

Chapter 16 Acid-Base Equilibria

16.1 Acids and Bases: A Brief Review

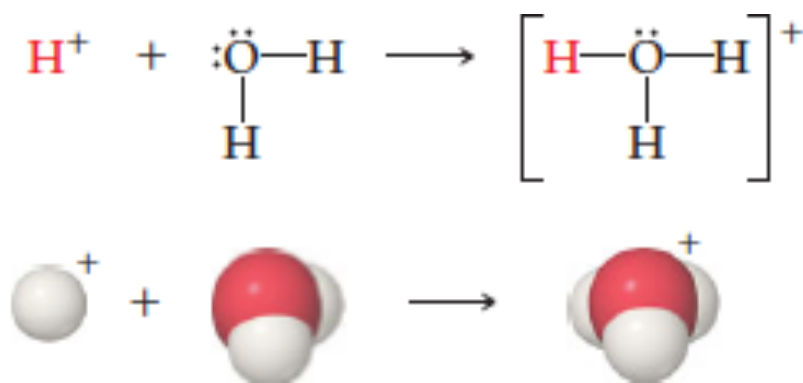
- Acids: taste sour and cause certain dyes to change color.
- Bases: taste bitter and feel soapy.
- **Arrhenius concept of acids and bases:**
 - An acid is a substance that, when dissolved in water, increases in concentration of H^+ ions.
 - ♣ Example: HCl is an acid
 - An Arrhenius base is a substance that, when dissolved in water, increases the concentration of OH^- .
 - ♣ Example: NaOH is a base.
 - This definition is quite narrow in scope as it limits us to aqueous solutions.

16.2 Bronsted-Lowry Acids and Bases

- More general definition for acids and bases is based on the fact that acid-base reactions involve proton transfer.

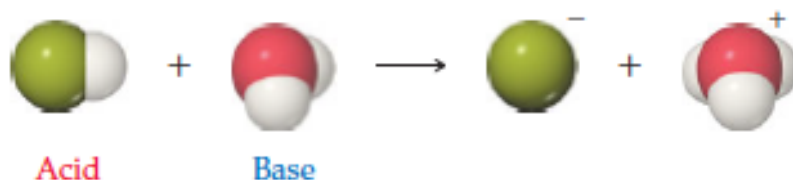
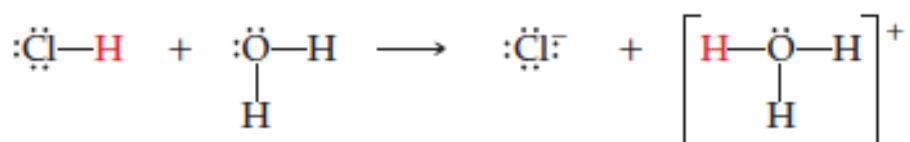
The Ion H^+ in Water

- The H^+ (aq) ion is simply a proton with no surrounding valence electrons.
- In water, clusters of hydrates of H^+ (aq) ions form.
- The simplest cluster is H_3O^+ (aq)
 - We call this a **hydronium ion**.
 - Larger clusters are also possible (such as H_5O_2^+ and H_9O_4^+)
- Generally we use H^+ (aq) and H_3O^+ (aq) interchangeably.

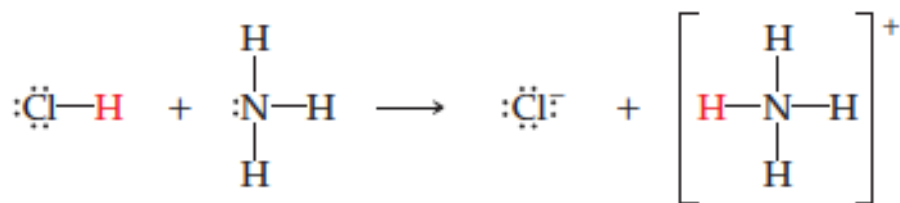


Proton-Transfer Reactions

- In the Bronsted-Lowry system, a **Bronsted-Lowry acid** is a species that donates H^+ and a **Bronsted-Lowry base** is a species that accepts H^+ .



- Therefore a Bronsted-Lowry base does not need to contain OH^-

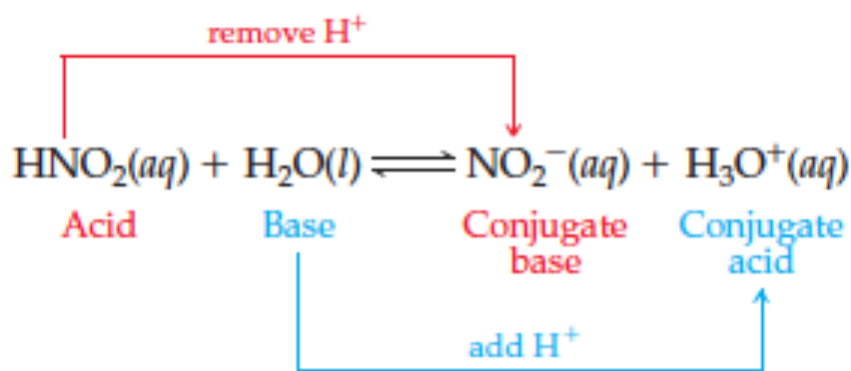


♣ NH_3 is a Bronsted-Lowry base but not an Arrhenius base.

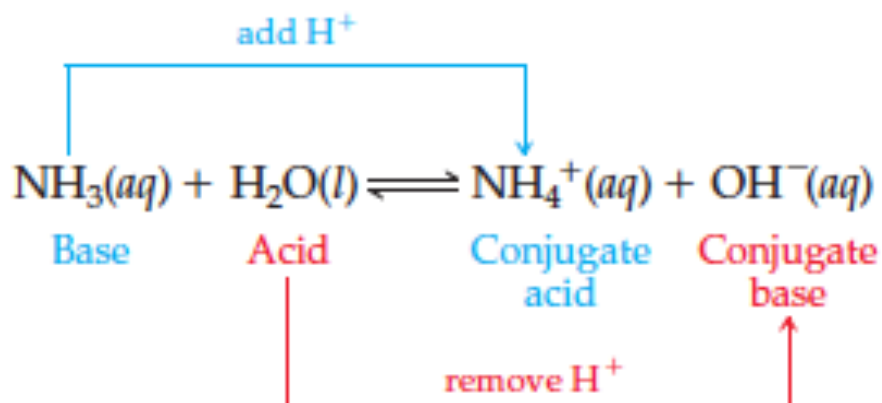
- Consider $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{NH}_4^+(aq) + \text{OH}^-(aq)$:
- H_2O donates a proton to ammonia.
 - Water is acting as an acid.
- NH_3 accepts a proton from water.
 - Ammonia is acting as a base.
 - Amphoteric substances** can behave as acids and bases.

Conjugate Acid-Base Pairs

- Whatever is left of the acid after the proton is donated is called its conjugate base.
- Similarly, a conjugate acid is formed by adding a proton to the base.
- Consider $\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$:
 - HA and A^- are **conjugate acid-base pair**
 - A^- is called the **conjugate base**.
- After H_2O (base) gains a proton it is converted into H_3O^+ (acid).
 - H_3O^+ is the **conjugate acid**.
 - Therefore, H_2O and H_3O^+ are a conjugate acid-base pair.

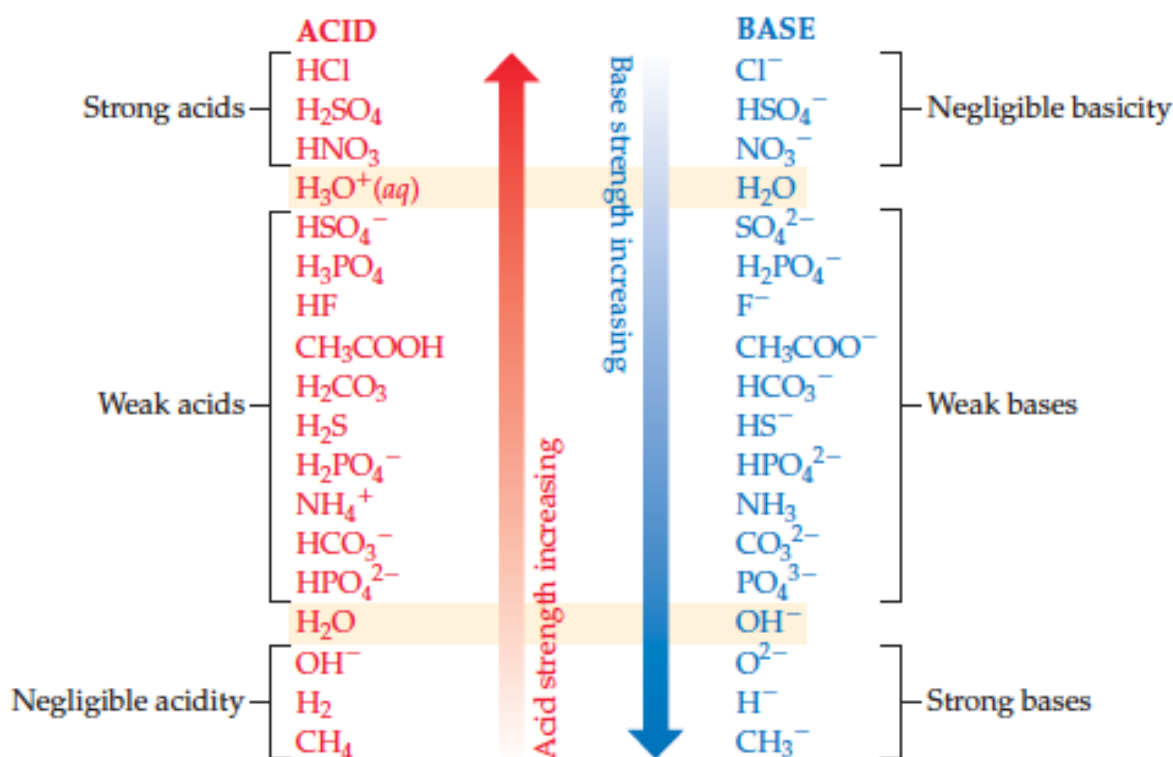


Likewise, for the reaction between NH_3 and H_2O , we have



Relative Strengths of Acids and Bases

- Show a slight tendency to abstract proton.
- In every **acid-base reaction, the position of the equilibrium favors the transfer of a proton from the stronger acid to the stronger base.**
 - H^+ is the strongest acid that can exist in equilibrium in aqueous solution.
 - OH^- is the strongest base that can exist in equilibrium in aqueous solution.

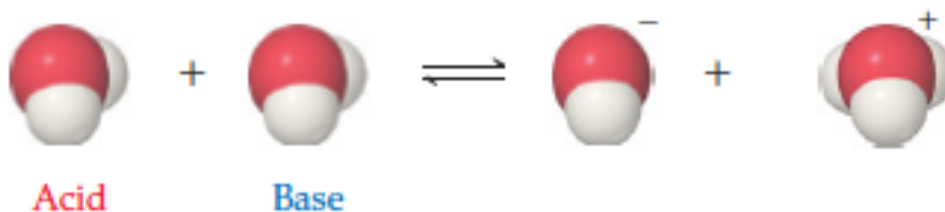
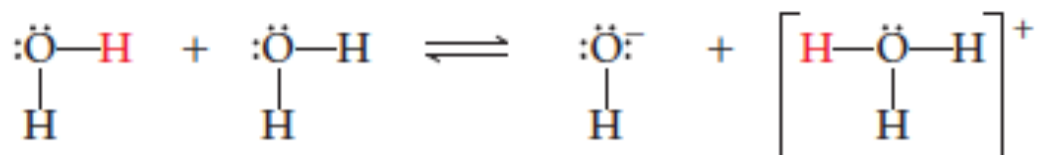


Strong acid: 100% ionized in H_2O

Strong base: 100% protonated in H_2O .



16.3 The Auto-ionization of Water



- We can write an equilibrium constant expression for the auto-ionization of water.

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

- Because $\text{H}_2\text{O}(l)$ is a pure liquid, we can simplify this expression:

$$[\text{H}_2\text{O}]^2 K_{\text{eq}} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

- K_w is called the ion-product constant.
- At 25°C the ion-product of water is:

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

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

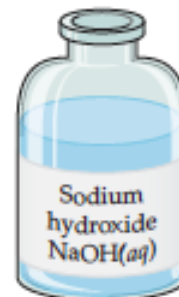
- This applies to pure water as well as to aqueous solutions.
 - A solution is neutral if $[\text{OH}^-] = [\text{H}_3\text{O}^+]$
 - If the $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, the solution is acidic.
 - If the $[\text{H}_3\text{O}^+] < [\text{OH}^-]$, the solution is basic.



Acidic solution
 $[\text{H}^+] > [\text{OH}^-]$
 $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$



Neutral solution
 $[\text{H}^+] = [\text{OH}^-]$
 $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$



Basic solution
 $[\text{H}^+] < [\text{OH}^-]$
 $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

16.4 The pH Scale

- In most solutions $[\text{H}^+]$ is quite small.
- We express the $[\text{H}^+]$ in terms of **pH**.

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

- This is a logarithmic scale
- A change in $[\text{H}^+]$ by a factor of 10 causes the pH to change by 1 unit.
- Most pH values fall between 0 and 14.
 - In neutral solutions at 25°C, $\text{pH} = 7.00$
 - In acidic solutions, $[\text{H}^+] > 1.0 \times 10^{-7}$ so $\text{pH} < 7.00$.**
 - ♣ As the pH decreases, the acidity of the solution increases.
 - In basic solutions, $[\text{H}^+] < 1.0 \times 10^{-7}$ so $\text{pH} > 7.00$.**
 - ♣ As the pH increases, the basicity of the solution increases (acidity decreases).

pOH and Other “p” Scales

- We can use a similar system to describe the [OH⁻].

$$\text{pOH} = -\log[\text{OH}^-]$$

- Recall that the value of K_w at 25°C is 1.0×10^{-14}
 - Thus we can describe a relationship between pH and pOH.









$$-\log[\text{H}^+] + (-\log[\text{OH}^-]) = \text{pH} + \text{pOH} = -\log K_w = 14.00$$

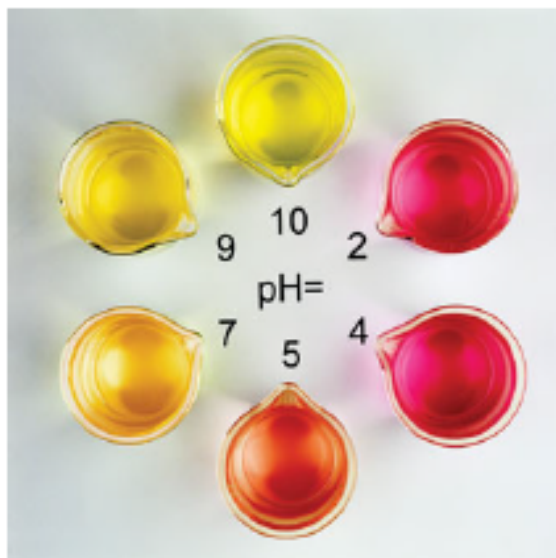
$$\text{pH} + \text{pOH} = 14.00$$

Measuring pH

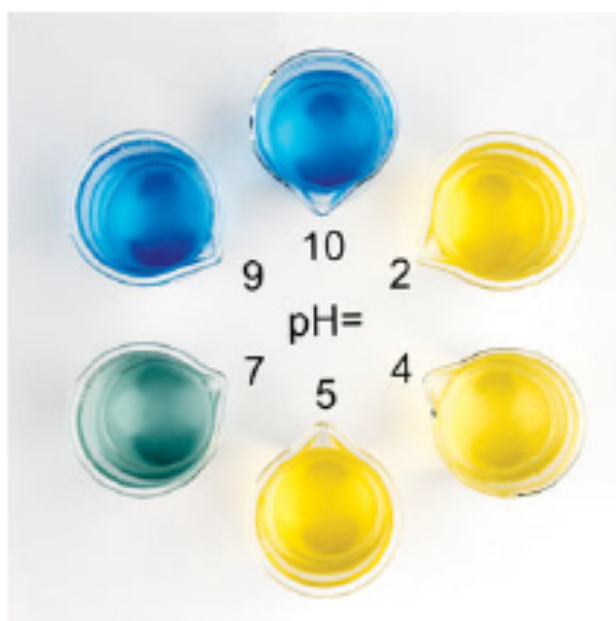
- The most accurate method to measure pH is to use a pH meter.
 - However, certain dyes change color as pH changes.
 - ♣ They are called acid-base indicators.
- Indicators are less precise than pH meters.
- Many indicators do not have a sharp color change as a function of pH.
- Most acid-base indicators can exist as either an acid or a base.
- Some natural products can be used as indicators (tea is colorless in acid and brown in base; red cabbage extract is another natural indicator).

Figure below is pH ranges for common acid–base indicators. Most indicators have a useful range of about 2 pH units.

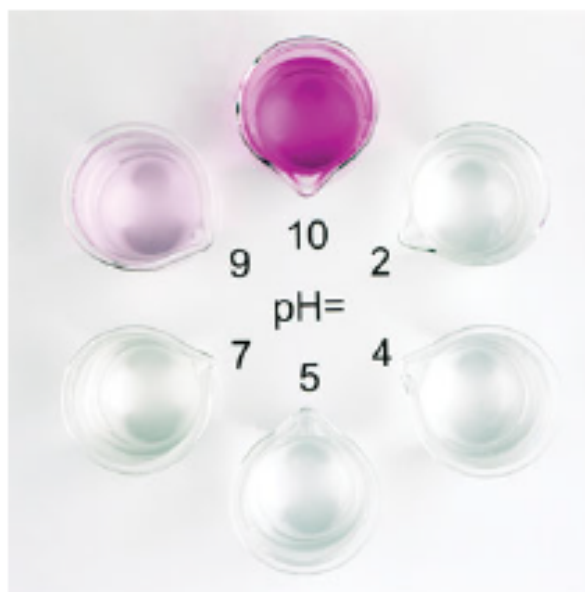
	pH range for color change							
	0	2	4	6	8	10	12	14
Methyl violet	Yellow		Violet					
Thymol blue	Red		Yellow		Yellow		Blue	
Methyl orange		Red		Yellow				
Methyl red			Red		Yellow			
Bromthymol blue				Yellow		Blue		
Phenolphthalein					Colorless		Pink	
Alizarin yellow R						Yellow		Red



Methyl red



Bromthymol blue

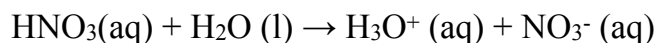


Phenolphthalein

16.5 Strong Acids and Bases

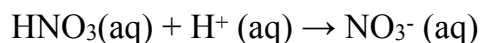
Strong Acids

- The most common strong acids are HCl, HBr, HI, HNO₃, HClO₃, HClO₄, and H₂SO₄.
- Strong acids are strong electrolytes.
 - Ionize completely in solution:



- Example: Nitric acid ionizes completely in solution.

♣ Since H⁺ and H₃O⁺ are used interchangeably, we write



- In solution the strong acid is usually the only source of H⁺.
 - Therefore, the pH of a solution of a monoprotic acid may usually be calculated directly from the initial molarity of the acid.

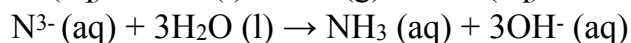
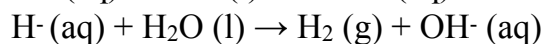
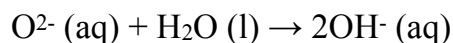
Strong Bases

- The most common strong bases are ionic hydroxides of the alkali metals or the heavier alkaline earth metals (e.g., NaOH, KOH, and Ca(OH)₂ are all strong bases.

- Strong bases are strong electrolytes and dissociate completely in solution.
 - For example: $\text{NaOH}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$

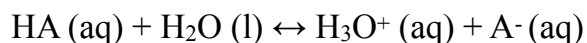
- The pOH (and thus the pH) of a strong base may be calculated using the initial molarity of the base.

- Not all bases contain the OH⁻ ion.
 - The oxide, hydride and nitride ions are stronger bases than hydroxide.
 - They are thus able to abstract a proton from water and generate OH⁻.



16.6 Weak Acids

- Weak acids are only partially ionized in aqueous solution.
 - There is a mixture of ions and un-ionized acid in solution.
 - Therefore, weak acids are in equilibrium.



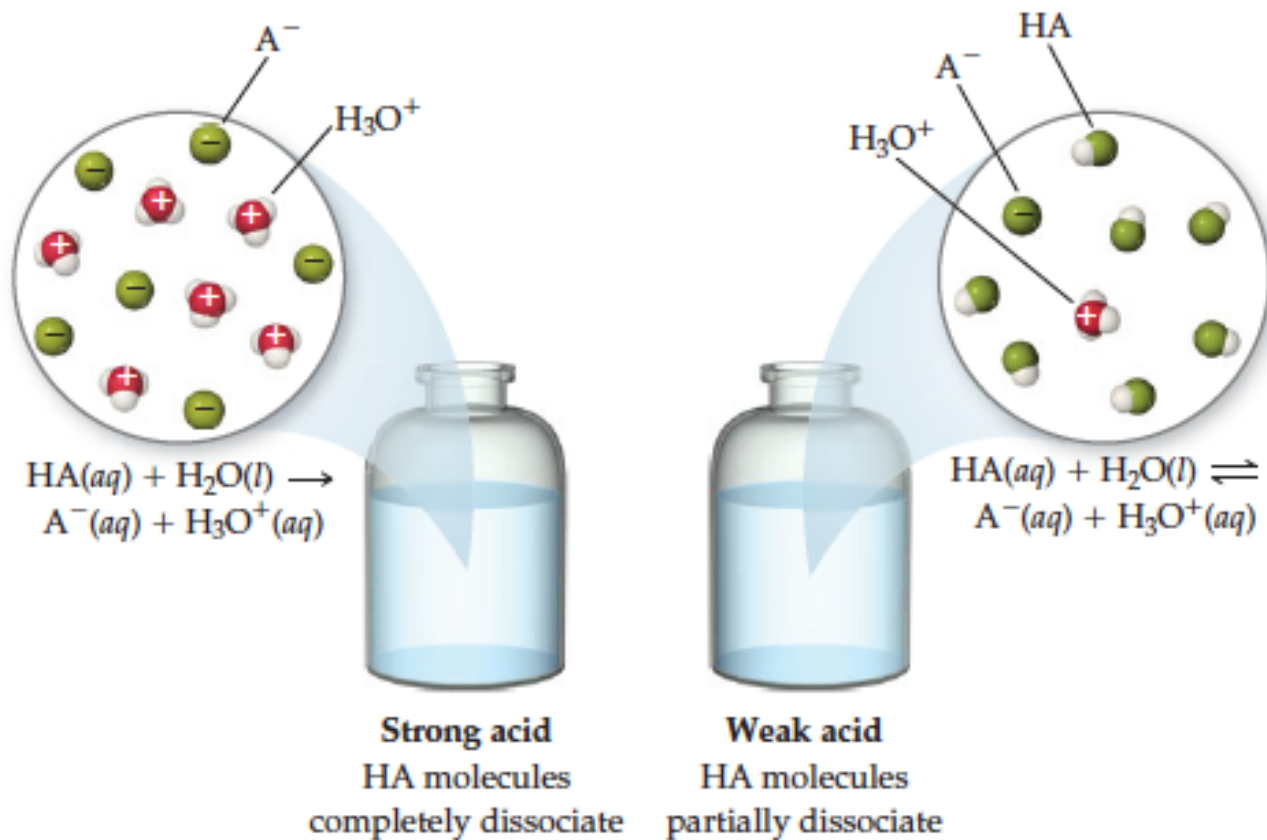
Or:



- We can write an equilibrium constant expression or this dissociation:

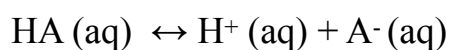
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

- K_a is called the **acid-dissociation constant**.
- The subscript “a” indicates that this is the equilibrium constant for the dissociation of an acid.
- Note that $[\text{H}_2\text{O}]$ is omitted from the K_a expression. (H_2O is a pure liquid.)
- The larger the K_a the stronger the acid.
- K_a is larger since there are more ions present at equilibrium relative to un-ionized molecules.
- If $K_a \gg 1$, then the acid is completely ionized and the acid is a strong acid.



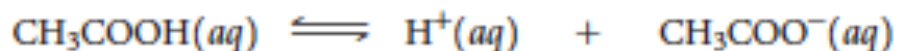
Using K_a to Calculate pH

- If the K_a value is quite small, we find that we can make a simplifying assumption.
 - Assume that x is the negligible compared to the initial concentration of the acid.
 - If x is $<5\%$ of the initial concentration, the assumption is probably a good one.
 - If x is $>5\%$ of the initial concentration, then it may be best to solve the quadratic equation or use successive approximations.
- Weak acids are only partially ionized.
- Percent ionization is another method to assess acid strength.
- For the reaction



$$\% \text{ ionization} = \frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HA}]_{\text{initial}}} \times 100$$

- Percent ionization relates to the equilibrium H^+ concentration, $[\text{H}^+]_{\text{equilibrium}}$ to the initial HA concentration, $[\text{HA}]_{\text{initial}}$.



Initial	0.30 M	0	0
Change	-x M	+x M	+x M
Equilibrium	(0.30 - x) M	x M	x M

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(x)}{0.30 - x} = 1.8 \times 10^{-5}$$

$$K_a = \frac{x^2}{0.30} = 1.8 \times 10^{-5}$$

$$x^2 = (0.30)(1.8 \times 10^{-5}) = 5.4 \times 10^{-6}$$

$$x = \sqrt{5.4 \times 10^{-6}} = 2.3 \times 10^{-3}$$

$$[\text{H}^+] = x = 2.3 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(2.3 \times 10^{-3}) = 2.64$$

$$\text{Percent ionization of CH}_3\text{COOH} = \frac{0.0023 \text{ M}}{0.30 \text{ M}} \times 100\% = 0.77\%$$

Polyprotic Acids

- **Polyprotic acids** have more than one ionizable proton.
- The protons are removed in successive steps

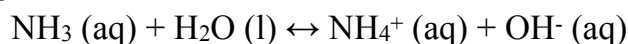
- Consider the weak acid, H₂SO₃ (sulfurous acid):



16.7 Weak Bases

- Weak bases remove protons from substances.
- There is an equilibrium between the base and the resulting ions:
Weak base + H₂O (l) ↔ conjugate acid + OH⁻ (aq)

- Example:



- The **base-dissociation constant**, K_b, is defined as

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

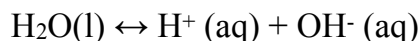
- The larger K_b, the stronger the base.

Types of Weak Bases

- Weak bases generally fall into one of two categories
 - Neutral substances with a lone pair of electrons that can accept protons.
 - ♣ Most neutral weak bases contain nitrogen.
 - ♣ **Amines** are related ammonia and have one or more N-H bonds replaced with N-C bonds (e.g., CH₃NH₂ is methylamine).
 - Anions of weak acids are also weak bases.
- Example: ClO⁻ is the conjugate base of HClO (weak acid):
ClO⁻ (aq) + H₂O(l) ↔ HClO (aq) + OH⁻(aq) K_b = 3.3 × 10⁻⁷

16.8 Relationship Between K_a and K_b

- The net reaction is the auto-ionization of water.



- Recall that:

$$K_w = [\text{H}^+][\text{OH}^-]$$

For a conjugate acid-base pair:

$$K_a \times K_b = K_w$$

- Alternatively,

$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00 \text{ (at } 25^\circ\text{C)}$$

- Thus, the larger K_a (and the smaller $\text{p}K_a$), the smaller K_b (and the larger $\text{p}K_b$).
 - The stronger the acid, the weaker its conjugate base and vice versa.

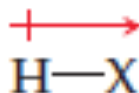
16.9 Acid-Base Properties of Salt Solutions

- Nearly all the salts are strong electrolytes.
- Many salt ions can react with water to form OH^- or H^+ .
- This process is called **hydrolysis**.
 - Anions from weak acids are basic.
 - Anions from strong acids are neutral.
 - Anions with ionizable protons (e.g., HSO_4^-) are amphoteric.
 - ♣ They are capable of acting as an acid or a base.
 - All cations, except those of the alkali metals or heavier alkaline earth metals are weak acids.
- The pH of a solution may be qualitatively predicted using the following guidelines:
 - Salts derived from a strong acid and strong base are neutral.
 - ♣ Examples: NaCl , $\text{Ca}(\text{NO}_3)_2$.
 - Salts derived from a strong base and weak acid are basic
 - ♣ Examples: NaClO_3 , $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$
 - Salts derived from a weak base and strong acid are acidic.
 - ♣ Example: NH_4Cl
 - Salts derived from a weak acid and weak base can be either acidic or basic.
 - ♣ Equilibrium rules apply!

16.10 Acid-Base Behavior and Chemical Structure

Factors That Affect Acid Strength

- Consider H-X
- For this substance to be an acid
 - The H-X bond must be polar with $H^{\delta+}$ and $X^{\delta-}$



- In ionic hydrides, the bond polarity is reversed
 - The H-X bond is polar with $H^{\delta-}$ and $X^{\delta+}$
 - In this case, the substance is a base.

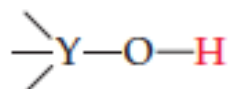
Binary Acids

- The H-X bond polarity is important in determining relative acid strength in any period of the periodic table.
 - Acid strength increases and base strength decreases from left to right across a period as the electronegativity of X increases.

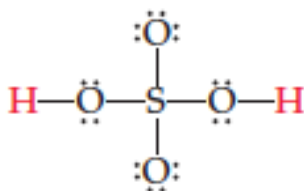
4A	5A	6A	7A
CH₄ Neither acid nor base	NH₃ Weak base $K_b = 1.8 \times 10^{-5}$	H₂O	HF Weak acid $K_a = 6.8 \times 10^{-4}$
SiH₄ Neither acid nor base	PH₃ Very weak base $K_b = 4 \times 10^{-28}$	H₂S Weak acid $K_a = 9.5 \times 10^{-8}$	HCl Strong acid
		H₂Se Weak acid $K_a = 1.3 \times 10^{-4}$	HBr Strong acid

Oxyacids

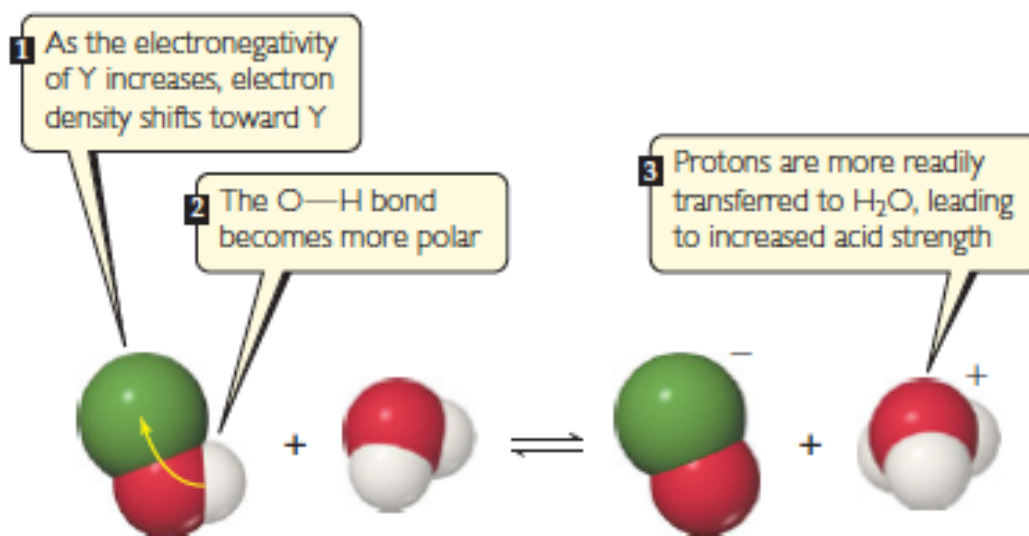
- Acids that contain OH groups (and often additional oxygen atoms) bound to the central atom are called **oxyacids**.



Example is sulfuric acid.

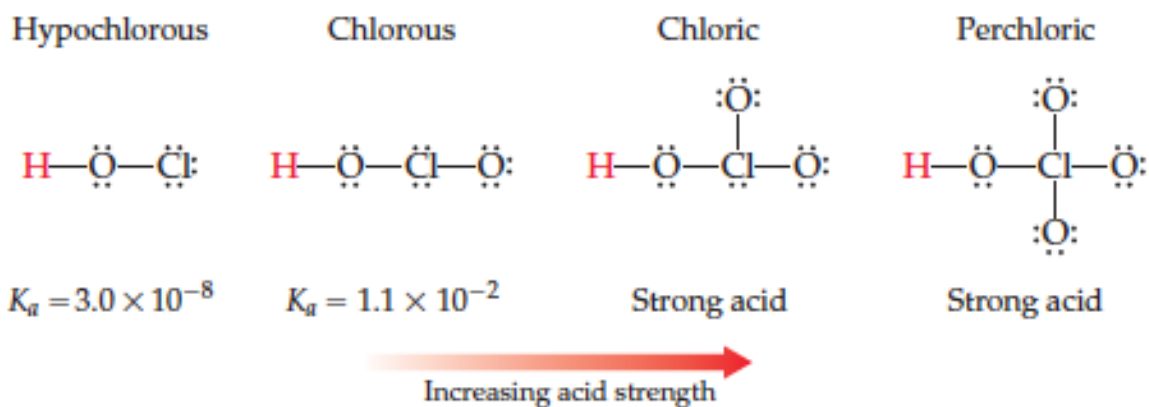


- The strength of the acid depends on Y and the atoms attached to Y.
 - As the electronegativity of Y increases, so does the acidity of the substance.



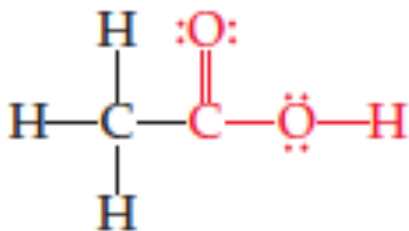
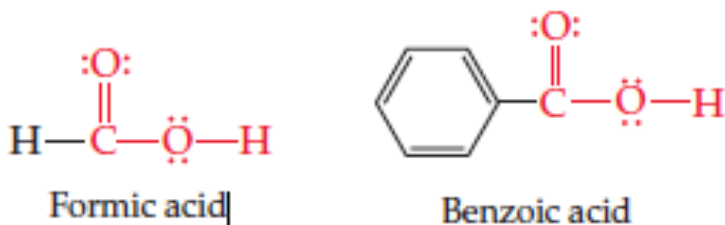
Substance	Y—OH	Electronegativity of Y	Dissociation constant
Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
Hypobromous acid	Br—OH	2.8	$K_a = 2.5 \times 10^{-9}$
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

- As the number of O atoms attached to Y increase the O-H bond polarity, and consequently the strength of the acid increases.
 - Example, HClO is a weaker acid than HClO₂ which is weaker than HClO₃ which is weaker than HClO₄

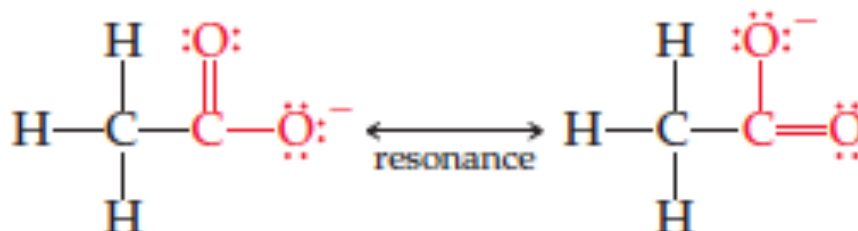


Carboxylic Acids

- There is a large class of acids that contain a =COOH group (a carboxyl group).
- Acids that contain this group are called **carboxylic acids**.
- Examples: acetic acid, benzoic acid, formic acid.



- Why are these molecules acidic?
- The additional oxygen atom on the carboxyl group increases the polarity of the O-H bond and stabilizes the conjugate base.
- The conjugate base exhibits resonance.
- This gives it the ability to delocalize the negative charge over the carboxylate group, further increasing the stability of the conjugate base.



16.11 Lewis Acids and Bases

- Lewis proposed a new definition of acids and bases that emphasizes the shared electron pair.
 - A **Lewis acid** is an electron pair acceptor
 - A **Lewis base** is an electron pair donor
 - ♣ Note: Lewis acids and bases do not need to contain protons.

