Summary of Acid/Base Theories

There are three basic acid-base theories:
1. Arrhenius,
2. Lowry-Bronsted, and
3. Lewis.

In this course, we will focus mainly on Arrhenius and Lowry- Bronsted theories.

Point #1 - about the definitions

As one moves from the Arrhenius to Lowry-Bronsted to Lewis theory, the definitions of acids and bases become broader and more reagents qualify to be acids and bases. All Arrhenius acids and bases are both Lowry-Bronsted and Lewis acids and bases along with other qualifying reagents. Of course, all Lowry-Bronsted acids and bases continue to be Lewis acids and bases along with other Lewis acid - base reagents.

Point #2 - about the differences

The major difference between Arrhenius and Lowry-Bronsted theories is in the broaden definition of bases. Lewis theory appears to be quite different in definition of both acids and bases and requires knowledge of the electronic structure of the reagent - mainly location of lone pair electrons and sites of electron deficiencies. We will find in the discussion below that the main difference between Lewis and Arrhenius/Lowry-Bronsted is a broaden definition of an acid.

Point #3 - about the applications

Arrhenius is normally used in the consideration of titrations of acid and bases. Lowry-Bronsted is useful in the study of equilibrium while Lewis finds an important application in reaction mechanism.

Arrhenius Theory:

An Arrhenius Acid has the form HX and undergoes the reaction

HX -----> H^{+1} + X^{-1} (note: the reactions describes a proton donor)

where H^{+1} is the hydrogen ion or proton and X^{-1} is normally a nonmetal or nonmetal group.

If the reaction HX -----> H^{+1} + X^{-1} goes 100% toward completion, the acid is an excellent donor of protons and is said to be a strong acid. Perhaps a few examples of acids* would be helpful at this point!

HCl --100%--> H^{+1} + Cl^{-1},	Hydrochloric Acid,	a strong acid
HNO_3 --100%--> H^{+1} + NO_3^{-1},	Nitric Acid,	a strong acid
HBr --100%--> H^{+1} + Br^{-1},	Hydrobromic Acid,	a strong acid
HI --100%--> H^{+1} + I^{-1},	Hydroiodic Acid,	a strong acid
$HClO_4$ --100%--> H^{+1} + ClO_4^{-1},	Perchloric Acid,	a strong acid
HF --~30%--> H^{+1} + F^{-1},	Hydrofluoric Acid,	a weak acid
$HC_2H_3O_2$ -- ~1% --> H^{+1} + $C_2H_3O_2^{-1}$	Acetic Acid,	a weak acid

*It is useful to remember the five above strong monoprotic acids!

An Arrhenius Base has the form of MOH and undergoes the reaction

MOH ---> M^{+1} + OH^{-1} (note: the reactions describes a hydroxide ion donor)

where OH^{-1} is the hydroxyl or hydroxide ion and M^{+1} is normally a metal. A notable exception is the nonmetal group NH_4^{+1} which is the cation part of the weak base NH_4OH.

If the reaction MOH ---> M^{+1} + OH^{-1} goes 100% toward completion, the base is an excellent donor of hydroxyl ions and is said to be a strong base. Perhaps a few examples of bases would be helpful at this point!

$NaOH$ --100% --> Na^{+1} + OH^{-1}	Sodium Hydroxide,	a strong base
KOH --100% --> K^{+1} + OH^{-1}	Potassium Hydroxide,	a strong base
NH_4OH --~1% --> NH_4^{+1} + OH^{-1}	Ammonium Hydroxide,	a weak base
$NH_3 \cdot H_2O$ --~1% --> NH_4^{+1} + OH^{-1}	Ammonium Hydroxide,	a weak base

Arrhenius acid-base theory is characterized by a neutralization reaction: the reaction of a acid plus a base to form water and a salt.

1. hydrochloric acid plus sodium hydroxide yields water plus sodium chloride (salt)

HCl + $NaOH$ -------> HOH + $NaCl$
or HCl + $NaOH$ -------> HOH + Na^{+1}_{aq} + Cl^{-1}_{aq}

2. sulfuric acid plus sodium hydroxide yields water plus sodium sulfate

H_2SO_4 + 2 $NaOH$ --------> 2 HOH + Na_2SO_4
or H_2SO_4 + 2 $NaOH$ --------> 2 HOH + 2 Na^{+1}_{aq} + $SO_4^{-2}{}_{aq}$

3. phosphoric acid plus sodium hydroxide yields water plus sodium phosphate

H_3PO_4 + 3 $NaOH$ --------> 3 HOH + Na_3PO_4
or H_3PO_4 + 3 $NaOH$ --------> 3 HOH + 3 Na^{+1}_{aq} + $PO_4^{-3}{}_{aq}$

Lowry-Bronsted Acid - Base Theory

<u>A Lowry Bronsted acid is a proton donor while a Lowry-Bronsted base is a proton acceptor</u>. Note that the definition of a Lowry-Bronsted acid is similar to the Arrhenius definition and all Arrhenius acids are also Lowry Bronsted acids.

The compound CO_2 is an example of a material that is not an Arrhenius acid but still causes acidic properties in water solution. If CO_2 is bubbled through water, the resulting solution is acidic. In fact, most water sitting around will be slightly acidic because of CO_2 absorption. The CO_2 interacts with the water and helps the water free up proton. In a sense CO_2 indirectly causes donation of proton to the system and functions as a Lowry-Bronsted acid.

$CO_2 + H_2O \text{ ------> } [\,H_2CO_3\,] \text{ -----> } H^{+1} + HCO_3^{-1}$
Carbon dioxide Carbonic Acid Hydrogen Carbonate

A Lowry-Bronsted base is a proton acceptor. Clearly, the hydroxide ion which is the particle involved in the definition of an Arrhenius base is a very good proton acceptor and also a Lowry-Bronsted base. There are, however, a number of particles other than the hydroxide ion that are also good proton acceptors and Lowry-Bronsted bases.

NH_3 (ammonia), NH_2^{-1} (amide ion), CH_3OH (methyl alcohol), and CH_3O^{-1} (Methoxide ion) are a few common examples of good proton acceptors and Lowry Bronsted bases beyond the OH^{-1}. Reactions for these bases are as follows.

Proton acceptor (Lowry-Bronsted Base)		Proton donor (Lowry-Bronsted Acid)				
NH_3 ammonia	+	HCl hydrochloric acid	------------->	NH_4^{+1}	+	Cl^{-1}
NH_2^{-1} amide ion	+	HCl	-------------->	NH_3	+	Cl^{-1}
CH_3OH methyl alcohol	+	HCl	-------------->	$CH_3OH_2^{+1}$	+	Cl^{-1}
CH_3O^{-1} Methoxide ion	+	HCl	------------->	CH_3OH	+	Cl^{-1}

Note that the products result from the transfer of a H^+ from the acid to the base (a H and a positive charge are transferred).

Most acids can be considered as a proton and anion bonded together. The anion is also called the conjugate base of the acid. A few examples.

Hydrochloric Acid,	a strong acid			
HCl	---->	H^{+1}	+	Cl^{-1}
uncharged		proton		chloride anion
acid				(conjugate base of HCl)

Nitric Acid,	a strong acid			
HNO_3	---->	H^{+1}	+	NO_3^{-1}
uncharged		proton		nitrate anion
acid				(conjugate base of HNO_3)

Hydrofluoric Acid,	a weak acid			
HF	<---->	H^{+1}	+	F^{-1}
uncharged		proton		fluoride anion
acid				(conjugate base of HF)

Again, NH_4^+ is a cationic acid and a notable exception to the notion of an acid being a proton bonded to anion. Since the acid is cationic (charged positively, +1), removal of a proton produces an uncharged conjugate base.

Ammonium Cation,	a weak acid			
NH_4^{+1}	------>	H^{+1}	+	NH_3
charged		proton		ammonia
acid				(uncharged conjugate base of NH_4^{+1})

Well, here is the major point! By definition weak acids do not give up proton well because their anions or conjugate bases have good affinity for the proton; therefore, the anion parts or the conjugate bases of a weak acids are a good proton acceptors and Lowry-Bronsted bases.

Perhaps a few examples:

Acetic Acid ($HC_2H_3O_2$) is a weak acid, and its anion or conjugate base is the acetate ion $C_2H_3O_2^{-1}$. To get the anion or conjugate base just remove a proton (H^+) from the acid. Acetate ion is a good proton acceptor and a Lowry-Bronsted base.

Acetate is 1. Anion of Weak Accid, 2. Conjugate base of the Weak Acid
3. Good Proton Acceptor and 4. a Lowry-Bronsted base

$C_2H_3O_2^{-1}$	+	HCl	----------->	$HC_2H_3O_2$	+	Cl^{-1}
Acetate ion		Hydrochloric Acid		Actetic Acid		Chloride ion

Nitrous acid and hydrofluoric acid are a weak acids; therefore, nitrite ion (the conjugate base of nitrous acid) and fluoride ion (the conjugate base of hydrofluoric acid) are Lowry-Bronsted bases.

NO_2^{-1} + HCl ------------> HNO_2 + Cl^{-1}
(nitrite from nitrous acid) (nitrous acid, a weak acid)

F^{-1} + HCl ------------> HF + Cl^{-1}
(fluoride from hydrofluoric acid) (hydrofluoric acid, a weak acid)

<u>Lowry-Bronsted acid base chemistry is characterized by a transfer of a proton (H^+) from an acid to a base</u>. When an acid gives up a proton, it forms its conjugate base. When a base gains a proton, it forms it conjugate acid.

________called conjugate pairs________
| base | acid
| |
$C_2H_3O_2^{-1}$ + HCl -----------> $HC_2H_3O_2$ + Cl^{-1}
| acid | base
| |
__________called conjugate pairs______

or

HCl $C_2H_3O_2^{-1}$
Lowry Bronsted Acid ---- Transfers a H^+-------->Lowry Bronsted Base
Proton donor Proton acceptor
| |
| |
Loss of a Proton Gain of a Proton
| |
| |
\/ \/
Generates the Conjugate base of the acid Generates the Conjugate acid of the base
Cl^{-1} $HC_2H_3O_2$

One last thought on Lowry-Bronsted acid-base theory. If a Lowry-Bronsted acid is good proton donor, then its conjugate base must not have much affinity for the proton, be a weak proton acceptor, and be a weak Lowry-Bronsted base. In fact there is a rule that states that the stronger a Lowry-Bronsted acid the weaker its conjugate base.

Remember that hydrochloric acid (HCl), nitric acid (HNO_3), hydrobromic acid (HBr), hydroiodic acid (HI), and perchloric acid ($HClO_4$), are all very strong acids (HX ----100%---> H^+ + X^-); therefore, the anions (or conjugate bases) of these acids (chloride (Cl^-), nitrate (NO_3^-), bromide (Br^-), iodide (I^-), and perchlorate (ClO_4^-)) are all very, very poor proton acceptors. In fact these anion have no affinity for proton and are called neutral anions. Put these anions into water and they do not attract or accept proton, and the resulting solution will be neutral.

X^- + H_2O --------> no reaction, neutral solution

where X is chloride, nitrate, bromide, iodide, or perchlorate

Remember that hydrofluoric, acetic, hydrocyanic, are weak acids (HX ---- not 100%---> H^+ + X^-); therefore, the anions (or conjugate bases) of these acids (fluoride (F^-), acetate ($C_2H_3O_2^-$), cyanide (CN^-)) are all good proton acceptors. Put these anions into water, and they will attract or accept proton, generate hydroxyl ions, and make the resulting solution will be basic. These anions are called basic anions.

X^- + H_2O --------> HX + OH^- (basic solution)

where X is the anion (conjugate base) of a weak acid

Remember the rule that states that the stronger an acid the weaker it conjugate base?

Weak Acid -----remove a proton and get ----> anion or conjugate base

/\ HF | F^-
| |
| $HC_2H_3O_2$ | $C_2H_3O_2^-$
| |
| HCN \/ CN^-
Stronger Acid
Stronger Conjugate Base

or

HF is a stronger acid than HCN; therefore, CN^- is a stronger base than F^-

Lewis Acid Base Theory

A Lewis acid is any molecule that can from a bond by accepting a pair of electrons from another molecule. The molecule that donates the electron pair is called a Lewis base. So, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.

The hydroxide ion which was the focus of the definition of the Arrhenius base has three lone pairs and is, therefore, a Lewis base. Molecules that are good proton acceptors (Lowry Bronsted bases) are so because they have lone pairs (i.e. $:NO_2^{-1}$ and $:CN^{-1}$). So hydroxide ion and other Lowry-Bronsted bases are also Lewis base molecules.

The proton which is so central to both Arrhenius and Lowry-Bronsted acid-base chemistry is electron deficient (no electrons) and a very good electron pair acceptor. The proton, therefore, is also a Lewis acid. There are, however, other molecules beyond the proton that are electron deficient, can accept electron pairs, and function as Lewis acids.

A few Lewis acid/base reactions follow:

1. Lewis Acid 2. Electron Pair Acceptor		1. Lewis Base 2. Electron Pair Donor		
H^+	+	OH^-	-------->	H_2O
H^+	+	H_2O	--------->	H_3O^+
H^+	+	CN^-	-------->	HCN
H^+	+	CH_3OH	--------->	$CH_3OH_2^+$
BF_3	+	NH_3	-------->	F_3BNH_3
Co^{+2}	+	H_2O	-------->	$Co(H_2O)^{+2}$
$FeCl_3$	+	Cl^-	--------->	$FeCl_4^{-1}$
$AlCl_3$	+	Cl^-	---------->	$AlCl_4^{-1}$

Acid-Base Character of Salts
A Summary

A salt is made up of a cation and anion. A few examples follow.

$NaCl$	Na^+	Cl^-	Sodium Chloride
KF	K^+	F^-	Potassium Fluoride
KNO_3	K^+	NO_3^-	Potassium Nitrate
NH_4Br	NH_4^+	Br^-	Ammonium Bromide

Remember also that the common strong acids and bases are as follows:

Common Strong Acids		Common Strong Bases	
Hydrochloric	HCl	Sodium Hydroxide	$NaOH$
Hydrobromic	HBr	Potassium Hydroxide	KOH
Hydroiodic	HI		
Nitric	HNO_3		
Perchloric	$HClO_4$		

1. Cations of strong bases (Na^+, K^+ ,Cs^+, Li^+, Rb^+, Ca^{+2}, and Ba^{+2}) have no affinity for hydroxide ion and are neutral in water.

2. Anions or conjugate bases of strong acids (Cl^-, Br^-, I^-, NO_3^-, and ClO_4^-) have no affinity for proton and are neutral in water.

3. Cations from weak bases (most notable NH_4^+ from the weak base NH_4OH) do have affinity for hydroxide ion and are acidic in water. In addition many metal ions (IA, Ca^{+2}, and Ba^{+2} are noted exceptions) are acidic in water. These cations attract hydroxyl ion and free up proton to make the solution acidic.

$$NH_4^+ + H_2O \longrightarrow H_3O^+ + NH_3$$

or

$$NH_4^+ + 2\ H_2O \longrightarrow H_3O^+ + NH_4OH$$

$$Al^{+3} + 2\ H_2O \longrightarrow H_3O^+ + Al(OH)^{+2}$$

$$Zn^{+2} + 2\ H_2O \longrightarrow H_3O^+ + Zn(OH)^{+1}$$

4. Anions or conjugate bases of weak acids have affinity for proton and <u>are basic in water.</u> A few examples of these types of anions are as follows:

Acetic acid ($HC_2H_3O_2$) is a weak acid; therefore, acetate ($C_2H_3O_2^-$) its anion or conjugate base is basic

$$C_2H_3O_2^- \quad + \quad H_2O \longrightarrow HC_2H_3O_2 \quad + \quad OH^-$$

Nitrous acid (HNO_2) is a weak acid; therefore, nitrite ion (NO_2^-) its anion or conjugate base is basic

$$NO_2^- \quad + \quad H_2O \longrightarrow HNO_2 \quad + \quad OH^-$$

Perhaps a few applications are necessary!

NaCl is made up of the cation Na^+ and the anion Cl^-. Both the Na^+ cation and Cl^- anion are neutral, so NaCl is neutral in water.

NaF is made up of the cation Na^+ and the anion F^-. The Na^+ cation is neutral; however, F^- is the anion from a weak acid and basic. NaF is, therefore, basic in water.

$$F^- \quad + \quad H_2O \longrightarrow HF \quad + \quad OH^-$$

NH_4Cl is made up of the cation NH_4^+ and the anion Cl^-. The NH_4^+ cation is acidic, and Cl^- which is an anion from a strong acid is neutral. NH_4Cl is acidic in water.

$$NH_4^+ + \quad 2\ H_2O \longrightarrow H_3O^+ \quad + \quad NH_4OH$$

$FeCl_3$ is made up of the cation Fe^{+3} and the anions Cl^-. The Fe^{+3} cation is acidic, and Cl^- which is an anion from a strong acid is neutral. $FeCl_3$ is acidic in water.

$$Fe^{+3} \quad + \quad 2\ H_2O \longrightarrow H_3O^+ \quad + \quad Fe(OH)^{+2}$$