

2. Polar Bonds & Their Consequences

We are familiar with Ionic bonds (electrostatic attraction between two oppositely charged ions) and covalent bonds in which there is an equal sharing of a pair of electrons between two atoms (one electron donated by each atom).

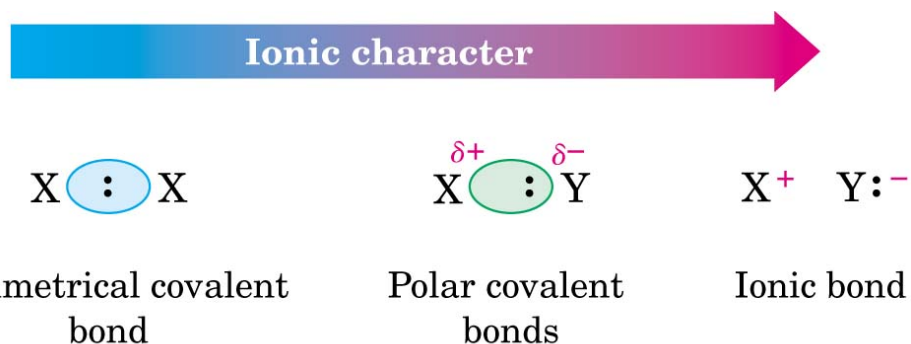
Many bonds however are neither ionic nor covalent and are referred to as polar covalent bond. The electron distribution in such a bond between two atoms is unequal; electrons are more highly attracted by one of the two atoms sharing the bond, the more electronegative atom.

2.1 Polar Covalent Bonds & Electronegativity

Covalent bonds can have ionic character

These are **polar covalent bonds**

Bonding electrons attracted more strongly by one atom than by the other, electron distribution between atoms is not symmetrical.



Bond Polarity and Electronegativity

Electronegativity (EN): intrinsic ability of an atom to attract the shared electrons in a covalent bond.

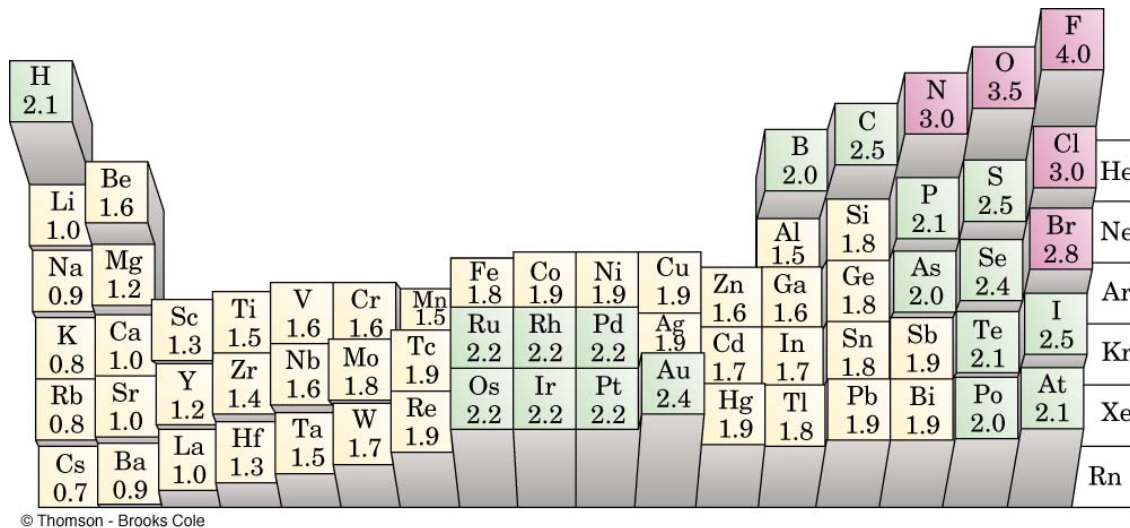
Differences in EN produce bond polarity

As shown in Figure 2.2, electronegativities are based on an arbitrary scale. F is most electronegative (EN = 4.0), Cs is least (EN = 0.7)

Metals on left side of periodic table attract electrons weakly, lower EN

Halogens and other reactive nonmetals on right side of periodic table attract electrons strongly, higher electronegativities

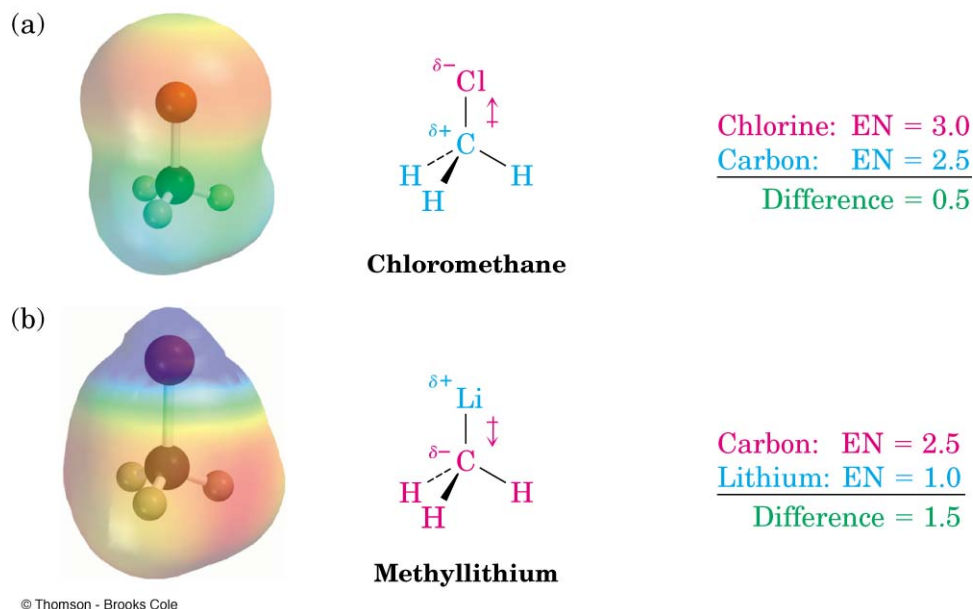
EN of C = 2.5



Bond Polarity and Inductive Effect

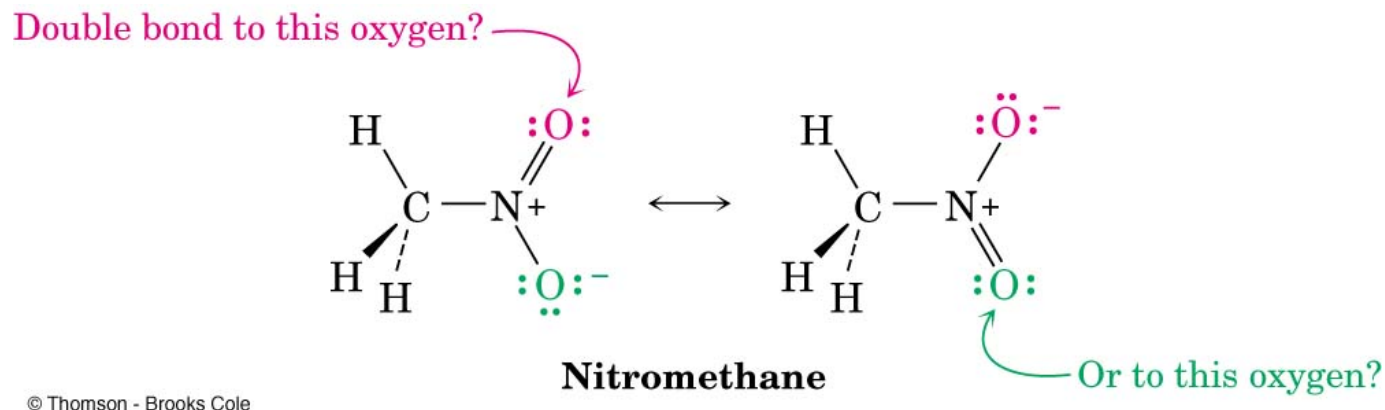
- Nonpolar Covalent Bonds: atoms with similar EN
- Polar Covalent Bonds: Difference in EN of atoms < 2
- Ionic Bonds: Difference in EN > 2
- C–H bonds, relatively nonpolar. C–O, C–X bonds (*more* electronegative elements) are polar. Bonding electrons reside toward the electronegative atom and C acquires partial positive charge, δ^+ .
- Electronegative atom acquires partial negative charge, δ^- .

Inductive effect: shifting of electrons in a bond in response to EN of nearby atoms



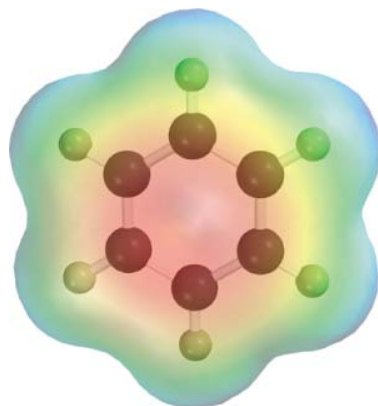
2.4 Resonance

- Some molecules have structures that cannot be represented with a single structural representation
- In these cases we draw structures that contribute to the final structure but which differ in the position of the π bond(s) or lone pair(s) of electrons
- Such a structure is delocalized and is represented by **resonance forms**
- The resonance forms are connected by a double-headed arrow (electrons and charges move in resonance structures, atoms do not)

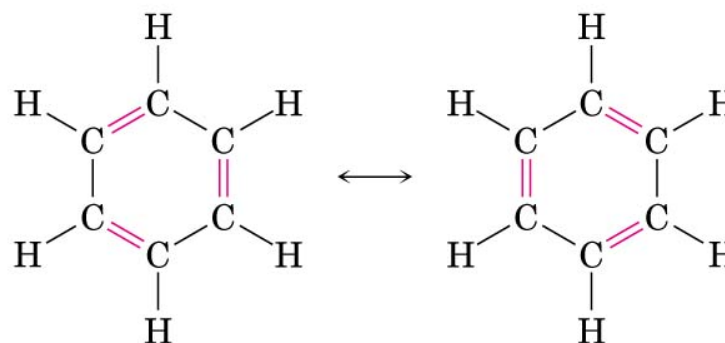


Resonance Hybrids

- A structure with resonance forms does not alternate between the forms (not an equilibrium)
- Instead, it is a *hybrid* of the two resonance forms, so the structure is called a **resonance hybrid**
- For example, benzene (C_6H_6) has two resonance forms with alternating double and single bonds
 - In the resonance hybrid, the actual structure, all its C-C bonds equivalent, midway between double and single



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Benzene (two resonance forms)

2.5 Rules for Resonance Forms

- Individual resonance forms are **imaginary** - the real structure is a hybrid (only by knowing the contributors can you visualize the actual structure)
- Resonance forms differ only in the placement of their π or nonbonding electrons
- Different resonance forms of a substance don't have to be equivalent; one form can contribute more to the actual structure than the rest.
- Resonance forms must be valid Lewis structures: the octet rule applies
- The resonance hybrid is more stable than any individual resonance form would be

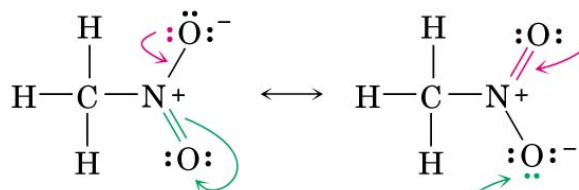
Curved Arrows and Resonance Forms

- We can imagine that electrons move in pairs to convert from one resonance form to another

- A curved arrow shows that a pair of electrons moves *from* the atom or bond at the tail of the arrow *to* the atom or bond at the head of the arrow

The red curved arrow indicates that a lone pair of electrons moves from the top oxygen atom to become part of an N=O double bond.

The new resonance structure has a double bond here . . .



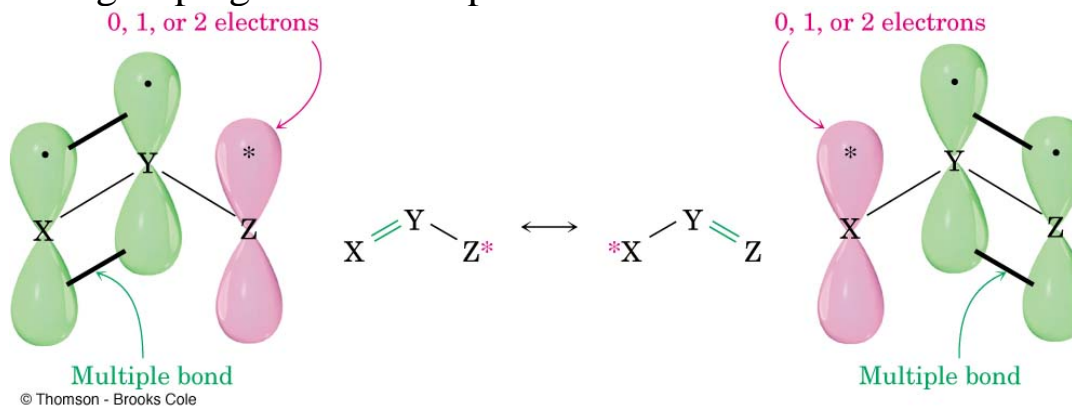
Simultaneously, two electrons from the N=O double bond move onto the bottom oxygen atom to become a lone pair.

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. . . and has a lone pair of electrons here.

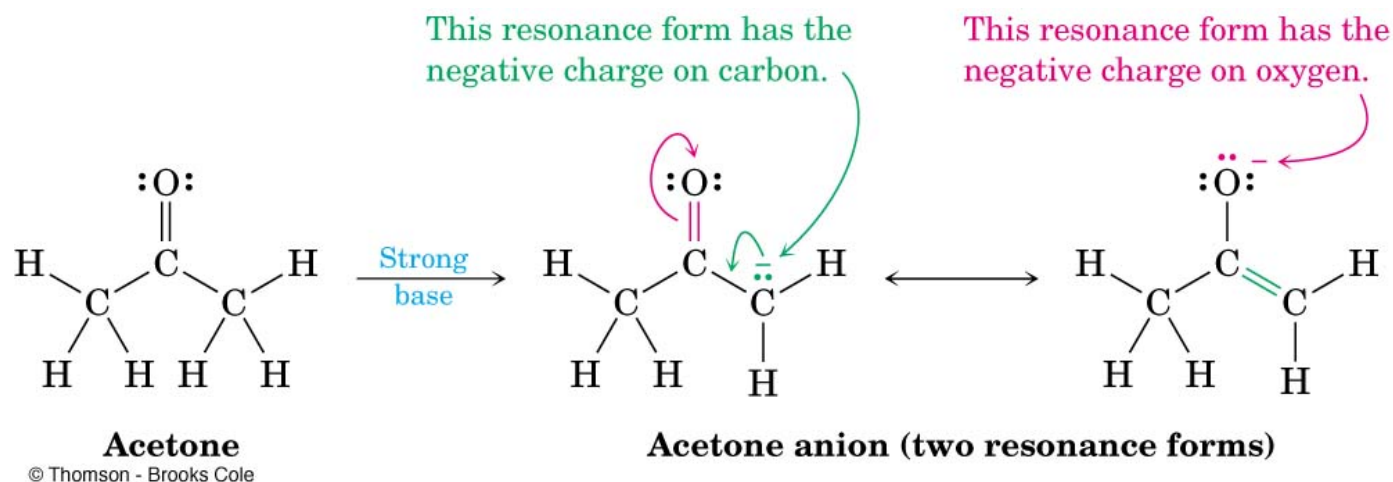
2.6 Drawing Resonance Forms

- Any three-atom grouping with a multiple bond has two resonance forms



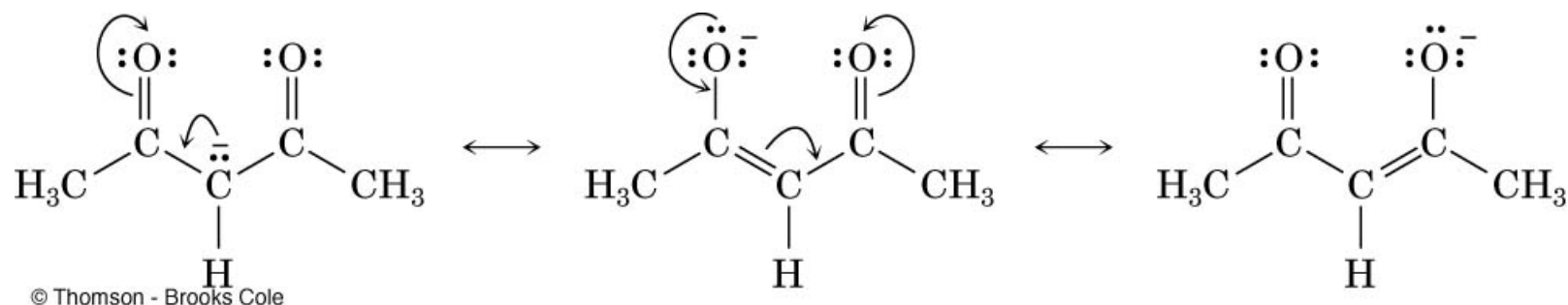
Different Atoms in Resonance Forms

- Sometimes resonance forms involve different atom types as well as locations
- The resulting resonance hybrid has properties associated with both types of contributors
- The types may contribute unequally
- The “enolate” derived from acetone is a good illustration, with delocalization between carbon and oxygen



2,4-Pentanedione

- The anion derived from 2,4-pentanedione
 - Lone pair of electrons and a formal negative charge on the central carbon atom, next to a C=O bond on the left and on the right
 - Three resonance structures result



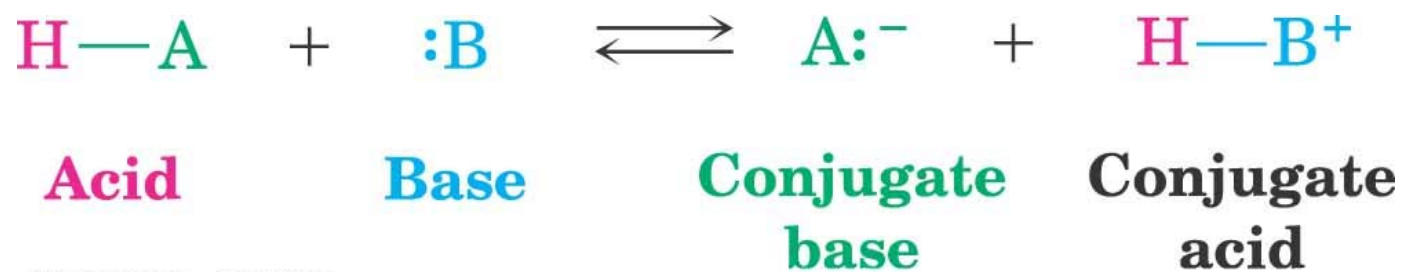
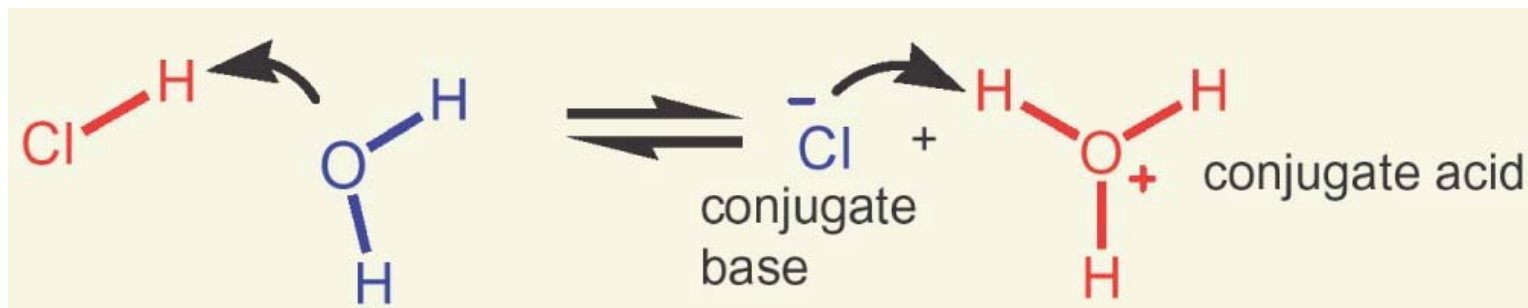
2.7 Acids and Bases: The Brønsted–Lowry Definition

- The terms “acid” and “base” can have different meanings in different contexts
- For that reason, we specify the usage with more complete terminology
- The idea that acids are solutions containing a lot of “ H^+ ” and bases are solutions containing a lot of “ OH^- ” is not very useful in organic chemistry
- Instead, Brønsted–Lowry theory defines acids and bases by their role in reactions that transfer protons (H^+) between donors and acceptors

Brønsted Acids and Bases

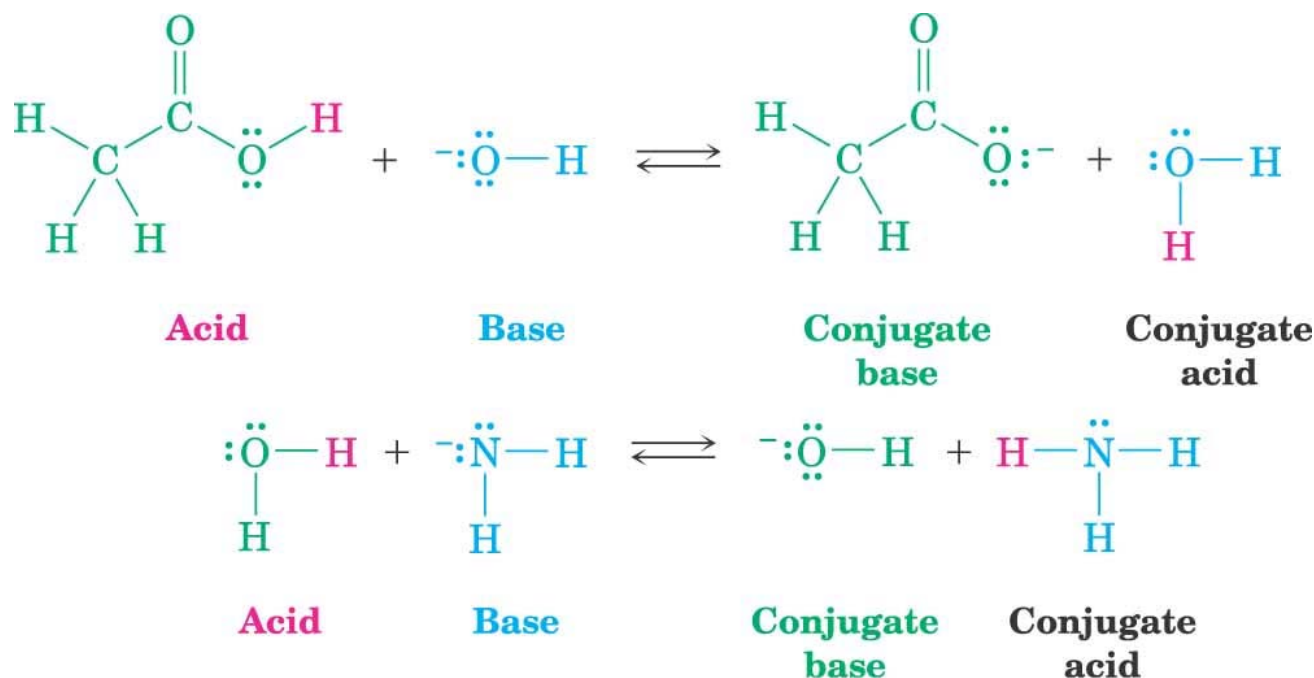
- A **Brønsted acid** is a substance that donates a hydrogen ion (H^+)
- A **Brønsted base** is a substance that accepts the H^+
 - “proton” is a synonym for H^+ , loss of an electron from H leaving the bare nucleus, a proton
- When HCl gas dissolves in water, a Brønsted acid–base reaction occurs
- HCl donates a proton to water molecule, yielding hydronium ion (H_3O^+) and Cl^-

- The reverse is also a Brønsted acid–base reaction of the conjugate acid and conjugate base



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Some other examples are:

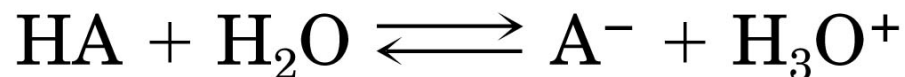


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Quantitative Measures of Acid Strength

Recall the definitions of a strong acid and a weak acid from General Chemistry I!!

- The equilibrium constant (K_{eq}) for the reaction of an acid (HA) with water to form hydronium ion and the conjugate base (A^-) is a measure related to the strength of the acid
- Stronger acids have larger K_{eq}
- Note that brackets [] indicate concentration, moles per liter, M.

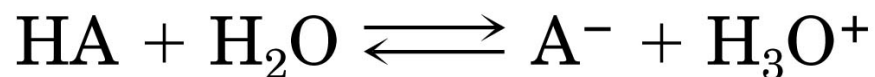


$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

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K_a – the Acidity Constant

- The concentration of water as a solvent does not change significantly when it is protonated
- The molecular weight of H₂O is 18 and one liter weighs 1000 grams, so the concentration is ~ 55.6 M at 25°
- The **acidity constant**, **K_a** for HA *K_{eq}* times 55.6 M (leaving [water] out of the expression)
- *K_a* ranges from 10¹⁵ for the strongest acids to very small values (10⁻⁶⁰) for the weakest

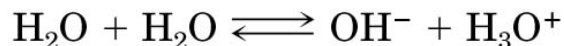


$$K_{\text{a}} = K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

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2.8 Acid and Base Strength

- The “ability” of a Brønsted acid to donate a proton to is sometimes referred to as the strength of the acid (imagine that it is throwing the proton – stronger acids throw it harder)
- The strength of the acid is measured with respect to the Brønsted base that receives the proton
- Water is used as a common base for the purpose of creating a scale of Brønsted acid strength
- $pK_a = -\log K_a$
- A smaller value of pK_a indicates a stronger acid and is proportional to the energy difference between products and reactants
- The pK_a of water is 15.74



$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad \text{and} \quad K_a = K_{\text{eq}} \times [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

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$$K_a = \frac{1.0 \times 10^{-14}}{55.6} = 1.80 \times 10^{-16} \quad \text{and} \quad pK_a = 15.74$$

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TABLE 2.3 Relative Strengths of Some Common Acids and Their Conjugate Bases

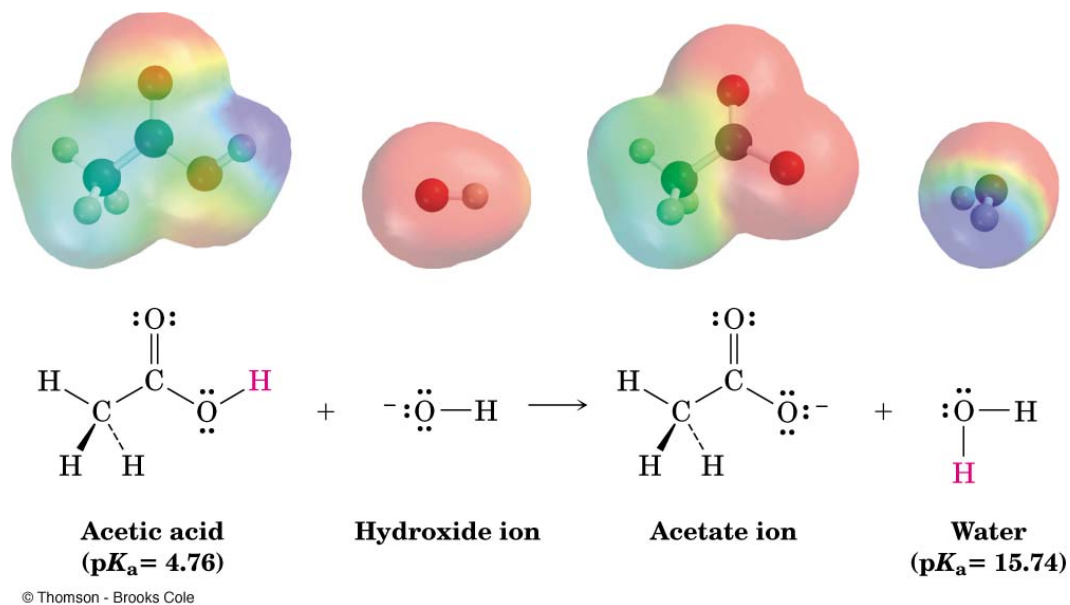
	Acid	Name	pK _a	Conjugate base	Name	
Weaker acid	CH ₃ CH ₂ OH	Ethanol	16.00	CH ₃ CH ₂ O ⁻	Ethoxide ion	Stronger base
	H ₂ O	Water	15.74	HO ⁻	Hydroxide ion	
	HCN	Hydrocyanic acid	9.31	CN ⁻	Cyanide ion	
	CH ₃ CO ₂ H	Acetic acid	4.76	CH ₃ CO ₂ ⁻	Acetate ion	
	HF	Hydrofluoric acid	3.45	F ⁻	Fluoride ion	
	HNO ₃	Nitric acid	-1.3	NO ₃ ⁻	Nitrate ion	
Stronger acid	HCl	Hydrochloric acid	-7.0	Cl ⁻	Chloride ion	Weaker base

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2.9 Predicting Acid–Base Reactions from pK_a Values

■ pK_a values are related as logarithms to equilibrium constants

H⁺ will always go from the stronger acid to the stronger base. An acid with a lower pK_a will react with the conjugate base of an acid with a higher pK_a.

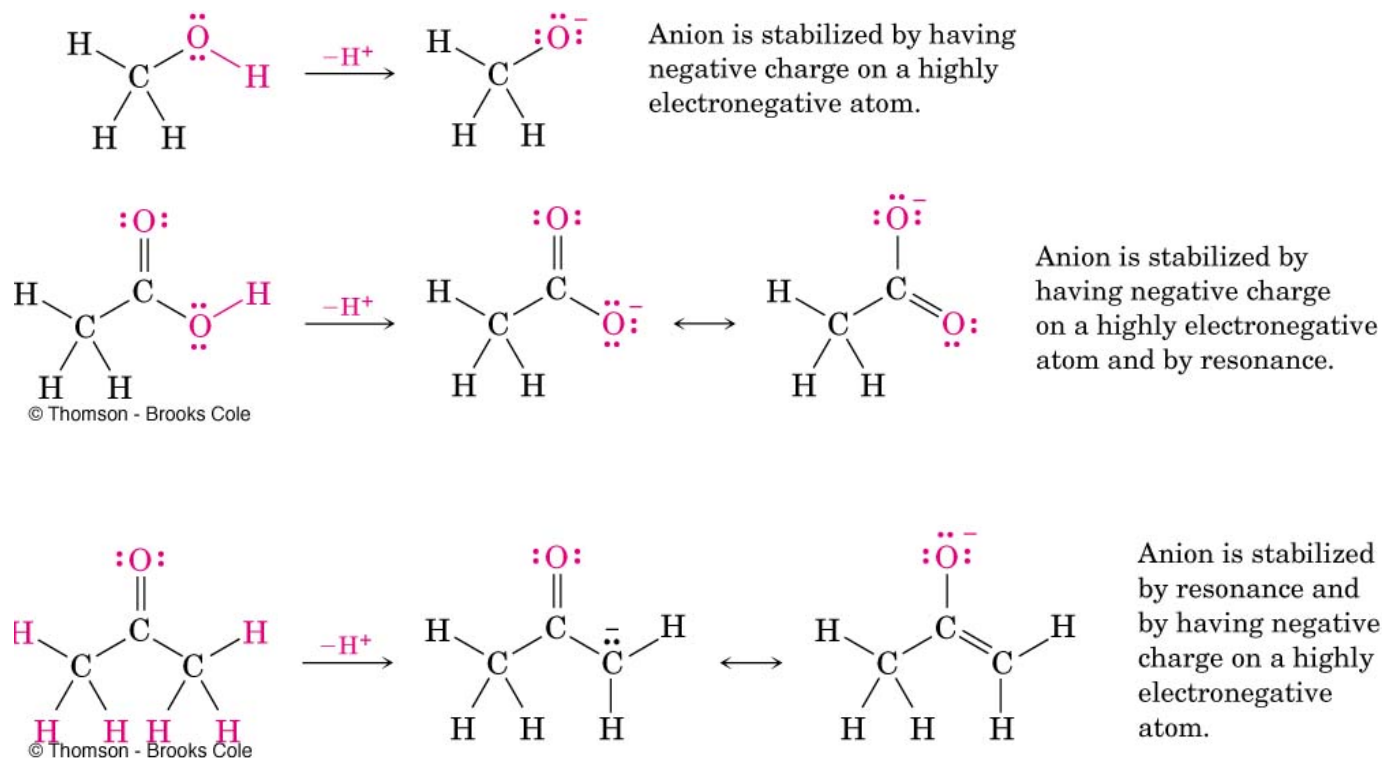


2.10 Organic Acids and Organic Bases

- The reaction patterns of organic compounds often are acid-base combinations
- The transfer of a proton from a strong Brønsted acid to a Brønsted base, for example, is a very fast process and will always occur along with other reactions

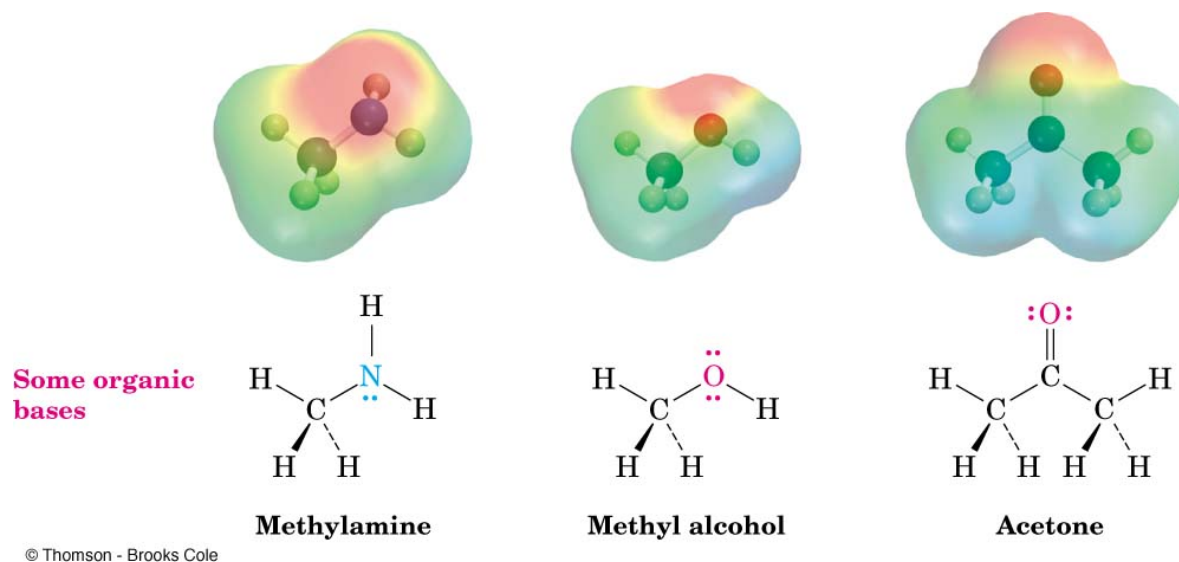
Organic Acids

- Those that lose a proton from O–H, such as methanol and acetic acid
- Those that lose a proton from C–H, usually from a carbon atom next to a C=O double bond (O=C–C–H)



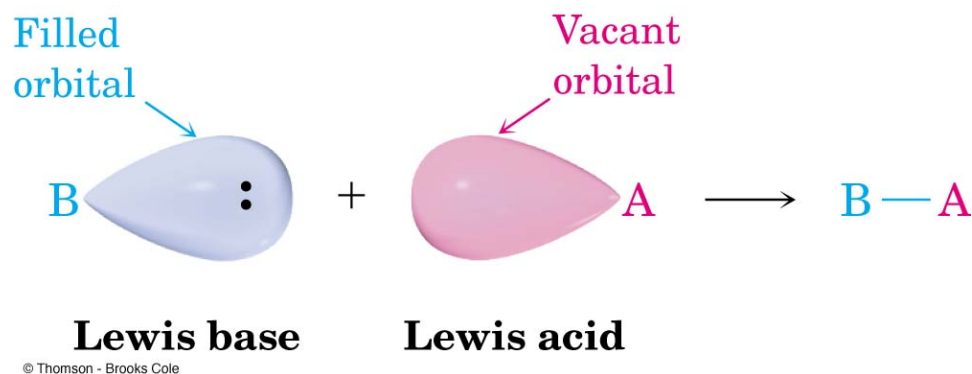
Organic Bases

- Have an atom with a lone pair of electrons that can bond to H⁺
- Nitrogen-containing compounds derived from ammonia are the most common organic bases
- Oxygen-containing compounds can react as bases when with a strong acid or as acids with strong bases



2.11 Acids and Bases: The Lewis Definition

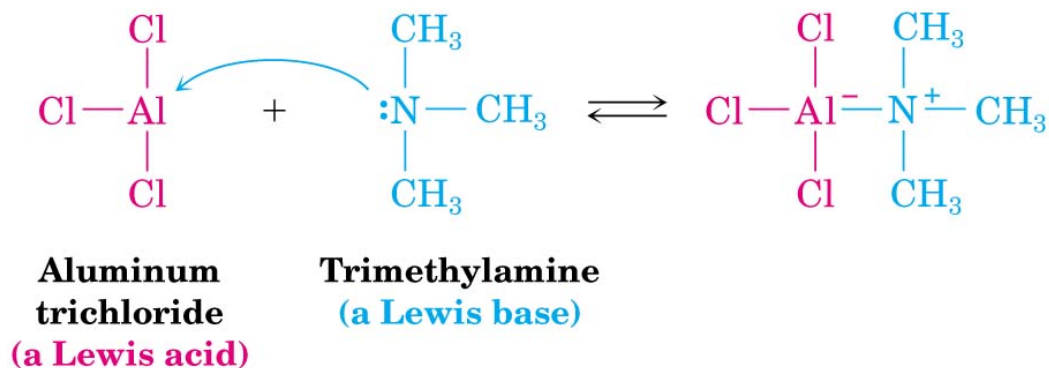
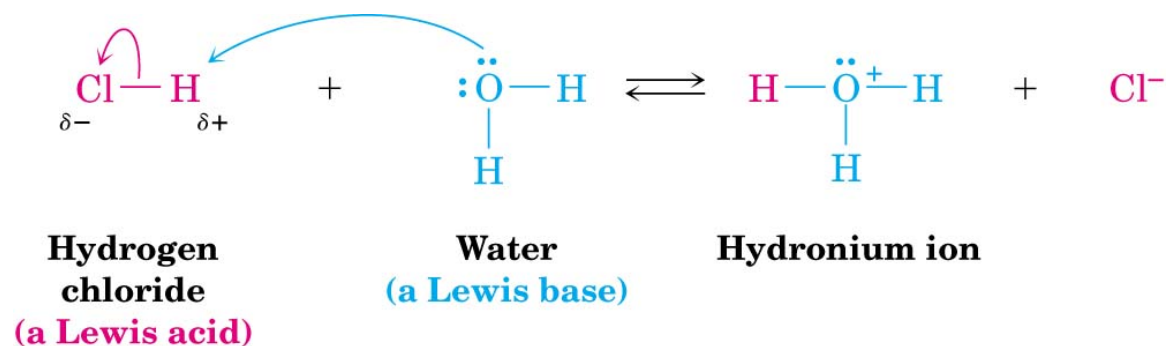
- Lewis acids are electron pair acceptors and Lewis bases are electron pair donors
- Brønsted acids are not Lewis acids because they cannot accept an electron pair directly (only a proton would be a Lewis acid)
- The Lewis definition leads to a general description of many reaction patterns but there is no scale of strengths as in the Brønsted definition of pK_a



Lewis Acids and the Curved Arrow Formalism

- The Lewis definition of acidity includes metal cations, such as Mg^{2+}
 - They accept a pair of electrons when they form a bond to a base
- Group 3A elements, such as BF_3 and AlCl_3 , are Lewis acids because they have unfilled valence orbitals and can accept electron pairs from Lewis bases
- Transition-metal compounds, such as TiCl_4 , FeCl_3 , ZnCl_2 , and SnCl_4 , are Lewis acids
- Organic compounds that undergo addition reactions with Lewis bases (discussed later) are called electrophiles and therefore Lewis Acids
- The combination of a Lewis acid and a Lewis base can be shown with a curved arrow from base to acid

Illustration of Curved Arrows in Following Lewis Acid-Base Reactions

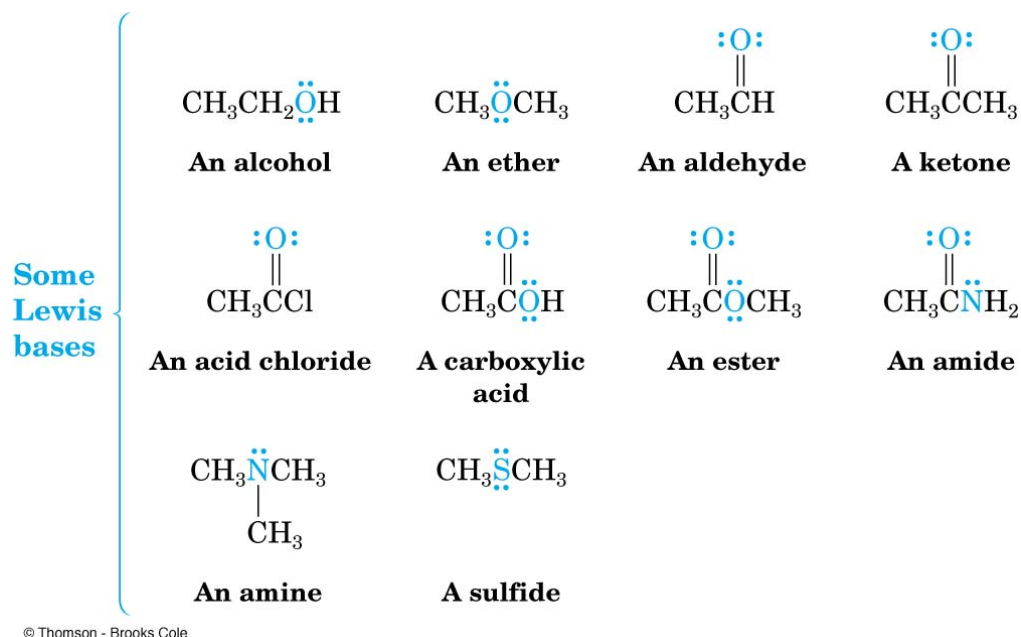


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Lewis Bases

- Lewis bases can accept protons as well as Lewis acids, therefore the definition encompasses that for Brønsted bases (in other words Lewis bases are Brønsted bases)

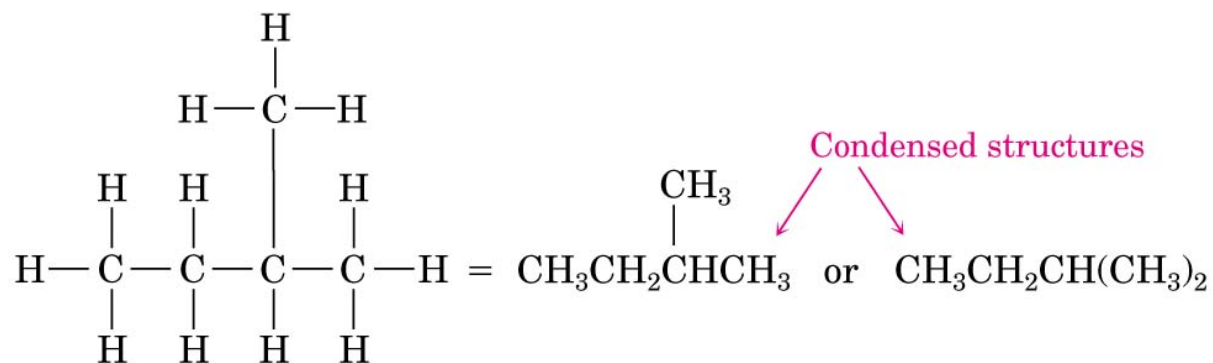
- Most oxygen- and nitrogen-containing organic compounds are Lewis bases because they have lone pairs of electrons
- Some compounds can act as both acids and bases, depending on the reaction



2.12 Drawing Chemical Structures

- Chemists use shorthand ways for writing structures
- **Condensed structures:** C-H and C-C and single bonds aren't shown but understood
 - If C has 3 H's bonded to it, write CH₃

- If C has 2 H's bonded to it, write CH₂; and so on. The compound called 2-methylbutane, for example, is written as follows:
- Horizontal bonds between carbons aren't shown in condensed structures—the CH₃, CH₂, and CH units are simply added without bonds but vertical bonds are added for clarity



2-Methylbutane

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Skeletal Structures (Line Formalism)

- Minimum amount of information but unambiguous
- C's not shown, assumed to be at each intersection of two lines (bonds) and at end of each line segment
- H's bonded to C's aren't shown – whatever number is needed will be there
- All atoms other than C and H *are* shown

