CHEM 131
ORGANIC CHEMISTRY

Chapter 1 Bonding and Isomerism

Organic Chemistry is the chemistry of carbon compounds

Why does sucrose melt at 185^0C while table salt melts at 801^o C?

Why do both substances dissolve in water and olive oil does not?

Why does methyl butyrate smell like pears while propyl acetate smell like apple yet they have the same number and kind of atoms?

Bonding is the key to the structure, physical properties and chemical behavior of different kinds of matter.

1.1 How Electrons are arranged in Atom

- The Structure of an Atom
- An atom consists of electrons, positively charged protons, and neutral neutrons
- Electrons form chemical bonds
- Atomic number: numbers of protons in its nucleus
- Mass number: the sum of the protons and neutrons of an atom
- Isotopes have the same atomic number but different mass numbers
- The atomic weight: the average weighted mass of its atoms
- Molecular weight: the sum of the atomic weights of all the atoms in the molecule

The ground-state electronic configuration describes the orbitals occupied by the atom's electrons with the lowest energy

Table 1.2 Electron Arrangements of the First 18 Elements

Atomic number	Element	Number of electrons in each orbital				
		1*s*	2*s*	2*p*	3*s*	3*p*
1	H	1				
2	He	2				
3	Li	2	1			
4	Be	2	2			
5	B	2	2	1		
6	C	2	2	2		
7	N	2	2	3		
8	O	2	2	4		
9	F	2	2	5		
10	Ne	2	2	6		
11	Na	2	2	6	1	
12	Mg	2	2	6	2	
13	Al	2	2	6	2	1
14	Si	2	2	6	2	2
15	P	2	2	6	2	3
16	S	2	2	6	2	4
17	Cl	2	2	6	2	5
18	Ar	2	2	6	2	6

Table 1.3 Valence Electrons of the First 18 Elements

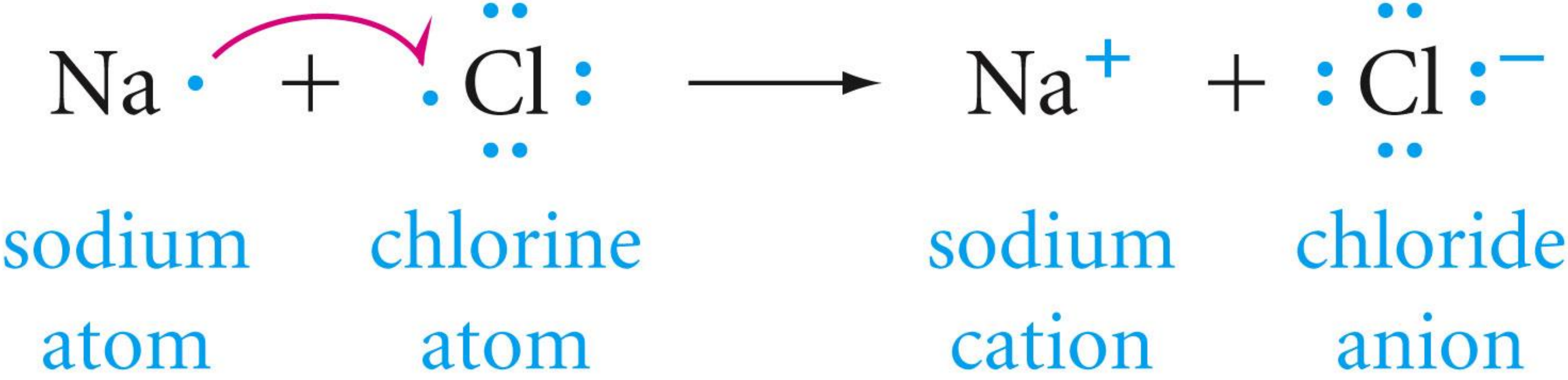
Group	I	II	III	IV	V	VI	VII	VIII
	H·							He:
	Li·	Ḃe·	·Ḃ·	·Ċ· (with one dot below)	·Ṅ: (with one dot below)	·Ö: (with one dot below)	:F̈: (with one dot below)	:N̈e: (with two dots below)
	Na·	Ṁg·	·Ȧl·	·Ṡi· (with one dot below)	·Ṗ: (with one dot below)	·S̈: (with one dot below)	:C̈l: (with one dot below)	:Är: (with two dots below)

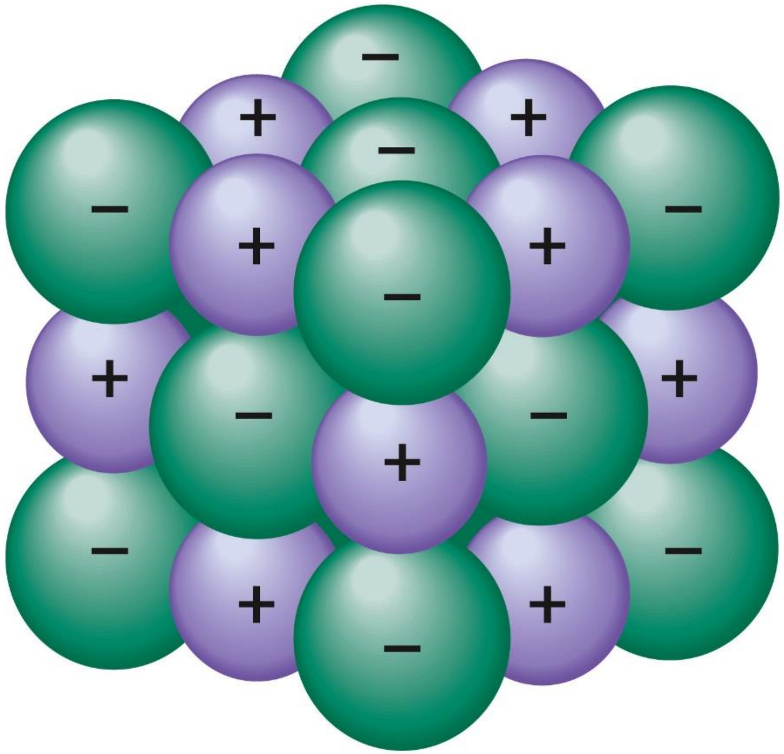
1.2 Ionic and Covalent bonding

Lewis's theory: an atom will give up, accept, or share electrons in order to achieve a filled outer shell or an outer shell that contains eight electrons

Ionic Compounds

are composed of positively charged cations and negatively charged anions





Sodium chloride, NaCl, is an ionic crystal. The purple spheres represent sodium ions, Na, and the green spheres are chloride ions, Cl_2.

Each ion is surrounded by six oppositely charged ions, except for those ions that are at the surface of the crystal.

The Covalent Bond

Covalent bonds are formed by sharing electrons

Bond energy (BE) is the energy necessary to break a mole of covalent bonds. The amount of energy depends on the type of bond broken.

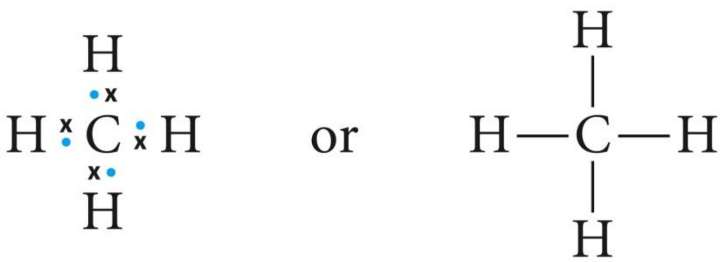
The bond length is the average distance between two covalently bonded atoms.

Problem 1.4

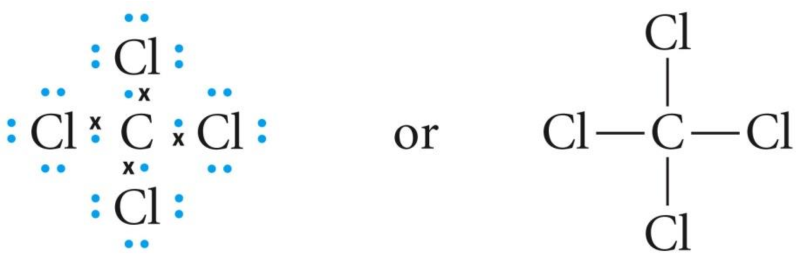
Write an equation for the formation of chlorine molecule

1.3 Carbon and the Covalent Bond

With four valence electrons, carbon usually forms covalent bonds with other atoms by sharing electrons.



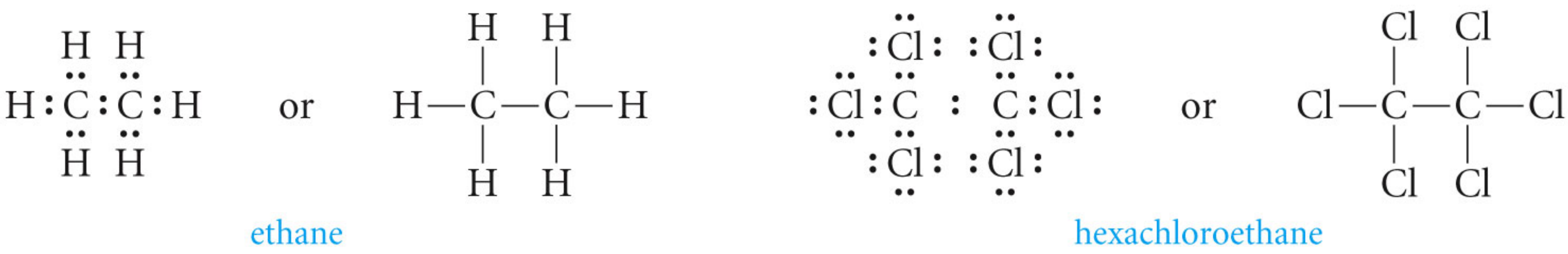
methane



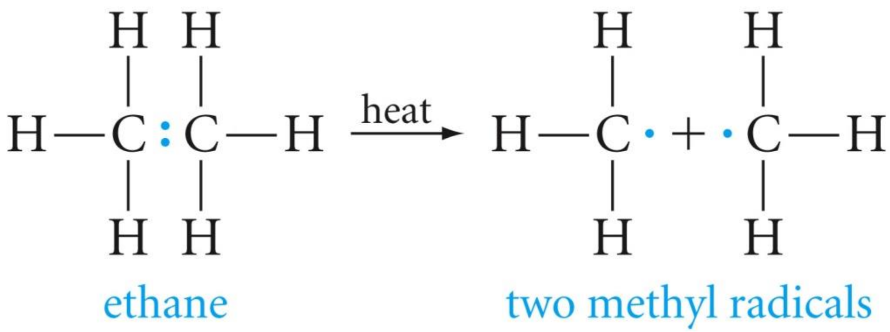
tetrachloromethane
(carbon tetrachloride)

1.4 Carbon-Carbon Single Bonds

Carbon could share electrons with not only different elements but also carbon.



Less heat is required to break the C-C bond in ethane than the H-H bond in a hydrogen molecule.The C-C-bond in ethane is 1.54 Å. The H-H bond in H2 molecule is 0.74 Å. The C-H is about 1.09 Å, close to the average of H-H bond and C-C bond.



A radical is a molecular fragment with an odd number of electrons

1.4 Polar Covalent Bonds

Is a covalent bond in which the electron are is not shared equally between the atoms

The bond polarization is indicated by an arrow whose head is negative and whose tail is marked with a plus sign. Alternatively, a partial charge, written as δ+ or δ -.

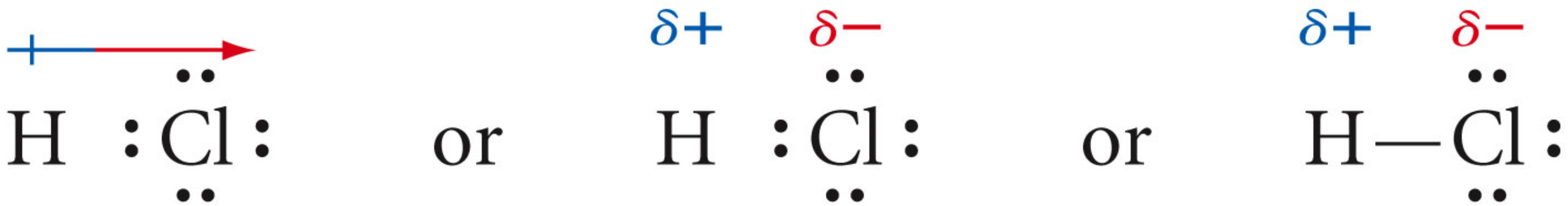


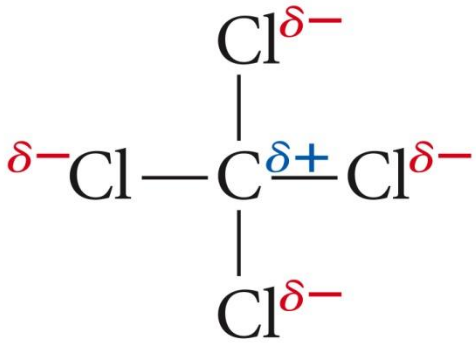
Table 1.4 Electronegativities of Some Common Elements

Group

I	II	III	IV	V	VI	VII
H 2.2						
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0					Br 3.0
						I 2.7

Pink	< 1.0
Orange	1.0–1.4
Yellow	1.5–1.9
Green	2.0–2.4
Light blue	2.5–2.9
Blue	3.0–3.4

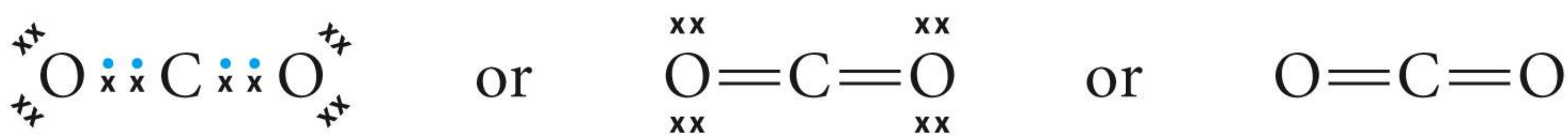
Bond polarization in tetrachloromethane



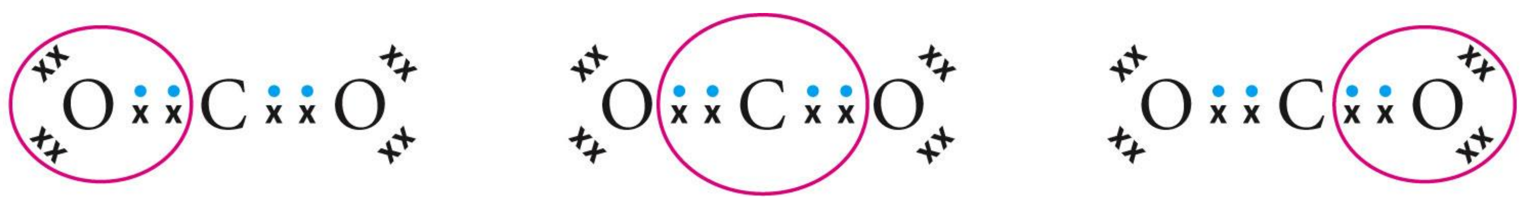
Problem 1.10

Predict the polarity of the P-Cl bond and the S-O bond

1.6 Multiple Covalent Bonds



A B C



hydrogen cyanide

1.7 Valance

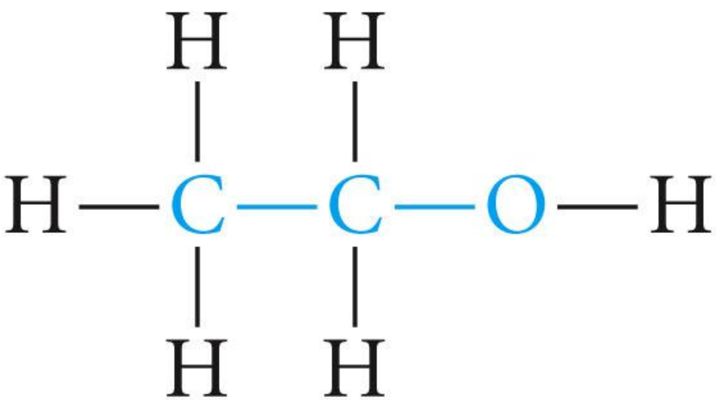
The valence of an element is simply the number of bonds that an atom of the element can form. The number is normally equal to the number of electron needed to fill the valence shell.

Table 1.5 Valences of Common Elements

Element	H·	·C· (4 dots)	·N: (5 dots)	·O: (6 dots)	:F: (7 dots)	:Cl: (7 dots)
Valence	1	4	3	2	1	1

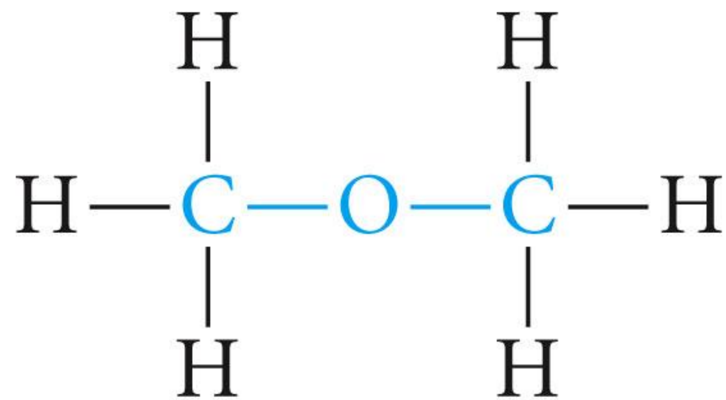
1.8 Isomerism

Isomers are molecules wit the same molecular formula
but different arrangement of atoms



ethanol
(ethyl alcohol)
bp 78.5°C

and

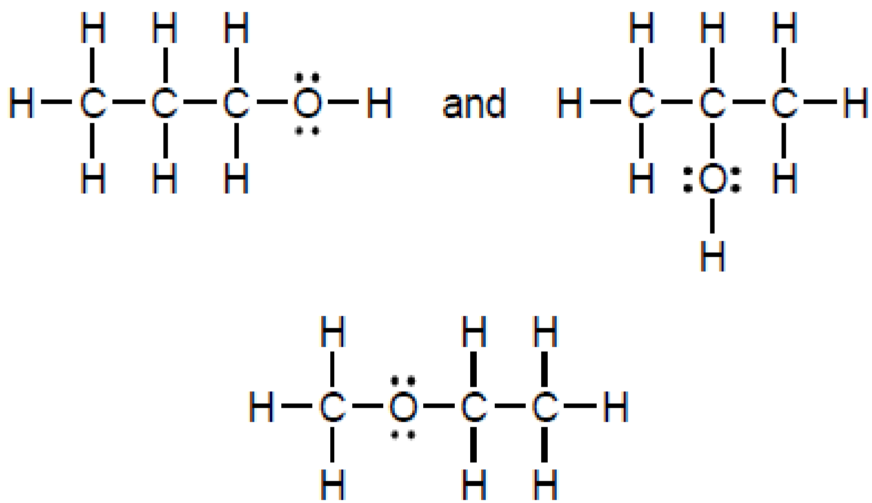


methoxymethane
(dimethyl ether)
bp −23.6°C

Structural (or constitutional) isomers are the compounds that have the same molecular formula but different structural formulas.

Problem 1.20

Draw structural formulas for the three possible isomers of C_3H_8O

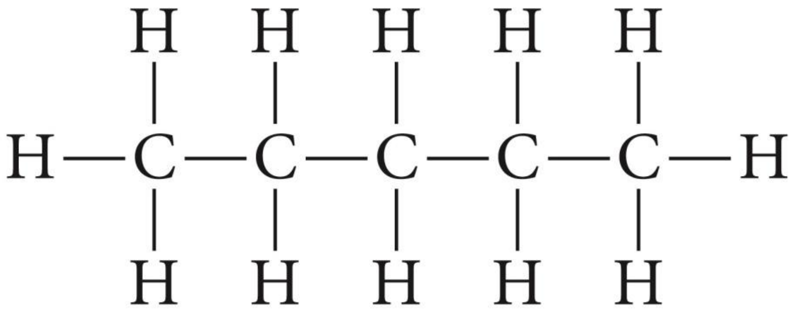


1.9 Writing Structural Formulas

Suppose we want to write out all possible structural formulas that correspond to the molecular formula C_5H_{12}.

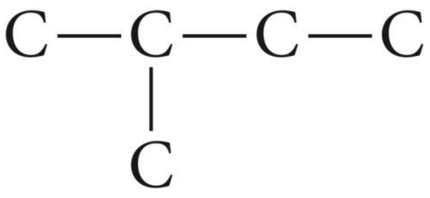
We begin by writing all five carbons in a continuous chain.

In a continuous chain, atoms are bonded one after another.

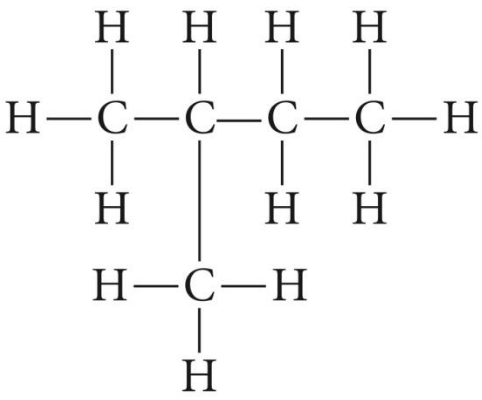


pentane, bp 36°C

In a branched chain, some atoms form branches from the longest continuous chain.

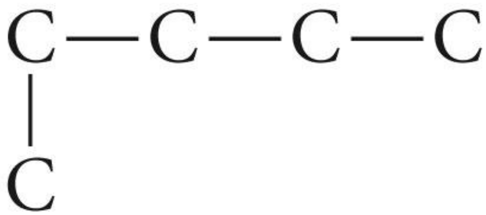


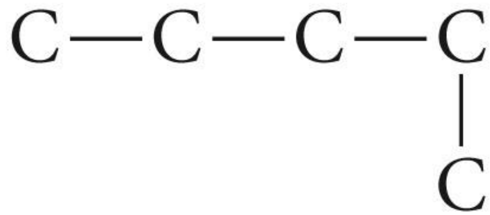
a branched chain

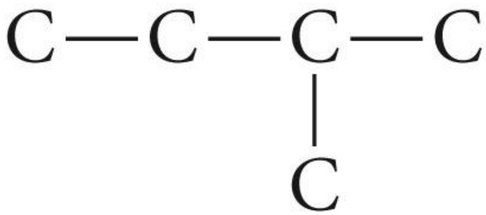


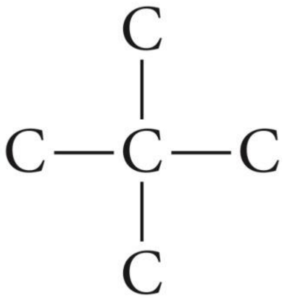
2-methylbutane, bp 28°C
(isopentane)

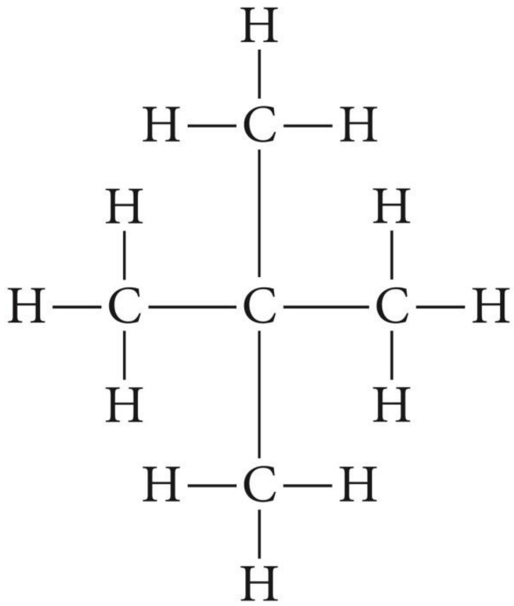
Suppose we keep the chain of four carbons and try to connect the fifth carbon somewhere else.







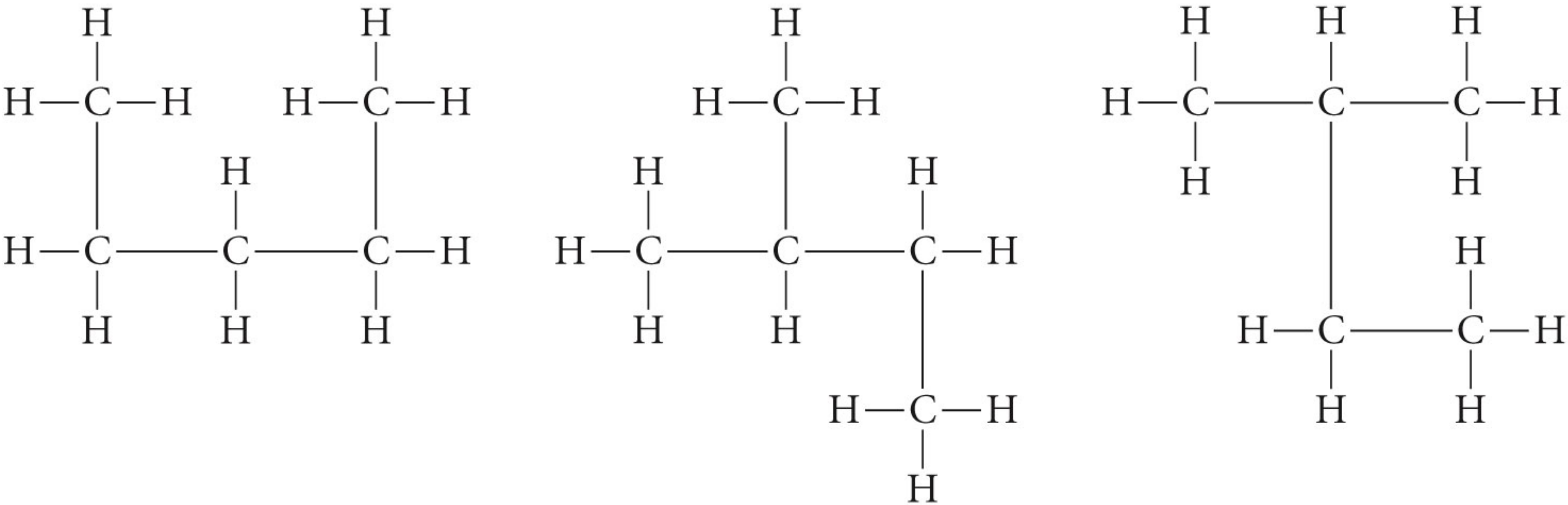




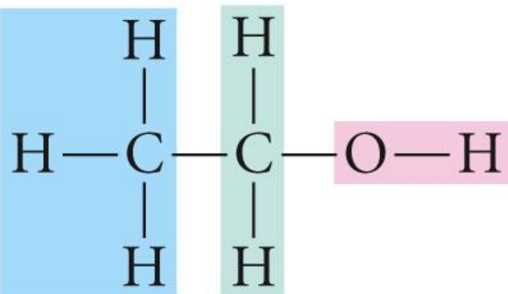
2,2-dimethylpropane, bp 10°C
(neopentane)

PROBLEM 1.21

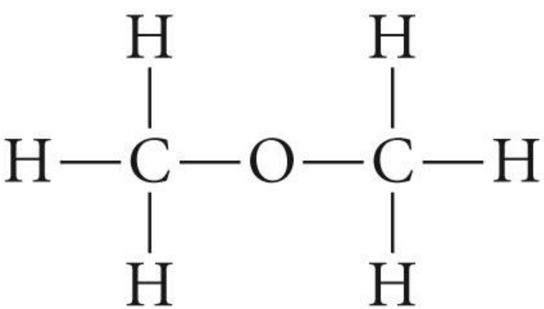
To which isomer of C_5H_{12} does each of the following structural formulas correspond?



1.10 Abbreviated Structural Formula



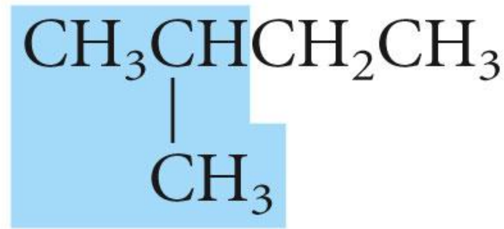
to $CH_3—CH_2—OH$ or CH_3CH_2OH



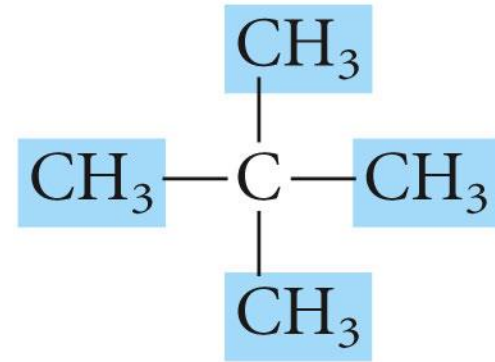
to $CH_3—O—CH_3$ or CH_3OCH_3

$CH_3CH_2CH_2CH_2CH_3$

n-pentane



isopentane



neopentane

$CH_3(CH_2)_3CH_3$

n-pentane

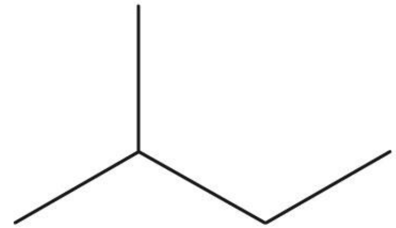
$(CH_3)_2CHCH_2CH_3$

isopentane

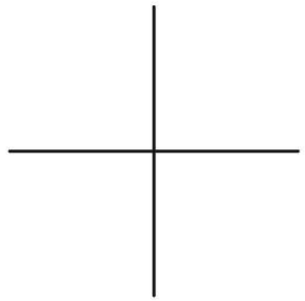
$(CH_3)_4C$

neopentane

n-pentane

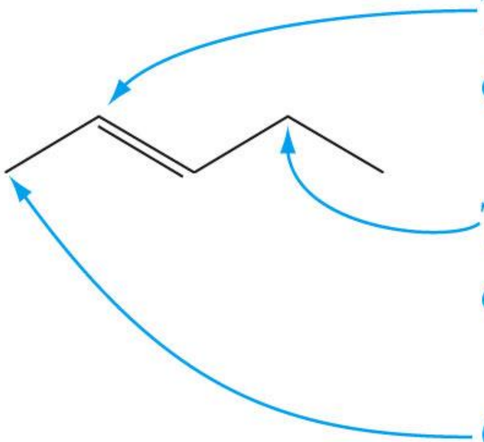


isopentane



neopentane

Each line segment have a carbon atom at each end



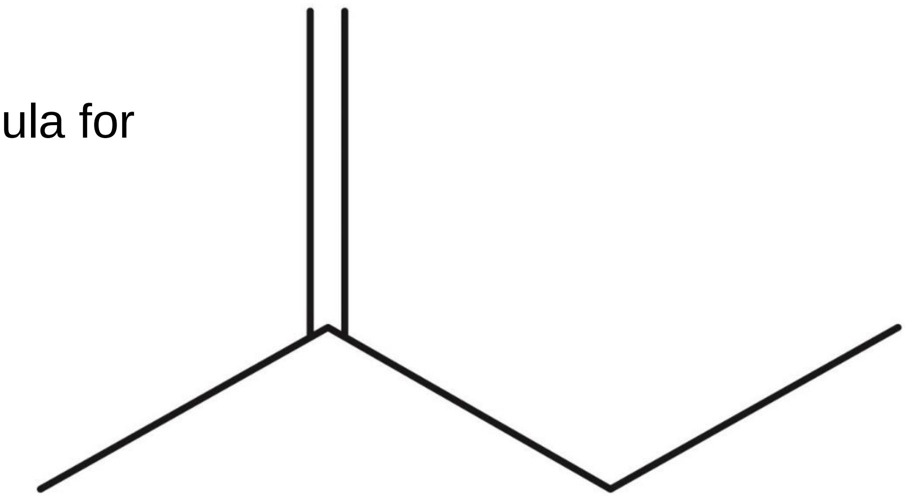
Three line segments emanate from this point; therefore, this carbon has one hydrogen $(4 - 3 = 1)$ attached to it.

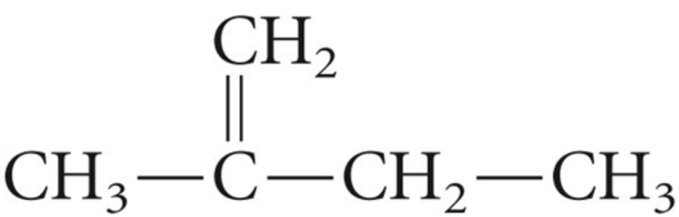
Two line segments emanate from this point; therefore, this carbon has two hydrogens $(4 - 2 = 2)$ attached to it.

One line segment emanates from this point; therefore, this carbon has three hydrogens $(4 - 1 = 3)$ attached to it.

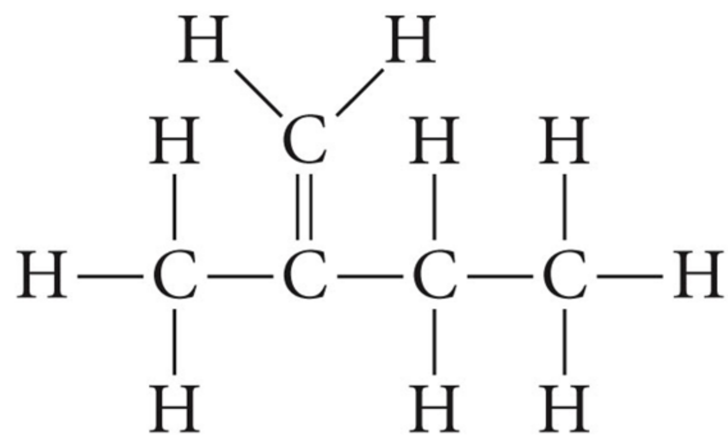
Example 1.12

Write a more detailed structural formula for





or



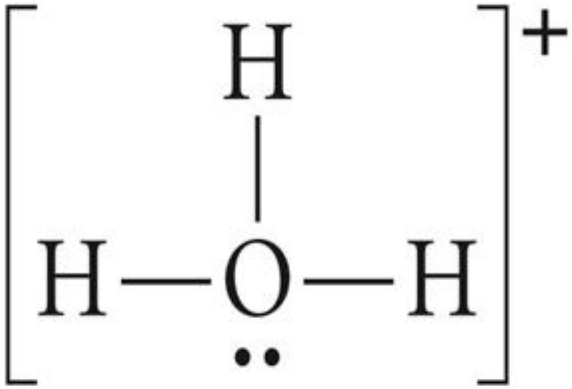
1.11 Formal Charge

The formal charge on an atom in a covalently bonded molecule or ion is the number of valence electrons in the neutral atom minus the number of covalent bonds to the atom and the number of unshared electrons on the atom.

$$\text{Formal charge} = \begin{matrix}\text{number of valence electrons}\\ \text{in the neutral atom}\end{matrix} - \left(\begin{matrix}\text{unshared}\\ \text{electrons}\end{matrix} + \begin{matrix}\text{half the shared}\\ \text{electrons}\end{matrix}\right)$$

or, in a simplified form,

$$\text{Formal charge} = \begin{matrix}\text{number of valence electrons}\\ \text{in the neutral atom}\end{matrix} - (\text{dots} + \text{bonds})$$



hydronium ion

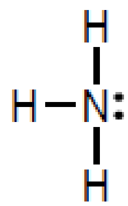
For H atom
Formal charge = 1 – (0 + 1) = 0

For O atom
Formal charge = 6 – (2 + 3) = 1 +1

Problem 1.25

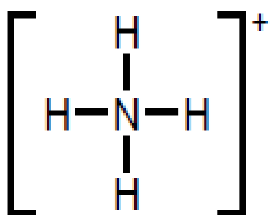
Calculate the formal charge on the nitrogen atom in ammonia, NH_3; in the ammonium ion, NH_4^+; and in the amide ion, NH_2^-

ammonia



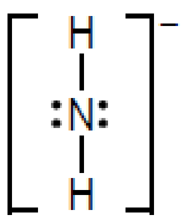
formal charge on nitrogen = 5 – (2 + 3) = 0

ammonium ion



formal charge on nitrogen = 5 – (0 + 4) = +1

amide ion

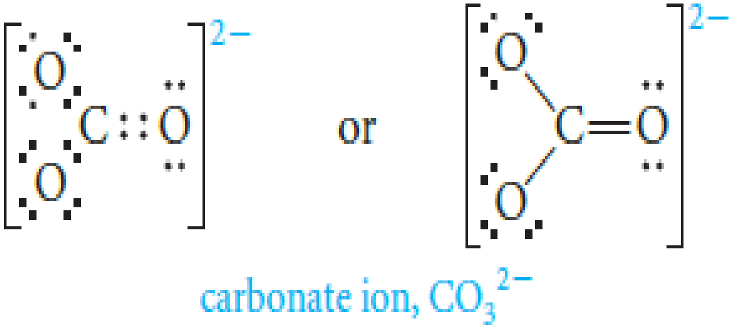


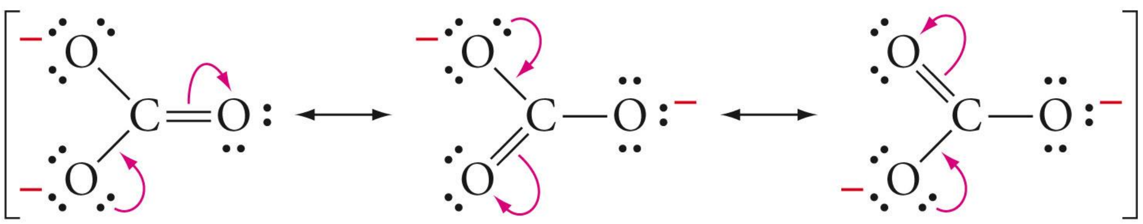
formal charge on nitrogen = 5 – (4 + 2) = –1

The formal charge on hydrogen in all three cases is zero [1 – (0 + 1) = 0].

1.12 Resonance

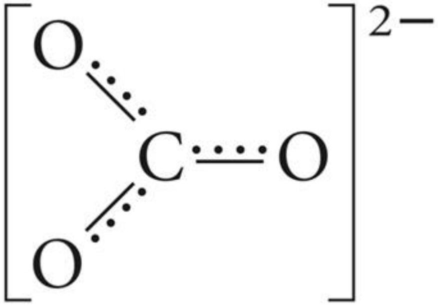
Sometimes, an electron pair is involved with more than two atoms. Molecules and ions in which this occurs can not be adequately represented by a single electron-dot structure. Please consider the structure of the carbonate ion, CO_3^{2-} .





- Only electrons can be moved (usually lone pairs or pi electrons).
- All the bond lengths are the same.
- The real structure is a resonance hybrid.

Physical measurement tell us that all three C-O bond length are identical: 1.31 Angstrom (Å).This distance is between the normal C=O (1.20 Å) and C-O (1.41 Å). We usually say the real carbonate ion has s structure that is resonance hydride of the three contributing resonance structures.



carbonate ion
resonance hybrid

1.13 Arrow Formalism

Arrow system is very important in Chemistry and has specific meaning.

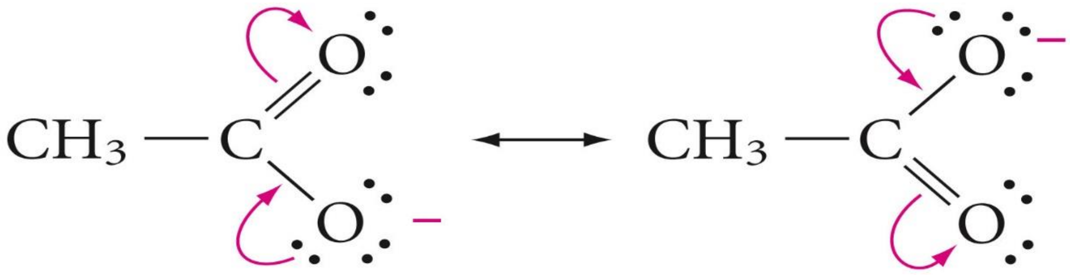
Curved arrows  a pair of electron moving

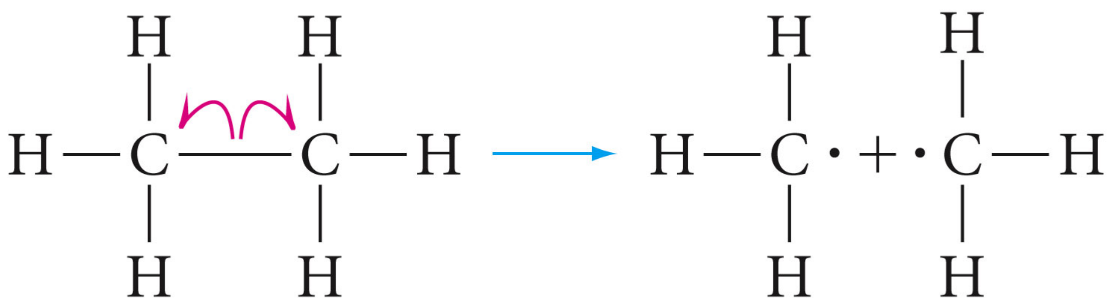
Fishhook arrows  single electron moving

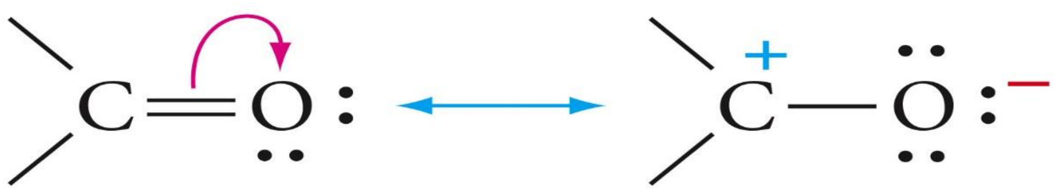
Straight arrows $\longrightarrow$ point from reactants to products in chemical reaction equactions

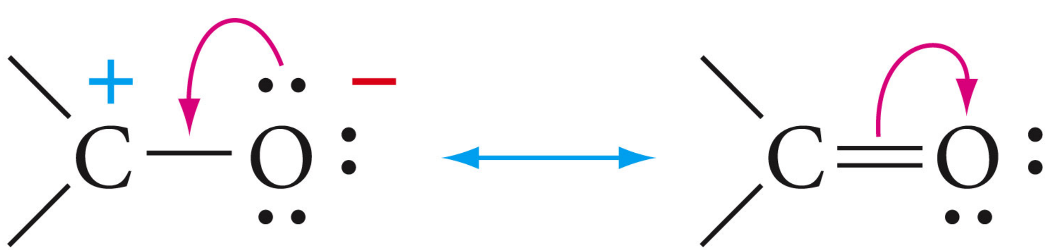
Straight arrow with half-heads $\rightleftharpoons$ used in pairs to indicate that the reaction is reversible.

double-headed straight arrow $\longleftrightarrow$ between two structures indicates that they are resonance structure









1.18 Classification According to Functional Group

Table 1.6 The Main Functional Groups

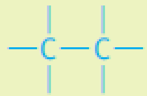
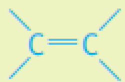
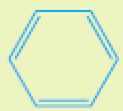
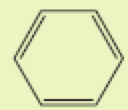
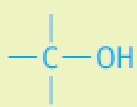
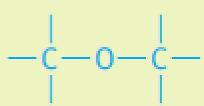
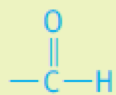
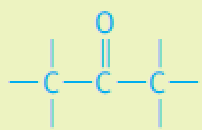
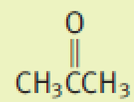
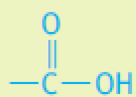
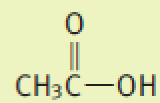
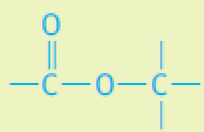
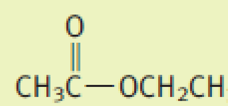
	Structure	Class of compound	Specific example	Common name of the specific example
A. Functional groups that are a part of the molecular framework		alkane	$CH_3—CH_3$	ethane, a component of natural gas
		alkene	$CH_2=CH_2$	ethylene, used to make polyethylene
	$—C \equiv C—$	alkyne	$HC \equiv CH$	acetylene, used in welding
		arene		benzene, raw material for polystyrene and phenol
B. Functional groups containing oxygen				
1. With carbon–oxygen single bonds		alcohol	CH_3CH_2OH	ethyl alcohol, found in beer, wines, and liquors
		ether	$CH_3CH_2OCH_2CH_3$	diethyl ether, once a common anesthetic

Table 1.6 ▬ continued

	Structure	Class of compound	Specific example	Common name of the specific example
*2. With carbon–oxygen double bonds**		aldehyde	$CH_2{=}O$	formaldehyde, used to preserve biological specimens
		ketone		acetone, a solvent for varnish and rubber cement
3. With single and double carbon–oxygen bonds		carboxylic acid		acetic acid, a component of vinegar
		ester		ethyl acetate, a solvent for nail polish and model airplane glue

*C. Functional groups containing nitrogen***	$-\overset{\vert}{\underset{\vert}{C}}-NH_2$	primary amine	$CH_3CH_2NH_2$	ethylamine, smells like ammonia
	$-C\equiv N$	nitrile	$CH_2{=}CH-C\equiv N$	acrylonitrile, raw material for making Orlon
D. Functional group with oxygen and nitrogen	$-\overset{O}{\overset{\Vert}{C}}-NH_2$	primary amide	$H-\overset{O}{\overset{\Vert}{C}}-NH_2$	formamide, a softener for paper
E. Functional group with halogen	$-X$	alkyl or aryl halide	CH_3Cl	methyl chloride, refrigerant and local anesthetic
F. Functional groups containing sulfur†	$-\overset{\vert}{\underset{\vert}{C}}-SH$	thiol (also called mercaptan)	CH_3SH	methanethiol, has the odor of rotten cabbage
	$-\overset{\vert}{\underset{\vert}{C}}-S-\overset{\vert}{\underset{\vert}{C}}-$	thioether (also called sulfide)	$(CH_2{=}CHCH_2)_2S$	diallyl sulfide, has the odor of garlic