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Lecture Presentation

Chapter 16

Acids and Bases

Stomach Acid and Heartburn

- The cells that line your stomach produce hydrochloric acid.
 - To kill unwanted bacteria
 - To help break down food
 - To activate enzymes that break down food
- If the stomach acid backs up into your esophagus, it irritates those tissues, resulting in heartburn.
 - Acid reflux

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Curing Heartburn

- Mild cases of heartburn can be cured by neutralizing the acid in the esophagus.
 - Swallowing saliva, which contains bicarbonate ion
 - Taking antacids that contain hydroxide ions and/or carbonate ions

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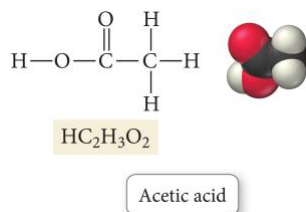
GERD

- Chronic heartburn is a problem for some people.
- GERD (gastroesophageal reflux disease) is chronic leaking of stomach acid into the esophagus.
- In people with GERD, the muscles separating the stomach from the esophagus do not close tightly, allowing stomach acid to leak into the esophagus.
- Physicians diagnose GERD by attaching a pH sensor to the esophagus to measure the acidity levels of the fluids over time.

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Properties of Acids

- Sour taste
- Ability to dissolve many metals
- Ability to neutralize bases
- Change blue litmus paper to red



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Common Acids

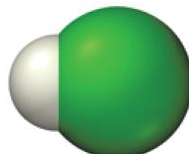
TABLE 16.1 Some Common Acids

Name	Occurrence / Uses
Hydrochloric acid (HCl)	Metal cleaning; food preparation; ore refining; primary component of stomach acid
Sulfuric acid (H_2SO_4)	Fertilizer and explosives manufacturing; dye and glue production; in automobile batteries; electroplating of copper
Nitric acid (HNO_3)	Fertilizer and explosives manufacturing; dye and glue production
Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$)	Plastic and rubber manufacturing; food preservation; active component of vinegar
Citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$)	In citrus fruits such as lemons and limes; used to adjust pH in foods and beverages
Carbonic acid (H_2CO_3)	In carbonated beverages due to the reaction of carbon dioxide with water
Hydrofluoric acid (HF)	Metal cleaning; glass frosting and etching
Phosphoric acid (H_3PO_4)	Fertilizer manufacturing; biological buffering; beverage preservation

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Structures of Acids

- Binary acid has the acid hydrogen (H^+) attached to a nonmetal atom.
- HCl , HF

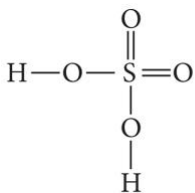


Hydrochloric acid

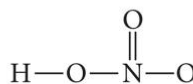
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Structure of Acids

- Oxyacids have the acid hydrogen attached to an oxygen atom.
- H_2SO_4 , HNO_3



Sulfuric acid



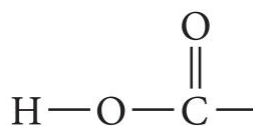
Nitric acid



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Structure of Acids

- Carboxylic acids have a -COOH group.
 - $\text{HC}_2\text{H}_3\text{O}_2$, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$
- Only the first H in the formula is acidic.
 - The H is on the COOH.



Carboxylic acid group



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Properties of Bases

- Taste bitter
 - alkaloids = plant product that is alkaline
 - often poisonous
- Feel slippery
- Ability to turn red litmus paper blue
- Ability to neutralize acids



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Common Bases

TABLE 16.2 Common Bases

Name	Occurrence / Uses
Sodium hydroxide (NaOH)	Petroleum processing; soap and plastic manufacturing
Potassium hydroxide (KOH)	Cotton processing; electroplating; soap production; batteries
Sodium bicarbonate (NaHCO ₃)	Sold as baking soda; antacid; source of CO ₂
Sodium carbonate (Na ₂ CO ₃)	Glass and soap manufacturing; general cleanser; water softener
Ammonia (NH ₃)	Detergent; fertilizer and explosives manufacturing; synthetic fiber production

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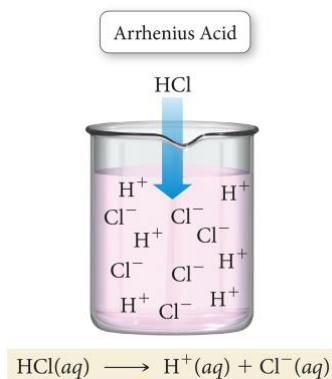
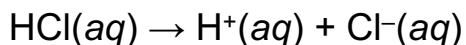
Definitions of Acids and Bases

- Arrhenius definition
 - Acid produces H⁺ in solution.
 - H⁺ ions always associate with H₂O to form a hydronium ion, H₃O⁺.
 - Base produces OH⁻ in solution.
- Brønsted–Lowry definition
 - H⁺ donor
 - H⁺ acceptor

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Arrhenius Theory

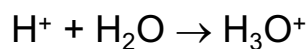
- Acids: produce H^+ ions in aqueous solution.



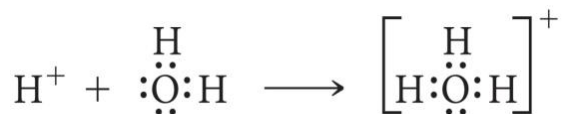
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Hydronium Ion

- The H^+ ions produced by the acid are so reactive that they cannot exist in water.
 - H^+ ions are protons!
- Instead, they react with water molecules to produce complex ions, mainly **hydronium ion, H_3O^+** .



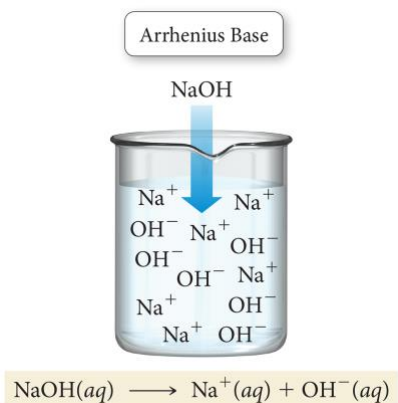
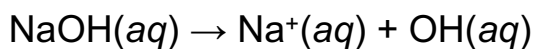
- There are also minor amounts of H^+ with multiple water molecules, $\text{H}(\text{H}_2\text{O})_n^+$.



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Arrhenius Theory

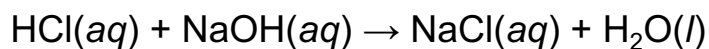
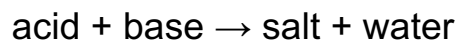
- Bases: produce OH^- ions in aqueous solution.



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Arrhenius Acid–Base Reactions

- The H^+ from the acid combines with the OH^- from the base to make a molecule of H_2O .
- The cation from the base combines with the anion from the acid to make a salt.



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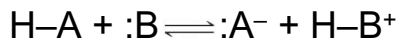
Brønsted–Lowry Acid–Base Theory

- Provides a more widely applicable definition of acids and bases
- Any reaction involving H^+ (proton) transfer from one molecule to another is an acid–base reaction, regardless of whether it occurs in aqueous solution or if there is OH^- present.
- All reactions that fit the Arrhenius definition also fit the Brønsted–Lowry definition.

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Brønsted–Lowry Theory

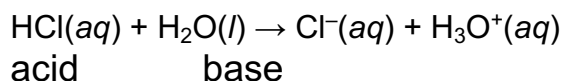
- The acid is an H^+ donor.
- The base is an H^+ acceptor.
 - Base structure must contain an atom with an unshared pair of electrons.
- In a Brønsted–Lowry acid–base reaction, the acid molecule donates an H^+ to the base molecule.



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Brønsted–Lowry Acids

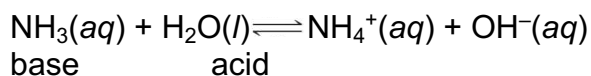
- Brønsted–Lowry acids are H^+ donors.
 - Any material that has H can potentially be a Brønsted–Lowry acid.
 - Because of the molecular structure, often one H in the molecule is easier to transfer than others.
- When HCl dissolves in water, the HCl is the acid because HCl transfers an H^+ to H_2O , forming H_3O^+ ions.
 - Water acts as a base, accepting H^+ .



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Brønsted–Lowry Bases

- Brønsted–Lowry bases are H^+ acceptors.
 - Any material that has atoms with lone pairs can potentially be a Brønsted–Lowry base.
 - Because of the molecular structure, often one atom in the molecule is more willing to accept H^+ transfer than others.
- When NH_3 dissolves in water, the $\text{NH}_3(\text{aq})$ is the base because NH_3 accepts an H^+ from H_2O , forming $\text{OH}^-(\text{aq})$.
 - Water acts as an acid, donating H^+ .

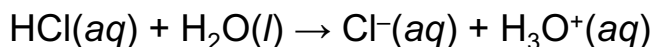


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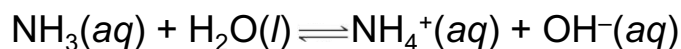
Amphoteric Substances

- **Amphoteric substances** can act as either an acid or a base because they have both a transferable H and an atom with lone-pair electrons.

- Water acts as a base, accepting H^+ from HCl .



- Water acts as an acid, donating H^+ to NH_3 .



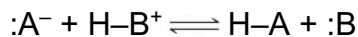
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Brønsted–Lowry Acid–Base Reactions

- One of the advantages of Brønsted–Lowry theory is that it illustrates **reversible** reactions to be as follows:



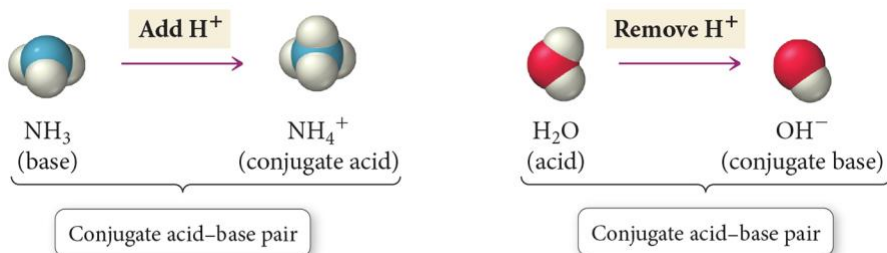
- The original base has an extra H^+ after the reaction, so it will act as an acid in the reverse process.
- And the original acid has a lone pair of electrons after the reaction, so it will act as a base in the reverse process:



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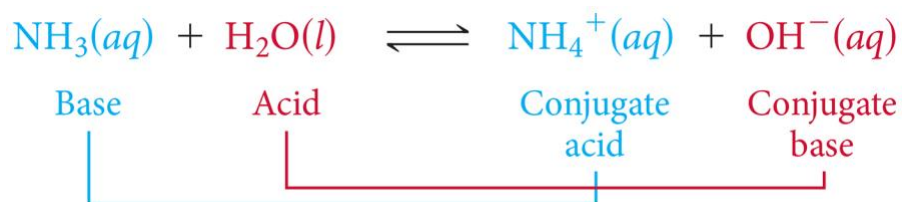
Conjugate Acid–Base Pairs

- In a Brønsted–Lowry acid–base reaction,
 - the original base becomes an acid in the reverse reaction.
 - the original acid becomes a base in the reverse process.
- Each reactant and the product it becomes is called a **conjugate pair**.



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Conjugate Pairs



A base accepts a proton and becomes a conjugate acid.

An acid donates a proton and becomes a conjugate base.

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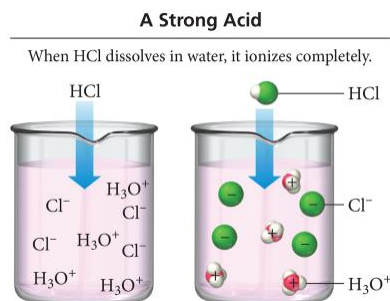
Acid Strength

- A strong acid is a strong electrolyte.
 - Practically all the acid molecules ionize.
- A strong base is a strong electrolyte.
 - Practically all the base molecules form OH^- ions, either through dissociation or reaction with water.
- A weak acid is a weak electrolyte.
 - Only a small percentage of the molecules ionize, \rightleftharpoons .
- A weak base is a weak electrolyte, \rightleftharpoons .
 - Only a small percentage of the base molecules form OH^- ions, either through dissociation or reaction with water, \rightleftharpoons .

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Strong Acids

- Strong acids donate practically all their H^+ ions.
 - 100% ionized in water
 - Strong electrolyte
- $[\text{H}_3\text{O}^+] = [\text{strong acid}]$
 - Species in brackets means the molarity of that species.



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Examples of Strong Acids

TABLE 16.3 Strong Acids

Hydrochloric acid (HCl)	Nitric acid (HNO ₃)
Hydrobromic acid (HBr)	Perchloric acid (HClO ₄)
Hydriodic acid (HI)	Sulfuric acid (H ₂ SO ₄) (<i>diprotic</i>)

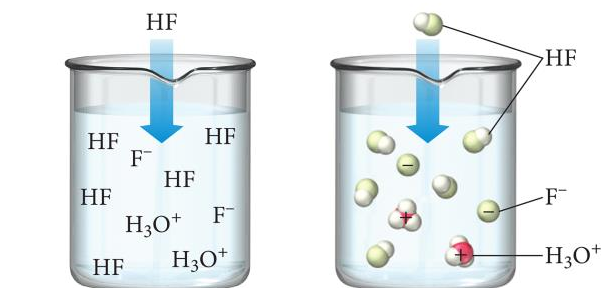
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Weak Acids

- Weak acids donate a small fraction of their H⁺ ions.
 - Most of the weak acid molecules do not donate H⁺ to water.
 - Much less than 1% ionized in water
- [H₃O⁺] << [weak acid]

A Weak Acid

When HF dissolves in water, only a fraction of the molecules ionize.



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Examples of Weak Acids

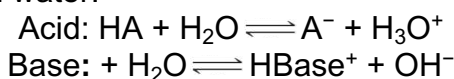
TABLE 16.4 Some Weak Acids

Hydrofluoric acid (HF)	Sulfurous acid (H ₂ SO ₃) (<i>diprotic</i>)
Acetic acid (HC ₂ H ₃ O ₂)	Carbonic acid (H ₂ CO ₃) (<i>diprotic</i>)
Formic acid (HCHO ₂)	Phosphoric acid (H ₃ PO ₄) (<i>triprotic</i>)

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Strengths of Acids and Bases

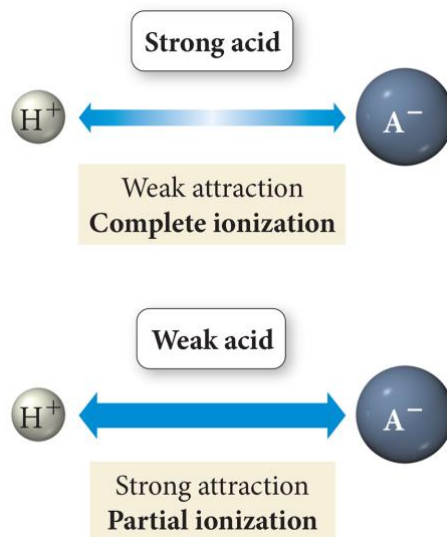
- Acid strength depends on the degree of attraction of the acid anion and the H⁺.
- Commonly, acid or base strength is measured by determining the equilibrium constant of a substance's reaction with water.



- The smaller ionization constant, K , the weaker the acid or base.
- The position of equilibrium depends on the strength of attraction between the base form and the H⁺.
 - Stronger attraction means stronger base or weaker acid.

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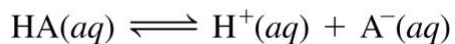
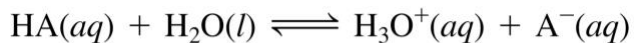
Ionic Attraction and Acid Strength



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Acid Ionization Constant, K_a

- Acid strength is measured by the size of the equilibrium constant when it reacts with H_2O .



- The equilibrium constant for this reaction is called the **acid ionization constant, K_a** .
 - larger K_a = stronger acid

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

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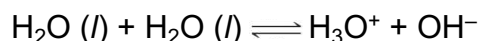
TABLE 16.5 Acid Ionization Constants (K_a) for Some Monoprotic Weak Acids at 25 °C					
Acid	Formula	Structural Formula	Ionization Reaction	K_a	pK_a
Chlorous acid	HClO_2	$\text{H}-\text{O}-\text{Cl}=\text{O}$	$\text{HClO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}_2^-(\text{aq})$	1.1×10^{-2}	1.96
Nitrous acid	HNO_2	$\text{H}-\text{O}-\text{N}=\text{O}$	$\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$	4.6×10^{-4}	3.34
Hydrofluoric acid	HF	$\text{H}-\text{F}$	$\text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq})$	6.8×10^{-4}	3.17
Formic acid	HCHO_2	$\text{H}-\text{O}-\text{C}(=\text{O})-\text{H}$	$\text{HCHO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CHO}_2^-(\text{aq})$	1.8×10^{-4}	3.74
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2$	$\text{H}-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_5$	$\text{HC}_7\text{H}_5\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_7\text{H}_5\text{O}_2^-(\text{aq})$	6.5×10^{-5}	4.19
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{H}-\text{O}-\text{C}(=\text{O})-\text{CH}_3$	$\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$	1.8×10^{-5}	4.74
Hypochlorous acid	HClO	$\text{H}-\text{O}-\text{Cl}$	$\text{HClO}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}^-(\text{aq})$	2.9×10^{-8}	7.54
Hydrocyanic acid	HCN	$\text{H}-\text{C}\equiv\text{N}$	$\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CN}^-(\text{aq})$	4.9×10^{-10}	9.31
Phenol	$\text{HC}_6\text{H}_5\text{O}$	$\text{H}-\text{O}-\text{C}_6\text{H}_5$	$\text{HC}_6\text{H}_5\text{O}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_6\text{H}_5\text{O}^-(\text{aq})$	1.3×10^{-10}	9.89

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Autoionization of Water

- Water is amphoteric; it can act as either an acid or a base.
 - Therefore, there must be a few ions present.

- When water acts with itself as an acid and a base to form ions, this process is called **autoionization**.



Can be written as $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+ + \text{OH}^-$.

- All aqueous solutions contain **both** H_3O^+ and OH^- .
 - The concentration of H_3O^+ and OH^- are equal in water.
 - $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7}\text{M}$ at 25 °C

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Ion Product of Water

- The product of the H_3O^+ and OH^- concentrations is always the same number.
- The number is called the **ion product of water** and has the symbol K_w .
 - Also known as the dissociation constant of water
- $[\text{H}_3\text{O}^+] \times [\text{OH}^-] = K_w = 1.00 \times 10^{-14}$ at 25°C
 - If you measure one of the concentrations, you can calculate the other.
- As $[\text{H}_3\text{O}^+]$ increases, the $[\text{OH}^-]$ must decrease so the product stays constant.
 - Inversely proportional

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Acidic and Basic Solutions

- All aqueous solutions contain both H_3O^+ and OH^- ions.
- Neutral solutions have equal $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$.
 - $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7}$
- Acidic solutions have a larger $[\text{H}_3\text{O}^+]$ than $[\text{OH}^-]$.
 - $[\text{H}_3\text{O}^+] > 1.00 \times 10^{-7}$; $[\text{OH}^-] < 1.00 \times 10^{-7}$
- Basic solutions have a larger $[\text{OH}^-]$ than $[\text{H}_3\text{O}^+]$.
 - $[\text{H}_3\text{O}^+] < 1.00 \times 10^{-7}$; $[\text{OH}^-] > 1.00 \times 10^{-7}$

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Measuring Acidity: pH

- The acidity or basicity of a solution is often expressed by **pH**.
- $\text{pH} = -\log[\text{H}_3\text{O}^+]$
 - $\text{pH}_{\text{water}} = -\log[10^{-7}] = 7$
 - Need to know the $[\text{H}_3\text{O}^+]$ concentration to find pH
- $\text{pH} < 7$ is acidic; $\text{pH} > 7$ is basic.
 $\text{pH} = 7$ is neutral.
- $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$
- From K_w , $[\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$

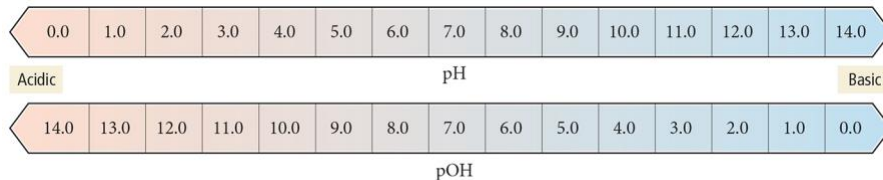
TABLE 16.6 The pH of Some Common Substances

Substance	pH
Gastric juice (human stomach)	1.0–3.0
Limes	1.8–2.0
Lemons	2.2–2.4
Soft drinks	2.0–4.0
Plums	2.8–3.0
Wines	2.8–3.8
Apples	2.9–3.3
Peaches	3.4–3.6
Cherries	3.2–4.0
Beers	4.0–5.0
Rainwater (unpolluted)	5.6
Human blood	7.3–7.4
Egg whites	7.6–8.0
Milk of magnesia	10.5
Household ammonia	10.5–11.5
4% NaOH solution	14

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What Does the pH Number Imply?

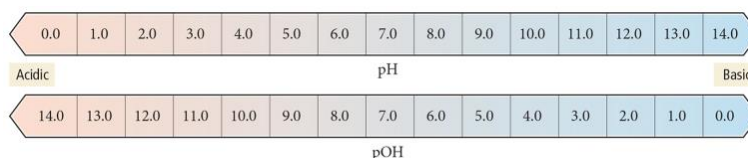
- The lower the pH, the more acidic the solution; the higher the pH, the more basic the solution.
 - 1 pH unit corresponds to a factor of 10 difference in acidity.
- Normal range of pH is 0 to 14.
 - pH 0 is $[\text{H}_3\text{O}^+] = 1 \text{ M}$; pH 14 is $[\text{OH}^-] = 1 \text{ M}$.
 - pH can be negative (very acidic) or larger than 14 (very alkaline).



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pOH

- Another way of expressing the acidity/basicity of a solution is **pOH**.
- $\text{pOH} = -\log[\text{OH}^-]$, $[\text{OH}^-] = 10^{-\text{pOH}}$
 - $\text{pOH}_{\text{water}} = -\log[10^{-7}] = 7$
 - Need to know the $[\text{OH}^-]$ concentration to find pOH
- $\text{pOH} < 7$ is basic; $\text{pOH} > 7$ is acidic; $\text{pOH} = 7$ is neutral.
- $\text{pH} + \text{pOH} = 14.0$



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Relationship between pH and pOH

- **$\text{pH} + \text{pOH} = 14.00$** at 25 °C.
 - You can use pOH to find the pH of a solution.

$$\begin{aligned}
 [\text{H}_3\text{O}^+][\text{OH}^-] &= K_w = 1.0 \times 10^{-14} \\
 (-\log([\text{H}_3\text{O}^+][\text{OH}^-])) &= -\log(1.0 \times 10^{-14}) \\
 (-\log([\text{H}_3\text{O}^+])) + (-\log([\text{OH}^-])) &= 14.00 \\
 \text{pH} + \text{pOH} &= 14.00
 \end{aligned}$$

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pK

- A way of expressing the strength of an acid or base is **pK**.
- $pK_a = -\log(K_a)$, $K_a = 10^{-pK_a}$
- $pK_b = -\log(K_b)$, $K_b = 10^{-pK_b}$
- **The stronger the acid, the smaller the pK_a .**
 - Larger K_a = smaller pK_a
 - Because pK_a is the $-\log$
- **The stronger the base, the smaller the pK_b .**
 - Larger K_b = smaller pK_b

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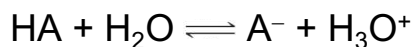
$[H_3O^+]$ and pH in an Acid Solution

- There are two sources of H_3O^+ in an aqueous solution of a strong acid—the acid and the water.
- For a strong acid, the contribution of the water to the total $[H_3O^+]$ is negligible.
- The $[H_3O^+]_{acid}$ shifts the K_w equilibrium so far that $[H_3O^+]_{water}$ is too small to be significant.
- $[H_3O^+]_{acid} = [HA]$

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Finding the pH of a Weak Acid

- There are also two sources of H_3O^+ in an aqueous solution of a weak acid—the acid and the water.
- However, finding the $[\text{H}_3\text{O}^+]$ is complicated by the fact that the acid undergoes only partial ionization.
- Calculating the $[\text{H}_3\text{O}^+]$ requires solving an equilibrium problem for the reaction that defines the acidity of the acid.



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Finding the pH of a Weak Acid

1. Write the equation for the acid, and use it as a guide to prepare the ICE table.
2. Complete the ICE table based on the given information. Keep in mind the reaction stoichiometry for the change line.
3. Substitute the expressions for equilibrium concentrations into the K expression.
4. Determine $[\text{H}_3\text{O}^+]$ from the calculated value of x , and calculate the pH as necessary.
5. Check the answer.

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Percent Ionization

- Another way to measure the strength of an acid is to determine the percentage of acid molecules that ionize when dissolved in water; this is called the **percent ionization**.
 - The higher the percent ionization, the stronger the acid.
 - Concentration of ionized acid = $[H_3O^+]$

$$\text{Percent ionization} = \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\% = \frac{[H_3O^+]_{\text{equil}}}{[HA]_{\text{init}}} \times 100\%$$

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Relationship between $[H_3O^+]_{\text{equilibrium}}$ and $[HA]_{\text{initial}}$

- Increasing the initial concentration of acid results in increased $[H_3O^+]$ at equilibrium.
- Increasing the initial concentration of acid results in decreased percent ionization.
- This means that the increase in $[H_3O^+]$ concentration is slower than the increase in acid concentration.

$$\text{Percent ionization} = \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\% = \frac{[H_3O^+]_{\text{equil}}}{[HA]_{\text{init}}} \times 100\%$$

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[H₃O⁺] and Percent Ionization

- The [H₃O⁺]_{equilibrium} of a weak acid increases with increasing [HA].
- Percent ionization of a weak acid decreases with increasing [HA].

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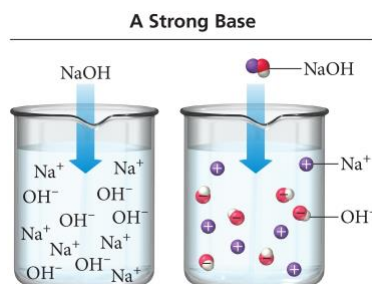
Finding the pH of Mixtures of Acids

- For a mixture of a strong acid with a weak acid, the complete ionization of the strong acid provides more than enough [H₃O⁺] to shift the weak acid equilibrium to the left so far that the weak acid's added [H₃O⁺] is negligible.
- For mixtures of weak acids, you generally need to consider only the stronger for the same reasons, as long as one is significantly stronger than the other and their concentrations are similar.

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Strong Bases

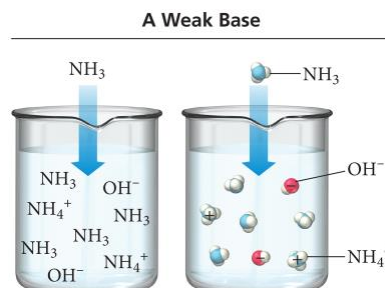
- The stronger the base, the more willing it is to accept H^+ .
 - Use water as the standard acid.
- For ionic bases, like $NaOH$, practically all units are dissociated into OH^- and cation, Na^+ .
 - Strong electrolytes
 - Multi- OH^- strong bases completely dissociate in one step.



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Weak Bases

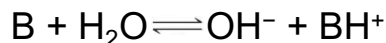
- In weak bases, only a small fraction of molecules accept H^+ .
 - Weak electrolyte
 - Most of the weak base molecules do not take H^+ from water.
 - Much less than 1% ionization in water
- $[OH^-] \ll [\text{weak base}]$
- Finding the pH of a weak base solution is similar to finding the pH of a weak acid.



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Base Ionization Constant, K_b

- Base strength is measured by the size of the equilibrium constant when it reacts with H_2O .



- The equilibrium constant is called the **base ionization constant, K_b** .
 - Larger K_b = stronger base

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

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Common Weak Bases

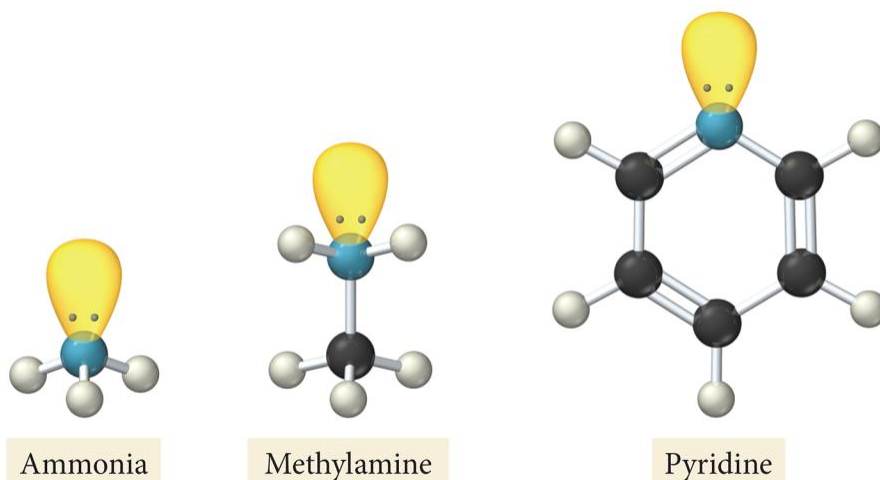
TABLE 16.8 Some Common Weak Bases

Weak Base	Ionization Reaction	K_b (at 25 °C)
Carbonate ion (CO_3^{2-})*	$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$	1.8×10^{-4}
Methylamine (CH_3NH_2)	$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$	4.4×10^{-4}
Ethylamine ($C_2H_5NH_2$)	$C_2H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$	5.6×10^{-4}
Ammonia (NH_3)	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	1.76×10^{-5}
Bicarbonate ion (HCO_3^-)* (or hydrogen carbonate)	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$	2.3×10^{-8}
Pyridine (C_5H_5N)	$C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$	1.7×10^{-9}
Aniline ($C_6H_5NH_2$)	$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$	3.9×10^{-10}

*The carbonate and bicarbonate ions must occur with a positively charged ion such as Na^+ that serves to balance the charge but does not have any part in the ionization reaction. For example, it is the bicarbonate ion that makes sodium bicarbonate ($NaHCO_3$) basic. We look more closely at ionic bases in Section 16.8.

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Structure of Amines



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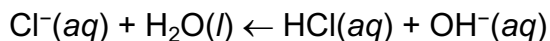
Acid–Base Properties of Ions and Salts

- Salts are ionic compounds.
- Soluble salts form ions in solution.
- Cation of a strong base and anion of a strong acid do not ionize water; hence, it doesn't affect solution pH.
- Cation of a weak base and anion of a weak acid will ionize water and affect the pH of solution.
 - NaHCO_3 solutions are basic.
 - Na^+ is the cation of the strong base NaOH .
 - HCO_3^- is the conjugate base of the weak acid H_2CO_3 .
- Anions tend to form basic or neutral solutions.
- Cations tend to form acidic or neutral solutions.

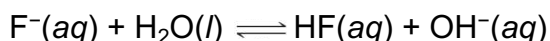
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Anions as Weak Bases

- Every anion can be thought of as the conjugate base of an acid.
- Therefore, every anion can potentially be a base.
 - $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$
- **The stronger the acid, the weaker the conjugate base.**
- An anion that is the conjugate base of a strong acid is pH neutral.



- An anion that is the conjugate base of a weak acid is basic.



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Strength of Conjugate Acid–Base Pairs

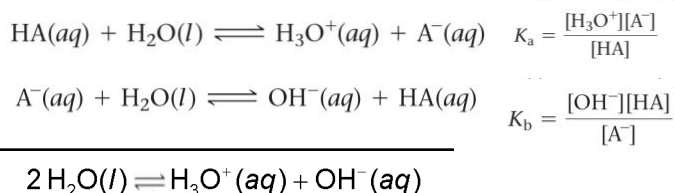
	Acid		Base		
↑ Acid Strength	Strong	HCl	Cl ⁻	Neutral	
		H ₂ SO ₄	HSO ₄ ⁻		
		HNO ₃	NO ₃ ⁻		
		H ₃ O ⁺	H ₂ O		
	Weak	HSO ₄ ⁻	SO ₄ ²⁻	Weak	
		H ₂ SO ₃	HSO ₃ ⁻		
		H ₃ PO ₄	H ₂ PO ₄ ⁻		
		HF	F ⁻		
		HC ₂ H ₃ O ₂	C ₂ H ₃ O ₂ ⁻		
		H ₂ CO ₃	HCO ₃ ⁻		
H ₂ S		HS ⁻			
HSO ₃ ⁻		SO ₃ ²⁻			
H ₂ PO ₄ ⁻		HPO ₄ ²⁻			
HCN		CN ⁻			
NH ₄ ⁺		NH ₃			
HCO ₃ ⁻		CO ₃ ²⁻			
HPO ₄ ²⁻		PO ₄ ³⁻			
H ₂ O		OH ⁻			
Negligible		HS ⁻	S ²⁻		Strong
		OH ⁻	O ²⁻		
				↓ Base Strength	

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Relationship between K_a of an Acid and K_b of Its Conjugate Base

- Many reference books give tables only of K_a values because K_b values can be found from them.

When you add equations, you multiply the K s.

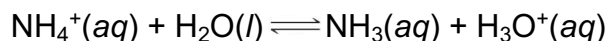


$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-][\text{OH}^-][\text{HA}]}{[\text{HA}][\text{A}]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

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Cations as Weak Acids

- The stronger the base, the weaker the conjugate acid.**
- A cation that is the counterion of a strong base is pH neutral.
- A cation that is the conjugate acid of a weak base is weakly acidic.

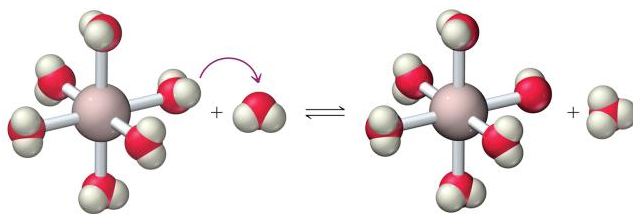
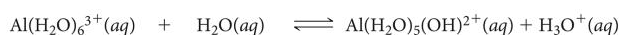
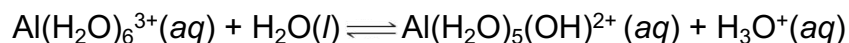


- A cation that is a small, highly charged metal ion forms weakly acidic solution.

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Metal Cations as Weak Acids

- Cations of small, highly charged metals are weakly acidic.
 - Alkali metal cations and alkali earth metal cations are pH neutral.
 - Cations are hydrated.



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Classifying Salt Solutions as Acidic, Basic, or Neutral

- If the salt cation is the counterion of a strong base and the anion is the conjugate base of a strong acid, it will form a neutral solution.
 - NaCl Ca(NO₃)₂ KBr
- If the salt cation is the counterion of a strong base and the anion is the conjugate base of a weak acid, it will form a basic solution.
 - NaF Ca(C₂H₃O₂)₂ KNO₂

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Classifying Salt Solutions as Acidic, Basic, or Neutral

- If the salt cation is the conjugate acid of a weak base and the anion is the conjugate base of a strong acid, it will form an acidic solution.
 - NH_4Cl
- If the salt cation is a highly charged metal ion and the anion is the conjugate base of a strong acid, it will form an acidic solution.
 - $\text{Al}(\text{NO}_3)_3$

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Classifying Salt Solutions as Acidic, Basic, or Neutral

- If the salt cation is the conjugate acid of a weak base and the anion is the conjugate base of a weak acid, the pH of the solution depends on the relative strengths of the acid and base.
 - NH_4F because HF is a stronger acid than NH_4^+ , and K_a of NH_4^+ is larger than K_b of the F^- ; therefore, the solution will be acidic.

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Ionization in Polyprotic Acids

- Because polyprotic acids ionize in steps, each H^+ has a separate K_a .
- $K_{a1} > K_{a2} > K_{a3}$
- Generally, the difference in K_a values is great enough so that the second ionization does not happen to a large enough extent to affect the pH.
 - For most pH problems, we just use the first ionization.
 - Except $\text{H}_2\text{SO}_4 \Rightarrow$ use $[\text{H}_2\text{SO}_4]$ as the $[\text{H}_3\text{O}^+]$ for the second ionization.
- $[\text{A}^{2-}] = K_{a2}$ as long as the second ionization is negligible.

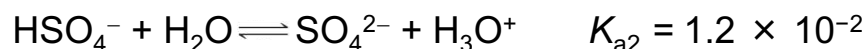
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Name (Formula)	Structure	Space-filling model	K_{a1}	K_{a2}	K_{a3}
Sulfuric Acid (H_2SO_4)			Strong	1.2×10^{-2}	
Oxalic Acid ($\text{H}_2\text{C}_2\text{O}_4$)			6.0×10^{-2}	6.1×10^{-5}	
Sulfurous Acid (H_2SO_3)			1.6×10^{-2}	6.4×10^{-8}	
Phosphoric Acid (H_3PO_4)			7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Citric Acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$)			7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Ascorbic Acid ($\text{H}_2\text{C}_6\text{H}_6\text{O}_6$)			8.0×10^{-5}	1.6×10^{-12}	
Carbonic Acid (H_2CO_3)			4.3×10^{-7}	5.6×10^{-11}	

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Ionization in H₂SO₄

- The ionization constants for H₂SO₄ are as follows:

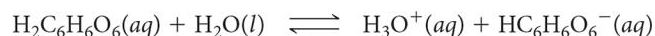


- For most sulfuric acid solutions, the second ionization is significant and must be accounted for.
- Because the first ionization is complete, use the given $[\text{H}_2\text{SO}_4] = [\text{HSO}_4^-]_{\text{initial}} = [\text{H}_3\text{O}^+]_{\text{initial}}$.

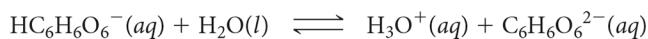
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Dissociation of a Polyprotic Acid

Dissociation of a Polyprotic Acid



$$[\text{H}_3\text{O}^+] = 2.8 \times 10^{-3} \text{ M}$$



$$[\text{H}_3\text{O}^+] = 1.6 \times 10^{-12} \text{ M}$$

$$\text{Total } [\text{H}_3\text{O}^+] = 2.8 \times 10^{-3} \text{ M} + 1.6 \times 10^{-12} \text{ M}$$

$$= 2.8 \times 10^{-3} \text{ M}$$



0.100 M H₂C₆H₆O₆

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Strengths of Binary Acids

- The more δ^+ H—X δ^- polarized the bond, the more acidic.
- The stronger the H—X bond, the weaker the acid.
- Binary acid strength increases to the right across a period.
 - Acidity: $\text{H—C} < \text{H—N} < \text{H—O} < \text{H—F}$
- Binary acid strength increases down the column.
 - Acidity: $\text{H—F} < \text{H—Cl} < \text{H—Br} < \text{H—I}$

Increasing electronegativity
Increasing acidity

Decreasing bond strength
Increasing acidity

6A	7A
H_2O	HF
H_2S	HCl
H_2Se	HBr
H_2Te	HI

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Strengths of Oxyacids, H—O—Y

- The more electronegative the Y atom, the stronger the oxyacid.
 - $\text{HClO} > \text{HIO}$
 - Acidity of oxyacids decreases down a group.**
 - Same trend as binary acids
 - Helps weaken the H—O bond
- The larger the oxidation number of the central atom, the stronger the oxyacid.
 - $\text{H}_2\text{CO}_3 > \text{H}_3\text{BO}_3$
 - Acidity of oxyacids increases to the right across a period.**
 - Opposite trend of binary acids
- The more oxygens attached to Y, the stronger the oxyacid.
 - Further weakens and polarizes the H—O bond
 - $\text{HClO}_3 > \text{HClO}_2$

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Relationship between Bond Strength and Acidity

Acid	Bond Energy (kJ/mol)	Type of Acid
H—F	565	Weak
H—Cl	431	Strong
H—Br	364	Strong

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Relationship between Electronegativity and Acidity

Acid	Electronegativity of Y	K_a
H—O—I	2.5	2.3×10^{-11}
H—O—Br	2.8	2.0×10^{-9}
H—O—Cl	3.0	2.9×10^{-8}

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Relationship between Number of Oxygens on the Central Atom and Acidity

Acid	Structure	K_a
HClO_4	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{O}-\text{Cl}=\text{O} \\ \\ \text{O} \end{array}$	Strong
HClO_3	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{O}-\text{Cl}=\text{O} \end{array}$	1
HClO_2	$\text{H}-\text{O}-\text{Cl}=\text{O}$	1.1×10^{-2}
HClO	$\text{H}-\text{O}-\text{Cl}$	2.9×10^{-8}

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Lewis Acid–Base Theory

- Lewis acid–base theory focuses on transferring an electron pair.
- Lewis acid—lone pair acceptor
- Lewis base—lone pair donor
- Does *not* require H^+

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Lewis Acids

- They are electron deficient, either from being attached to electronegative atom(s) or not having an octet.
- They must have an empty orbital willing to accept the electron pair.
- H^+ has empty 1s orbital.
- B in BF_3 has empty 2p orbital and an incomplete octet.
- Many small, highly charged metal cations have empty orbitals that they can use to accept electrons.
- Atoms that are attached to highly electronegative atoms and have multiple bonds can be Lewis acids.

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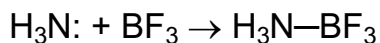
Lewis Bases

- The Lewis base has electrons it is willing to give away to or share with another atom.
- The Lewis base must have a lone pair of electrons on it that it can donate.
- Anions are better Lewis bases than neutral atoms or molecules.
 - $\text{N} < \text{N}^-$
- Generally, the more electronegative an atom, the less willing it is to be a Lewis base.
 - $\text{O} < \text{S}$

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Lewis Acid–Base Reactions

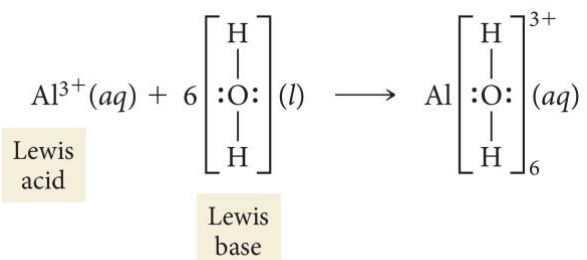
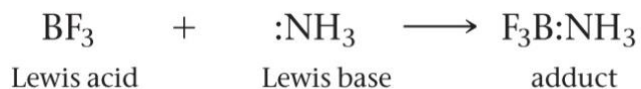
- The base donates a pair of electrons to the acid.
- It generally results in the formation of a covalent bond.



- The product that forms is called an **adduct**.
- Arrhenius and Brønsted–Lowry acid–base reactions are also Lewis reactions.

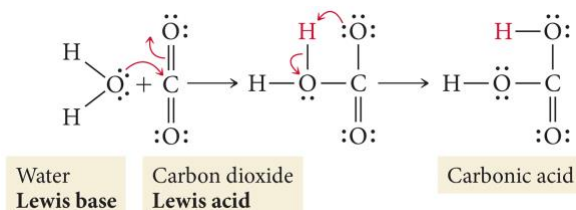
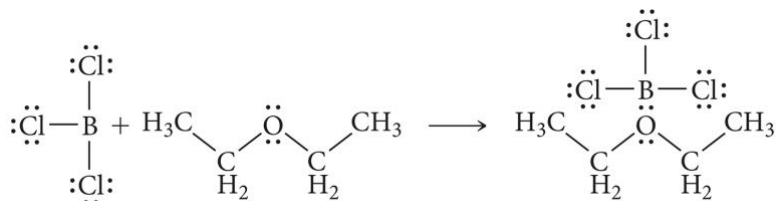
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Examples of Lewis Acid–Base Reactions



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Examples of Lewis Acid–Base Reactions



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U.S. Fuel Consumption

- About 82% of the energy used in the United States comes from the combustion of fossil fuels.
 - Oil, natural gas, coal
- Combustion of fossil fuels produces CO_2 .

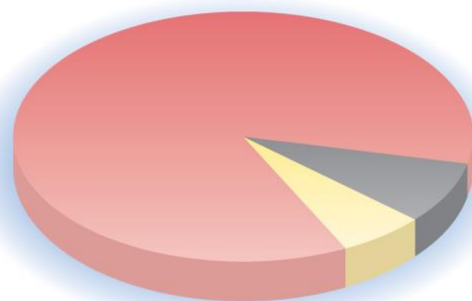
$$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$$
- Natural fossil fuels also contain small amounts of S that burn to produce SO_2 gas, which reacts with O_2 to form SO_3 .

$$2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3$$
- The high temperatures of combustion allow N_2 in the air to combine with O_2 to form oxides of nitrogen.

$$\text{N}_2 + 2 \text{O}_2 \rightarrow 2 \text{NO}_2$$

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U.S. Energy Consumption
by Source, 2013



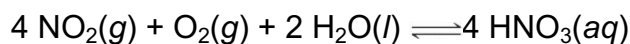
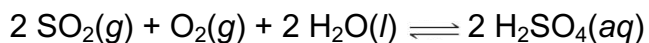
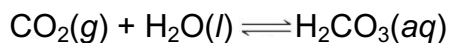
- Fossil Fuels: 82%
- Nuclear: 10%
- Renewable Energy: 8%

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What Causes Acid Rain?

- Many natural and pollutant gases dissolved in the air are nonmetal oxides.
 - CO_2 , SO_2 , NO_2

- Nonmetal oxides are acidic.

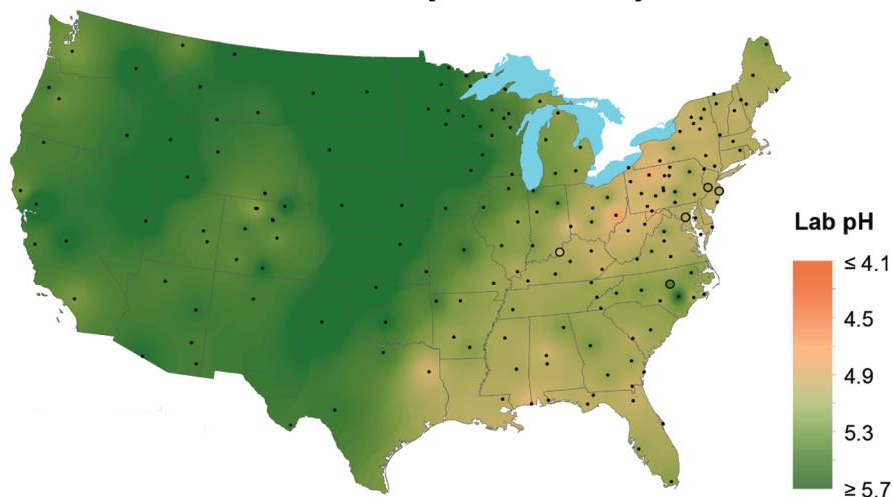


- Processes that produce nonmetal oxide gases as waste increase the acidity of the rain.
 - Natural—volcanoes and some bacterial action
 - Human-made—combustion of fuel

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pH of Rain in Different U.S. Regions

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2013



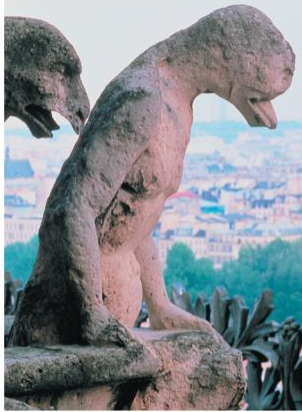
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Damage from Acid Rain

- Acids react with metals and damages bridges, cars, and other metallic structures.
- It degrades materials and structures that contain carbonates, like buildings and other structures made of limestone or cement.
- Acidifying lakes affects aquatic life.
- Soil acidity causes more dissolving of minerals and leaching more minerals from soil, making it difficult for trees.

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Effects of Acid Rain



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Acid Rain Legislation

- 1990 Clean Air Act attacks acid rain.
 - Forces utilities to reduce SO_2
- The result is acid rain in the Northeast has stabilized and is beginning to be reduced.

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U.S. Sulfur Dioxide Pollutant Levels



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