PART I: Acids & Bases

- Several concepts of acid-base theory:

The Arrhenius concept

The Bronsted-Lowry concept

The Lewis concept

Acids & Bases

- According to the Arrhenius concept of acids and bases

  An acid is a substance that, when dissolved in water, increases the concentration of Hydrogen ion, $H^+(aq)$

- The $H^+(aq)$ ion, called the Hydrogen ion is actually chemically bonded to water, that is, H_3O^+, called the Hydronium ion

  A base is a substance that when dissolved in water increases the concentration of the Hydroxide ion, $OH^-(aq)$

Acids & Bases

- An Arrhenius acid is any substance which ***increases*** the concentration of Hydrogen ions (H^+) in solution. Acids generally have a sour taste

$$\mathbf{HBr(aq) \rightarrow H^+(aq) + Br^-(aq)}$$

- An Arrhenius base is any substance which ***increases*** the concentration of Hydroxide ions (OH^-) in solution. Bases generally have a bitter taste

$$\mathbf{KOH(s) \rightarrow K^+(aq) + OH^-(aq)}$$

- Hydrogen and Hydroxide ions are important in aqueous solutions because - Water reacts to form both ions

$$\mathbf{H_2O(l) \leftrightarrow H^+(aq) + OH^-(aq)}$$

- HBr and KOH are examples of a ***strong acid*** and a ***strong base***; strong acids & bases dissociate completely

Acids & Bases

- Monoprotic acids are those acids that are able to donate one proton per molecule during the process of dissociation (sometimes called ionization) as shown below (symbolized by HA):

  $$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

  Common examples of monoprotic acids in mineral acids include Hydrochloric Acid (HCl) and Nitric Acid (HNO_3)

- Polyprotic acids are able to donate more than one proton per acid molecule.
  - Diprotic acids have two potential protons to donate

    $$H_2A(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HA^-(aq)$$

  - Triprotic acids have three potential protons to donate

    $$H_3A(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2A^-(aq)$$

Acids & Bases

- Oxoacids
  - Oxoacids with one oxygen have the structure: HOY

    HOCl HOBr HOI

  - Oxoacids with multiple oxygen have the structure:

    $(OH)_mYO_n$

$HOClO_3$ $(HClO_4)$ $HOClO_2$ $(HOCLO_3)$

$HOClO$ $(HCLO_2)$ HOCL (HClO)

The more oxygen atoms, the <u>greater the acidity</u>; thus $HOCLO_3$ is a stronger acid than HOCl

<u>Acidity</u> refers to the relative <u>acid strength</u>, i.e. the degree to which the acid <u>dissociates</u> to form H^+ (H_3O^+) & OH^-

Bronsted-Lowry Acids & Bases

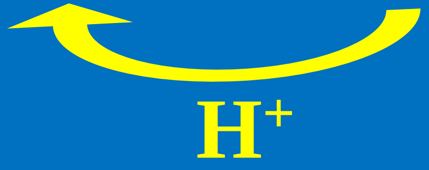
- Brønsted-Lowry Concept of Acids and Bases
  - In the Brønsted-Lowry concept:
    - An Acid is a species that <u>donates protons</u>
    - A Base is a species that <u>accepts protons</u>
    - Acids and bases can be ions as well as molecular substances
    - Acid-base reactions are not restricted to aqueous solution
    - Some species can act as either acids or bases (Amphoteric species) depending on what the other reactant is

Bronsted-Lowry Acids & Bases

- Amphoteric Species
  - A species that can act as either an acid or base is:

    Amphoteric
  - Water is an important amphoteric species in the acid-base properties of aqueous solutions
    - Water can react as an acid by donating a proton to a base

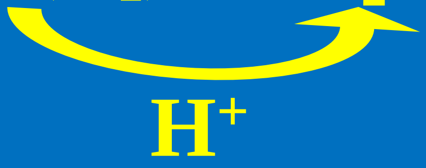
$$\mathbf{NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)}$$



$\mathbf{H^+}$

    - Water can also react as a base by accepting a proton from an acid

$$\mathbf{HF(aq) + H_2O(l) \rightarrow \mathit{F}^-(aq) + H_3O^+(aq)}$$



$\mathbf{H^+}$

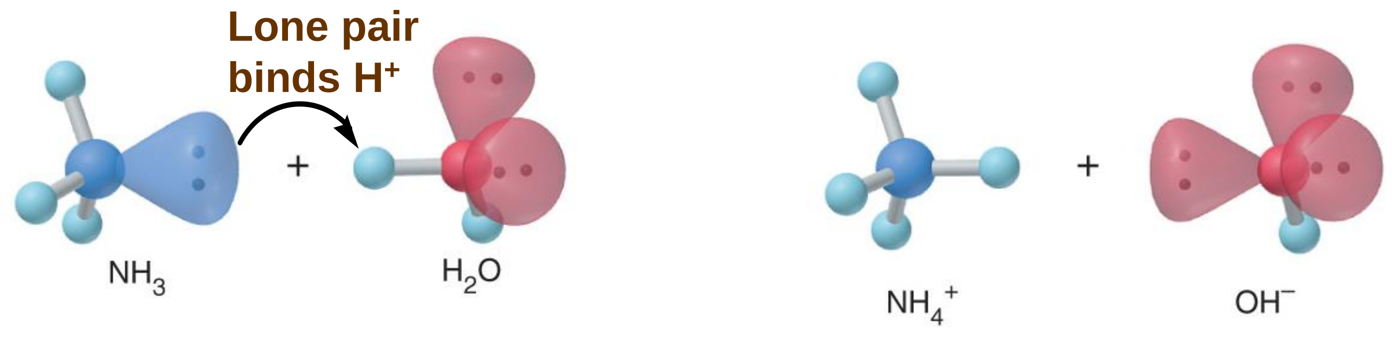
Bronsted-Lowry Acids & Bases

- Brønsted-Lowry Concept of Acids and Bases

Proton transfer as the essential feature of a Brønsted-Lowry acid-base reaction

Acid
H^+ donor

Base
H^+ acceptor



Base
H^+ acceptor

Acid
H^+ donor

Acids & Bases

- **Bronsted-Lowery Concept – Conjugate Pairs**
  - In Bronsted theory, acid and base reactants form:

<u>Conjugate Pairs</u>

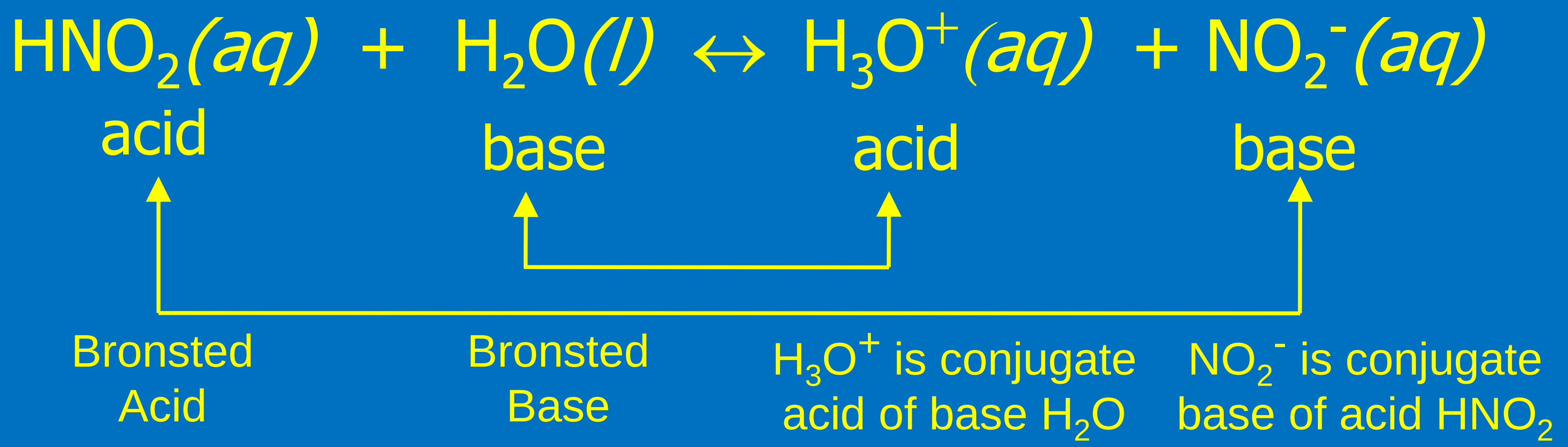
  - The acid (HA) donates a proton to water leaving the conjugate Base (A^-)
  - The base (H_2O) accepts a proton to form the conjugate acid (H_3O^+)

$$HA(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad A^-(aq) \quad + \quad H_3O^+(aq)$$

Acid	Base	Conjugate Base	Conjugate Acid

Bronsted-Lowry Acids & Bases

Bronsted-Lowery Acid-Base Conjugate Pairs



$$HNO_2(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + NO_2^-(aq)$$

Bronsted Acid

Bronsted Base

H_3O^+ is conjugate acid of base H_2O

NO_2^- is conjugate base of acid HNO_2

- Conjugate acid-base pairs are shown connected
- Every acid has a conjugate base
- Every base has a conjugate acid
- The conjugate base has one fewer H and one more "minus" charge than the acid
- The conjugate acid has one more H and one fewer minus charge than the base

Bronsted-Lowry Acids & Bases

- Bronsted-Lowery Acid-Base Conjugate Pairs

$$NH_3(aq) \quad + \quad H_2O(l) \quad \leftrightarrows \quad NH_4^{+}\square aq) \quad + \quad OH^{-}(aq)$$

base acid acid base

Bronsted Base	Bronsted Acid	NH_4^+ is conjugate acid of base NH_3	OH^- is conjugate base of acid H_2O
Accepts Proton	Donates Proton		

Bronsted-Lowry Acids & Bases

Bronsted-Lowery Acid-Base Conjugate Pairs

acid base acid base

$$H_2S \quad + \quad NH_3 \quad \leftrightarrows \quad NH_4^+ \quad + \quad HS^-$$

Bronsted Acid

Donates Proton

Bronsted Base

Accepts Proton

NH_4^+ is conjugate acid of base NH_3

HS^- is conjugate Base of acid H_2S

Bronsted-Lowry Acids & Bases

- Bronsted_Lowry Concept – **The Leveling Effect**
  - All Bronsted_Lowry acids yield H_3O^+ ions (Cation)
  - All Bronsted_Lowry bases yield OH^- ions (Anion)
  - All strong acids are equally strong because all of them form the strongest acid possible - H_3O^+
  - Similarly, all strong bases are equally strong because they form the strongest base possible - OH^-
  - Strong acids and bases dissociate completely yielding H_3O^+ and OH^-
  - Any acid stronger than H_3O^+ simply donates a proton to H_2O
  - Any base stronger than OH^- simply accepts proton from H_2O
  - Water exerts a leveling effect on any strong acid or base by reacting with it to form water ionization products

Practice Problem

- Identify the conjugate acid-base pairs in the following:

$H_2PO_4^-(aq) + CO_3^{-2}(aq)$ □ $HCO_3^-(aq) + HPO_4^{2-}(aq)$

Base

Conjugate Acid

Acid

Conjugate base

$H_2PO_4^-$ has one more H^+ than HPO_4^{2-} and

CO_3^{2-} has one fewer H^+ than HCO_3^-

$H_2PO_4^-$ & HCO_3^- are acids

HPO_4^{2-} & CO_3^{2-} are bases

$H_2PO_4^- / HPO_4^{2-}$ is a conjugate acid-base pair

HCO_3^- / CO_3^{2-} is a conjugate acid-base pair

Lewis Acids & Bases

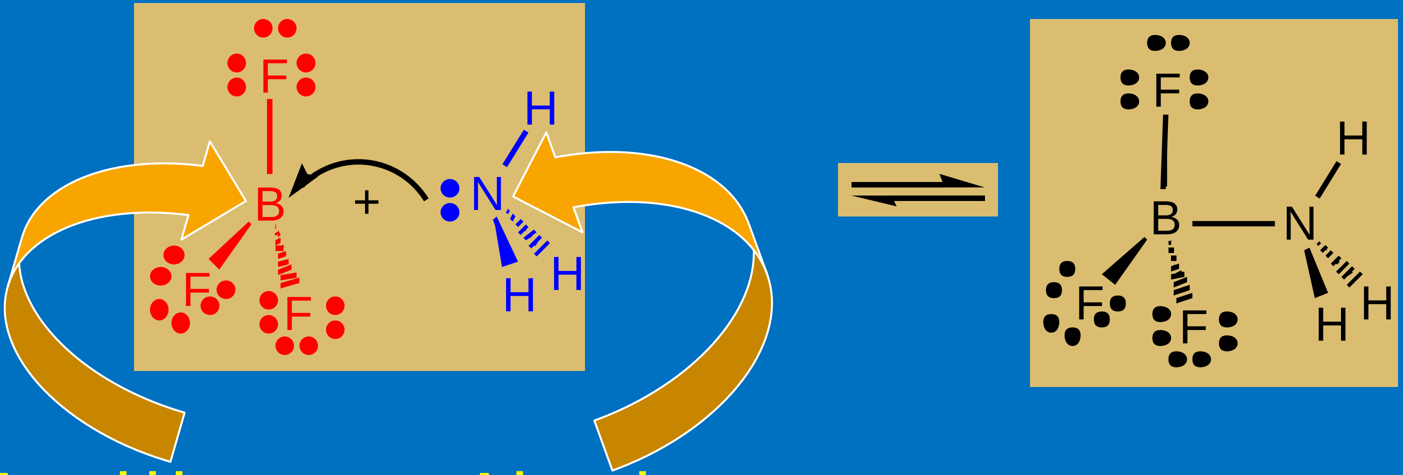
- **Lewis Acids & Bases**
  - Some acid base reactions don’t fit the Bronsted-Lowry or Arrhenius classifications
  - The Lewis acid-base concepts expands the acid class
  - Such reactions involve a “sharing” of electron pairs between atoms or ions
  - Lewis Acid – An electron deficient species (Electrophile) that accepts an electron pair
  - Lewis Base – An electron rich species (Nucleophile) that donates an electron pair

Lewis Acids & Bases

- **Lewis Acids & Bases**
- The product of any Lewis acid-base reaction is called an "Adduct", a single species that contains a new covalent bond (shared electron pair)

$$\mathbf{A^{+} \quad + \quad :B \quad \rightarrow \quad A-B}$$

Acid (Electrophile) **Base (Nucleophile)** **Adduct**



An acid is an electron-pair acceptor

A base is an electron-pair donor

Adduct

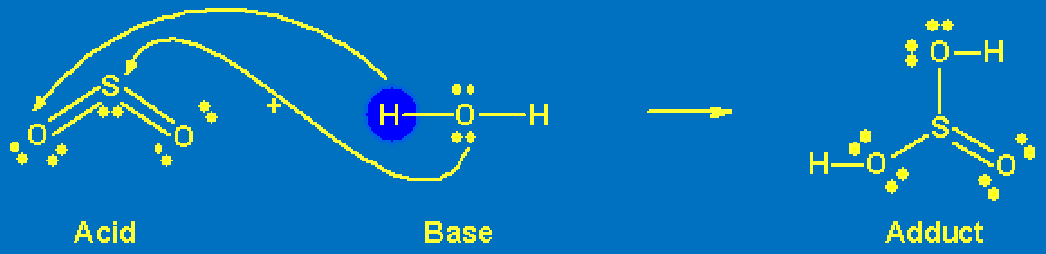
Lewis Acids & Bases

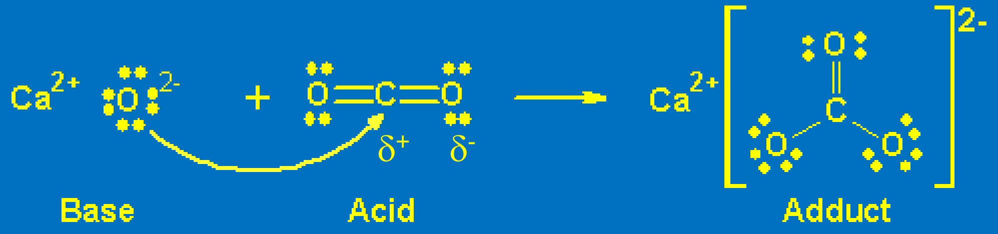
- Species that do not contain Hydrogen in their formulas, such as CO_2 and Cu^{++} function as Lewis acids by accepting an electron pair
- The donated proton of a Bronsted-Lowry acid acts as a Lewis acid by accepting an electron pair donated by the base:
  - The Lewis acids are Yellow and the Lewis bases are Blue in following reaction

$$BF_3 \quad + \quad {:}NH_3 \quad \leftrightarrow \quad BF_3NH_3$$

$$Fe^{3+} \quad + \quad 6\ H_2O \quad \leftrightarrow \quad Fe(H_2O)_6{}^{3+}$$

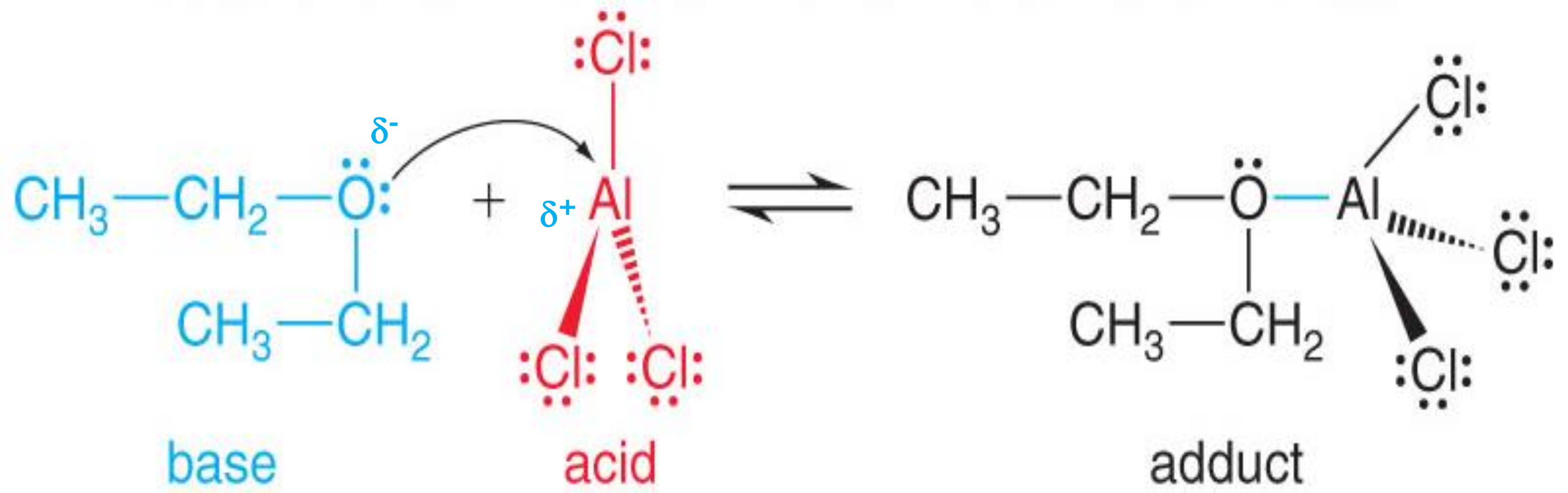
$$HF \quad + \quad H_2O \quad \leftrightarrow \quad F^- \ + \ H_3O^+$$





Lewis Acids & Bases

- Solubility Effects
  - A Lewis acid-base reaction between nonpolar Diethyl Ether and normally insoluble Aluminum Chloride



  - The solubility of Aluminum Chloride in Dimethyl Ether results from the Oxygen acting as a base by donating an electron pair to the Aluminum acting as an acid forming a water-soluble polar covalent bond

PART II: Acids & Bases

- Self Ionization of Water
- Pure water undergoes auto-ionization to produce Hydronium and Hydroxide ions

$$2\,H_2O(l) \leftrightarrow H_3O^+(aq) + OH^-(aq)$$

- The extent of this process is described by an auto-ionization (ion-product) constant, K_w

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

- The concentrations of Hydronium and Hydroxide ions in any aqueous solution must obey the auto-ionization equilibrium
- Classification of solutions using K_w:

Acidic: $[H_3O^+] > [OH^-]$

Basic: $[H_3O^+] < [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Acids & Bases

- Because of the auto-ionization constant of water, the amounts of Hydronium and Hydroxide ions are always related
  - For example, pure water at 25 °C,

$$K_w = [H_3O^+][OH^-] = 1.0\times 10^{-14}$$
$$[H_3O)^+] = [OH^-] = 1.0\times 10^{-7}$$

- The Definition of pH
  - The amount of Hydronium ion (H_3O^+) in solution is often described by the pH of the solution

$$pH = -\log[H_3O^+]$$
$$[H_3O^+] = 1\times 10^{-pH}$$

- The Definition of pOH
  - Hydroxide (OH^-) can be expressed as pOH

$$pOH = -\log_{10}[OH^-]$$
$$[OH^-] = 1\,x\,10^{-pOH}$$

Acids & Bases

- pH scale ranges from 0 to 14
  - The pH of pure water = -log(1.00×10^{-7}) = 7.00

    pH = 0.00 - 6.999^{+} = acidic $[H_3O^+] > [OH^-]$

    pH = 7.00 = neutral $[H_3O^+] = [OH^-]$

    pH = 7.00^{+} - 14.00 = basic $[H_3O^+] < [OH^-]$
  - Acidic solutions have a lower pH (higher $[H_3O^+]$ and a higher pOH (lower $[OH^-]$ than basic solutions

Acids & Bases

- Relations among pH, pOH, and pK_w

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

$$-\log(K_w) = -\log([H_3O^+][OH^-]) = -\log(1 \times 10^{-14})$$

$$-\log(K_w) = -\log[H_3O^+] - \log[OH^-] = -\log(1 \times 10^{-14})$$

$$pK_w = pH + pOH = 14 \quad (\text{at } 25^{o}C)$$

Equilibrium & Acid-Base Conjugates

- Equilibrium Constants (K) for acids & bases can also be expressed as pK
  - Reaction of an Acid (HA) with water as a base

$HA(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	$+$	A^-
Acid		**Base**		**Conjugate Acid**		**Conjugate Base**

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad pK_a = -\log_{10}[K_a]$$

  - Reaction of a Base (A^-) with water as an acid

$A^-(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$HA(aq)$	$+$	$OH^-(aq)$
Base		**Acid**		**Conjugate Acid**		**Conjugate Base**

$$K_b = \frac{[HA][OH^-]}{[A^-]} \qquad pK_b = -\log_{10}[K_b]$$

Equilibrium & Acid-Base Conjugates

- Relationship between:

K_a and HA

K_b and A^-

- Setup two dissociation reactions:

$$\begin{array}{rcl} \cancel{HA} + H_2O & \rightleftharpoons & H_3O^+ + \cancel{A^-} \\ \cancel{A^-} + H_2O & \rightleftharpoons & \cancel{HA} + OH^- \\ \hline 2H_2O & \rightleftharpoons & H_3O^+ + OH^- \end{array}$$

(autoionization)

- The sum of the two dissociation reactions is the autoionization of water
- The overall equilibrium constant is the product of the individual equilibrium constants

$$\frac{[H_3O^+][\cancel{A^-}]}{[\cancel{HA}]} \times \frac{[\cancel{HA}][OH^-]}{[\cancel{A^-}]} = [H_3O^+][OH^-]$$

$$K_a \times K_b = K_w$$

Equilibrium & Acid-Base Conjugates

$$K_w = K_a \times K_b$$

$$-\log(K_w) = -\log([K_a][K_b])$$

$$-\log(K_w) = -\log[K_a] - \log[K_b]$$

$$pK_w = pK_a + pK_b = 14 \quad (\text{at } 25^{o}\text{C})$$

$$pK_w = pH + pOH = 14 \quad (\text{at } 25^{o}\text{C})$$

- From this relationship, K_a of the acid in a conjugate pair can be computed from K_b and vice versa
- Reference tables typically have K_a & K_b values for molecular species, but not for ions such as F- or $CH_3NH_3^+$

Equilibrium & Acid-Base Conjugates

- Acid strength [H_3O^+] increases with increasing value of K_a

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base strength [OH^-] increases with increasing value of k_b

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

- A low pK corresponds to a high value of K

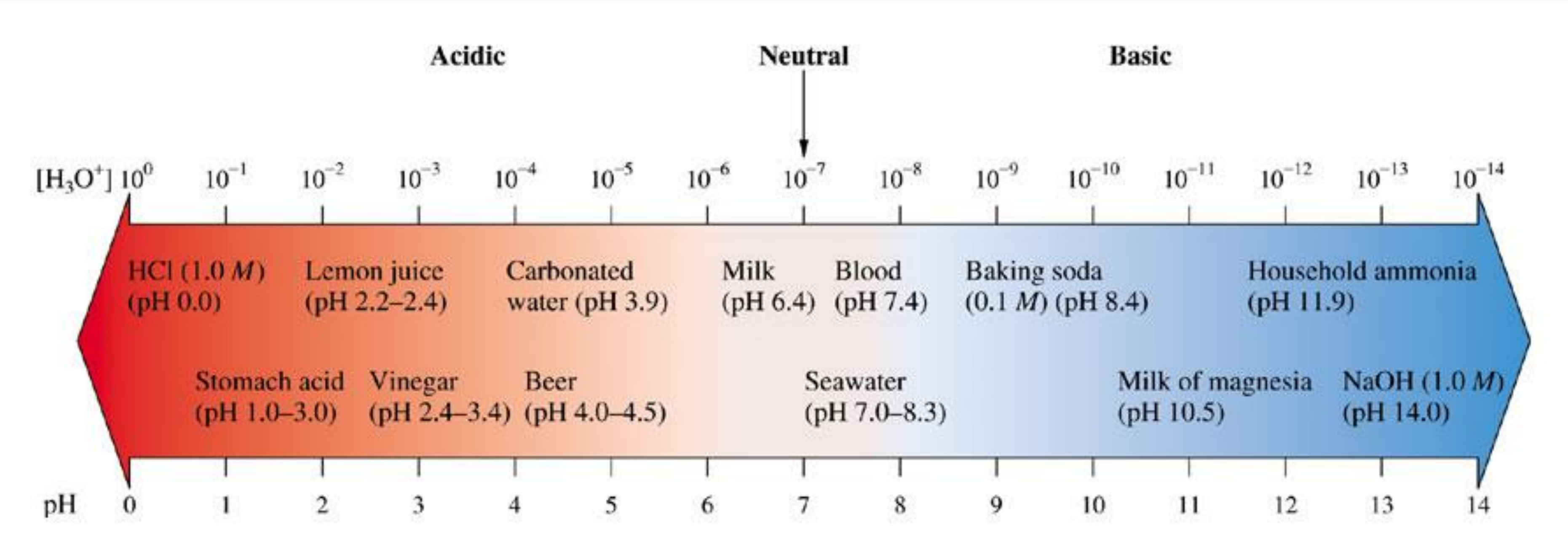
$$pK_a = -\log_{10}[K_a]$$

$$pK_b = -\log_{10}[K_b]$$

- A reaction that reaches equilibrium with mostly products present (proceeds to far right) has a "low pK" (high K)

Acids & Bases

The pH Scale



PART III: Acids & Bases

- Strong Acids & Bases
  - Strong acids and bases dissociate completely in aqueous solutions

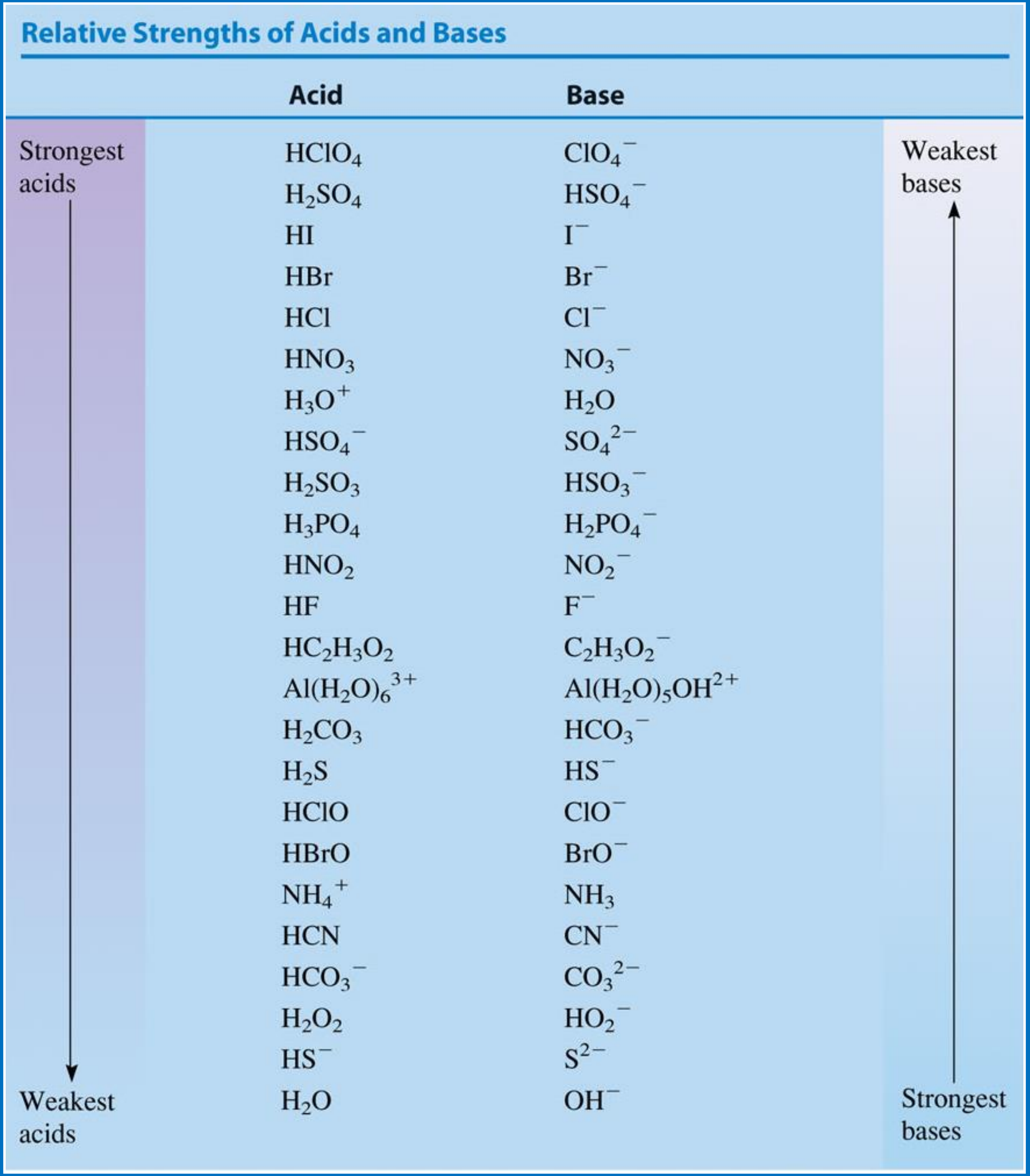
    Strong acids: HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$

    Strong bases: all Group I & II Hydroxides

    NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$
  - The term strong has nothing to do with the concentration of the acid or base, but rather the extent of dissociation
  - In the case of HCl, the dissociation lies very far to the right because the conjugate base (Cl^-) is extremely weak, much weaker than water

    $$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
  - H_2O is a much stronger base than Cl^- and "out competes it" for available protons

Acids & Bases



Relative Strengths of Acids and Bases

	Acid	Base	
Strongest acids	$HClO_4$	ClO_4^-	Weakest bases
	H_2SO_4	HSO_4^-	
	HI	I^-	
	HBr	Br^-	
	HCl	Cl^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HNO_2	NO_2^-	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	$Al(H_2O)_6^{3+}$	$Al(H_2O)_5OH^{2+}$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$HClO$	ClO^-	
	$HBrO$	BrO^-	
	NH_4^+	NH_3	
	HCN	CN^-	
	HCO_3^-	CO_3^{2-}	
	H_2O_2	HO_2^-	
	HS^-	S^{2-}	
Weakest acids	H_2O	OH^-	Strongest bases

Activity Series

Strengths of acids and bases

Strength determined by K, not concentration

PART IV: Weak Acid Equilibria Problems

- Solving Problems involving Weak-Acid Equilibria
  - Types
    - Given equilibrium concentrations, find K_a
    - Given K_a and some concentrations, find other concentrations
  - Approach
    - Determine "Knowns" and "Unknowns"
    - Write the Balanced Equation
    - Set up equilibrium expression – $K_a = \dfrac{[C]^c[D]^d.....}{[A]^a[B]^b....}$
    - Define "x" as the unknown change in [HA]
      - Typically, $x = [A]_{diss}$ (conc. of HA that dissociates)

$$x = [A]_{diss} = [H_3O^+] = [A^-]$$

Weak Acid Equilibria Problems

- Construct a "Reaction" table
- Make assumptions that simplify calculations
  - ♦ Usually, "x" is very small relative to initial concentration of HA
  - ♦ Assume $[HA]_{init} \approx [HA]_{eq}$ & Apply 5% rule

    If "x" < 5% $[HA]_{init}$; assumption is valid
- Substitute values into K_a expression, solve for "x"

➢ The Notation System

- Brackets – [HA]; $[HA]_{diss}$; $[H_3O^+]$

  indicate "Molar" concentrations
- Bracket with "no" subscript refers to molar concentration of species at equilibrium

Weak Acid Equilibria Assumptions

- Assumptions

$$\mathbf{HA(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad H_3O^+(aq) \quad + \quad A^-}$$

- The $[H_3O^+]$ from the "autoionization" of water is "Negligible"

  It is much smaller that the $[H_3O^+]$ from the dissociation of HA

$$[H_3O^+] = [H_3O^+]_{\text{from HA}} + [H_3O^+]_{\text{from } H_2O} \approx [H_3O^+]_{\text{from HA}}$$

- A weak acid has a small K_a

- Therefore, the change in acid concentration can be neglected in the calculation of the equilibrium concentration of the acid

$$[HA] = [HA]_{\text{init}} - [HA]_{\text{dissoc}} \approx [HA]_{\text{init}}$$

Weak Acid Equilibria Assumptions

- Assumption Criteria - 2 approaches

$$HA(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad H_3O^+(aq) \quad + \quad A^-$$

$$K = \frac{\left[H_3O^+\right]\left[A^-\right]}{\left[HA\right]}$$

  - For K_c relative to $[HA]_{init}$ (or K_p relative to $P_{A(init)}$)

$$\text{if} \quad \frac{[HA]_{init}}{Kc} > 400, \text{ the assumption } [HA] \approx [Ha]_{init} \text{ is justified}$$

$$\text{Neglecting } x \text{ introduces an error } < 5\%$$

$$\text{if} \quad \frac{[HA]_{init}}{Kc} < 400, \text{ the assumption } [HA] \approx [HA]_{init} \text{ is not justified}$$

$$\text{Neglecting } x \text{ introduces an error } > 5\%$$

  - For $[HA]_{diss}$ relative to $[HA]_{init}$

$$\text{if } [HA]_{diss} < 5\% \; [HA]_{init}, \text{ the assumption } ([HA] \approx [HA]_{init}) \text{ is valid}$$

Weak Acid Equilibria

- Effect of Concentration on Extent of Acid Dissociation

Case 1: $[HPr]_{init} = 0.10\ M$

$$K_a = \frac{[H_3O^+][Pr^-]}{[HPr]} = 1.3 \times 10^{-5} \approx \frac{(x)(x)}{0.10}$$

$$x = 1.1 \times 10^{-3} M = [H_3O^+] = [Pr^-] = [HPr]_{diss}$$

$$\%\ HA_{diss} = \frac{[HPr]_{diss}}{[HPr]_{init}} = \frac{1.1 \times 10^{-3} M}{1.0 \times 10^{-1} M} \times 100 = 1.1\%$$

Case 2: $[HPr]_{init} = 0.01\ M$

$$x = 3.6 \times 10^{-4} M = [H_3O^+] = [Pr^-] = [HPr]_{diss}$$

$$\%\ HA_{diss} = \frac{3.6 \times 10^{-4} M}{1.0 \times 10^{-2} M} \times 100 = 3.6\%$$

As the concentration decreases the percent dissociation increases

Weak Acid Equilibria

- Polyprotic Acids
  - Acids with more than one ionizable proton are polyprotic acids.
  - One proton at a time dissociates from the acid molecule
  - Each dissociation step has a different K_a

$$H_3PO_4(aq) + H_2O(l) \leftrightarrows H_2PO_4^{-} + H_3O^{+}(aq)$$

$$K_{a1} = \frac{[H_2PO_4^{-}][H_3O^{+}]}{[H_3PO_4]} = 7.2 \times 10^{-3}$$

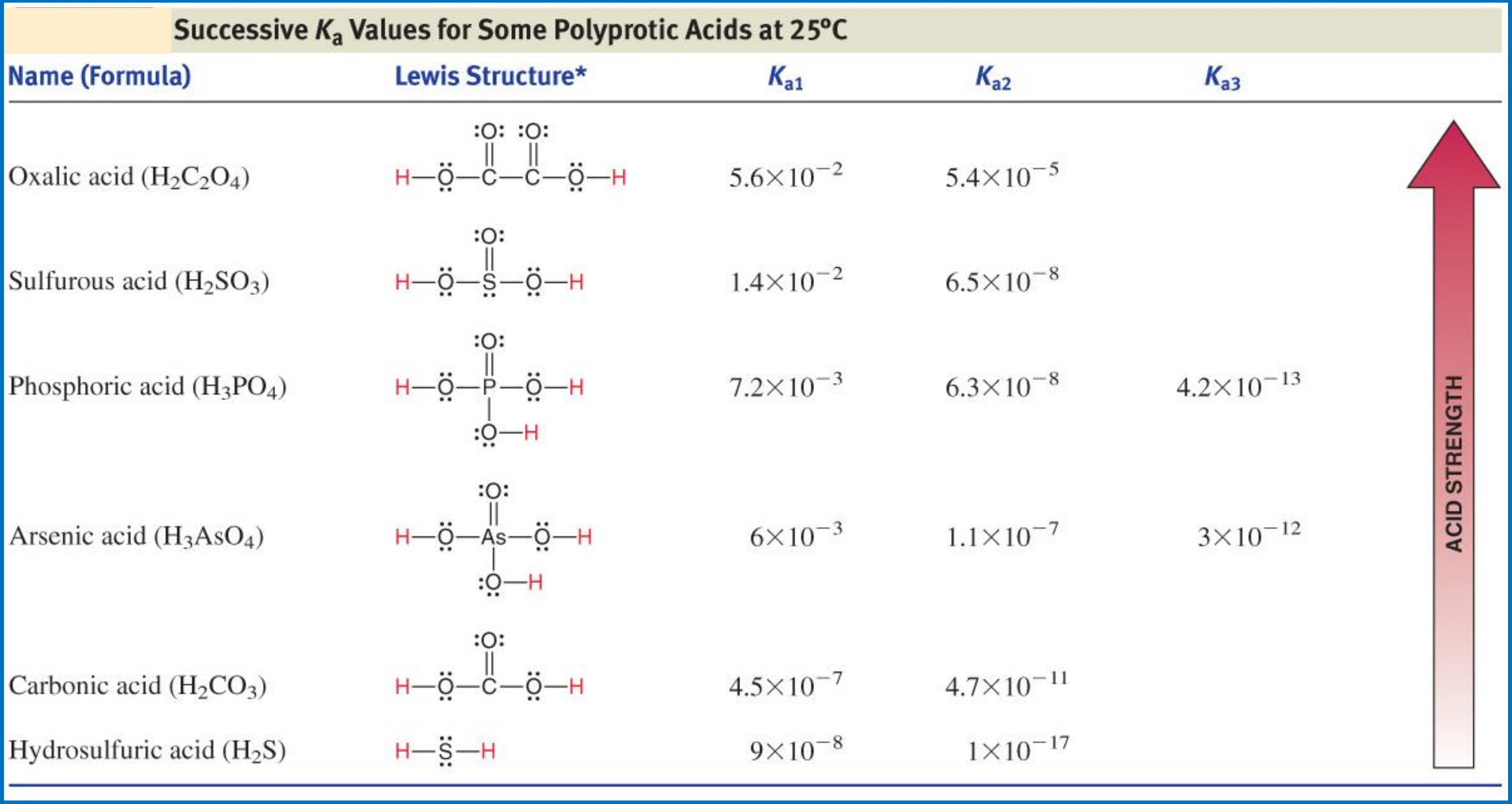
$$H_2PO_4^{-}(aq) + H_2O(l) \leftrightarrows HPO_4^{-2} + H_3O^{+}(aq)$$

$$K_{a2} = \frac{[HPO_4^{-2}][H_3O^{+}]}{[H_2PO_4^{-}]} = 6.3 \times 10^{-8}$$

$$HPO_4^{-2}(aq) + H_2O(l) \leftrightarrows PO_4^{-3} + H_3O^{+}(aq)$$

$$K_{a3} = \frac{[PO_4^{-3}][H_3O^{+}]}{[HPO_4^{-}]} = 4.2 \times 10^{-13}$$

Weak Acid Equilibria



Successive K_a Values for Some Polyprotic Acids at 25°C

Name (Formula)	Lewis Structure*	K_{a1}	K_{a2}	K_{a3}
Oxalic acid ($H_2C_2O_4$)	$\mathrm{H{-}\ddot{O}{-}\overset{:O:}{\overset{\Vert}{C}}{-}\overset{:O:}{\overset{\Vert}{C}}{-}\ddot{O}{-}H}$	5.6×10^{-2}	5.4×10^{-5}	
Sulfurous acid (H_2SO_3)	$\mathrm{H{-}\ddot{O}{-}\overset{:O:}{\overset{\Vert}{S}}{-}\ddot{O}{-}H}$	1.4×10^{-2}	6.5×10^{-8}	
Phosphoric acid (H_3PO_4)	$\mathrm{H{-}\ddot{O}{-}\overset{:O:}{\overset{\Vert}{\underset{:\ddot{O}{-}H}{\underset{\vert}{P}}}}{-}\ddot{O}{-}H}$	7.2×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
Arsenic acid (H_3AsO_4)	$\mathrm{H{-}\ddot{O}{-}\overset{:O:}{\overset{\Vert}{\underset{:\ddot{O}{-}H}{\underset{\vert}{As}}}}{-}\ddot{O}{-}H}$	6×10^{-3}	1.1×10^{-7}	3×10^{-12}
Carbonic acid (H_2CO_3)	$\mathrm{H{-}\ddot{O}{-}\overset{:O:}{\overset{\Vert}{C}}{-}\ddot{O}{-}H}$	4.5×10^{-7}	4.7×10^{-11}	
Hydrosulfuric acid (H_2S)	$\mathrm{H{-}\ddot{S}{-}H}$	9×10^{-8}	1×10^{-17}	

Successive dissociation equilibrium constants (Ka) for polyprotic acids have significantly lower values

Ka1 >> Ka2 >> Ka3

Weak Bases & Relation to Weak Acids

- Base – Any species that accepts a proton (Bronsted)
- In water the base accepts a proton from water acting as an acid (water is amphoteric) and leaves behind a OH$^-$ ion

$$\mathrm{B(aq)} \;+\; \mathrm{H_2O(l)} \;\rightleftharpoons\; \mathrm{BH^+(aq)} \;+\; \mathrm{OH^-(aq)}$$

$$K_c = \frac{[\mathrm{BH^+}][\mathrm{OH^-}]}{[\mathrm{B}][\mathrm{H_2O}]}$$

- The water term is treated as a constant in aqueous reactions and is incorporated into the value of K_c

$$K_c[\mathrm{H_2O}] = K_b = \frac{[\mathrm{BH^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$$

$$pK_b = -\log K_b$$

- Base strength increases with increasing K_b (pK_b deceases)

Weak Base Equilibria

- Ammonia is the simplest Nitrogen-containing compound that acts as a weak base in water

$$NH_3(aq) + H_2O(l) \;\square\; NH_4^+(aq) + OH^-(aq)$$

- Ammonium Hydroxide (NH_4OH) in aqueous solution consists largely of unprotonated NH_3 molecules, as its small K_b indicates:

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]\left[H_2O\right]} = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}$$

$$K_b = 1.76 \times 10^{-5}$$

Weak Base Equilibria

In a 1.0 M NH_3 solution:

$$[OH^-] = [NH_4^+] = 4.2 \times 10^{-3}\ M$$

The NH_3 is about 99.58% <u>un</u>dissociated

- If one or more of the Hydrogen atoms in ammonia is replaced by an "organic" group (designated as R), an "Amine" results:

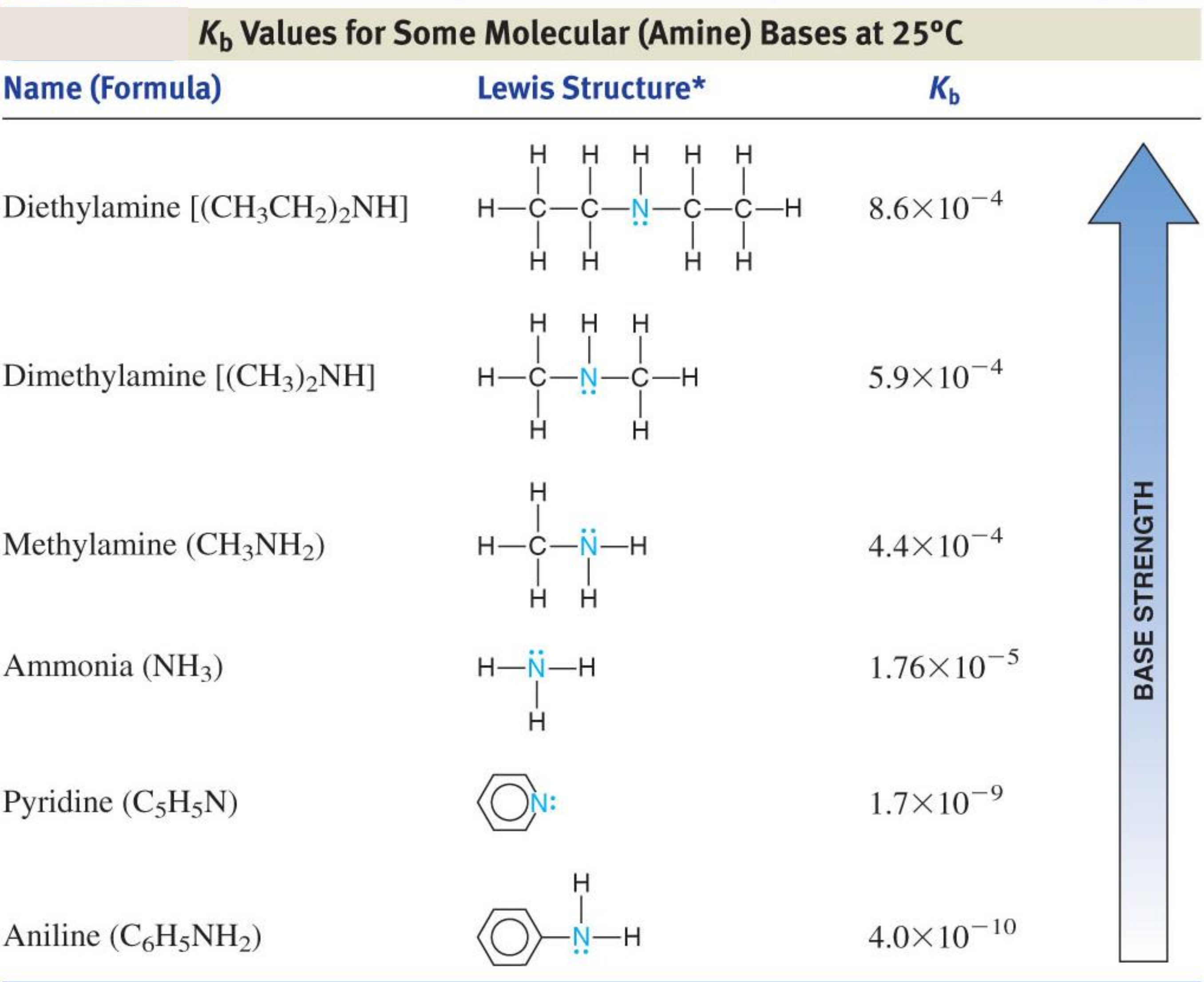
Primary Amine

Secondary Amine

Tertiary Amine

- The Nitrogen atom in each compound has a "lone-pair" of unbonded electrons, a Bronsted Base characteristic, i.e., the electron pair(s) can accept protons

Weak Base Equilibria



K_b Values for Some Molecular (Amine) Bases at 25°C

Name (Formula)	Lewis Structure*	K_b
Diethylamine [$(CH_3CH_2)_2NH$]		8.6×10^{-4}
Dimethylamine [$(CH_3)_2NH$]		5.9×10^{-4}
Methylamine (CH_3NH_2)		4.4×10^{-4}
Ammonia (NH_3)		1.76×10^{-5}
Pyridine (C_5H_5N)		1.7×10^{-9}
Aniline ($C_6H_5NH_2$)		4.0×10^{-10}

Anions of Weak Acids & Bases

- The anions of weak acids are Bronsted-Lowry bases

$$A^-(aq) + H_2O(l) \quad \square \quad HA(aq) + OH^-(aq)$$

Base (A^-) accepts a proton from water to form conjuate acid (HA)

$$F^-(aq) + H_2O(l) \quad \square \quad HF(aq) + OH^-(aq)$$

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

F^-, anion of weak acid HF, acts as weak base and accepts a proton to form HF

Anions of Weak Acids & Bases

- The acidity of HF vs F^-
  - HF is a weak acid, very little dissociates
  - Very little H_3O^+ and F^- produced

$$\mathbf{HF(aq) + H_2O(l) \overset{\longleftarrow}{\rightleftharpoons} H_3O^+(aq) + F^-(aq)}$$

  - Water autoionization also contributes H_3O^+ and OH^-, but in much smaller amounts than H_3O^+ from HF

$$\mathbf{2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)}$$

  - The Acidity of a solution is influenced mainly by the

H_3O^+ from HF and OH^- from water

$$[H_3O^+]_{\text{from HF}} \gg [OH^-]_{\text{from } H_2O} \qquad \text{(solution acidic)}$$

Anions of Weak Acids & Bases

- Basicity of $A^-(aq)$
  - Consider 1 M solution of NaF
  - Salt dissociates completely to yield stoichiometric concentrations of F^- , assume Na^+ is spectator ion
  - Some of the F^- reacts with water to form OH^-

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

  - Water autoionization also contributes H_3O^+ and OH^-, but in much smaller amounts than OH^- from reaction of F^- and H_2O

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$[OH^-]_{\text{from } F^-} \gg [H_3O^+]_{\text{from } H_2O} \qquad \text{(solution basic)}$$

Anions of Weak Acids & Bases

- Summary
  - The relative concentration of HA & A^- determine the acidity or basicity of the solution
    - In an HA solution, [HA] >> $[A^-]$ and

      $[H_3O^+]_{\text{from HA}}$ >> $[OH^-]_{\text{from } H_3O^+}$

      "Solution is Acidic"
    - In an A^- solution, $[A^-]$ >> [HA] and

      $[OH^-]_{\text{from } A^-}$ >> $[H_3O^+]_{\text{from } H_3O^+}$

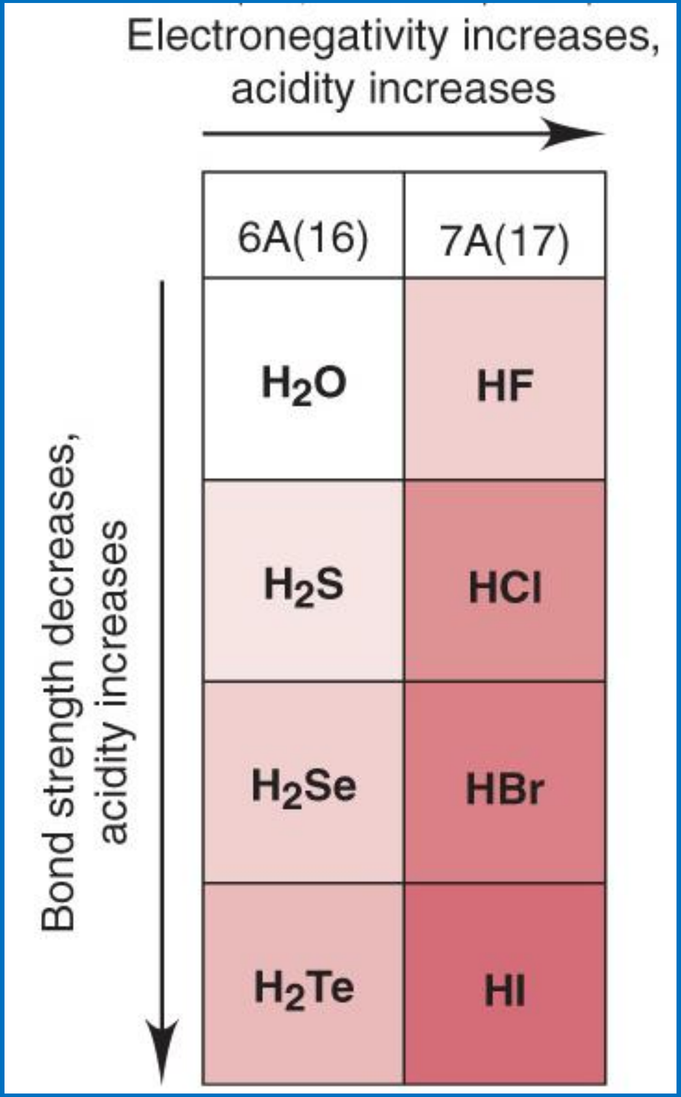
      "Solution is Basic"

Acid Strength

- Trends in Acid Strength of Nonmetal Hydrides

- As the electronegativity of the nonmetal (E) bonded to the ionizable proton increases (left to right), the acidity increases
- As the length of the E-H bond increases (top to bottom), the bond strength decreases, so the acidity increases
- The "strong" monoprotic halide acids (HCl, HBr, HI) are equally strong

  Note: (HF) is a <u>weak</u> acid)



6A(16)	7A(17)
H_2O	HF
H_2S	HCl
H_2Se	HBr
H_2Te	HI

Acid Strength in Oxoacids

- Oxoacids
  - An Oxoacid is an acid that contains Oxygen
  - To be more specific, it is an acid that:
    - contains oxygen
    - contains at least one other element (S, N, X)
    - has at least one Hydrogen atom (acid hydrogen) bound to oxygen
    - forms an ion by the loss of one or more protons
    - acidity of an Oxoacid is not related to bond strength as in nonmetal hydrides

Acid Strength in Oxoacids

- Oxoacids with 1 Oxygen - HOE structure:

The more electronegative is E, the stronger the acid

Acid Strength: $HOCl > HOBr > HOI$

- Oxoacids with multiple Oxygens - $(OH)_mEO_n$ structure

The more Oxygen atoms, the greater the acidity

$HOClO_3$ $(HClO_4)$ > $HOClO_2$ $(HCLO_3)$ >

$HOClO$ $(HCLO_2)$ > $HOCL$ $(HClO)$

Acid Strength in Oxoacids

- For oxoacids with the same number of oxygen atoms around E, acid strength increases with the electronegativity of E

$K_a(HOCl) = 2.9x10^{-8} > K_a(HOBr) = 2.3x10^{-9} > K_a(HOI) = 2.3x10^{-11}$

- For oxoacids with different numbers of oxygen atoms around a <u>given</u> E, acid strength increases with the number of oxygen atoms.
  - K_a ($HOCl$ Hypochorous acid) = $2.9x10^{-8}$ (Weak)
  - K_a ($HOCLO$ Chlorous acid) = $1.12x10^{-2}$
  - K_a ($HOCLO_2$ Chloric acid) ≈ 1
  - K_a ($HOCLO_3$ Perchloric acid) = $> 10^7$ (Strong)

Acid-Base Properties – Salt Solutions

- Neutral Salt Solutions
  - Salts consisting of the Anion of a Strong Acid and the Cation of a Strong Base yield a neutral solutions because the ions do not react with water

$$HNO_3(l) + H_2O(l) \rightarrow NO_3^-(aq) + H_3O^+(aq)$$

Nitrate (NO_3^-) is a weaker base than water (H_2O) ; reaction goes to completion as the NO_3^- becomes fully hydrated; does not react with water

$$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$$

Sodium becomes full hydrated; does not react with water

$$NaNO_3(s) \xrightarrow{H_2O} Na^+(aq) + NO_3^-(aq) + H_3O^+(aq) + OH^-(aq)$$

Na^+ & NO_3^- do not react with water, leaving just the "autoionization of water, i.e., a neutral solution

$$2H_2O \quad \square \quad H_3O^+ + OH^-$$

Acid-Base Properties – Salt Soln

- Salts that produce Acidic Solutions
  - A salt consisting of the anion of a strong acid and the cation of a weak base yields an acidic solution
    - The cation acts as a weak acid
    - The anion does not react with water (previous slide)
    - In a solution of NH_4Cl, the NH_4^+ ion that forms from the weak base, NH_3, is a weak acid
    - The Chloride ion, the anion from a strong acid does not react with water

$$\mathbf{NH_4Cl(s) + H_2O \xrightarrow{H_2O} NH_4^+(aq) + Cl^-}$$

$$\mathbf{NH_4^+(aq) + H_2O \; \square \; NH_3(aq) + H_3O^+ \quad (Acidic)}$$

Acid-Base Properties – Salt Soln

- Salts that produce Basic Solutions
  - A salt consisting of the anion of a weak acid and the cation of a strong base yields a basic solution
  - The anion acts as a weak base
  - The cation does not react with water
  - The anion of the weak acid accepts a proton from water to yield OH^- ion, producing a "Basic" solution

$$\mathbf{CH_3COONa(s)\ +\ H_2O\ \xrightarrow{H_2O}\ Na^+(aq)\ +\ CH_3COO^-(aq)}$$

(dissoluton & hydration)

$$\mathbf{CH_3COO^-\ +\ H_2O(l)\ \rightleftharpoons\ CH_3COOH(aq)\ +\ OH^-\ \ (Basic)}$$

(reaction of weak base - Acetate Anion))

Salts of Weakly Acidic Cations and Weakly Basic Anions

- Overall acidity of solution depends on relative acid strength (K_a) or base strength (K_b) of the separated ions

  Ex. NH_4CN - Acidic or Basic?

  Write equations for any reactions that occur between the separated ions and water

$NH_4^+(aq) + H_2O(l)$ □ $NH_3(aq) + H_3O^+$

$CN^-(aq) + H_2O(l)$ □ $HCN(aq) + OH^-$

Salts of Weakly Acidic Cations and Weakly Basic Anions

- Ex. NH_4CN - Acidic or Basic? (Con't)

  Compare K_a of NH_4^+ & K_b of CN^-

  Recall: Molecular compounds only in tables of K_a & K_b

$$K_a \text{ of } NH_4^+ = \frac{K_w}{K_b \text{ of } NH_3} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.7 \times 10^{-10}$$

$$K_b \text{ of } CN^- = \frac{K_w}{K_a \text{ of } HCN} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-5}} = 1.6 \times 10^{-5}$$

Magnitude of K_b ($K_b > K_a$) (1.6×10^{-5} / 5.7×10^{-10} = 3×10^4)

K_b of CN^- >> K_a of NH_4^+ Solution is Basic

Acceptance of proton from H_2O by CN^- proceeds much further than the donation of a proton to H_2O by NH_4^+