

# Chapter 2: Why Is An Acid-Base Theme Important?

- The operational theme of this book suggests that understanding acid and base chemistry will lead to a better understanding of Organic chemistry.
- Applying acid-base principles to many reactions allows one to understand and predict that reaction rather than simply memorizing it.
- To examine this premise, the acid-base reactions found in General chemistry must be reexamined to determine how they can be applied directly, or when they must be modified.

## To begin, you should know:

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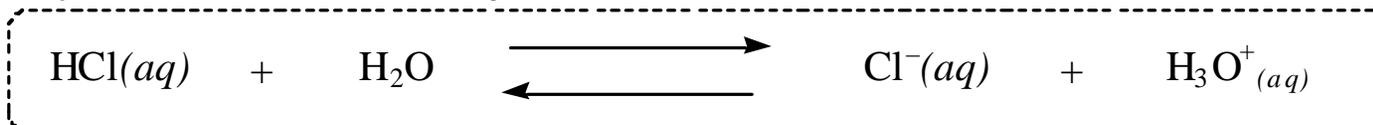
- Define and recognize the structures of simple Brønsted-Lowry acids and bases as well as simple Lewis acids and bases.
- Understand the definitions of conjugate acid and conjugate base.
- Understand the fundamentals of acid-base strength in aqueous media
- Understand the role of water in acid base equilibria.
- Understand  $K_a$  and  $pK_a$  and how to manipulate them.
- Recognize classical mineral acids.
- Recognize classical Brønsted-Lowry bases.

## When completed, you should know:

- There is an inverse relationship between  $K_a$  and  $pK_a$ , and a large  $K_a$  or a small  $pK_a$  is associated with a stronger acid.
- It is important to put water back into the acid-base reaction for aqueous media.
- The fundamental difference between a Brønsted-Lowry acid and a Lewis acid is that the former is a proton that accepts electrons and the latter is any other atom that accepts electrons. The fundamental difference between a Brønsted-Lowry base and a Lewis base is that the former donates electrons to a proton and the latter donates electrons to another atom.
- Curved arrows are used to indicate electron flow from a source of high electron density to a point of low electron density.
- Acid strength in an acid X–H is largely determined by the stability of the conjugate acid and base, and the strength of the X–H bond. For example, HI is a stronger acid than HF due to a weaker X–H bond and charge dispersal in the larger anionic conjugate base. An acid such as perchloric acid is stronger than sulfuric acid due to charge dispersal in the conjugate base that results from resonance.
- Base strength is largely determined by the stability of the conjugate acid and base, and the electron donating ability of the basic atom. Water is a stronger acid than ammonia because hydroxide ion is more stable than the amide anion and the OH bond is weaker than the NH bond. Ammonia is a stronger base than water because oxygen is more electronegative than nitrogen, and the ammonium ion is more stable than the hydronium ion.
- Reaction of a Lewis acid and a Lewis base leads to an ate complex as the product.

## Brønsted-Lowry Acids and Bases

- In 1884, Svante A. Arrhenius (Sweden, 1859-1927) defined an acid as a material that can release a proton or hydrogen ion ( $\text{H}^+$ ).
- When hydrogen chloride ( $\text{HCl}$ ) is dissolved in water, a solution is formed via ionization that leads to hydrated hydrogen ions and hydrated chloride ions. Using the original definition, a base (then called an alkali) is a material that can donate a hydroxide ion ( $\text{OH}^-$ ). Sodium hydroxide in water solution ionizes to hydrated sodium ions and hydrated hydroxide ions.
- This concept led to a definition of acids and bases as reported independently in 1923, by Thomas M. Lowry (England, 1874-1936) and Johannes Nicolas Brønsted (Denmark, 1879-1947).
- *According to this definition, an acid is a material that donates a proton and a base is a material that can accept a proton, the Brønsted-Lowry definitions mentioned above.*



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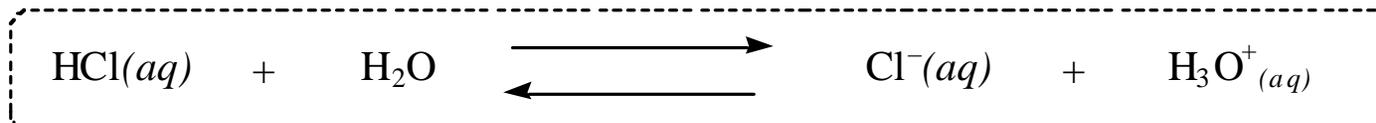
**Svante A. Arrhenius**  
(Sweden, 1859-1927)

**Johannes Nicolas Brønsted**  
(Denmark, 1879-1947)

**Thomas M. Lowry**  
(England, 1874-1936)

## Brønsted-Lowry Acids and Bases

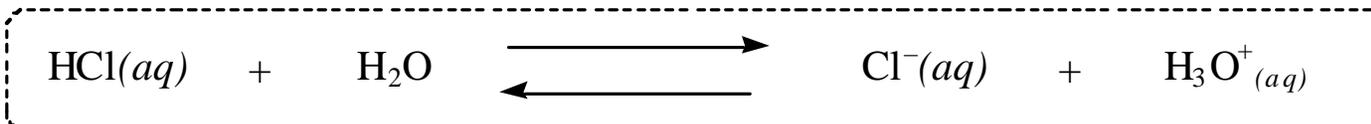
According to Brønsted and Lowry, an acid-base reaction is defined in terms of a proton transfer. By this definition, the reaction of HCl in water is:



### *Water is the base in this reaction.*

- Acid and base reactions in General chemistry are always done in water.
- When a Brønsted-Lowry acid such as HCl is placed in water, a proton is transferred to a water molecule (water is the base); a conjugate acid is formed (the hydronium ion  $\text{H}_3\text{O}^+$ ) as well as a conjugate base (the chloride ion).
- In neutral pure water (no acid is present), the hydrogen ion concentration is about  $1.0 \times 10^{-7}$  M (pH of 7).
- **An increase in the concentration of hydrogen ions above  $1.0 \times 10^{-7}$  M gives an acidic solution, with a pH less than 7.**
- **If the pH is  $>7$ , it is considered a basic solution.**

## Strong Brønsted-Lowry Acids and Bases



**The criterion for acid strength is the extent of ionization in water.**

- The mineral acids HCl, HBr, HI, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and HClO<sub>4</sub> are all strong acids.

**Strong bases are extensively ionized in water.**

- Common strong bases include NaOH (soda lye), KOH (potash lye), LiOH, CsOH, Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub>.

**The relative strength of these acids and bases are defined by their reaction with water.**

## Weak Brønsted-Lowry Acids and Bases

**The criterion for acid strength is the extent of ionization in water.**

**Weak acids and weak bases will ionize to a lesser extent in water relative to the strong acids or bases.**

- Weak acids are solutes that react reversibly with water to form  $\text{H}_3\text{O}^+$  ions, and there are two categories.
  - molecules containing an ionizable hydrogen atom such as nitrous acid ( $\text{HNO}_2$ )
  - cations such as the ammonium ion ( $\text{NH}_4^+$ ).
- Weak bases are defined as solutes that react with water molecules to acquire a  $\text{H}^+$  ion and leave an hydroxide ion ( $\text{HO}^-$ ) behind.
- An example of a weak base is the reaction of ammonia + water to give the ammonium cation and hydroxide anion.
- Weak acids that will be discussed in this book are acetic acid ( $\text{CH}_3\text{COOH}$ ), boric acid ( $\text{H}_3\text{BO}_3$ ), butanoic acid ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ ), formic acid ( $\text{HCOOH}$ ), hydrocyanic acid ( $\text{HCN}$ ), and uric acid ( $\text{HC}_5\text{H}_3\text{N}_4\text{O}_3$ ), and the fatty acid known as stearic acid [ $\text{CH}_2(\text{CH}_2)_{15}\text{CH}_2\text{COOH}$ , an 18-carbon acid].
- Weak bases include ammonia ( $\text{NH}_3$ ), and amines such as methylamine ( $\text{CH}_3\text{NH}_2$ ), triethylamine [ $(\text{CH}_3)_3\text{N}$ ], and pyridine ( $\text{C}_5\text{H}_5\text{N}$ ).

**The relative strength of these acids and bases are defined by their reaction with water.**

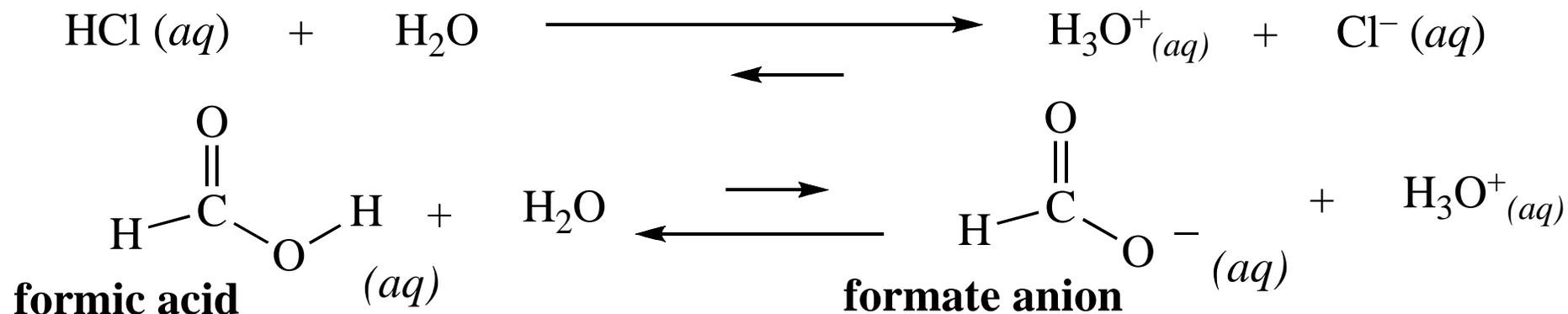
## Organic Acids and Bases

***Acid-Base chemistry is important in Organic chemistry.***

- *Many organic acids and bases are insoluble in water, so the classical Brønsted-Lowry definition does not formally apply.*
- *A very weak acid can react with a particularly strong base, and a very weak base may react with a particularly strong acid.*
- **If an organic molecule is a very weak base, for example, an acid-base reaction occurs only if that base is treated with a very strong acid.**
- **A solvent other than water is required to put organic acids or bases into solution, and this “other” solvent is typically another organic compound.**
- **Diethyl ether ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ), hexane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) are common solvents.**
- **A water-organic solvent mixture is often required to make the acid-base components soluble.**

## Comparing an Organic Acid and HCl

- Water reacts with the strong acid HCl, and the much weaker organic acid formic acid (HCOOH).
- The reaction of formic acid and water generates the conjugate base known as the formate anion, and the conjugate acid, the hydronium ion.
- Formic acid is a weaker acid than HCl, so ***the equilibrium lies to the left for HCOOH when compared with the equilibrium for HCl.***
- Note the (aq) term, which indicates solvation of that molecule or ion by the solvent, which is water.
- Note also that ***the term reaction is used for the acid-base equilibrium.***

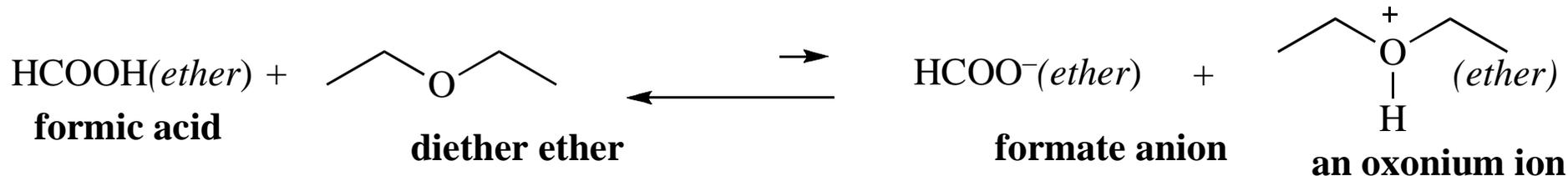




## Acids in Organic Solvents

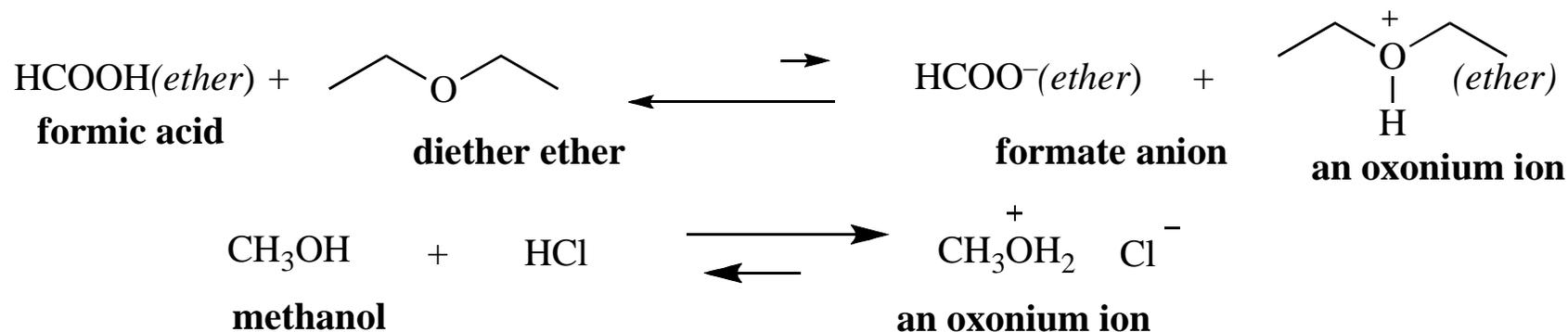
Consider the reaction of formic acid using diethyl ether as a solvent rather than water. Note the (*ether*) term in the reaction, indicating solvation by ether rather than by water.

- The organic solvent diethyl ether is also the base, just as water is the base in reactions with HCl or HCOOH.
  - The basic atom in diethyl ether is the oxygen, and it reacts with the weak acid (formic acid) to give the formate anion (the conjugate base).
  - The conjugate acid is the protonated form of ether (an oxonium ion).
  - The equilibrium lies to the left in the reaction because that formic acid is a weak acid in ether, but ***the definition of strong or weak acid relating to dissociation in water no longer applies.***
  - It is the same reaction, in principle, but the solvent is different and that influences the position of the equilibrium. In fact, *the equilibrium for formic acid lies further to the left in ether than in water, so formic acid is a weaker acid in ether than in water.*
- <sup>a</sup> This important statement suggests that ***the strength of the acid depends on the base it reacts with,*** which is critical for establishing where the equilibrium lies, to the left or to the right.



## Acids in Different Organic Solvents

- If HCl is placed in anhydrous (no water) methanol, where methanol is the solvent, the oxygen of the methanol is the only available base for reaction with the acid HCl.
- The oxygen of methanol reacts with HCl to form oxonium ion (the conjugate acid), with chloride ion as the counterion (the conjugate base).
- The term (*ether*) is used for solvation in the formic acid reaction to show the analogy to the water reaction, but the (*methanol*) designation is omitted in this case.
- Although *it is understood that all components are solvated by the solvent methanol, the solvation term is usually omitted in Organic chemistry and it will be omitted throughout the book.*
- The important point of this reaction is the same as the formic acid reaction in ether. ***The definition for ionization in water does not apply, but ionization is still the key to the acid base reaction regardless of solvent.***
- This leads to the idea that ***an acid reacts with a base, regardless of solvent, but the extent of ionization changes with the solvent and with the base.***
- **In fact, the degree of ionization changes as the acid and the base are changed and also as the solvent is changed.**



## Equilibrium Constants



Remember from General chemistry that the equilibrium constant,  $K_a$  (acidity constant) is given by the following generalized equation when the reaction is done in water.

$$K_a = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]}$$

and for HCl in water

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}]}$$

However, the actual equation for the equilibrium constant for this particular reaction is:

$$K_a = \frac{[\text{conjugate acid}][\text{conjugate base}]}{[\text{acid}][\text{base}]}$$

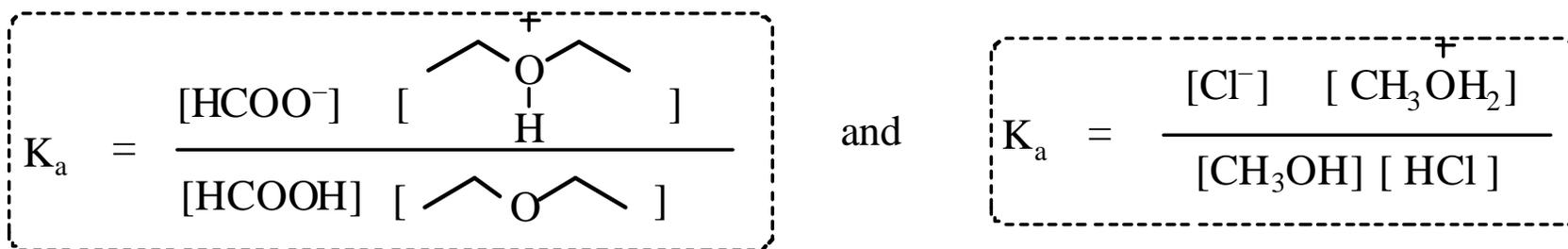
so,

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}][\text{base}]}$$

- The base in the HCl reaction is actually the water from the solvent. ***Where is the term for water in the first set of equations?***
- In General chemistry the water is *removed* from the equation to simplify calculations.
- ***However, when water is removed from the equilibrium constant equation this act also removes the **base** from the acid base equation.***
- If water is not the solvent and there is a different base in the reaction, *the base certainly must be put back in the equation*

## Put the Base Back Into Acid-Base Reactions

The equilibrium constants for the formic acid reaction with ether as well as the methanol and HCl reaction must use the  $K_a$  equations:

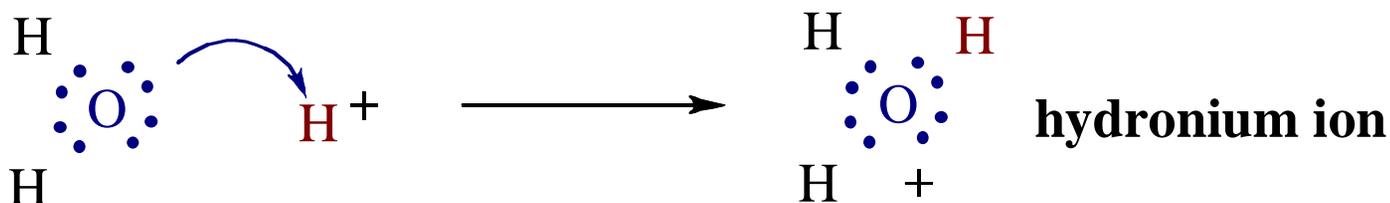


- This analysis relies on the Brønsted-Lowry definitions of an acid and a base as used in General chemistry, as well as an extension of the fundamental ionization equations to solvents other than water.
- Water is not used for many reactions found in Organic chemistry, and it is important to ***change the focus from acids that ionize in water to the concept that acids react with bases in order to ionize.***
- **This concept is the basis for many of the reactions that will be introduced in succeeding chapters.**
- **It is important to remember that both the acid and the base must be identified in a reaction based on their reactivity.**

## There are Two Acid-Base Definitions. How Are They Related?

- A Brønsted-Lowry acid is defined as a proton donor and a Brønsted-Lowry base is a proton acceptor.
- A Lewis acid accepts an electron pair from a Lewis base, which donates an electron pair.
- How are these definitions related, not just how do they differ?
- Part of the problem may lie with removing the base (water) from acid-base reactions done in water?
- When HCl reacts with water, the Brønsted-Lowry definition states that the proton ( $H^+$ ) is “donated” to water, forming the hydronium ion.
- In this reaction, the oxygen atom of the water “accepts” the proton, but to accept the proton, the oxygen must *donate* two electrons to the H and the H accept two electrons from the oxygen - so the two definitions merge.
- The Brønsted-Lowry definition is useful in water, where it is convenient to monitor transfer of a proton and measurement of pH.
- The Lewis definition is more general because it focuses on transfer of electrons, and those atoms that are electron rich and electron donors, and those atoms that are electron deficient, and accept electrons. This definition is more important for tracking chemical reactions.

## What Happens When Water Accepts a Proton to Form the Hydronium Ion?



- Remember that the Lewis definition of a base is an electron donor and a Lewis base donates electrons to an atom other than hydrogen.
- *In this case the base donates two electrons to a proton. At this point, the definitions merge.*
- A Brønsted-Lowry base accepts a proton by donating two electrons to that proton.

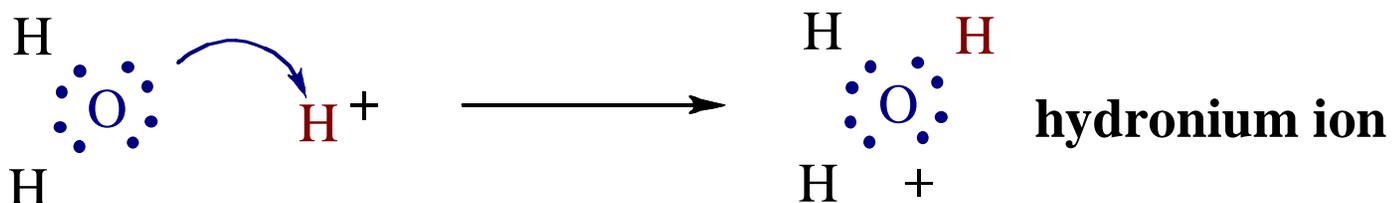
### Why two electrons?

- A covalent bond requires two electrons. Therefore, *bases may be defined as two electron donors to an electron deficient center.*
- If the base donates electrons to a proton, it is a Brønsted-Lowry base.
- If the base donates electrons to an atom other than hydrogen, it is formally a Lewis base.

The key concept is that *a base is a two-electron donor.*

- To donate two electrons, a base must have an excess of electron density.

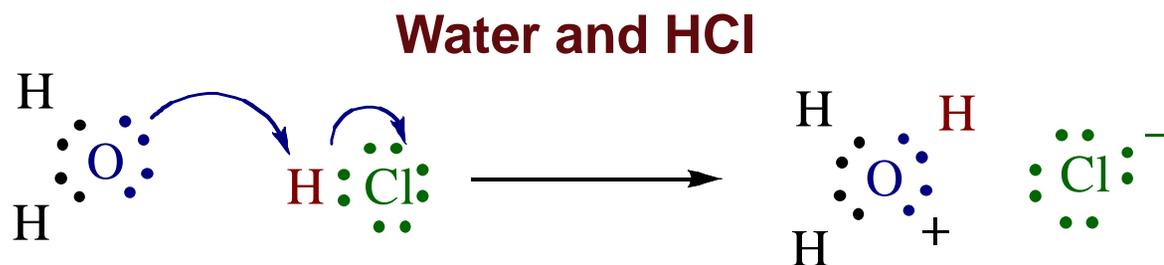
## Electron Flow and the Curved Arrow Formalism



- All bases donate two electrons, and *the electron flow is from the base to the acid, not from the acid to the base.*
- An acid does **not** donate the proton, but rather the proton is “attacked” by the base to form a new bond to the proton, as shown for water and  $\text{H}^+$  to give the hydronium ion.
- A **blue curved arrow** is used to indicate the flow of electrons, and *the electron flow is always from a source of high electron density to a point of low electron density.*
- The direction of the arrow is **always** from the base to the proton of the acid, as illustrated.
- The color **blue** is used for the electron rich base, as well as the electron flow represented by the arrow, the color **red** is used for the electron deficient acid, here a proton. This convention is used throughout the book.

## No “Free” Protons

- A base is electron rich and will donate two electrons to an electron deficient atom, such as a proton, to form the conjugate acid.
- The reaction with water showed  $H^+$  as a free proton, but *there is no such thing as a free proton; i.e.,  $H^+$  by itself.*
- The proton in common acids such as HCl or HCOOH have the hydrogen atom attached to another atom by a covalent bond.
- Electronegativity differences make the hydrogen atom in HCl polarized such that H is electron deficient and positive (a proton-like atom), whereas the Cl is electron rich and negative.
- Therefore, ***a base does not react with a free proton but rather with an electron deficient hydrogen atom that is attached to another atom, as in HCl.***
- When the base donates two electrons to the hydrogen atom, it literally pulls the proton away.



- When HCl reacts with water, what happens to the two electrons in the bond between H and Cl?
- The oxygen atom of water donates two electrons (it is the base) to the H of HCl, and the H-Cl bond breaks as the two electrons are used to form a new bond (O-H). The two electrons from the H-Cl bond will migrate towards the chlorine atom, forming chloride ion, which is formally the conjugate base.
- The new bond between O and H (O-H) is the third bond to O of the hydronium ion, which is the conjugate acid.
- A **curved arrow** represents the electron flow from the basic oxygen to the **electron deficient H** of HCl, and the entire acid-base process is written as a chemical reaction.

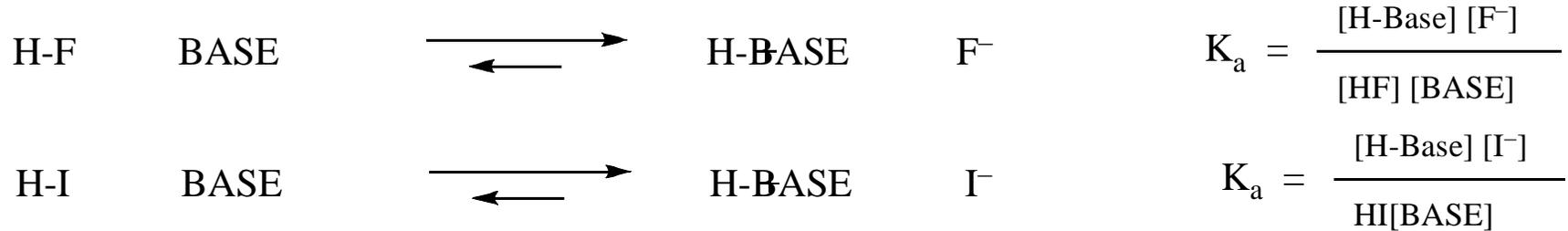
The electron rich atom in water is the oxygen atom (the basic atom), and it donates two electrons to the electron deficient hydrogen of HCl (the acid), forming a new O-H bond in the hydronium ion, which is the conjugate acid.

As the O-H bond is formed by using the two electrons from the oxygen, the H-Cl bond breaks and the two electrons in that bond are transferred to chlorine, forming the chloride ion, which has a negative charge.

## Strength of Acids and Bases

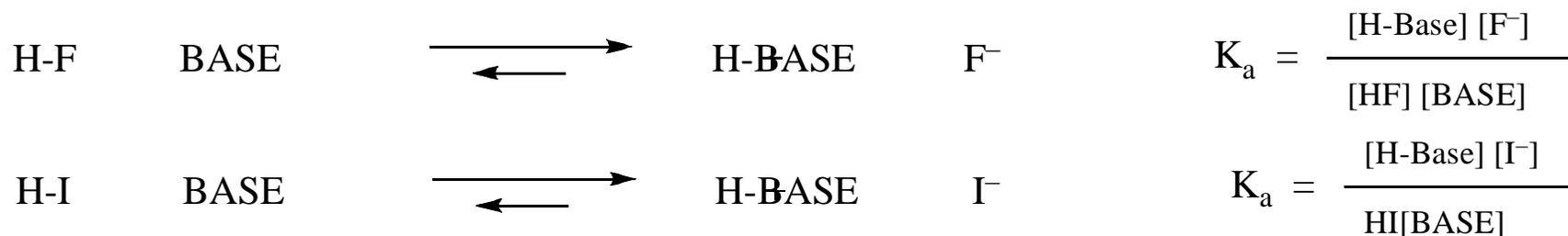
- Why is one base stronger than another?
- Why is one acid stronger or weaker than another?
  
- To probe acid or base strength in an equilibrium, the structure of the acid must be compared with the structure of its conjugate acid, and the structure of the base compared with that of its conjugate base.
- Determining the  $K_a$  for two different acids that react with the same base will make it possible to identify the stronger acid.
- Determining the  $K_a$  for two reactions in which a common acid reacts with two different bases will make it possible to identify the stronger base.
  
- Such comparisons reveal structural differences of the acid/conjugate acid and base/conjugate base pair *for both reactions*.

## Why is HI more acidic than HF?



- In the presence of a common but unspecified base, the  $K_a$  for the HI reaction is larger than the  $K_a$  for the HF reaction (HI is a stronger acid than HF).
- The reaction of HF with the base, gives H-BASE as the conjugate acid and fluoride ion as the conjugate base.
- The reaction with HI gives H-BASE, but the conjugate base is the iodide ion.
- *Both sides of each equation must be examined.* First, examine the left side of each reaction: the strength of the HF bond and the HI bond.

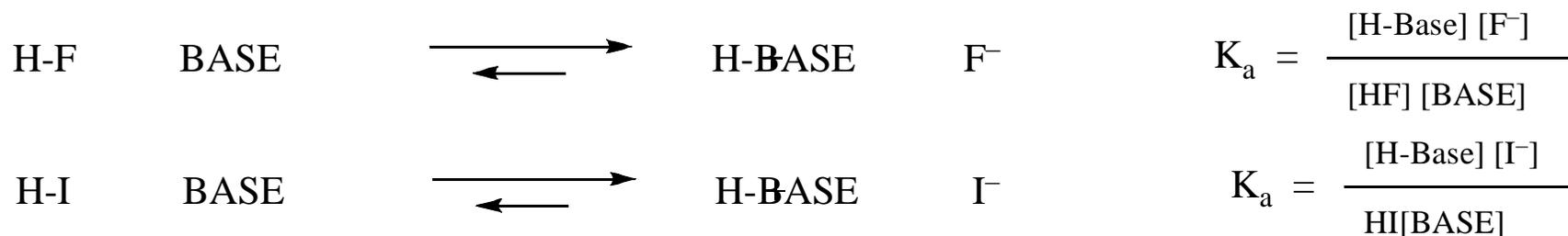
## Why is HI more acidic than HF?



### A weaker X-H bond makes $K_a$ larger

- The bond dissociation energy of the H-I bond is  $298.3 \text{ kJ mol}^{-1}$ , making it weaker than the H-F bond ( $569.7 \text{ kJ mol}^{-1}$ ).
- The covalent radius of I (135 pm) is much greater than that of F (71 pm), so the bond distance between H and I will be longer than the bond distance between H-F.
- The distance between the H and F nuclei along that bond is less than the distance between the H and I nuclei, due to the much larger radius of the iodine. This is the bonding distance, and generally, *a longer bond is a weaker bond*.
- If the H-I bond is weaker, it should break more easily when attacked by the base, pushing the reaction to the *right*, towards the conjugate acid and base.
- If the equilibrium is pushed to the right,  $K_a$  is larger, so a weaker bond is consistent with a more acidity compound.

## Why is HI more acidic than HF?



**These are equilibrium reactions, so determining the strength of HI and HF is not sufficient to answer the question. The conjugate bases, fluoride ion and iodide ion, must also be examined.**

- If one conjugate base is more stable than the other, the more stable ion will be less reactive.
- In this example, the fluoride ion reacts with the conjugate acid or iodide ion reacts with the conjugate base. The reactivity here refers to pushing the acid-base equilibrium to the left.
- The iodide ion is less reactive because it is larger and less able to donate electrons (it is a weaker base) when compared with the fluoride ion (iodide ion is more stable than the fluoride ion).
- **The iodide ion is less reactive and therefore more stable.**
- If iodide ion is less reactive, there is a higher concentration of iodide relative to fluoride, which means that the equilibrium in the HI reaction is pushed more to the right, and the equilibrium for HF is pushed further to the left.
- If the equilibrium is pushed to the left, there is a lower concentration of the conjugate base.
- **If there is a lower concentration of the conjugate base (iodide ion),  $K_a$  is smaller.**
- **If there is a higher concentration of the conjugate base (iodide ion),  $K_a$  is larger.**

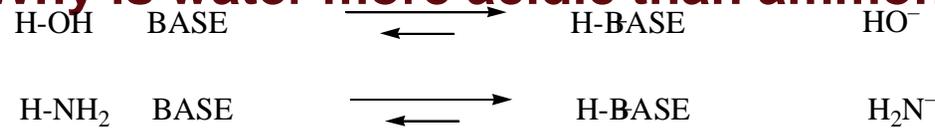
## Why does a more stable conjugate base make $K_a$ larger?

Why is iodide ion more stable and less reactive?

- First, compare the size of the ions using the ionic radii rather than the covalent radii used above.
- The ionic radius of the iodide ion ( $I^{-1}$ ) is reported to be 215 pm and that of the fluoride ion ( $F^{-1}$ ) is 136 pm. It is clear that the iodide ion is significantly larger.
- The fluoride ion and the iodide ion have the same charge (an excess of two electrons and a total of eight electrons).
- The charge is dispersed over a much larger area in the larger iodide ion, making it more difficult to donate those electrons to the acid. *It is less reactive.*
- The larger size of the ion and dispersal of charge over a larger area makes the ion less reactive, and less basic, so there will be a higher concentration of the conjugate base/conjugate acid and a lower concentration of the acid/base, so  $K_a$  is larger (a stronger acid).
- If a conjugate base is more reactive (less stable) there will be a lower concentration of the conjugate base/conjugate acid and a higher concentration of the acid/base, so  $K_a$  is smaller (a weaker acid).

HI is a stronger acid ( $K_a$  is larger) because of the weaker HI bond and because the larger size of the iodide ion disperses the charge and makes that conjugate base less reactive.

## Why is water more acidic than ammonia?



The reported  $\text{pK}_a$  of water is 15.74 and ammonia has a reported  $\text{pK}_a$  of 38.

Why is water so much more acidic?

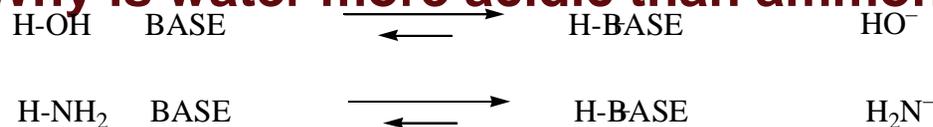
- Water and ammonia react with an unspecified but generic BASE that give the same conjugate acid (H-BASE).
- Water leads to hydroxide ion as the conjugate base and ammonia leads to the amide anion as the conjugate base.

**The bond strength of the O-H and N-H bonds must be determined, as well as the relative stability (reactivity) of the conjugate bases, hydroxide versus amide.**

- The reported bond dissociation energy of H-O is  $429.9 \text{ kJ mol}^{-1}$ , and the bond dissociation energy of H-N is  $<338.9 \text{ kJ mol}^{-1}$ .
- These numbers indicate that the O-H bond is stronger, and should be more difficult to break, but this is inconsistent with water as the stronger acid.

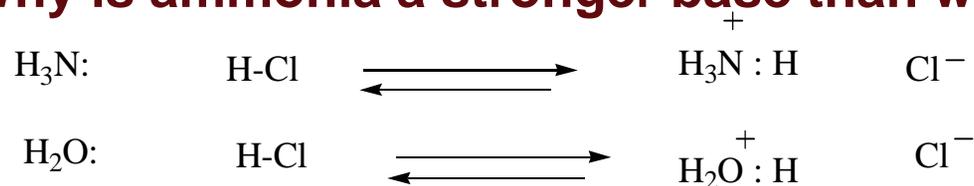
**Do not determine OH versus NH bond strength of the acid-base pair without looking at the products. *This is a misuse of bond dissociation energies because it does not take into account all bond making and bond breaking.***

## Why is water more acidic than ammonia?



- **The hydroxide ion less basic than the amide anion.**
- Oxygen is more electronegative than nitrogen, which indicates that oxygen tends to retain electrons more than nitrogen, and if oxygen retains electron density, it is less likely to donate electrons (it is a weaker base).
- The ionic radius of the hydroxide ion is 252 pm, and that of the amide ion is 168 pm, so the charge is dispersed over a larger area in hydroxide, making it more stable and less reactive.
- The relative basicity (stability-reactivity) of the conjugate base plays a major role in determining relative base strength. The base strength obviously influences the relative stability (reactivity) of the conjugate acid.
- This example reinforces the idea that simply looking at the left side of the reaction (the acid-base pair) and asking which is the stronger bond is *not* sufficient. To compare the strength of two acids or of two bases, both acid-base reactions must be examined, and the nature of the acid, the base, the conjugate acid and the conjugate base must be examined.

## Why is ammonia a stronger base than water?



- The reaction of ammonia and HCl gives the ammonium ion as the conjugate acid and the chloride ion as the conjugate base. For the reaction with water, the conjugate acid is the hydronium ion, and the conjugate base is the chloride ion. The  $\text{pK}_a$  of the hydronium ion is estimated to be  $-2$ , the  $\text{pK}_a$  of HCl is  $-7$  and the  $\text{pK}_a$  of  $\text{NH}_4^+$  is  $9.24$ .
- Oxygen is more electronegative than nitrogen, so oxygen will retain electron density more efficiently than nitrogen. If electron density is retained, oxygen cannot donate electrons as well, so it is less basic than nitrogen.
- The hydronium ion is a stronger acid than ammonia, so the equilibrium for that reaction will be pushed to the left (smaller  $K_a$ ), whereas the equilibrium for the ammonium ion will be more to the right (larger  $K_a$ ).
- The reaction of ammonia and HCl has a larger  $K_a$ , with formation of more ammonium chloride, so ammonia reacts with HCl better than water, consistent with ammonia as a stronger base.

**Ammonia is a stronger base because it is better able to donate electrons, but also because the conjugate acid is more stable (less reactive) when compared to the conjugate acid formed from water.**

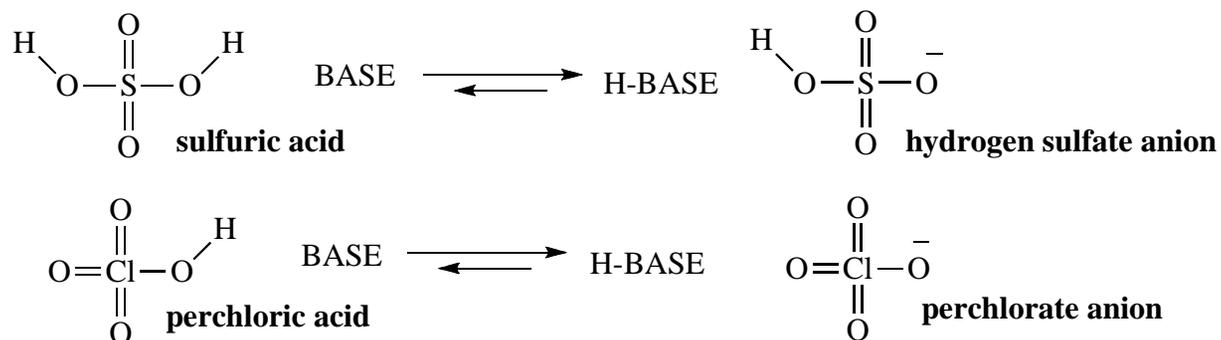
## Why is $\text{NH}_2^-$ more basic than $\text{NH}_3$ ?

- The amide anion has a charge of  $-1$ , which means that there is an excess of electron density on the nitrogen when compared to ammonia.
- Ammonia has three covalent bonds, and although there is one unshared pair of electrons, the molecule is neutral (no charge).
- The amide anion has two pairs of unshared electrons.
- **The amide anion is more basic simply because there is a higher concentration of electron density that can be donated to an acid.**

In general, a base that has a charge of  $-1$  should be stronger than a base that is uncharged.

Note that the amide anion is the conjugate base of ammonia, when ammonia undergoes reaction as an acid. A proton must be removed from ammonia to form the amide anion.

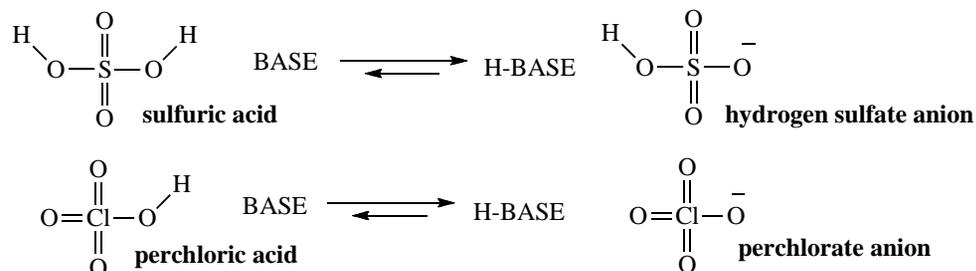
## Why is sulfuric acid less acidic than perchloric acid?



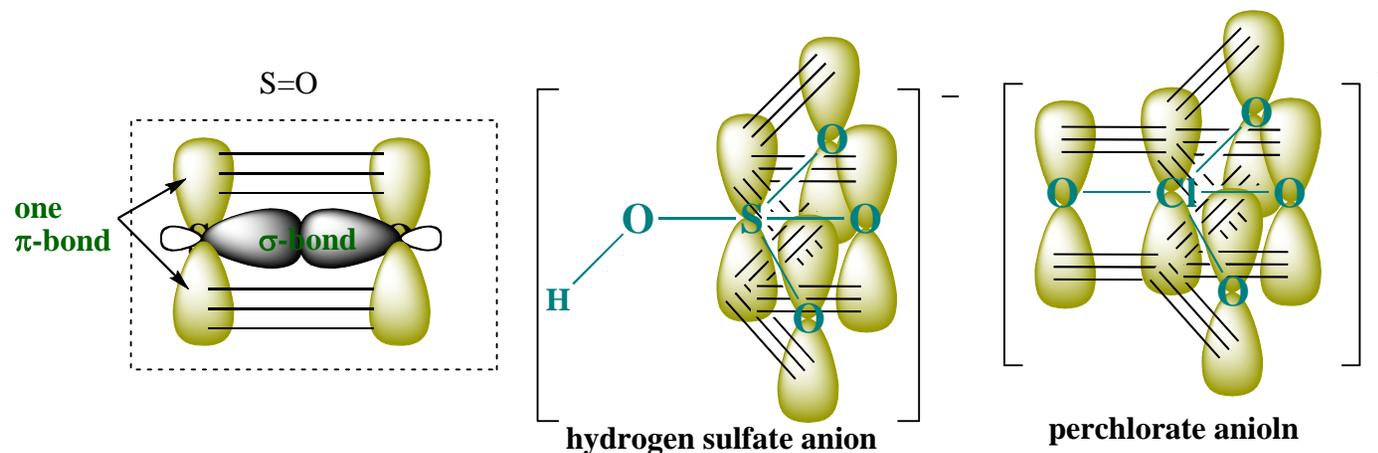
The reported  $\text{pK}_a$  of perchloric acid is  $-10$  and that of sulfuric acid is about  $-1.9$ .

- Both perchloric acid and sulfuric acid have an O-H group, and the acidic proton is part of an O-H unit for both acids.
- Any differences in bond strength may be due to differences in the sulfur versus the chlorine.
- The covalent radii of S is 102 pm and that of Cl is 99 pm, so there is minimal difference.
- If there is little difference in bond strength in the acids, there may be more subtle factors, but remember to examine the conjugate bases.
- The hydrogen sulfate anion has an ionic radius of 221 pm whereas the perchlorate anion has an atomic radius of 225 pm. There is little difference in the size of the anions.

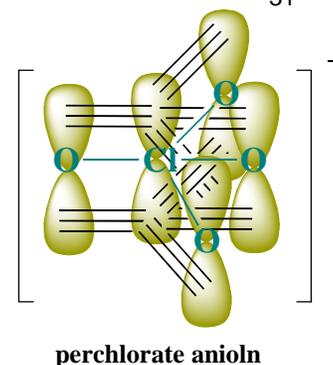
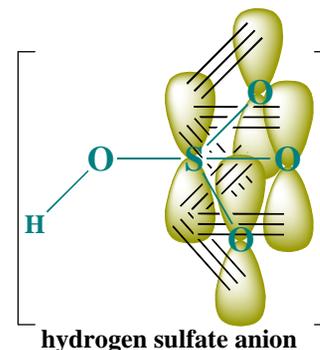
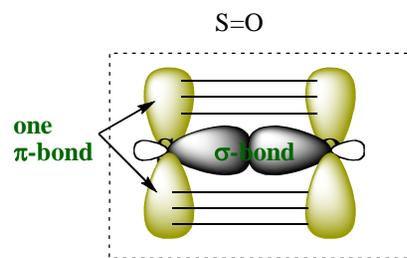
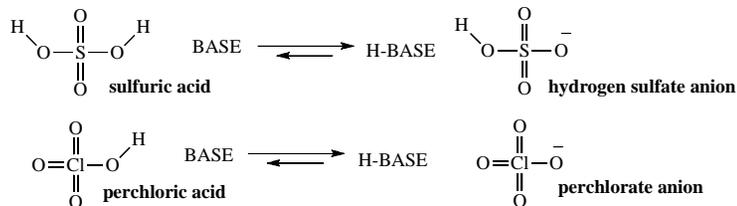
## Why is sulfuric acid less acidic than perchloric acid?



- There is one difference in the  $\text{HSO}_4^-$  anion and the  $\text{ClO}_4^-$  anion relative to the fluoride ion, iodide ion, hydroxide ion or amide anion discussed previously.
- There are  $\pi$ -bonds, and  $\text{S}=\text{O}$  indicates the presence of two bonds between S and O, one  $\sigma$ -bond and one  $\pi$ -bond.
- The  $\sigma$ -bond is stronger than the  $\pi$ -bond, because the  $\sigma$ -bond is formed by sharing electron density on a line between the two nuclei but the  $\pi$ -bond is formed sharing electron density between parallel adjacent p-orbitals on S and O.
- Since less electron density is shared, the  $\pi$ -bond is weaker.



## Why is sulfuric acid less acidic than perchloric acid?



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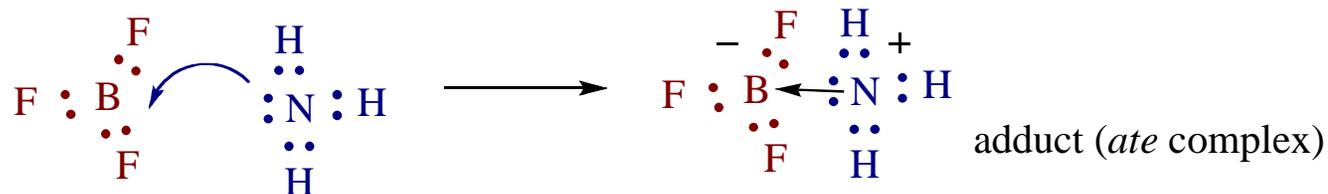
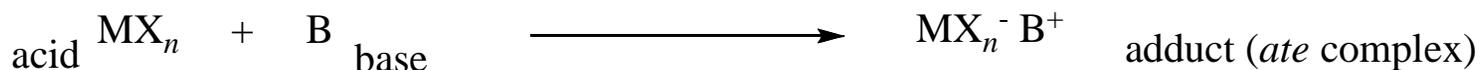
- In these anions, the p-orbitals can overlap, and the excess electron density (the negative charge) is dispersed over several atoms.
- This type of charge dispersal is also called charge delocalization, and is given the name **resonance**. **Resonance delocalization leads to greater stability and lower reactivity.**
- The charge is dispersed over five atoms (the Cl and four O atoms) in the perchlorate anion, but only over four atoms in the hydrogen sulfate anion.
- Greater resonance delocalization makes the perchlorate anion more stable.
- Greater charge dispersal due to resonance leads to greater stability (less reactive), just as charge dispersal due to the larger size of an anion leads to greater stability.
- If the perchlorate anion is more stable, the equilibrium is pushed to the right (larger  $K_a$ ), consistent with perchloric acid as the stronger acid.

**Sulfuric acid is a weaker acid, in part, because the perchlorate anion has greater resonance stability than the hydrogen sulfate anion, so it is less reactive as a base.**

## Lewis Acids and Lewis Bases

- Lewis acids are electron pair acceptors and Lewis bases are electron pair donors.
- A Lewis base must be electron rich in order to donate electrons. Likewise, a Lewis acid must be electron deficient.
- In this book, Lewis bases will be confined to molecules that contain oxygen, nitrogen, a halogen atom, and sometimes sulfur or phosphorus.
- Defining acids as electron pair acceptors and bases as electron pair donors bypasses the need for ionization in water, and simply focuses on transfer of electrons from one species to another.
- Apart for acids and bases, electron transfer is the fundamental requirement for a chemical reaction.

## Ate Complexes



- Group 13 atoms such as boron and aluminum can only form three covalent bonds and remain neutral, so they are electron deficient.
- When boron or aluminum atoms that have three bonds accept an electron pair from a Lewis base, the resulting fourth bond will provide the two electrons needed to satisfy the octet rule. The B and Al take on a (-) charge.
- This reaction forms the so-called Lewis-acid-Lewis base complex, which is a charged complex called an **ate complex**.
- A typical reaction is shown between  $\text{BF}_3$  and ammonia, in which the Lewis base (ammonia) donates two electrons to the electron deficient boron (note the direction of the arrow), forming the ate complex, in which the boron and the nitrogen share two electrons.
- The nitrogen takes on a positive charge in the complex, and the boron takes on a negative charge.
- The arrow in the ate complex represents what is called a **dative bond**, indicative of the electron donating nature of the bond in a Lewis acid-Lewis base ate complex.

## Strength of Lewis Acids

- The relative order of Lewis acidity is not always straightforward because the electrophilic atom (here a metal) may have different valences and several groups or atoms may be attached to the metal (known as *ligands*).
  - Lewis acids usually take the form  $\text{MX}_n$ , where X may be a halogen atom or X may be a molecule that contains oxygen, nitrogen or phosphorus (other X units will be introduced later in the book).
  - The metal is M and  $n$  in  $\text{X}_n$  is the number of units attached to M. Reaction with a Lewis base leads to formation of a conjugate acid-base adduct ( $\text{MX}^- \text{B}^+$ , the *ate complex*).
1. In  $\text{MX}_n$  ( $n < 4$ ) acidity arises from the central atom's requirement for completion of an outer electron octet by accepting one or more pairs of electrons from the base. Acidity is diminished when two electron pairs are required. Group 13 acids are more acidic than transition metal acids:  $\text{BF}_3 > \text{AlCl}_3 > \text{FeCl}_3$
  2. The acidity of M will decrease within any group with increasing atomic volume (effectively, with increasing atomic number) owing to the weaker attraction between nuclear charge and incoming electron pairs. The result of these effects leads to the order:  
$$\text{BX}_3 > \text{AlX}_3 > \text{GaX}_3 > \text{InX}_3$$
  3. In general, the availability of  $d$  orbitals for donation will be easier (especially with  $d$  outer orbitals) and more effective, the heavier the element.

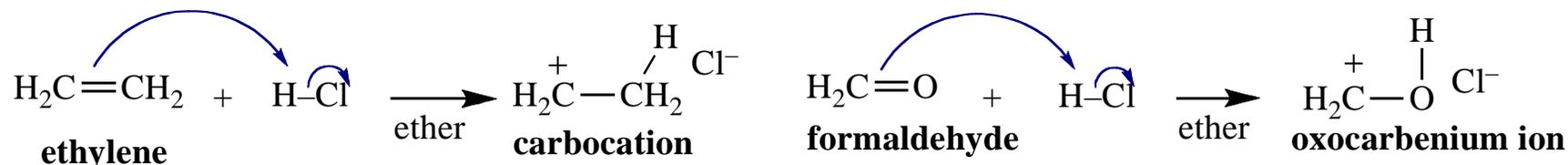
This leads to a decrease in acidity, as in the series (B→Al→Ga→In) above.

It is therefore possible to order the more common Lewis acids by decreasing acid strength:



## Relevance to Organic Chemistry

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### If an organic molecule can donate electrons, it may react as a base

- Modify thinking as to what constitutes a weak or strong acid or base.
- In ethylene there are two bonds between adjacent carbon atoms, a double bond (C=C), a strong (the  $\sigma$ -bond) and a weak  $\pi$ -bond.
- When ethylene is mixed with the strong acid HCl, the weaker p-bond reacts with the HCl by donating two electrons from the weak  $\pi$ -bond to form a new C-H bond and generate a positive charge on the adjacent carbon (a carbocation), with a chloride counterion.
- The reaction between HCl and ethylene involves donating two electrons from the alkene to the acidic proton of HCl, so it is clearly an acid-base reaction.
- Formaldehyde also has a strong  $\sigma$ -bond and a weak  $\pi$ -bond, this time in a carbon-oxygen double bond (C=O).
- Formaldehyde reacts with HCl to give an oxocarbenium ion, which has an O-H bond along with the positive charge on the adjacent carbon and the chloride counterion. The oxocarbenium ion is the conjugate acid and chloride ion is the conjugate base.
- Both reactions are done in ether as a solvent, as indicated by the term ether on the arrow, so the acid-base definitions from General chemistry for reactions in water do not apply.
- It is clear that ethylene and formaldehyde react as weak bases with the strong acid HCl to give the indicated products.

- ***Categorizing reactions by their ability to donate electrons from one source to another, or from one atom or group to another.***
- ***A focus on the bond making-bond breaking process is a key to understanding how reactions work.***

## Define Nucleophiles

- If a species donates two electrons to an atom such as B or Al, it is called a Lewis base.
- In some cases, ***a molecule, a compound or an ion can donate two electrons to a carbon atom, forming a new bond to that carbon.***
- ***A special name is given to a species that donates electrons to carbon. It is called a **nucleophile**.***
- A **nucleophile** is essentially a Lewis base that reacts with a carbon species that functions as a Lewis acid. In most Organic chemistry books, a fundamental theme is the reaction of nucleophiles with various carbon species.
- ***With an acid-base theme, a nucleophile is simply a modified Lewis base and the carbon it react with is a modified Lewis acid.***