

# CONCEPTS OF ACIDS AND BASES

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# Acid-Base Concepts

- Acids and bases are among the most familiar and important of all chemical compounds. You encounter them each and everyday. Vinegar- acetic acid, lemon juice - citric acid, milk of magnesium - magnesium hydroxide, there is even HCl in your stomach to digest food
- Antoine Lavoisier was one of the first chemists to try to explain what makes a substance acidic.

In 1777, he proposed that oxygen was an essential element in acids. There is one definition involving oxygen (Lux Flood) but many other ways more useful and we will discuss those.

- The actual cause of acidity and basicity was ultimately explained in terms of the **effect these compounds have on water** by Arrhenius in 1884.

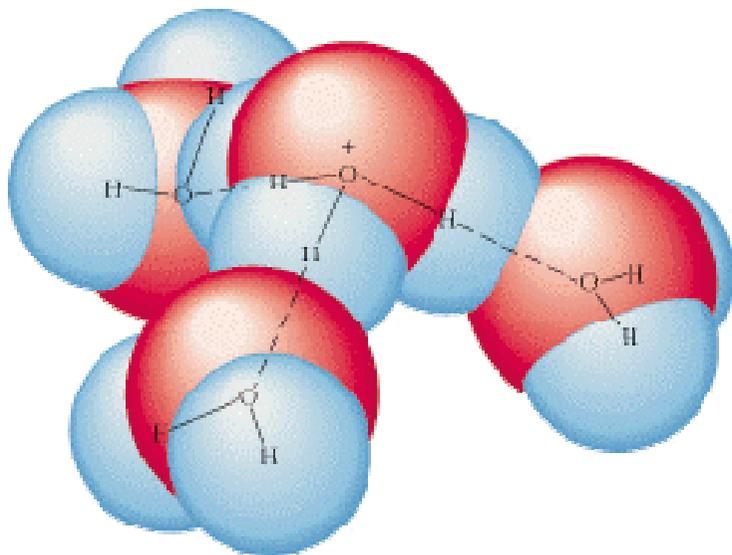
# Definitions of Acids and Bases

- We will look at several (not all) concepts of acid-base theory including:
  - The Arrhenius concept
  - The Bronsted Lowry concept
  - The Lewis concept

# The Arrhenius Definition

- According to the Arrhenius concept of acids and bases, an acid is a **substance that, when dissolved in water, increases the concentration of hydronium ion ( $\text{H}_3\text{O}^+$ ) (produces  $\text{H}^+$ ).**
  - Chemists often use the notation  $\text{H}^+(\text{aq})$  for the  $\text{H}_3\text{O}^+(\text{aq})$  ion, and call it the hydrogen ion.
  - Remember, however, that the aqueous hydrogen ion is actually chemically bonded to water, that is,  $\text{H}_3\text{O}^+$ .

# Arrhenius Concept of Acids and Bases



The  $\text{H}_3\text{O}^+$  is shown here hydrogen bonded to three water molecules.

# Arrhenius Concept of Acids and Bases

- A base, in the Arrhenius concept, is a substance that, when dissolved in water, increases the concentration of hydroxide ion,  $\text{OH}^-(\text{aq})$  (produces  $\text{OH}^-$ ).

# Arrhenius Concept of Acids and Bases

- In the Arrhenius concept, a **strong (100%) acid** is a substance that **ionizes completely** in aqueous solution to give  $H_3O^+(aq)$  and an anion.
  - An example is perchloric acid,  $HClO_4$ .



- 6 strong acids include **HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>**. **Must memorize; work future problems**

# Arrhenius Concept of Acids and Bases

- In the Arrhenius concept, a strong (100%) base is a substance that **dissociates completely** in aqueous solution to give OH<sup>-</sup>(aq) and a cation.
  - An example is sodium hydroxide, NaOH (ionic).

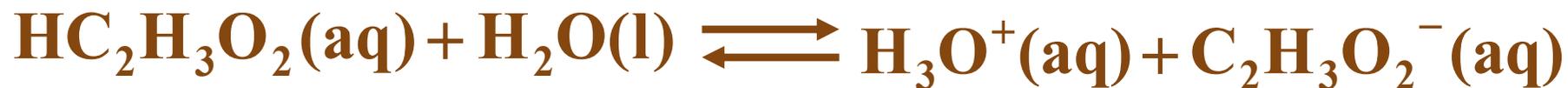


- 6 strong bases include NaOH, LiOH, KOH, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub>.
- memorize

# Arrhenius Concept of Acids and Bases

- Rest of acids and bases ( $\text{NH}_3$ ,  $\text{NH}_2^-$ ,  $\text{NH}^-$ , anions) that you encounter are **weak**. They are **not completely ionized** and exist in reversible reaction with the corresponding ions.

– An example is acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ .



– Ammonium hydroxide,  $\text{NH}_4\text{OH}$ , is a weak base.



# Arrhenius Concept of Acids and Bases

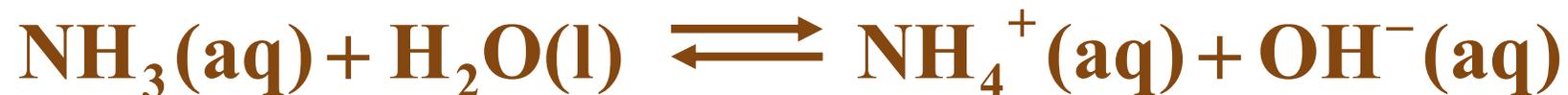
- The Arrhenius concept is limited in that it looks at acids and bases in aqueous solutions only involving  $H^+$  and  $OH^-$ . There are many substances with acid/base properties that do not involve these and cannot be classified by this theory.
  - In addition, it singles out the  $OH^-$  ion as the source of base character, when other species can play a similar role
  - There are broader definitions of acids and bases which we will cover.

# The Brønsted-Lowry Definition

- According to the Brønsted-Lowry concept, an **acid** is the species **donating the proton** in a proton-transfer reaction.
- A **base** is the **species accepting the proton** in a proton-transfer reaction.
  - In any reversible acid-base reaction, both forward and reverse reactions involve proton transfer.
  - notice this theory is only looking at proton not even looking at hydroxide. This theory is useful in aqueous solution and the one we will use the most in this chapter since dealing with aq chemistry

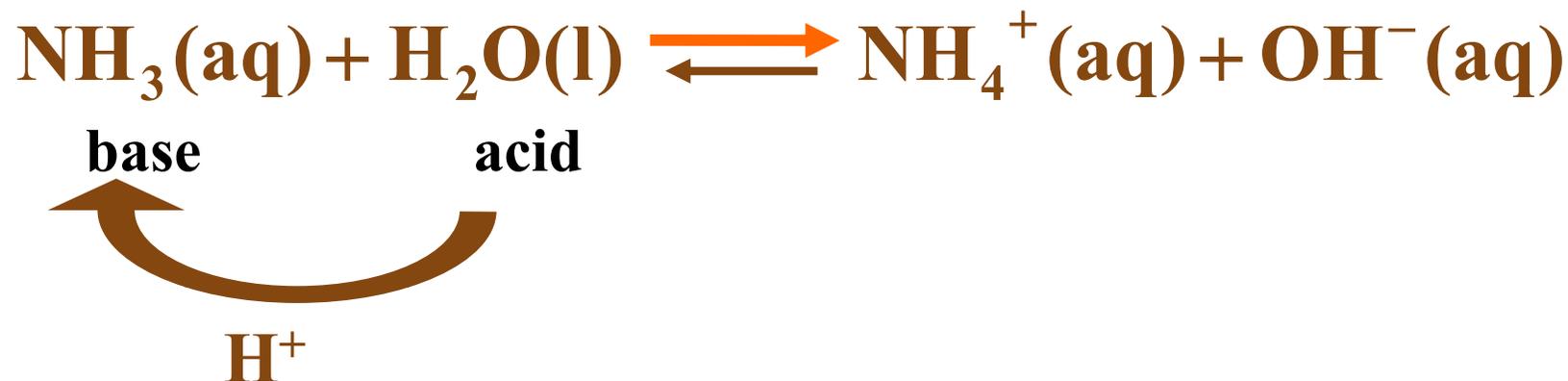
# Brønsted-Lowry Concept of Acids and Bases

- Consider the reaction of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ .  
Based on Arrhenius theory (produces  $\text{OH}^-$ )  
therefore  $\text{NH}_3$  is a base in water.



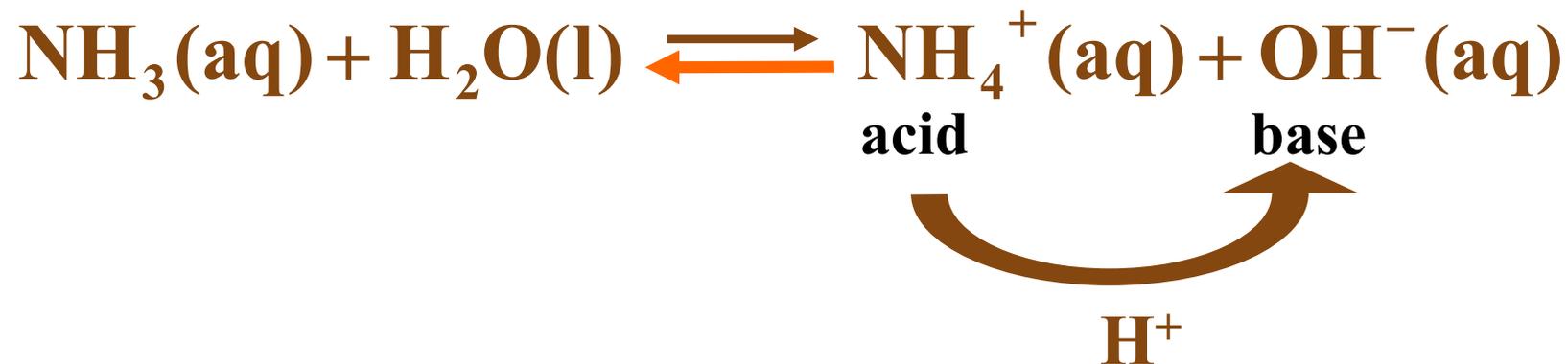
# Brønsted-Lowry Concept of Acids and Bases

- What is it by Bronsted-Lowry?



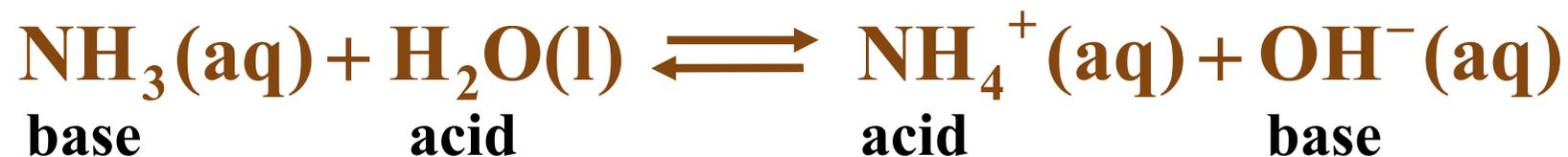
- In the **forward reaction**, NH<sub>3</sub> accepts a proton from H<sub>2</sub>O. Thus, NH<sub>3</sub> is a base and H<sub>2</sub>O is an acid. Same conclusion without looking at OH<sup>-</sup>

# Brønsted-Lowry Concept of Acids and Bases



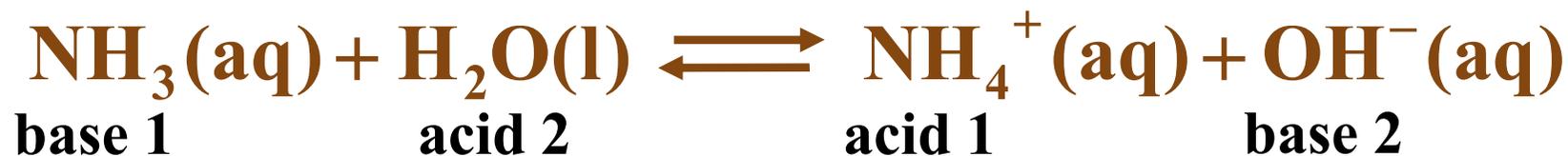
- Since this is a **reversible reaction**, there is also acid/base components on the reverse rxn.  $\text{NH}_4^+$  donates a proton to  $\text{OH}^-$ . **The  $\text{NH}_4^+$  ion is the acid and  $\text{OH}^-$  is the base.**

# Brønsted-Lowry Concept of Acids and Bases



- The species  $\text{NH}_4^+ / \text{NH}_3$  and  $\text{H}_2\text{O} / \text{OH}^-$  are conjugate acid-base pair.
- A **conjugate acid-base pair** consists of two species in an acid-base reaction, one acid and one base, that **differ by the loss or gain of one proton.**

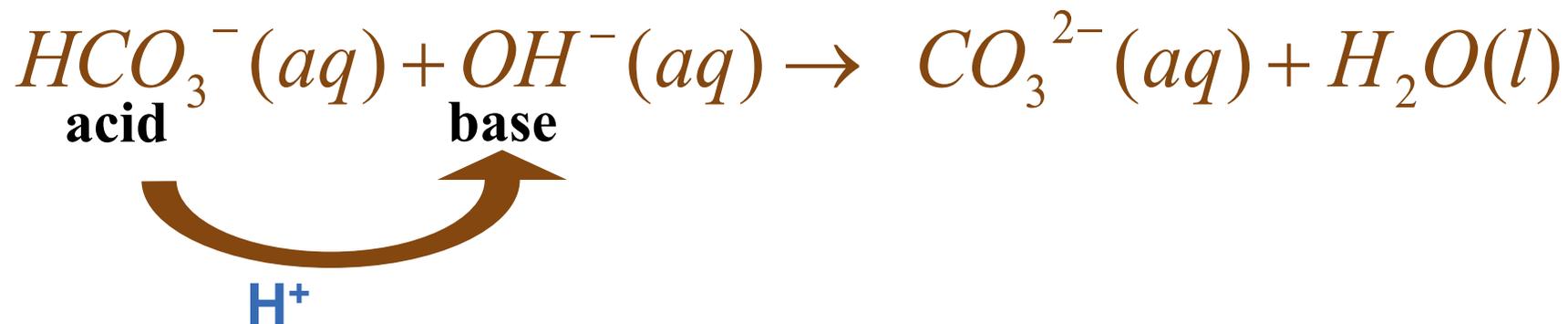
# Brønsted-Lowry Concept of Acids and Bases



- $\text{NH}_4^+$  is the conjugate acid of  $\text{NH}_3$  and  $\text{NH}_3$  is the conjugate base of  $\text{NH}_4^+$  ( $\text{NH}_4^+/\text{NH}_3$ ).  $\text{H}_2\text{O}$  is the conjugate acid of  $\text{OH}^-$  and  $\text{OH}^-$  is the conjugate base of  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}/\text{OH}^-$ ).
- The Brønsted-Lowry concept defines a species as an acid or a base according to its function in the proton-transfer reaction.

# Brønsted-Lowry Concept of Acids and Bases

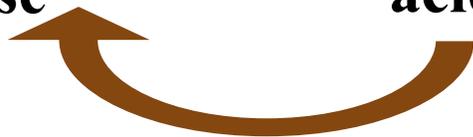
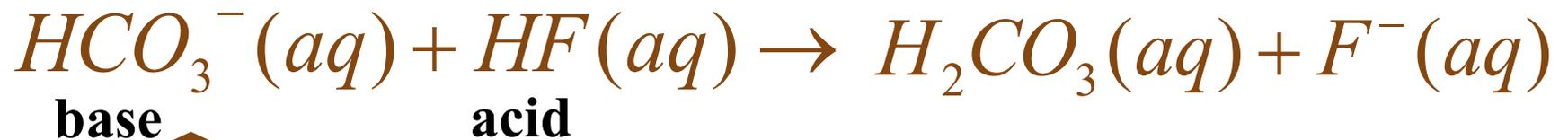
- Some species can act as an acid or a base.
  - An **amphoteric species** is a species that can act either as an acid or a base (it can gain or lose a proton).
  - For example,  $\text{HCO}_3^-$  acts as a proton donor (an acid) in the presence of  $\text{OH}^-$



- $\text{HCO}_3^-$  acid and  $\text{CO}_3^{2-}$  conj base
- $\text{OH}^-$  base and  $\text{H}_2\text{O}$  conj acid

# Brønsted-Lowry Concept of Acids and Bases

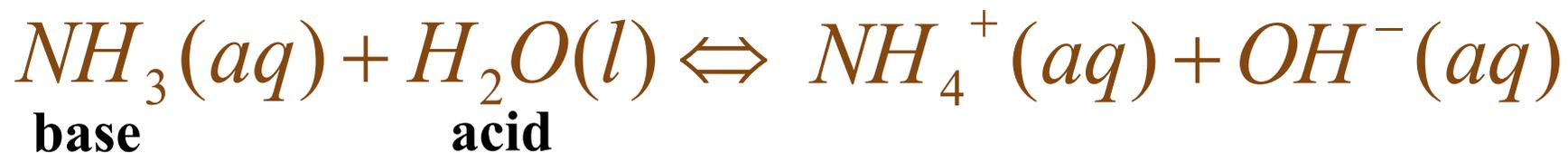
- Alternatively,  $\text{HCO}_3^-$  can act as a proton acceptor (a base) in the presence of HF. Proton acceptor and base in this reaction.  $\text{HCO}_3^-$  base,  $\text{H}_2\text{CO}_3$  conj acid, HF acid,  $\text{F}^-$  conj base



- $\text{HCO}_3^-$  base and  $\text{H}_2\text{CO}_3$  conj acid
- HF acid and  $\text{F}^-$  conj base

# Brønsted-Lowry Concept of Acids and Bases

- The amphoteric characteristic of water is important in the acid-base properties of aqueous solutions.
  - Water reacts as an acid with the base  $\text{NH}_3$ .



- $\text{NH}_3$  base and  $\text{NH}_4^+$  conj acid
- $\text{H}_2\text{O}$  acid and  $\text{OH}^-$  conj base



Amphoteric in H<sub>2</sub>O?

H<sub>2</sub>SO<sub>4</sub>      No, always strong acid in water

HSO<sub>4</sub><sup>-</sup>      yes

SO<sub>4</sub><sup>2-</sup>      No, always base in water

conj acid      conj base

HF      F<sup>-</sup>

HSO<sub>4</sub><sup>-</sup>      SO<sub>4</sub><sup>2-</sup>

H<sub>2</sub>SO<sub>4</sub>      HSO<sub>4</sub><sup>-</sup>

NH<sub>4</sub><sup>+</sup>      NH<sub>3</sub>

H<sub>2</sub>O      OH<sup>-</sup>

H<sub>3</sub>O<sup>+</sup>      H<sub>2</sub>O

# Brønsted-Lowry Concept of Acids and Bases

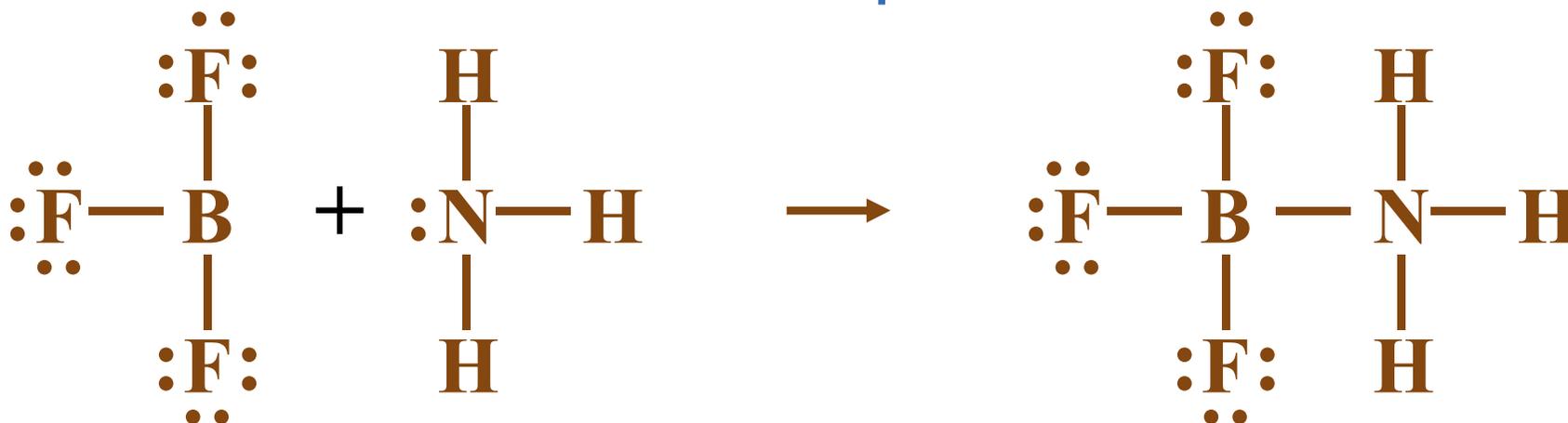
- In the Brønsted-Lowry concept:
  1. A base is a species that accepts protons;  $\text{OH}^-$  is only one example of a base.
  2. Acids and bases can be ions as well as molecular substances.
  3. Acid-base reactions are not restricted to aqueous solution but most of what we do will be.
  4. Some species can act as either acids or bases depending on what the other reactant is. Molecular species that we call acids and bases will always be that in water; water will be the other.

# The Lewis Definition

- The Lewis concept defines an **acid as an electron pair acceptor** and a **base makes available electron pair**.
  - This concept broadened the scope of acid-base theory to include reactions that did not involve  $H^+$ .
  - The Lewis concept embraces many reactions that we might not think of as acid-base reactions. Most useful definition.

# Lewis Concept of Acids and Bases

- The reaction of boron trifluoride with ammonia is an example.



- Boron trifluoride accepts the electron pair, so it is a **Lewis acid**. Ammonia makes available the electron pair, so it is the **Lewis base**.

# Acids and Bases Strengths

- The Brønsted-Lowry concept introduced the idea of **conjugate acid-base pairs** and proton-transfer reactions.
  - We consider such acid-base reactions to be a competition between species for hydrogen ions.
  - The stronger acids are those that lose their hydrogen ions more easily than other acids; donate proton quicker.
  - From this point of view, **we can order acids by their relative strength as hydrogen ion donors.**
  - Similarly, the stronger bases are those that hold onto hydrogen ions more strongly than other bases; harder to lose proton.

Bottom line:

easier give up proton, stronger the acid

harder to give up proton, stronger the base.



# Strengths of Binary Acids, Oxoacids, and Polyprotic Acids

- How do we determine the strength of acids/bases that are in the same class (all strong or weak). Two factors are important in determining the relative acid strengths.

- One is the polarity of the bond to which the hydrogen atom is attached.

- The H atom has a partial positive charge:



- The more polarized (larger EN difference) the bond, the more easily the proton is removed and the greater the acid strength.

# Molecular Structure and Acid Strength

- The second factor is the strength of the bond or, in other words, how tightly the proton is held.
- This depends on the size,  $d$ , of atom X.



- The larger atom X, the weaker the bond and the greater the acid strength. (less attraction between atoms, easier to pull off proton).

Larger EN difference and size of anion,  
stronger the acid (easier to pull proton off)

# Molecular Structure and Acid Strength

- Consider a series of binary acids from a given column of elements.
  - Let's predict the following order of acidic strength.
  - As you go down the column of elements, the radius increases markedly and dictates result (adding shell further away) and the H-X bond strength decreases.

smaller radius, harder  
ionize, weakest acid

larger radius, easiest  
ionize, strongest acid



Aqueous soln:



This acid strength for the strong acids does not hold true for water as the solvent. Remember that we discussed earlier that some acids are strong and others are weak. The strength is related to the amount it ionizes . In water, the strong acids/bases ionize 100% meaning these species break up 100%. All these acids look the same in water which is called the "leveling effect" of water. The tendency of a solvent to accept or donate protons determines the strength of a solute acid or base dissolved in it. The strong species all completely ionize and are the same strength.

–  $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$  If 1M solution, 0M HCl and 1M hydronium

– both strong acid

–  $\text{HBr} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Br}^-$  If 1M solution, 0M HBr and 1M hydronium

– Therefore strongest acid in water is hydronium ion and strongest base hydroxide ion. However, in another organic solvent you would find that based on bond strengths (radius) that HBr would ionize more (easier) than HCl and is truly the stronger acid but in water there is no difference in ionization therefore same strength hence "leveling effect" of water.

## Molecular Structure and Acid Strength

- As you go across a row of elements, the polarity of the H-X bond becomes the dominant factor.
  - As electronegativity increases going to the right, the polarity of the H-X bond increases by large amount as compare to change in size and the acid strength increases.
  - Let's predict the following order of acidic strength.

smaller EN diff, harder  
ionize, weakest acid

larger EN diff, easiest  
ionize, strongest acid



- note: ammonium typically base in water

# Molecular Structure and Acid Strength

- Consider the oxoacids. An oxoacid has the structure:



- The acidic H atom is always attached to an O atom
- Bond polarity is the dominant factor in the relative strength of oxoacids.
- This, in turn, depends on the electronegativity of the atom Y.

# Molecular Structure and Acid Strength



- If the electronegativity of Y is large, then the O-H bond is relatively polar and the acid strength is greater. Easier to remove proton, stronger acid
- Let's predict the following order of acidic strength.



Larger EN , easiest  
ionize, strongest acid

smallest EN diff, hardest  
ionize, weakest acid

# Molecular Structure and Acid Strength

- With each additional O atom, Y becomes effectively more electronegative.



- As a result, the H atom becomes more acidic as more O are on the species.
- The acid strengths of the oxoacids of chlorine increase in the following order.



- another way to look at it is charge on Y gets higher stronger pull on O and weakens O-H bond, easier to remove

# Molecular Structure and Acid Strength

- Consider polyprotic (more than one ionizable proton) acids and their corresponding anions.
  - Each successive H atom becomes more difficult to remove (species is negatively charged therefore harder to pull positive proton off).
  - Therefore the acid strength of a polyprotic acid and its anions decreases with increasing negative charge.



# Autoionization of Water

- **Self-ionization** is a reaction in which two like molecules react to give ions (amphiprotic therefore can react with self)
  - In the case of water, the following equilibrium is established.

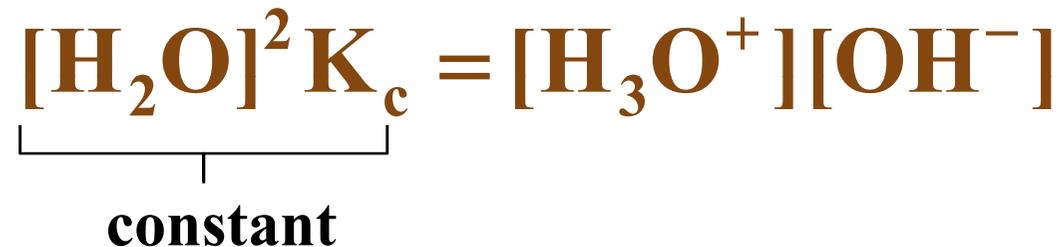


- The equilibrium-constant expression for this system is:

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

# Self-ionization of Water

- The concentration of ions is extremely small (equil lies to far left), so the concentration of H<sub>2</sub>O remains essentially constant. This gives:



and fact pure liquid activity 1 in K

# Self-ionization of Water



- We call the equilibrium value for the ion product  $[\text{H}_3\text{O}^+][\text{OH}^-]$  the **ion-product constant for water**, which is written  $K_w$ .

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

- At 25 °C, the **value of  $K_w$  is  $1.0 \times 10^{-14}$** .
- Like any equilibrium constant,  $K_w$  varies with temperature.  $K_w$  means water + water and basis of acid/base scale in aqueous solutions



# Self-ionization of Water

- These ions are produced in equal numbers in pure water, so if we let  $x = [H^+] = [OH^-]$

$$1.0 \times 10^{-14} = x^2 \quad \text{at } 25 \text{ } ^\circ\text{C}$$

$$x = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M} = [H_3O^+] = [OH^-]$$

- Thus, the concentrations of  $H^+$  and  $OH^-$  in pure water are both  $1.0 \times 10^{-7} \text{ M}$ . Baseline for what we call a neutral solution with water as solvent.
- If you add acid or base to water they are no longer equal but the  $K_w$  expression still holds. One goes up other goes down to keep product equal to  $K_w$

# Solutions of Strong Acid or Base

- In a solution of a strong acid you can normally ignore the self-ionization of water as a source of  $\text{H}^+(\text{aq})$ . You have the self ionization equil and the strong acid ionization; however one drop of strong acid ionizes 100% and typically produces far greater amount of hydronium ion than that produced from water itself.
  - The  $\text{H}^+(\text{aq})$  concentration is usually determined by the strong acid concentration.
  - However, the self-ionization still exists and is responsible for a small concentration of  $\text{H}_3\text{O}^+$  ion but we typically neglect it.

# Solutions of Strong Acid or Base

- By dissolving substances in water, you can alter the concentrations of  $H^+(aq)$  and  $OH^-(aq)$ .
  - In a **neutral solution**, the concentrations of  $H^+(aq)$  and  $OH^-(aq)$  are **equal**, as they are in pure water.
$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} M$$
  - In an **acidic solution**, the concentration of  $H^+(aq)$  is greater than that of  $OH^-(aq)$ .  $[H_3O^+] > 1.0 \times 10^{-7} M > [OH^-]$
  - In a **basic solution**, the concentration of  $OH^-(aq)$  is greater than that of  $H^+(aq)$ .  $[H_3O^+] < 1.0 \times 10^{-7} M < [OH^-]$

# Solutions of Strong Acid or Base

- At 25°C, you observe the following conditions.
  - In an acidic solution,  $[H^+] > 1.0 \times 10^{-7} \text{ M}$ .
  - In a neutral solution,  $[H^+] = 1.0 \times 10^{-7} \text{ M}$ .
  - In a basic solution,  $[H^+] < 1.0 \times 10^{-7} \text{ M}$ .

Realize these definitions for acid/base/neutral solutions is based as water as solvent. If different solvent or temperature, the concentration would be different.

# pH

- Although you can quantitatively describe the acidity of a solution by its  $[H^+]$ , it is often more convenient to give acidity in terms of pH (power of the hydrogen ion). Easier to see larger value:  $10^{-7}$  vs  $10^{-8}$ 
  - The **pH** of a solution is defined as the negative logarithm of the molar hydrogen-ion concentration.
  - Basically changing  $1.0 \times 10^{-7}$  M to log scale.  
 $1.0$  number indicates where between the  $10^{-6}$  and  $10^{-7}$  -->  $7.00$

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

# The pH of a Solution

- For a solution in which the hydrogen-ion concentration is  $1.0 \times 10^{-3}$  M, the pH is:

$$pH = -\log(1.0 \times 10^{-3}) = 3.00$$

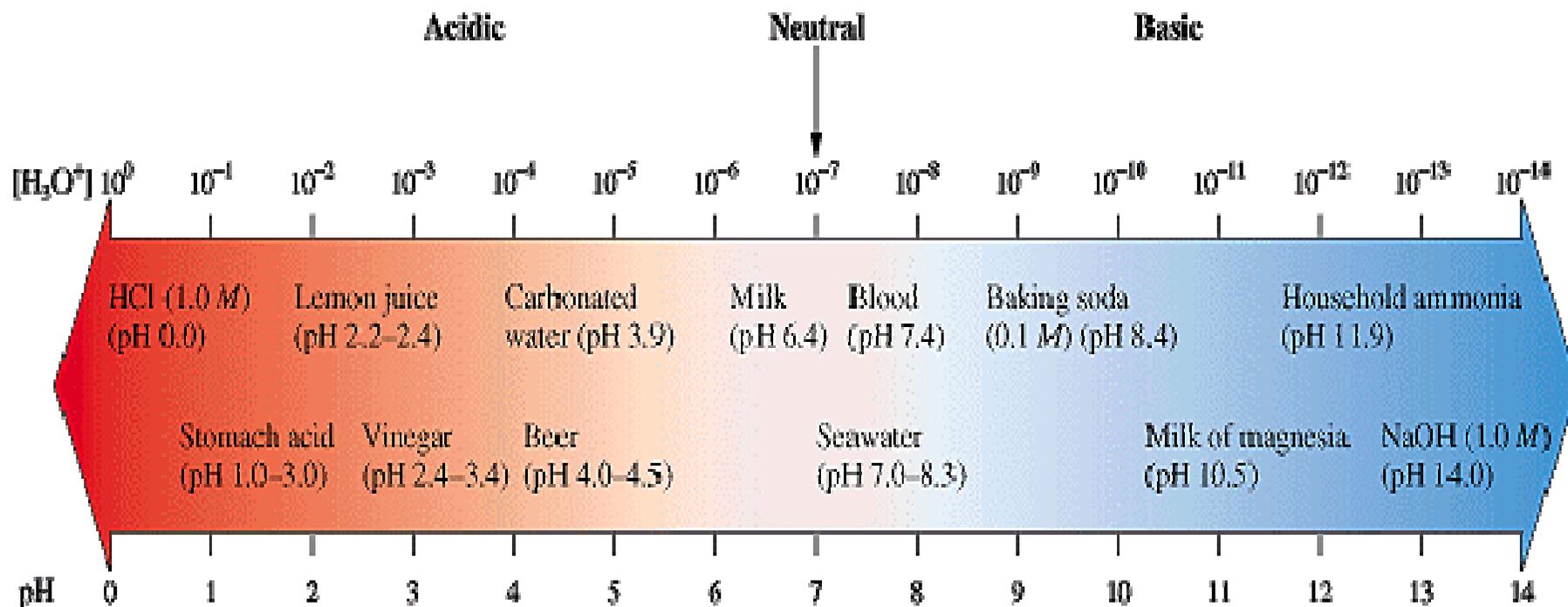
- Note that the number of decimal places in the pH equals the number of significant figures in the hydrogen-ion concentration.

note:  $[H_3O^+] \uparrow$       pH  $\downarrow$

# The pH of a Solution

- In a **neutral solution**, whose hydrogen-ion concentration is  $1.0 \times 10^{-7}$  M, the **pH = 7.00**.
- For **acidic solutions**, the hydrogen-ion concentration is greater than  $1.0 \times 10^{-7}$  M, so the **pH is less than 7.00**.
- Similarly, a **basic solution** has a **pH greater than 7.00**.
- Realize pH scale is greater than 14 and less than 0 and that it is dependent on solvent being water; different solvent different scale; not necessarily neutral equal 7 with different solvent. Also lower pH more acidic solution not necessarily stronger acid. Strength is based on ionization not pH although pH affected by strength. Weaker acid can have lower pH if have much higher conc.

# The pH Scale



## A Problem to Consider

- A sample of orange juice has a hydrogen-ion concentration of  $2.9 \times 10^{-4}$  M. What is the pH?

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

$$\text{pH} = -\log(2.9 \times 10^{-4})$$

$$\text{pH} = 3.54$$

## A Problem to Consider

- The pH of human arterial blood is 7.40. What is the hydrogen-ion concentration?
- calculator 2nd function log

$$[\text{H}^+] = 10^{-\text{pH}}$$

$$[\text{H}^+] = \text{anti log}(-\text{pH})$$

$$[\text{H}^+] = \text{anti log}(-7.40)$$

$$[\text{H}^+] = 10^{-7.40} = 4.0 \times 10^{-8} \text{ M}$$

## pOH

- A measurement of the hydroxide ion concentration, similar to pH, is the pOH.
  - The **pOH** of a solution is defined as the negative logarithm of the molar hydroxide-ion concentration.

$$pX = -\log[X]$$

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

$$[OH^-] = 10^{-pOH}$$

# The pH of a Solution

- Using  $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$  at 25 °C, we can show another important eq

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

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

$$-\log K_w = -\log 1.0 \times 10^{-14} = -\log[H^+] + (-\log[OH^-])$$

$$pK_w = 14.00 = pH + pOH$$

$$[H^+] = 10^{-pH}$$

$$[OH^-] = 10^{-pOH}$$

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

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

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

## A Problem to Consider

- An ammonia solution has a hydroxide-ion concentration of  $1.9 \times 10^{-3}$  M. What is the pH of the solution?

You first could calculate the pOH:

$$pOH = -\log(1.9 \times 10^{-3}) = 2.72$$

Then the pH is:  $pH = 14.00 - 2.72 = 11.28$

Optional way:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-3}} \\ = 5.26 \times 10^{-12} \text{ M}$$

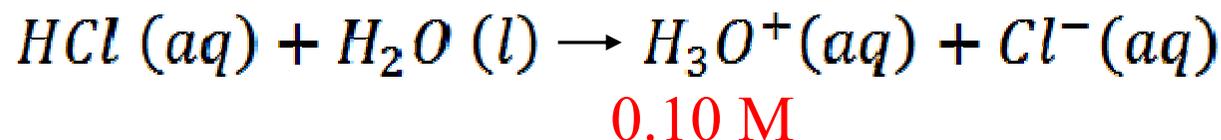
$$pH = -\log 5.26 \times 10^{-12} = 11.28$$

# The pH of a Solution

- The pH of a solution can accurately be measured using a pH meter.
  - Although less precise, acid-base indicators are often used to measure pH because they usually change color within a narrow pH range.

## pH of Strong Acids or Bases

- Calculate the  $[H_3O^+]$ ,  $[OH^-]$ , pH, and pOH in 0.10 M HCl.



$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

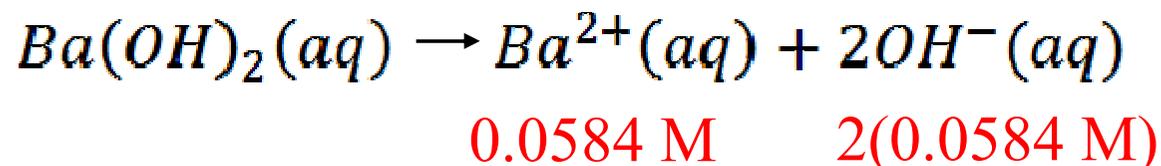
$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.10}$$
$$= 1.0 \times 10^{-13} \text{ M}$$

$$pH = -\log[H_3O^+] = -\log 0.10 = 1.00$$

$$pOH = 14.00 - pH = 14.00 - 1.00 = 13.00$$

- Ex. Calculate the  $[H_3O^+]$ ,  $[OH^-]$ , pH, and pOH in solution prepared by dissolving 10.0g of  $Ba(OH)_2$  per liter.

$$[Ba(OH)_2] = \frac{10.0g}{1.0L} \times \frac{1 \text{ mol}}{171.3 \text{ g}} = 0.0584M$$



$$[OH^-] = 2(0.0584) = 0.117M$$

$$pOH = -\log[OH^-] = -\log[0.117] = 0.932$$

$$pH = 14.00 - pOH = 14.00 - 0.932 = 13.07$$

$$[H^+] = 10^{-pH} = 10^{-13.07} = 8.5 \times 10^{-14} M$$

**Thank you**