Molecular Structure and Bonding

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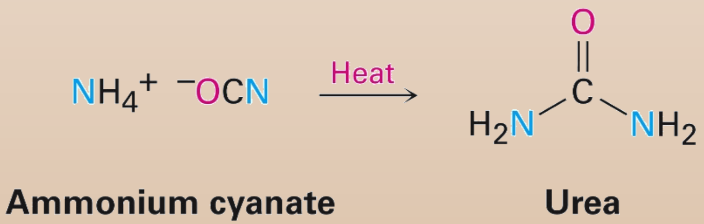
Origins of Organic Chemistry

- Initially thought to be chemicals that were obtained from plants and animals only.
- Thought to have a “vital force” as they from natural sources.
- Distinctions were made between organic and inorganic chemistry because of this vital force.
- It was also supposed that inorganic chemicals could not make organic chemicals until in 1828, Woehler synthesized urea from ammonium cyanate.



What is Organic Chemistry?

- It is the study of compounds containing carbon bonded with hydrogen, oxygen, sulfur, nitrogen, phosphorous and halogens.
- Carbon is the only non metal in group IV; Si and Ge are metalloids and Sn and Pb are metals.
- Bonding for carbon can be covalent and ionic.
- It can combine with only group I and II metals.
- Some compounds of carbon 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

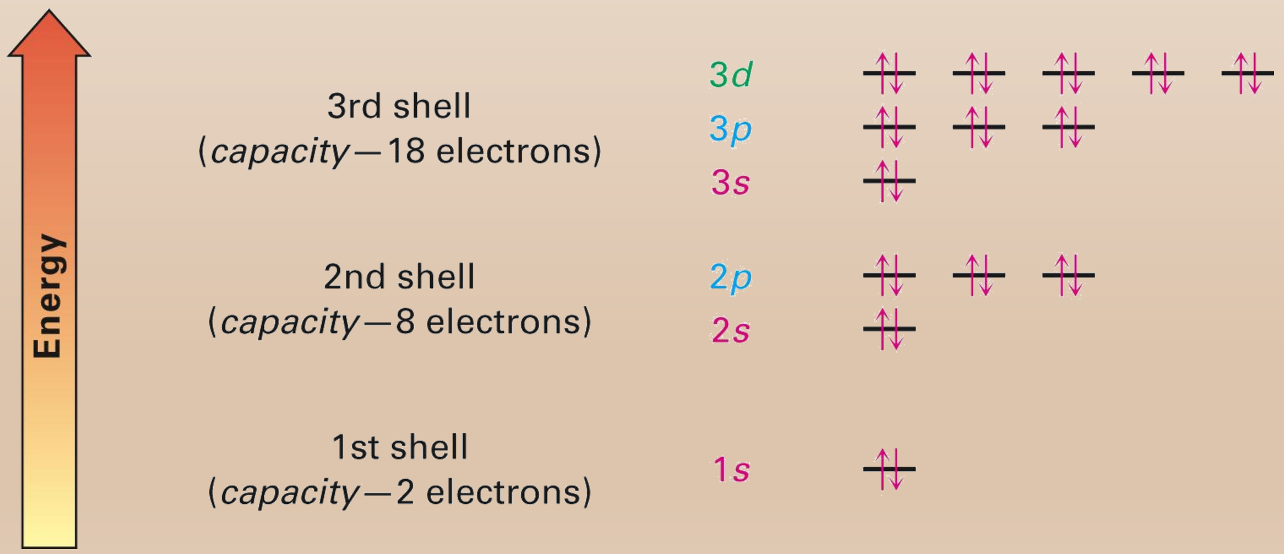
- Atoms have electrons, protons and neutrons. Protons and neutrons are found in the nucleus in the center of the atom and electrons are in shells outside the nucleus.
- Atomic weight is the number of protons and neutrons in an atom.
- Atomic number is the number of protons in an atom.
- Isotopes are atoms with same atomic number and different number of neutrons.

Electronic Configuration

- Electrons are found in specific regions called shells and in specific regions – spdf.
- Energy:
  - s – lowest in energy ($2e^-$); p – higher in energy ($6e^-$); d – transition elements ($10e^-$); f – lanthanides and actinides ($14e^-$)
- Shape:
  - s subshell is spherical shape (only one); p is dumbbell (3 shapes); d has 5 shapes and f has 7.
- Electrons are filled by energy level and in opposite spins. (Aufbau principle, Pauli Exclusion principle and Hund's rule)

Electronic Configuration diagrams

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

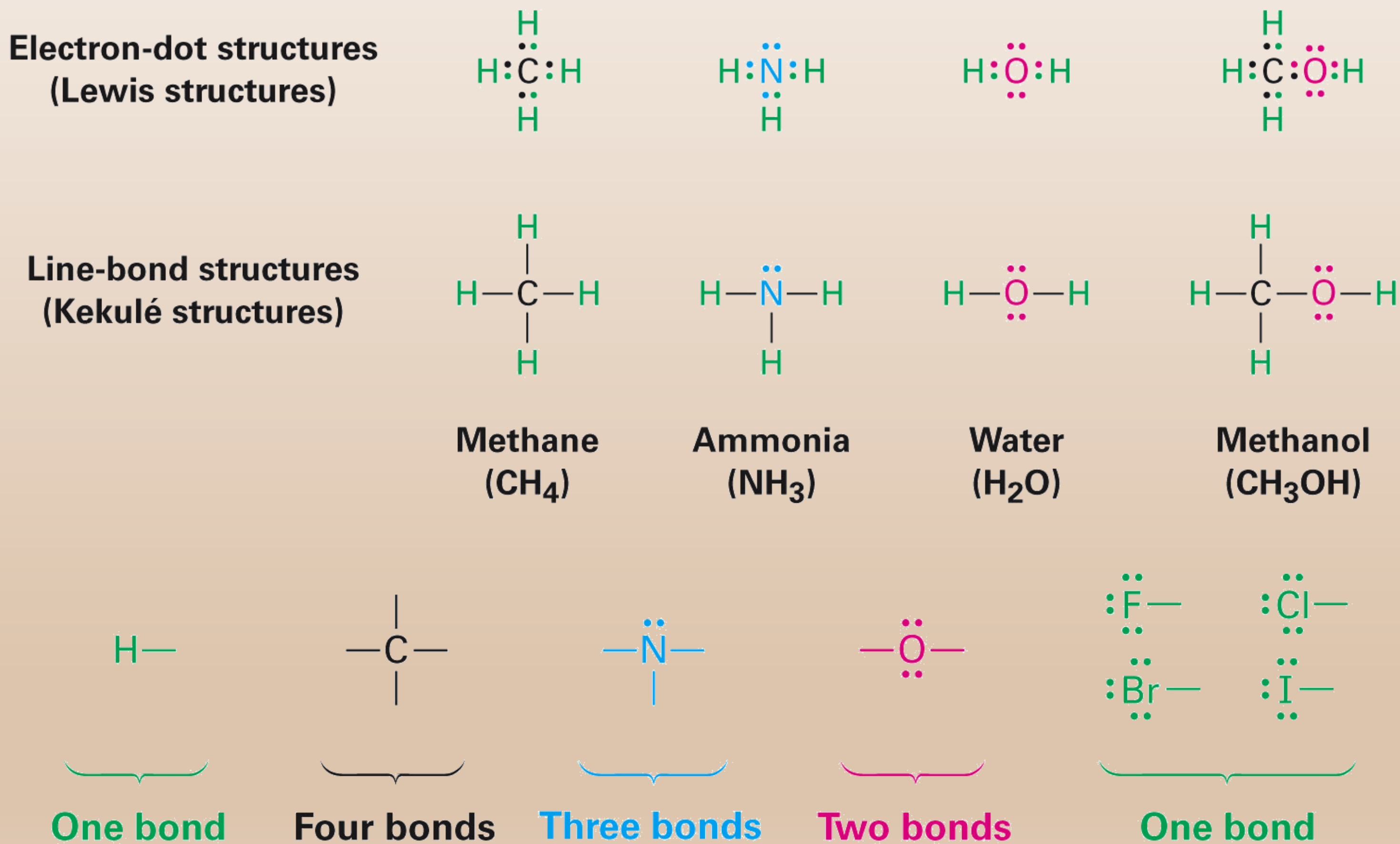


Bonding

- Lewis structures – shows electrons as dots.
- Two kinds of bonding: covalent and ionic. Covalent is sharing of electrons and ionic is transfer of electrons.
- Covalent is found in non metals and ionic is metals and non metals.
- In organic chemistry we deal more with covalent bonding.

Lewis Structures

- Representing the bonds (electron pairs) using lines is common. Lone pair of electrons can be represented by just dots.



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.

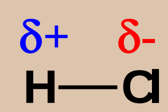
$$H\bullet \;+\; \bullet H \longrightarrow H\text{-}H \qquad \Delta H^0 = -435\text{ kJ } (-104\text{ kcal})/\text{mol}$$

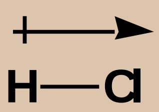
- The number of shared pairs gives the number of bonds.
  - One shared pair forms a single bond (e.g. hydrogen, halogens)
  - Two shared pairs form a double bond (e.g. oxygen, carbon dioxide)
  - Three shared pairs form a triple bond (e.g. nitrogen, hydrogen cyanide)

Types of Covalent Bonds

- We divide covalent bonds into
  - nonpolar covalent bonds and
  - polar covalent bonds.
- Non polar 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.
- An example of a polar covalent bond is that of H-Cl.
- The difference in electronegativity between Cl and H is 3.0 - 2.1 = 0.9.
- We show polarity 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.

Difference in Electronegativity Between Bonded Atoms	Type of Bond
Less than 0.5	Nonpolar covalent
0.5 to 1.9	Polar covalent
Greater than 1.9	Ions form

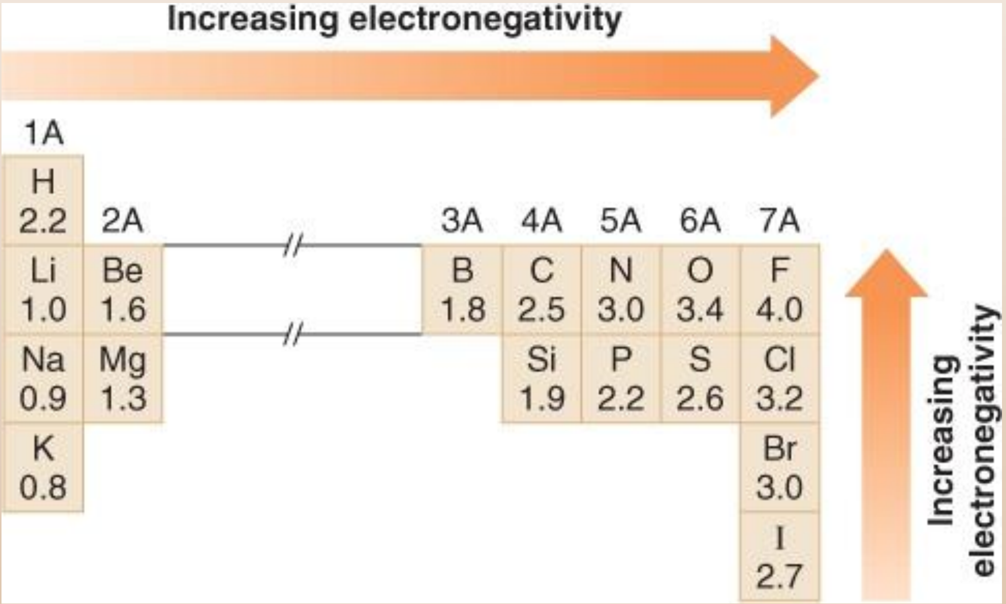




Dipole Moment and Electronegativity

Dipole moment is a measure of the polarity of a covalent bond, which comes from the difference in electronegativity.

Electronegativity is a measure of an atom's attraction for electrons in a bond.



Bond	Bond Dipole (D)	Bond	Bond Dipole (D)	Bond	Bond Dipole (D)
$+\!\!\longrightarrow$		$+\!\!\longrightarrow$		$+\!\!\longrightarrow$	
H-C	0.3	C-F	1.4	C-O	0.7
H-N	1.3	C-Cl	1.5	C=O	2.3
H-O	1.5	C-Br	1.4	C-N	0.2
H-S	0.7	C-I	1.2	C≡N	3.5

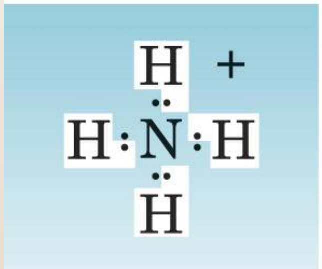
Formal Charge

- It is the charge on an atom in a molecule or a polyatomic ion.
- To derive formal charge
  - Write a correct Lewis structure for the molecule or ion.
  - Assign each atom all its unshared (nonbonding) electrons and one-half its shared (bonding) electrons.
  - Compare this number with the number of valence electrons in the neutral, unbonded atom.
  - The sum of all formal charges is equal to the total charge on the molecule or ion.

$$\text{Formal charge} = \begin{pmatrix}\text{Number of valence electrons}\\ \text{in the neutral, unbonded atom}\end{pmatrix} - \left(\begin{matrix}\text{All unshared}\\ \text{electrons}\end{matrix} + \begin{matrix}\text{One half of all}\\ \text{shared electrons}\end{matrix}\right)$$

Calculating Formal Charge

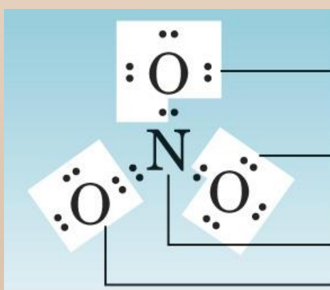
- Ammonium ion $(NH_4)^+$



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 $(NO_3)^-$



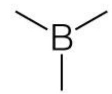
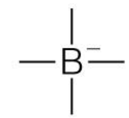
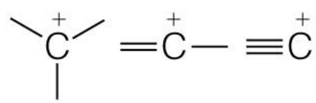
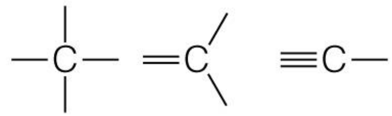
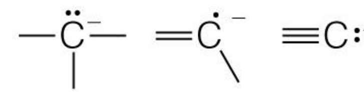
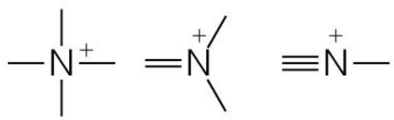
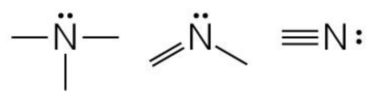
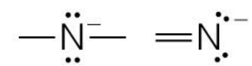
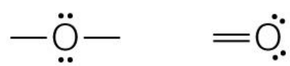
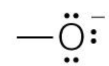
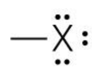
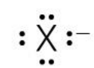
Formal charge = 6 − 7 = −1

Formal charge = 5 − 4 = +1

Formal charge = 6 − 6 = 0

Charge on ion = 2(−1) + 1 + 0 = −1

Formal Charges Table

Group	Formal Charge of +1	Formal Charge of 0	Formal Charge of −1
3A			
4A			
5A			
6A			
7A		 (X = F, Cl, Br, or I)	

Problem: Lewis Structure and Formal Charge

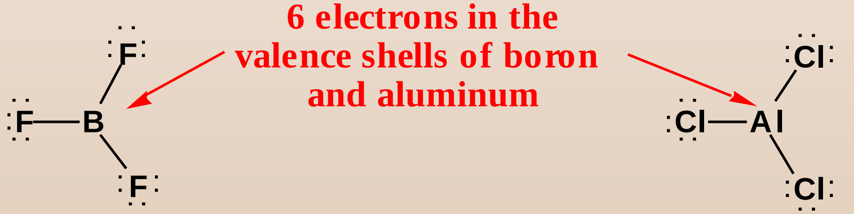
Draw Lewis structures, and show which atom in each bears the formal charge

(a) NH_2^- (b) HCO_3^- (c) CO_3^{2-}

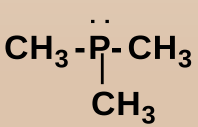
(d) $CH_3NH_3^+$ (e) $HCOO^-$ (f) CH_3COO^-

Exceptions to the Octet Rule

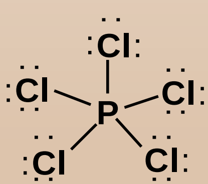
- There are three exceptions:
- Incomplete valence shell – usually group III
- Expanded valence shell – usually covalent compounds of the 3rd row e.g. P, S, Cl, I etc.
- Unpaired electrons – usually N



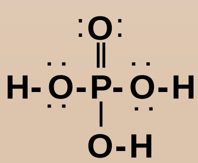
Boron trifluoride **Aluminum chloride**



Trimethyl-phosphine



Phosphorus pentachloride



Phosphoric acid

Key Words/Concepts

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