Chapter 15 ACIDS AND BASES

These Notes are to SUPPLIMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

The author is providing these notes as an addition to the students reading the text book and listening to the lecture. Although the author tries to keep errors to a minimum, the student is responsible for correcting any errors in these notes.

Acids: have a sour taste. Turn litmus from blue to red, basic phenolphthalein from red to colorless
Bases: are bitter. Turn litmus red to blue [Blue = Base], phenolphthalein from colorless to pink.

	Acid	**Base**
Arrhenius	H^+, Proton Donor	OH^-, Hydroxide Donor
Bronstead-Lowry	H^+, Proton Donor	H^+, Proton Acceptor
Lewis	Accepts an Electron Pr	Donates an Electron Pr

1. Arrhenius Acid Base: Acid is a H^+ donor, Base is an OH^- donor. H^+ is really a Hydronium Ion H_3O^+

Water Soln: $HCl + NH_3 \rightarrow NH_4Cl$ in water soln and products ionize

In Benzene: $HCl + NH_3 \rightarrow NH_4Cl$ salt products is ppt

In Gas Phase $HCl + NH_3 \rightarrow NH_4Cl$

Reactions in Benzene and Gas Phase do not have a OH- donor!

A strong acid completely ionizes in aqueous solution to give H_3O^+

e.g. $HClO_4$, H_2SO_4, Hi, HBr, HCl, HNO_3

A strong base completely ionizes in aqueous solution to give OH-

e.g. LiOH, NaOH, KOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

A weak acid is NOT completely ionized in aqueous solution: acetic acid $CH_3\text{-}COOH \leftarrow\rightarrow CH_3\text{-}COO^- + H^+$

If you remember, the Net Ionic Equation for the reaction of an acid and a base is:

$H^+ + OH^- \rightarrow H_2O$ and the ΔH for this reaction is -55.90 kJ / Mole H^+

The reaction is exothermic, so it will go to completion!

2. Bronsted-Lowry Acid Base

An acid donates a proton in a proton transfer reaction
A base accepts the proton in a proton transfer reaction

H_3O^+ is the proton donor, NH_3 is the proton acceptor

$$H_3O^+(aq) + NH_3(aq) \longrightarrow H_2O(l) + NH_4^+(aq)$$

In Benzene they are not ionized, HCl is the proton donor or acid.

$$\underset{\text{acid}}{HCl(benzene)} + \underset{\text{base}}{NH_3(benzene)} \longrightarrow NH_4Cl(s)$$

In a reversible acid base reaction, both the forward and reverse reactions involve proton transfers.
Students point out the acids and bases.

$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

Conjugate acid base pair is the two species in an acid base reaction that differ by the loss or gain of a proton.

$$\underset{\text{acid}}{HC_2H_3O_2(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{C_2H_3O_2^-(aq)}$$

conjugate acid-base pairs

NH_3	+	H_2O ←→	NH_4^+	+	OH^-
Base		Acid	Acid		Base

NH_3 and NH_4^+ differ by a proton, so NH_3 and NH_4^+ are the conjugate acid base pair
The NH4+ is the conjugate acid The NH_3 is the conjugate base.

Example 15.1 Id the acid, base, conjugate acid-base pair

a. $HCO_3^- + HF \leftrightarrow H_2CO_3 + F^-$

b. $HCO_3^- + OH^- \leftrightarrow CO_3^{-2} + H_2O$

Exercise 15.1 $H_2CO_3 + CN^- \leftrightarrow HCN + HCO_3^-$

An **Amphiprotic** species can act as an acid or a base. [Amphoteric]

$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

$$\underset{\text{acid}}{HC_2H_3O_2(aq)} + \underset{\text{base}}{H_2O(aq)} \rightleftharpoons \underset{\text{base}}{C_2H_3O_2^-(aq)} + \underset{\text{acid}}{H_3O^+(aq)}$$

Class Question: Write the Amphoteric ionization of water, label the acids and bases.

Bronsted-Lowry Concept of acids and bases

1. A base accepts protons. OH^- is only one example
2. Acids and bases can be ions or molecular substances
3. Acid-Base reactions are not restricted to water solutions
4. A species can act as an acid or base, depending upon the other reactant

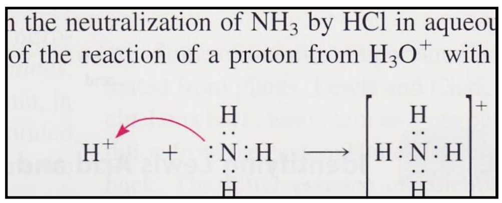
Concept Check 15.1 Write the acid base equilibrium for formic acid H-CO-OH

3. Lewis Acid Base

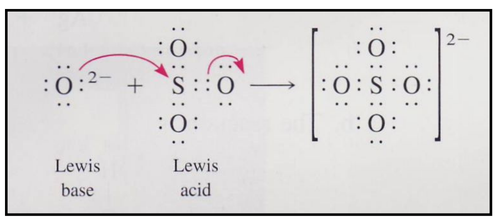
Lewis Acid: species that can form a covalent bond by accepting an electron pair from another species.
Lewis Base: species that can form a covalent bond by donating an electron pair to another species.

The Lewis and the Bronsted are the same, but the look at different ends of the reactants/products.

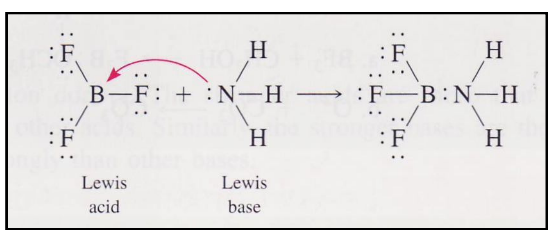
The proton accepts the electron pair and is the Lewis Acid



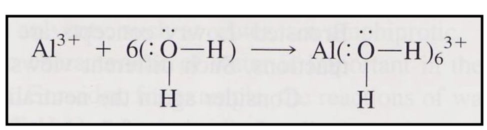
The SO_3 accepts the electron pair [which moves to the oxygen]. The SO_3 is the Lewis Acid



Boron TriFluoride accepts the electron pair and is the Lewis Acid

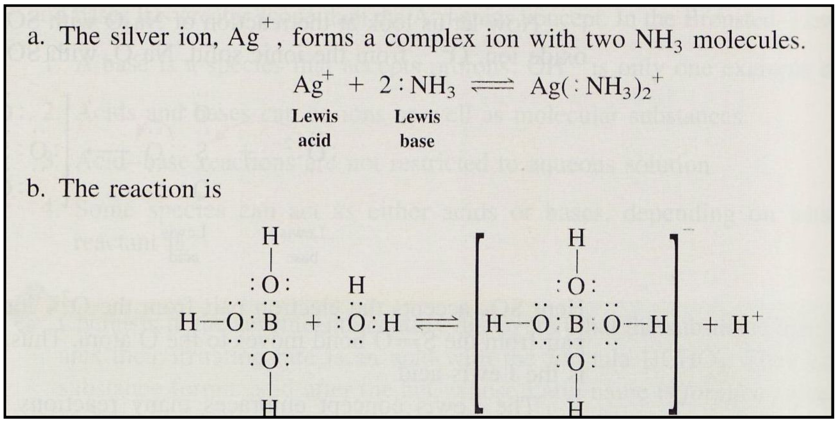


Complex Ions: Aluminum accepts the electron pairs – the Lewis Acid



Example 15.2 Identify the Lewis Acid and Base: $Ag^+ + 2\ NH_3 \leftarrow\rightarrow Ag(NH_3)_2^+$

$$B(OH)_3 + H_2O \leftarrow\rightarrow B(OH)_4^- + H^+$$



a. The silver ion, Ag^+, forms a complex ion with two NH_3 molecules.

$$\underset{\text{Lewis acid}}{Ag^+} + \underset{\text{Lewis base}}{2:NH_3} \rightleftharpoons Ag(:NH_3)_2^+$$

b. The reaction is

Exercise 15.2

Id the Lewis Acids and Bases: $BF_3 + CH_3OH \leftarrow\rightarrow F_3B:\overset{H}{\underset{\cdot\cdot}{O}}\text{-}CH_3$

$$O^{-2} + CO_2 \leftarrow\rightarrow CO_3^{-2}$$

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

- Stronger Acids loose their H^+ ions more easily than other acids.
- An acid base reaction normally goes in the direction of the **WEAKER ACID**.
- If an acid is **STRONG**, the acids conjugate base is **WEAK**
- Saying an acid loses its proton readily is the same as saying it's conjugate base does not hold onto it's proton very tightly [see HCl and Cl^- below]
- The strongest acid has the weakest conjugate base

HCl	+	$H_2O \leftarrow\rightarrow$	**Cl^-**	+	H_3O^+
Strong Acid		Base	**Weak Base**		Acid

Because the forward reaction occurs almost completely, HCl is a stronger acid than H_3O^+
Or you could say H_3O^+ is a weaker acid than HCl.

$$CH_3\text{-}COOH + H_2O \leftarrow\rightarrow CH_3\text{-}COO^- + H_3O^+$$

0.1 M AcOH goes about 1% ionized. Therefore acetic acid is a weaker acid than H_3O^+

HCl and HI dissolved in water are 100% ionized.

But when dissolved in acetic acid, more HI is ionized than HCl. So HI is a stronger acid than HCl.
Water inhibits the **LEVELING EFFECT** on the strengths of the acids.

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

Example 15.3 Which species is favored: SO_4^{-2} + HCN ← → HSO_4^- + CN^-

HSO_4^- is a stronger acid than HCN. Or, HCN is a weaker acid than HSO_4^-

CN^- is a stronger base than SO_4^{-2} Or SO_4^{-2} is a weaker base

The reaction will go towards the weaker acid – from Right to Left.

Exercise 15.3 Which species is favored: H_2S + CH_3-COO^- ← → CH_3-COOH + HS^- **<u>CLASS DO</u>**

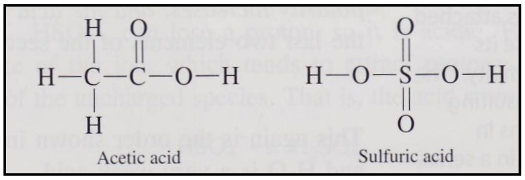
<u>Molecular Structure and Acid Strength:</u> Two factors determine the relative acid strength

1. Acid Strength - Polarity of the Bond

$$\overset{\delta+}{\mathbf{H}} - \overset{\delta-}{\mathbf{X}}$$

The more polarized the bond, the easier the molecule can loose the H+. Remember the table on Electronegativity [Table 9.15, page 346].

Acetic Acid is a weak acid, Sulfuric Acid is a very strong acid.
The electronegative Oxygen on the Sulfur make it easy for sulfuric to loose it's H^+.



Hydrogen bonded to Oxygen will have a partial positive charge

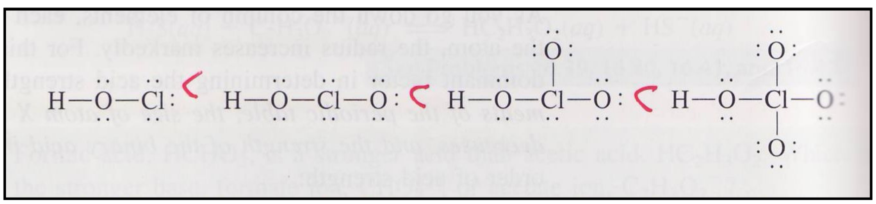
2. Acid Strength - Strength of the bond
The strength of a bond depends on the size of the X atom. The lager X is, the weaker is the bond and the stronger is the acid strength. **[Class Question WHY?].**

So, going down the Halogens: **HF < HCl < HBr < HI** X radius increases, the acid strength increases.

Going across the periodic table, the electronegativity increases [See Table 9.15] = the HX polarity increases and the acid strength increases.

The Oxoacids: H-O-Y H-O-Cl < H-O-Br < H-O-I
In going down the halogens, the electronegativity decreases, so Cl is the most electronegative, it pulls the electrons from the Oxygen and the Hydrogen and the Hydrogen can leave easier so H-O-Cl is the strongest.

Adding more electronegative groups also increases the acidity by withdrawing electrons away from the Hydrogen making it easier for the H^+ to leave.



$HClO_4$ > $HClO_3$ > $HClO_2$ > $HClO$ [acid strength increases with more oxygen]

Polyprotic Acids: $H_2SO_4 \rightarrow H^+ + HSO_4^{-1} \rightarrow H^+ + SO_4^{-2}$
The first H^+ is lost easily. But due to the negative charge on the HSO_4^{-1} is will hold onto the proton stronger so it will not loose it's H^+ easily. So, loosing the 1st is easy, the 2nd and 3rd hard.

<u>Self Ionization of Water and pH</u>
Auto Ionization / Amphoteric water: $H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$

Kw =→ [H_3O^+] [OH^-] / [H_2O]

The concentration of the ions is very small compared to the concentration of water [56 M], so:

CLASS PROVE WATER IS 56 M

[H_2O] * Kw = [H_3O^+] [OH^-] = 1.0×10^{-14} at 25 °C.

In pure water the OH^- and H_3O^+ are the same:
Kw = [H_3O^+] [OH^-]
$1.0 \times 10^{-14} = x * x$
1.0×10^{-7} M = x = [H_3O^+] = [OH^-]

Solutions of Strong Acid or Base:

Dissolve 0.10 mole of HCl in 1.0 L of water and you get 0.10 mol / 1.0 L = 0.10 M HCl.

HCl is a strong acid and is essentially completely ionized: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

So, starting with 0.10 M HCl, complete ionization, you get 0.10 M H_3O^+.

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

$$[OH^-] = 1.0 \times 10^{-14} / [0.10 \text{ M}] = 1.0 \times 10^{-13} \text{ M}$$

What is the hydrogen ion concentration in **0.010 M NaOH?**

NaOH is a strong base and is essentially completely ionized: $NaOH + H_2O \rightarrow Na^+ + OH^- + H_2O$

$$Kw = 1.0 \times 10^{-14} = [H_3O^+][OH^-] = [H_3O^+][0.010 \text{ M}]$$

$$[H_3O^+] = 1.0 \times 10^{-14} / [0.010 \text{ M}] = 1.0 \times 10^{-12} \text{ M}$$

Example 15.4, p 638 Calculate the hydronium and hydroxide ion concentration in 0.15 M HNO_3 and 0.010 M $Ca(OH)_2$? **Class Exercise at the Board**

Exercise 15.5, Calculate the hydronium and hydroxide ion concentration in 0.125 M $Ba(OH)_2$?
Hint: Remember there are 2 OH^{-1} in $Ba(OH)_2$

Summary: Acid Solutions:	$[H_3O^+] > 1.0 \times 10^{-7}$ M	between 10^{-1} M and 10^{-7} M
Neutral Solutions:	$[H_3O^+] = 1.0 \times 10^{-7}$ M	
Basic Solutions:	$[H_3O^+] < 1.0 \times 10^{-7}$ M	between 10^{-7} M and 10^{-14} M

Exercise 15.6 The hydroxide ion concentration is 1.0×10^{-5} M, is the solution acid, base or neutral?

<u>pH of a Solution:</u> pH is the negative of the log [base 10] of the molar hydronium ion concentration.

$$pH = -\log[H_3O^+] \quad \text{or} \quad -\log[H^+]$$

A solution has the hydronium ion concentration of 1.0×10^{-3}, what is it's pH?

$$pH = -\log[H_3O^+] = -\log[1.0 \times 10^{-3}] = 3.00$$

What is the pH of a neutral solution? $pH = -\log[H_3O^+] = -\log[1.0 \times 10^{-7}] = 7.00$

What is the pH of the 0.10 M HCl from above? $pH = -\log[H_3O^+] = -\log[1.0 \times 10^{-1}] = 1.00$

What is the pH of the 0.010 M NaOH from above? $pH = -\log[H_3O^+] = -\log[1.0 \times 10^{-12}] = 12.00$

Example 15.5 What is the pH of orange juice with a hydronium ion concentration of 2.9×10^{-4} M?

$pH = -\log[H_3O^+] = -\log[2.9 \times 10^{-4} \text{ M}] = 3.54$ which is less then 7, so it's acid

Exercise 15.7 What is the pH of digestive juice in the stomach with a hydronium ion concentration of 0.045 M? **Class Exercise at the board.**

$pOH = - \log [OH^-]$ $pH + pOH = 14$

An ammonia solution has a hydroxide ion concentration of 1.9×10^{-3} M, what is the pH?

pOH $= - \log [OH^-] = - \log [1.9 \times 10^{-3} \text{ M}] = 2.72$

$pH + pOH = 14$ $pH = 14.00 - pOH = 14 - 2.72 = 11.28$

Exercise 15.8 A calcium hydroxide solution has a hydroxide ion concentration of 0.025 M. What's the pH?

Exercise 15.9 A soda has a pH of 3.16. What is the hydronium ion concentration?

Exercise 15.10 A 0.010 M ammonia solution has a pH of 10.6. What is the concentration of hydroxide ion?

Acid Base Indicators: