

## 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



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

If the reaction  $\text{HX} \text{ ----> } \text{H}^{+1} + \text{X}^{-1}$  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!

$\text{HCl} \rightarrow 100\% \rightarrow \text{H}^{+1} + \text{Cl}^{-1}$ ,	Hydrochloric Acid,	a strong acid
$\text{HNO}_3 \rightarrow 100\% \rightarrow \text{H}^{+1} + \text{NO}_3^{-1}$ ,	Nitric Acid,	a strong acid
$\text{HBr} \rightarrow 100\% \rightarrow \text{H}^{+1} + \text{Br}^{-1}$ ,	Hydrobromic Acid,	a strong acid
$\text{HI} \rightarrow 100\% \rightarrow \text{H}^{+1} + \text{I}^{-1}$ ,	Hydroiodic Acid,	a strong acid
$\text{HClO}_4 \rightarrow 100\% \rightarrow \text{H}^{+1} + \text{ClO}_4^{-1}$ ,	Perchloric Acid,	a strong acid
$\text{HF} \rightarrow \sim 30\% \rightarrow \text{H}^{+1} + \text{F}^{-1}$ ,	Hydrofluoric Acid,	a weak acid
$\text{HC}_2\text{H}_3\text{O}_2 \rightarrow \sim 1\% \rightarrow \text{H}^{+1} + \text{C}_2\text{H}_3\text{O}_2^{-1}$	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

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

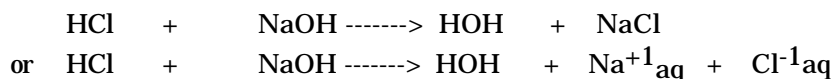
where  $\text{OH}^{-1}$  is the hydroxyl or hydroxide ion and  $\text{M}^{+1}$  is normally a metal. A notable exception is the nonmetal group  $\text{NH}_4^{+1}$  which is the cation part of the weak base  $\text{NH}_4\text{OH}$ .

If the reaction  $\text{MOH} \rightarrow \text{M}^{+1} + \text{OH}^{-1}$  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!

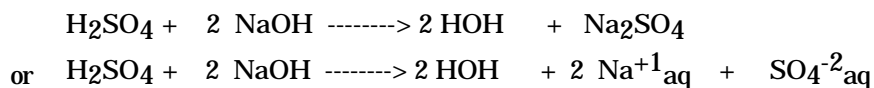
$\text{NaOH} \rightarrow 100\% \rightarrow \text{Na}^{+1} + \text{OH}^{-1}$	Sodium Hydroxide,	a strong base
$\text{KOH} \rightarrow 100\% \rightarrow \text{K}^{+1} + \text{OH}^{-1}$	Potassium Hydroxide,	a strong base
$\text{NH}_4\text{OH} \rightarrow \sim 1\% \rightarrow \text{NH}_4^{+1} + \text{OH}^{-1}$	Ammonium Hydroxide,	a weak base
$\text{NH}_3\text{-H}_2\text{O} \rightarrow \sim 1\% \rightarrow \text{NH}_4^{+1} + \text{OH}^{-1}$	Ammonium Hydroxide,	a weak base

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

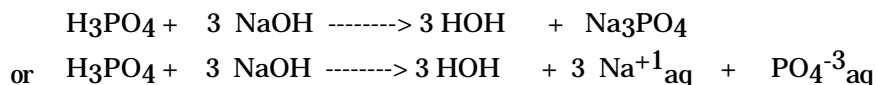
1. hydrochloric acid plus sodium hydroxide yields water plus sodium chloride (salt)



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



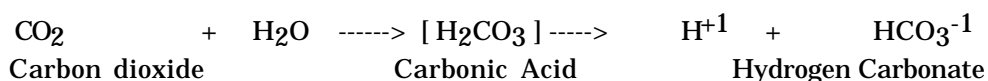
3. phosphoric acid plus sodium hydroxide yields water plus sodium phosphate



## Lowry-Bronsted Acid - Base Theory

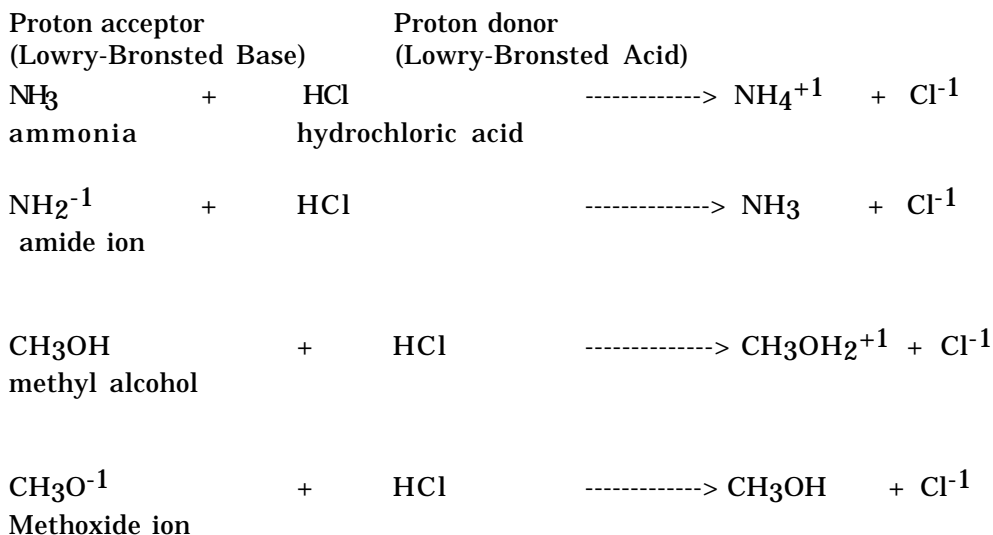
A Lowry Bronsted acid is a proton donor while a Lowry-Bronsted base is a proton acceptor. Note that the definition of a Lowry-Bronsted acid is similar to the Arrhenius definition and all Arrhenius acids are also Lowry Bronsted acids.

The compound CO<sub>2</sub> is an example of a material that is not an Arrhenius acid but still causes acidic properties in water solution. If CO<sub>2</sub> is bubbled through water, the resulting solution is acidic. In fact, most water sitting around will be slightly acidic because of CO<sub>2</sub> absorption. The CO<sub>2</sub> interacts with the water and helps the water free up proton. In a sense CO<sub>2</sub> indirectly causes donation of proton to the system and functions as a Lowry-Bronsted acid.



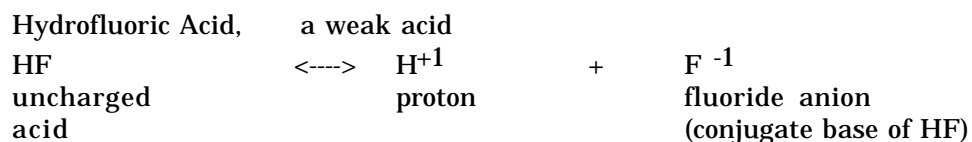
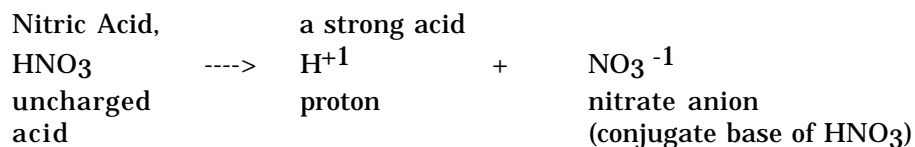
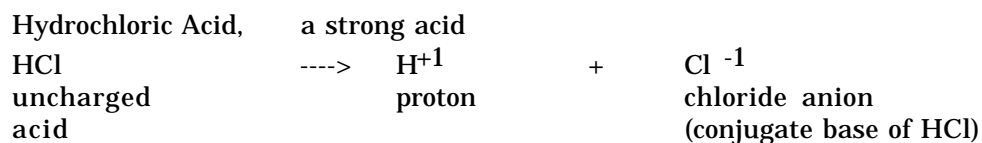
A Lowry-Bronsted base is a proton acceptor. Clearly, the hydroxide ion which is the particle involved in the definition of an Arrhenius base is a very good proton acceptor and also a Lowry-Bronsted base. There are, however, a number of particles other than the hydroxide ion that are also good proton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

NH<sub>3</sub> (ammonia), NH<sub>2</sub><sup>-1</sup> (amide ion), CH<sub>3</sub>OH (methyl alcohol), and CH<sub>3</sub>O<sup>-1</sup> (Methoxide ion) are a few common examples of good proton acceptors and Lowry Bronsted bases beyond the OH<sup>-1</sup>. Reactions for these bases are as follows.

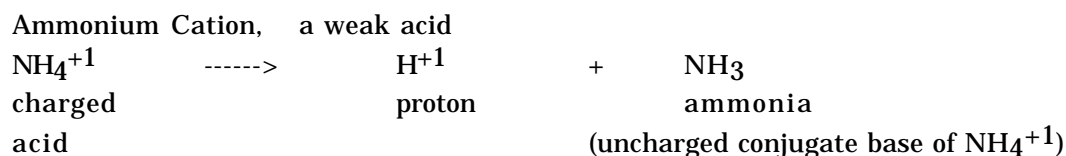


Note that the products result from the transfer of a H<sup>+</sup> from the acid to the base (a H and a positive charge are transferred).

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.



Again, NH<sub>4</sub><sup>+</sup> 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.

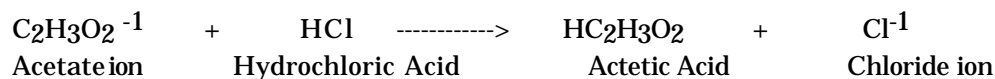


Well, here is the major point! By definition weak acids do not give up proton well because their anions or conjugate bases have good affinity for the proton; therefore, the anion parts or the conjugate bases of a weak acids are a good proton acceptors and Lowry-Bronsted bases.

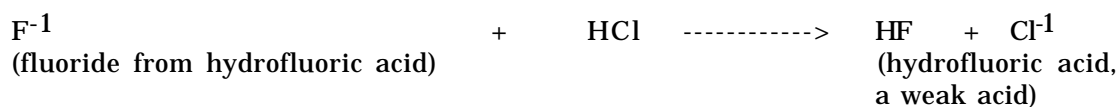
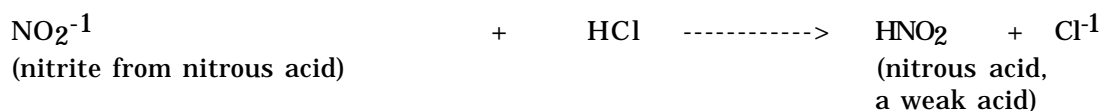
Perhaps a few examples:

Acetic Acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) is a weak acid, and its anion or conjugate base is the acetate ion C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-1</sup>. To get the anion or conjugate base just remove a proton (H<sup>+</sup>) from the acid. Acetate ion is a good proton acceptor and a Lowry-Bronsted base.

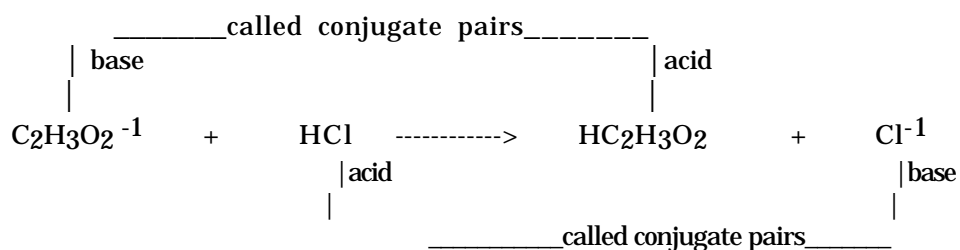
Acetate is 1. Anion of Weak Acid, 2. Conjugate base of the Weak Acid  
3. Good Proton Acceptor and 4. a Lowry-Bronsted base



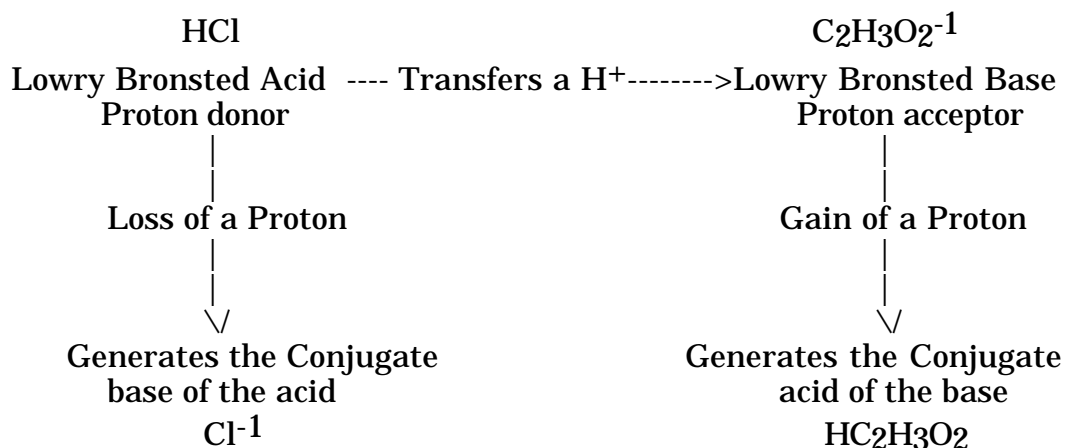
Nitrous acid and hydrofluoric acid are weak acids; therefore, nitrite ion (the conjugate base of nitrous acid) and fluoride ion (the conjugate base of hydrofluoric acid) are Lowry-Bronsted bases.



Lowry-Bronsted acid base chemistry is characterized by a transfer of a proton ( $\text{H}^+$ ) from an acid to a base. When an acid gives up a proton, it forms its conjugate base. When a base gains a proton, it forms its conjugate acid.

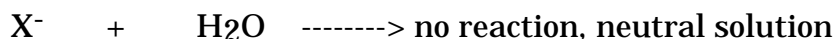


or



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<sub>3</sub>), hydrobromic acid (HBr), hydroiodic acid (HI), and perchloric acid (HClO<sub>4</sub>), are all very strong acids (HX  $\rightarrow$  100%  $\rightarrow$  H<sup>+</sup> + X<sup>-</sup>); therefore, the anions (or conjugate bases) of these acids (chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), bromide (Br<sup>-</sup>), iodide (I<sup>-</sup>), and perchlorate (ClO<sub>4</sub><sup>-</sup>)) are all very, very poor proton acceptors. In fact these anions 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.



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

Remember that hydrofluoric, acetic, hydrocyanic, are weak acids (HX  $\rightarrow$  not 100%  $\rightarrow$  H<sup>+</sup> + X<sup>-</sup>); therefore, the anions (or conjugate bases) of these acids (fluoride (F<sup>-</sup>), acetate (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>), cyanide (CN<sup>-</sup>)) 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.



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

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

Weak Acid  $\rightarrow$  remove a proton and get  $\rightarrow$  anion or conjugate base



or

HF is a stronger acid than HCN; therefore, CN<sup>-</sup> is a stronger base than F<sup>-</sup>

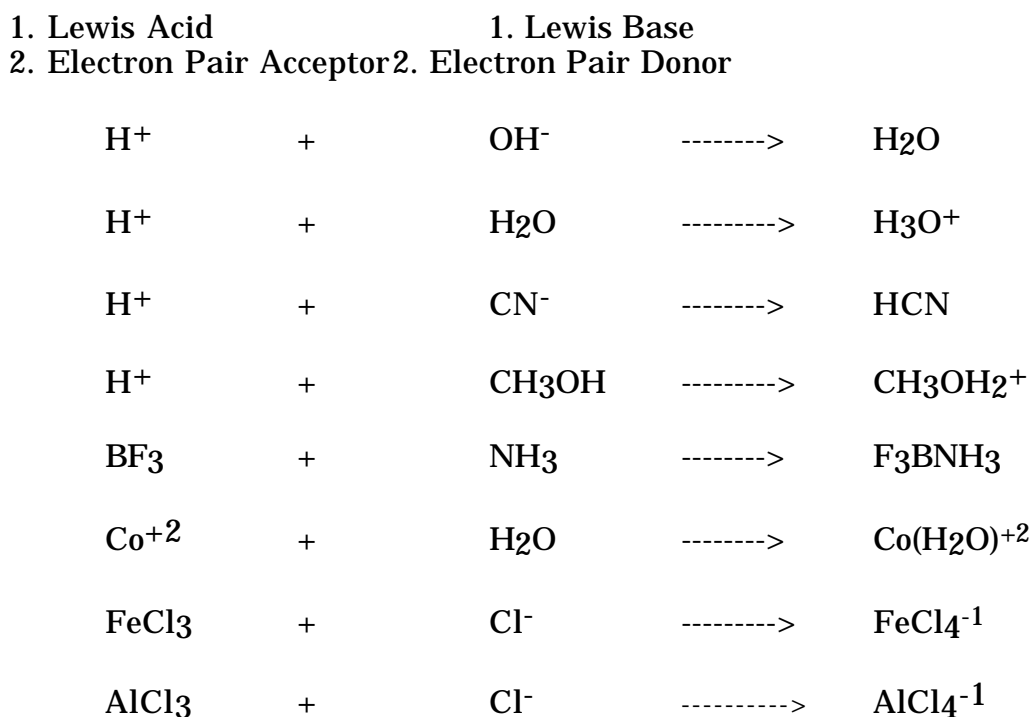
## Lewis Acid Base Theory

A Lewis acid is any molecule that can form 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.  $:\text{NO}_2^{-1}$  and  $:\text{CN}^{-1}$ ). 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:



## Acid-Base Character of Salts A Summary

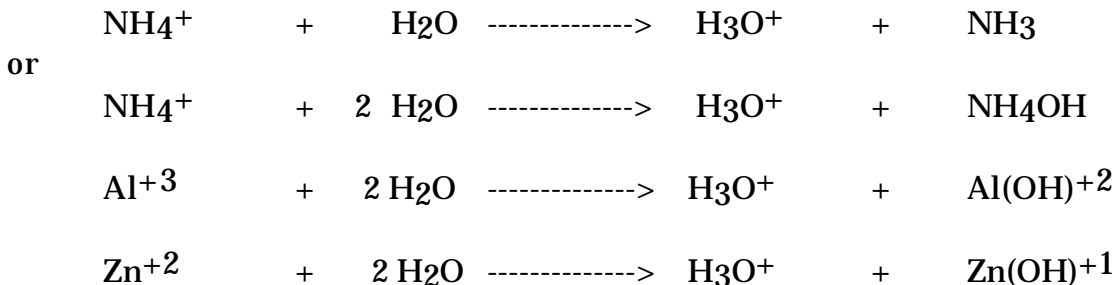
A salt is made up of a cation and anion. A few examples follow.

NaCl	Na <sup>+</sup>	Cl <sup>-</sup>	Sodium Chloride
KF	K <sup>+</sup>	F <sup>-</sup>	Potassium Fluoride
KNO <sub>3</sub>	K <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	Potassium Nitrate
NH <sub>4</sub> Br	NH <sub>4</sub> <sup>+</sup>	Br <sup>-</sup>	Ammonium Bromide

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

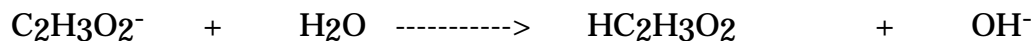
Common Strong Acids	Common Strong Bases
Hydrochloric HCl	Sodium Hydroxide NaOH
Hydrobromic HBr	Potassium Hydroxide KOH
Hydroiodic HI	
Nitric HNO <sub>3</sub>	
Perchloric HClO <sub>4</sub>	

1. Cations of strong bases (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Li<sup>+</sup>, Rb<sup>+</sup>, Ca<sup>+2</sup>, and Ba<sup>+2</sup>) have no affinity for hydroxide ion and are neutral in water.
2. Anions or conjugate bases of strong acids (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup>) have no affinity for proton and are neutral in water.
3. Cations from weak bases (most notable NH<sub>4</sub><sup>+</sup> from the weak base NH<sub>4</sub>OH) do have affinity for hydroxide ion and are acidic in water. In addition many metal ions (IA, Ca<sup>+2</sup>, and Ba<sup>+2</sup> are noted exceptions) are acidic in water. These cations attract hydroxyl ion and free up proton to make the solution acidic.



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

Acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) is a weak acid; therefore, acetate ( $\text{C}_2\text{H}_3\text{O}_2^-$ ) its anion or conjugate base is basic



Nitrous acid ( $\text{HNO}_2$ ) is a weak acid; therefore, nitrite ion ( $\text{NO}_2^-$ ) its anion or conjugate base is basic



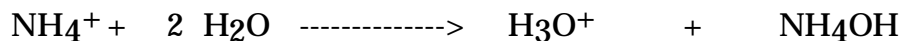
Perhaps a few applications are necessary!

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

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



$\text{NH}_4\text{Cl}$  is made up of the cation  $\text{NH}_4^+$  and the anion  $\text{Cl}^-$ . The  $\text{NH}_4^+$  cation is acidic, and  $\text{Cl}^-$  which is an anion from a strong acid is neutral.  $\text{NH}_4\text{Cl}$  is acidic in water.



$\text{FeCl}_3$  is made up of the cation  $\text{Fe}^{+3}$  and the anions  $\text{Cl}^-$ . The  $\text{Fe}^{+3}$  cation is acidic, and  $\text{Cl}^-$  which is an anion from a strong acid is neutral.  $\text{FeCl}_3$  is acidic in water.

