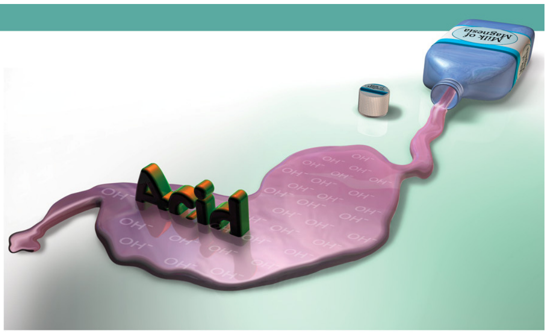
Chapter 15
Acids and Bases



Chemistry: A Molecular Approach, 2nd Ed.
Nivaldo Tro
Some Powerpoint lecture slides in this set were prepared by Roy Kennedy
Massachusetts Bay Community College
Wellesley Hills, MA
2008, Prentice Hall

Stomach Acid

- The cells that line our stomach produce ***hydrochloric acid***, **HCl** $_{(aq)}$
  - to kill unwanted bacteria
  - to help break down food
  - to activate enzymes that help break down food

Stomach Acid & Heartburn

- If the stomach acid backs up into your esophagus, it irritates those tissues, resulting in heartburn
  - ***Acid reflux***
  - ***GERD*** = gastroesophageal reflux disease = chronic leaking of stomach acid into the esophagus

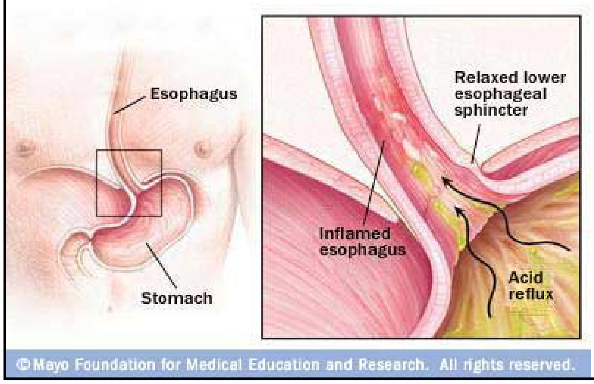


Image available at http://www.mayoclinic.com/images/image_popup/r7_heartburn.jpg

Curing Heartburn

Mild cases of heartburn can be cured by neutralizing the acid in the esophagus

- Swallowing saliva which contains bicarbonate ion (HCO_3^-), a weak <u>base</u>
- Taking antacids containing hydroxide ions (OH^-, a <u>base</u>) and/or carbonate ions (CO_3^{2-}, a weak <u>base</u>)

Carlsbad Cavern. Image available at J. Suchocki, “Conceptual Chemistry: Understanding Our World Of Atoms and Molecules.” 3rd Edition, Benjamin Cummings, Wesley: San Francisco, 2007.

How Carlsbad Cavern was Formed

Most of the caves people are familiar with (such as Mammoth Cave in Kentucky) were formed by rainwater slowly dissolving limestone. Water sinking through enlarged fractures and sinkholes eventually grew to become underground streams and rivers carving out complex cave systems. The caves of the Guadalupe Mountains were formed in a much different way.

Between 4 and 6 million years ago hydrogen-sulfide-rich (H_2S) waters began to migrate through fractures and faults in the Capitan Limestone. This water mixed with rainwater moving downward from the surface. When the two waters mixed, the H_2S combined with the oxygen carried by the rainwater and formed sulfuric acid (H_2SO_4). This acid dissolved the limestone along fractures and folds in the rock to form Carlsbad Cavern. This process left behind massive gypsum ($CaSO_4$) deposits, clay, and silt as evidence of how the cave was formed. With time, the active level dropped to form deeper cave passages.

http://www.nps.gov/cave/naturescience/cave.htm

How Carlsbad Cavern was Formed

- (H_2S) Hydrogen sulfide-rich rainwater runoff forms sulfuric acid in the presence of dissolved O_2
- Sulfuric acid, H_2SO_4, is a strong acid
  - vs. carbonic acid, H_2CO_3, in soda and rainwater, which is a weak acid
- Strong acids react faster and more completely with bases, like limestone, than weak acids
  - Reason for larger caverns in NM

http://www.nps.gov/cave/naturescience/cave.htm

Another chemical equilibrium involved in nature: Gypsum Formations

Gypsum = hydrated calcium sulfate, $CaSO_4{\bullet}H_2O$
= insoluble in water

The giant **gypsum crystals** in Mexico's "Cueva de los Cristales" are a stunning natural wonder featuring crystals up to 11 metres long. Image accessed from http://www.webelements.com/nexus/search/results/taxonomy:281
See Geology: April, 2007, v. 35, no. 4, where the crystals are featured on the cover.

What are Acids?

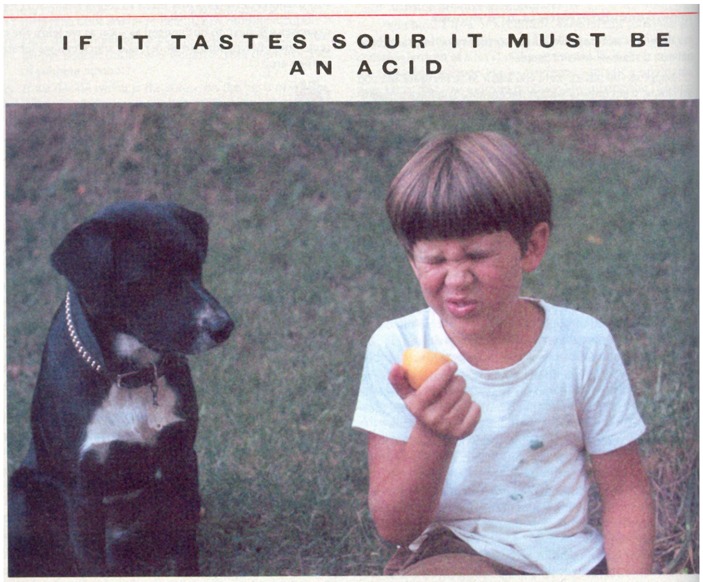
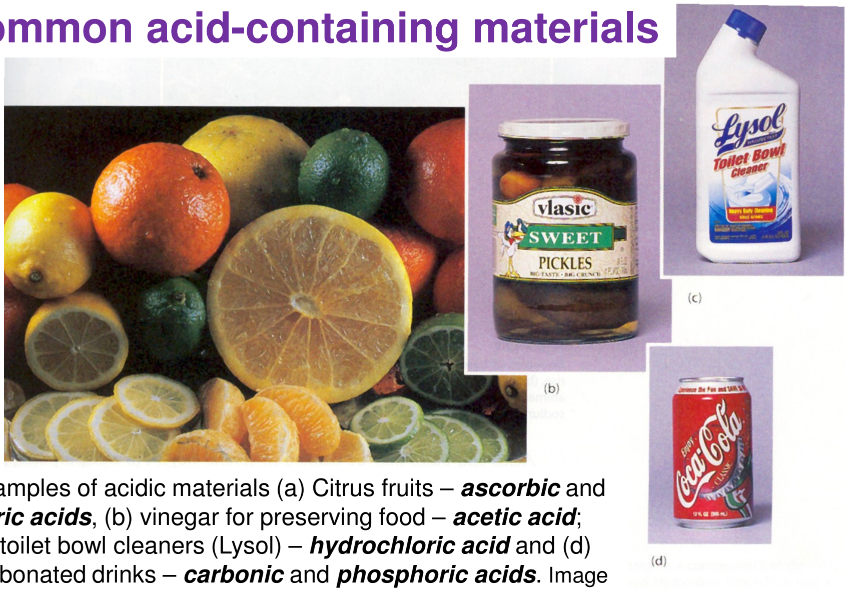


Image available at C. Snyder, “The Extraordinary Chemistry of Ordinary Things,” 4th ed. Wiley, 2003.

Common acid-containing materials

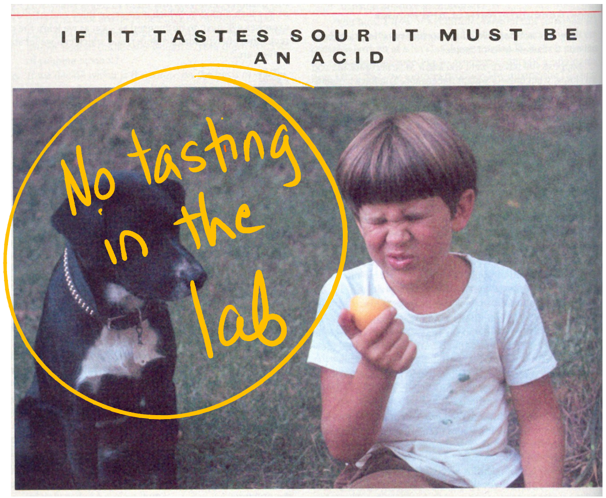


Examples of acidic materials (a) Citrus fruits – ***ascorbic*** and ***citric acids***, (b) vinegar for preserving food – ***acetic acid***; (c) toilet bowl cleaners (Lysol) – ***hydrochloric acid*** and (d) carbonated drinks – ***carbonic*** and ***phosphoric acids***. Image available at J. Suchocki, “Conceptual Chemistry: Understanding Our World Of Atoms and Molecules.” 3rd ed.

Common base-containing materials

Figure 10.2 Examples of bases. (a) Baking soda – ***sodium bicarbonate***, (b) wood ash – ***potassium carbonate***; (c) bar soap and (d) Drain clog remover – ***sodium hydroxide.***

How can we tell if a solution is acidic?



No tasting in the lab

Image available at C. Snyder, “The Extraordinary Chemistry of Ordinary Things,” 4th ed. Wiley, 2003.

General Properties of Acids

- Sour taste
- React with “active” metals – producing H_2 gas
  - i.e., Al, Zn, Fe, but not Cu, Ag, or Au

$$2\ Al + 6\ HCl \longrightarrow 2\ AlCl_3 + 3\ H_2$$

  - Corrosive
- React with carbon*ate*s (weak base), producing CO_2
  - Marble, baking soda, chalk, limestone

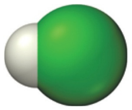
$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

- Change color of vegetable dyes
  - Blue litmus turns red = acid
- React with bases to form ionic salts = ***neutralization***

Structures of Acids

- ***Binary acids*** have acidic hydrogens attached to a nonmetal atom
  - HCl, HF, H_2S

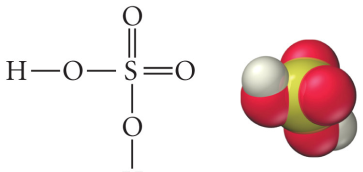
HCl



Hydrochloric acid

Structure of Acids – Cont.

- **Oxy acids** have acidic hydrogens attached to an oxygen atom
  - H_2SO_4, HNO_3, H_3PO_4



H_2SO_4

Sulfuric Acid

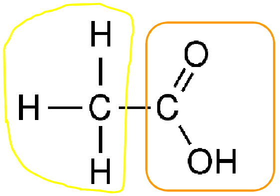
HNO_3

Nitric Acid

Structure of Acids – Cont.

Organic acids – contain a *hydrocarbon group* and *acidic H* attached to O

- **Carboxylic acids** have - COOH (called *carboxylate*) group
  - Ex. Acetic acid, CH_3COOH (also written as $HC_2H_3O_2$)

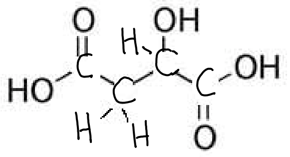


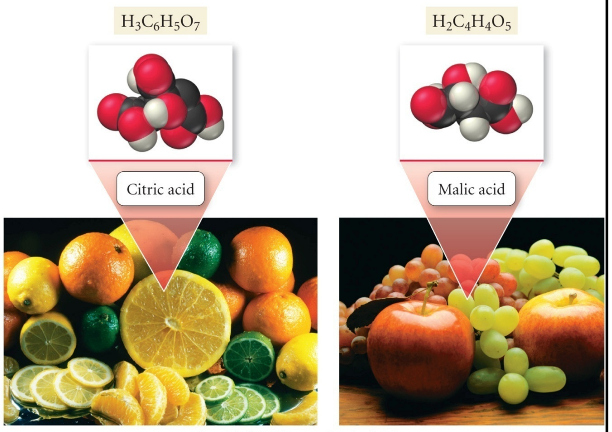
- Only the first H in the formula is acidic
- The acidic H is on the COOH

Carboxylic acids – *Cont.*

- Ex. Malic acid, $\mathbf{H_2}C_4H_4O_5$ = 2 acidic H, two COOH group

  Citric acid, $\mathbf{H_3}C_6H_5O_7$ = 3 acidic H, three COOH group





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Properties of Bases

- Also known as ***alkalis*** (vs. solutions of bases in water = ***alkaline***, or ***basic*** solutions)
- Taste bitter
  - Alkaloids = naturally-occurring bases in plants
    - Ex. Nicotine; Caffeine
- Solutions feel slippery
- Change color of vegetable dyes
  - Red litmus turns blue = basic
- React with acids to form ionic salts
  - *Neutralization*

Structure of Bases

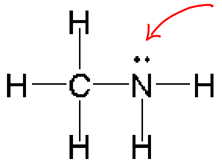
- Most ionic bases contain ***hydroxide*** (OH^-) ions

  Ex. NaOH, $Ca(OH)_2$

- Some contain ***carbonate*** CO_3^{2-} ions

  Ex. $CaCO_3$ $NaHCO_3$

- Organic bases called ***amines*** containing amino ($R-NH_2$ or R_2-NH or R_3-N) groups



Methylamine

Nonbonding e^- pair attracts H^+

ion-diple

How do we explain the difference in properties and behavior of acid and bases?

Arrhenius Theory

An **acid** is a substance that increases the concentration of H^+ ions when dissolved in water

Ex. Hydrogen chloride, HCl, is an Arrhenius acid. Gaseous HCl dissolves in water to produce hydrated H^+ and Cl^-

$$HCl_{(g)} \xrightarrow{H_2O} \mathbf{H^+}_{(aq)} + Cl^-_{(aq)}$$

Note: An aqueous solution of HCl is known as *hydrochloric acid*. Concentrated hydrochloric acid is about 37 % HCl by mass and is 12 M in HCl.

Reference: Brown, LeMay, Bursten and Murphy, Chemistry: The Central Science, Pearson, 2009.

Arrhenius Theory

A **base** is a substance that increases the concentration of hydroxide, OH^-, ions when dissolved in water

Ex. Sodium hydroxide, NaOH

- Because NaOH is *ionic*, it dissociates into Na^+ and OH^- when it dissolves in water, releasing OH- into the solution

$$NaOH_{(aq)} \xrightarrow{H_2O} Na^+_{(aq)} + \mathbf{OH^-}_{(aq)}$$

Hydroxide ion

Reference: Brown, LeMay, Bursten and Murphy, Chemistry: The Central Science, Pearson, 2009.

Arrhenius Theory

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

HCl ionizes in water, producing H^+ and Cl^- ions

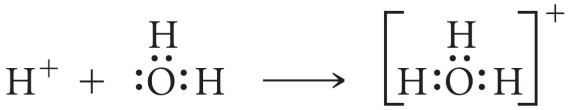
$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

NaOH dissociates in water, producing Na^+ and OH^- ions

Hydronium Ion, H_3O^+

- The H^+ ions produced by the acid are so reactive they cannot exist in water
  - H^+ ions are *protons!!* [i.e. a hydrogen atom stripped off of its only electron; leaves only one proton in the nucleus]
- Instead, they react with a water molecule(s) to produce complex ions, mainly **hydronium ion, H_3O^+**

$$H^+ + H_2O \rightarrow H_3O^+$$



Problems with Arrhenius Theory

- Does not explain why molecular substances, like NH_3, dissolve in water to form basic solutions – even though they do not contain $OH^–$ ions
- Does not explain how some ionic compounds, like Na_2CO_3 or Na_2O, dissolve in water to form basic solutions – even though they do not contain $OH^–$ ions
- Does not explain why molecular substances, like CO_2, dissolve in water to form acidic solutions – even though they do not contain H^+ ions
- Does not explain acid-base reactions that take place *outside aqueous solution*

Bronsted-Lowry (B-L) Theory
of Acids and Bases

An **acid** is a proton (hydrogen ion, H^+) donor.
A **base** is a proton (hydrogen ion, H^+) acceptor.

Example 1:

$$\underset{\text{B-L Acid}}{HCl} + \underset{\text{B-L Base}}{H_2O} \rightleftharpoons H_3O^+ + Cl^-$$

$$HCl + H_2O \rightleftharpoons H_3O^+ + \underset{\text{One less H than HCl}}{Cl^-}$$

Transfer of H^+ from HCl (donor) to H_2O …

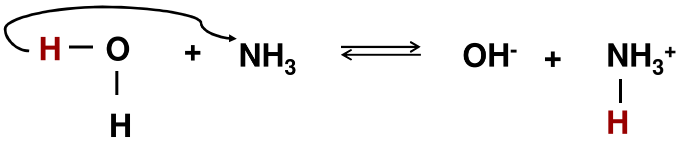
forming H_3O^+ and Cl^-

Bronsted-Lowry (B-L) Theory – *Cont.*

Example 2:

$$H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+$$

Identify the B-L acid and B-L base in example 2 above



$$H{-}\underset{\displaystyle H}{\overset{}{O}} + NH_3 \rightleftharpoons OH^- + \underset{\displaystyle H}{NH_3^+}$$

B-L **Acid** B-L **Base**

Transfer of H⁺ from H_2O (donor) to NH_3 …

… produces hydroxide and ammonium ions

Amphoteric Substances

Note: In both Examples 1 and 2, water behaved as an acid or a base. A species that can act as an acid or a base is called ***amphoteric***.

Amphoteric substances:

- have both ***transferable H⁺*** and atom with ***lone pair***

Ex. 1: Water acts as base, accepting H^+ from HCl *due to* attraction between H^+ and lone pair of e^- in O

$$\underset{\approx}{HCl}_{(aq)} + H_2\ddot{O}\!:_{(l)} \rightarrow Cl^-_{(aq)} + H_3O^+_{(aq)}$$

Ex. 2: Water acts as acid, donating H^+ to NH_3

$$NH_{3\,(aq)} + H_2O_{(l)} \Leftrightarrow NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

Bronsted-Lowry (B-L) Theory – *Cont.*

Note: In both examples, water behaved as an acid or a base. A species that can act as an acid or a base is called ***amphoteric***.

Drill: Identify the B-L ***acid*** and ***base*** in each of the following. Circle any amphoteric species

1) $\underset{\text{acid}}{HNO_3} + \underset{\text{base}}{CO_3^{2-}} \Rightarrow NO_3^- + HCO_3^-$

2) $\underset{\text{base}}{HPO_4^{2-}} + \underset{\text{acid}}{H_2O} \Rightarrow H_2PO_4^- + OH^-$

3) $\underset{\text{acid}}{HPO_4^{2-}} + \underset{\text{base}}{H_2O} \Rightarrow PO_4^{-3} + H_3O^+$

Bronsted-Lowry (B-L) Theory – *Cont.*

NOTE: The B-L theory of acids and bases …
(a) *does not require that H_3O^+ or OH^- be formed* and
(b) *is not limited to aqueous solutions*.

Example of acid-base reaction in nonaqueous solution:

$$\underset{\text{Acid}}{HCl_{(g)}} + \underset{\text{Base}}{NH_{3(g)}} \rightleftharpoons \underset{\text{Ammonium chloride}}{NH_4^+Cl^-_{(s)}}$$

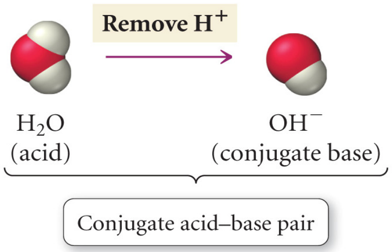
Salt

- A **salt** is an ionic compound formed by an acid-base reaction.
- *All acid-base reactions* (**neutralization**) *form a salt*. In aqueous solutions, water is also produced.

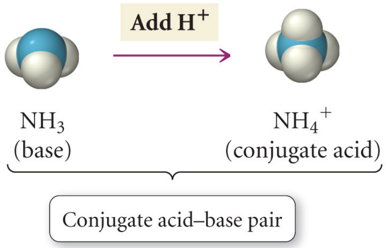
Conjugate Acids and Bases

In the reaction $H_2O + NH_3 \Leftrightarrow OH^{-} + NH_4^{+}$

H_2O and OH^{-} constitute an
Acid/Conjugate Base pair



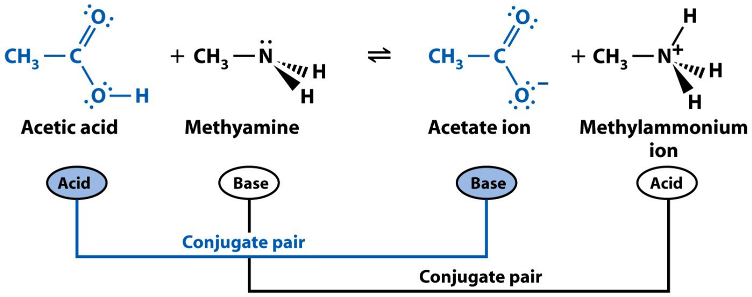
NH_3 and NH_4^{+} constitute a
Base/Conjugate Acid pair



NOTE: Conjugates differ by 1 H^{+}

Conjugate Acid-Base Pairs – *Cont.*

- The products of neutralization reactions are also classified as acids and bases:



Unnumbered figure pg 105
Quantitative Chemical Analysis, Seventh Edition
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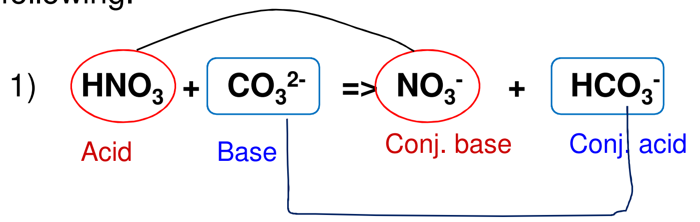
- Notice that the base derived from acetic acid is its conjugate base. Likewise, the acid produced from methylamine is its conjugate acid.
- **Conjugate acid** and **base pairs** are related to each other by one hydrogen (as H^{+})

Conjugate Acid-Base Pairs – *Cont.*

Drill: Identify the conjugate acid-base pairs in each of the following.



1) **HNO_3 + CO_3^{2-} => NO_3^- + HCO_3^-**

Acid Base Conj. base Conj. acid

NOTE: The species in the pair with one more H is always the acid

2) **HPO_4^{2-} + H_2O => $H_2PO_4^-$ + OH^-**

Base Acid Conj. acid Conj. base

Acid-base indicators

Indicators = substances (like natural dyes) that *change colors* in acidic or basic (alkaline) solutions

Examples:

- Litmus
- Anthocyanins *Anthos* = flower; *Cyan* = blue
  - Red cabbage
  - Cranberries
  - Radishes

Anthocyanins give many fruits and flowers their ***stunning color*** and ***acid-base behavior***.

Source: P. Kelter, J. Carr and A. Scott, “Chemistry: A World of Choices.” Boston: McGraw-Hill, 1999. (p. 288)

Acidic soil

Alkaline soil

Figure 11.17 Hydrangeas. These flowers are blue when grown in ______ soil and pink when grown in ______ ______ *(Diane Hirsch/Fundamental Photographs)*

Source: C. Baird and W. Gloffke, “Chemistry In Your Life.” New York: Freeman, 2003. (p. 437)

Strengths of Acids and Bases

Strong acids are those that ionize completely to form H^+ ions

- Forward reaction (ionization) is highly favored; No equilibrium involved

Single arrow indicates 100 % ionization

Ex. $HNO_{3\,(aq)} \longrightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$

Strong bases are those that dissociate completely to form OH^- ions

- Forward reaction (dissociation) is highly favored; No equilibrium involved

Single arrow indicates 100 % dissociation

Ex. $Ca(OH)_{2\,(aq)} \longrightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$

Strong Acids

- Strong acids are ***strong electrolytes***. Why?
  - 100% ionized in water
  - More ions in water, better electrolyte
- $[H_3O^+]$ = [strong acid]

$HCl \longrightarrow H^+ + Cl^-$

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

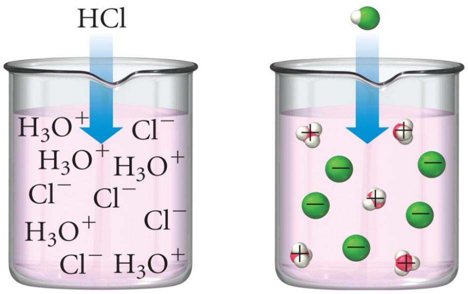


TABLE 15.3 Strong Acids

- Hydrochloric acid (HCl)
- Hydrobromic acid (HBr)
- Hydriodic acid (HI)
- Nitric acid (HNO_3)
- Perchloric acid ($HClO_4$)
- Sulfuric acid (H_2SO_4) (*diprotic*)

NOTE: Only the 1st ionization of H_2SO_4 is 100 % complete

TO MEMORIZE THESE

TABLE 15.7 Strong Bases

- Lithium hydroxide ($LiOH$)
- ↗Sodium hydroxide ($NaOH$)
- ↗Potassium hydroxide (KOH)
- Strontium hydroxide [$Sr(OH)_2$]
- ↗Calcium hydroxide [$Ca(OH)_2$]
- Barium hydroxide [$Ba(OH)_2$]

↗ **Memorize!**

Strengths of Acids and Bases

Weak acids partially ionize to form H^+ ions

- Acid-base equilibrium is involved

Equilibrium arrow indicates partial ionization.

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

- Extent of ionization indicated by magnitude of K (or **K_a** for acids)

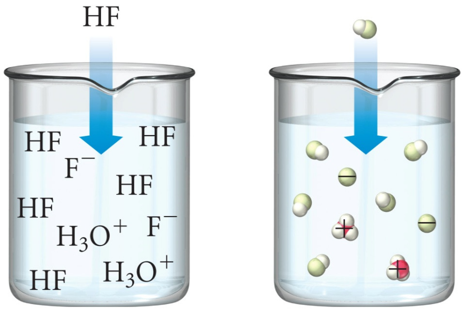
  Exercise: Write the K_a expression for the ionization of HF.

Weak Acids

- ***Weak acids*** ionize a small fraction of their H's
  - Most of the weak acid molecules do not donate H^+ to water
  - Usually less than 5 % ionize in water
- $[H_3O^+] << [\text{Weak acid}]$

$HF \rightleftharpoons H^+ + F^-$

$HF + H_2O \rightleftharpoons H_3O^+ + F^-$



Polyprotic Acids

- ***Polyprotic acids*** have more than one ionizable H
  - 1 H = **mono**protic, 2 H = **di**protic, 3 H = **tri**protic

    Ex. HCl = *mono*protic, H_2SO_4 = *di*protic, H_3PO_4 = *tri*protic
- Polyprotic acids ionize in steps
  - Each ionizable H removed sequentially

    Ex. $H_2SO_4 \longrightarrow H^+ + HSO_4^-$ Step 1

    $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ Step 2
- Removing the first H is easier than the second
  - H_2SO_4 is a stronger acid than HSO_4^-

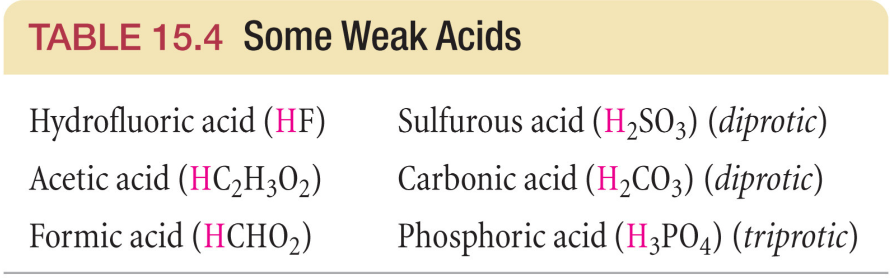


TABLE 15.4 Some Weak Acids

- Hydrofluoric acid (HF)
- Acetic acid ($HC_2H_3O_2$)
- Formic acid ($HCHO_2$)
- Sulfurous acid (H_2SO_3) (*diprotic*)
- Carbonic acid (H_2CO_3) (*diprotic*)
- Phosphoric acid (H_3PO_4) (*triprotic*)

Remember acetic, carbonic and phosphoric acids

TABLE 15.1 Some Common Acids

Name	Occurrence/Uses
Hydrochloric acid (HCl)	Metal cleaning; food preparation; ore refining; main component of stomach acid
Sulfuric acid (H_2SO_4)	Fertilizer and explosives manufacturing; dye and glue production; automobile batteries; electroplating of copper
Nitric acid (HNO_3)	Fertilizer and explosives manufacturing; dye and glue production
Acetic acid ($HC_2H_3O_2$)	Plastic and rubber manufacturing; food preservative; active component of vinegar
Citric acid ($H_3C_6H_5O_3$)	Present in citrus fruits such as lemons and limes; used to adjust pH in foods and beverages
Carbonic acid (H_2CO_3)	Found 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 manufacture; biological buffering; preservative in beverages

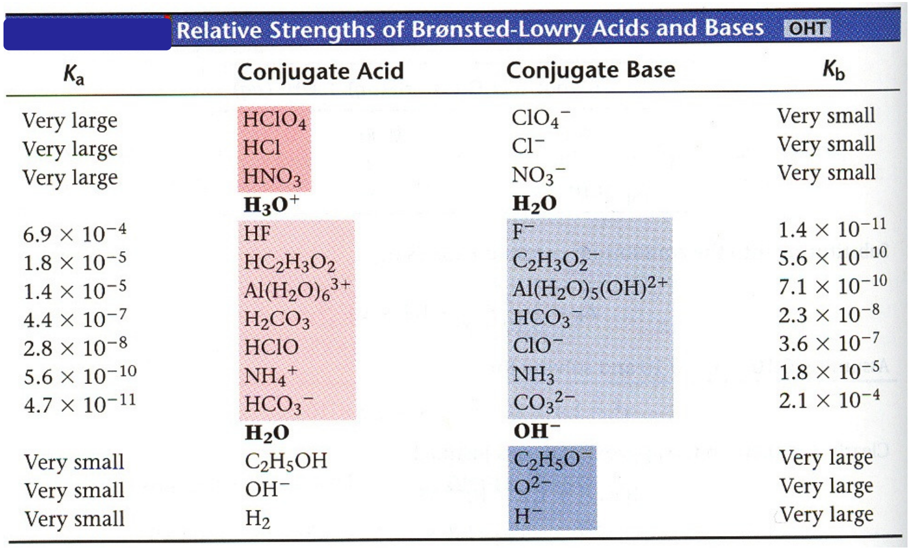
General Trends in Acidity

- The ***stronger an acid***, the ***weaker*** the ***conjugate base*** at accepting H^+
- Generally the more O, the stronger <u>oxyacid</u>

  Acid strength: $H_2SO_4 > H_2SO_3$; $HNO_3 > HNO_2$
- For conjugates: The cation is stronger acid than neutral molecule; neutral molecule is stronger acid than its anion

  Acid strength: $H_3O^+ > H_2O > OH^-$

  $NH_4^+ > NH_3 > NH_2^-$
  - Base trend opposite



Relative Strengths of Brønsted-Lowry Acids and Bases OHT

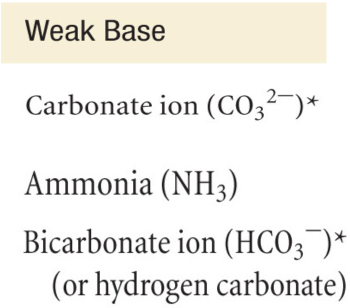
K_a	Conjugate Acid	Conjugate Base	K_b
Very large	$HClO_4$	ClO_4^-	Very small
Very large	HCl	Cl^-	Very small
Very large	HNO_3	NO_3^-	Very small
	H_3O^+	**H_2O**	
6.9×10^{-4}	HF	F^-	1.4×10^{-11}
1.8×10^{-5}	$HC_2H_3O_2$	$C_2H_3O_2^-$	5.6×10^{-10}
1.4×10^{-5}	$Al(H_2O)_6^{3+}$	$Al(H_2O)_5(OH)^{2+}$	7.1×10^{-10}
4.4×10^{-7}	H_2CO_3	HCO_3^-	2.3×10^{-8}
2.8×10^{-8}	$HClO$	ClO^-	3.6×10^{-7}
5.6×10^{-10}	NH_4^+	NH_3	1.8×10^{-5}
4.7×10^{-11}	HCO_3^-	CO_3^{2-}	2.1×10^{-4}
	H_2O	**OH^-**	
Very small	C_2H_5OH	$C_2H_5O^-$	Very large
Very small	OH^-	O^{2-}	Very large
Very small	H_2	H^-	Very large

Weak Bases

Weak bases partially ionize to form OH^- ions

- Acid-base equilibrium is involved
- Extent of ionization indicated by magnitude of K (= **K_b** for bases)

Some Common weak bases (Table 15.8, Tro) – ***Memorize!***



Weak Base
Carbonate ion (CO_3^{2-})*
Ammonia (NH_3)
Bicarbonate ion (HCO_3^-)* (or hydrogen carbonate)

* Conjugates

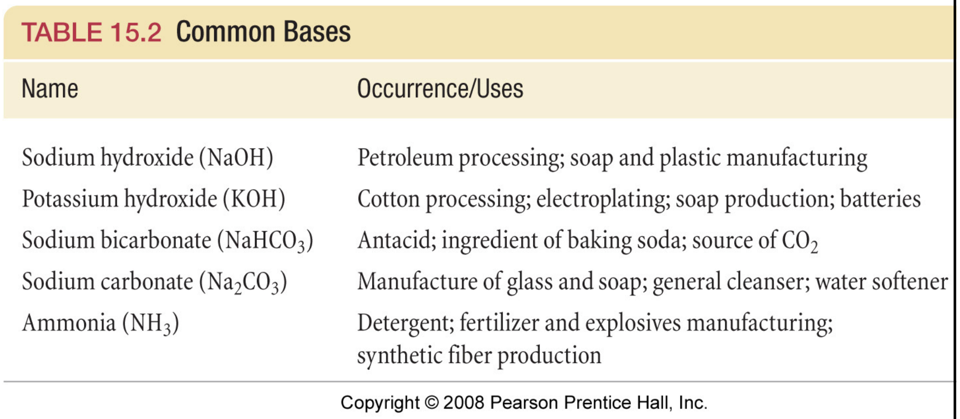


TABLE 15.2 Common Bases

Name	Occurrence/Uses
Sodium hydroxide (NaOH)	Petroleum processing; soap and plastic manufacturing
Potassium hydroxide (KOH)	Cotton processing; electroplating; soap production; batteries
Sodium bicarbonate ($NaHCO_3$)	Antacid; ingredient of baking soda; source of CO_2
Sodium carbonate (Na_2CO_3)	Manufacture of glass and soap; general cleanser; water softener
Ammonia (NH_3)	Detergent; fertilizer and explosives manufacturing; synthetic fiber production

Major Types of Weak Acids and Bases

Acids and bases can be classified as electrically neutral or charged species

(1) **Electrically neutral** species – *Examples:*

Acids: All 6 strong acids; $HC_2H_3O_2$ **(acetic)**; H_2CO_3 **(carbonic)**

Bases: All 6 strong bases; NH_3

Is CH_4 an acid? No, none of its H's is acidic (H is not written first)

(2) **Electrically charged** species – *Examples:*

Acids: $H_2PO_4^-$, HSO_4^-, HCO_3^- (from polyprotic acids; each has at least ***1 acidic H*** *left*; includes amphoteric species)

Bases: $C_2H_3O_2^-$, PO_4^{-3}, SO_4^{-2}, CO_3^{-2} $H_2PO_4^-$, HSO_4^-, HCO_3^- (conj. bases of acids; includes amphoteric species)

Major Types of Weak Acids and Bases – *Cont.*

Electrically charged species – *More* examples:

Acids: $\mathbf{NH_4^+}$

Some metal cations like $\mathbf{Al^{3+}}$, $\mathbf{Mg^{2+}}$, $\mathbf{Fe^{2+}}$ and $\mathbf{Zn^{2+}}$

Q. *How can metal cations like Al^{3+} be acidic?*

- In aqueous solutions, these metals exist as hydrated metal ions (associated with H_2O), which ionize to form H_3O^+

$$\underset{\textbf{Acid}}{Al(H_2O)_6^{3+}{}_{(aq)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Conj. Base}}{Al(H_2O)_5(OH)^{2+}{}_{(aq)}} + \underset{\textbf{Conj. acid}}{\mathbf{H_3O^+{}_{(aq)}}}$$

Acidic!

Self-Ionization (Autoprotolysis) of Water

- Water is *amphiprotic* - can act as a B-L acid or base
- H_2O can donate H^+ to another H_2O molecule

$$\mathbf{H_2O + H_2O \overset{K_w}{\rightleftharpoons} H_3O^+ + OH^-}$$

Autoprotolysis of water

Transfer of H⁺

Or simply $\mathbf{H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^-}$ $K_w = [H^+]\,[OH^-]$

At 25 ^{0}C, $\mathbf{K_w = 1.0 \times 10^{-14}}$

The pH Scale

- In pure water, $[H^+] = [OH^-]$
- A solution where $[H^+] = [OH^-]$ is called a **neutral solution**

Since $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25 ^{0}C, what is $[H^+]$ if $[H^+] = [OH^-]$?

Answer: Let **x = $[H^+]$** = $[OH^-]$

$$K_w \quad = \quad [H^+][OH^-] \qquad K_w = 1.0 \times 10^{-14} \text{ at } 25\ ^0\text{C}$$

$$1.0 \times 10^{-14} = (x)(x) \quad \Rightarrow \quad x^2 = 1.0 \times 10^{-14}$$

$$\sqrt{x^2} = \sqrt{1.0 \times 10^{-14}}$$

- In neutral solutions: **x** = **1.0×10^{-7} M = $[H^+]$**

The pH Scale – *Cont.*

pH scale = numeric scale used to measure acidity or basicity of solutions.

- Mathematically, pH is the negative logarithm (base 10) of $[H^+]$

$\text{pH} = -\log [H^+]$ or **$\text{pH} = -\log [H_3O^+]$**

Recall: At 25 ^{0}C, $K_w = 1.0 \times 10^{-14}$.
What is the pH of pure water at 25 ^{0}C?

Since $[H^+] = 1.0 \times 10^{-7}$ M in neutral solutions like pure H_2O:

$$\text{pH} = -\log [H^+] \quad = \; -\log (1.0 \times 10^{-7}) = -(-7.00)$$

pH = 7.00 (In neutral solutions and for pure H_2O)

Relationship between $[H^+]$ and $[OH^-]$

- In most aqueous solutions, $[H^+]$ and $[OH^-]$ are not equal.
- What happens to $[OH^-]$ when $[H^+]$ is increased? Decreased?

Since $[H^+]$ $[OH^-]$ = 1.0×10^{-14} = K_w at 25 ^{0}C:

$\uparrow[H^+]$, $[OH^-]$ must decrease so their product, K_w equals 1.0×10^{-14}

Thus, when *$[H^+]$ is very high*, *$[OH^-]$ is very low*, and vice versa.

- In **acidic solution**, **$[H^+] > [OH^-]$**
- In **neutral solution**, **$[H^+] = [OH^-]$**
- In **basic solution**, **$[H^+] < [OH^-]$**

Relationship between pH and $[H^+]$

if pH < 7.0, solution is acidic
if pH = 7.0, solution is neutral
if pH > 7.0, solution is basic

Notes:
(1) The lower the pH, the more acidic the solution.

(2) A factor-of-10 increase in $[H^+]$ changes pH by 1 unit

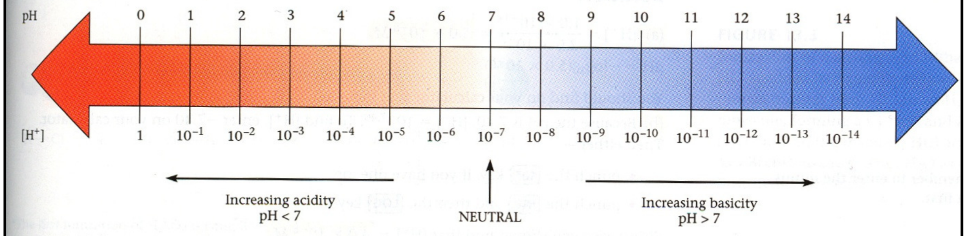


FIGURE 13.2
pH-$[H^+]$ relationship. Acidity is inversely related to pH; the higher the H^+ ion concentration, the lower the pH. In neutral solution, $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ *M*; pH = 7.00 at 25°C. OHT

pH and pOH

Since **pH = - log [H$^+$]** **pOH = - log [OH$^-$]**

- Since **[H$^+$] [OH$^-$] = 1.0 x 10^{-14}** = K_w at 25 ^{0}C:

Take the −log of both sides

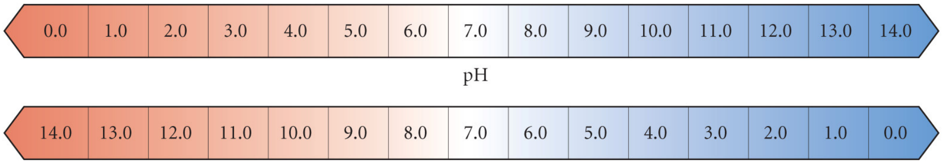
$$-\log([H^+][OH^-]) = -\log 1\times10^{-14}$$

$$\underbrace{-\log[H^+]}_{pH} + \underbrace{(-\log[OH^-]}_{pOH} = -(-14))$$

Note:
$\log M\cdot N =$
$\log M + \log N$

pH + pOH = 14.00 at 25 ^{0}C

Relationship Between pH and pOH



0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	12.0	13.0	14.0

pH

14.0	13.0	12.0	11.0	10.0	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0	0.0

pOH

Determining pH of solutions

(1) Solutions of $\underbrace{\textbf{strong acids}}_{\textbf{S.A.}}$ or $\underbrace{\textbf{strong bases}}_{\textbf{S.B.}}$

Recall that S.A. and S.B. are 100 % ionized in water.

Challenge: a) What is the $[H^+]$ in 0.100 M $HCl_{(aq)}$? b) What is the pH of this solution? c) Repeat for 0.100 M $Ba(OH)_{2\ (aq)}$, but this time calculate $[OH^-]$ and pH. Assume 25 ^0C temperature.

Solution: First, you must recognize that HCl is a S.A. and $Ba(OH)_2$ is a S.B.

Determining pH of solutions – *Cont.*

Ionization equation:

	$HCl_{(aq)}$	$\xrightarrow{100\ \%}$	$H^+_{(aq)}$	+	$Cl^-_{(aq)}$
Before ioniz'n:	0.100 M		?		?
After ioniz'n:	$\underbrace{0}$		0.100 M		0.100 M

No HCl left since ionization is 100 % complete (No equilibrium established)

Thus, $[H^+] = \underbrace{[S.A.]_{ini}}_{\text{Initial [ ] of strong acid}} = 0.100\ M$

and $pH = -\log [H^+]$

$= -\log (0.100)$

$\boxed{pH = 1.00}$

Acidic!

Determining pH of solutions – *Cont.*

Similarly, for a S.B like $Ba(OH)_2$,

Ionization equation:

$$\mathbf{Ba(OH)_{2\,(aq)}} \xrightarrow{100\,\%} \mathbf{Ba^{2+}_{(aq)} + 2OH^{-}}_{(aq)}$$

0.100 M this base — produces — **2 x 0.100 M** of hydroxide

Thus, $\mathbf{[OH^-] = n \times \underbrace{[S.B.]_{ini}}}$ = 0.200 M

Initial [ ] of strong base; n = number of moles OH^- per mole of S.B.

Recall: pH + pOH = 14.00

$$\left.\begin{aligned} \text{and pOH} &= -\log[OH^-] \\ &= -\log(0.100) \end{aligned}\right\} \text{pOH} = 1.00$$

pH = 14.00 - 1.00

$$\boxed{\text{pH} = 13.00}$$

Basic!

<u>Caution</u> with very dilute (< 10^{-7} M) solutions of S.A. or S.B.

Example: The pH of 1 x 10^{-8} M HCl ≠ 8.0

The pH of 1 x 10^{-8} M NaOH ≠ 6.0. WHY?

- These very dilute solutions are mostly H_2O.
  - Thus, the dissociation of water produces more H^+ or OH^- (both = 10^{-7} M) than the S.A. or the S.B.

Bottomline: The pH of very dilute (< 10^{-7} M) solutions of S.A. or S.B. ≈ 7.0, the pH of pure water.