removal of the excess hydronium will continue until most of the *base form* of the conjugate pair is depleted.

- It is for this reason that buffers are made of relatively *high concentrations* of the buffering conjugate pairs, and that we say, “a buffer is a solution that will resist pH changes when *small* amounts of acid or base are added.”

Addition of Base to a Buffer Solution

If a small amount base was added to a _____ *buffered solution*, it would increase the pH.

- The pH would increase because the hydroxide ion concentration would increase, and therefore *the concentration of hydronium ions will decrease*.

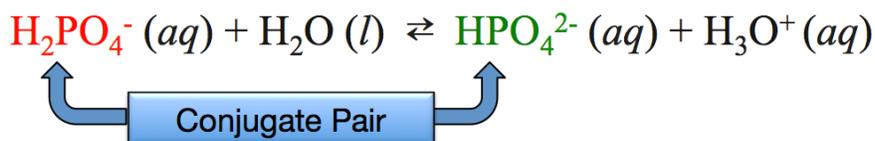
However, if a small amount of base was added to a *buffered solution*, *the hydronium ion concentration would be maintained because of a decrease in the reverse reaction rate of the buffer conjugate pair equilibrium*, as predicted by Le Châtelier's Principle.



The concentration of **hydronium ions** will be **maintained** because it is replenished by the greater rate of the forward reaction.

Biological Buffers

An important _____ (within cells) buffer is the dihydrogen phosphate/hydrogen phosphate conjugate pair:



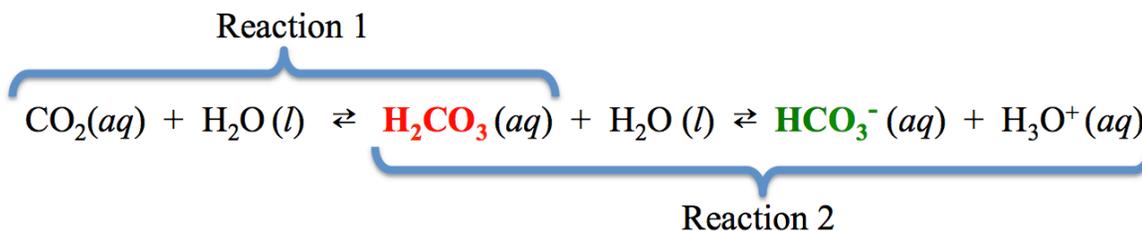
Proteins also act as *intracellular* buffers.

- In chapter 13 you will learn how proteins can donate or accept H^+ .

Important _____ (outside of cells) buffers, in solutions such as blood or interstitial fluids, are the carbonic acid (H_2CO_3)/bicarbonate (HCO_3^-) and the ammonium (NH_4^+)/ammonia (NH_3) conjugate pairs.

In blood, the carbonic acid (H_2CO_3)/bicarbonate (HCO_3^-) buffering pair is especially useful because the buffer conjugate pair concentrations ($[\text{H}_2\text{CO}_3]$ and $[\text{HCO}_3^-]$) are replenished through cellular respiration and can be controlled through breathing.

- To understand how this happens, we must consider these two reactions:



- The CO_2 in Reaction 1 is constantly produced in the body during cellular respiration. Most of the CO_2 produced is exhaled; however, there is always some CO_2 dissolved in the blood.
- Reaction 2 is the carbonic acid/bicarbonate equilibrium, which acts as a **buffer**.