

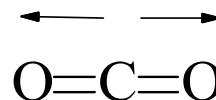
## Ch 2 Polar Covalent Bonds

Two primary bond types: Covalent (shared  $e^{-1}$ 's) and Ionic (transferred  $e^{-1}$ 's)

- Ionic bonds can have covalent character, such as with Na:Cl.  
An  $e^{-1}$  pair on  $Cl^{-1}$  can fill the 3s orbital of  $Na^{+1}$ , so that the  $e^{-1}$  pair is shared by both atoms.
- Covalent bonds have ionic character when the bonding  $e^{-1}$ 's are attracted more strongly to one atom ( $\delta^{-}$ ) than to the other ( $\delta^{+}$ ).
- The result of unequal sharing of  $e^{-1}$ 's is a polar covalent bond.
- An atom's attraction to its valence  $e^{-1}$ 's is called its [electronegativity](#) (e/n) value.  
The e/n difference between [two atoms](#) of different elements is the cause of [bond polarity](#).
- The e/n is measured on an arbitrary scale with Cs as the lowest (0.7) in the bottom left of the periodic table and F as the highest (4.0) in the top right of the table.
- Bond polarity can be measured from the difference in e/n values for the two atoms.  
Generally, a difference of  $< 0.5$  is nonpolar, from 0.5 to 1.5 is polar, and  $> 1.5$  is ionic.
- C is 2.5 and H is 2.1. The difference is 0.4.  
So, hydrocarbons are practically (but not completely) nonpolar.
- If an element with  $e/n > 2.5$  is bonded to C, it is  $\delta^{-}$ , while C is  $\delta^{+}$ .  
For instance, in  $H_3CCl$  (chloromethane), the Cl is  $\delta^{-}$ .
- If an element with  $e/n < 2.5$  is bonded to C, it is  $\delta^{+}$ , while C is  $\delta^{-}$ .  
For instance, in  $H_3CLi$  (methyl lithium), the Li is  $\delta^{+}$ .
- The direction of the polarity is indicated with a crossed arrow pointing from  $\delta^{+}$  to  $\delta^{-}$ .
- The shifting of  $e^{-1}$  density towards the  $\delta^{-}$  atom in a  $\sigma$  bond is called the Inductive Effect.

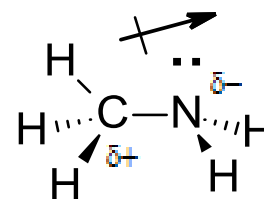
### Dipole Moment (Charge Separation)

- As individual bonds have polarities that can be measured from e/n differences, molecules have polarities which are measured as Dipole Moments.
- A dipole moment ( $\mu$ ) is the distance (in meters) between the + and - centers on a molecule times the magnitude of the charge (in coulombs).
- The dipole moment is expressed in Debyes, where  $1 D = 3.34 \times 10^{-30}$  Coul·m.
- The charge on an  $e^{-1}$  is  $1.602 \times 10^{-19}$  Coul, so two atoms with +1 and -1 charges, and separated by 100 pm (or  $1 \times 10^{-10}$  m) will have  $\mu = 1.602 \times 10^{-29}$  Coul·m = 4.80 D.
- For  $H_3CCl$ , the bond length is 178 pm and  $\mu = 1.87$  D.  
Since  $(178/100) \times (4.80 D) = 8.54 D$  for full +1 and -1 charges, and  $1.87/8.54 = 0.22$ , we can say that the C-Cl bond is 22% ionic.
- The dipole moment for a molecule can be reinforced or cancelled as a result of geometry.  
For instance,  $O=C=O$  has two polar bonds, but the molecule is linear and symmetrical.  
So, the oxygen atoms pull the  $e^{-1}$ 's in opposing directions.  
As a result, the individual dipoles cancel each other completely, and the molecule is completely nonpolar ( $\mu = 0$ ).



## The Dipole Moment for Methylamine (CH<sub>3</sub>NH<sub>2</sub>)

- The arrow points from the  $\delta^+$  C nucleus to the lone pair on the  $\delta^-$  N.



## Formal Charges

- Assigns integer + and - charges on atoms in a molecule based on the number of valence  $e^{-1}$ 's owned by an atom compared with the number that is normally owned.
- The charge is determined using the Lewis dot structure for the molecule.
- The number of  $e^{-1}$ 's owned is the total of all nonbonding valence  $e^{-1}$ 's plus *half* of all  $e^{-1}$ 's in shared pairs.

The N in NH<sub>3</sub> has one lone pair (2  $e^{-1}$ 's) and six shared  $e^{-1}$ 's (3  $e^{-1}$ 's owned), so that a total of 5  $e^{-1}$ 's are owned. How many  $e^{-1}$ 's should N own?

- The number of  $e^{-1}$ 's normally owned is the same as its column number in the periodic table. C is in column IV-A, so it normally owns 4  $e^{-1}$ 's.

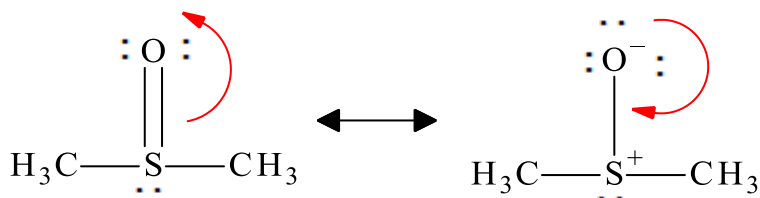
In CH<sub>4</sub>, the C has eight shared  $e^{-1}$ 's in four bonds. How many are owned?

- An instance involving charges can be seen in one resonance form of dimethylsulfoxide (H<sub>3</sub>CSOCH<sub>3</sub>), where the S and O share a single bond and both atoms have an octet.

In this structure, the O "owns" 7 of the surrounding 8  $e^{-1}$ 's, while S "owns" 5 of the surrounding 8  $e^{-1}$ 's. Both atoms are in column VI-A, and should own 6  $e^{-1}$ 's.

As a result, O has an extra  $e^{-1}$ , which is a -1 formal charge.

On the other hand, S has one less  $e^{-1}$ , which is a +1 formal charge.

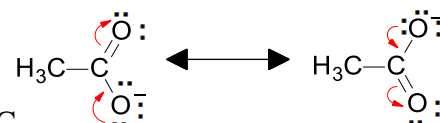


## Resonance

- Sometimes more than one equivalent Lewis or Kekulé structure is possible for molecules with double and triple bonds.
- In the acetate anion (H<sub>3</sub>CCOO<sup>-1</sup>), one O has a double bond with C, while the other O has a single bond and a negative charge.

It doesn't matter which O is which, so two structures are possible.

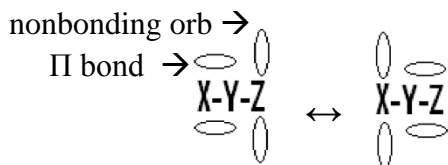
- The two structures are called resonance forms, and the only difference between the two forms is that two  $e^{-1}$  pairs have moved. The negatively charged O can donate an  $e^{-1}$  pair to C to create a double bond, while the two  $\pi$  bonded  $e^{-1}$ 's on the C=O double bond can be accepted by the O to give it the negative charge.
- In truth, neither resonance form is correct by itself, and the actual molecule is an average of the forms. This average is called a resonance hybrid and gives both O's half of a  $\pi$  bond and half of a negative charge. Both O's are in reality identical and have the same bond length.



## Rules for Resonance Forms

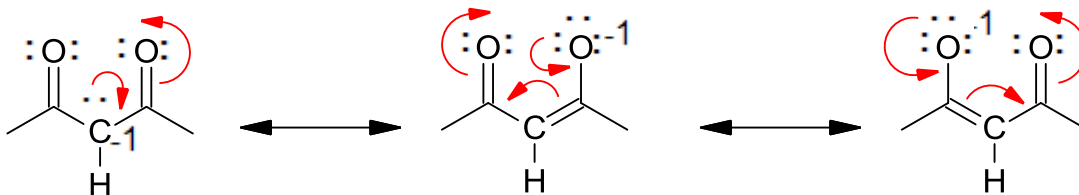
1. Individual resonance forms are not continuously occupied, as molecules resonate perpetually. The actual structure is a resonance hybrid, which is a composite of all individual forms.
2. Resonance forms differ only in the placement of the  $\Pi$  and nonbonding  $e^{-1}$ 's. Nuclear positions and orbital hybridizations do not change.
3. Resonance forms do not need to be equivalent, such as for the acetone anion. The double bond with the central C can be with the O or with the  $\text{CH}_2$ , while the charge would be on the other atom.
4. Resonance forms must have valid Lewis structures and follow valence rules. For instance, the acetate anion cannot have a negative charge on C because there would be no way for all of the atoms to follow the octet rule.
5. The resonance hybrid is more stable than any of the resonance forms. Resonance leads to stability by distributing the  $e^{-1}$ 's over more atoms. This distribution of  $e^{-1}$ 's is called delocalization. Generally, the more resonance forms that are possible, the greater the molecule's stability will be.

A three-atom grouping with a  $\Pi$  bond next to a lone pair can typically have two resonance forms.



Note that the nonbonding orb (on X or Z) can be empty or have either one or two  $e^{-1}$ 's. In all three cases, the two resonance forms are valid.

Five atoms with two  $\Pi$  bonds can have three resonance forms. This is the case with the anion of 2,4-pentanedione:



## Acids and Bases

- The Bronsted-Lowry definitions are that an acid is a proton ( $H^{+1}$ ) donor, and a base is a proton acceptor.
- Acid and base react together to form the acid's conjugate base anion (has lost an  $H^{+1}$ ) and the base's conjugate acid cation (has gained an  $H^{+1}$ ).
- The stronger an [acid or base](#) is, the weaker its conjugate ion is.

## Acid/Base Strength

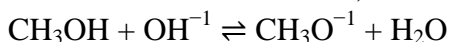
- An acid has a hydrolysis reaction with water:  $HA + H_2O \rightleftharpoons A^{-1} + H_3O^{+1}$
- The reaction has an overall equilibrium constant:  $K_c = \frac{[H_3O^{+1}][A^{-1}]}{[HA][H_2O]}$
- From this we get the acid ionization constant:  $K_a = K_c[H_2O] = \frac{[H_3O^{+1}][A^{-1}]}{[HA]}$
- We use a logarithm to obtain:  $pK_a = -\log[K_a]$
- We use an exponent to reverse that equation:  $K_a = 10^{-pK_a}$
- The strongest of acids has  $K_a \sim 10^{+15}$  and  $pK_a \approx -15$ . (This  $pK_a$  is a negative number.)
- The weakest of acids has  $K_a \sim 10^{-60}$  and  $pK_a \approx +60$ . (This  $pK_a$  is a large positive number.)
- Water has an auto-ionization reaction:  $2H_2O \rightleftharpoons H_3O^{+1} + OH^{-1}$
- $K_c = \frac{[H_3O^{+1}][OH^{-1}]}{[H_2O]^2} = \frac{1.00 \times 10^{-14}}{[H_2O]^2}$
- We can find the  $K_a$  for water from  $K_c$ :  
 $K_a = K_c[H_2O] = \frac{[H_3O^{+1}][OH^{-1}]}{[H_2O]} = \frac{1.00 \times 10^{-14}}{55.6} = 1.8 \times 10^{-16}$
- Also, we can then find the  $pK_a$  for water from its  $K_a$ :  
 $pK_a = -\log[K_a] = -\log[1.8 \times 10^{-16}] = 15.74$
- See Appendix B in McMurry, as well as [this table](#), for  $pK_a$  values of organic acids.

## Predicting acid-base rxns from $pK_a$ 's

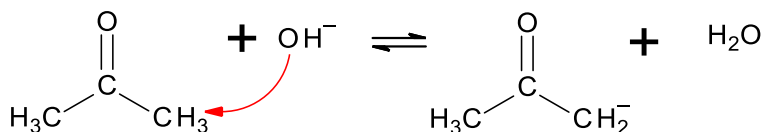
- Since reactions usually occur as reactive substances converting into less reactive products, the acid-base eqm favors the side of the reaction with the weaker acid and weaker base.
- This means the reaction goes from lower  $pK_a$  to higher  $pK_a$ .
- Consider the neutralization of acetic acid:  $CH_3COOH + OH^{-1} \rightleftharpoons CH_3COO^{-1} + H_2O$
- The  $pK_a$  of acetic acid is 4.76 and the  $pK_a$  of water is 15.74.
- So, water is the weaker of the two acids, and the equilibrium favors the products: acetate and water.

## Organic Acids

- An organic acid possesses a positively polarized H.
- The H is either bonded to an O, such as in CH<sub>3</sub>OH (methanol):



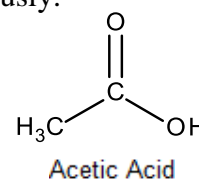
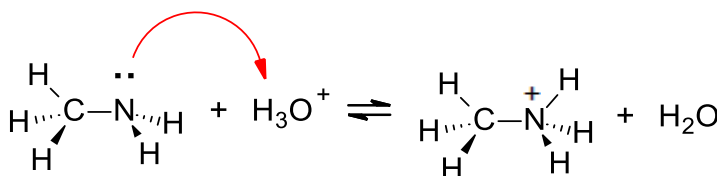
or is bonded to a C that is next to C=O (carbonyl), such as in CH<sub>3</sub>C=OCH<sub>3</sub> (acetone):



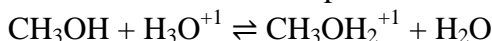
- Acidity results if the resulting anion can be stabilized either by placing the negative charge on the electronegative O, like in CH<sub>3</sub>O<sup>-1</sup>, or by distributing the charge among two or more resonance forms, like in the anions of acetic acid and 2,4-pentanedione seen previously.
- Acetic acid and other acids with the formula RCOOH are called carboxylic acids.

## Organic Bases

- An organic base possesses a lone (nonbonding) e<sup>-1</sup> pair that can bond with an H<sup>+1</sup>.
- Typically, the lone pair is on an N, such as in CH<sub>3</sub>NH<sub>2</sub> (methylamine):



- Lone pairs on O can be basic as well. (normally, O has two lone pairs)
- Note that in CH<sub>3</sub>OH (methanol), the O can either be an acid that donates H<sup>+1</sup>, or be a base that uses a lone pair to bond with an H<sup>+1</sup>:



## Lewis Acids and Bases

- A Lewis acid is an e<sup>-1</sup> pair acceptor, and a Lewis base is an e<sup>-1</sup> pair donor.
- Acids have either a vacant (empty) orbital, or a polar covalent bond with a δ<sup>+</sup> H. H<sup>+1</sup> is a Lewis acid because it has an empty 1s orbital.
- Examples of Lewis acids include metal cations (such as Mg<sup>+2</sup>), compounds with trivalent atoms (such as BF<sub>3</sub> and AlCl<sub>3</sub>), and some compounds with transition metals (such as FeCl<sub>3</sub>).
- Bases have a nonbonding e<sup>-1</sup> pair, often on an O or N atom, that can be donated to an acid.
- Examples of Lewis bases include alcohol (ROH), ethers (ROR), and amines (RNH<sub>2</sub>).
- The carbonyl O in acetic acid has two lone pairs and it can donate one of those pairs. So, acetic acid can be basic in the presence of a much stronger acid! For instance, HCl, HBr, and HI can all protonate CH<sub>3</sub>COOH to form CH<sub>3</sub>C(OH)<sub>2</sub><sup>+1</sup>.