

Organic Chemistry, *Fourth Edition*

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Chapter 2 Acids and Bases

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Chapter 2 Acids and Bases

- 2.1 Brønsted-Lowry Acids and Bases
- 2.2 Reactions of Brønsted-Lowry Acids and Bases
- 2.3 Acid Strength and pK_a
- 2.4 Predicting the Outcome of Acid-Base Reactions
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2.1 Brønsted-Lowry Acids and Bases

- A hydrogen atom without its electron is a proton.
 H^+ = proton
- A **Brønsted-Lowry acid** is a proton donor.
• It must have a proton.
- A **Brønsted-Lowry base** is a proton acceptor.
• It must be able to form a bond to a proton.

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Brønsted-Lowry Acids and Bases

Figure 2.1

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Brønsted-Lowry acids [H – A]		Brønsted-Lowry bases [B:]	
Inorganic	Organic	Inorganic	Organic
HCl	CH ₃ CO ₂ H		CH ₃ NH ₂
H ₂ SO ₄	acetic acid	H ₂ O:	methoxide
HSO ₄ [–]		:NH ₃	
H ₂ O	OH		CH ₃ C(=O)CH ₃
H ₃ O ⁺	HO ₂ CCH ₂ –C–CH ₂ CO ₂ H	[–] OH	acetone
	COOH	[–] NH ₂	CH ₂ =CH ₂
	citric acid		ethylene

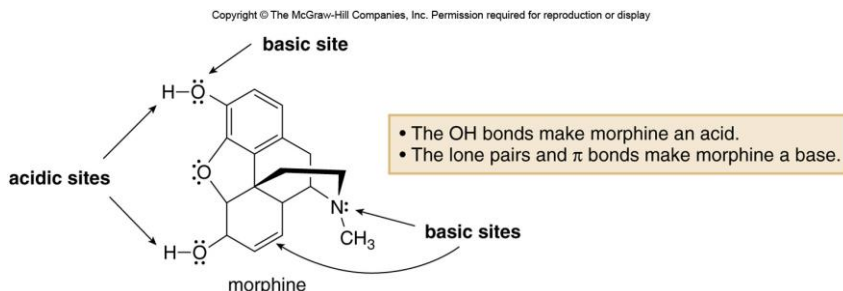
- All Brønsted-Lowry acids contain a proton.
- The net charge may be zero, (+), or (–).

- All Brønsted-Lowry bases contain a lone pair of electrons or a π bond.
- The net charge may be zero or (–).

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Acidic and Basic Sites in Morphine

Some molecules contain both hydrogen atoms and lone pairs and thus, can act either as acids or bases, depending on the particular reaction.

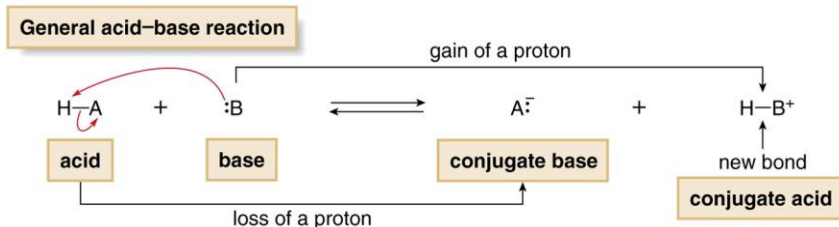


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2.1 Reactions of Brønsted-Lowry Acids and Bases

- A Brønsted-Lowry acid base reaction results in the transfer of a proton from an acid to a base.
- The electron pair of the base $B:$ forms a new bond to the proton of the acid forming the **conjugate acid** of the base.
- The acid $H-A$ loses a proton, leaving the electron pair in the $H-A$ bond on A . This forms the **conjugate base** of the acid.

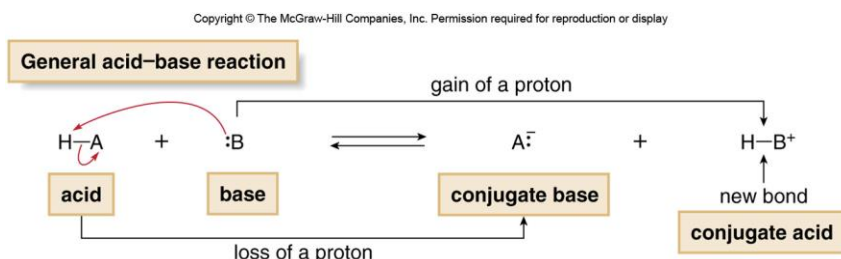
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Reactions of Brønsted-Lowry Acids and Bases

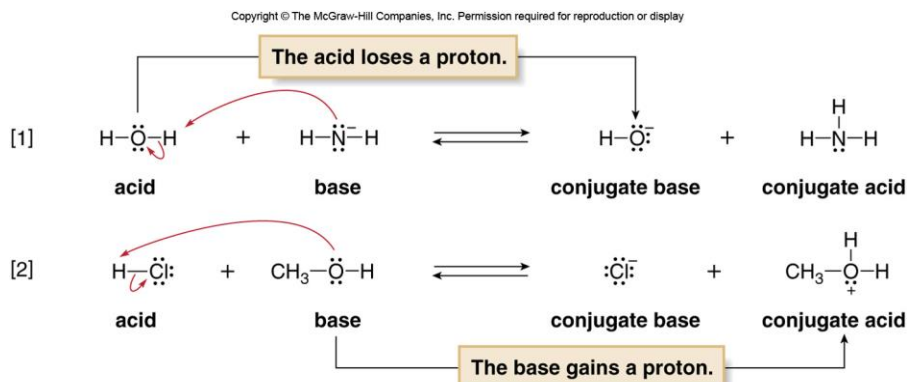
- The movement of electrons in reactions can be illustrated using **curved arrow** notation.
- Because two electron pairs are involved in this reaction, two curved arrows are needed.



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Examples of Brønsted-Lowry Acid-Base Reactions

- A double reaction arrow (indicating equilibrium) is used between starting materials and products to indicate that the reaction can proceed in the forward and reverse directions.



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General Reactivity

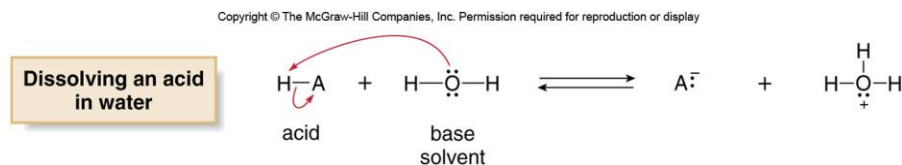
These reactions illustrate a general pattern of reactivity:

- **Electron-rich** species react with **electron-deficient** species
 - Bases are electron rich
 - While the H of an acid has a partial positive charge making it electron deficient
- Therefore, acids and bases react with one another

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2.3 Acid Strength and pK_a

- Acid strength is the tendency of an acid to donate a proton.
- The more readily a compound donates a proton, the stronger an acid it is.



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Acid-Base Equilibrium

- Acidity is measured by an **equilibrium constant**.
- When a Brønsted-Lowry acid H-A is dissolved in water, an acid-base reaction occurs, and an **equilibrium constant** can be written for the reaction.

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Equilibrium constant

$$K_{\text{eq}} = \frac{[\text{products}]}{[\text{starting materials}]} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H-A}][\text{H}_2\text{O}]}$$

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Acidity Constant

- Because the concentration of the solvent H₂O is essentially constant, the equation can be rearranged and a new equilibrium constant, called the **acidity constant**, K_a , can be defined.

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$$\text{Acidity constant} = K_a = [\text{H}_2\text{O}]K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H-A}]}$$

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K_a and pK_a

- It is generally more convenient when describing acid strength to use " pK_a " values than K_a values.

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Definition: $pK_a = -\log K_a$

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K_a	$pK_a = -\log K_a$
K_a values of typical organic acids	pK_a values of typical organic acids
10^{-5} to 10^{-50} ↑ larger number stronger acid	$+5$ to $+50$ ↑ smaller number stronger acid
↑ smaller number weaker acid	↑ larger number weaker acid

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Acidity of Some Common Compounds

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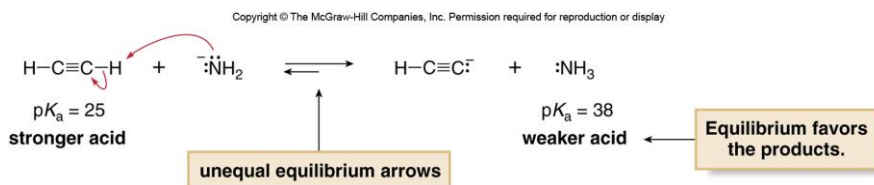
Table 2.1 Selected pK_a Values

	Acid	pK_a	Conjugate base	
	H-Cl	-7	Cl ⁻	
	CH ₃ COO-H	4.8	CH ₃ COO ⁻	
	HO-H	15.7	HO ⁻	
	CH ₃ CH ₂ O-H	16	CH ₃ CH ₂ O ⁻	
	HC≡CH	25	HC≡C ⁻	
	H-H	35	H ⁻	
	H ₂ N-H	38	H ₂ N ⁻	
	CH ₂ =CH ₂	44	CH ₂ =C ⁻ H	
	CH ₃ -H	50	CH ₃ ⁻	

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2.4 Outcome of Acid-Base Reactions

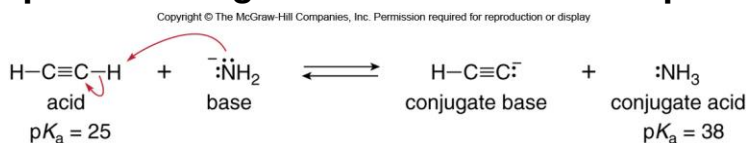
- The position of the equilibrium depends on the relative strengths of the acids and bases.
- Equilibrium always favors formation of the weaker acid and base.



- Because the pK_a of the starting acid (25) is lower than that of the conjugate acid (38), equilibrium favors the products.

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Steps in Solving Acid-Base Reaction Equilibria



- Step [1]** Identify the acid and base in the starting materials. Assume :NH_2^- is the base because it bears a net negative charge. That makes $\text{HC}\equiv\text{CH}$ the acid.
- Step [2]** Draw the products of proton transfer and identify the conjugate acid and base in the products. Acetylene gives up its proton to :NH_2^- .
- Step [3]** Compare the pK_a values of the acid and the conjugate acid. Equilibrium favors formation of the weaker acid with the higher pK_a . The pK_a of NH_3 is higher; therefore products are favored.

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2.5 Factors that Determine Acid Strength

- Anything that stabilizes a conjugate base $A:^-$ makes the starting acid H-A more acidic.
- Four factors affect the acidity of H-A. These are:
 - Element effects
 - Inductive effects
 - Resonance effects
 - Hybridization effects

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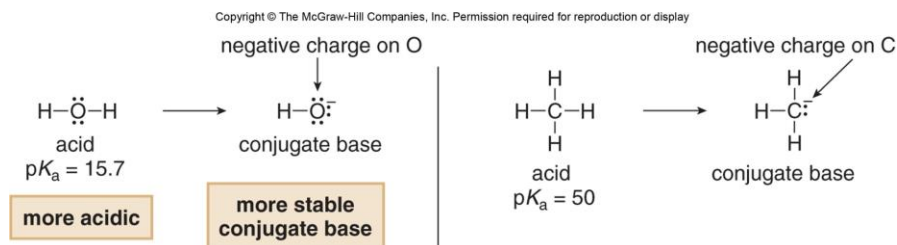
Comparing the Acidity of Any Two Acids

- Always draw the conjugate bases.
- Determine which conjugate base is more stable.
- The **more stable** the conjugate base, the **more acidic** the acid.

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Element Effects—Trends in the Periodic Table

Why does H_2O have a much lower $\text{p}K_{\text{a}}$ than CH_4 ?

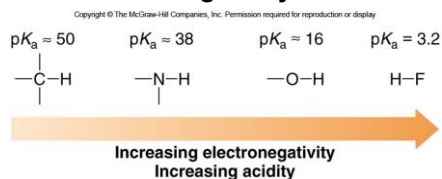


Since oxygen is much more electronegative than carbon, it more readily accepts a negative charge.

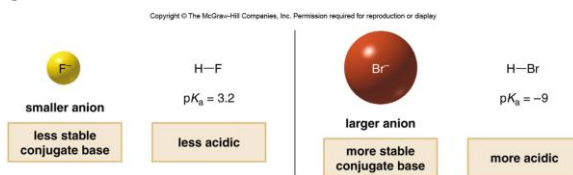
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Element Effects—Trends in the Periodic Table

Across a row of the periodic table, the acidity of H-A increases as the electronegativity of A increases.



Positive or negative charge is stabilized when it is spread over a larger volume.

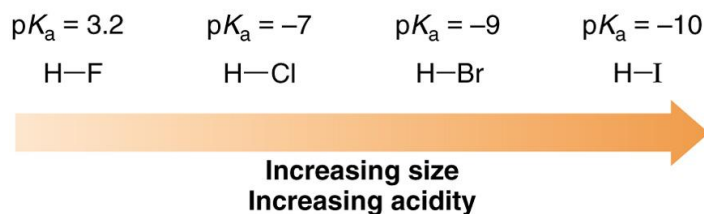


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Element Effects Down a Column in the Periodic Table

- Down a column of the periodic table, size, and not electronegativity, determines acidity.
- The acidity of H-A increases as the size of A increases.

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Inductive Effects

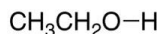
- An **inductive effect** is the pull of electron density through σ bonds caused by electronegativity differences of atoms.
- More electronegative atoms stabilize regions of high electron density by an electron withdrawing inductive effect.
- The more electronegative the atom and the closer it is to the site of the negative charge, the greater the effect.
- The acidity of H-A increases with the presence of electron withdrawing groups in A.

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Inductive Effects in Trifluoroethanol

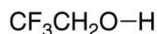
- In the example below, note that 2,2,2-trifluoroethanol is more acidic than ethanol.

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ethanol

$$\text{p}K_{\text{a}} = 16$$



2,2,2-trifluoroethanol

$$\text{p}K_{\text{a}} = 12.4$$

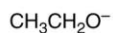
← stronger acid

- The reason for the increased acidity of 2,2,2-trifluoroethanol is that the three electronegative fluorine atoms stabilize the negatively charged conjugate base.

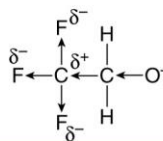
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Rationale for Inductive Effects

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No additional electronegative atoms stabilize the conjugate base.

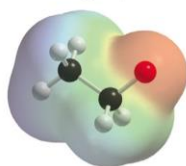


CF_3 withdraws electron density, stabilizing the conjugate base.

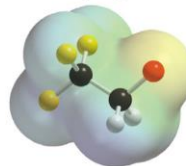
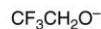
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Figure 2.2



The dark red of the O atom indicates a region of high electron density.



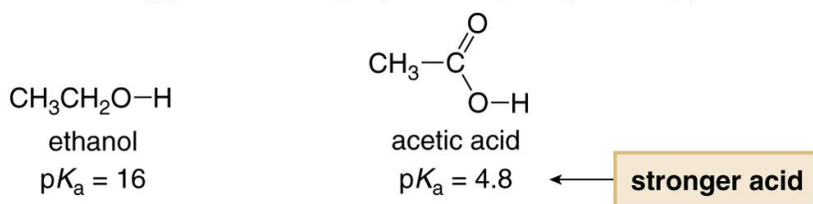
The O atom is yellow, indicating it is less electron rich.

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Resonance Effects

- Delocalization of charge through resonance influences acidity.
- Acetic acid is more acidic than ethanol, even though both conjugate bases have the negative charge on the same element, O.

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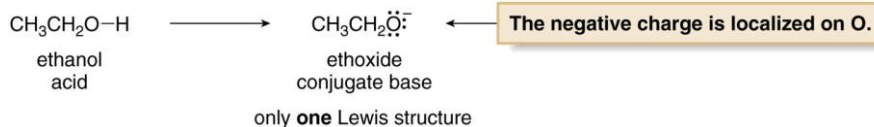


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Comparison of Ethoxide and Acetate ions

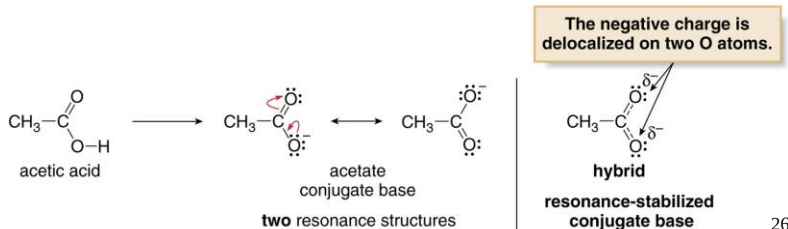
- The conjugate base of ethanol has a localized charge.

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- The conjugate base of acetic acid is resonance delocalized.

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Electrostatic Potential Plots of Ethoxide and Acetate

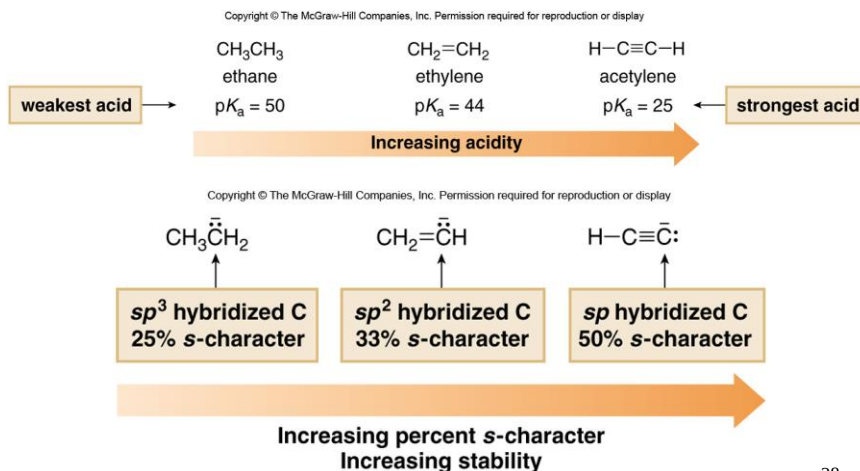
Figure 2.3



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Hybridization Effects

Consider the relative acidities of three different compounds containing C-H bonds.



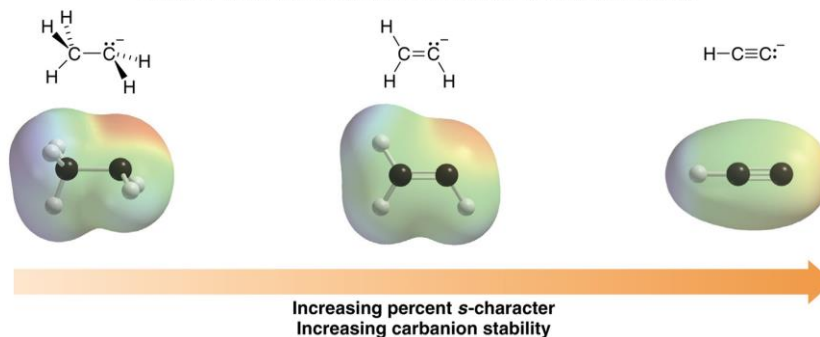
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Stability of Conjugate Bases

The higher the percent of s-character of the hybrid orbital, the more stable the conjugate base.

Figure 2.4

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- As the lone pair of electrons is pulled closer to the nucleus, the negatively charged carbon appears less intensely red.

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Summary of Factors that Determine Acid Strength

Figure 2.5

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Factor	Example	
1. Element effects: The acidity of H–A increases both left-to-right across a row and down a column of the periodic table.	CH_4 NH_3 H_2O HF H_2S HBr HI Increasing acidity → ↑ Increasing acidity	
2. Inductive effects: The acidity of H–A increases with the presence of electron-withdrawing groups in A.	$\text{CH}_3\text{CH}_2\text{O}-\text{H}$	$\text{CF}_3\text{CH}_2\text{O}-\text{H}$ more acidic
3. Resonance effects: The acidity of H–A increases when the conjugate base A^- is resonance stabilized.	$\text{CH}_3\text{CH}_2\text{O}-\text{H}$	$\text{CH}_3\text{COO}-\text{H}$ more acidic
4. Hybridization effects: The acidity of H–A increases as the percent s-character of A^- increases.	CH_3CH_3 $\text{CH}_2=\text{CH}_2$ $\text{H}-\text{C}\equiv\text{C}-\text{H}$ → Increasing acidity	

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How To: Determine the Relative Acidity of Protons

Step [1] Identify the atoms bonded to hydrogen, and use periodic trends to assign relative acidity.

- The most common H-A bonds in organic compounds are C-H, N-H and O-H.
- Acidity increases left to right across a row, the relative acidity of these bonds is C-H < N-H < O-H.
- H atoms bonded to C atoms are usually *less acidic* than H atoms bonded to any heteroatom.

Step [2] If the two H atoms in question are bonded to the same element, draw the conjugate bases and look for other points of difference.

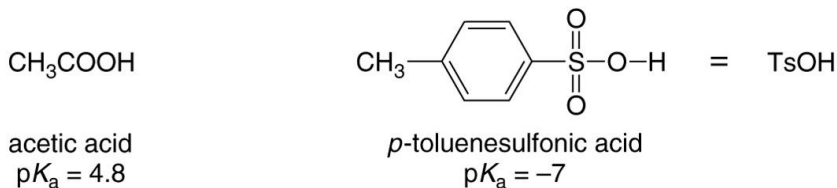
- Do electron-withdrawing groups stabilize the conjugate base?
- Is the conjugate base resonance stabilized?
- How is the conjugate base hybridized?

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2.6 Commonly Used Acids in Organic Chemistry

- The familiar acids HCl and H₂SO₄ are often used in organic reactions.
- Various organic acids are also commonly used (e.g., acetic acid and *p*-toluenesulfonic acid (TsOH)).

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Commonly Used Bases in Organic Chemistry

- Common strong bases used in organic reactions are more varied in structure.

Figure 2.6

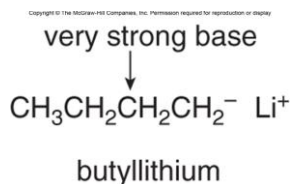
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oxygen bases	nitrogen bases
$\text{Na}^+ \text{ } ^-\text{OH}$ sodium hydroxide	$\text{Na}^+ \text{ } ^-\text{NH}_2$ sodium amide
$\text{Na}^+ \text{ } ^-\text{OCH}_3$ sodium methoxide	$\text{Li}^+ \text{ } ^-\text{N}[\text{CH}(\text{CH}_3)_2]_2$ lithium diisopropylamide
$\text{Na}^+ \text{ } ^-\text{OCH}_2\text{CH}_3$ sodium ethoxide	
$\text{K}^+ \text{ } ^-\text{OC}(\text{CH}_3)_3$ potassium <i>tert</i> -butoxide	hydride
	$\text{Na}^+ \text{ } ^-\text{H}$ sodium hydride

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Characteristics of Strong Organic Bases

- Strong bases have weak conjugate acids with high $\text{p}K_{\text{a}}$ values, usually > 12 .
- Strong bases have a net negative charge, but not all negatively charged species are strong bases. For example, none of the halides F^- , Cl^- , Br^- , or I^- , is a strong base.
- Carbanions, negatively charged carbon atoms, are especially strong bases. A common example is butyllithium:

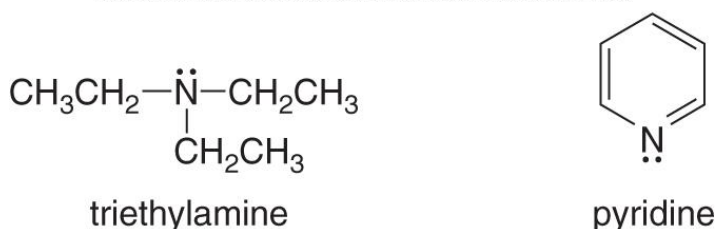


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Other Common Bases in Organic Chemistry

- Amines (e.g., triethylamine and pyridine) are organic bases.
- They are basic due to having a lone pair on N.
- They are weaker bases since they are neutral, not negatively charged.

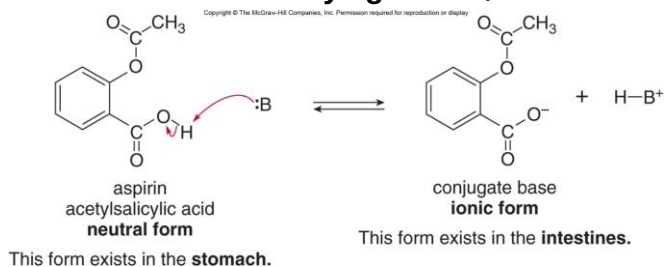
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2.7 Example: Aspirin

- **Aspirin (acetylsalicylic acid)** is one of the most well known drugs. It functions as an analgesic مسكن, anti-pyretic خافض الحرارة and anti-inflammatory agent مضاد للالتهابات.



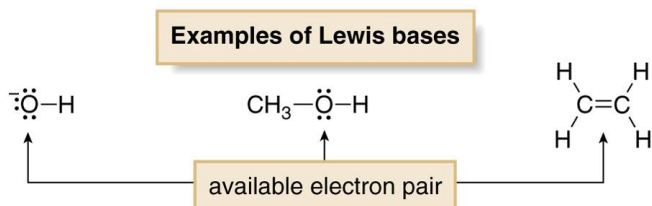
- In **ionic form**, it is soluble in the aqueous blood stream and transported to tissues where it is needed.
- When **protonated**, it becomes neutral and can pass through cell membranes to inhibit certain chemical reactions.

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2.8 Lewis Acids and Bases

- A **Lewis base** is an electron pair donor.
- Lewis bases are structurally the same as Brønsted-Lowry bases. Both have an available electron pair—a lone pair or an electron pair in a π bond.
- A Brønsted-Lowry base always donates this electron pair to a proton, but a Lewis base donates this electron pair to anything that is electron deficient.

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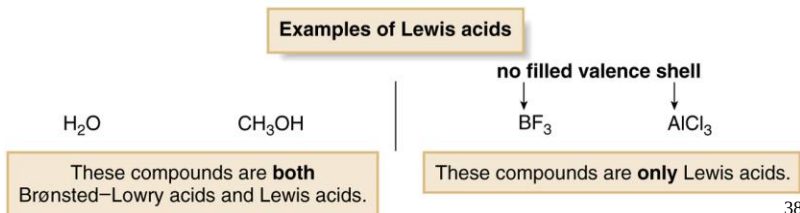


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Lewis Acids

- A **Lewis acid** is an electron pair acceptor.
- Any species that is electron deficient and capable of accepting an electron pair is also a Lewis acid.
- All Brønsted-Lowry acids are also Lewis acids, but the reverse is not necessarily true.
- Common Lewis acids (which are not Brønsted-Lowry acids) contain elements in group 3A that can accept an electron pair because they do not have filled valence shells.

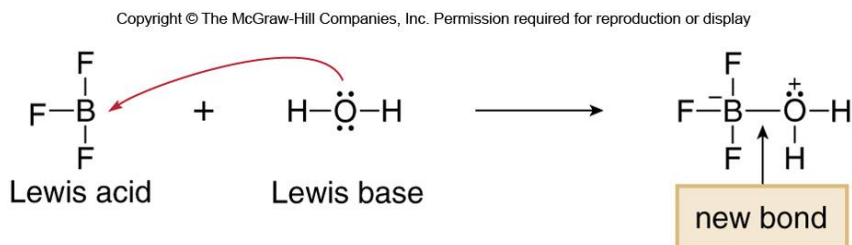
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Lewis Acid-Base Reactions

- In a Lewis acid-base reaction, a Lewis base donates an electron pair to a Lewis acid.
- This is illustrated in the reaction of BF_3 with H_2O . H_2O donates an electron pair to BF_3 to form a new bond.



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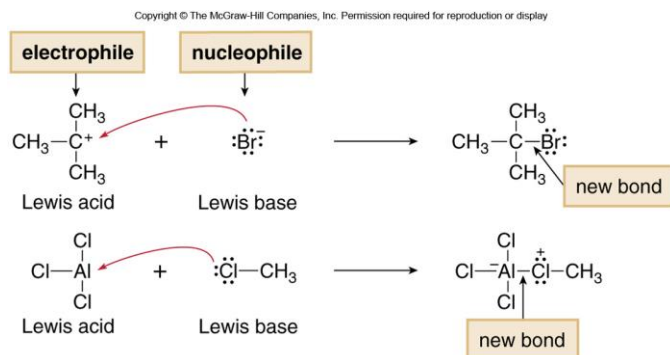
Electrophiles and Nucleophiles

- Lewis acid-base reactions illustrate a general pattern in organic chemistry.
- Electron-rich species react with electron-poor species.
- A Lewis acid is also called an **electrophile**.
- When a Lewis base reacts with an electrophile other than a proton, the Lewis base is also called a **nucleophile**.
- In this example, BF_3 is the electrophile and H_2O is the nucleophile.

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Lewis Acid-Base Reactions that Form One New Covalent Bond

- Note that in each reaction below, the electron pair is not removed from the Lewis base.
- Instead, it is donated to an atom of the Lewis acid and one new covalent bond is formed.



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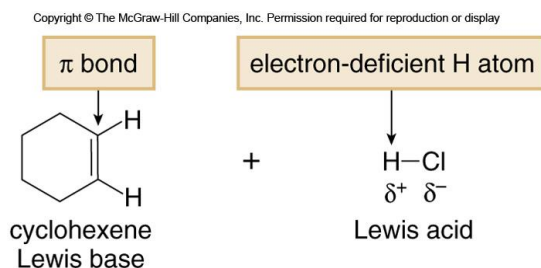
Drawing Products of Lewis Acid-Base Reactions

- In other Lewis acid-base reactions, one bond is formed and one bond is broken.
- To draw the products of these reactions, keep in mind the following steps:
 - Always identify the Lewis acid and base first.
 - Draw a curved arrow from the electron pair of the base to the electron-deficient atom of the acid.
 - Count electron pairs and break a bond when needed to keep the correct number of valence electrons.

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Alkene-HCl Reaction

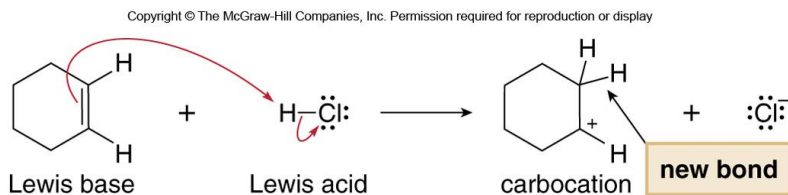
- The reaction between cyclohexene and HCl can be treated as a Lewis acid-base interaction.
- HCl acts as the Lewis acid, and cyclohexene, having a π bond, is the Lewis base.



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Drawing the Product of the Reaction of HCl with Cyclohexene

- The electron pair in the π bond of the Lewis base forms a new bond to the proton of the Lewis acid, generating a carbocation.
- The H-Cl bond must break, giving its two electrons to Cl, forming Cl^- .
- Because two electron pairs are involved, two curved arrows are needed.



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