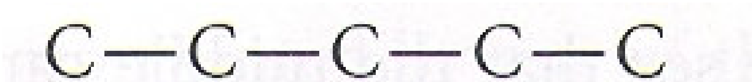
1.9 Writing Structural Formulas

- Useful Hints:
- Example: for the formula C_5H_{12}.
- What are the possible structural formulas ?

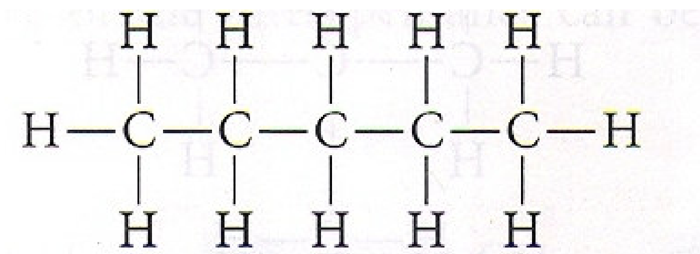
Useful Hints

- Begin by writing all carbons in a continuous chain.



a continuous chain

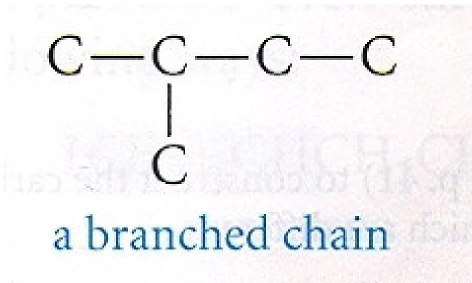
- Add Hydrogens



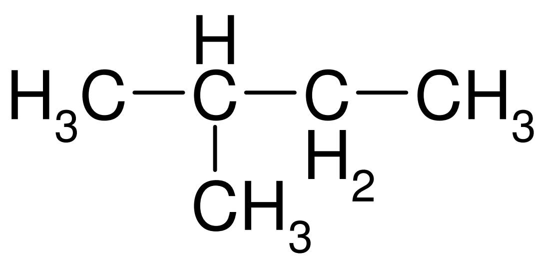
pentane, bp 36°C

Useful Hints

- For other isomers, consider branched chains.

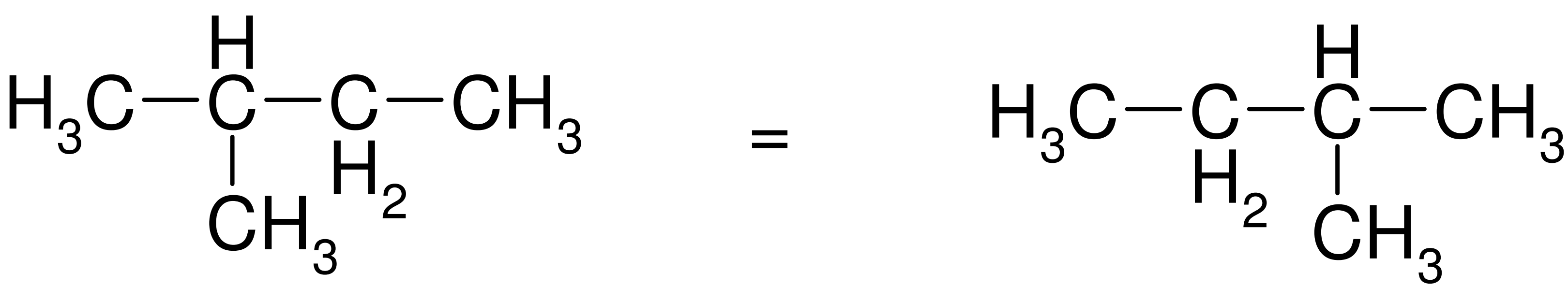


- Fill-in hydrogen



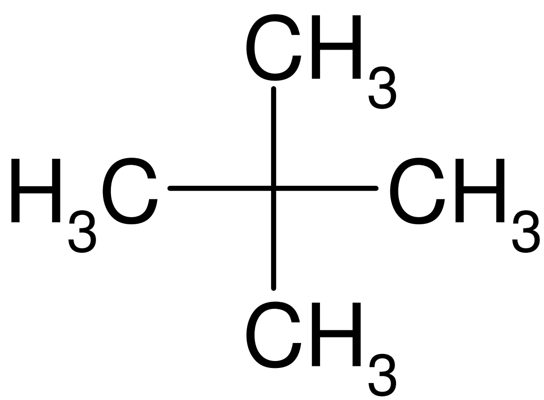
Useful Hints

- Any other possible branching?



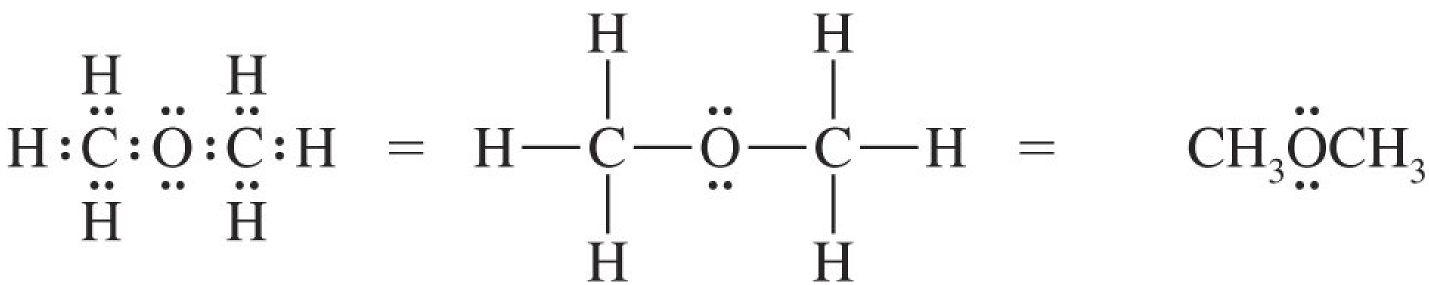
Useful Hints

- Is there a third isomer!



1.10 Abbreviated Structural Formulas

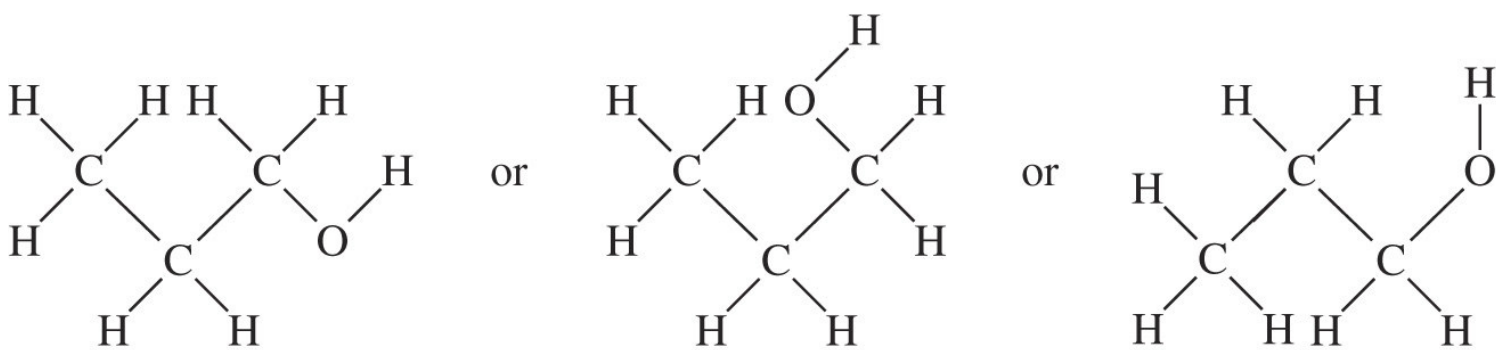
- Dot formulas are more cumbersome to draw than dash formulas and condensed formulas
- Lone-pair electrons are often (but not always) drawn in, especially when they are crucial to the chemistry being discussed



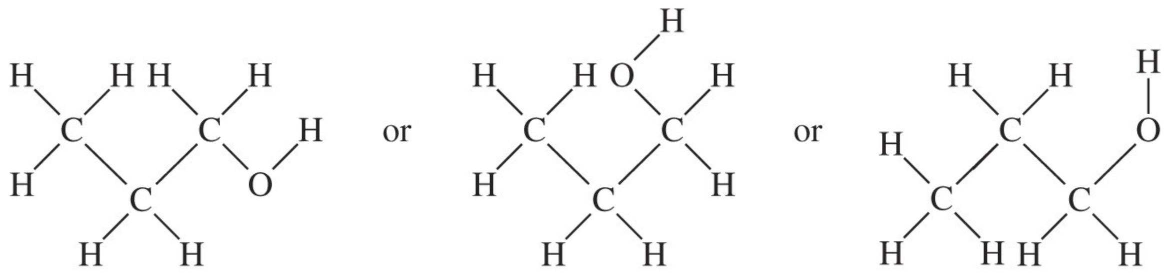
Dot structure   Dash formula   Condensed formula

Dash Formulas

- Each dash represents a pair of electrons
  - This type of representation is meant to emphasize connectivity and does not represent the 3-dimensional nature of the molecule
    - The dash formulas of propyl alcohol appear to have 90^{o} angles for carbons which actually have tetrahedral bond angles (109.5^{o})
  - There is relatively free rotation around single bonds so the dash structures below are all equivalent

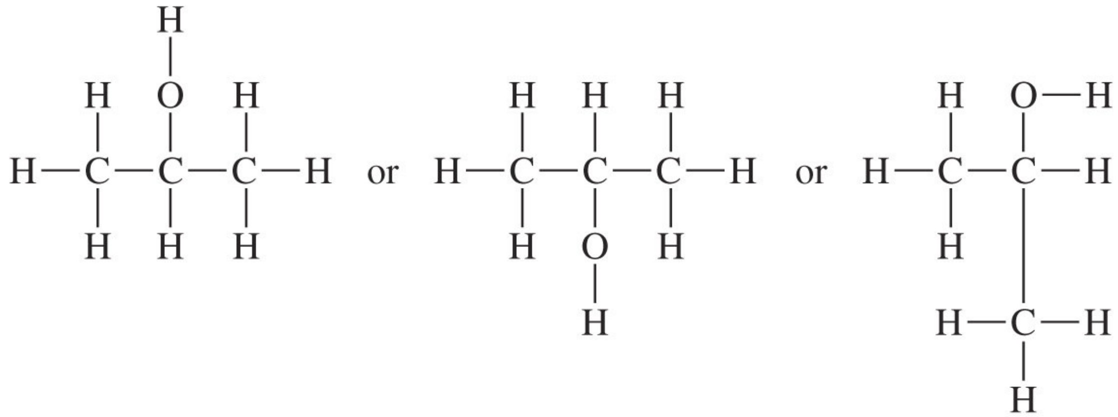


Equivalent dash formulas for propyl alcohol



Equivalent dash formulas for propyl alcohol

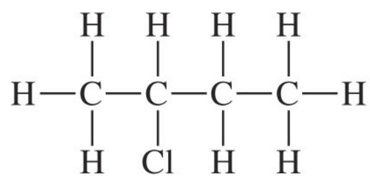
Propyl alcohol (above) is a constitutional isomer of isopropyl alcohol (below)



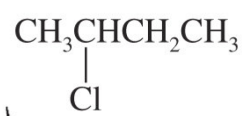
Equivalent dash formulas for isopropyl alcohol

Condensed Structural Formulas

- In these representations, some or all of the dash lines are omitted
- In partially condensed structures all hydrogens attached to an atom are simply written after it but some or all of the other bonds are explicitly shown
- In fully condensed structure all bonds are omitted and atoms attached to carbon are written immediately after it
- For emphasis, branching groups are often written using vertical lines to connect them to the main chain

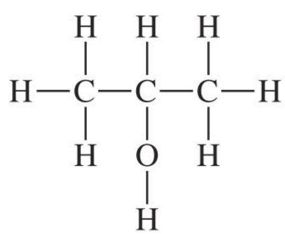


Dash formula

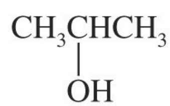


or $CH_3CHClCH_2CH_3$

Condensed formulas



Dash formula



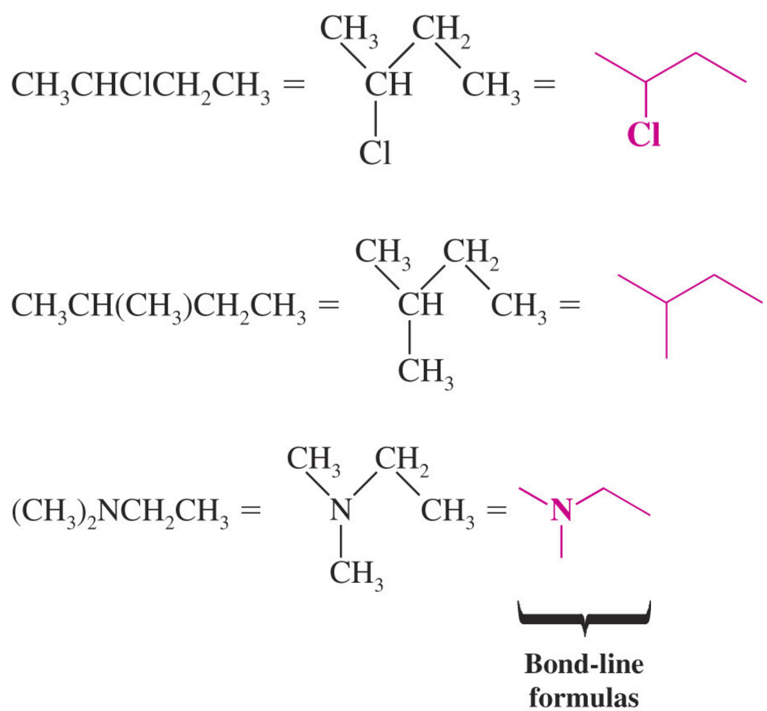
$CH_3CH(OH)CH_3$

$CH_3CHOHCH_3$ or $(CH_3)_2CHOH$

Condensed formulas

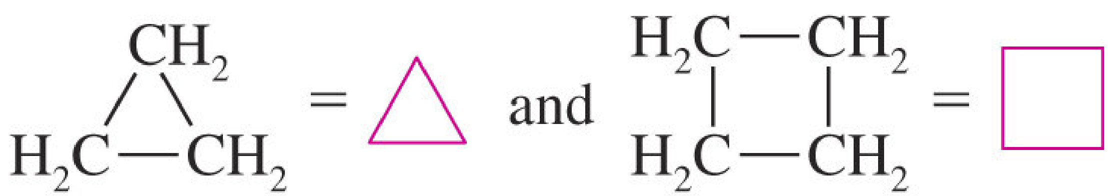
Bond-Line Formulas

- A further simplification of drawing organic molecules is to completely omit all carbons and hydrogens and only show heteroatoms (*e.g.* O, Cl, N) explicitly
- Each intersection or end of line in a zig-zag represents a carbon with the appropriate amount of hydrogens
  - Heteroatoms with attached hydrogens must be drawn in explicitly

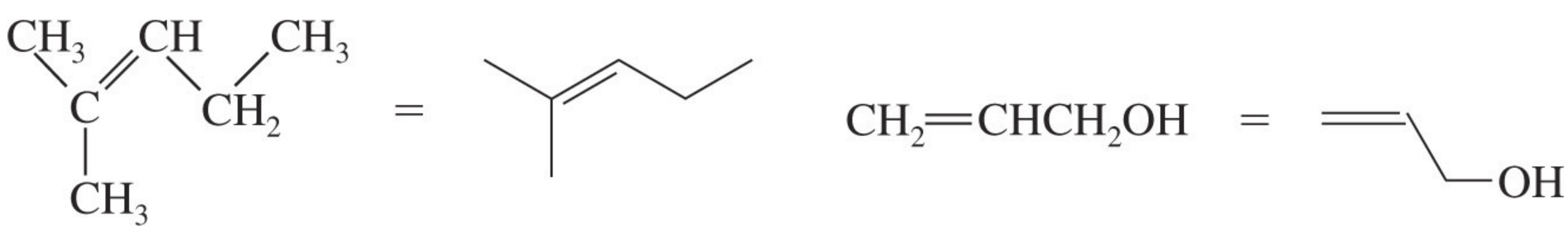


For Cyclic Compounds & Multiple Bonds

- Cyclic compounds are condensed using a drawing of the corresponding polygon



- Multiple bonds are indicated by using the appropriate number of lines connecting the atoms



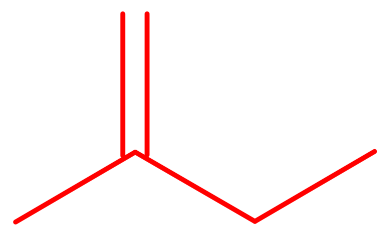
On-board exercises

1. Write a structural formula that shows all bonds for each of the following:

$(CH_3)_2CHCH_2OH$

$Cl_2C{=}CCl_2$

2. Write a more detailed formula for



3. Write a line-segment formula for $CH_3CH_2CH{=}CHCH_2CH(CH_3)_2$

1.11 Formal Charge

- A formal charge is a positive or negative charge on an individual atom
- The sum of formal charges on individual atoms is the total charge of the molecule or ion
- The formal charge is calculated by subtracting the assigned electrons on the atom in the molecule from the electrons in the neutral atom
- Electrons in bonds are evenly split between the two atoms; one to each atom
- Lone pair electrons belong to the atom itself

Formal Charge

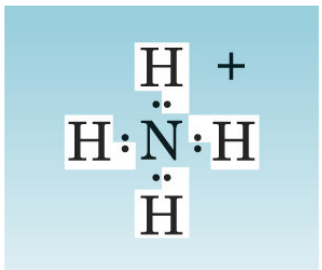
- An atom's ***formal charge*** is the difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

$$\text{formal charge on an atom in a Lewis structure} = \text{total number of valence electrons in the free atom} - \text{total number of nonbonding electrons} - \frac{1}{2}\left(\text{total number of bonding electrons}\right)$$

The sum of the formal charges of the atoms in a molecule or ion must equal the charge on the molecule or ion.

Examples

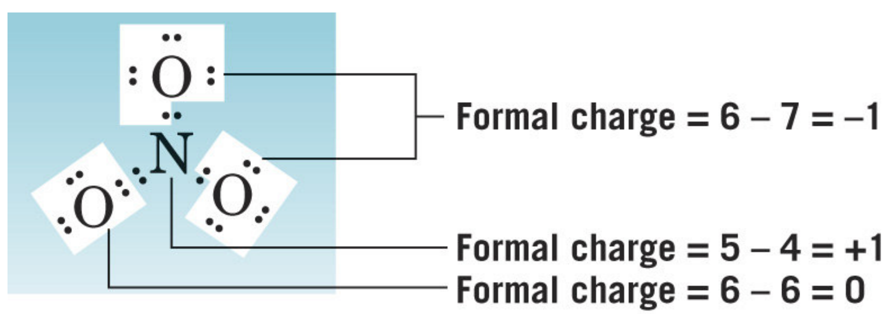
- Ammonium ion $(NH_4)^+$



For hydrogen:	valence electrons of free atom	=	1
	subtract assigned electrons	=	–1
	Formal charge	=	0
For nitrogen:	valence electrons of free atom	=	5
	subtract assigned electrons	=	–4
	Formal charge	=	+1

Charge on ion = 4(0) + 1 = +1

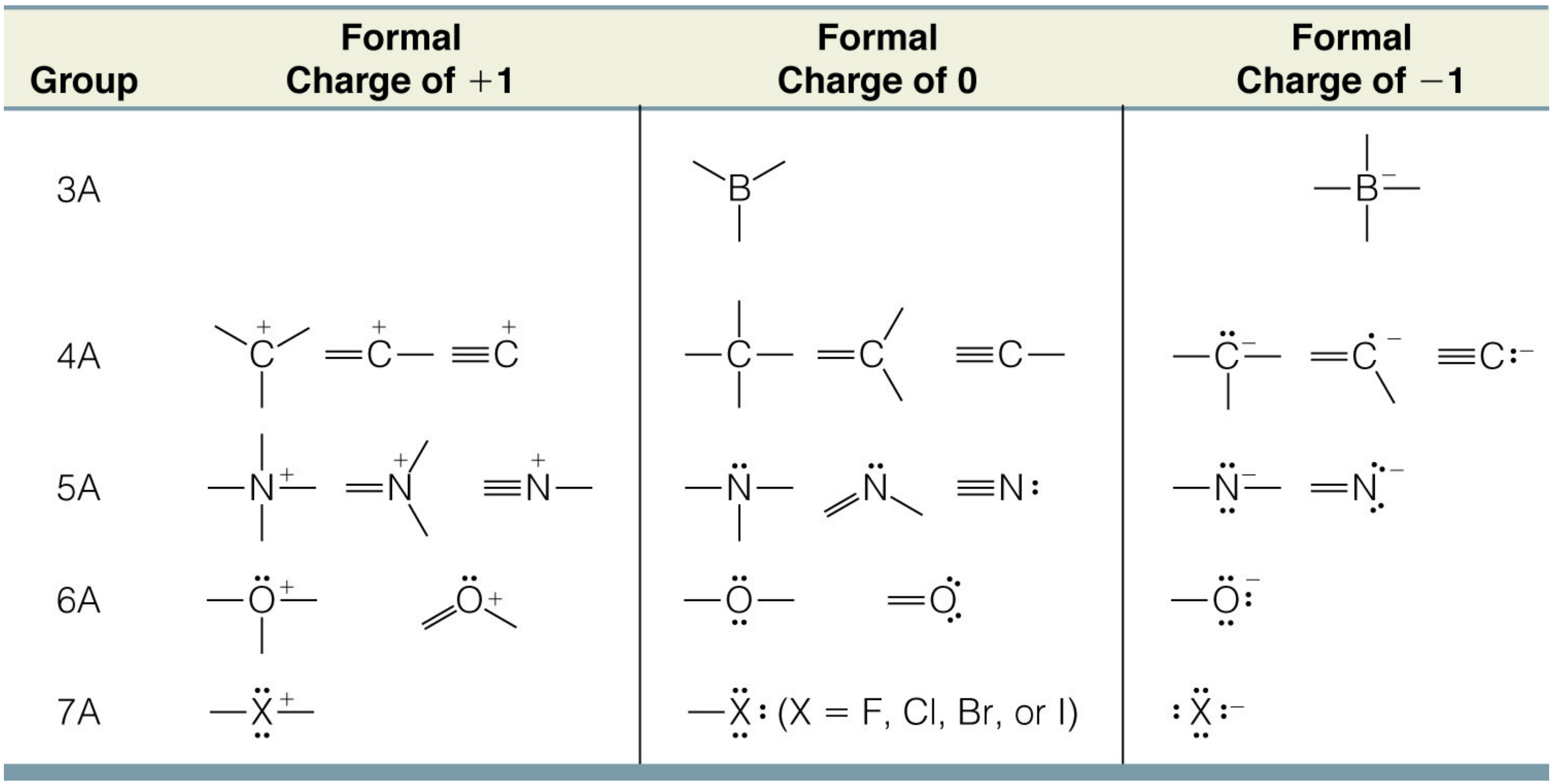
- Nitrate ion $(NO_3)^-$



Charge on ion = 2(–1) + 1 + 0 = –1

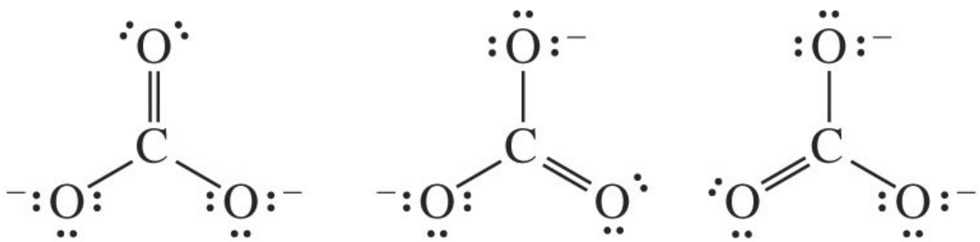
- An atom will always have the same formal charge depending on how many bonds and lone pairs it has regardless of which particular molecule it is in
- For example a singly bonded oxygen with 3 lone pairs will always have a negative charge and an oxygen with three bonds and one lone pair will always have a positive charge
- Knowing these forms of each atom is invaluable in drawing Lewis structures correctly and rapidly (See table next page)

A Summary of Formal Charges



1.12 Resonance

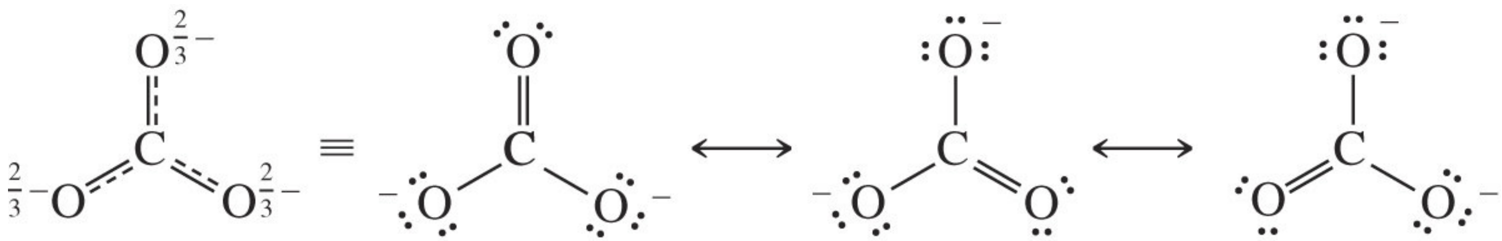
- Often a single Lewis structure does not accurately represent the true structure of a molecule
- The real carbonate ion is not represented by any of the structures 1,2 or 3 ***(Resonance Structures)***



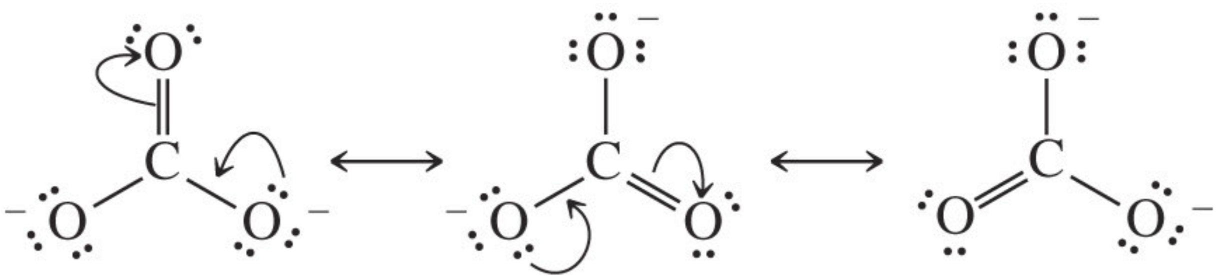
1 2 3

- Experimentally carbonate is known not to have two carbon-oxygen single bonds and one double bond; all bonds are equal in length and the charge is spread equally over all three oxygens

- The real carbonate ion can be represented by a drawing in which partial double bonds to the oxygens are shown and partial negative charge exists on each oxygen
- The real structure is a *resonance hybrid* or mixture of all three Lewis structures
- Double headed arrows are used to show that the three Lewis structures are resonance contributors to the true structure
  - The use of equilibrium arrows is incorrect since the three structures do not equilibrate; the true structure is a hybrid (average) of all three Lewis structures

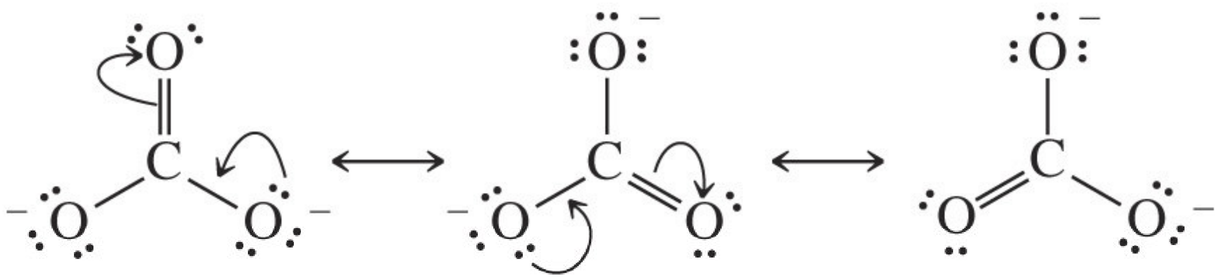


- One resonance contributor is converted to another by the use of curved arrows which show the movement of electrons
  - The use of these arrows serves as a bookkeeping device to assure all structures differ only in position of electrons

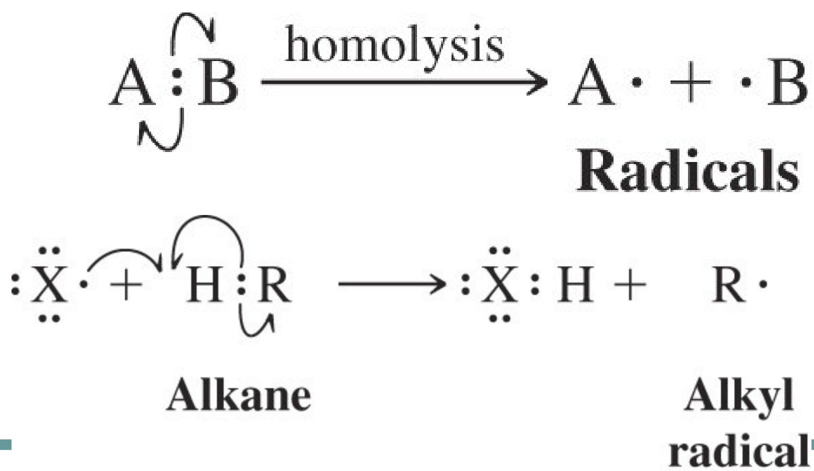


1.13 Arrow Formalism

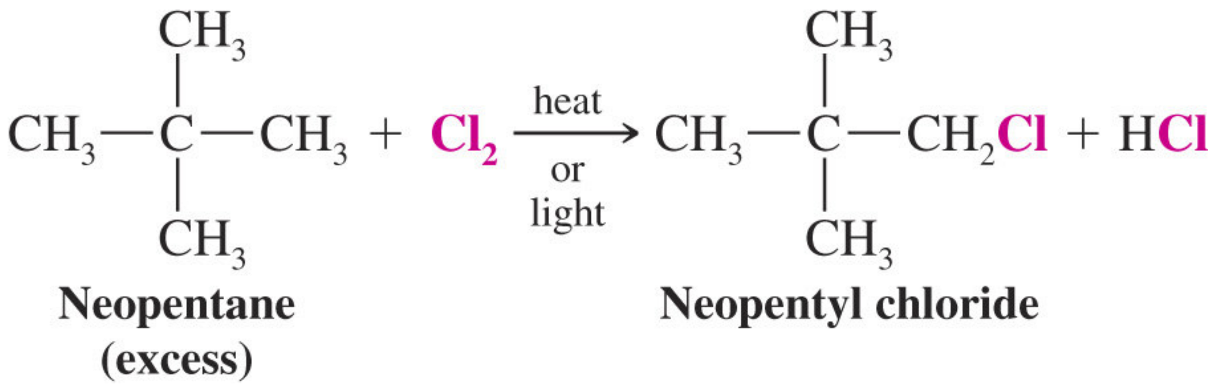
1. Curved Arrows: show how electrons are moved in resonance structures and in reactions.

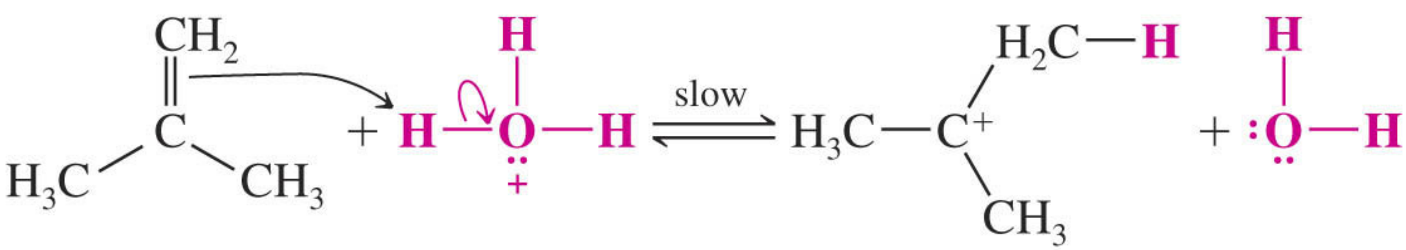


2. Fishhook Arrows: indicate the movement of single electrons.



3. Straight Arrows: point from reactants to products in chemical reaction equations.





The alkene donates an electron pair to a proton to form the more stable 3° carbocation.

4. Double-Headed Straight Arrows: between two structures indicates resonance structures.