Ch. 16 Acids and Bases

Acid/base character (pH) of a solution has enormous impact

- a. lake biosystem (acid rain)
- b. farming/gardening (soil pH, alkalinity, etc)
- c. rusting/corrosion
- d. biology
  - cells, proteins, blood, enzymes, hormones need very tight pH control
  - Most bio reaction mechanisms involve H^+ transfer → $[H^+]$ has huge impact on rates

16.1 Bronsted-Lowry Concept of Acids/Bases

	Bronsted-Lowry Definition	Lewis Definition
Acid	**$H^{\oplus}$ donor**	Lone-pair acceptor
Base	**$H^{\oplus}$ acceptor**	Lone-pair donor

Acid and water: $HCl + H_2O \rightarrow H_3O^{\oplus} + Cl^{\ominus}$

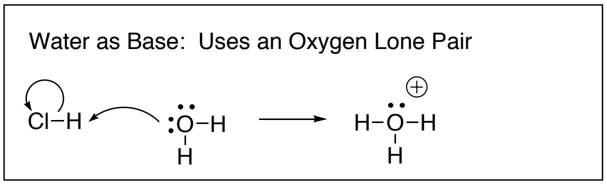
Base and water: $NH_3 + H_2O \rightleftharpoons HO^{\ominus} + NH_4^{\oplus}$

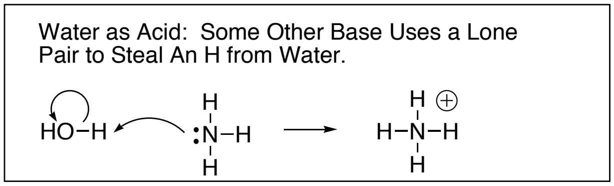
Notes:

1. An **acid** **loses** an $H^{\oplus}$ and gets more negative
   - A neutral acid becomes an **anion** after loss of $H^{\oplus}$ — $HCl \rightarrow Cl^{\ominus}$
   - A cationic acid becomes neutral after loss of $H^{\oplus}$ — $H_3O^{\oplus} \rightarrow H_2O$
2. A **base** **gains** an $H^{\oplus}$ and gets more positive
   - A neutral base becomes a **cation** after gain of $H^{\oplus}$ — $H^{\oplus} + NH_3 \rightarrow NH_4^{\oplus}$
   - An anionic base becomes neutral after gain of $H^{\oplus}$ — $H^{\oplus} + {}^{\ominus}OH \rightarrow H_2O$

The change in either charge or number of H's can help identify whether a chemical is functioning as an acid or a base.

3. Every base needs a lone pair which gets used to bond to the new hydrogen
   - The two electrons involved in the new bond to hydrogen always come from an electron pair on the base


Water as Base: Uses an Oxygen Lone Pair


Water as Acid: Some Other Base Uses a Lone Pair to Steal An H from Water.

4. Water can function as either a base (accepting an $H^{\oplus}$ when an acid is placed in water) or as an acid (donating an $H^{\oplus}$ when a base is placed in water)

5. In every acid-base reaction, you must have both an acid (a chemical functioning as the $H^{\oplus}$ donor) and also a base (a lone-pair donating chemical functioning as the $H^{\oplus}$ acceptor)
   - An acid can't give unless there is some basic lone-pair to take.….

Terminology: $H^{\oplus}$ = "proton"

<u>Conjugate Acid-Base Pairs</u>

Structures that <u>differ by one H and one charge unit</u> are referred to as conjugate acid-base pairs

Conjugate Acid	Conjugate Base	Conjugate Acid	Conjugate Base
HF	$F^{\ominus}$	$H_3O^{\oplus}$	H_2O
HCl	$Cl^{\ominus}$	H_2O	$HO^{\ominus}$
H_2SO_4	$HSO_4^{\ominus}$	$NH_4^{\oplus}$	NH_3
$HSO_4^{\ominus}$	SO_4^{2-}		

1. Draw the conjugate bases	2. Draw the conjugate acids
a. HCN	a. SO_4^{2-}
b. HBr	b. NH_3
c. CH_4	c. $Cl^{\ominus}$

<u>Relative Strengths of Acids and Bases</u>

	Acid	Base	
Strong acids, 100% Ionized in H_2O	HCl	$Cl^{\ominus}$	Nonbases
	H_2SO_4	$HSO_4^{\ominus}$	
	$H^{\oplus}(aq) = H_3O^+$	H_2O	
	HSO_4^-	SO_4^{2-}	
	HF	$F^{\ominus}$	
	H_2CO_3	$HCO_3^{\ominus}$	
	$NH_4^{\oplus}$	NH_3	
	$HCO_3^{\ominus}$	CO_3^{2-}	
	H_2O	$OH^{\ominus}$	
Nonacids	$OH^{\ominus}$	O^{2-}	Strong bases, 100% Protonated in H_2O
	H_2	$H^{\ominus}$	

- Stronger acids have weaker conjugate bases and weaker acids have stronger conjugate bases
- Stronger bases have weaker conjugate acids and weaker bases have stronger conjugate acids

Conjugate Pairs in Acid-Base Reactions and Acid-Base Equilibria

1. Note: Some acid-base reactions go entirely to the product side, or stay entirely on left side
2. But many acid-base reactions involve equilibria, in which a proton is shuffling back and forth from side to side
3. In the example shown, a proton ($H^{\oplus}$) jumps back and forth between F and O.
   a. Going from left to right, F is the giver (HF = acid) and O the acceptor (H_2O = base)
   b. Returning from right back to left, O is the giver ($H_3O^{\oplus}$ = acid) and F the acceptor ($F^{\ominus}$ = base)

$$HF + H_2O \rightleftharpoons H_3O^{\oplus} + F^{\ominus}$$

Notes

1. Each side of every acid-base reaction has one thing that functions as an acid and the other as a base. (This is true on the right side as well as on the left side).
2. Every acid-base reaction has 2 conjugate pairs
   a. For the acid on the left, it's conjugate base appears on the right side
   b. For the base on the left, it's conjugate acid appears on the right side.

Problems: For each of the species in the following equilibria, mark whether it functions as an acid or a base?

- For each of the species in the following equilibrium, draw an arrow to it's conjugate.

a. $NH_3 + HClO \rightleftharpoons NH_4^{\oplus} + ClO^{\ominus}$

b. $HCN + H_2PO_3^{\ominus} \rightleftharpoons H_3PO_3 + CN^{\ominus}$

c. $CH_3NH_2 + CH_3OH_2^{\oplus} \rightleftharpoons CH_3NH_3^{\oplus} + CH_3OH$

d. $H_2O + HSO_4^{\ominus} \rightleftharpoons H_3O^{\oplus} + SO_4^{-2}$

Notes/Notice:

1. Notice the change in H-count and the change in charge for each of these
2. The acid on the left always loses a hydrogen and becomes one step unit more negative
3. The base on the left always gains a hydrogen and becomes more positive
4. **Cations usually function as acids**
   - They are positive, and want to get rid of $H^{\oplus}$ to alleviate positive charge
5. **An anion usually function as a base**
   - It usually wants to get more positive, and the negative charge always means it has a lone-pair available
   - Some exceptions, such as example "d"

Acid/Base Strength

1. **Strong acids** are better $H^{\oplus}$ donors than **weaker acids**
   Strong bases are better $H^{\oplus}$ acceptors than weaker bases

2. Acid/base strength depends on love for $H^{\oplus}$

- Consider the conjugate pair of $Z^{\ominus}$ and HZ
  - a. High $H^{\oplus}$ Love: Suppose $Z^{\ominus}$ really loves $H^{\oplus}$
    1. Then $Z^{\ominus}$ is a strong base
       - It aggressively grabs $H^{\oplus}$ from somebody else
    2. Then HZ is a very weak acid or a total non-acid
       - Z tightly holds onto the $H^{\oplus}$
       - It doesn't let anybody else steal $H^{\oplus}$ unless it's a base who loves $H^{\oplus}$ even more
  - b. Low $H^{\oplus}$ Love: Suppose $Z^{\ominus}$ doesn't have much love for $H^{\oplus}$
    1. Then $Z^{\ominus}$ is a weak base or a totally non-base
       - It's very weak about grabbing $H^{\oplus}$ from somebody else
    2. Then HZ is acidic
       - Z is very weak about holding onto the $H^{\oplus}$
       - Some base who loves $H^{\oplus}$ more can easily steal the $H^{\oplus}$ away and leave $Z^{\ominus}$ behind

3. Love for $H^{\oplus}$ and the Competition between Competing Bases

$$\underset{\text{acid}}{HX} \quad + \quad \underset{\text{base}}{Z^{\ominus}} \quad \rightleftharpoons \quad \underset{\text{base}}{X^{\ominus}} \quad + \quad \underset{\text{acid}}{HZ}$$

NOTICE: There is one hydrogen, but two things ($Z^{\ominus}$ and $X^{\ominus}$) competing for it.

- a. Whichever base loves $H^{\oplus}$ **more** will be the **stronger base**, and the equilibrium will drive to the opposite direction → to the conjugate acid of the strong base
- b. Whichever base loves $H^{\oplus}$ **less** will lose the competition and remain in its basic form

1. Strong love for $H^{\oplus}$ = strong base
2. Equilibrium goes from strong base to weak base, favors the side where the weaker base lies.
3. In the same way, the equilibrium always goes from the stronger acid to the weaker acid, and always favors the side with the weaker acid
4. The weaker acid and weaker base are always on the same side, and the stronger acid and stronger base are always together on the other side

4. Acid-Base Strength and the Direction of Acid-Base Equilibria

*Acid/base reactions **always** go from stronger acid/base to weaker acid + base

K favors weaker

HCl	+	NaOH	→	H_2O +	$Na^{\oplus}Cl^{\ominus}$	K large (K >>1)
Stronger acid		stronger base		weaker acid	weaker base	
H_2S	+	$F^{\ominus}$	←	HF +	$HS^{\ominus}$	K small (K <1)
weaker acid		weaker base		stronger acid	stronger base	

a. Stronger acid + base always on same side
b. If you know any of relative strengths, can predict sense, K
c. If given K info, can identify weaker/stronger

Problems

1. HF is stronger than HNO_2. Predict the "direction" of the reaction, and say whether K will be greater or less than 1. (ID each as acid or base)

   $HF + Na^{\oplus}NO_2^{\ominus}$ $Na^{\oplus}F^{\ominus} + HNO_2$ K 1

2. Predict the "direction" of the reaction, and say whether K will be greater or less than 1.

   $HF + Cl^{\ominus}$ $HCl + F^{\ominus}$ K 1

3. Classify each as the weaker or stronger acid or base.

   $HA + B^{\ominus}$ $A^{\ominus} + HB$ $K = 10^3$

4. Classify each as the weaker or stronger acid or base.

   $HCN + SO_4^{2-}$ $HSO_4^{\ominus} + CN^{\ominus}$ $K = 10^{-5}$

5. Direct Relationship between strengths of conjugate acid/base

Acid Strength	**Strength of Conjugate Base**
Strong	Nonbasic
Weak	Weak
Nonacid	Strong base

Note: there is a huge range of strengths within the "weak" category

	Acid	Base	
Strong acids, 100% Ionized in H_2O	HCl	$Cl^{\ominus}$	Nonbases
	H_2SO_4	$HSO_4^{\ominus}$	
	$H^{\oplus}$ (aq) = H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	HF	$F^{\ominus}$	
	H_2CO_3	$HCO_3^{\ominus}$	
	$NH_4^{\oplus}$	NH_3	
	$HCO_3^{\ominus}$	CO_3^{2-}	
	H_2O	$OH^{\ominus}$	
Nonacids	$OH^{\ominus}$	O^{2-}	Strong bases, 100% Protonated in H_2O
	H_2	$H^{\ominus}$	

The weaker the acid, the stronger it's conjugate base
The stronger the acid, the weaker it's conjugate base

6. Strong Acids versus Weak Acids versus Nonacids. How do they Differ in Water?

a. **Strong acids** ionize completely in water

$$HCl + H_2O \rightarrow H_3O^{\oplus} + Cl^{\ominus}$$

- There is **NO** acid left, no acid where the H and the Cl are bonded.
- Goes completely to the product side.

b. **Weak acids** ionize incompletely in water
- An equilibrium exists
- Normally only a small amount of product ion is present at equilibrium, and most of the weak acid is in it's undissociated form

$$HF + H_2O \rightleftharpoons H_3O^{\oplus} + F^{\ominus} \qquad K = 10^{-5}$$

- There is plenty of HF left. But meaningful amounts of $H_3O^{\oplus}$ + $F^{\ominus}$ ions present.
- Some "weak" acids are stronger or weaker than others.

c. **Nonacids:** Don't ionize at all in water.
- No equilibrium exists
- Stays completely on the left side

$$CH_4 + H_2O \leftarrow H_3O^{\oplus} + CH_3^{\ominus}$$

16.1,2 Recognizing Acids

1. **Memorize** Six **strong acids**

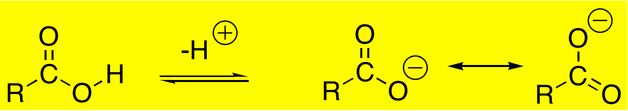
HCl HBr HI HNO_3 H_2SO_4 $HClO_4$

- **Assume all other acids are weak acids**
- The conjugate anions of these strong acids are nonbasic

2. Weak acids
   a. Usually formula written with H in front
   HF HCN H_2S H_2CO_3 → acids
   CH_4 NH_3 SiH_4 → nonacids

*** Note: NOT ALL H's are acidic!!**

   b. Carboxylic acids



- The "R" group can be anything, but is usually hydrocarbon
- The anion is stabilized by resonance
- Carboxylic acids are often written as: CH_3COOH, C_2H_5COOH, etc.

   c. Transition-metal Cations: in water they are "hydrated" and function as <u>weak</u> <u>acids</u> (Section 16.5, p. 784)

General: $M^{\oplus}(H_2O)_x + H_2O \rightleftharpoons H_3O^{\oplus} + M(H_2O)_{x-1}(OH)$

Ex: $Fe^{3+}(H_2O)_6 + H_2O \rightleftharpoons [Fe(H_2O)_5\,OH]^{2+} + H_3O^{\oplus}$

$Cu^{2+}(H_2O)_4 + H_2O \rightleftharpoons [Cu(H_2O)_3\,OH]^{\oplus} + H_3O^{\oplus}$

   d. Ammonium Ions are <u>weak acids</u> (see more under bases, amines)
   - Conjugate acids of neutral amine bases
   - Formal positive charge on nitrogen
   - Unlike most acids, these are cationic species

$NH_4^{\oplus}$, $CH_3NH_3^{\oplus}$, $(CH_3)_2NH_2^{\oplus}$, $C_6H_5NH_3^{\oplus}$, etc.

Recognizing Bases

1. Soluble metal hydroxides ⇒ strong bases
    - All **Group 1 metal hydroxides, many Group 2**…
    - Group 1 metal hydroxides produce 1 mole of hydroxide per mole of formula
    - Soluble Group 2 metal hydroxides produce 2 moles of hydroxide per formula

Group 1	Group 2
LiOH, NaOH, KOH …	$Ca(OH)_2$, $Ba(OH)_2$ …

$NaOH\ (aq) \rightarrow Na^{\oplus}\ (aq) + {}^{\ominus}OH(aq)$ (Complete)
1mole 1 mole

$Ca(OH)_2\ (aq) \rightarrow Na^{\oplus}\ (aq) + 2\ {}^{\ominus}OH(aq)$ (Complete)
1mole 2 mole

- most Transition-metal hydroxides have limited solubility and aren't effectively strong

$CuOH(S) \rightleftharpoons Cu^{+}(aq) + OH^{-}(aq)$
1mole less than 1mole (Incomplete)

2. Amines: Neutral N Compounds ⇒ weak bases

Parent: $H_3N{:} + H_2O \rightleftharpoons {}^{\ominus}OH + NH_4{}^{\oplus}$
weak base weak acid

- Other amines have N: in common, but replace one or more of the hydrogens with other thing, usually carbon groups

Amines Bases (examples)	Conjugate acids = "Ammonium" Ions
NH_3	$NH_3{}^{\oplus}$
CH_3NH_2	$CH_3NH_2{}^{\oplus}$
$(CH_3)_2NH$	$(CH_3)_2NH^{\oplus}$
$C_6H_5NH_2$	$C_6H_5NH_2{}^{\oplus}$

- N lone pairs accept $H^{\oplus}$
- Amines are the only "neutral bases". All other bases have anionic charge.
- The conjugate acids are called "ammonium ions" (see earlier)
    - "Amines" = neutral, weakly basic
    - "Ammoniums" = cationic, weakly acidic
- The ammonium ions have formal $\oplus$ charge on N

3. **Any conjugate base of a weak acid is weak base**

4. **Any conjugate base of a non-acid is a strong base**

Note: Most Anions are Basic. Whenever you see an anion, consider whether it will be basic!

5. **Evaluating the Basicity of Anions**
   a. Draw the conjugate acid of the anion
   b. Evaluate the acidity of the conjugate "acid" as strongly acidic, weakly acidic, or nonacidic
   c. Based on the acidity of the acid, decide what the strength of the anion base would be.

Conjugate Acid Strength	**Strength of Conjugate Base**
Strong acid	Nonbasic
Weak acid	Weak Base
Non-acid	Strong base

Base Strength	Anion	Conjugate Acid	Acid Strength
	$F^{\ominus}$	HF	
	${}^{\ominus}CN$	HCN	
	$H_2PO_4^{\ominus}$	H_3PO_4	
	$Cl^{\ominus}$	HCl	
	$H^{\ominus}$	H_2	
	${}^{\ominus}CH_3$	CH_4	

Note: Most anions are basic

- Memorize the six anions derived from strong acids that are not basic
- Assume any other anion is basic

Six strong Acids	HCl	HBr	HI	HNO_3	H_2SO_4	$HClO_4$
Six Non-Basic Anions	$Cl^{\ominus}$	$Br^{\ominus}$	$I^{\ominus}$	$NO_3^{\ominus}$	$HSO_4^{\ominus}$	$ClO_4^{\ominus}$

Recognizing and Classifying Acid/Base Character of Ionic Formulas

1. Distinguish molecular from ionic formulas
2. **For ionics, check each ion separately**
   a. Is the cation acidic?
      1. No if it's a group 1 or group 2 metal cation
      2. Yes if it's a transition metal cation
      3. Yes if it's an ammonium cation
   b. Is the anion basic?
      1. No if it's one of the six non-basic anions derived from strong acids
      2. Yes if it's any other anion

1. Classify as Strong Acid, Weak Acid, Strong Base, Weak Base, or Non-acid/base

   a. HBr

   b. HF

   c. $CH_3CH_2NH_2$

   d. CH_3CH_2COOH

   e. H_2SO_4

   f. H_3PO_4

   g. HClO

   h. $ClO^{\ominus}$

   i. $Cl^{\ominus}$

   j. $NO_3^{\ominus}$

   k. O^{2-}

   l. CH_4

   m. NaOH

   n. NaF

   o. KCl

   p. NH_4NO_3

   q. $FeBr_3$

16.3 Autoionization of water

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq)^{+}\ OH^{\ominus}(aq) \qquad \mathbf{K_w = 1.00 \times 10^{-14}} =$$

1. Water is both weakly acidic and basic
2. Amount of ions is teensy but very important
3. $K_w = 1.00 \times 10^{-14}$ always true
4. If either $[H_3O^{\oplus}]$ or $[HO^{\ominus}]$ known, can calculate other

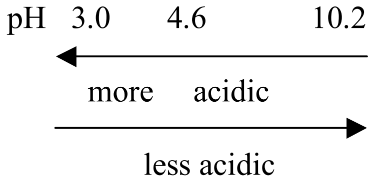
$$\boxed{[H_3O^{\oplus}][OH^{\ominus}] = \mathbf{1.00 \times 10^{-14}} \qquad \textbf{Memorize!}}$$

Neutral: $[H_3O^{\oplus}] = 1 \times 10^{-7} = [OH^{\ominus}]$ pH = 7 Acidic: $[H_3O^{\oplus}] > 1 \times 10^{-7} > [OH^{\ominus}]$ pH <7 Basic: $[H_3O^{\oplus}] < 1 \times 10^{-7} < [OH^{\ominus}]$ pH > 7	Note: $H^{\oplus}$ vs. $H_3O^{\oplus}$ • $H^{\oplus}$ (proton) in water exists as $H_3O^{\oplus}$ (hydronium). • But $H^{\oplus}$ is easier to write! • They are really the same thing.

16.4 The pH Scale

$pH = -\log[H_3O^{\oplus}]$	$[H_3O^+] = 10^{-pH}$	Much nicer numbers
On calculator: enter $[H^+]$, hit "log", and correct the sign from negative to positive	**On calculator**: enter pH, switch the sign from positive to negative, and hit 10^x button (depending on calculator)	

1. Higher numberer pH → less $H^{\oplus}$, less acidic, more basic
   Lower numbered pH → more $H^{\oplus}$, more acidic, more less$^+$



2. pH = 7 neutral pH < 7 acidic pH > 7 basic

3. pH change of 1 = tenfold change in $[H^{\oplus}]$
   Change of 2 = 100-fold change
   pH change of 8 → 4 isn't double the acid or half the acid, it's 10 thousand times more!

4. Number of significant figures in $[H^+]$ = number of digits after decimal in pH

   $[H^+] = 3.6 \times 10^{-6}$ → pH = 5.44
   2 sig fig → 2 after decimal

5. Small pH changes → death
   - 7.35 < blood < 7.45
   - bio rates are often strongly H^+ catalyzed, with 2nd or 3rd order rate dependence on $[H^+]$

6. pOH = - log[OH$^-$] just like $pH = -\log [H^+]$	**[OH$^-$] = 10^{-pOH}** just like $[H^+] = 10^{-pH}$

7. Since $10^{-14} = [H^+][OH^-]$ → take negative log of both sides → $\boxed{\mathbf{14.00 = pH + pOH}}$

Skills: interconvert among

$[H^+] \Leftrightarrow [OH^-]$

$\Updownarrow \quad \Updownarrow$

$pH \Leftrightarrow pOH$

To know any one allows you to find any of the others!

Problems

1. Find pH for following

a. $[H_3O^+] = 1.0 \times 10^{-4}$

b. $[H^+] = 1.0 \times 10^{-11}$

c. $[H^+] = 3.2 \times 10^{-4}$

d. $[OH^-] = 1.0 \times 10^{-8}$

e. $[OH^-] = 5.8 \times 10^{-4}$

f. pOH = 8.30

2. Find pOH:

a. $[H^+] = 3.9 \times 10^{-5}$

b. $[OH^-] = 3.9 \times 10^{-5}$

c. pH = 3.95

3. Find both $[H^+]$ $[OH^-]$

a. pH = 3.72

b. pH = 9.81

c. $[H^+] = 3.5 \times 10^{-8}$

d. $[OH^-] = 4.1 \times 10^{-3}$

16.5 Equilibrium Expressions and Ionization Constants for Acids, Bases.

A. Acids

$HA\ (aq) + H_20\ (l) \rightleftharpoons H_30^{\oplus}\ (aq) + A^{\ominus}\ (aq)$ $\qquad K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$

Shorthand: $HA \rightleftharpoons H^{\oplus} + A^{\ominus}$ $\qquad \mathbf{K_a} = \dfrac{[H_3O^+][A^-]}{[HA]}$

1. Strong acids: ionize completely (K_a = infinity)
2. Weak acids: $K_a < 1$
3. Larger $K_a \Rightarrow$ stronger acid   Smaller $K_a \Rightarrow$ weaker acid
4. For weak acids, ionizations may be minimal but is still significant
    - for math calculations, the "simplifying assumption" is usually useful
5. Since $A^{\ominus}$ and HA are conjugates:
    - larger $K_a \Rightarrow$ less basic $A^{\ominus}$ (stronger acid → weaker base)
    - smaller $K_a \Rightarrow$ more basic $A^{\ominus}$ (weaker acid → stronger base)

B. Bases

Generic	$Base(aq) + H_20(l) \rightleftharpoons OH^{\ominus}(aq) + Base\text{-}H^{\oplus}(aq)$ Conjugate acid	$\mathbf{K_b} = \dfrac{[OH^-][BH^+]}{[B]}$
Anionic Base	$A^{\ominus} + H_20 \rightleftharpoons OH^{\ominus} + HA$ Conjugate acid	$\mathbf{K_b} = \dfrac{[OH^-][HA]}{[A^-]}$
Neutral Amine Base	$NH_3 + H_20 \rightleftharpoons OH^{\ominus} + NH_4^{\oplus}$ Amine Ammonium	$\mathbf{K_b} = \dfrac{[OH^-][NH_4^+]}{[NH_3]}$

16.7 Calculations involving K_a, K_b, pH, pOH

A. **Strong Acids**: $[HA] = [H^{\oplus}] \Rightarrow$ pH

- Complete ionization $HCl \rightarrow H^{\oplus} + Cl^{\ominus}$
- To know the concentration of the strong acid is to know the concentration of $H^{\oplus}$

B. **Strong Bases**: complete formation of $OH^{\ominus}$

- $[NaOH] = [OH^{\ominus}] \Rightarrow$ pOH, pH
    - for a group one metal hydroxide (NaOH, etc.), you get exactly as many moles of hydroxide as you put in of NaOH, and $[NaOH] = [OH^{\ominus}]$
    - $NaOH \rightarrow Na^{\oplus} + OH^{\ominus}$
- For a group two metal hydroxide, you get two moles of hydroxide for every one mole of formula that you put in.
    - $1\ Ba(OH)_2 \rightarrow 1\ Ba^{2+} + 2\ OH^{\ominus}$
    - $[OH^{\ominus}] = 2\ ([Ba(OH)_2])$
- Since $[OH^{\ominus}]$ is knowable, you can then plug in, and find pOH, pH, and/or $[H^{\oplus}]$

Some pH Calculations Involving Strong Acids or Bases

1. What is the pH of 1.36×10^{-3} M H_2SO_4?

2. An HCl solution has pH = 2.16. what is [HCl]?

3. What is pH for 0.013 M KOH solution?

4. What is pH for a solution that is 0.013 M in $Ca(OH)_2$?

5. What is the pH if 22 g of $Ba(OH)_2$ (90 g/mol) is dissolved in 760 mL of water?

C. Weak Acids Calculation: Equilibrium, K_a, and pH ICE-able (Section 16.7, p 789-792)

Two Key Equations	$K_a = \frac{[H^+]^2}{[HA]_{init}}$	$[H^+] = \sqrt{K_a \cdot [HA]}$;

1. **Major Application 1**: $\boxed{\text{Given a known } K_a \text{, Solve for pH}}$ When a Known Amount of Weak Acid is Placed in a Known Amount of Water

$\boxed{\text{Logic: Use } K_a \rightarrow \text{solve for } [H^{\oplus}] \rightarrow \text{solve for pH}}$

Steps

1. Whether it's given in molarity or not, convert the sample/solvent ratio into Molarity
2. Set up an ICE table
3. Solve for equilibrium $[H^{\oplus}]$
   - Use simplifying assumption if K_a is reasonably small
   - Use another simplifying assumption that the original population of $H^{\oplus}$ is also reasonably small relative to the final, equilibrium amount of $H^{\oplus}$
4. Use $[H^{\oplus}]$ to solve for pH

5. Or: If K_a is small enough so that the simplifying assumption is reasonable, you can directly plug into the equation shown above

	HA	$\rightleftharpoons$	$H^{\oplus}$	+	$A^{\ominus}$
Initial	$[HA]_{init}$		1.0×10^{-7}		0
Change					
Equilibrium					
Equilibrium After Simplifying Assumptions					

K_a =

When the simplifying assumptions are used:	$\mathbf{K_a}= \dfrac{[H^+]^2}{[HA]_{init}}$	$[\mathbf{H}^{\oplus}]=\sqrt{K_a \times [HA]_{init}}$
When the first simplifying assumption is not used (but the second one is)	$K_a= \dfrac{[H^+]^2}{[HA]_{init} - [H^+]}$	$[H^{\oplus}]$ requires a quadratic solution

2. **<u>Major Application 2</u>**: $\boxed{\text{Given a measured pH, Solve for } K_a}$ When a Known Amount of Weak Acid is Placed in a Known Amount of Water

$$\boxed{\text{Logic: Use pH} \rightarrow \text{solve for } [H^{\oplus}] \rightarrow \text{solve for K}}$$

$$K_a= \frac{[H^+]^2}{[HA]_{init}}$$

<u>Weak Acid pH/K_a Problems</u>

1. pH → K_a What is K_a for an acid if an 0.15 M solution is prepared and found to have pH = 4.86?

Logic:

Equation(s):

2. $K_a \rightarrow$ pH What is pH for a 0.15 M solution of an acid with $Ka = 2.2 \times 10^{-6}$?
Logic:

Equation(s):

3. If an 0.23 M solution of an acid gives pH = 3.82, what is K_a for acid?

4. If a 0.11 M solution has a $Ka = 1.3 \times 10^{-8}$ acid, what is pH?

D. Weak Base Calculations involving K_b and pH (Section 16.7, p 792-793)

	$A^{\ominus}$	$+ H_2O$	$\rightleftharpoons$	HA	+	$HO^{\ominus}$
Initial	$[A^{\ominus}]_{init}$			0		1.0×10^{-7}
Change						
Equilibrium						
Equilibrium After Simplifying Assumptions						

$K_b =$

When the simplifying assumptions are used:	$\mathbf{K_b}=\dfrac{[HO^-]^2}{[A^-]_{init}}$	$\mathbf{[HO^{\ominus}]}=\sqrt{K_b \times [A^-]_{init}}$
When the first simplifying assumption is not used but the second one is	$K_b=\dfrac{[HO^-]^2}{[A^-]_{init} - [HO^-]}$	$[HO^{\ominus}]$ requires a quadratic solution

Applications

1. pH → K_b Strategy: pH → pOH → $[HO^{\ominus}]$ → K_b

2. K_b → pH Strategy: K_b → $[HO^{\ominus}]$ → pOH → pH

Problems: pH and K_b

1. pH → K_b What is K_b if a 0.123 M solution of a weak base gives pH=10.62?

2. K_b → pH If K_b for a weak base is 1.6×10^{-5}, what is the pH of a 0.222 M solution of the base?

E. Relationship Between K_a and K_b for Conjugate acids/bases (Section 16.7, p 794)

- Review: stronger the acid, weaker the conjugate base (and vice versa)

$$\boxed{K_a \times K_b = 1.0 \times 10^{-14}}$$

Review Table 16.2

1. Given one, can solve for other.
2. Tables routinely provide only one; expect you to solve for other
3. Can rank relative strengths of acids(or bases) given info about conjugates
4. Toughest problem: given K_a for conjugate acid, calculate pH for a solution of weak base
   - Logic: $K_a \rightarrow K_b \rightarrow [HO^{\ominus}] \rightarrow pOH \rightarrow pH$

Derivation of $K_aK_b=10^{-14}$ (not responsible for derivation, just for interest)

$$K_a = \frac{[H_3 0^+][A^-]}{[HA]} \qquad K_b = \frac{[OH^-][HA]}{[A^-]}$$

$$\text{So } K_aK_b = \left(\frac{[H_3O^+][A^-]}{[HA]}\right)\frac{[OH^-][HA]}{[A^-]} = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus $\mathbf{K_aK_b=K_w=10^{-14}}$

Acid Strength	**K_a**	**K_b**	**Strength of Conjugate Base**
Strong	$K_a > 1$	$K_b < 1 \times 10^{-14}$	Nonbasic
Weak	$1 \times 10^{-14} < K_a < 1$	$1 \times 10^{-14} < K_b < 1$	Weak
Nonacid	$K_a < 1 \times 10^{-14}$	$K_b > 1$	Strong base

Problems Involving Relationship between K_a and K_b for Conjugated Acid/Base

Substance	HF	HN_3	HCN
K_a	6.8×10^{-4}	1.9×10^{-3}	4.9×10^{-10}
Relative Acidity			
Conjugate Base			
Relative Basicity			
K_b			

1. Rank the acidity for the three weak acids, 1 being strongest.

2. Rank the basicity, 1 being the stongest, for: NaCN NaF NaN_3

Substance	HF	HN_3	HCN
K_a	6.8×10^{-4}	1.9×10^{-3}	4.9×10^{-10}
Conjugate Base			
K_b			

3. What is K_b for N_3^-?

4. What is pH for a solution that is 0.12 M in NaF^-?

Logic:

5. What is pH for a solution that is 0.20 M in NaCN?

Logic:

C. Polyprotic Acids: More than One H^+ Available (Section 16.5, p. 783)

H_2SO_4, H_3PO_4, H_2CO_3,…

1. Each H^+ gets successively **less** acidic (by > 1000)

Relative Acidity	Acid		Conjugate Base	Relative Basicity
	H_3PO_4	$K_{a1} = 10^{-3}$	$H_2PO_4^-$	
	$H_2PO_4^-$	$K_{a2} = 10^{-8}$	HPO_4^{2-}	
	HPO_4^{-2}	$K_{a3} = 10^{-13}$	PO_4^{3-}	

2. As acids in water, only consider the first ionization.
3. When base is added, however, all H^+'s come off (stoichiometry permitting)

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

But $H_3PO_4 + 3\ OH^- \rightarrow 3\ H_20 + PO_4^{3-}$

4. H_2SO_4: 1st strong, 2nd weak

$$\underset{\text{none}}{H_2SO_4} \xrightarrow[\boxed{\text{Complete}}]{\text{water}} H^+ + \underset{\text{lot}}{HSO_4^-} \underset{\boxed{\text{weak}}}{\overset{\text{water}}{\rightleftharpoons}} 2H^+ + \underset{\text{little}}{SO_4^{2-}}$$

5. Some anions are complex: both acidic and basic!!

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$HCO_3^- \xrightarrow{H_20} OH^- + H_2CO_3$$

Polyprotic Acid/Base Problems

1. Which is the stronger acid?

H_3PO_4	$H_2PO_4^-$
H_2SO_4	HSO_4^-

2. Which is the stronger base?

HCO_3^-	CO_3^{2-}
HSO_4^-	SO_4^{2-}

16.8 Acid-Base Properties of Salts (Ionic Compounds)

$FeCl_2$	$MgBr_2$	NaCN
pH<7	pH=7	pH>7
acidic	neutral	basic

Recall: "salts" formed by acid/base reactions

"salt"=<u>ionic</u>

Example:	SA/SB	$HCl + NaOH \rightarrow H_20 + NaCl$	neutral
	WA/SB	$HF + NaOH \rightarrow H_2O + NaF$	basic
	SA/WB	$HCl + NH_3 \rightarrow NH_4^+Cl^-$	acidic
	WA/WB	$HF + NH_3 \rightarrow NH_4^+F^-$	can't tell

Observations:

1. Salts can be acidic, basic, or neutral.
2. Depends on strengths of acids/bases from which they form.
3. The "ions" in the salts are conjugates; may be acidic or basic!!

A. General Logic to Predict: Identify Ions individually

1. Cations: acidic or neutral
   a. $\boxed{\text{Group I or II cations are } \underline{\text{neutral}}}$
      Li^+, Na^+, K^+, Mg^{2+}, Ba^{2+}, …
      No impact on pH
   b. Al^{3+}, T-metal cations are <u>acidic </u>(see 16.5 pg.)

$$Al^{3+} \xrightarrow{\text{water}} \underbrace{[Al(H_2O)_6]^{3+}}_{\text{Weak acid}} \rightleftharpoons H^+ + [Al(OH)(H_20)_5]^{2+}$$

   c. Ammoniums are acidic
      NH_4^+, $CH_3NH_3^+$ etc.

2. Anions: basic or neutral
   a. Neutral: conjugates of strong acids
      Cl^-, Br^-, I^-, NO_3^-, ClO_4^-
   b. basic: conjugates of weak acids (or non acids)
      F^-, ClO^-, …
3. "Amphoteric" anions derived from polyprotic acids: can be acidic or basic
   -not test responsible
      HCO_3^-, $H_2PO_4^-$, HSO_3^-

B. Predicting acidic/neutral/basic (qualitatively)

Cation	anion	salt solution	example
Neutral	neutral	neutral	NaCl, KNO_3
Acidic	neutral	acidic	NH_4Cl, $Fe(NO_3)_3$
Neutral	basic	basic	NaF, K(ClO)
Acidic	basic	can't predict (without K's)	NH_4F, $Fe(N_3)_3$

Predicting Acid/Base Character for Ionic Formulas

1. Predict as acidic, basic, neutral, or can't tell.

   a. Na_2SO_3

   b. $MgCl_2$

   c. NH_4CN

   d. $CoCl_2$

   e. $NaNO_3$

   f. KN_3

   g. $AlCl_3$

   h. CH_3NH_3Br

2. Rank the following in terms of increasing pH, 1 being the lowest. (ID as strong/weak acid, strong/weak base, or neutral first!)

   NaCl CaF_2 $ZnBr_2$ HNO_3 KOH

16.6 Molecular Structure and Acid/Base Strength

- Why is something strong or weak? Acidic or Basic? Can we predict from structure,without K's?

A. 3 Factors on Acid Strength

1. **H-A bond strength: stronger → <u>less</u> acidic**
    - Why H-F (strong bond) is weak acid, but H-Cl, H-Br, H-I are strong acids
    - Row 2 bonds (H-F, O-H, N-H, C-H) usually stronger than row 3,4 analogs
2. H-A polarity
    - Reflects electronegativity and polarity in the bond to the acidic hydrogen
        - CH_4 non polar → nonacidic
        - H-Br polar → acidic
3. Stability of conjugate $A^{\ominus}$
    - -electron love again a factor

$CH_4 \rightarrow H^+ + {}^{\ominus}CH_3$ Horrible. Carbon not electronegative, can't handle $\ominus$

$HF \rightarrow H^+ + F^{\ominus}$ Way stronger. Fluorine electronegative, can handle $\ominus$

B. Practical Pattern

1. Horizontal Periodic Pattern: Acidity increase left → right

	CH_4	NH_3	H_2O	HF
K_a	10^{-50}	10^{-32}	10^{-14}	10^{-4}

Note: e^- love, electronegativity/bond-polarity, anion stability all agree

Rank: Acidity of: SiH_4 SH_2 HCl PH_3

2. Vertical Periodic Pattern: Acidity Increases Top → Bottom
-due to decreasing H-A bond strength (even though contrary to e^- love)

HF < HCl
Weak strong

$H_2O < H_2S < H_2Se$
$K_a=10^{-14}$ 10^{-9} 10^{-6}

<u>Note: Basicity of conjugates linked!!</u>

Horizontal: ${}^{\ominus}NH_2 > F^{\ominus}$ Vertical: $F^{\ominus} > Cl^{\ominus}$

C. "Oxoacids" (Nonmetal hydroxides)

*Many structures have OH $Z(OH)_y(O)_x$

KOH	$H_2CO_3 = C(OH)_2O$	$H_2SO_4 = S(OH)_2O_2$
Base	weak acid	strong acid

1. **<u>Metals</u>** with OH are **<u>basic</u>** NaOH, $Mg(OH)_2$, etc. $NaOH \rightarrow Na^{\oplus} + HO^{\ominus}$
2. **<u>Nonmetals</u>** with OH are **<u>acidic</u>** F-O-H $F\text{-}O\text{-}H \rightarrow H^{\oplus} + FO^{\ominus}$
3. Oxoacid <u>acidity</u> increases as you move left → right across a row

$$Si(OH)_4 < P(OH)_3 < S(OH)_2 < Cl(OH)$$

- -electron love increases polarity of O-H bond

4. "Extra" Oxygens's increase acidity

$HClO_4 > HClO_3 > HClO_2 > HClO$ $H_2SO_4 > H_2SO_3$

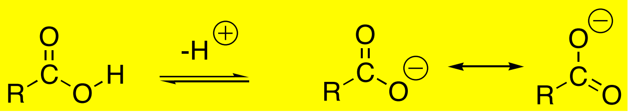
Strong weak strong weak

<u>Why</u>? Extra electron-loving oxygen
1. Stabilizes resulting anion
2. Polarizes O-H
3. Weakens O-H

5. Any <u>Neutral</u> Oxoacid with ≥ 2 extra O's is a <u>strong</u> Acid

Strong: H_2SO_4, $HClO_3$ weak: H_2CO_3, H_3PO_4, H_2SO_3

D. Carboxylic Acids: Famous class of oxoacids



E. "Hydrides"
1. M-H metal hydride → basic

   $NaH + H_2O \rightarrow$

2. Non-metal "hydrides" neutral or acidic

   CH_4

   H-Cl

Polarity Reveral: Compare Na-H to H-Cl

Predicting Acid/Base Properties and Trends Why?

1. Which are acidic vs. basic vs. neutral in water?

   $HClO_3$ CH_3COOH CH_3NH_2 $Ca(OH)_2$

2. Rank Acidity (1 strongest)

   HF H_2O H_2SO_4 CH_4

3. Rank Acidity (1 strongest)

   $HClO_4$ $HClO_3$ H_2SO_4 H_2SO_3

4. Rank Acidity (1 strongest)

   H_2O H_2S H_2Se

5. Rank Acidity (1 strongest)

   HBr H_2Se H_3As H_4Ge

6. Which would be stronger?

   $HBrO_3$ vs $HBrO$

7. Rank Basicity (1 strongest)

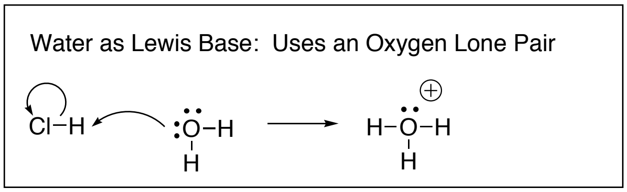
   $^{\ominus}CH_3$ $^{\ominus}NH_2$ $^{\ominus}OH$ $F^{\ominus}$

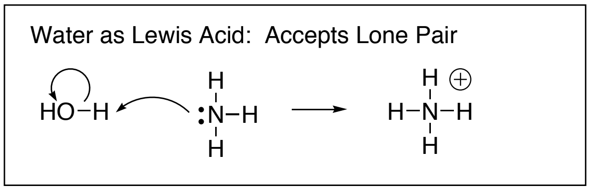
8. Rank Basicity (1 strongest)

   HPO_4^{2-} $H_2PO_4^{\ominus}$ $HSO_4^{\ominus}$

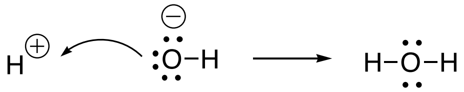
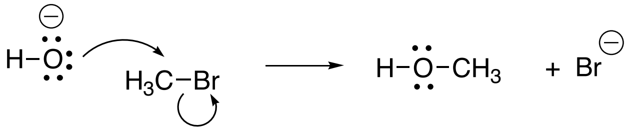
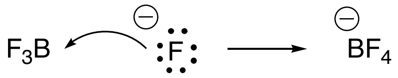
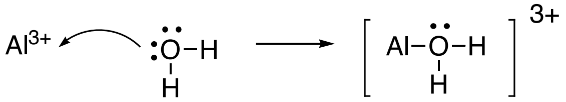
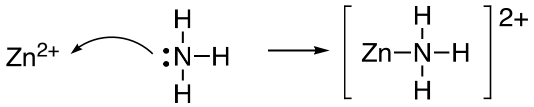
16.10 Lewis Acids and Bases: focus on electron pairs, not H^+ movement

Lewis acid: e- pair acceptor **Lewis base: e- pair donor**	Covers "acid-base" chemistry that doesn't involve H^+


Water as Lewis Base: Uses an Oxygen Lone Pair


Water as Lewis Acid: Accepts Lone Pair

Other Examples

a. 	b. 
c. 	d.  How metal hydrates form
e. 	

Notes: 1. A "base" must have a lone pair
(F^-, OH_2, NH_3, ….)
2. All anions have lone pairs → Lewis Base potential
3. An "acid" must be able to accept a lone pair
-all cations can!!
-some neutrals: BF_3, SO_2, …

Lewis Acid/Base Problems

1. Which would not be a Lewis acid?

$AlCl_3$ Ti^{4+} $NO_3^{\ominus}$ $ZnSO_4$

2. Identify the Lewis acid and Lewis Base

a. $Fe^{3+} + 6\,H_2O \rightarrow [Fe(H_2O)_6]^{3+}$

b. $H^+ + CH_3NH_2 \rightarrow CH_3NH_3$

c. $Br\text{-}CH_3 + I^{\ominus} \rightarrow Br^{\ominus} + I\text{-}CH_3$

d. $Ni^{2+} + 4\,N_3^{\ominus} \rightarrow [Ni(N_3)_4]^{2-}$

CH. 16 Acid-Base Chemistry Math

Key Equations, Numerical Relationships

1. $[H^+][HO^-] = 1.00 \times 10^{-14}$

2. $pH = -\log[H^+]$ $[H^+] = 10^{-pH}$ (on calculator, enter –pH, then punch the **10^x** button)

   $pOH = -\log[OH^-]$ $[OH^-] = 10^{-pOH}$ (on calculator, enter –pOH, then punch the **10x** button)

3. $pH + pOH = 14$ $pH = 14 - pOH$

Weak acid problems

$K_a = [H^+][A^-]/[HA]$ but when HA is placed in water, $[H^+] = [A^-]$ so:

When the simplifying assumptions are used:

4. $K_a = \dfrac{[H^+]^2}{[HA]_{init}}$

5. $[H^{\oplus}] = \sqrt{K_a \times [HA]_{init}}$

When the first simplifying assumption is not used (but the second one is)

6. $K_a = \dfrac{[H^+]^2}{[HA]_{init} - [H^+]}$

$[H^{\oplus}]$ requires a quadratic solution

7. Quadratic Equation: for $ax^2 + bx = c = 0 x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Weak base problems

$K_b = [Base\text{-}H^+][OH^-]/[Base]$ but when Base is place in water, $[Base\text{-}H^+] = [OH^-]$ so:

When the simplifying assumptions are used:

8. $K_b = \dfrac{[HO^-]^2}{[Base]_{init}}$

9. $[HO^{\ominus}] = \sqrt{K_b \times [Base]_{init}}$

When the first simplifying assumption is not used but the second one is

10. $K_b = \dfrac{[HO^-]^2}{[Base]_{init} - [HO^-]}$

$[HO^{\ominus}]$ requires a quadratic solution

11. $K_aK_b = 10^{-14}$ for a conjugate acid/base pair.

Note: This relationship is routinely used when a K value for your acid or base is not provided, but the K value for it's conjugate is. So get it indirectly.

Some Calculation Logic Scenarios

1. Strong acid → pH [Strong acid] → $[H^{\oplus}]$ → pH
2. Strong base → pH [Strong base] → $[HO^{\ominus}]$ → pOH → pH
3. Weak acid + K_a → pH [Weak acid] + K_a → $[H^{\oplus}]$ → pH
4. pH of weak acid → K_a pH → solve for $[H^{\oplus}]$ → K_a
5. Weak base + K_b → pH [Weak base] + K_b → $[HO^{\ominus}]$ → pOH → pH
6. pH of weak base → K_b pH → solve for $[HO^{\ominus}]$ → pOH → pH
7. Weak base + K_a of conjugate acid → pH K_a → K_b → $[HO^{\ominus}]$ → pOH → pH

Simple Acid-Base Concept Map