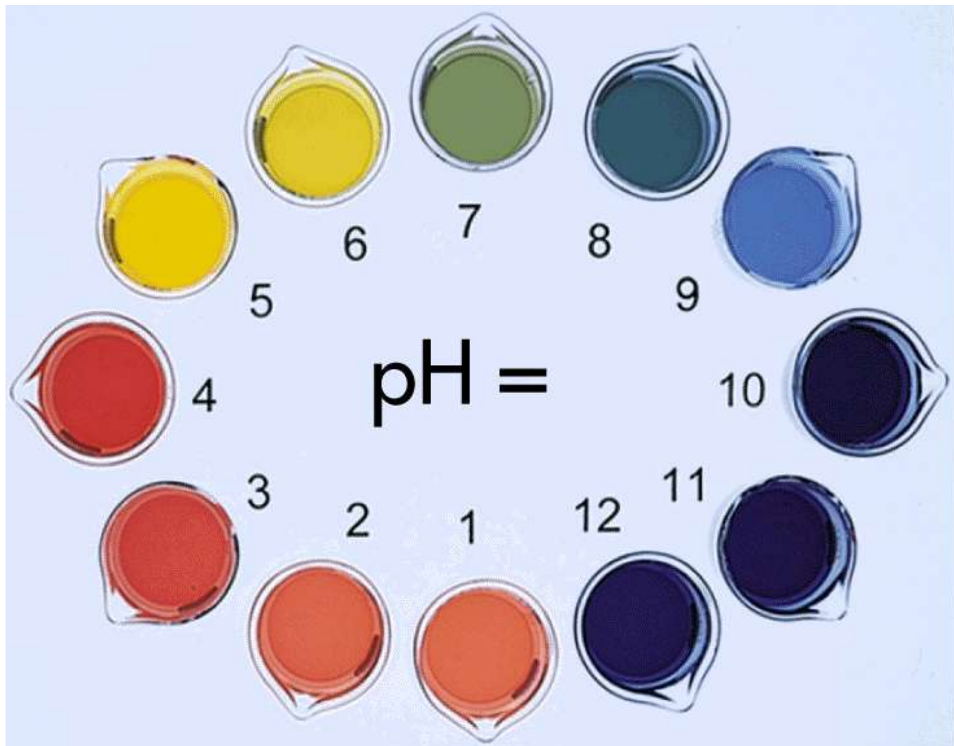
Chapter 16: Acid-Base Equilibria



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Section 16.1 – Acids and Bases: A Brief Review

- Acids taste sour, react with metals, and change the color of indicators.
- Bases taste bitter, feel slippery, and change the color of indicators.

Arrhenius

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

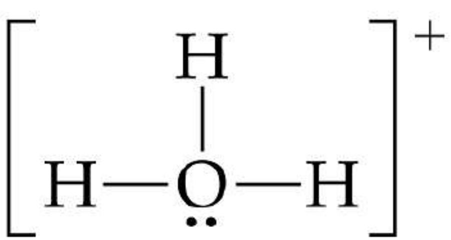
$$HCl \rightarrow \mathbf{H^+} + Cl^-$$

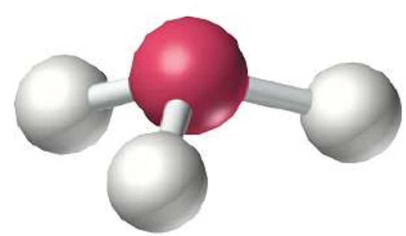
- An Arrhenius base is a substance that increases the concentration of OH^- ions when dissolved in water.

$$NaOH \rightarrow Na^+ + \mathbf{OH^-}$$

Section 16.2 – Bronsted-Lowry Acids and Bases

- The Bronsted-Lowry definitions involve the transfer of H^+ ions from one substance to another.
- H^+ is sometimes called a proton.
- H_3O^+ is called the hydronium ion and it forms when water gains an H^+.





Bronsted-Lowry

- A Bronsted-Lowry acid is a substance that donates a proton (H^+) to another substance.

$$\mathbf{HBr} + H_2O \rightarrow H_3O^+ + Br^-$$

- A Bronsted-Lowry base is a substance that accepts a proton (H^+) from another substance.

$$\mathbf{NH_3} + H_2O \rightarrow NH_4^+ + OH^-$$

Bronsted-Lowry

- To be a Bronsted-Lowry acid, the substance must be able to lose an H^+ ion.
- To be a Bronsted-Lowry base, the substance must have a nonbonding pair of electrons to bond with an H^+ ion.
- A substance that can act as an acid or base is amphiprotic. (Ex. H_2O)

Conjugate Acid-Base Pairs

- A conjugate base is formed when an acid loses a proton.
- A conjugate acid is formed when a base gains a proton.
- A conjugate acid-base pair is a pair of substances that differ by one proton.

$$HNO_2 + H_2O \leftrightarrow NO_2^- + H_3O^+$$

acid	base	conjugate base	conjugate acid

Sample Exercise 16.1

a. What is the conjugate base of each of the following acids: $HClO_4$, H_2S, PH_4^+, HCO_3^-?

b. What is the conjugate acid of each of the following bases: CN^-, SO_4^{-2}, H_2O, HCO_3^-?

Practice Exercise

- Write the formula for the conjugate acid for each of the following: HSO_3^-, F^-, PO_4^{3-}, CO.

Sample Exercise 16.2

- The hydrogen sulfite ion (HSO_3^-) is amphiprotic.

a. Write an equation for the reaction of HSO_3^- with water, in which the ion acts as an acid. Identify the conjugate acid-base pairs.

Sample Exercise 16.2 con't

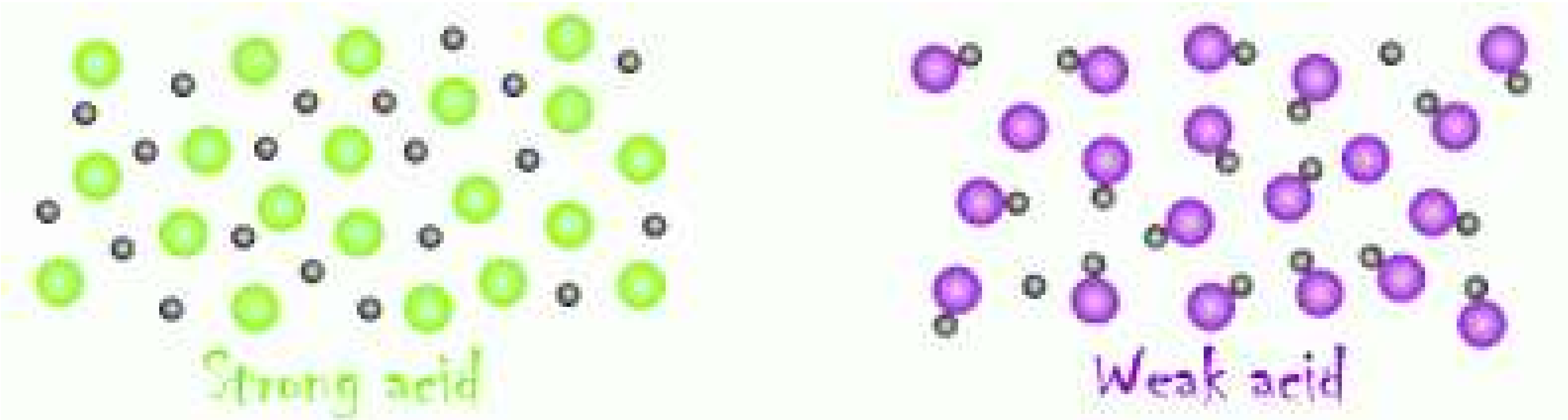
b. Write an equation for the reaction of HSO_3^- with water, in which the ion acts as a base. Identify the conjugate acid-base pairs.

Practice Exercise

- When lithium oxide (Li_2O) is dissolved in water, the solution turns basic from the reaction of the oxide ion (O^{2-}) with water. Write the reaction that occurs, and identify the conjugate acid-base pairs.

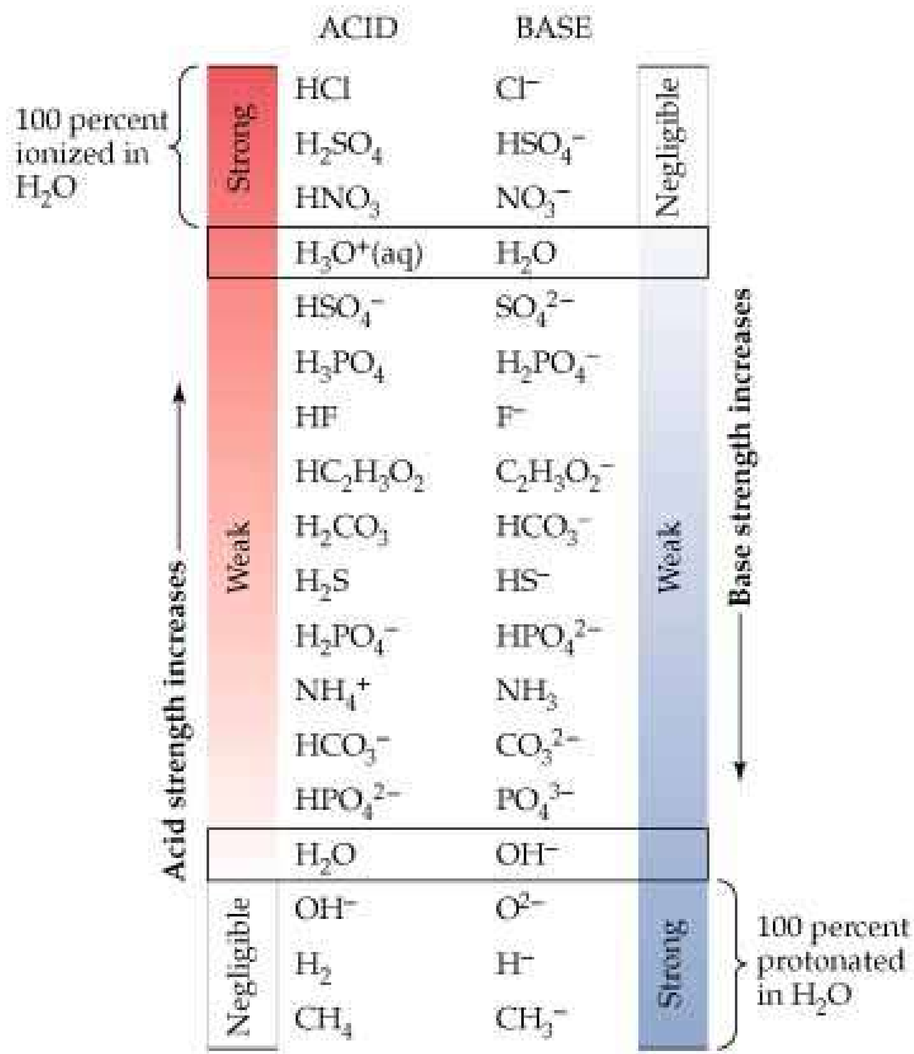
Strong vs. Weak

- A strong acid or base fully dissociates into ions in solution.
- A weak acid or base on partially dissociates into ions in solution.



Strong vs. Weak

- If an acid is strong, then is conjugate base is weak.
- If an acid weak, then the conjugate base is strong.



Strength

$$HX + H_2O \leftarrow\rightarrow H_3O^+ + X^-$$

- If H_2O is a stronger base than X^-, then the equilibrium will lie to the right.
- If H_2O is a weaker base than X^-, then the equilibrium will lie to the left.

Equilibrium

- Equilibrium favors the transfer of a proton between the stronger acid and stronger base to form the weaker acid and weaker base.

Sample Exercise 16.3

- For the following proton-transfer reaction, use Figure 16.4 to predict whether the equilibrium lies predominately to the left (K_c <1) or to the right (K_c >1):

$$HSO_4^- + CO_3^{2-} \leftarrow\rightarrow SO_4^{2-} + HCO_3^-$$

Practice Exercise

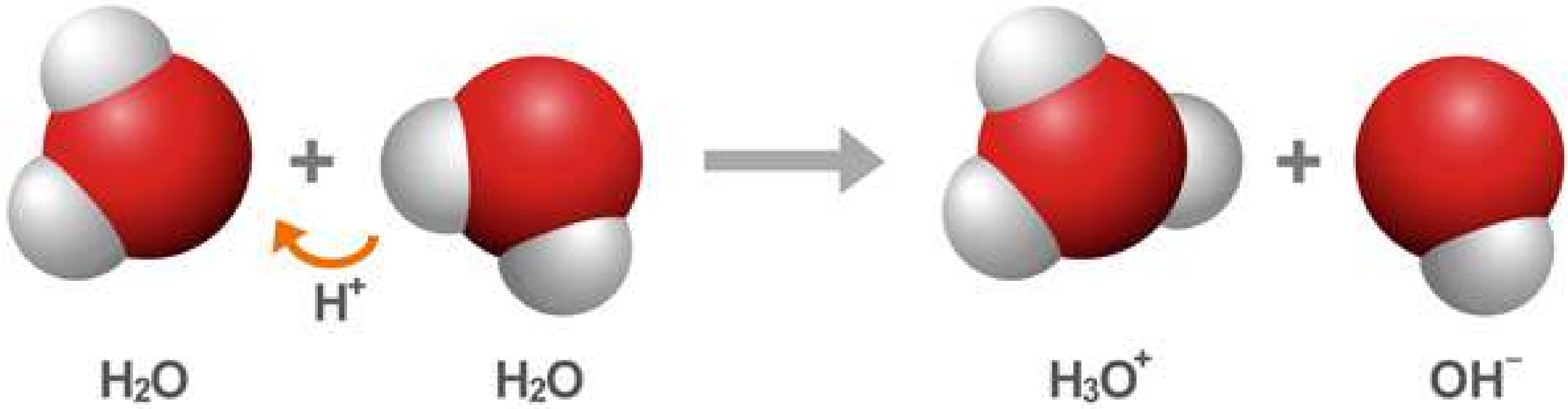
- For each of the following reactions, use Figure 16.4 to predict whether the equilibrium lies predominately to the left or to the right:

a. $HPO_4^- + H_2O \leftrightarrow H_2PO_4^- + OH^-$

b. $NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$

Section 16.3 – The Autoionization of Water

- Autoionization is when a water molecule donates a proton to another water molecule.



K_w

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

$$K_c = [H_3O^+][OH^-]$$

$$H_3O^+ = H^+$$

At 25^oC, $K_w = [H^+][OH^-] = 1 \times 10^{-14}$

When $[H^+] = [OH^-]$, the solution is neutral.

K_w

- The value of K_w does not change with concentration.
- If $[H^+]$ increases, then $[OH^-]$ decreases and vice versa.

Sample Exercise 16.4

- Calculate the values of $[H^+]$ and $[OH^-]$ in a neutral solution at 25^oC.

Practice Exercise

- Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic:

a. $[H^+] = 4 \times 10^{-9} M$
b. $[OH^-] = 1 \times 10^{-7} M$
c. $[OH^-] = 7 \times 10^{-13} M$

Sample Exercise 16.5

- Calculate the concentration of H^+ in

a. A solution in which $[OH^-]$ is 0.010M.

b. A solution in which $[OH^-]$ is 1.8×10^{-9}M.

Practice Exercise

- Calculate the concentration of OH^- in a solution in which

a. $[H^+] = 2 \times 10^{-6} M$

b. $[H^+] = [OH^-]$

c. $[H^+] = 100 \times [OH^-]$

Section 16.4 – The pH Scale

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

- pH has no units.
- As pH decreases as $[H^+]$ increases.
- A change in $[H^+]$ by a factor or 10 causes the pH to change by 1.

Solution H^+ concentration compared to distilled water	pH	Solutions at this pH
1×10^7	0	Strong hydrofluoric acid
1×10^6	1	Battery acid
1×10^5	2	Lemon juice, gastric juice
1×10^4	3	Vinegar, orange juice, soda
1×10^3	4	Tomato juice
1×10^2	5	Black coffee Rainwater
10	6	Urine Saliva
1	7	"Pure" water
0.1	8	Seawater
1×10^{-2}	9	Baking soda
1×10^{-3}	10	Milk of magnesia
1×10^{-4}	11	Household ammonia
1×10^{-5}	12	Soapy water
1×10^{-6}	13	Bleach Oven cleaner
1×10^{-7}	14	Liquid drain cleaner

Sample Exercise 16.6

- Calculate the pH values for

a. A solution in which $[OH^-] = 0.010M$

b. A solution in which $[OH^-] = 1.8 \times 10^{-9}M$

Practice Exercise

a. In a sample of lemon juice $[H^+]$ is 3.8×10^{-4}M. What is the pH?

b. A commonly available window-cleaning solution has $[OH^{-}]$ = 1.9×10^{-6}M. What is the pH?

Sample Exercise 16.7

- A sample of freshly pressed apple juice has a pH of 3.76. Calculate $[H^+]$.

Practice Exercise

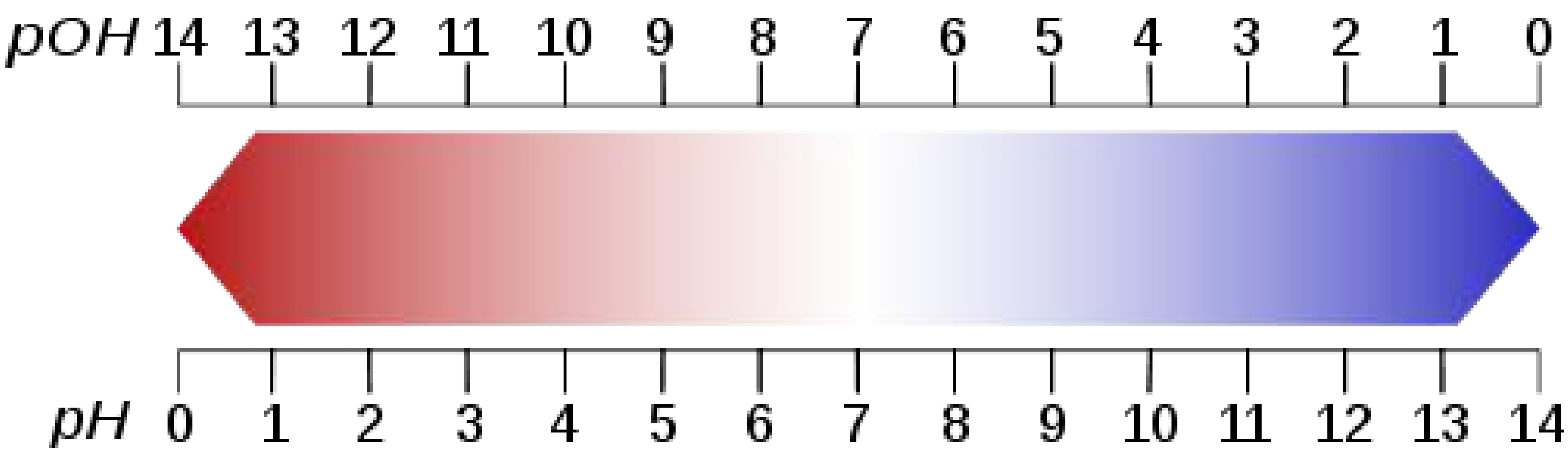
- A solution formed by dissolving an antacid tablet has a pH of 9.18. Calculate $[H^+]$.

pOH

$$pOH = -\log[OH^-]$$

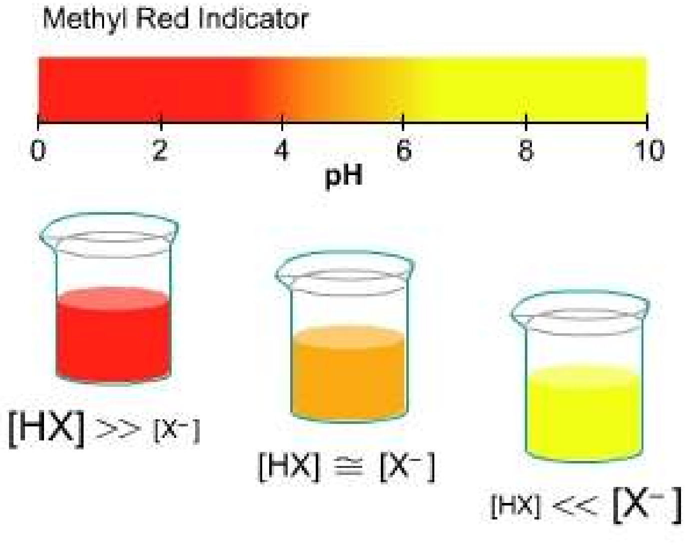
- The pOH scale is the opposite of the pH scale.

$$pH + pOH = 14.00$$



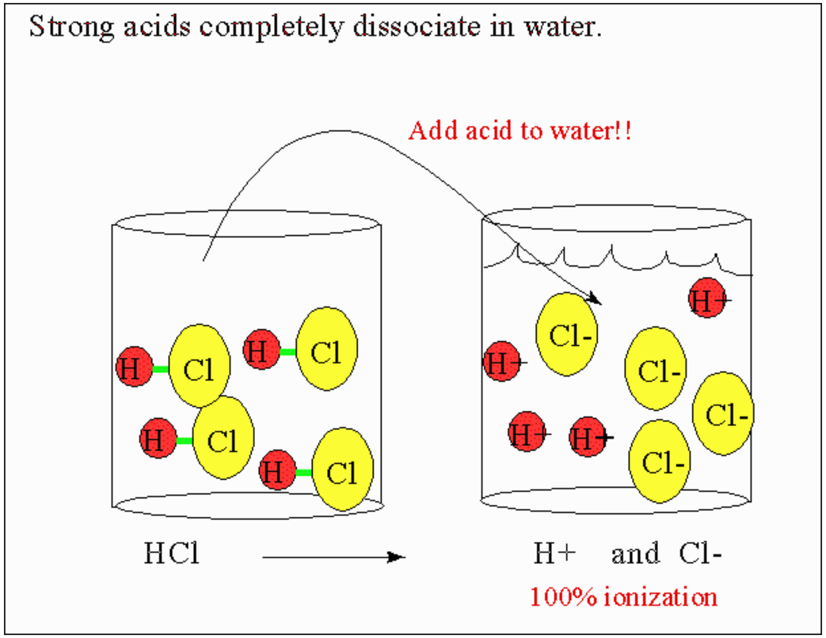
Indicators

- Indicators are chemicals that change color as pH changes.
- Each indicator has its own pH range.



Section 16.5 – Strong Acids and Bases

- Strong acids and bases are strong electrolytes and fully dissociate into ions in solution.



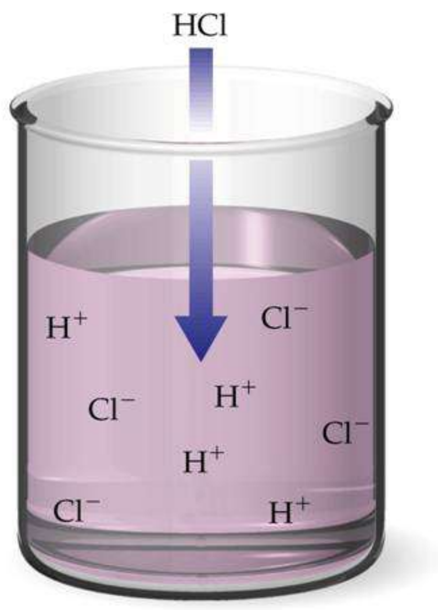
Strong Acids

- Seven commons strong acids:

1. HCl
2. HBr
3. HI
4. HNO_3
5. $HClO_3$
6. $HClO_4$
7. H_2SO_4

Strong Acids

- When a strong acid is present in a solution, the $[H^+]$ from water is negligible compared to the acid.



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

Sample Exercise 16.8

- What is the pH of a 0.040M solution of $HClO_4$?

Practice Exercise

- An aqueous solution of HNO_3 has a pH of 2.34. What is the concentration of the acid?

Strong Bases

- Common strong bases:

1. Alkali metal hydroxides
2. Heavy alkaline metal hydroxides (Ca, Sr, and Ba)

Sample Exercise 16.9

- What is the pH of

a. A 0.028M solution of NaOH

b. A 0.0011M solution of $Ca(OH)_2$

Practice Exercise

- What is the concentration of a solution of

a. KOH for which the pH is 11.89

b. $Ca(OH)_2$ for which the pH is 11.68

Metal Oxides

- Metal oxides dissolve to form a basic solution.

$$Na_2O \rightarrow 2Na^+ + O^{2-}$$

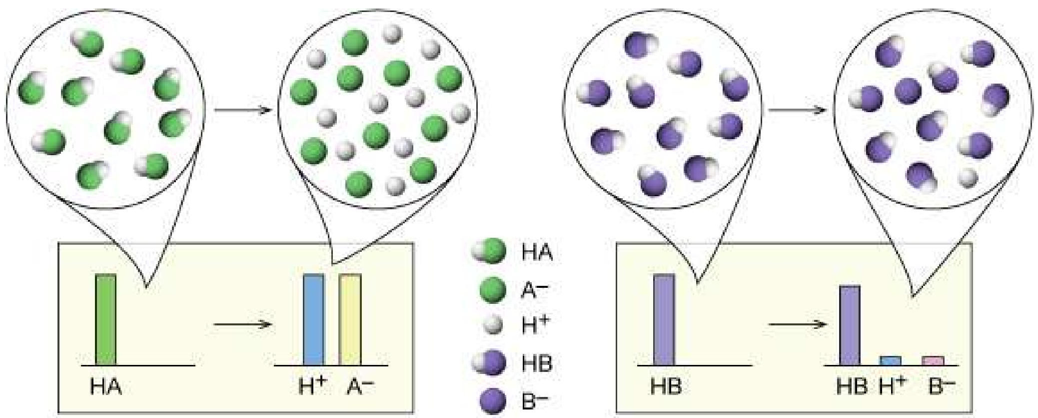
$$O^{2-} + H_2O \rightarrow 2OH^-$$

Section 16.6 – Weak Acids

$$HA \leftrightarrow H^+ + A^-$$

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

- K_a is the acid-dissociation constant.
- The larger the value of K_a, the stronger the acid.



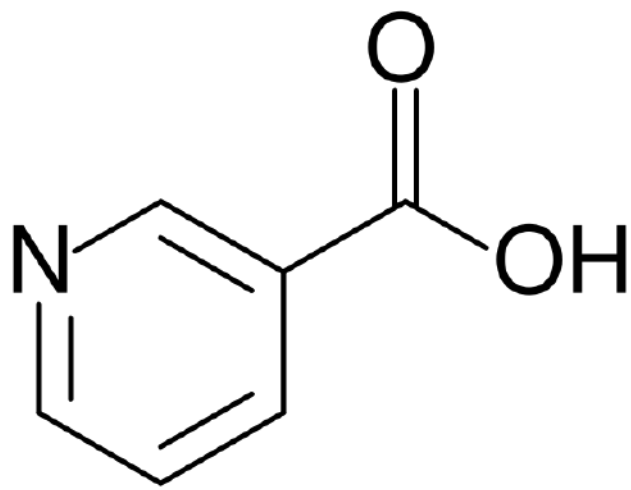
(a) Strong acid (b) Weak acid

Sample Exercise 16.10

- A student prepared a 0.10M solution of formic acid (HCOOH) and measured its pH. The pH at 25°C was found to be 2.38. Calculate K_a for formic acid at this temperature.

Practice Exercise

- Niacin, one of the B vitamins, has the following molecular structure:

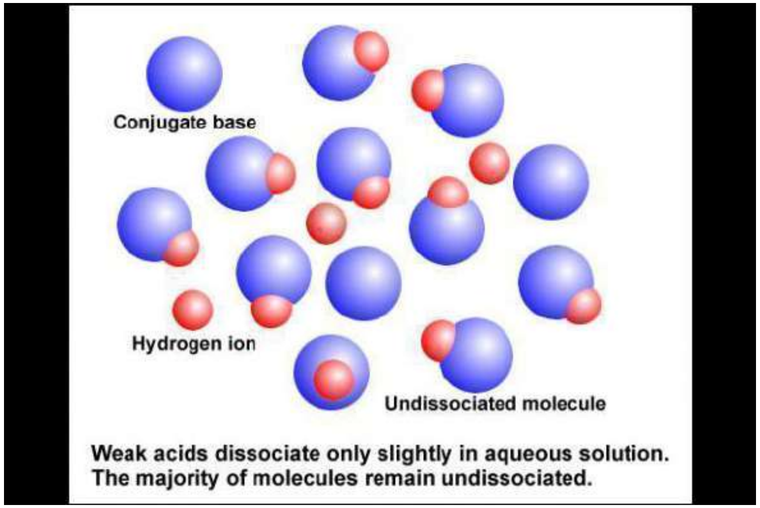


A 0.020M solution of niacin has a pH or 3.26. What is the acid-dissociation constant, K_a, for niacin?

Percent Ionization

- Percent ionization can also measure acid strength.

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



Sample Exercise 16.11

- A 0.10M solution of formic acid (HCOOH) contains 4.2×10^{-3}M H^+. Calculate the percentage of the acid that is ionized.

Practice Exercise

- A 0.020M solution of niacin has a pH of 3.26. Calculate the percent ionization of the niacin.

Using K_a to Calculate pH

- Set up an ICE chart like we did in the previous chapter.
- However, if K_a is small (normally 10^{-5} or less), then we can skip the quadratic equation by making an assumption.

	B	+ H_2O ⇄	BH^+	+ OH^-
I	[B]	—	0	0
C	-x	—	+x	+x
E	[B] - x	—	x	x

Sample Exercise 16.12

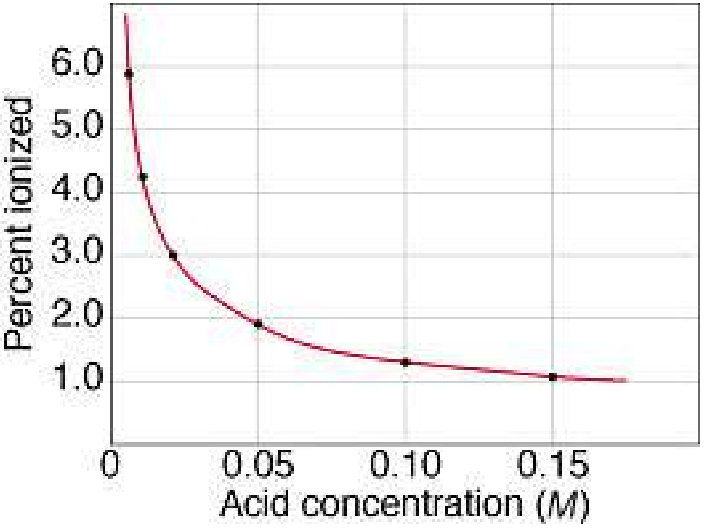
- Calculate the pH of a 0.20M solution of HCN. The K_a value is 4.9×10^{-10}.

Practice Exercise

- The K_a for niacin is 1.5×10^{-5}. What is the pH of a 0.010M solution of niacin?

Equilibrium Concentrations

- As the concentration of a weak acid increases, the equilibrium concentration of $[H^+]$ increases.
- However, as the concentration increases, the percent ionization decreases.



Sample Exercise 16.13

- Calculate the percentage of HF molecules ionized in

a. A 0.1M HF solution

b. A 0.010M HF solution

Practice Exercise

- The percent ionization of niacin ($K_a = 1.5 \times 10^{-5}$ in a 0.020M solution of 2.7%. Calculate the percentage of niacin molecules ionized in a solution that is

a. 0.010M

b. 1.0×10^{-3}M

Polyprotic Acids

- Polyprotic acids have more than 1 ionizable H. (Ex. H_2SO_4)
- It is easier to remove the first hydrogen, and the K_a values become smaller for each hydrogen that is removed.

$$H_3PO_{4(aq)} \rightleftharpoons H^+_{(aq)} + H_2PO_4^-{}_{(aq)} \qquad \text{1st Step}$$

$$H_2PO_4^-{}_{(aq)} \rightleftharpoons H^+_{(aq)} + HPO_4^{2-}{}_{(aq)} \qquad \text{2nd Step}$$

$$HPO_4^{2-}{}_{(aq)} \rightleftharpoons H^+_{(aq)} + PO_4^{3-}{}_{(aq)} \qquad \text{3rd Step}$$

Polyprotic Acids

- As long as the K_a values differ by a factor of 10^3 or more, then only the K_{a1} should be used in calculations.

TABLE 14.2 Acid-Dissociation Constants of some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

Sample Exercise 16.14

- The solubility of CO_2 in pure water at 25°C and 0.1atm pressure is 0.0037M. The common practice is the assume that all of the dissolved CO_2 is in the form of carbonic acid (H_2CO_3), which is produced by reaction between the CO_2 and H_2O:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

What is the pH of a 0.0037M solution of H_2CO_3?

Practice Exercise

a. Calculate the pH of a 0.020M solution of oxalic acid ($H_2C_2O_4$). $K_{a1} = 5.9 \times 10^{-2}$ and $K_{a2} = 6.4 \times 10^{-5}$.

b. Calculate the concentration of oxalate ion, [$C_2O_4^{-2}$], in solution.

Section 16.7 – Weak Bases

- The base-dissociation, K_b, constant can be written as follows:

$$B + H_2O \leftrightarrow HB^+ + OH^-$$

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

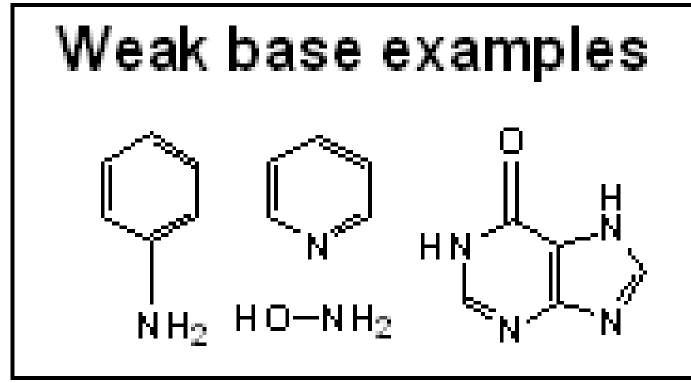
Sample Exercise 16.15

- Calculate the concentration of OH^- in a 0.15M solution of NH_3.

Practice Exercise

- Which of the following compounds should produce the highest pH as a 0.05M solution: pyridine, methylamine, or nitrous acid? (Refer to p. 691 in the book.)

Types of Weak Bases



- 2 Categories:

1. Neutral substance with a nonbonding electron pair to act as a proton acceptor. (NH_3) Amines which have N-H bonds are weak bases.
2. The anions of weak acids. (ClO^-)

Sample Exercise 16.16

- A solution made by adding solid sodium hypochlorite (NaClO) to enough water to make 2.00L of solution has a pH or 10.50. Calculate the number of moles of NaClO that were added to the water. ($K_b = 3.3 \times 10^{-7}$)

$$ClO^- + H_2O \leftarrow\rightarrow HClO + OH^-$$

Practice Exercise

- A solution of NH_3 in water has a pH of 11.17. What is the molarity of the solution?

Section 16.8 – Relationship between K_a and K_b

$$K_a \times K_b = K_w = 1 \times 10^{-14}$$

- As the strength of an acid increases (larger K_a), the strength of its conjugate base must decrease (smaller K_b).
- This formula only works for conjugate acid-base pairs.

K_a and K_b

- You can also use the formula below by taking the negative log of each component:

$$pK_a + pK_b = pK_w = 14.00$$

Sample Exercise 16.17

- Calculate

a. The base-dissociation constant, K_b, for the fluoride ion (F^-). (HF, $K_a = 6.8 \times 10^{-4}$)

b. The acid-dissociation constant, K_a, for the ammonium ion (NH_4^+). (NH_3, $K_b = 1.8 \times 10^{-5}$)

Practice Exercise

a. Which of the following anions has the largest base-dissociation constant: NO_2^-, PO_4^{3-}, or N_3^-?

b. The conjugate acid of the base quinoline has a pK_a of 4.90. What is the base-dissociation constant for quinoline?

Section 16.9 – Acid-Base Properties of Salt Solutions

- Nearly all salts are strong electrolytes, so they fully dissociate in solution.
- Hydrolysis is when a substance reacts with water to form H^+ or OH^-.

Anions

- In general, an anion (X^-), in solution can be considered the conjugate base of an acid.
- If the acid is strong, then the conjugate base will have no effect on the pH of the solution.

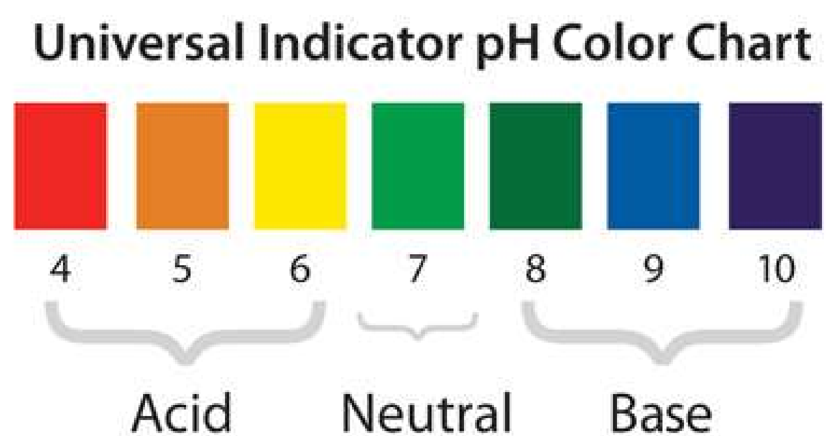
Anions

- If the acid is weak, then the conjugate base is a weak base and will form hydroxide ions which increase the pH making it basic.

$$X^- + H_2O \leftrightarrow HX + OH^-$$

Amphiprotic Anions

- Amphiprotic anions can act as an acid or a base (HSO_3^-).
- If $K_a > K_b$, the solution will be acidic.
- If $K_b > K_a$, the solution will be basic.



Cations

- Polyatomic cations whose formulas contain one or more protons can be considered the conjugate acids or weak bases. (NH_4^+)
- The weak acid will donate a proton to water an form H_3O^+ lowering the pH.

$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$$

Metal Cations

- Metal cations will react with water to lower the pH unless it is a metal cation from a strong base (alkali metals and heavy alkaline earth metals).
- The mechanism of metal cations is no longer a part of the curriculum.

Combined Effect of Cations and Anions

To summarize:

1. An anion that is a conjugate base of a strong acid will not affect pH.
2. An anion that is a conjugate base of a weak acid will increase pH.
3. A cation that is a conjugate acid of a weak base will decrease pH.

Combined Effect of Cations and Anions

4. A cation that is part of a strong base will not effect pH.

5. Other metal ions will cause a decrease in pH.

When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the ion with the largest K influences pH.

Sample Exercise 16.18

- Determine whether aqueous solutions of each of the following salts will be acidic, basic, or neutral:

a. $Ba(CH_3COO)_2$

b. NH_4Cl

c. CH_3NH_3Br

d. KNO_3

e. $Al(ClO_4)_3$

Practice Exercise

- In each of the following indicate which salt in each of the following pairs will form the more acidic (or less basic) 0.010M solution:

a. $NaNO_3$ or $Fe(NO_3)_3$

b. KBr or KBrO

c. CH_3NH_3Cl or $BaCl_2$

d. NH_4NO_2 or NH_4NO_3

Sample Exercise 16.19

- Predict whether the salt Na_2HPO_4 will form an acidic solution or a basic solution on dissolving in water. ($H_2PO_4^-$, $K_a = 4.2 \times 10^{-13}$)

Practice Exercise

- Predict whether the dipotassium salt of citric acid ($K_2HC_6H_5O_7$) will form an acidic or basic solution in water. (see Table 16.3 for data.)

Section 16.10 – Acid-Base Behavior and Chemical Structure

- Factors affecting the strength of an acid:

1. Bond Polarity (H – X) – The more polar the bond, the stronger the acid. As you move across a row on the periodic table, electronegativity increases so acidity increases.

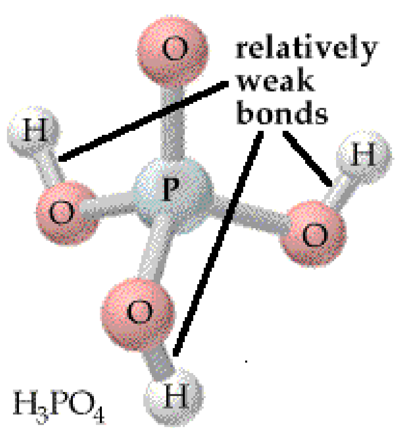
Factors Affecting Acid Strength

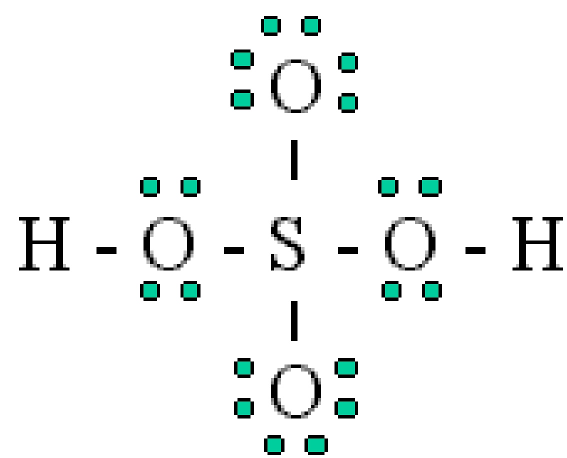
2. Bond Strength – A stronger bond is less likely to break. Bond strength decreases as you move down a group on the periodic table, so acid strength increases.

3. Stability of the conjugate base X^-.

Oxyacids

- Oxyacids are acids with –OH groups and sometimes other oxygen atoms are bonded to a central atom. (H_2SO_4)
- The generic formula is Y-O-H.



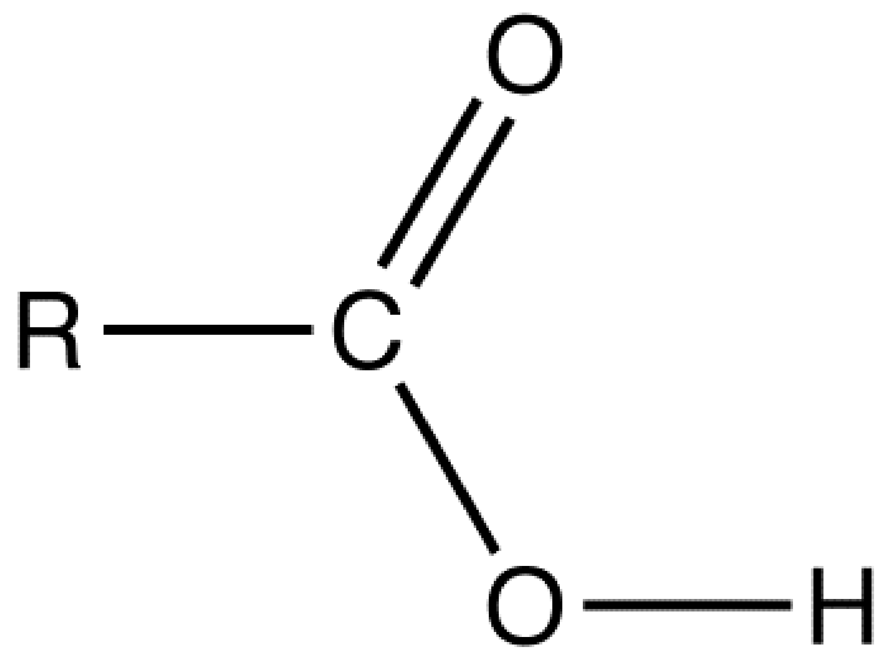


Oxyacid Strength

- For oxyacids with the same number of –OH groups, the acid with the most electronegative Y is more acidic.
- For oxyacids with the same Y, the acid with the most oxygens attached to Y is more acidic.

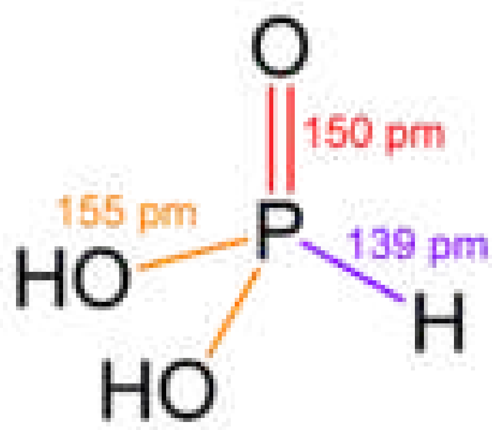
Carboxylic Acids

- Carboxylic acids contain a carboxyl group –COOH.



Sample Integrative Exercise

- Phosphorous acid (H_3PO_3) has the following Lewis structure:



a. Explain why H_3PO_3 is diprotic and not triprotic.

Sample Integrative Exercise

b. A 25.0mL sample of a solution of H_3PO_3 is titrated with 0.102M NaOH. It requires 23.3mL of NaOH to neutralize both acidic protons. What is the molarity of the H_3PO_3 solution?

Sample Integrative Exercise

c. The original solution from part b has a pH of 1.59. Calculate the percent ionization and K_{a1} for H_3PO_3.