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### Chapter 2 Polar Covalent Bonds; Acids and Bases

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## Learning Objectives



### (2.1)

- Polar covalent bonds: Electronegativity
   (2.2)
- Polar covalent bonds: Dipole moments (2.3)
- Formal charges
- (2.4)
- Resonance
- (2.5)
- Rules for resonance forms

## Learning Objectives



### (2.6)

- Drawing resonance forms
- (2.7)
- Acids and bases: The Brønsted–Lowry definition
   (2.8)
- Acid and base strength
- (2.9)
- Predicting acid—base reactions from pKa values
   (2.10)
- Organic acids and organic bases

### Learning Objectives



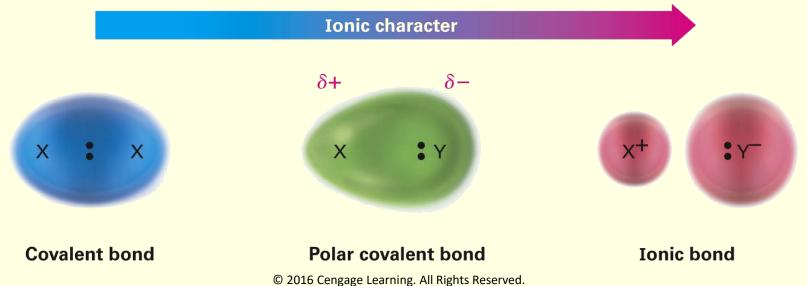
### (2.11)

- Acids and bases: The Lewis definition
   (2.12)
- Noncovalent interactions between molecules

## Polar Covalent Bonds: Electronegativity



- Covalent bonds can have ionic character
- Polar covalent bonds: Bonding electrons are attracted more strongly by one atom than by the other
  - Electron distribution between atoms is not symmetrical



## Electronegativity



- Intrinsic ability of an atom to attract the shared electrons in a covalent bond
- Differences in EN produce bond polarity
- F is most electronegative (EN = 4.0), Cs is least (EN = 0.7)
- Metals on left side of periodic table attract electrons weakly
- Halogens and other reactive nonmetals on right side of periodic table attract electrons strongly
- EN of C = 2.5

## Figure 2.2 - Electronegativity Values and Trends

H 2.1														He			
Li 1.0	Be 1.6											В 2.0	C 2.5	N 3.0	0 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											AI 1.5	Si 1.8	P 2.1	S 2.5	CI 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Тс 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Та 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	TI 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1	Rn

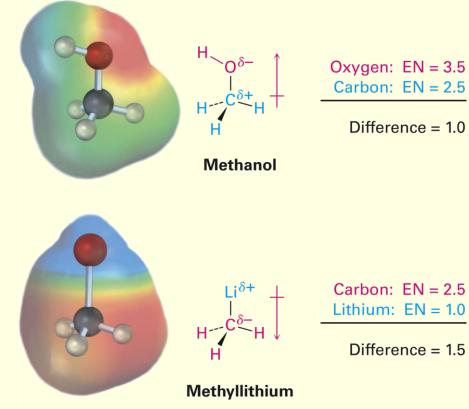
# Bond Polarity and Inductive Effect



- Difference in EN of atoms < 2 in polar covalent bonds
- Difference in EN > 2 in ionic bonds
  - C–H bonds are relatively nonpolar
  - C–O, C–X bonds are polar
- Bonding electrons toward electronegative atom
  - C acquires partial positive charge,  $\delta$ +
  - Electronegative atom acquires partial negative charge,  $\delta$ -
- Inductive effect: Shifting of electrons in a σ bond in response to EN of nearby atoms

### **Electrostatic Potential Maps**

- Show calculated charge distributions
- Colors indicate electron-rich (red) and electron-poor (blue) regions
- Arrows indicate direction of bond polarity





- Which element in each of the following pairs is more electronegative?
  - (a) Li or H
  - (b) CI or I
- Solution:
  - Using Figure 2.2
  - (a) Li (1.0) is less electronegative when compared to H (2.1)
  - (b) CI (3.0) is more electronegative when compared to I (2.5)

### Polar Covalent Bonds: Dipole Moments

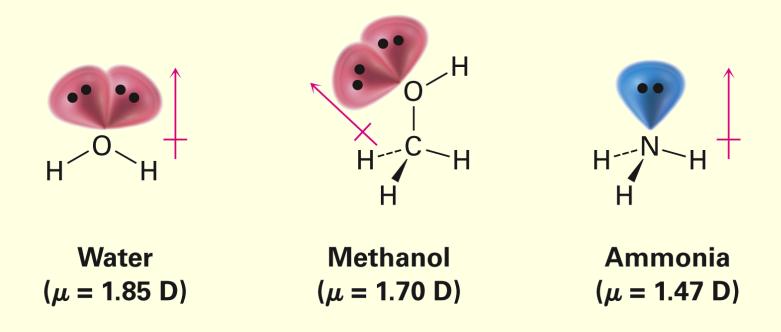


- Molecules are often polar from vector summation of individual bond polarities and lone-pair contributions
- Strongly polar substances are soluble in polar solvents like water
  - Nonpolar substances are insoluble in water
- Dipole moment (µ): Net molecular polarity, due to difference in summed charges
  - µ Magnitude of charge Q at end of molecular dipole times distance r between charges

### Polar Covalent Bonds: Dipole Moments



- $\mu = Q \times r$ , in debyes (D), 1 D = 3.336 × 10<sup>-30</sup> coulomb meter
- Length of an average covalent bond, the dipole moment would be 1.60 × 10<sup>-29</sup> C⋅m, or 4.80 D



# Dipole Moments in Water and Ammonia

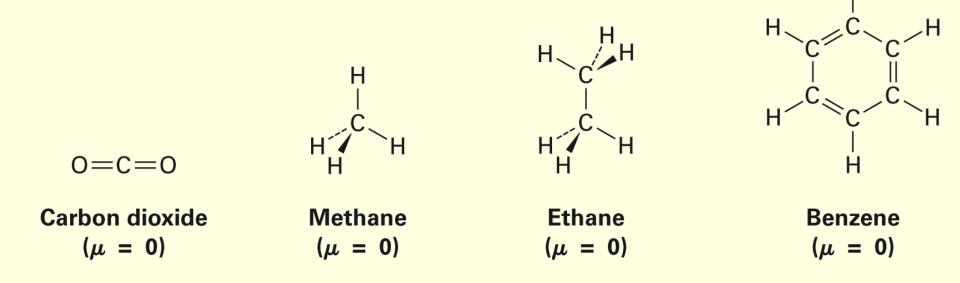


- Large dipole moments
  - EN of O and N > H
  - Both O and N have lone-pair electrons oriented away from all nuclei

TABLE 2-1 Dipole Moments of Some Compounds									
Compound	Dipole moment (D)	Compound	Dipole moment (D)						
NaCl	9.00	NH <sub>3</sub>	1.47						
CH <sub>2</sub> O	2.33	CH <sub>3</sub> NH <sub>2</sub>	1.31						
CH <sub>3</sub> CI	1.87	CO <sub>2</sub>	0						
H <sub>2</sub> O	1.85	CH <sub>4</sub>	0						
CH₃OH	1.70	CH <sub>3</sub> CH <sub>3</sub>	0						
CH <sub>3</sub> CO <sub>2</sub> H	1.70		0						
CH <sub>3</sub> SH	1.52								
		Benzene							

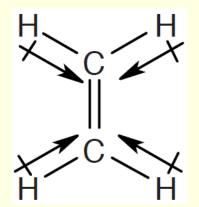
### Absence of Dipole Moments

- In symmetrical molecules, the dipole moments of each bond have one in the opposite direction
  - The effects of the local dipoles cancel each other





- Draw three-dimensional drawing of H<sub>2</sub>C=CH<sub>2</sub> molecules
  - Predict whether it has dipole moment
- Solution:
  - Drawing an arrow that points from the least electronegative element to the most electronegative element

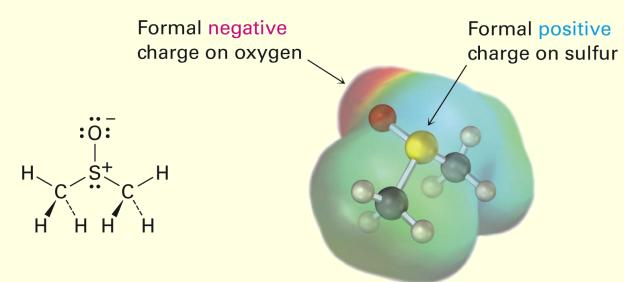


Has zero dipole moment

### **Formal Charges**



- At times it is necessary to have structures with formal charges on individual atoms
- Bonding of the atom in the molecule is compared to valence electron structure

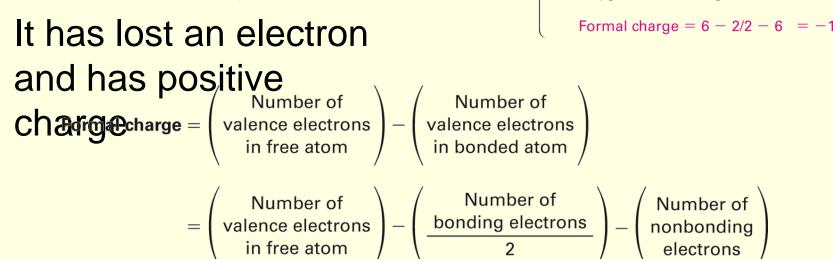


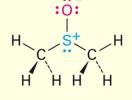
#### **Dimethyl sulfoxide**

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### Formal Charge for Dimethyl Sulfoxide

- Atomic sulfur has 6 valence electrons
- Dimethyl sulfoxide sulfur has only 5





#### For sulfur:

Sulfur valence electrons	= 6
Sulfur bonding electrons	= 6
Sulfur nonbonding electrons	= 2

#### Formal charge = 6 - 6/2 - 2 = +1

#### For oxygen:

Dxygen	valence electrons	=	6
Dxygen	bonding electrons	=	2
Dxygen	nonbonding electrons	=	6

# Table 2.2 - A Summary ofCommon Formal Charges



Atom		С		N	I.	C	)	S	;	Р
Structure	—ċ—	ċ	—ē—	—N	— <u>.</u>	—ö—	— <u>ö:</u>	— <u>;</u> + 	— <u>:</u> :-	P
Valence electrons	4	4	4	5	5	6	6	6	6	5
Number of bonds	3	3	3	4	2	3	1	3	1	4
Number of nonbonding electrons	1	0	2	0	4	2	6	2	6	0
Formal charge	0	+1	-1	+1	-1	+1	-1	+1	-1	+1

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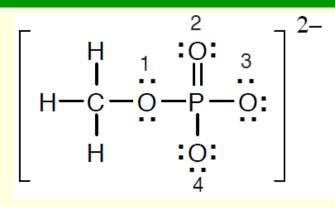
 Calculate formal charges on the four O atoms in the methyl phosphate dianion

$$\begin{bmatrix} H & :0: \\ I & I \\ H-C-O-P-O: \\ I & I \\ H & :O: \\ H & :O: \end{bmatrix}^{2-2}$$

Solution:

Formal charge (FC) = 
$$\begin{bmatrix} \# \text{ of valence} \\ \text{electrons} \end{bmatrix} - \begin{bmatrix} \# \text{ of bonding electrons} \\ 2 \end{bmatrix} - \begin{bmatrix} \# \text{ of } \\ nonbonding \end{bmatrix} = \begin{bmatrix} \# \text{ of } \\ nonbonding \end{bmatrix}$$





Methyl phosphate

• For oxygen 1: FC = 
$$6 - \frac{4}{2} - 4 = 0$$

• For oxygen 2: FC = 6 - 
$$\frac{4}{2}$$
 - 4 = 0

• For oxygen 3: FC = 
$$6 - \frac{2}{2} - 6 = -1$$



• For oxygen 4: FC = 
$$6 - \frac{2}{2} - 6 = -1$$

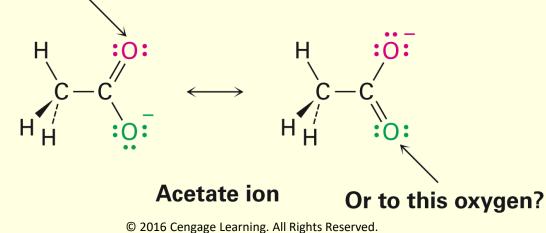
- Formal charge of oxygen atoms 1 and 2 is 0
- Formal charge of oxygen atoms 3 and 4 is -1

### Resonance



- Some molecules have structures that cannot be shown with a single representation
- Represented by structures that contribute to the final structure but differ in the position of the π bond or lone pair
  - Such structures are delocalized and are represented by resonance forms

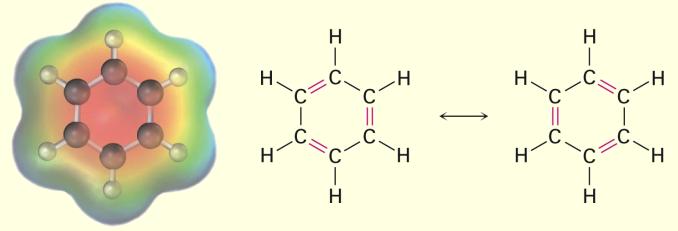
Double bond to this oxygen?



### **Resonance Hybrids**



- Structure with resonance forms, that does not alternate between the forms
- Example Benzene (C<sub>6</sub>H<sub>6</sub>) has two resonance forms with alternating double and single bonds
  - Is a hybrid of the two individual forms
  - All six carbon—carbon bonds are equivalent



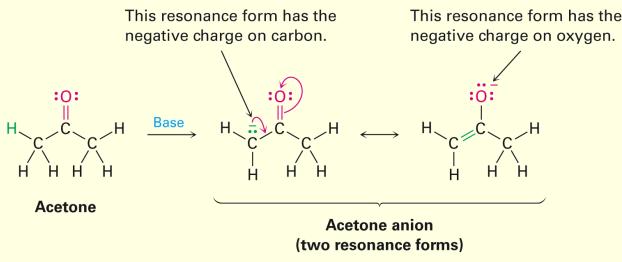
Benzene (two resonance forms)

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### **Rules for Resonance Forms**



- Individual resonance forms are imaginary
  - Real structure is a hybrid of different forms
- Resonance forms differ only in the placement of their  $\pi$  or nonbonding electrons
  - Curved arrow indicates movement of electrons, not of the atoms



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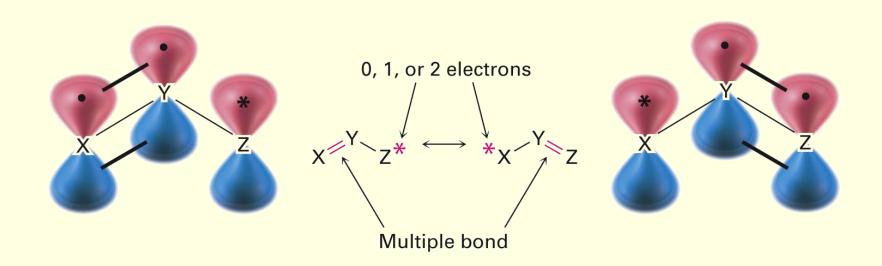
### **Rules for Resonance Forms**



- Different resonance forms of a substance do not have to be equivalent
  - When two resonance forms are nonequivalent, the actual structure of the resonance hybrid resembles the more stable form
- Resonance forms obey normal rules of valency
- Resonance hybrid is more stable than any individual resonance form
  - Resonance leads to stability

### **Drawing Resonance Forms**

- Any three-atom grouping with a p orbital on each atom has two resonance forms



### **Drawing Resonance Forms**

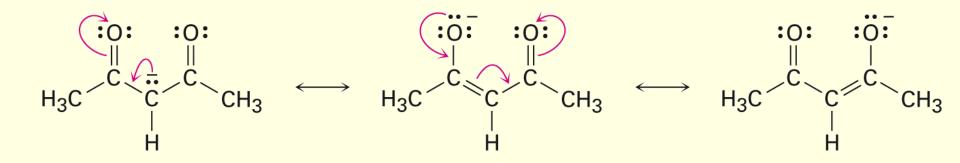


- Resonance forms differ by an exchange in position of the multiple bonds and the asterisk
  - From one end of the three-atom grouping to the other
- Recognizing three-atom groupings within larger structures help generate resonance forms, symmetrically

### 2,4-Pentanedione Anion

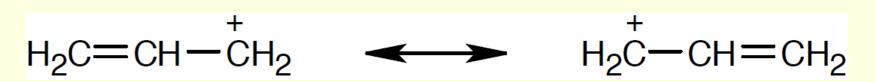


- Has a lone pair of electrons
- Has a formal negative charge on the central carbon atom, next to a C=O bond on the left and on the right
- Has three resonance structures





- Draw the indicated number of resonance forms for:
  - The allyl cation,  $H_2C=CH CH_2^{2-}$  (2)
- Solution:
  - Locating three-atom groupings that contain a multiple bond next to an atom with a p orbital
  - Exchanging the positions of the bond and the electrons in the p orbital, we have:



### Acids and Bases: The Brønsted-Lowry Definition

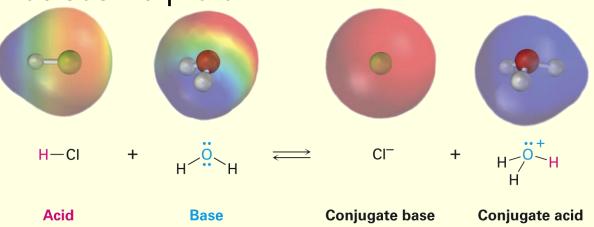


- Idea that acids are solutions containing a lot of "H<sup>+</sup>" and bases are solutions containing a lot of "OH<sup>-</sup>" is not very useful in organic chemistry
- Brønsted-Lowry theory defines acids and bases by their role in reactions that transfer protons (H<sup>+</sup>) between donors and acceptors

## Acids and Bases: The Brønsted-Lowry Definition



- Brønsted-Lowry acid: Substance that donates a hydrogen ion, H<sup>+</sup>
- Brønsted-Lowry base: Substance that accepts a hydrogen ion, H<sup>+</sup>
  - Proton is a synonym for H<sup>+</sup>
    - Loss of valence electron from H leaves only the nucleus—a proton

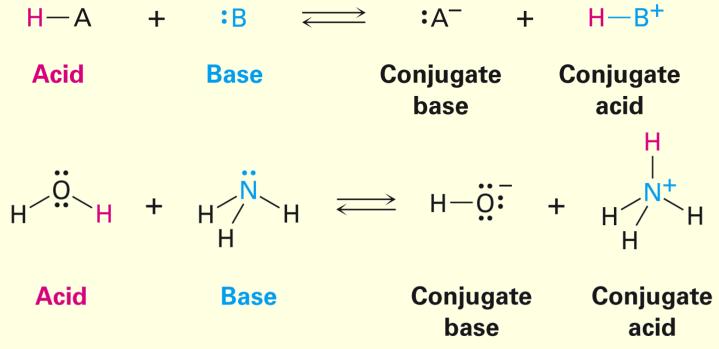


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## Acids and Bases: The Brønsted-Lowry Definition



- Conjugate base: Product that results from deprotonation of a Brønsted-Lowry acid
- Conjugate acid: Product that results from protonation of a Brønsted-Lowry base



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### Acid Base Strength



- Acidity constant (K<sub>a</sub>): Measure of acid strength
  - For the reaction of an acid (HA) with water to form hydronium ion
- Conjugate base (A<sup>-</sup>) is a measure related to the strength of the acid
- Brackets [] indicate concentration in moles per liter

$$\mathbf{K}_{\mathbf{a}} = \frac{\left[\mathbf{H}_{3}\mathbf{O}^{+}\right]\left[\mathbf{A}^{-}\right]}{\left[\mathbf{H}\mathbf{A}\right]}$$

### Acid and Base Strength

- Acid strengths are normally expressed using pK<sub>a</sub> values
  - $\mathbf{p}K_{a}$ : Negative common logarithm of the  $K_{a}$

$$\mathbf{pK}_{a} = -\log \mathbf{K}_{a}$$

- Stronger acids have smaller pK<sub>a</sub>
- Weaker acids have larger pK<sub>a</sub>

### Acid and Base Strength



• Water is both an acid and base solvent  $H_2O + H_2O \square OH^- + H_3O^+$ 

$$K_{a} = \frac{\left[H_{3}O^{+}\right]\left[OH^{-}\right]}{\left[HA\right]} = \frac{\left[H_{3}O^{+}\right]\left[OH^{-}\right]}{\left[H_{2}O\right]}$$
$$K_{a} = \frac{\left[1.0 \times 10^{-7}\right]\left[1.0 \times 10^{-7}\right]}{55.4} = 1.8 \times 10^{-15}$$

 $pK_a = 15.74$ 

- Ion product of water,  $K_w = [H_3O^+][OH^-]$
- Molar concentration of pure water,  $[H_2O] = 55.4 \text{ M at } 25^{\circ} \text{ C}$

# Table 2.3 - Relative Strengths of Some Common Acids and Their Conjugate Bases

	Acid	Name	pK <sub>a</sub>	Conjugate base	Name		
Weaker acid	CH₃CH₂OH	Ethanol	16.00	CH <sub>3</sub> CH <sub>2</sub> O <sup>-</sup>	Ethoxide ion	Stronger base	
	H <sub>2</sub> O	Water	15.74	HO-	Hydroxide ion		
	HCN	Hydrocyanic acid	9.31	CN-	Cyanide ion		
	H <sub>2</sub> PO <sub>4</sub> <sup></sup>	Dihydrogen phosphate ion	7.21	HPO4 <sup>2-</sup>	Hydrogen phosphate ion		
	CH₃CO₂H	Acetic acid	4.76	$CH_3CO_2^-$	Acetate ion		
	H <sub>3</sub> PO <sub>4</sub>	Phosphoric acid	2.16	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Dihydrogen phosphate ion		
	HNO <sub>3</sub>	Nitric acid	-1.3	NO <sub>3</sub> -	Nitrate ion		
Stronger acid	HCI	Hydrochloric acid	-7.0	CI-	Chloride ion	Weaker base	



- The amino acid phenylalanine has  $pK_a = 1.83$ , and tryptophan has  $pK_a = 2.83$ 
  - Which is the stronger acid?
- Solution:
  - Stronger acid has a smaller pK<sub>a</sub> and a weaker acid has a larger pK<sub>a</sub>
  - Accordingly, phenylalanine (p $K_a = 1.83$ ) is a stronger acid than tryptophan (p $K_a = 2.83$ )

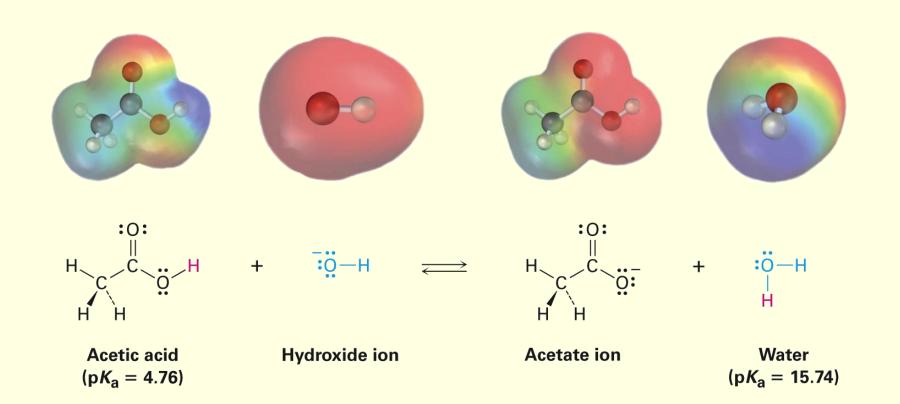
# Predicting Acid-Base Reactions from pK<sub>a</sub> Values



- pK<sub>a</sub> values are related as logarithms to equilibrium constants
- Useful for predicting whether a given acid-base reaction will take place
- Difference in two pK<sub>a</sub> values is the log of the ratio of equilibrium constants, and can be used to calculate the extent of transfer

## Predicting Acid-Base Reactions from pK<sub>a</sub> Values





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- Will the following reaction take place to a significant extent as written, according to the data in Table 2.3?
- $HCN + CH_3CO_2^-Na^+ \xrightarrow{?} Na^+^-CN + CH_3CO_2H$
- Solution:
  - $HCN + CH_3CO_2^-Na^+ \xrightarrow{?} Na^+^-CN + CH_3CO_2H$

 $\begin{array}{ll} \mathsf{pK}_{\mathsf{a}} = \ 9.3 & \qquad \mathsf{pK}_{\mathsf{a}} = \ 4.7 & \\ \text{Weaker acid} & \qquad & \text{Stronger acid} \end{array}$ 

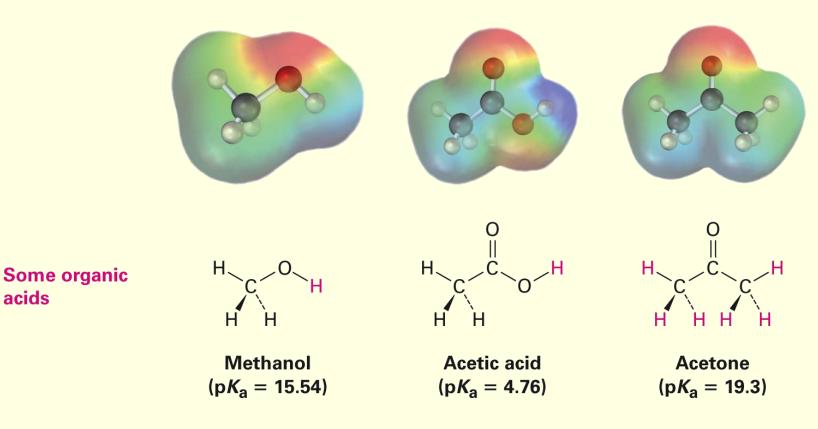
 Since CH<sub>3</sub>CO<sub>2</sub>H is stronger than HCN the reaction will not take place to a significant extent the direction written

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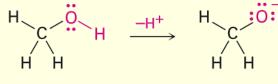
#### Characterized by the presence of positively polarized hydrogen atom



## Organic Acids

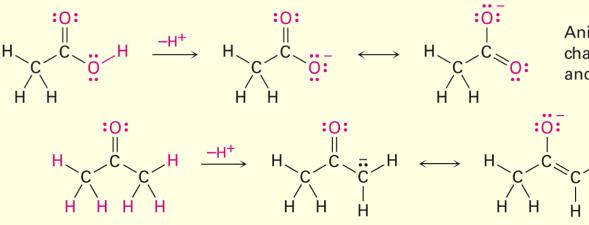


- Two main kinds, those that contain:
  - Hydrogen atom bonded to a electronegative oxygen atom(O–H)
  - A hydrogen atom bonded to a carbon atom next to a C=O bond(O=C-C-H)



Anion is stabilized by having negative charge on a highly electronegative atom.

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Anion is stabilized both by having negative charge on a highly electronegative atom and by resonance.

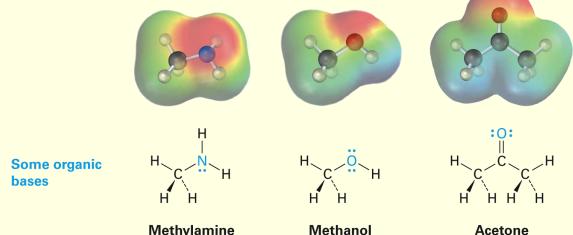
> Anion is stabilized both by resonance and by having negative charge on a highly electronegative atom.

#### **Organic Bases**



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

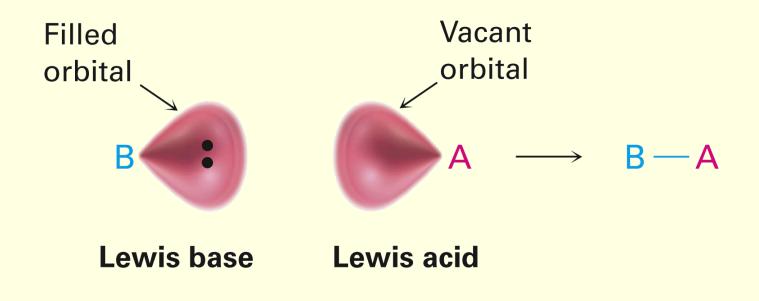
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# Acids and Bases: The Lewis Definition



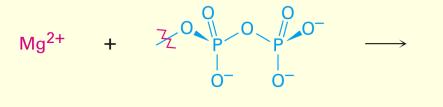
- Lewis acid: Electron pair acceptors
- Lewis bases: Electron pair donors
- Brønsted acids are not Lewis acids because they cannot accept an electron pair directly

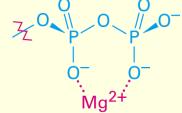


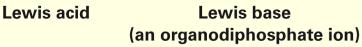
#### Lewis Acids and the Curved Arrow Formalism



- Lewis definition of acidity includes metal cations, such as Mg<sup>2+</sup>
  - They accept a pair of electrons when they form a bond to a base







Acid-base complex

- Group 3A elements, such as BF<sub>3</sub> and AlCl<sub>3</sub>, are Lewis acids
  - Have unfilled valence orbitals and can accept electron pairs from Lewis bases

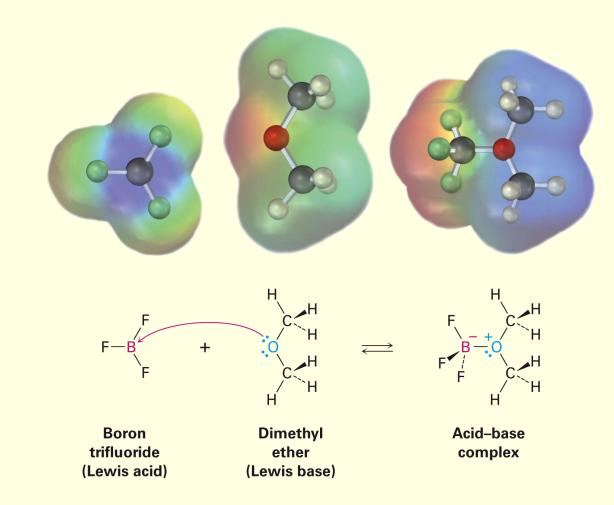
#### Lewis Acids and the Curved Arrow Formalism



- Transition-metal compounds, such as TiCl<sub>4</sub>, FeCl<sub>3</sub>, ZnCl<sub>2</sub>, and SnCl<sub>4</sub>, are Lewis acids
- Curved arrow means that a pair of electrons move from the atom at the tail of the arrow to the atom at the head of the arrow

#### **Figure 2.5** - The Reaction of Boron Trifluoride with Dimethyl Ether





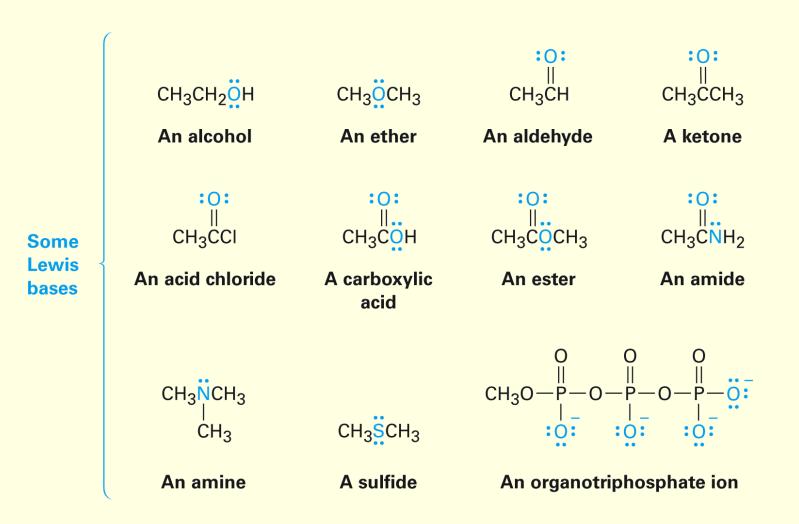
#### Lewis Bases



- Compound with a pair of nonbonding electrons that it can use to bond to a Lewis acid
- Can accept protons as well as Lewis acids
  - Definition encompasses that for Brønsted bases
- Oxygen-and nitrogen-containing organic compounds are Lewis bases; they have lone pairs of electrons
- Some compounds can act as both acids and bases

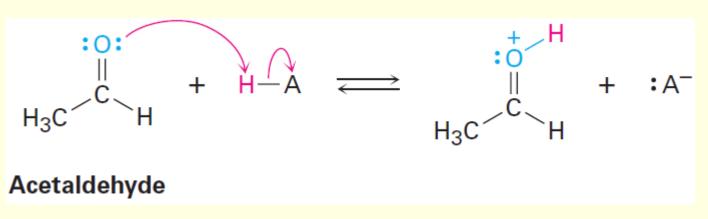
#### Lewis Bases







- Using curved arrows, show how acetaldehyde, CH<sub>3</sub>CHO, can act as a Lewis base
- Solution:
  - A Lewis base donates an electron pair to a Lewis acid
  - Using a curved arrow to show the movement of a pair toward the H atom of the acid



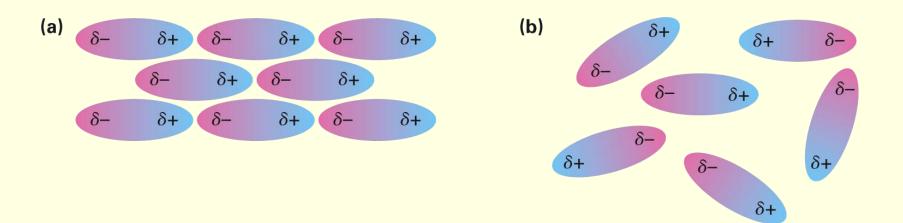
#### Noncovalent Interactions Between Molecules



- Noncovalent interactions: One of a variety of nonbonding interactions between molecules
  - Dipole–dipole forces
  - Dispersion forces
  - Hydrogen bonds

#### **Dipole–Dipole Forces**

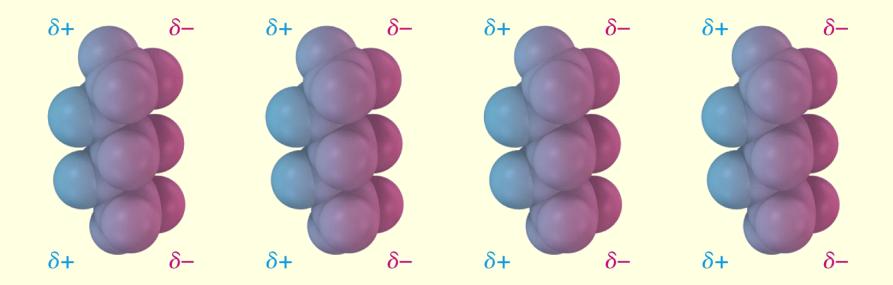
- Occur between polar molecules as a result of electrostatic interactions among dipoles
- Depending on orientation of the molecules, the forces can be either attractive or repulsive



#### **Dispersion Forces**

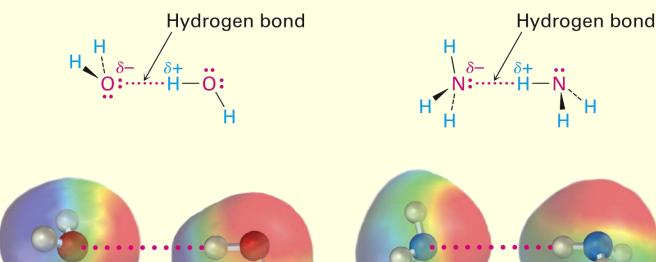


- Occur between all neighboring molecules
  - Arise due to constant change in electron distribution within molecules



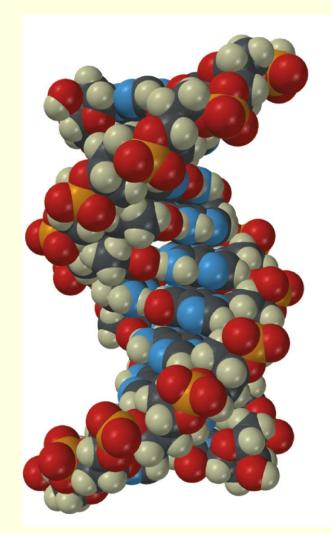
## Hydrogen Bond Forces

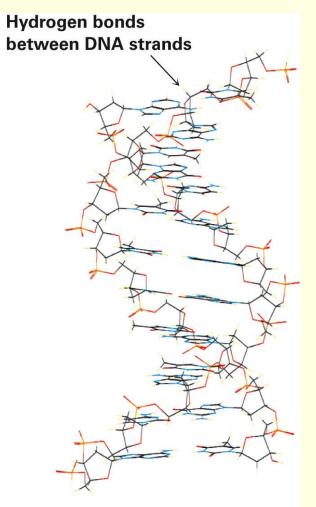
- Forces are the result of attractive interaction between a hydrogen bonded to an electronegative O or N atom and an unshared electron pair on another O or N atom



## A Deoxyribonucleic Acid Segment

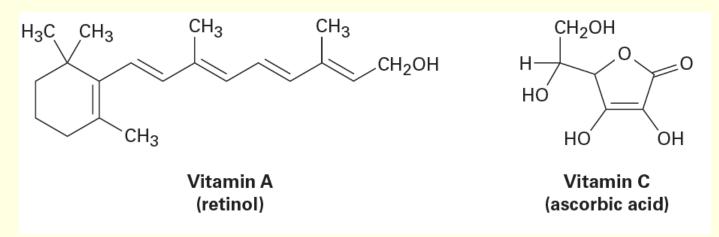




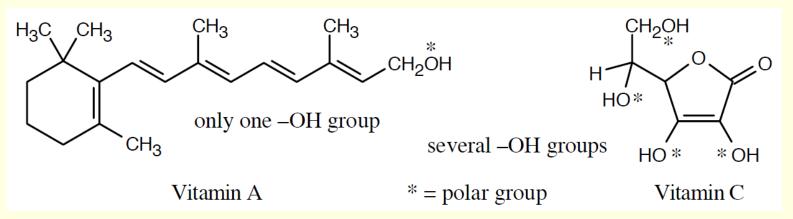




- Of the two vitamins A and C, one is hydrophilic and water-soluble while the other is hydrophobic and fat-soluble
  - Which is which?



#### Solution:



- Vitamin C has several polar —OH groups that can form hydrogen bonds with water
  - It is water soluble(hydrophilic)
- Most of Vitamin A's atoms can't form hydrogen bonds with water
  - It is fat-soluble(hydrophobic)

## Summary



- Organic molecules often have polar covalent bonds as a result of unsymmetrical electron sharing caused by differences in the electronegativity of atoms
- Polarity of a molecule is measured by its dipole moment, μ
- (+) and (-) indicate formal charges on atoms in molecules to keep track of valence electrons around an atom

#### Summary



- Some substances must be shown as a resonance hybrid of two or more resonance forms that differ by the location of electrons
- A Brønsted(–Lowry) acid donates a proton
- A Brønsted(–Lowry) base accepts a proton
- Strength of Brønsted acid is related to the negative logarithm of the acidity constant, pK<sub>a</sub>
- Weaker acids have higher values of pK<sub>a</sub>

### Summary



- Lewis acid has an empty orbital that can accept an electron pair
- Lewis base can donate an unshared electron pair
- Noncovalent interactions have several types Dipole–dipole, dispersion, and hydrogen bond forces