CHAPTER 10
Reactions in Aqueous Solutions I: Acids, Bases & Salts

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Properties of Aqueous Solutions of Acids and Bases

acidic solutions	basic solutions
They have a sour taste	They have a bitter taste
They change the colors of many indicators	They change the colors of many indicators
React with metals to generate hydrogen	
They react with metal oxides and hydroxides to form salts and water	They react with acids to form salts and water
Acidic aqueous solutions conduct electricity	Aqueous basic solutions conduct electricity

The Arrhenius Theory	The Brønsted-Lowry Theory	The Lewis Theory
Acids are substances that contain hydrogen Bases are substances that contain hydroxyl, OH, group	An acid is a proton donor (H^+). A base is a proton acceptor.	Acids are electron pair acceptors. Bases are electron pair donors.
HCl and NaOH	NH_3 and H_2O	BF_3 and NH_3

The Arrhenius Theory

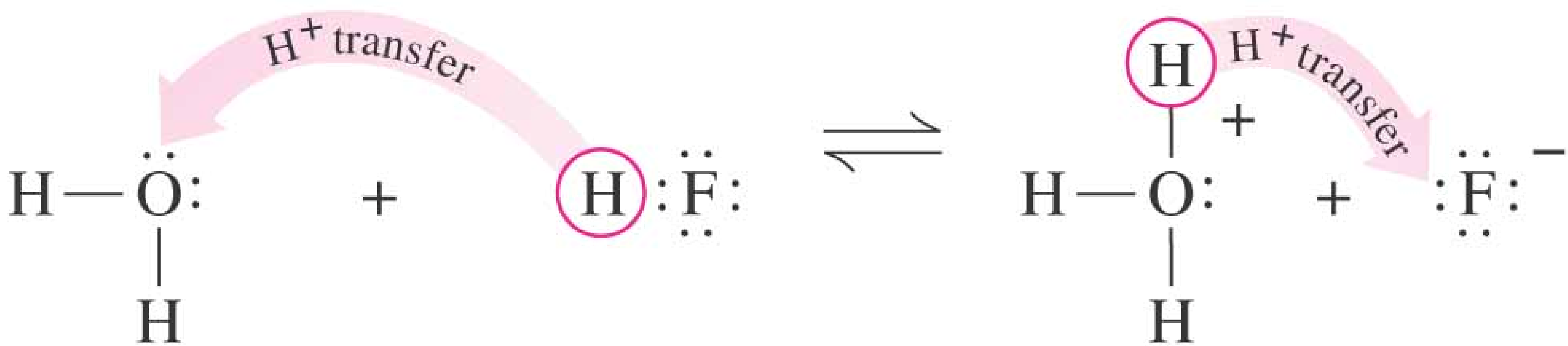
- Svante Augustus Arrhenius first presented this theory of acids and bases in 1884.
- Acids are substances that contain hydrogen and produces H^+ in aqueous solutions.
- Bases are substances that contain the hydroxyl, OH, group and produce hydroxide ions, OH^-, in aqueous solutions.

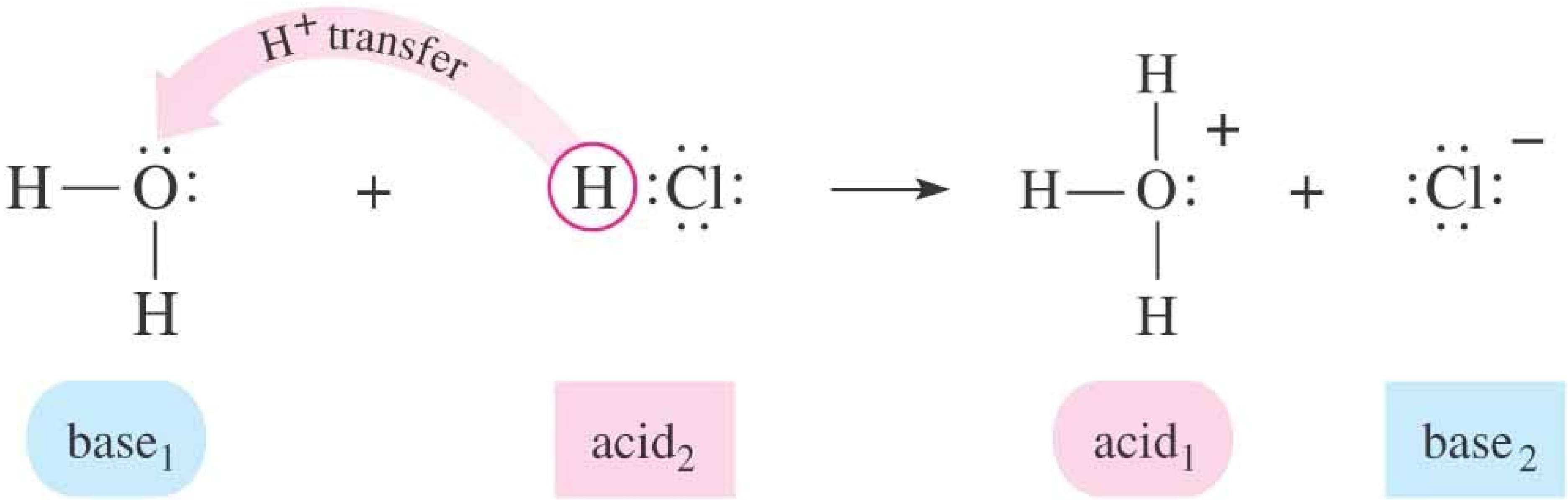
The Brønsted-Lowry Theory

- J.N. BrØnsted and T.M. Lowry developed the acid-base theory in 1923.
- An acid is a proton donor (H^+).
- A base is a proton acceptor.

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

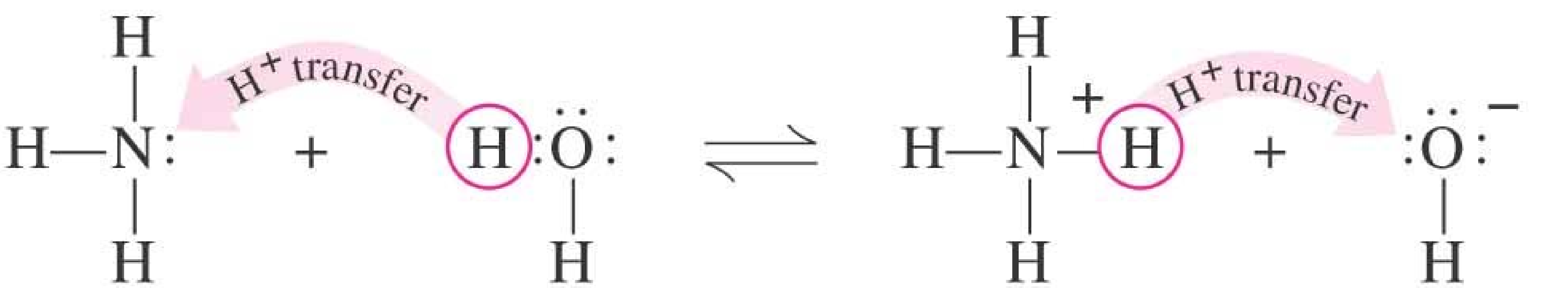
$base_1$ | $acid_2$ | $acid_1$ | $base_2$



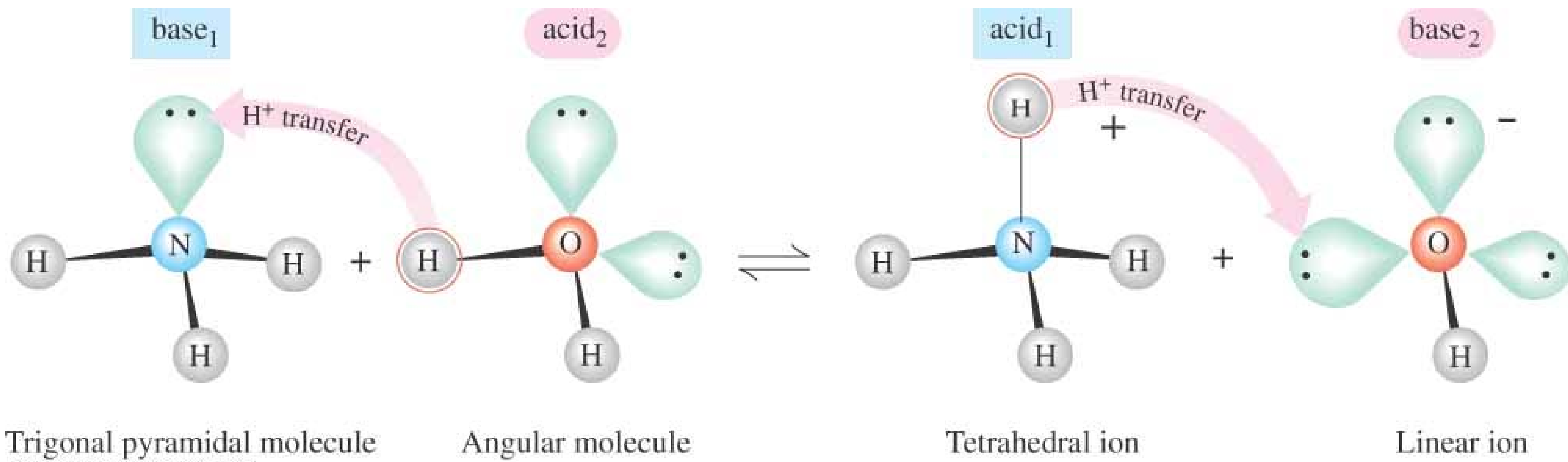

H+ transfer
base1
acid2
acid1
base2

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

base$_1$ | acid$_2$ | acid$_1$ | base$_2$



amnonia | water | ammonium ion | hydroxide ion


base$_1$
acid$_2$
acid$_1$
base$_2$
H^+ transfer
H^+ transfer
Trigonal pyramidal molecule
Angular molecule
Tetrahedral ion
Linear ion

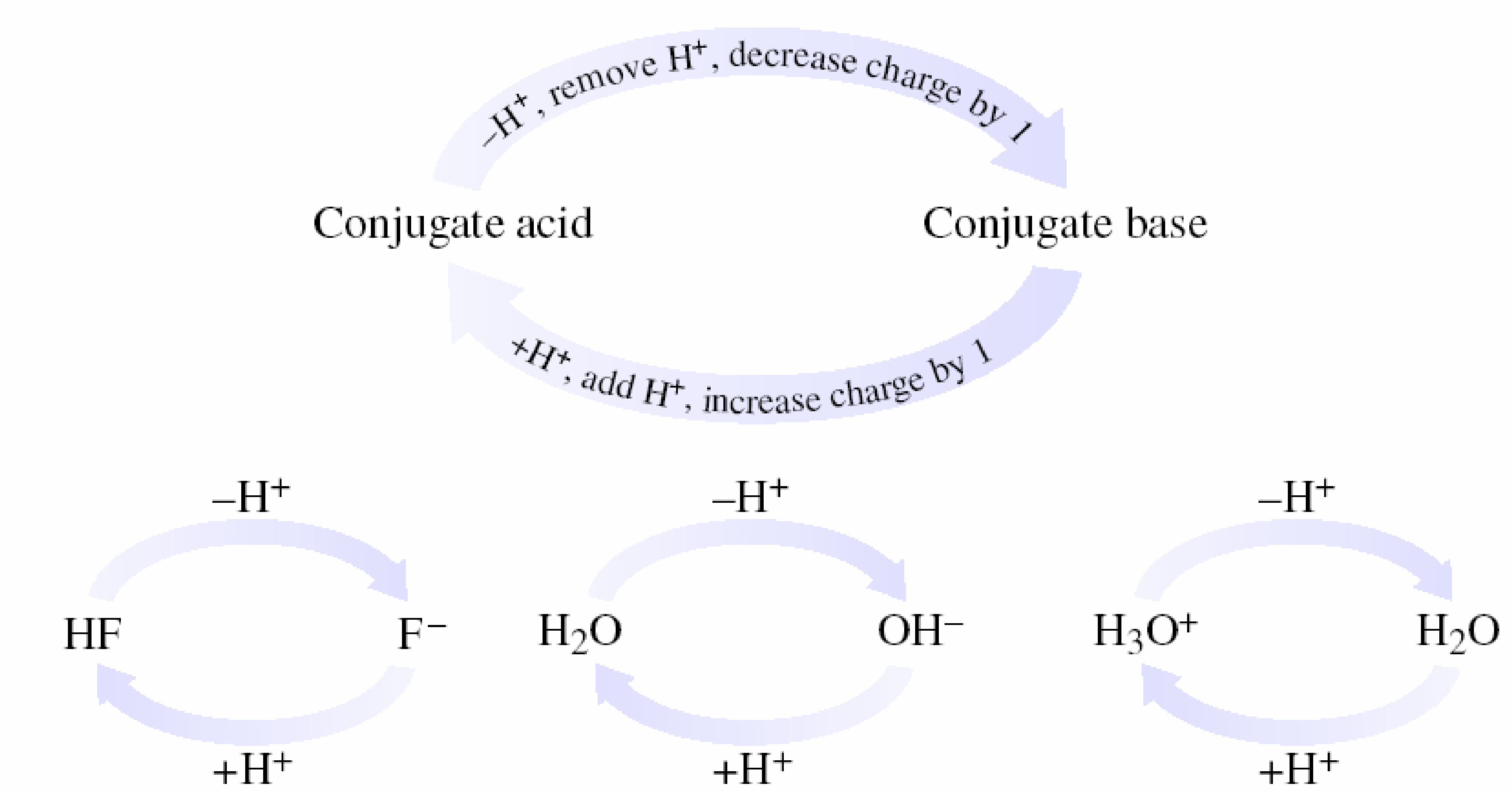
The Brønsted-Lowry Theory

- An important part of BrØnsted-Lowry acid-base theory is the idea of ***conjugate acid-base pairs***.
  - Two species that differ by a proton are called acid-base conjugate pairs.
- $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

- HNO_3 is the acid, conjugate base is NO_3^-
- H_2O is the base, conjugate acid is H_3O^+

The Brønsted-Lowry Theory

- Conjugate acid-base pairs are species that differ by a proton.



The Brønsted-Lowry Theory

- The major differences between Arrhenius and Brønsted-Lowry theories.

1. The reaction does not have to occur in an aqueous solution.
2. Bases are not required to be hydroxides.

The Brønsted-Lowry Theory

- An important concept in BrØnsted-Lowry theory involves the relative strengths of acid-base pairs.
- ***<u>Weak acids have strong conjugate bases.</u>***
- ***<u>Weak bases have strong conjugate acids.</u>***
- **The weaker the acid or base, the stronger the conjugate partner.**
- The reason why a weak acid or base is weak is because the conjugate is so strong it reforms the original acid or base.

The Brønsted-Lowry Theory

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

- Since NH_3 is a weak base, NH_4^+ must be a strong acid.
  - NH_4^+ gives up H^+ to reform NH_3.
- Compare that to

$$NaOH \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

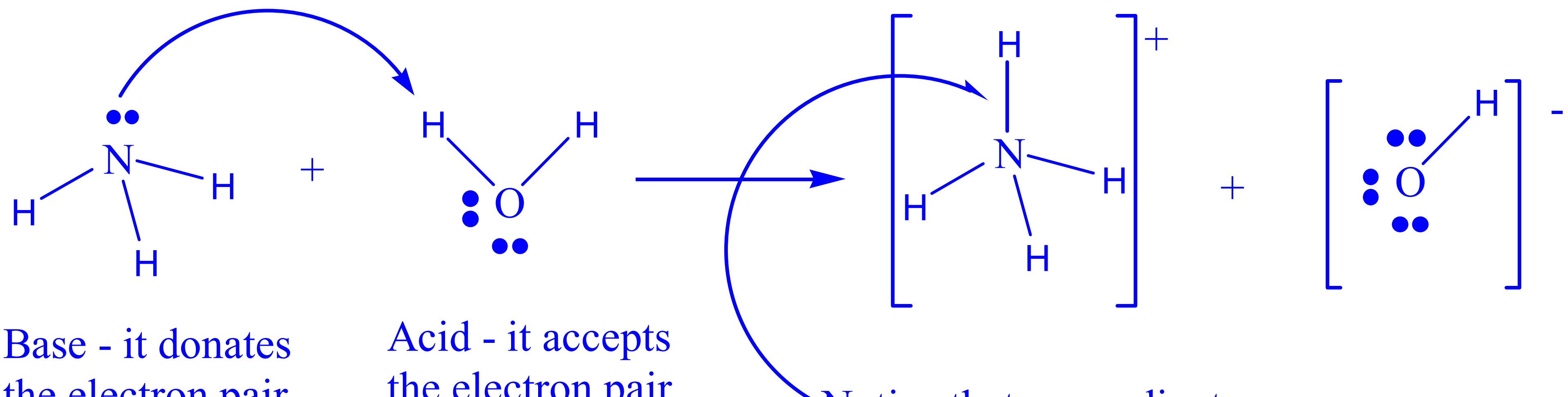
  - Na^+ must be a weak acid or it would recombine to form NaOH

The Lewis Theory

- Developed in 1923 by G.N. Lewis.
  - **Emphasis on what the electrons are doing** as opposed to what the protons are doing.
- Acids are defined as **electron pair acceptors**.
- Bases are defined as **electron pair donors**.

The Lewis Theory

- One Lewis acid-base example is the ionization of ammonia. Look at this reaction in more detail paying attention to the electrons.



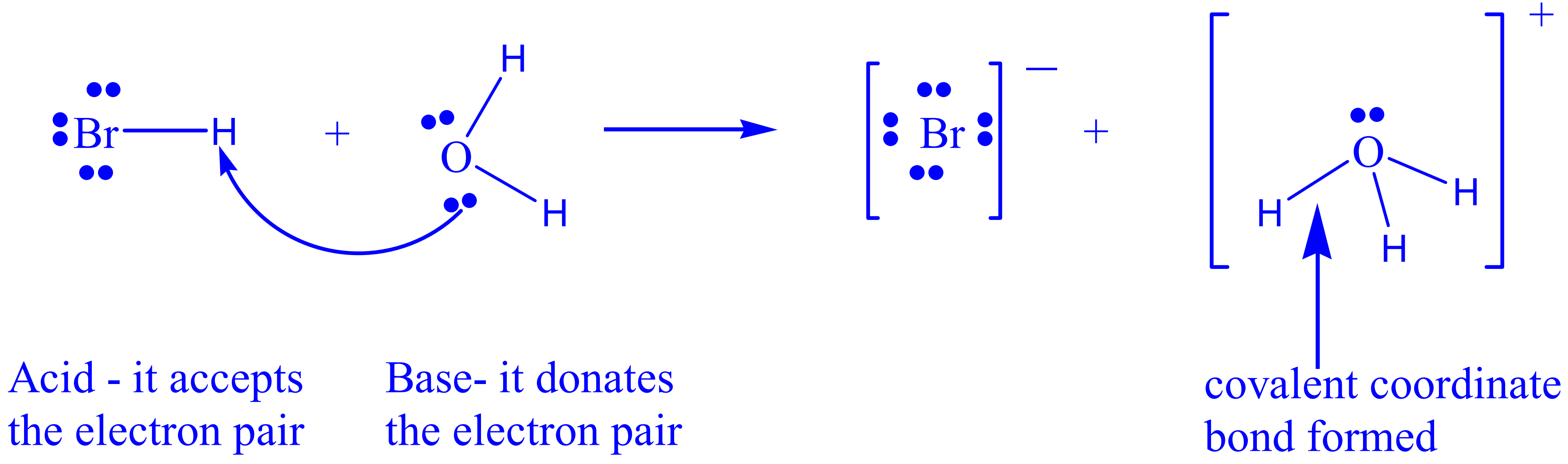
Base - it donates the electron pair

Acid - it accepts the electron pair

Notice that a coordinate covalent bond is formed on the ammonium ion.

The Lewis Theory

- A second example is the ionization of HBr. Again, a more detailed examination keeping our focus on the electrons.



The Lewis Theory

- A third Lewis example is the autoionization of water.

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

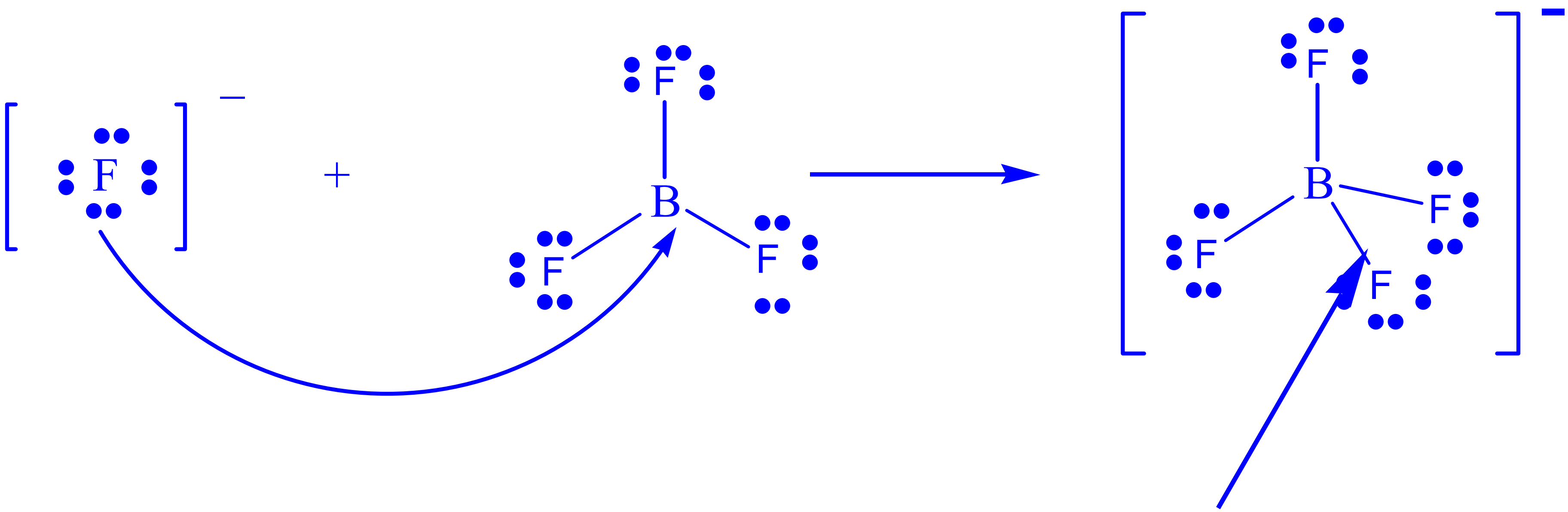
acid base

The Lewis Theory

- The reaction of sodium fluoride and boron trifluoride provides an example of a Lewis acid-base reaction.
  - It does not involve H^+ at all, thus it cannot be an Arrhenius nor a Brønsted-Lowry acid-base reaction.

$$NaF + BF_3 \rightarrow Na^+ + BF_4^-$$

The Lewis Theory



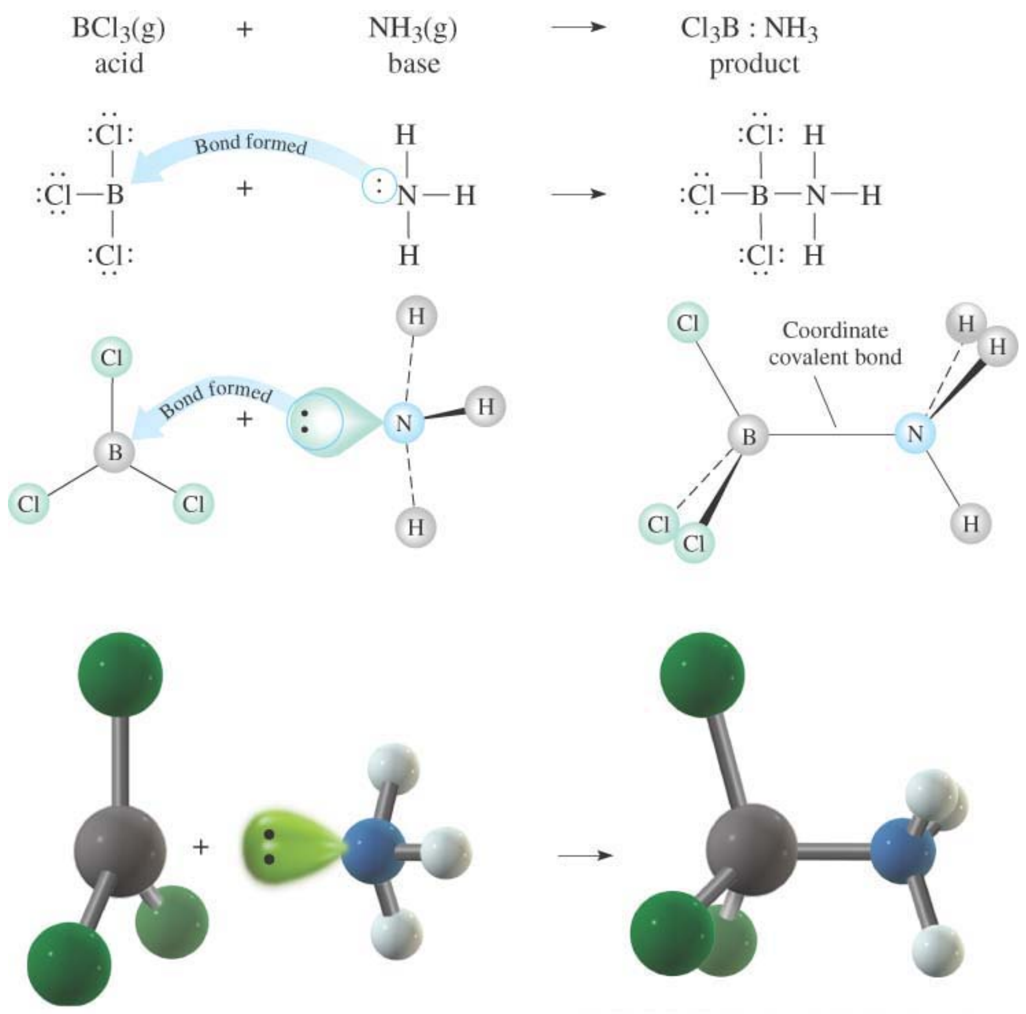
Base - it donates the electron pair

Acid - it accepts the electron pair

coordinate covalent bond formed

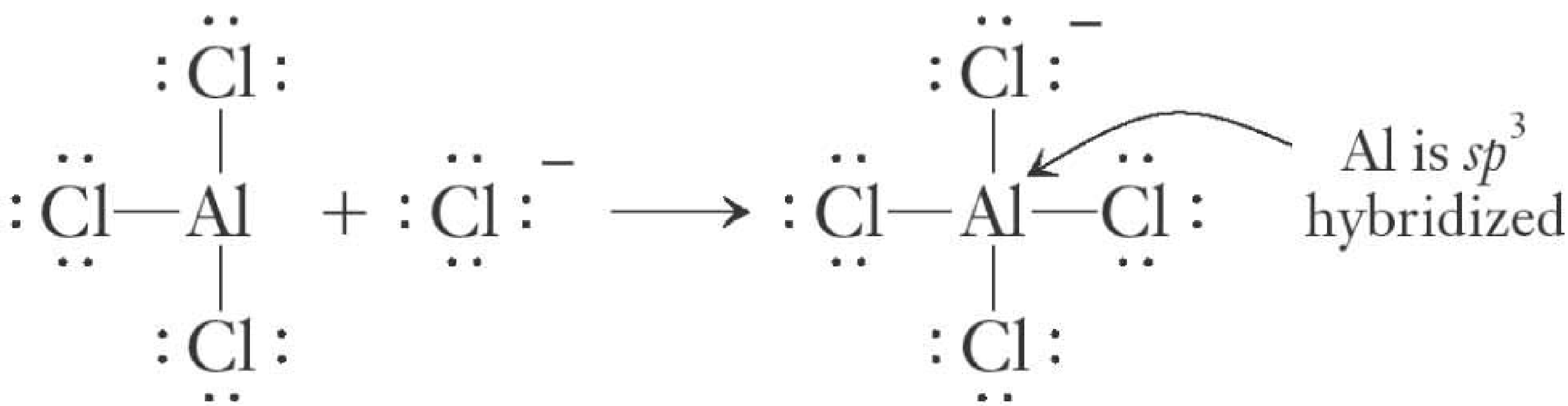
The Lewis Theory

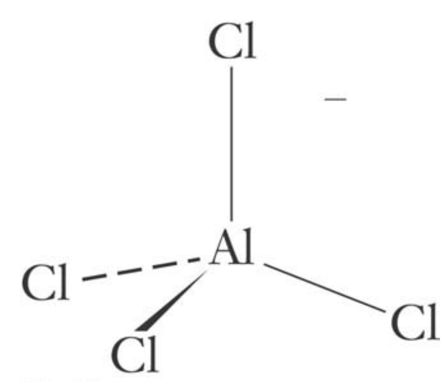
- BF_3 is a strong Lewis acid.

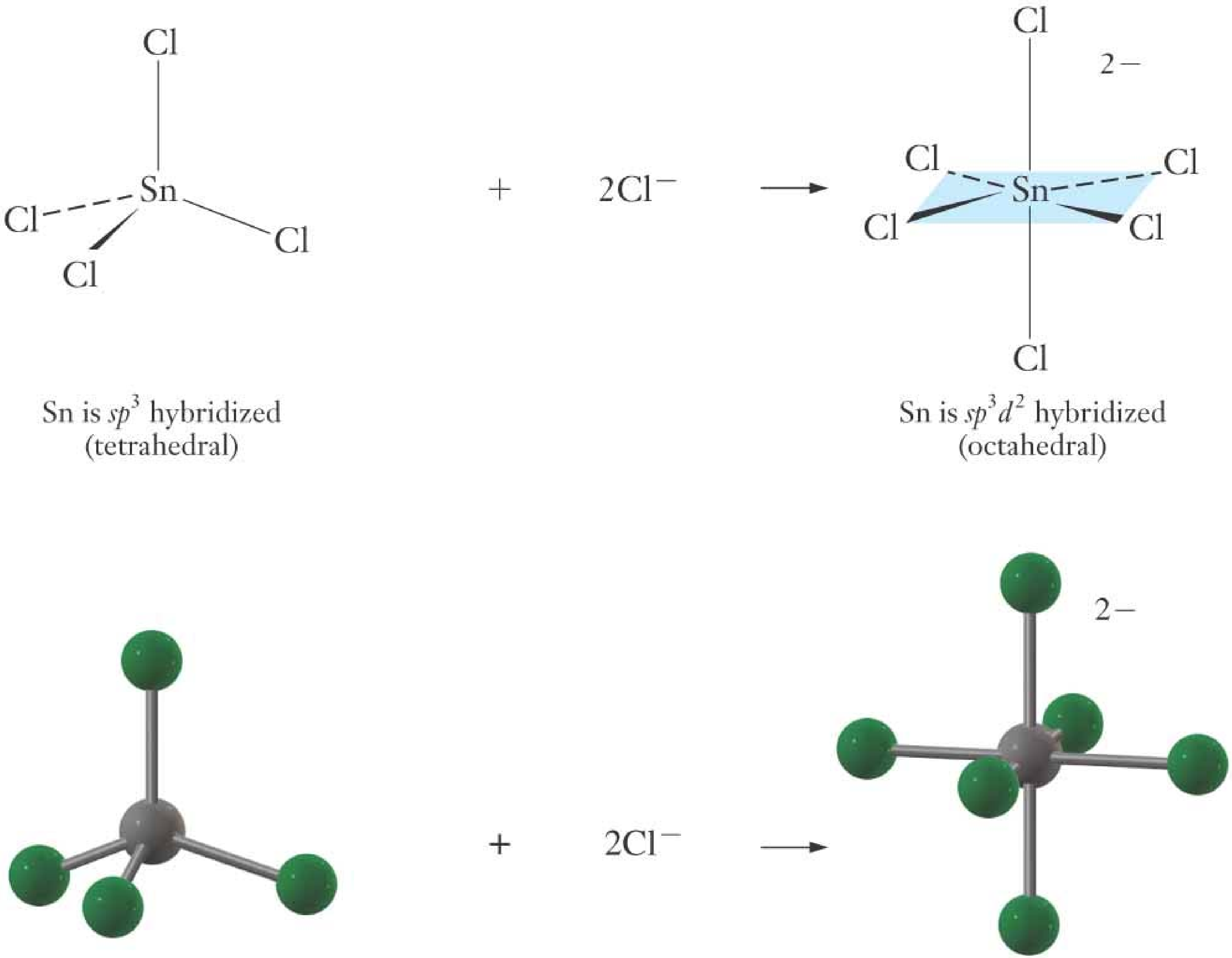


$$AlCl_3(s) + Cl^-(aq) \longrightarrow AlCl_4^-(aq)$$

acid base product







Cl
Sn
Cl
Cl
Cl
+
2Cl−
Cl
2−
Cl
Sn
Cl
Cl
Cl
Cl
Sn is sp3 hybridized
(tetrahedral)
Sn is sp3d2 hybridized
(octahedral)
+
2Cl−
2−

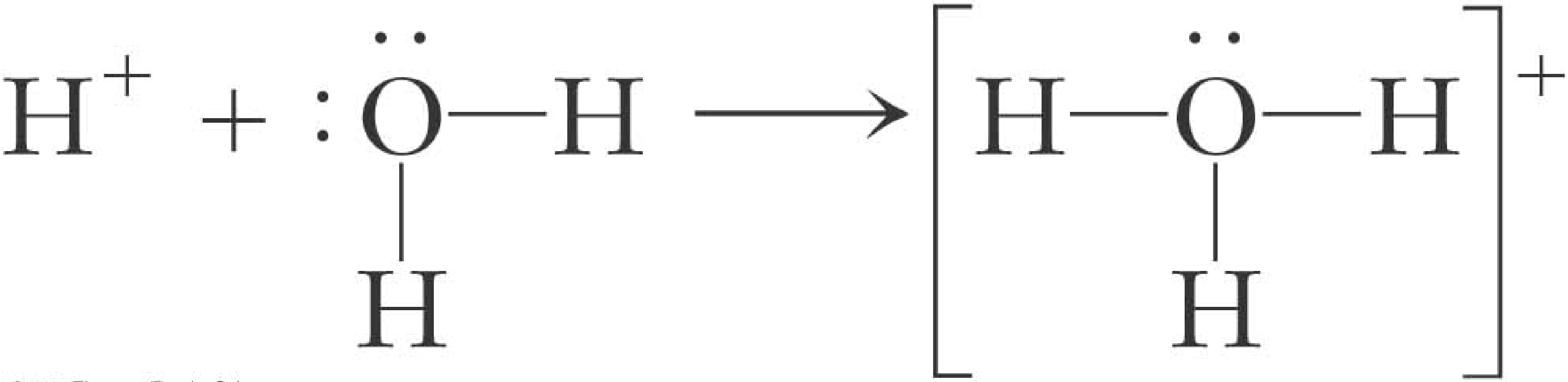
The Autoionization of Water

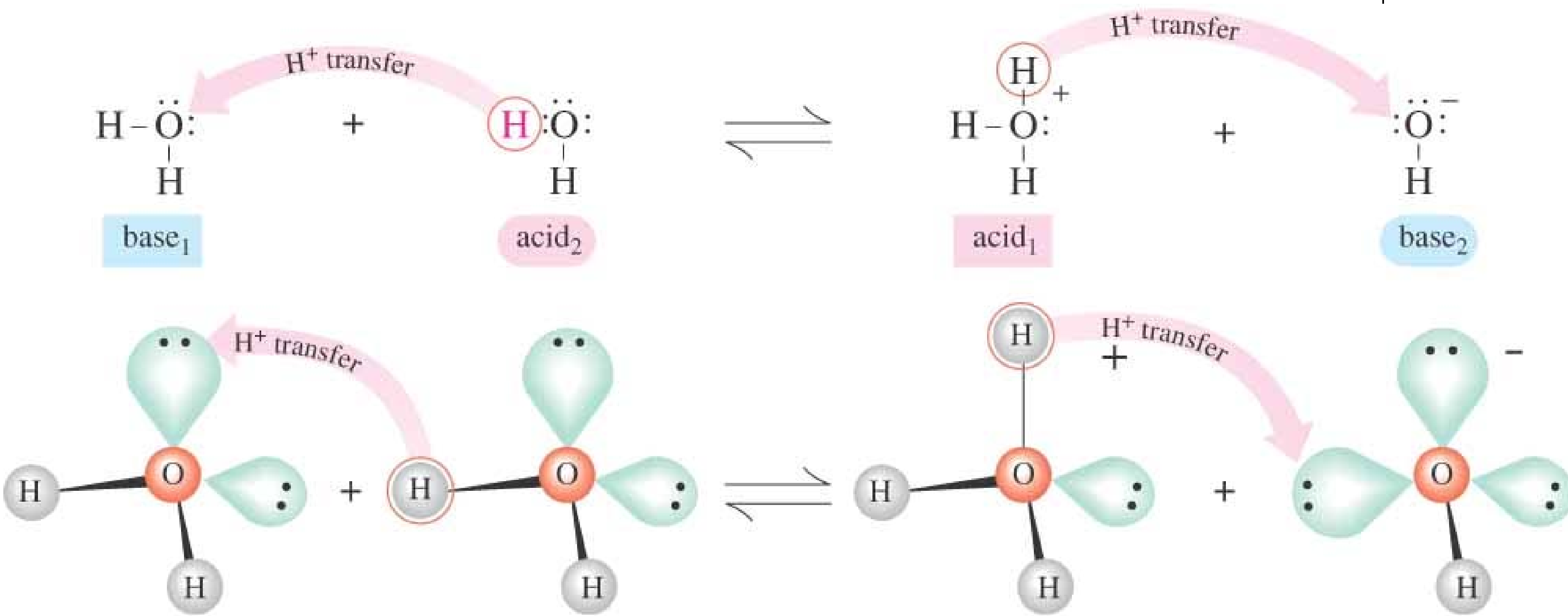
- Water can be either an acid or base in Bronsted-Lowry theory.
- Consequently, water can react with itself.
  - This reaction is called autoionization.
- One water molecule acts as a base and the other as an acid.

$$\underset{\text{base}_1}{H_2O} + \underset{\text{acid}_2}{H_2O} \rightleftarrows \underset{\text{acid}_1}{H_3O^+} + \underset{\text{base}_2}{OH^-}$$

The Hydronium Ion (Hydrated Hydrogen Ion)

- The protons that are generated in acid-base reactions are not present in solution by themselves.
- Protons are surrounded by several water molecules and called the hydronium ions.
- $H^{+}_{(aq)}$ is really $H(H_2O)_n^{+}$




H⁺ transfer
base1
acid2
acid1
base2

Amphoterism

- Species that can behave as an acid or base are called **amphoteric**.

Amphoterism

- Examples of amphoteric species are hydroxides of elements with intermediate electronegativity.
  - Zn and Al hydroxides for example.
- $Zn(OH)_2$ behaves as a base in presence of strong acids.
- $Zn(OH)_2$ behaves as an acid in presence of strong bases.

$$Zn(OH)_2 + 2\,HNO_3 \rightarrow Zn(NO_3)_2 + 2\,H_2O$$

$$Zn(OH)_2 + 2KOH \rightarrow K_2Zn(OH)_4$$

Strengths of Acids

For **binary acids**, acid strength increases with decreasing H-X bond strength.

- Bond strength has this periodic trend.

  HF >> HCl > HBr > HI

- Acid strength has the reverse trend.

  HF << HCl < HBr < HI

The same trend applies to the VIA hydrides.

- Their bond strength has this trend.

  $H_2O >> H_2S > H_2Se > H_2Te$

- The acid strength is the reverse trend.

  $H_2O << H_2S < H_2Se < H_2Te$

TABLE 10-2 *Relative Strengths of Conjugate Acid–Base Pairs*

Acid strength increases (↑)

Acid			Base
$HClO_4$	100% ionized in dilute aq. soln. No molecules of nonionized acid.	Negligible base strength in water.	ClO_4^-
HI			I^-
HBr			Br^-
HCl			Cl^-
HNO_3			NO_3^-
H_3O^+	Equilibrium mixture of nonionized molecules of acid, conjugate base, and $H^+(aq)$.		H_2O
HF			F^-
CH_3COOH			CH_3COO^-
HCN			CN^-
NH_4^+			NH_3
H_2O		Reacts completely with H_2O to form OH^-; cannot exist in aqueous solution.	OH^-
NH_3			NH_2^-

$$\text{Acid} \underset{\text{base gains } H^+}{\overset{\text{acid loses } H^+}{\rightleftharpoons}} \text{Base}$$

Base strength increases (↓)

Strengths of Acids

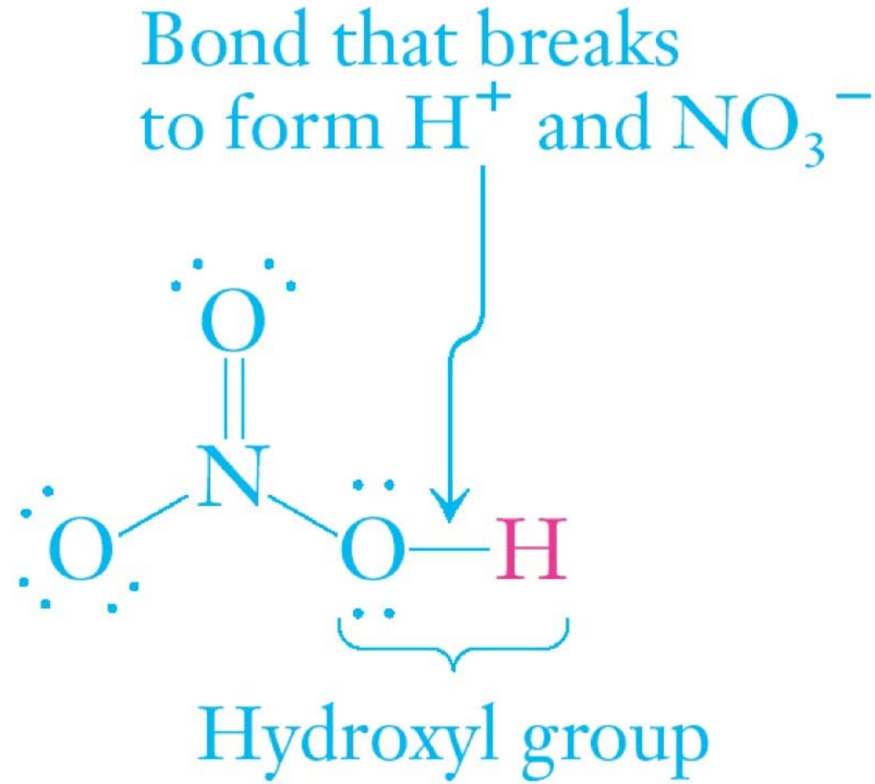
- Remember that for **binary acids**, acid strength increased with decreasing H-X bond strength.
- Ternary acids have the same periodic trend.
- Strong ternary acids have weaker H-O bonds than weak ternary acids.
- For example, compare acid strengths:

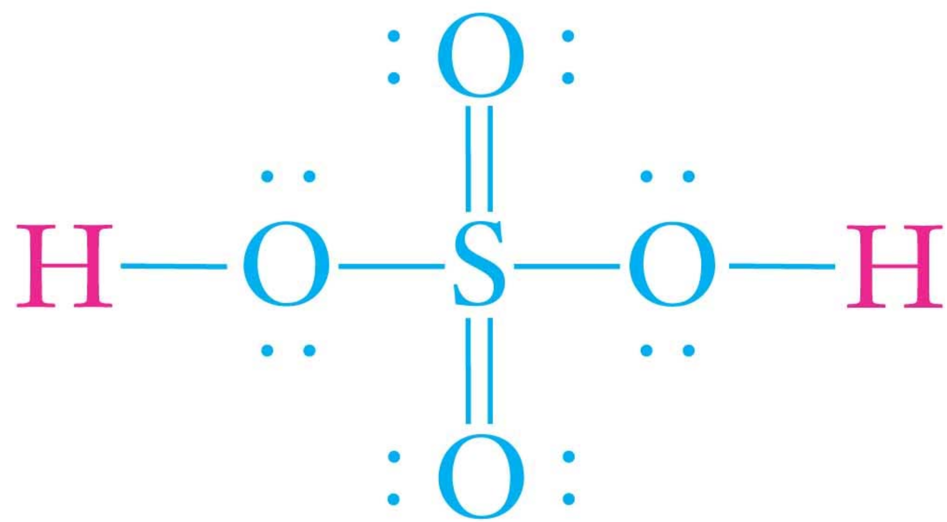
$$HNO_2 < HNO_3 \qquad H_2SO_3 < H_2SO_4$$

- This implies that the H-O bond strength is:

$$HNO_2 > HNO_3 \qquad H_2SO_3 > H_2SO_4$$

Ternary acids are hydroxides of nonmetals that produce H_3O^+ in water.





Strengths of Acids

- Ternary acid strength usually increases with:

1. an increasing number of O atoms on the central atom.
2. an increasing oxidation state of central atom.
   - Every additional O atom increases the oxidation state of the central atom by 2.

Strengths of Acids

- For ternary acids having the same central atom:

  the **highest oxidation state** of the central atom is **usually strongest acid**.
- For example, look at the strength of the Cl ternary acids.

$HClO < HClO_2 < HClO_3 < HClO_4$

weakest **strongest**

Acid-Base Reactions in Aqueous Solutions

- There are four acid-base reaction combinations that are possible:
  1. Strong acids – strong bases
  2. Weak acids – strong bases
  3. Strong acids – weak bases
  4. Weak acids – weak bases

Acid-Base Reactions in Aqueous Solutions

1. Strong acids - strong bases
   - forming soluble salts

$$2\ HBr_{(aq)} + Ca(OH)_{2(aq)} \rightarrow CaBr_{2(aq)} + 2\ H_2O_{(\ell)}$$

2. Strong acids-strong bases
   - forming **<u>insoluble</u>** salts

**** There is only one reaction of this type:

$$H_2SO_{4(aq)} + Ba(OH)_{2(aq)} \rightarrow BaSO_{4(s)} + 2H_2O_{(\ell)}$$

3. Weak acids - strong bases
   - forming soluble salts

$$HNO_{2(aq)} + NaOH_{(aq)} \rightarrow NaNO_{2(aq)} + H_2O_{(\ell)}$$

Acid-Base Reactions in Aqueous Solutions

4. Strong acids - weak bases
   - forming soluble salts

$$HNO_{3(aq)} + NH_{3(aq)} \rightarrow NH_4NO_{3(aq)}$$

5. Weak acids - weak bases
   - forming soluble salts

$$CH_3COOH_{(aq)} + NH_{3(aq)} \rightarrow NH_4CH_3COO_{(aq)}$$

Chemistry is fun!