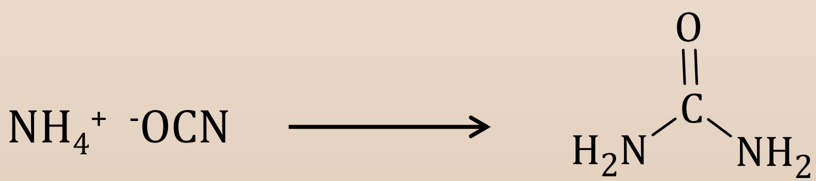
Molecular Structure
1 - Bonding

Dr. Sapna Gupta

Origins of Organic Chemistry

Organic chemicals were initially thought to be chemicals that were obtained from plants and animals only. The chemicals were thought to have a “vital force” as they from natural sources.

It was also supposed that inorganic chemicals could not make organic chemicals until in 1828, Woehler synthesized urea, an organic compound from ammonium cyanate.



Ammonium cyanate Urea

What is Organic Chemistry?

Organic chemistry is the study of compounds containing carbon bonded with hydrogen, oxygen, sulfur, nitrogen, phosphorous and halogens.

- Carbon is the only nonmetal in group IV; Si and Ge are metalloids and Sn and Pb are metals.
- Bonding for carbon can be covalent and ionic, although it can combine with only group I and II metals in ionic bonding.
- Some compounds of carbon that not considered to be organic are CO, CO_2, CO_3^{2-}, HCO_3^-, CN^-.
- There are over 10 million organic compounds.

Review: Atomic Structure

Atoms have electrons, protons and neutrons. Protons (electrically positive) and neutrons (electrically neutral) are found in the nucleus in the center of the atom and electrons (electrically negative) are in shells outside the nucleus.

- Atomic weight is the number of protons and neutrons in an atom.
- Atomic number is the number of protons in an atom.
- Isotopes are atoms with same atomic number and different number of neutrons.

Electronic Configuration

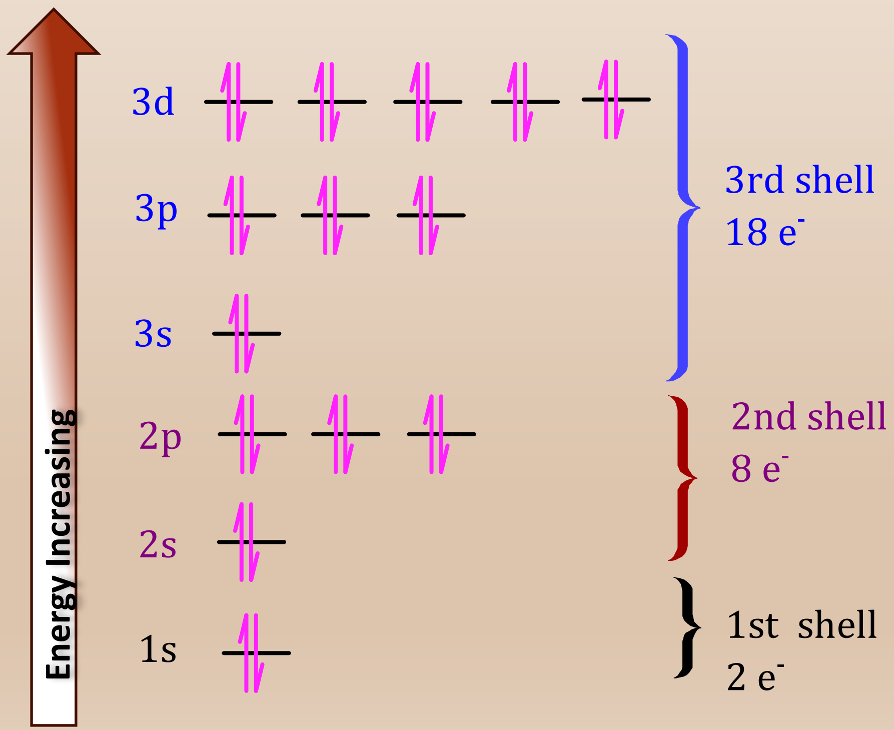
Electrons are found in specific regions called shells and in specific regions, subshells – spdf. The table below shows all the properties of these subshells.

Electrons are filled from lowest energy level and in opposite spins in each orientation. Follow Aufbau principle, Pauli Exclusion principle and Hund's rule to fill electrons.

Orbitals	s	p	d	f
Energy	Lowest			Highest
Number of electrons possible	2	6	10	14
Shape	Spherical	Dumbbell	Various	Various
Orientations in space	One	Three	Five	Seven

Electronic Configuration Diagrams

- First shell (n=1) contains one s orbital, denoted 1s, holds only two electrons.
- Second shell (n=2) contains one s orbital (2s) and three p orbitals (2p), eight electrons.
- Third shell (n=3) contains an s orbital (3s), three p orbitals (3p), and five d orbitals (3d), 18 electrons.



Bonding

Bonding is association of various atoms to get to a lower energy state. This is attained by having eight electrons in the valence shell. This is called the octet rule. Only valence electrons are involved in bonding.

- Lewis structures are drawn to show valence electrons as dots.
- There are two kinds of bonding: covalent and ionic. Covalent is sharing of electrons and ionic is transfer of electrons.
- Covalent bonding is found between nonmetals and ionic bonding is between metals and nonmetals, where metals give electrons, becoming cations, and nonmetals accept electrons becoming anions.
- In organic chemistry we deal more with covalent bonding.

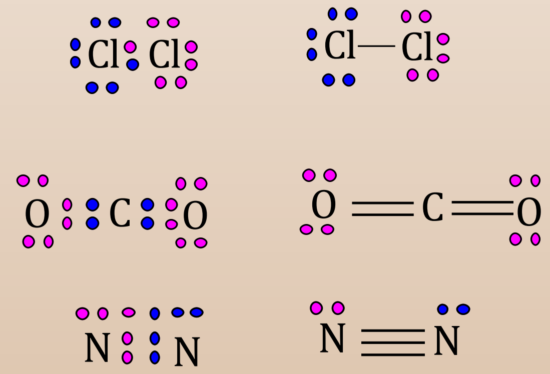
Covalent Bonds

The simplest covalent bond is that in H_2. The single electrons from each atom combine to form an electron pair which are shared equally in the valence shell

$$\mathrm{H}\cdot \quad + \quad \cdot\mathrm{H} \longrightarrow \mathrm{H}:\mathrm{H} \quad \text{or} \quad \mathrm{H{-}H}$$

The number of shared pairs gives the number of bonds.

- One shared pair forms a single bond (e.g. hydrogen, halogens).
- Two shared pairs form a double bond (e.g. oxygen, carbon dioxide).
- Three shared pairs form a triple bond (e.g. nitrogen, hydrogen cyanide).

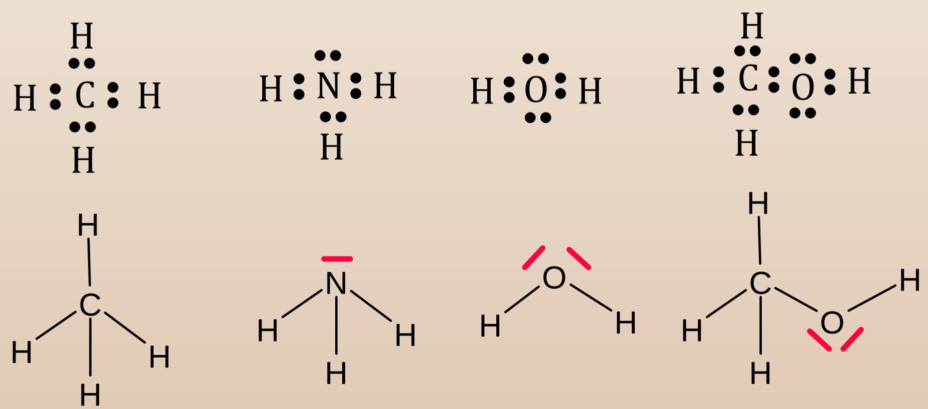


Lewis Structures

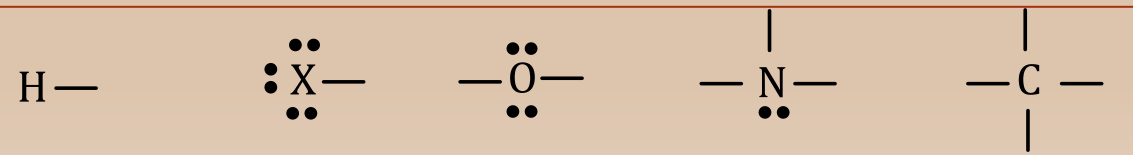
Bonds (electron pairs) are represented by using lines. Lone pair of electrons can be represented by just dots or lines. Below are some examples of Lewis structures of common covalent compounds. Bonding becomes easier if you can remember how many bonds each atom is going to form, which is generally determined from which group they are in. (Halogens are generally represented as X).

Electron dot structures

Line structures



Molecular Formula	CH_4	NH_3	H_2O	CH_3OH
	Methane	Ammonia	Water	Methanol

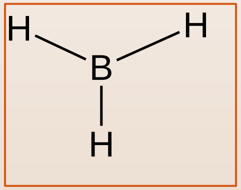


one bond one bond two bonds three bonds four bonds

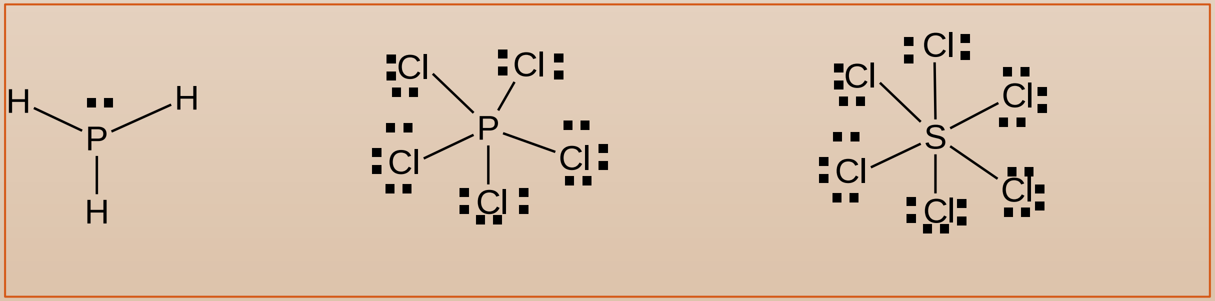
Exceptions to the Octet Rule

Most molecules will follow the octet rule, however there are three exceptions:

1) Incomplete valence shell – when there are less than 8 e- in the valence shell. This usually occurs in group III compounds since there are only 3 electrons for bonding so maximum valence electrons possible are 6.



2) Expanded valence shell – when there are more than 8 e- in the valence shell. This is usually in covalent compounds of the 3rd row e.g. P, S, Cl, I etc. This occurs because of the d orbitals in the third shell available to accommodate the extra electrons.



3) Unpaired electrons in the valence shell – this usually happens for nitrogen N, since it has odd number of electrons.

$:\dot{N}=O$

Types of Covalent Bonds

We can classify covalent bonds into

- **nonpolar** covalent bonds and
- **polar** covalent bonds.

- Nonpolar covalent bonds are either the bonds between the same atoms or with less than 0.5 electronegativity difference. E.g., H_2, Cl_2, CH_4.
- Polar covalent bond is when the subtraction of electronegativity number is more than 0.5.
- The electronegative values are given on the next slide.
- An example is H-Cl. The difference in electronegativity between Cl and H is 3.0 - 2.1 = 0.9.

Difference in Electronegativity	Type of Bond
Less than 0.5	Nonpolar covalent bond
0.5-0.9	Polar covalent
More than 0.9	Ionic bond

Electronegativity

Electronegativity is a measure of an atom's attraction for electrons in a covalent bond. Electronegativity increases across the periodic table and decreases down a group. The measured values are given below but it is not a good idea to memorize these numbers. A better way to remember if a bond is polar or not is do a few subtractions of atoms e.g., C and I, C and H to get an idea. N, O, F are the highest electronegative elements, followed closely by Cl. The rest can have some effect on bond polarity but not as much as N, O, F and Cl.

Increasing Electronegativity →

Decreasing Electronegativity ↓

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA
1 **H** 2.1																
3 **Li** 1.0	4 **Be** 1.5											5 **B** 2.0	6 **C** 2.5	7 **N** 3.0	8 **O** 3.5	9 **F** 4.0
11 **Na** 0.9	12 **Mg** 1.2											13 **Al** 1.5	14 **Si** 1.8	15 **P** 2.1	16 **S** 2.5	17 **Cl** 3.0
19 **K** 0.8	20 **Ca** 1..0	21 **Sc** 1.3	22 **Ti** 1.5	23 **V** 1.6	24 **Cr** 1.6	25 **Mn** 1.5	26 **Fe** 1.8	27 **Co** 1.9	28 **Ni** 1.9	29 **Cu** 1.9	30 **Zn** 1.6	31 **Ga** 1.6	32 **Ge** 1.8	33 **As** 2.0	34 **Se** 2.4	35 **Br** 2.8
37 **Rb** 0.8	38 **Sr** 1.0	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In** 1.7	50 **Sn** 1.8	51 **Sb** 1.9	52 **Te** 2.1	53 **I** 2.1
55 **Cs** 0.7	56 **Ba** 0.9	57 **La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl** 1.9	82 **Pb** 1.8	83 **Bi** 1.9	84 **Po** 2.0	85 **At** 2.2

Dipole Moment

Dipole moment (mu - μ) is the movement of a molecule in an electric current. This movement occurs a) when there is polarity in a covalent bond, which comes from the difference in electronegativity, and b) when the molecule is asymmetric.

When the dipole difference is very large, an ionic bond forms. When the difference is large, the bond is polar. When the difference is small, the bond is nonpolar.

Polarity in a bond is shown by using the symbols δ+ and δ-, or by using an arrow with the arrowhead pointing toward the negative end and a plus sign on the tail of the arrow at the positive end, as shown below.

δ+ δ-

H – Cl

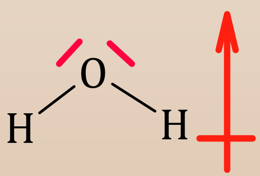
Bond Dipole	Bond Dipole	Bond Dipole
H-C 0.3 H-N 1.3 H-O 1.5 H-S 0.7	C-F 1.4 C-Cl 1.5 C-Br 1.4 C-I 1.2	C-O 0.7 C=O 2.3 C-N 0.2 C=N 3.5

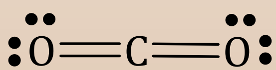
Solved Problem: Determining direction of polarity/dipole moment

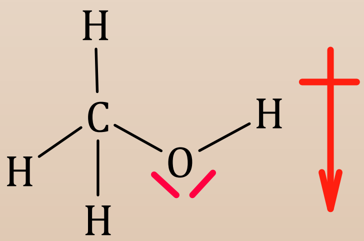
Determine the direction of polarity in the following molecules and ions. Draw the crosshair arrow to indicate the dipole moment.

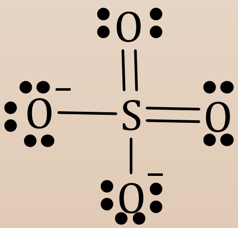
H_2O, CO_2, CH_3OH, SO_4^{-2}

Answer: First draw the Lewis structures of all molecules. If this is wrong, then all else will be wrong. Write the molecule in the appropriate shape and then determine the polarity of the bonds. Dipole moment will be towards the most electronegative element. (Note: you can draw the lone pairs as a line or dots).









Formal Charge

It is the charge on an atom in a molecule or a polyatomic ion.

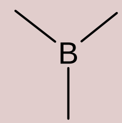
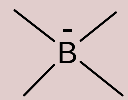
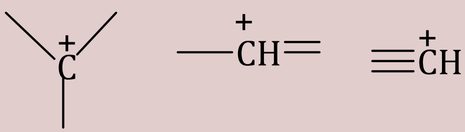
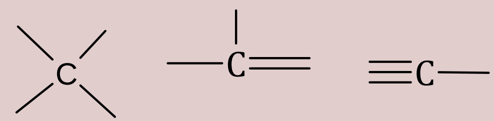
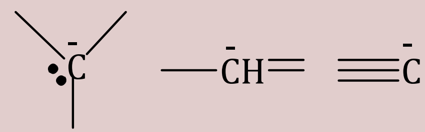
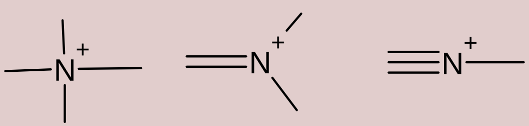
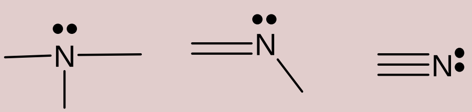
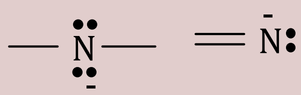
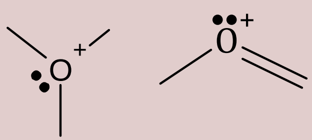
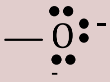
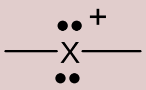
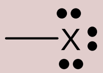
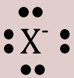
- To calculate formal charge:
  - Write a correct Lewis structure for the molecule or ion with all bonding and nonbonding electrons.
  - Formal charge is subtraction of half of bonding electrons (or just the number of bonds - BE) and nonbonding electrons (NE) from the valence electrons (VE).
  - The sum of all formal charges is equal to the total charge on the molecule or ion.

Formal charge, FC = VE – BE – NE

- The overall molecule may have a formal charge of -3 or +2, as calculated, but the individual atom will always be +/- 1.

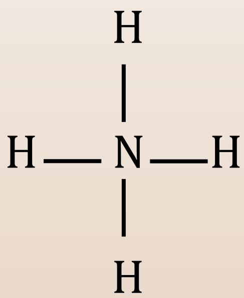
Formal Charges Table

The table below shows how the formal charge changes with the number of electrons/bonds on the central atom. The pattern generally is the if the atom as the octet, then formal charge is zero, less than octet is +1 and more than octet is -1.

Group	Formal Charge +1	Formal Charge 0	Formal Charge -1
III			
IV			
V			
VI			
VII			

Calculating Formal Charge

Ammonium ion $(NH_4)^+$



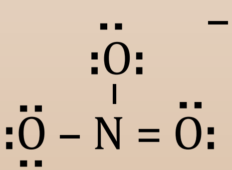
VE – BE – NE = FC

H = 1 – 1 – 0 = 0

N = 5 – 4 – 0 = +1

Formal charge on ion = +1

Nitrate ion $(NO_3)^-$



VE – BE – NE = FC

Double bond O = 6 – 2 – 4 = 0

Single bond O = 6 – 1 – 6 = -1 (two oxygens) = -2

Central atom N = 5 – 4 – 0 = +1

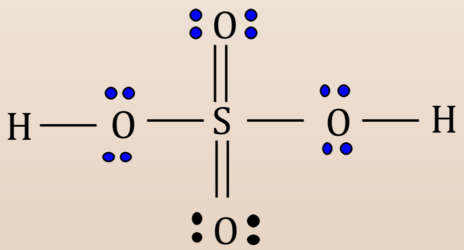
Formal charge on ion = -1

Solved Problem: Determining formal charge

Determine the formal charge on each atom in the following polyatomic ions.

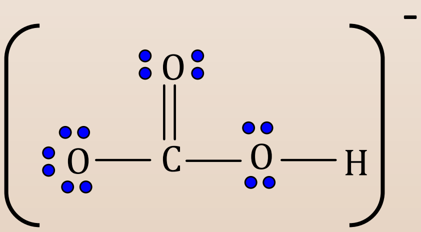
H_2SO_4, HCO_3^-

Answer: First draw the Lewis structures of all molecules. If this is wrong, then all else will be wrong.



	H	-O-	=O	S
VE	1	6	6	6
-BE	-1	-2	-2	-6
-LE	-0	-4	-4	-0
FC	0	0	0	0

TOTAL CHARGE =
2(0) + 2(0) + 2(0) + (-0) = 0



	-O	C	=O	-O-	H
VE	6	4	6	6	1
-BE	-1	-4	-2	-2	-1
-LE	-6	-0	-4	-4	-0
FC	-1	0	0	0	0

TOTAL CHARGE =
(-1) + (0) + (0) + (0) + (0) = **-1**

Key Words/Concepts

- Electronic Configurations
- Lewis structures
- Bonding
  - Ionic
  - Covalent
  - Polar Covalent
- Exceptions to Octet Rule
- Electronegativity
- Formal Charge