

# Acid-Base Behavior and Chemical Structure

## Factors that Affect Acid Strength

Consider H-X. For this substance to be an acid we need:

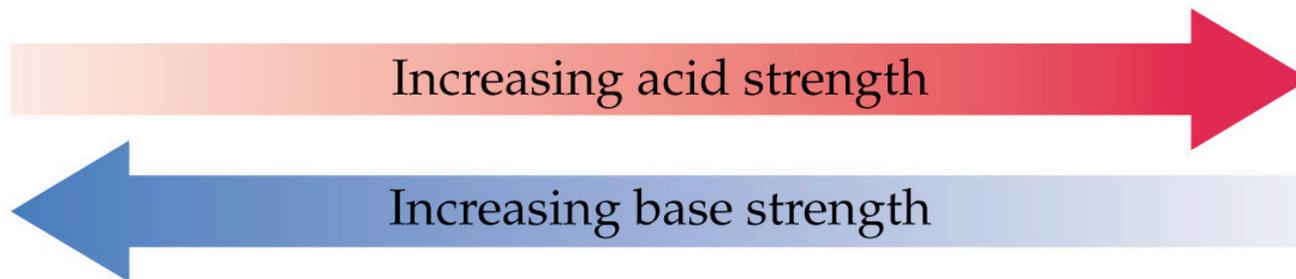
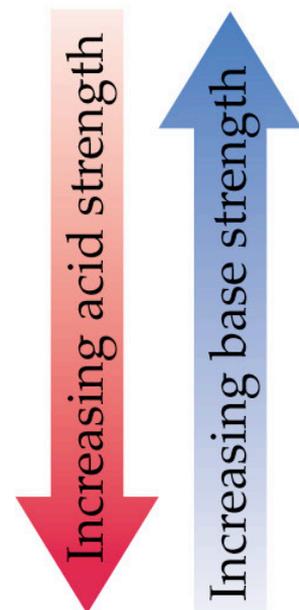
- H-X bond to be polar with  $H\delta^+$  and  $X\delta^-$  (if X is a metal then the bond polarity is  $H\delta^-$ ,  $X\delta^+$  and the substance is a base),
- the H-X bond must be weak enough to be broken,
- the conjugate base,  $X^-$ , must be stable.

## Binary Acids

- Acid strength increases across a period and down a group.
- Conversely, base strength decreases across a period and down a group.
- HF is a weak acid because the bond energy is high.
- The electronegativity difference between C and H is so small that the C-H bond is non-polar and CH<sub>4</sub> is neither an acid nor a base.

# Binary Acids

	GROUP			
	4A	5A	6A	7A
Period 2	$\text{CH}_4$ No acid or base properties	$\text{NH}_3$ Weak base	$\text{H}_2\text{O}$ ---	$\text{HF}$ Weak acid
Period 3	$\text{SiH}_4$ No acid or base properties	$\text{PH}_3$ Weak base	$\text{H}_2\text{S}$ Weak acid	$\text{HCl}$ Strong acid



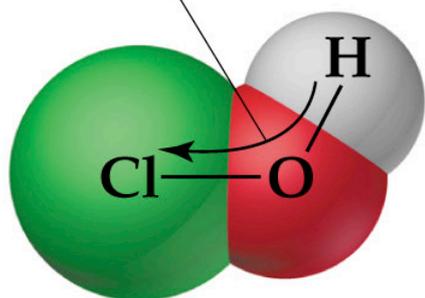
# Oxyacids

- Oxyacids contain O-H bonds.
- All oxyacids have the general structure Y-O-H.
- The strength of the acid depends on Y and the atoms attached to Y.
  - If Y is a metal (low electronegativity), then the substances are bases.
  - If Y has intermediate electronegativity (e.g. I, EN = 2.5), the electrons are between Y and O and the substance is a weak oxyacid.

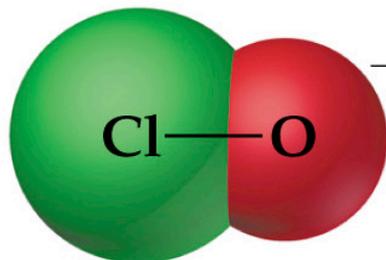
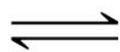
- If Y has a large electronegativity (e.g. Cl, EN = 3.0), the electrons are located closer to Y than O and the O-H bond is polarized to lose H<sup>+</sup>.
- The number of O atoms attached to Y increase the O-H bond polarity and the strength of the acid increases (e.g. HOCl is a weaker acid than HClO<sub>2</sub> which is weaker than HClO<sub>3</sub> which is weaker than HClO<sub>4</sub> which is a strong acid).

# Oxyacids

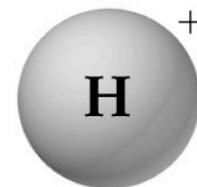
Electron drift



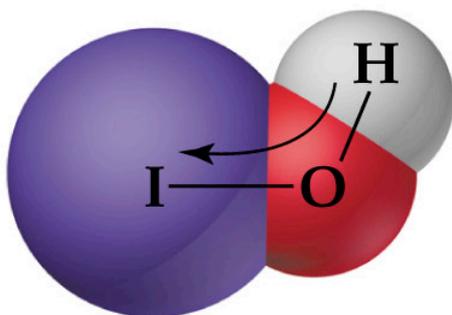
EN = 3.0



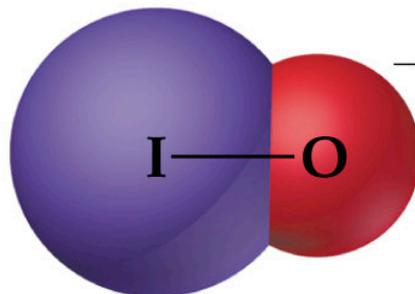
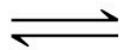
+



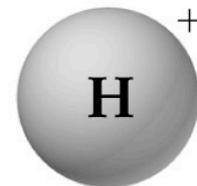
$$K_a = 3.0 \times 10^{-8}$$



EN = 2.5



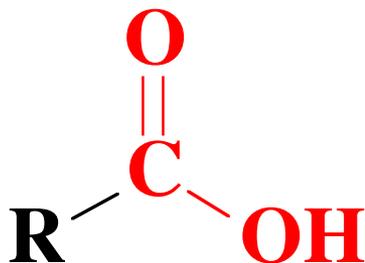
+



$$K_a = 2.3 \times 10^{-11}$$

## Carboxylic Acids

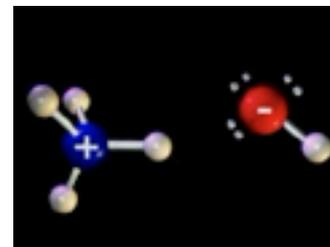
- Carboxylic acids all contain the COOH group.
- All carboxylic acids are weak acids.
- When the carboxylic acid loses a proton, it generate the carboxylate anion, COO<sup>-</sup>.



# Lewis Acids and Bases

- Brønsted-Lowry acid is a proton donor.
- Focusing on electrons: a Brønsted-Lowry acid can be considered as an electron pair acceptor.
- Lewis acid: electron pair acceptor.
- Lewis base: electron pair donor.
- Note: Lewis acids and bases do not need to contain protons.
- Therefore, the Lewis definition is the most general definition of acids and bases.

- Lewis acids generally have an incomplete octet (e.g.  $\text{BF}_3$ ).
- Transition metal ions are generally Lewis acids.
- Lewis acids must have a vacant orbital (into which the electron pairs can be donated).
- Compounds with  $\pi$ -bonds can act as Lewis acids:



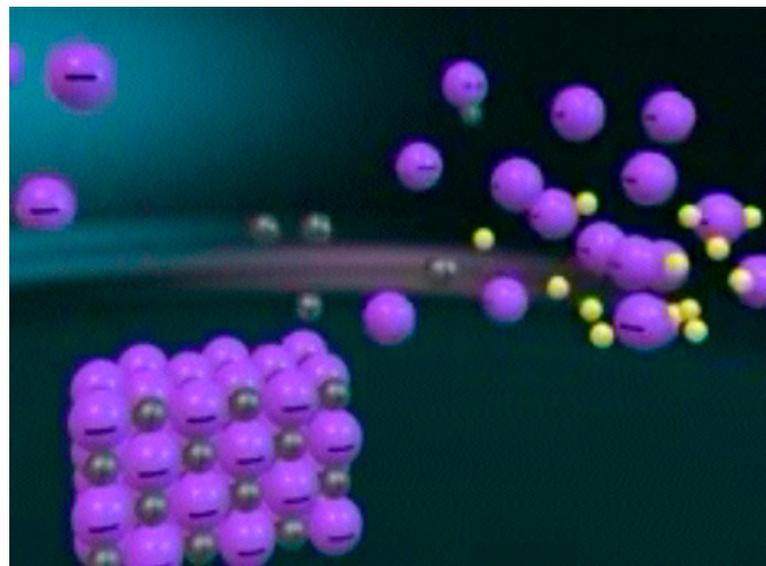
# The Common Ion Effect

- The solubility of a partially soluble salt is decreased when a common ion is added.
- Consider the equilibrium established when acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , is added to water.
- At equilibrium  $\text{H}^+$  and  $\text{C}_2\text{H}_3\text{O}_2^-$  are constantly moving into and out of solution, but the concentrations of ions is constant and equal.

- Consider the addition of  $\text{C}_2\text{H}_3\text{O}_2^-$ , which is a common ion. (The source of acetate could be a strong electrolyte such as  $\text{NaC}_2\text{H}_3\text{O}_2$ .)
- Therefore,  $[\text{C}_2\text{H}_3\text{O}_2^-]$  increases and the system is no longer at equilibrium.
- So,  $[\text{H}^+]$  must decrease.



The equilibrium will shift to the left.



# Buffered Solutions

## Composition and Action of Buffered Solutions

- A buffer consists of a mixture of a weak acid (HX) and its conjugate base ( $X^-$ ):



- The  $K_a$  expression is

$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$
$$\therefore [\text{H}^+] = K_a \frac{[\text{HX}]}{[\text{X}^-]}$$

- A buffer resists a change in pH when a small amount of  $\text{OH}^-$  or  $\text{H}^+$  is added.
- When  $\text{OH}^-$  is added to the buffer, the  $\text{OH}^-$  reacts with HX to produce  $\text{X}^-$  and water. But, the  $[\text{HX}]/[\text{X}^-]$  ratio remains more or less constant, so the pH is not significantly changed.
- When  $\text{H}^+$  is added to the buffer,  $\text{X}^-$  is consumed to produce HX. Once again, the  $[\text{HX}]/[\text{X}^-]$  ratio is more or less constant, so the pH does not change significantly.

## Example

Write the reaction that occurs in a buffer solution containing HF/F<sup>-</sup> when:

1. H<sup>+</sup> is added
2. OH<sup>-</sup> is added

## Example

Write the reaction that occurs in a buffer solution containing HF/F<sup>-</sup> when:

1. H<sup>+</sup> is added



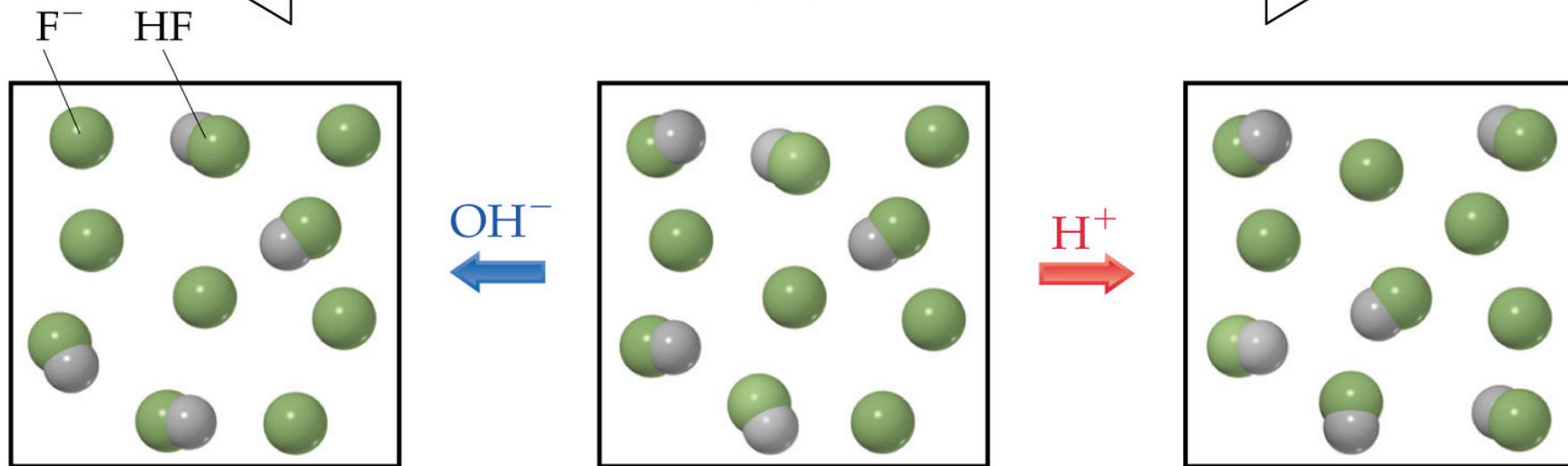
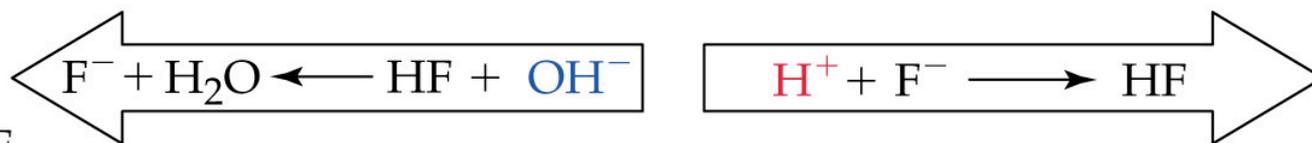
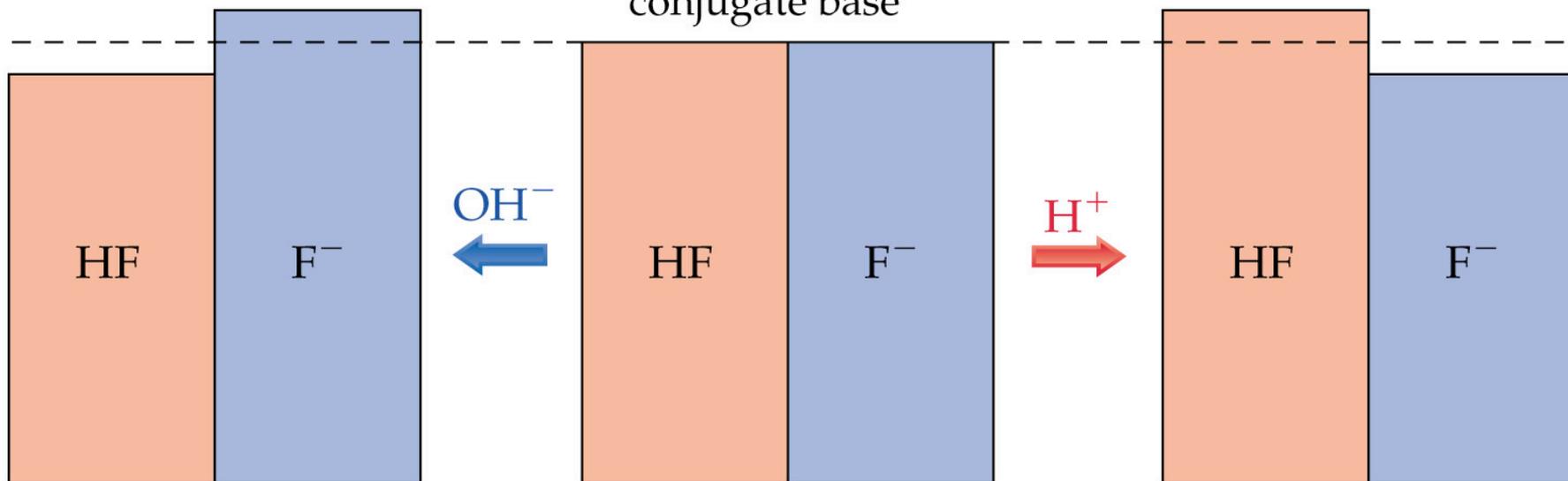
2. OH<sup>-</sup> is added



Buffer after  
addition of  $\text{OH}^-$

Buffer with equal  
concentrations of  
weak acid and its  
conjugate base

Buffer after  
addition of  $\text{H}^+$



## Buffer Capacity and pH

- Buffer capacity is the amount of acid or base neutralized by the buffer before there is a significant change in pH.
- Buffer capacity depends on the composition of the buffer.
- The greater the amounts of conjugate acid-base pair, the greater the buffer capacity.
- The pH of the buffer depends on  $K_a$ .
- In general, the effective range of a buffer is within the pH range:  
$$\text{pK}_a - 1 \text{ to } \text{pK}_a + 1.$$