



Organic Chemistry

Chemical Bonding and Structure

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Chemical Bonding and Structure By Seema Zareen <u>http://ocw.ump.edu.my/course/view.php?id=152</u>

Expected Outcomes

In the end of this chapter, student will have the ability to:

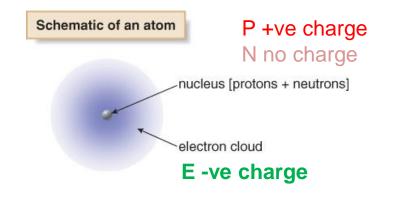
- Draw Lewis structure
- Identify ionic and covalent bond in a compounds
- Differentiate isomers and resonance Lewis drawing
- Explain characteristic and properties of constitutional isomers, enantiomers, diastereoisomers, and racemic mixture
- Predict the shape of molecules
- Draw condensed structures and skeletal structure

Contents

- Bonding
- Lewis Structure
- Resonance
- Stereochemistry
- Molecular shapes
- Drawing organic structure

Organic Chemistry

- The branch of Science in which we study of the carbon containing compounds is called Organic Chemistry.
 OR
- The study of hydrocarbons and their derivatives known as Organic Chemistry.
- Over 10 million structures have been identified
 - about 1000 new ones are identified each day! (Scifinder website)
- C is a small atom
 - it forms single, double, and triple bonds
 - it is intermediate in electronegativity (2.5)
 - it forms strong bonds with C, H, O, N, and some metals



- The nucleus contains positively charged protons and uncharged neutrons.
- The electron cloud is composed of negatively charged electrons.

$$N = A - Z$$

- \therefore N = No. of proton
 - A = Atomic number = No. of proton = No. of electron
 - Z = Mass Number or Atomic Mass = No. of proton + No. of neutron

Periodic Table of Elements



	1	2	3	4		5	6	7	8		9	10)	11	12	2	13	14		15	16	17	18	
1	1 ¹ H Hydrogen 1.00794	Atomic # Symbol	C	Solid	I				Meta	Is				Nonme									2 He Helum 4.002002	2 К
2	3	4 3 Be Deyllum 9.012102	=	g Liqui Gas	d		Alkali metals	Alkaline earth me	Lantha	noid	metals	Poor metals Transition		Other nonmetals	Noble ga		5 3 B B 10.011	6 C Carbon 12.0107		7 8 N Vitrogen 14.0067	8 O Crypen 15.9994	8 F Pluotre 15.9904032	10 Ne Nacn 20.1797	a K
3	11 Na ^{Sodium} 22.96976928	12 Mg Magnatum 24.300	R	f Unkr	nown		tals	ne metals	Actino	ids		n tals		<u>ज</u>	gases		13 3 Al Aluminium 26.9015366	14 Si 58con 20.085		15 P hosphorus xx,973762	16 S Sutur 32.005	2 17 CI CNotte 35.453	18 Ar Argon 39.940	R 13
4	19 K Potassium 39.0903	20 Ca Calclum 40.070	21 Sc Scandum 44.900912	22 Ti Tianium 47.007	23 22 Vana 5094		24 Cr ^{Chromlum} 51.9901	25 Mn Marganese St. 830045	26 Fe	unter 10	27 Co '	28 Ni Nickel 50.0934	2802	29 Cu Copper 60.546	30 Zn 2m	2000.2	31 Galum Galum	32 Ge Germanium 72.63	A Tax	33 As Intenic Na2160	34 See Selenium 75.90	35 Br Bromine 73.804	36 Kr Krypton 63.796	N BB R
5	37 Rb Ruteklum 65.4670	38 Sr 5tontum 67.62	39 Y	40 Zr 21100nium 91.224	2 10 2 Nobi \$2.90	an '	42 Mo Molybdenum 85.90	43 Tc Technetum (97,9072)	44 Ruteriur 101.07	ų,	15 Rh	46 Pd Paladum 106.42	28880	47 Ag	48 Cd Cadmium 112.411	o li lino	49 2 In 19 Indian 19	50 Sn Th 118.710	1	51 5 Sb 5 kritmony 121.760	52 Te Telutum 127.00	53 lotine 125,90447	54 Xe Xaron 131,280	200 MLMNO
6	55 Cs Creature 132,9054519	56 Ba 1 Datum 137.327	57–71	72 Hf Hattlum 178.49	73 100 100 100 100 100 100 100 100	lum 2	74 W Tungeten 103.04	75 Re Rhenlum	76 05 005 000 000 000 000 000 000 000 000	1	77 IF 1 Mum 82.217	78 Pt Pathum 195.004	10000000	79 Au	80 Hg Mercury 200.59	10 BB 0 mo	81 1 Ti 1 Thailum 3	82 Pb 1072	8	B3 Bi Ilemuth	84 Po Polenium (200.9624)	85 At Astatine (209.9071)	86 Rn Radon (222.0176)	* OCENY
7	87 Fr Pandum	88 1 Ra 1 Radum	89–103	104 Rf Retwitedur (201)) 11 11 11	106 Sg Seeborgium (200)	107 Bh Bohrum (254)	108 Hs 1987 1987 1987 1987 1987 1987 1987 1987	1232		110 Ds	1.2188 B mo	111 Rg	112 Cn Coperation	10 10 10 10 10 10 10 10 10 10 10 10 10 1	113 Uut 1 (24)	114 Fl Flerovtum (209)	121	115 Uup 2007		117 Uus ^{Uhanesptam}	118 Uuo Unurodium (294)	C + OK R T X
For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.																								
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	58 Ce ¹ Sentum 140.116	59 Pr Prawoo	2 31 5ymtum 2 705	60 Nd Neodymian 144.242	2010202	61 Pm Promethium (145)	28828282	62 Sm 5amartum 150.36	2003022	63 Eu 51.904	2000002	64 Gd Gadolinium 157.25		65 Tb ³ Terblum 150.92535	200702	66 Dy Dysproslum 162:500		67 Ho Holmium 164.93022	2 8 18 2 8 2	68 Er :	2899282	69 Tm ³ Thulum 160,93421	10010101	70 Yb Yttertslum 173.054	288282	71 Lutetum 174.9000
89 Ac	90 Th	91 Pa	5 this = 5	92 U	2 8 1931	93 Np	28 1822	94 Pu	2000	95 Am	20000	96 Cm		97 Bk	28827	98 Cf		99 Es	2 8 8 2 9	100 Fm	28920	101 Md	28831	102 No	28800	103 i Lr i

Californium

Einsteinium

Femium

Michael Dayah

For a fully interactive experience, visit www.ptable.com.

Actinium

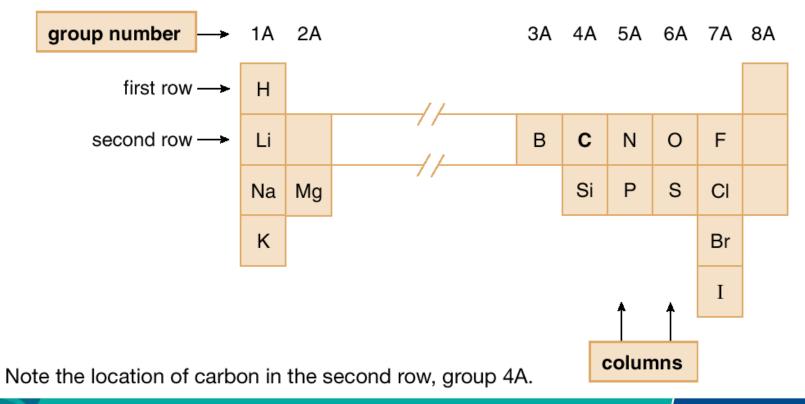
michael@dayah.com

Lawrencium

The Periodic Table

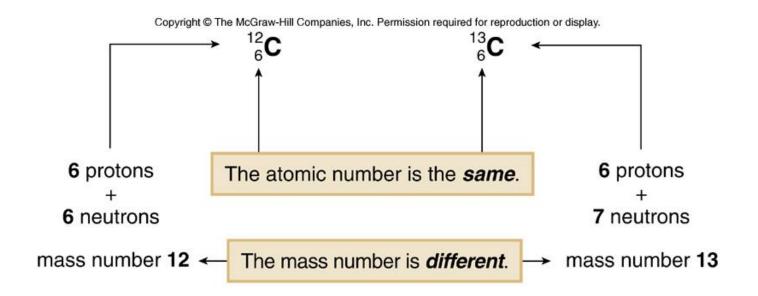
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A periodic table of the common elements seen in organic chemistry



The Periodic Table

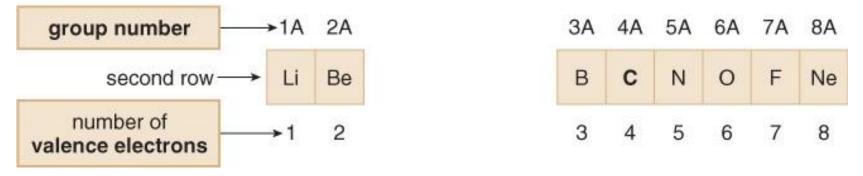
A comparison of two isotopes of the element carbon



- Elements in the same row are similar in size.
- Elements in the same column have similar electronic and chemical properties.

Second Row Elements

- Since each of the four orbitals available in the second shell can hold two electrons, there is a maximum capacity of eight electrons for elements in the second row.
- The second row of the periodic chart consists of eight elements, obtained by adding electrons to the 2s and three 2p orbitals.



• Chemical bond: attractive force holding two or more atoms together.

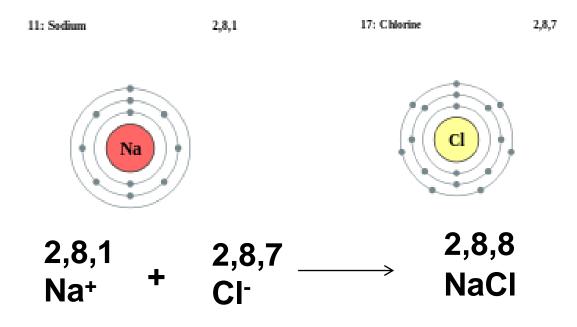
There are 2 extreme forms of connecting or bonding atoms:

- Ionic Bond—complete transfer of electrons from one atom to another
- Covalent Bond—electrons shared between atoms

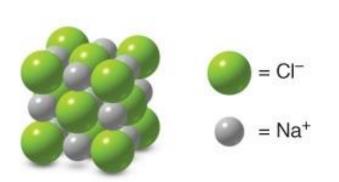
Most bonds are somewhere in between.

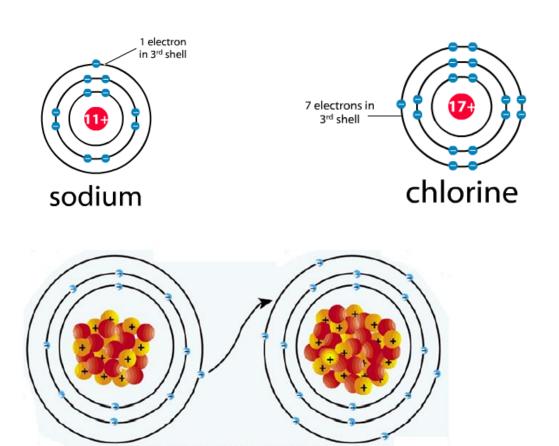
IONIC BOND FORMATION

Sodium loss one electron get positive charge and Chlorine get electron be come negative charge, both ions form ionic bond through electrostatic force of attraction



- An ionic bond generally occurs when elements on the far left side of the periodic table combine with elements on the far right side, ignoring noble gases.
- A positively charged cation formed from the element on the left side attracts a negatively charged anion formed from the element on the right side. An example is sodium chloride, NaCl. NaCl—An ionic crystalline lattice





Ionic Bond – Sodium Takes an Electron From Chlorine to Make a Salt Molecule

Covalent Bonding

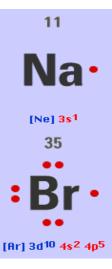
Covalent bond is the <u>sharing</u> of the VALENCE ELECTRONS of each atom in a bond

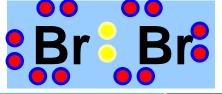
Recall: Electrons are divided between **COre**

and valence electrons.

	ATOM	core	valence				
Na	$1s^2 2s^2 2p^6 3s^2$	¹ [Ne]	$3s^1$				

Br [Ar] $3d^{10} 4s^2 4p^5$ [Ar] $3d^{10} 4s^2 4p^5$

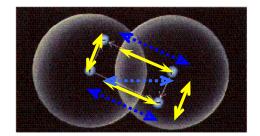




Covalent Bonding

The bond arises from the mutual attraction of 2 nuclei for the same electrons.

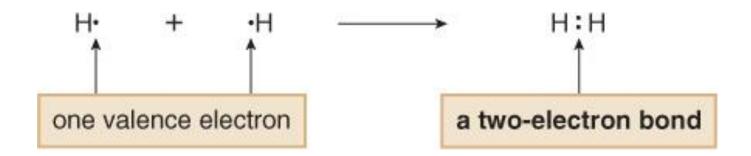
 $H_A^{\bullet} + H_B^{\bullet} \longrightarrow H$ A covalent bond is a balance of attractive and repulsive forces.



Covalent Bond

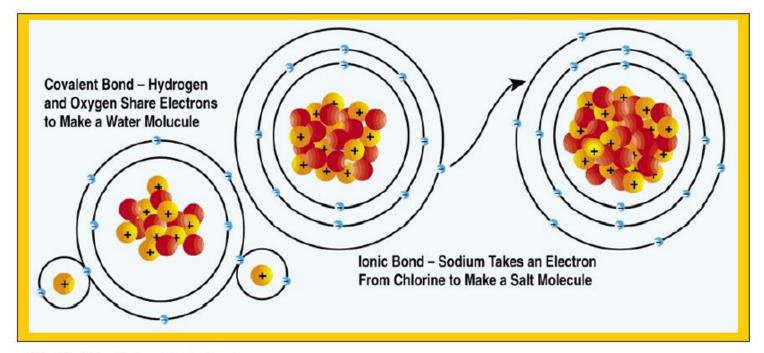
COVALENT BOND in Hydrogen (H₂)

- Hydrogen forms one covalent bond.
- When two hydrogen atoms are joined in a bond, each has a filled valence shell of two electrons.



Ionic and Covalent Bonds

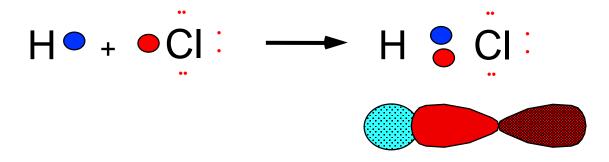
Ionic and Covalent Bonds:



Model of Covalent and Ionic Bonds

Bond Formation

A bond can result from a "head-to-head" overlap of atomic orbitals on neighboring atoms.

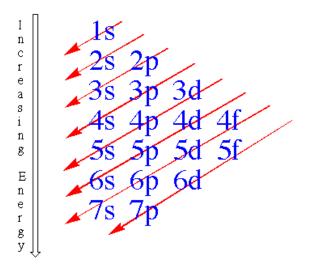


Overlap of H (1s) and Cl (2p)

This type of overlap places bonding electrons in a $MOLECULAR \ ORBITAL$ along the line between the two atoms and forms a $SIGMA \ BOND(\sigma)$.

Electronic Configuration

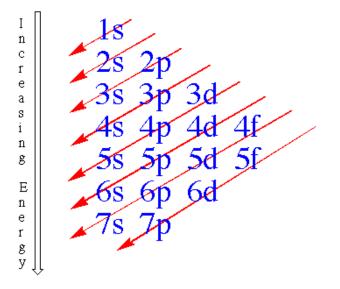
What is Electronic Configuration of Na (11), Mg (12) and Cl (17) atoms



1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s

 $\mathbf{CI}_{(17)} = 1s^{2}2s^{2}2p^{6}3s^{2}3p^{5} \qquad 2+2+6+2+5 = 17 \text{ e}$

Electronic Configuration



Mg =Is², 2s², 2p⁶, 3s²
$$2 + 2 + 6 + 2 = 12$$
 electronsNa =Is², 2s², 2p⁶, 3s¹ $2 + 2 + 6 + 1 = 11$ electrons

- Second row elements can have no more than eight electrons around them. For neutral molecules, this has two consequences:
 - Atoms with one, two, or three valence electrons form one, two, or three bonds, respectively, in neutral molecules.
 - Atoms with four or more valence electrons form enough bonds to give an octet. This results in the following equation:

predicted number of bonds

= 8 - number of valence electrons

When second-row elements form fewer than four bonds their octets consist of both bonding (shared) and nonbonding (unshared) electrons. Unshared electrons are also called *lone pairs*.

Electronic Contribution in Molecule

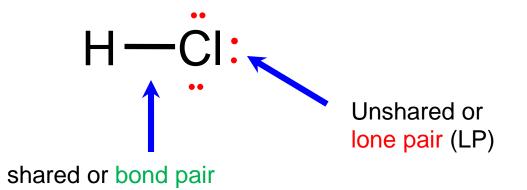
Electron distribution is depicted with Lewis electron dot structures

Electrons are distributed as:

- shared or BOND PAIRS and
- unshared or LONE PAIRS.

Bond and Lone Pairs

 Electrons are distributed as shared or BOND PAIRS and unshared or LONE PAIRS.



This is a LEWIS ELECTRON DOT structure.

Rule for Lewis Dot Structure:

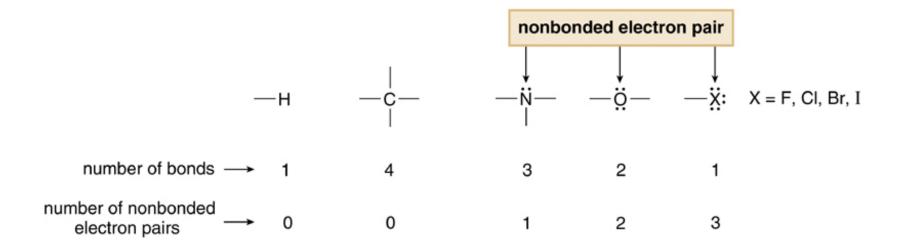


- 1. Identify the **central atom** (less electronegative atom) of molecule.
 - Connect the central atom with other atoms with single bonds.
- 2. Calculate the number of the **electron in pi-bonds** (multiple bonds) using formula **1** as given below:

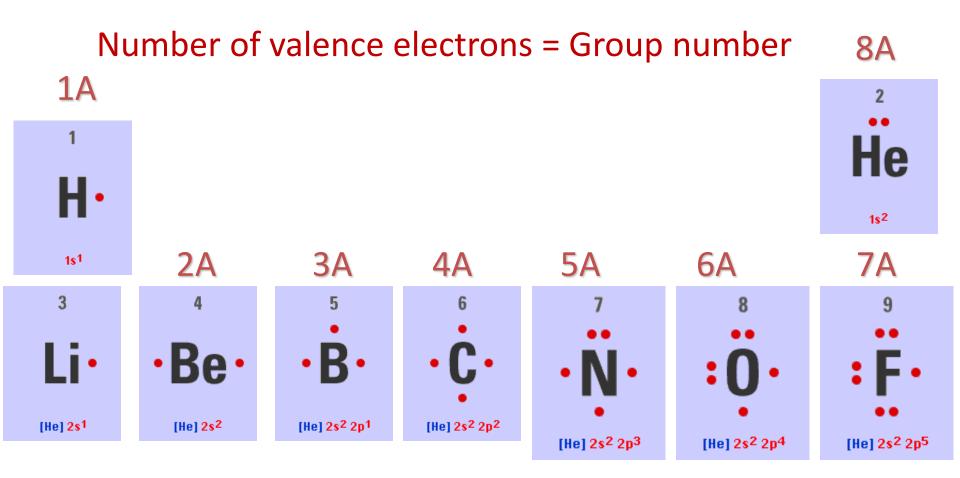
P = 6n + 2 - V ----- (1)
where as P is the number of electrons in pi-bond
n is the number of atom in the molecule

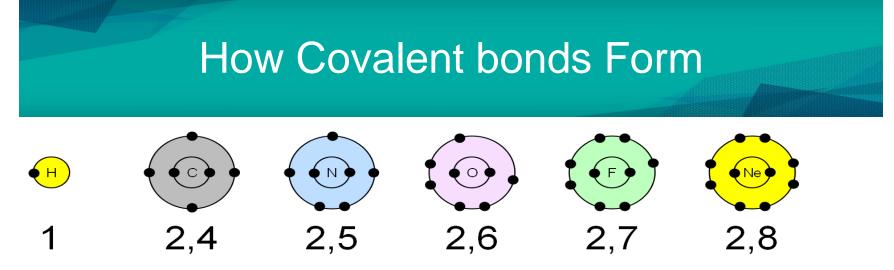
- & V is the valence electrons in the molecule = (Sum of atom group numbers) Charge
- 3. Add **double or triple bonds** to the structure in Step 1 according to the results obtained in Step 2.
 - Add unshared pairs of electrons around each atom so that all of them have octets around them (except for the H atom)
- 4. Calculate the Formal Charge of the atoms in the molecule as follows:
 Formal Charge of Element =
 Group Number Total number of electrons "owned" by the atom concerned

Summary: The usual number of bonds of common neutral atoms



Valence Electrons



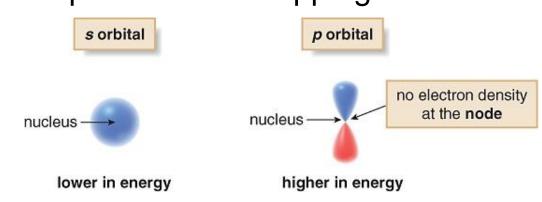


The process of sharing electrons is known as covalent bonding. In order to achieve a full outer shell...

Hydrogen atoms each need one electron; Carbon atoms each need four electrons; Nitrogen atoms each need three electrons; Oxygen atoms each need two electrons; Fluorine atoms each need one electron; Neon atoms already have a full outer electron shell.

TYPES OF COVALENT BOND or Molecular Orbitals

- An sigma orbital has a sphere of electron density and is lower in energy than the other orbitals of the same shell.
- A *p* orbital has a dumb bell shape and contains a node of electron density at the nucleus. It is higher in energy than an *s* orbital.

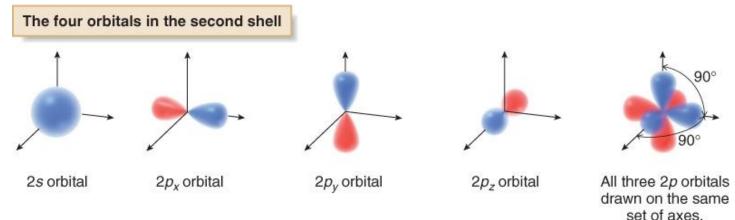


Sigma & pi-bond: *overlapping of orbitals.

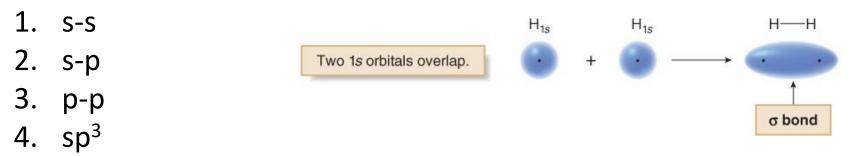
Since there is only one orbital in the first shell, and each shell can hold a maximum of two electrons, there are two elements in the first row, H and He.

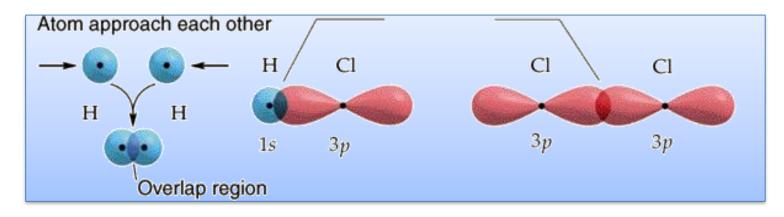


Each element in the second row of the periodic table has four orbitals available to accept additional electrons: one 2s orbital, and three 2p orbitals.



Types of sigma bonds:

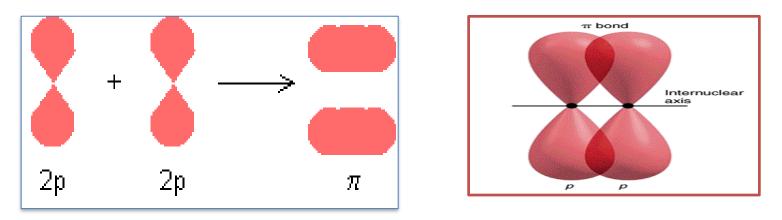




*All single bond is sigma bond.

Pi- bond:

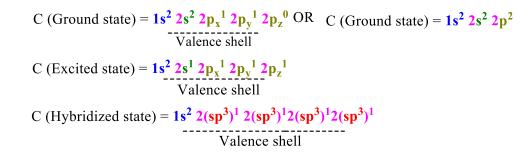
• The second kind of bonding is Pi(T) bonding. It occurs when p orbitals overlap side by side or parallel to each other.

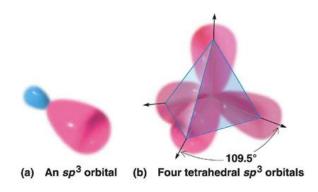


The increased electron density is concentrated above and below the nuclear axis.

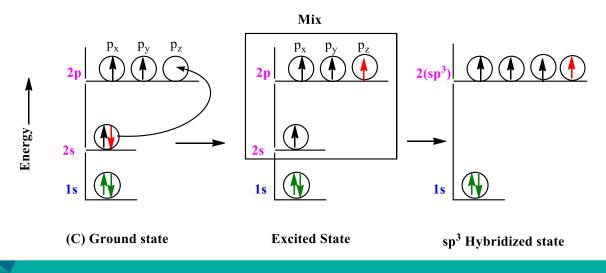
bonding occurs in molecules with multiple bonds.

Electronic Configration of carbon in its ground or atomic state

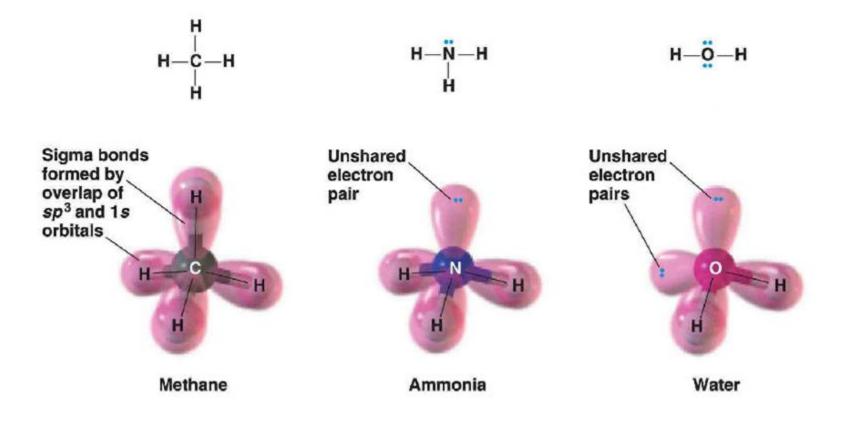




Energy-level diagram



orbital overlap pictures of methane, ammonia, and water

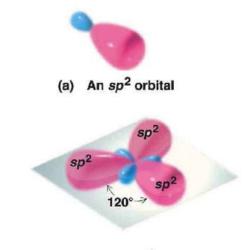


Electronic Configration of carbon in its ground or atomic state

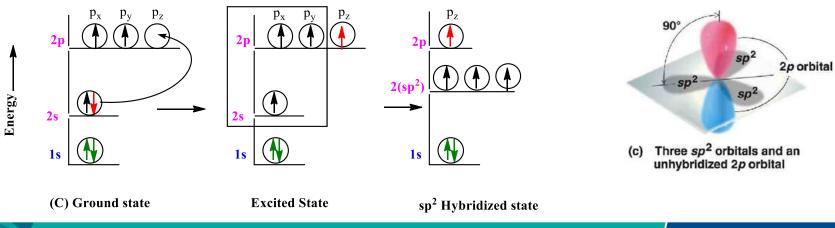
Energy-level diagram

C (Ground state) =
$$1s^2 2s^2 2p_x^{-1} 2p_y^{-1} 2p_z^{-0}$$
 OR C (Ground state) = $1s^2 2s^2 2p^2$
Valence shell
C (Excited state) = $1s^2 2s^1 2p_x^{-1} 2p_y^{-1} 2p_z^{-1}$
Valence shell
C (Hybridized state) = $1s^2 2(sp^2)^{-1} 2(sp^2)^{-1} 2(sp^2)^{-1} 2p_z^{-1}$
Valence shell

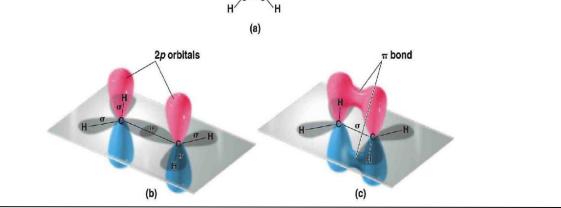
Mix



(b) Three sp² orbitals



Bonding in Ethylene

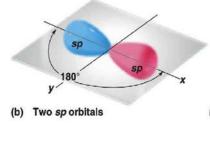


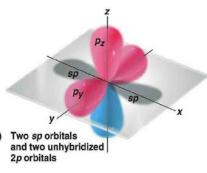
Electronic Configration of carbon in its ground or atomic state

C (Ground state) =
$$1s^2 2s^2 2p_x^{-1} 2p_y^{-1} 2p_z^{-0}$$
 OR C (Ground state) = $1s^2 2s^2 2p^2$
Valence shell
C (Excited state) = $1s^2 2s^1 2p_x^{-1} 2p_y^{-1} 2p_z^{-1}$
Valence shell
C (Hybridized state) = $1s^2 2(sp)^{-1} 2(sp)^{-1} 2p_y^{-1} 2p_z^{-1}$
Valence shell

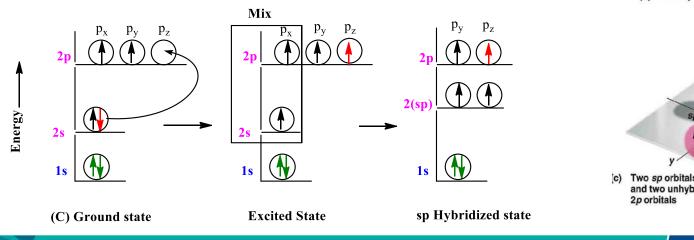




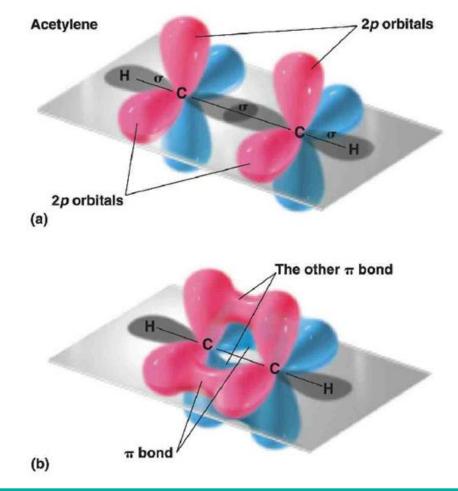




Energy-level diagram formate



Bonding in Acetylene



σ-bond Single bond = σ bond Double bond = σ + π π -bond (weaker) Triple bond = σ + 2 π

e.g.

Resonances

Resonances: occurs whenever a molecule can be represented by two or more structures differing only in the arrangement of electrons, without shifting any atoms. It only involves the delocalization of electrons.

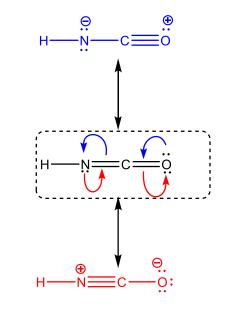
When one or more valid Lewis dot diagram can be drawn. e.g. HNCO and SO₃

no change in

- 1. net # of e
- 2. net charge
- 3. sigma bond (connectivity)

Resonance contribution

- 1. closed shells
- 2. minimize Formal charge
- 3. If F.C. is present then
 - (-) with electronegative atoms
 - (+) w/o electronegative atoms



- A compound with delocalized e⁻ is said to have *resonance*
 - resonance contributor
 - resonance structure
 - contributing resonance structure

- Benzene
 - contributing resonance structures





resonance contributor

resonance contributor



resonance hybrid



Drawing resonance hybrids

- Only e⁻ move (not atoms)
- Only π and non-bonding e⁻ move
- Total # e⁻ stays same (as does unpaired e⁻)

e⁻ can be moved only by...

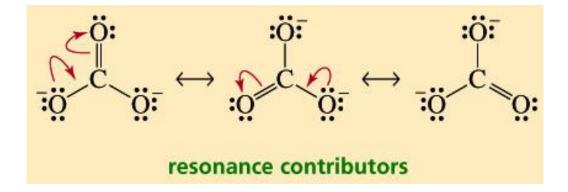
πe^{-} move toward + or toward π bond

$$CH_{3}CH \stackrel{+}{=} CH \stackrel{+}{-} CHCH_{3} \longleftrightarrow CH_{3} \stackrel{+}{CH} - CH \stackrel{+}{=} CHCH_{3}$$
resonance contributors
$$CH_{3}^{\delta +} \stackrel{\delta +}{-} CH \stackrel{\delta +}{=} CHCH_{3}$$
resonance hybrid

Communitising Technology

e⁻ can be moved only by...

Nonbonding pair e⁻ toward a π bond



e⁻ can be moved only by...

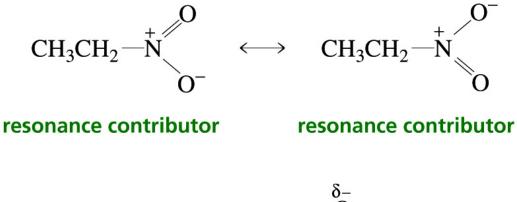
Nonbonding single e^{-} toward a π bond

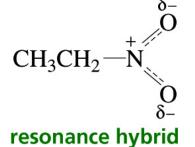
$$CH_3 - CH = CH \stackrel{\frown}{\longrightarrow} CH_2 \longleftrightarrow CH_3 - \dot{C}H - CH = CH_2$$

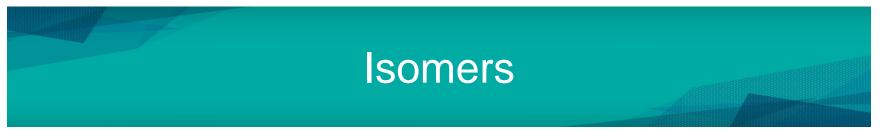
resonance contributors



• Drawing resonance hybrids of nitro ethane



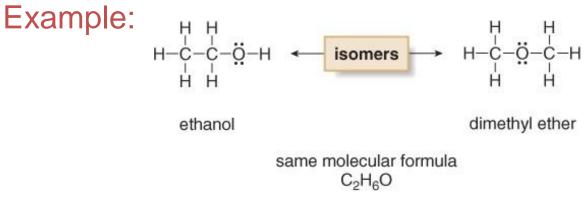




Isomers

Isomers have same molecular formula but different molecular structure called isomer.

In drawing a Lewis structure for a molecule with several atoms, sometimes more than one arrangement of atoms is possible for a given molecular formula.



Both are valid Lewis structures and both molecules exist. These two compounds are called isomers.

Ethanol and dimethyl ether are constitutional isomers.

Isomers

Examples of isomers:

 $CH_2 = CH - CH_2 - CH_3$

I-butene

 C_4H_8

CH₃-CH₂-CH₂-OH

1-Propanol C_3H_8O

CH₃-CH=CH-CH₃

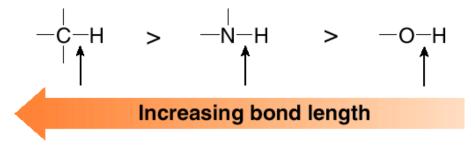
2-butene C₄H₈

> CH₃-CH-CH₃ OH **2-Propanol** C_3H_8O

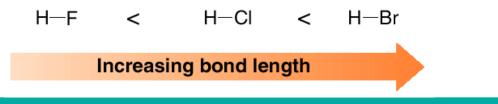
Determining Molecular Shape

Two variables define a molecule's structure: bond length and bond angle.

• Bond length *decreases* across a row of the periodic table as the size of the atom *decreases*.



• Bond length *increases* down a column of the periodic table as the size of an atom *increases*.



Average Bond Lengths						
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)	
н-н	0.74	H-F	0.92	C-F	1.33	
С-Н	1.09	H-CI	1.27	C-CI	1.77	
N-H	1.01	H-Br	1.41	C-Br	1.94	
0-н	0.96	H-I	1.61	C-I	2.13	

Determining Molecular Shape—Bond Angle

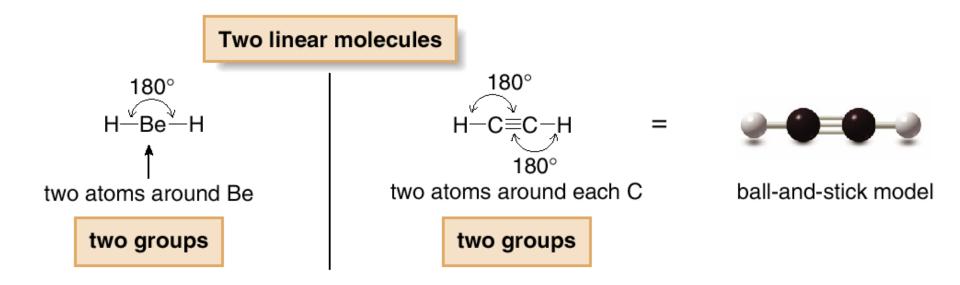
Bond angle determines the shape around any atom bonded to two other atoms.

• The number of groups surrounding a particular atom determines its geometry. <u>A group is either an atom or a lone pair of electrons.</u>

Number of groups	Geometry	Bond angle	
• two groups	linear	180°	
 three groups 	trigonal planar	120°	
 four groups 	tetrahedral	109.5°	

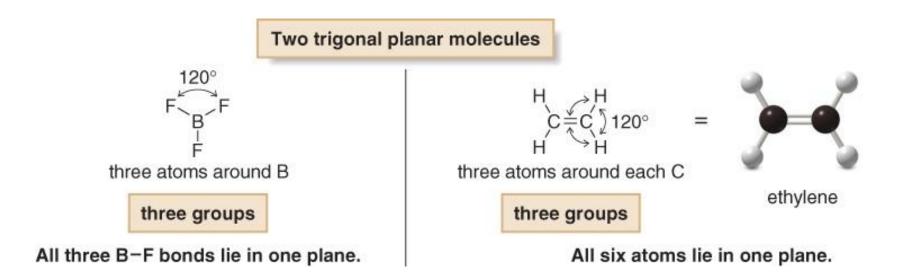
Determining Molecular Shape—Bond Angle

Two groups around an atom—



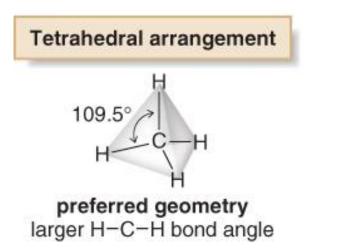
Determining Molecular Shape—Bond Angle

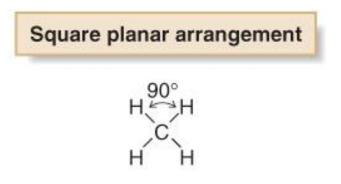
Three groups around an atom—



Determining Molecular Shape

Four groups around an atom—

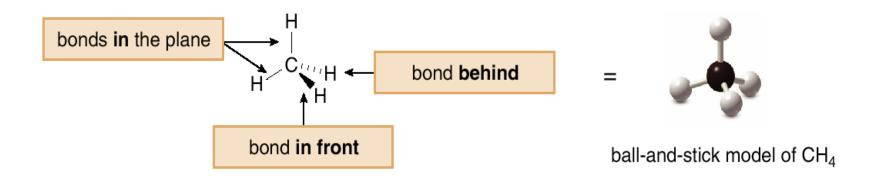




This geometry does not occur.

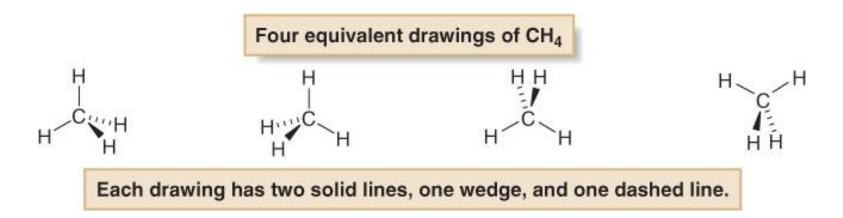
Drawing Three Dimensional Structures

- A solid line is used for a bond in the plane.
- A wedge is used for a bond in front of the plane.
- A dashed line is used for a bond behind the plane.



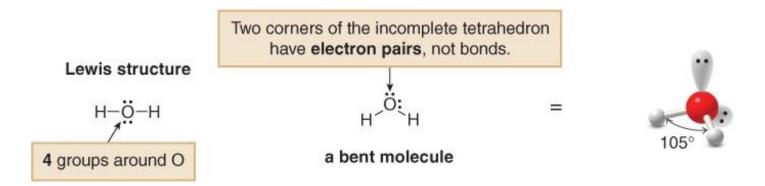
Drawing Three Dimensional Structures

The molecule can be turned in many different ways, generating many equivalent representations. All of the following are acceptable drawings for CH_4 .



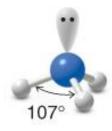
A Nonbonded Pair of Electrons is Counted as a "Group"

In water (H₂O), two of the four groups attached to the central O atom are lone pairs. The two H atoms and two lone pairs around O point to the corners of a tetrahedron. The H-O-H bond angle of 105° is close to the theoretical tetrahedral bond angle of 109.5°. Water has a bent shape, because the two groups around oxygen are lone pairs of electrons.





Methane (CH₄)



Ammonia (NH₃)



In both NH_3 and H_2O , the bond angle is smaller than the theoretical tetrahedral bond angle (109.5°) because of repulsion of the lone pairs of electrons. The bonded atoms are compressed into a smaller space with a smaller bond angle.

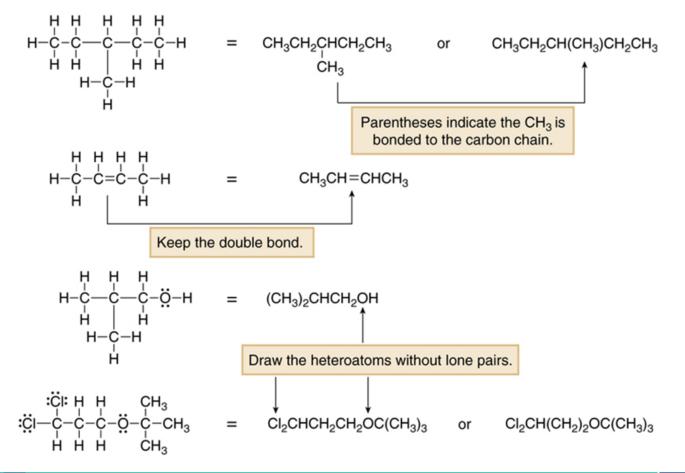
Predicting Geometry Based on Counting of Groups Around the Central Atom

Number of groups Examples around an atom Geometry Bond angle 2 linear 180° $BeH_2, HC \equiv CH$ 3 120° $BF_3, CH_2 = CH_2$ trigonal planar 109.5° 4 tetrahedral CH_4 , NH_3 , H_2O

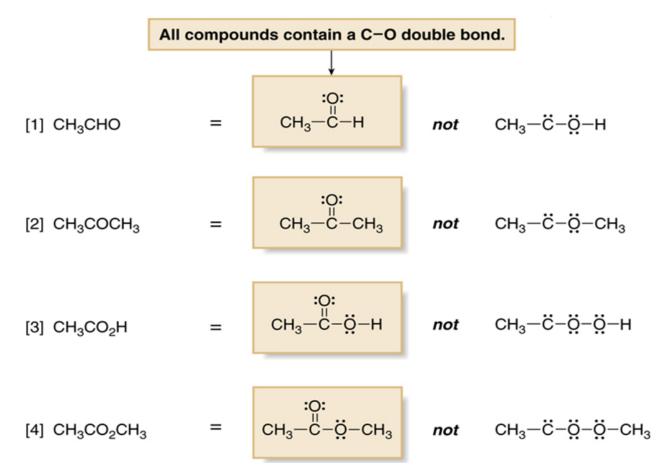
Drawing Organic Molecules—Condensed Structures

- All atoms are drawn in, but the two-electron bond lines are generally omitted.
- Atoms are usually drawn next to the atoms to which they are bonded.
- Parentheses are used around similar groups bonded to the same atom.
- Lone pairs are omitted.

Examples of Condensed Structures

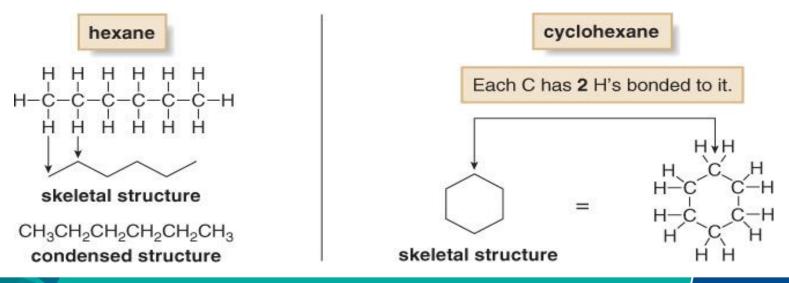


Examples of Condensed Structures Containing a C-O Double Bond



Skeletal Structures

- Assume there is a carbon atom at the junction of any two lines or at the end of any line.
- Assume there are enough hydrogens around each carbon to make it tetravalent.
- Draw in all heteroatoms and hydrogens directly bonded to them.



Examples of Skeletal Structures

