Lewis Structures. Sections 3.3-3.7

Learning goals:

(1) Writing valid Lewis structures for the constitutional structure of molecular substances for a given composition.

(2) Predicting molecular geometry (positions of atoms in space) from Lewis structures (VSEPR theory).

(3) Understanding electronegativity and how this concept allows the distinction between polar bonds and non-polar bonds.

(4) Using Lewis structures and molecular geometry to determine whether a molecule has a dipole moment or not.

(5) Using the octet rule to compute formal charges on atoms and multiple bonding between atoms.

Lecture 5. Chem C1403 Wed Sept 21, 2005

Understanding electronis structure of atoms and molecules: Composition, constitution and configuration.

Composition: Core electrons (inert) and outer valence electrons (reactive).

Constitution: Electronic connections of two or more atoms (Lewis structures).

Configuration: Distribution of outer electrons in space (Shapes of electronic distributions about atoms).

Today's Lecture: How to write "valid" Lewis Structures

(1) Drawing "valid" Lewis structures which follow the "doublet" &"octet" rule (holds almost without exception for first full row)

(2) Drawing structures with single, double and triple bonds

(3) Dealing with isomers (same composition, different constitution)

(4) Dealing with resonance structures (same constitution, different bonding (electronic structure) between atoms)

(5) Dealing with "formal" charges on atoms in Lewis structures

(6) Dealing with violations of the octet rule:

Molecules which possess an odd number of electrons

Molecules which are electron deficient

Hypervalent molecules which are capable of making more than four covalent bonds to a central atom.

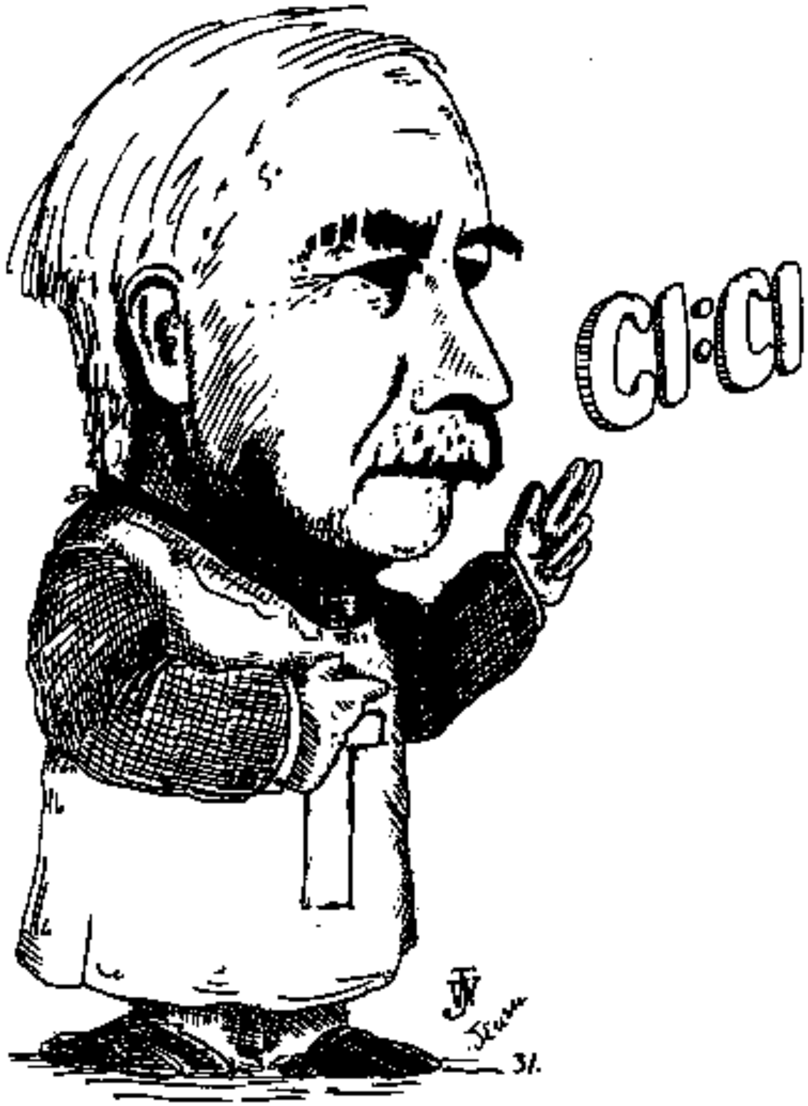
Chemical features of molecules that can be addressed by Lewis structures:

(1) Describe rules for making bonds between atoms in molecules

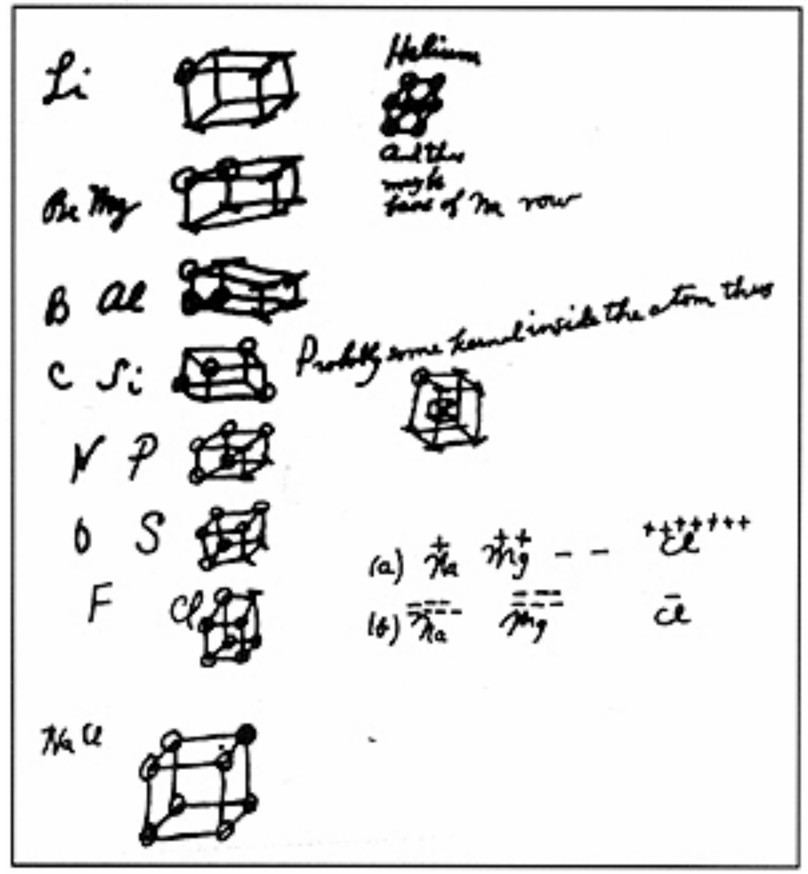
(2) Describe bond lengths, bond angles, bond polarity

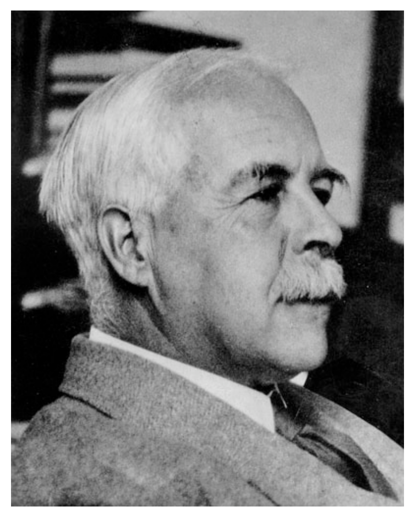
(3) Describe chemical reactivity with formal charge and resonance structures

(4) Predict the existence and stability of isomers



G. N. Lewis (1875-1946)





Lewis: Atoms try to lower their energy by gaining, losing or sharing electrons.

(1) Atoms seek the noble gas closed shell electronic structure, which is particularly stable.

(2) Atoms will share, donate or accept electrons in order to achieve the noble gas electronic configuration.

(3) For two atoms with very different electronegativities, one atom will donate an electron to the other atom to achieve the noble gas electronic configuration.

(4) For two atoms of similar electronegativities, one atom will share electrons with the other atoms to achieve the noble gas electronic configuration.

3-3 Lewis dot electronic structures of atoms

Chapters 16 and 17 (after Exam 1) will show how quantum mechanics describes how the structure of the periodic table arises from the electronic structure of atoms.

We start the process by understanding the basis of the periodic table by considering the Lewis dot electronic model of the atom.

The Lewis model attempts to explain in a very simple way the basis for the similarities in compositions of binary compounds formed by metals and non metals.

The atomic valence of an atom is the number of other atoms that which an atom can make a strong bond. A convenient measure of valence is the number of atoms of hydrogen to which an atom will combine, since H has a strict atomic valence of 1.

Carbon:	valence of 4	CH_4
Nitrogen:	valence of 3	NH_3
Oxygen:	valence of 2	OH_2
Fluorine:	valence of 1	FH

Lewis invented a theory to explain these differences in valence by means of a simple electron count. A count of the valence electrons about the atoms in a molecule.

Lewis "dot-line" representations of atoms and molecules

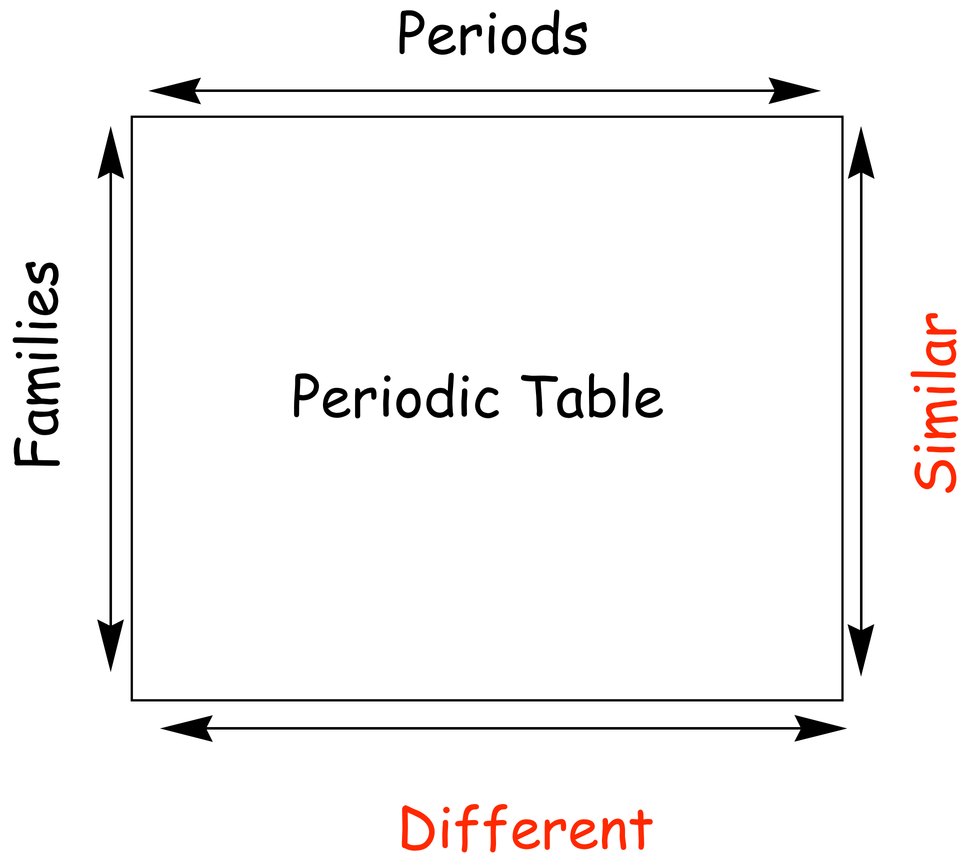
(1) Electrons of an atom are of two types: ***core*** electrons and ***valence*** electrons. Only the valence electrons are shown in Lewis dot-line structures.

(2) The number of valence electrons is equal to the group number of the element for the representative elements.

(3) For atoms the first four dots are displayed around the four "sides" of the symbol for the atom. If there are more than four electrons, the dots are paired with those already present until an octet is achieved.

(4) Ionic compounds are produced by complete ***transfer*** of an electron from one atom to another.

(5) Covalent compounds are produced by ***sharing*** of one or more pairs of electrons by two atoms.



Elements in columns possess similar chemical properties.

Elements in rows possess different periodic properties.

Start with the first three periods of the periodic table: How many electrons do each atom possess? How many are valence electrons?

I	II	III	IV	V	VI	VII	VIII
1	2	3	4	5	6	7	8
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

***The connection between the Periodic Table and atomic structure*.**

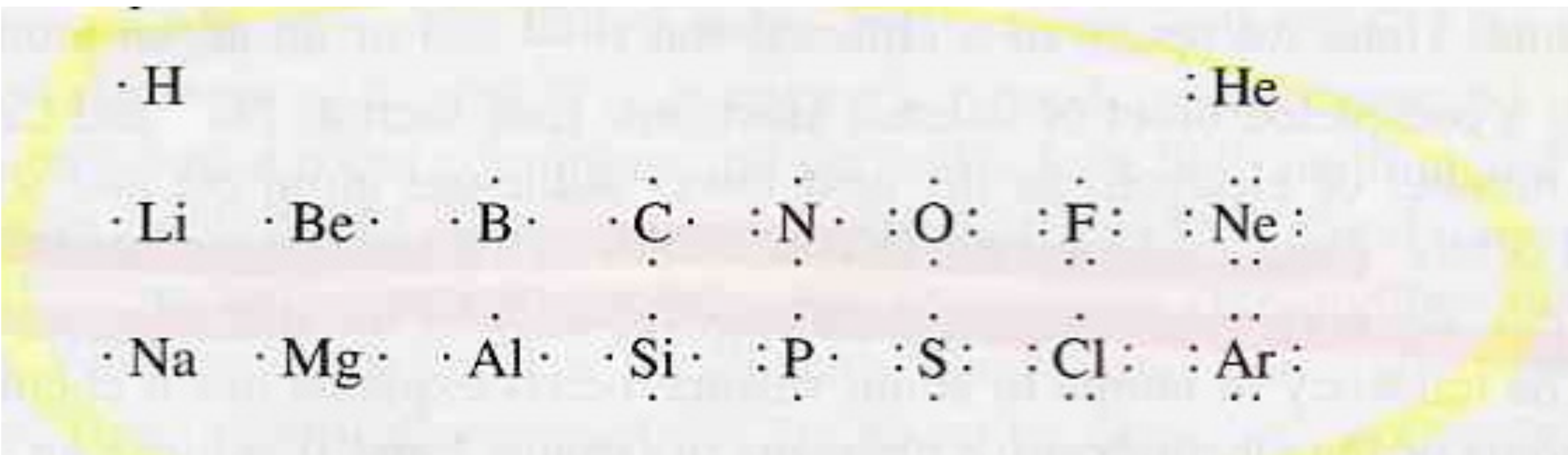
Periodic Table: The group number of the group of a column for the main group elements in the periodic table is the number of valence electrons possessed by the neutral atom = atomic number = number of protons in the nucleus of an atom.

Total electrons for elements 1-18

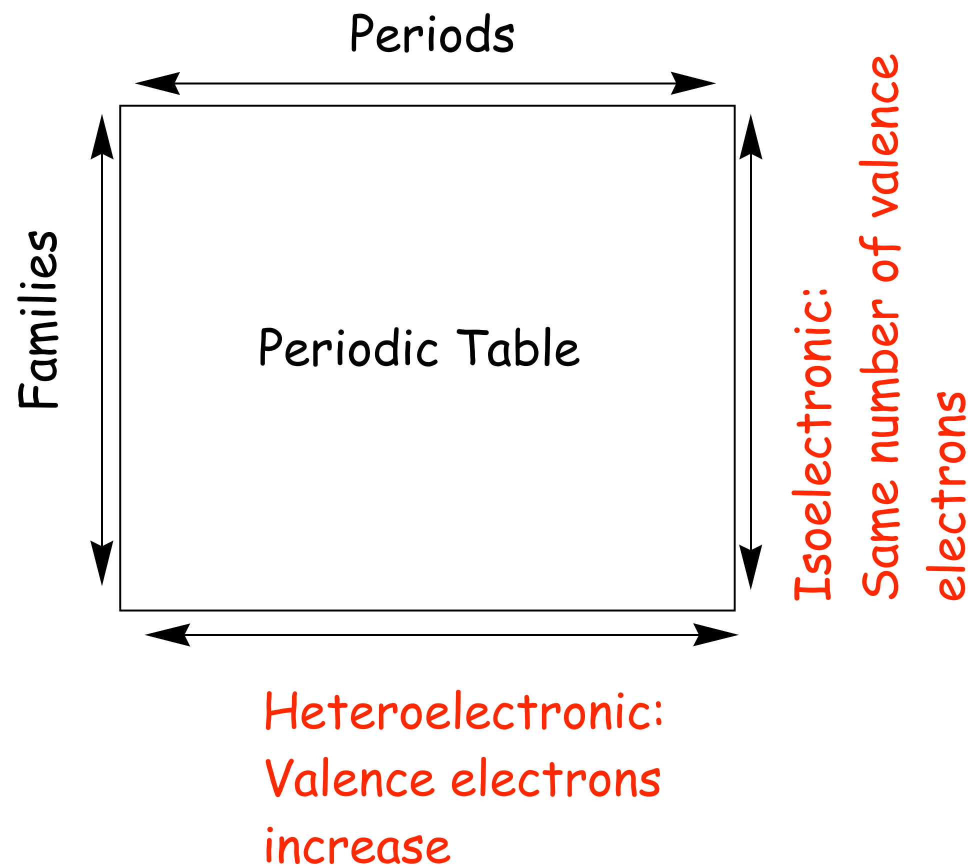
I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
^{1}H							^{2}He = 2 core electrons
^{3}Li	^{4}Be	^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne = 10 core electrons
^{11}Na	^{12}Mg	^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}Ar = 18 core electrons

Lewis structures for the valence electrons for the elements of the 2ed and 3rd periods of the periodic table: for a neutral atom, the number of valence electrons = group number = all electrons - core of previous noble gas (Except for H and He).

I	II	III	IV	V	VI	VII	VIII
Valence electrons:							
1	2	3	4	5	6	7	8



Lewis' explanation of the periodic table: periodic properties appear because of periodic electronic structure of atoms.



Elements in columns possess the same number of valence electrons and therefore have similar chemical properties. The atoms are "isoelectronic" with respect to the number of valence electrons.

Elements in rows possess different numbers of valence electrons and therefore have different periodic properties. The atoms are "heteroelectronic".

Basic rules for writing Lewis structures (a useful, if imperfect model of reality) for molecules containing only H, C, N, O, F

the ***doublet*** rule for H: ***hydrogen*** is most stable when it has two valence electrons surrounding it.

The ***octet*** rule for C, N, O, F: The valence electrons of the atoms of C, N, O and F are distributed in such a way that eight electrons (an octet of electrons) surround an atom of these.

The octet rule holds with very few exceptions for compounds possessing only H, C, N, O and F. There are no violations in which the octet is exceeded in stable molecules. Odd electron molecules (NO) are exceptions where less than an octet occurs.

Lewis dot-line constitutional structures of covalent bonds in molecules

Compounds with very different electronegativities (metals versus non-metals) transfer electrons from one atom to another for form ions:

Li & F, Be & O

Compounds with similar electronegativies share electrons:

C & H, C & O, C & N, C & F

Lewis Structure Mechanics

- Three steps for “basic” Lewis structures:

1. Sum the valence electrons for all atoms to determine total number of electrons.

2. Use pairs of electrons to form a bond between each pair of atoms (bonding pairs).

3. Arrange remaining electrons around atoms (lone pairs) to satisfy the “octet rule” (“duet” rule for hydrogen).

Writing valid Lewis structures for molecules containing only H, C, N, O and F atoms.

Start with diatomic molecules:

Elements: H_2, C_2, N_2, O_2, F_2

Compounds: CO, CN, CF, NO, NF, OF

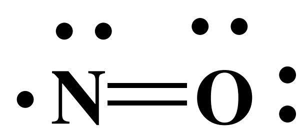
Extend ideas to polyatomic molecules:

H_2CO, H_2C_2, H_4C_2 and friends

Writing Valid Lewis Structures Which Do Not Obey the Octet Rule for H, C, N, O, F: Odd electron molecules (Rare)

Odd electron molecules: If a molecule possess an odd number of electrons, obviously a valid structure cannot be written which possess an octet of electron about each atom.

Rule for valid Lewis structures: In this case valid Lewis structures are defined as those which maximize the number of atoms which possess an octet and which place the odd electron on the least electronegative atom.



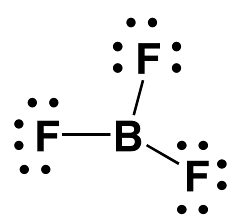
Example: NO
N = 5 VE, O = 6 VE
Total = 11 valence electrons

Writing Valid Lewis Structures Which Do Not Obey the Octet Rule: Hypovalent molecules (even electron, but less than 8 electrons around a central atom)

Hypovalent molecules (electron deficient molecules): If a molecule does not possess a sufficient number of valence electrons to make octets about each of the atoms, obviously, a valid structure cannot be written which shows an octet about each.

Rule for valid Lewis structures: In this case, valid Lewis structures are defined as those for which octets are assigned the more electronegative atoms so that the lack of an octet occurs on the least electronegative atom (typically a Be or B atom).

Example: BF_3
Be = 3 VE
3 F = 21 VE



Writing Valid Lewis Structures Which Do Not Obey the Octet Rule: Hypervalent atoms (more than eight electrons around a central atom)

Hypervalent atoms (valence shell expanded atoms): Some atoms in the third row of the periodic table (examples: P, S, Cl) and beyond can accommodate more than 4 pairs of electrons. In this case the hypervalent atom is termed a ***central*** atom and the atoms bounded to it are called the ***outer*** atoms.

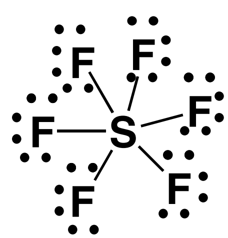
Examples: SF_4, SF_6, PF_5

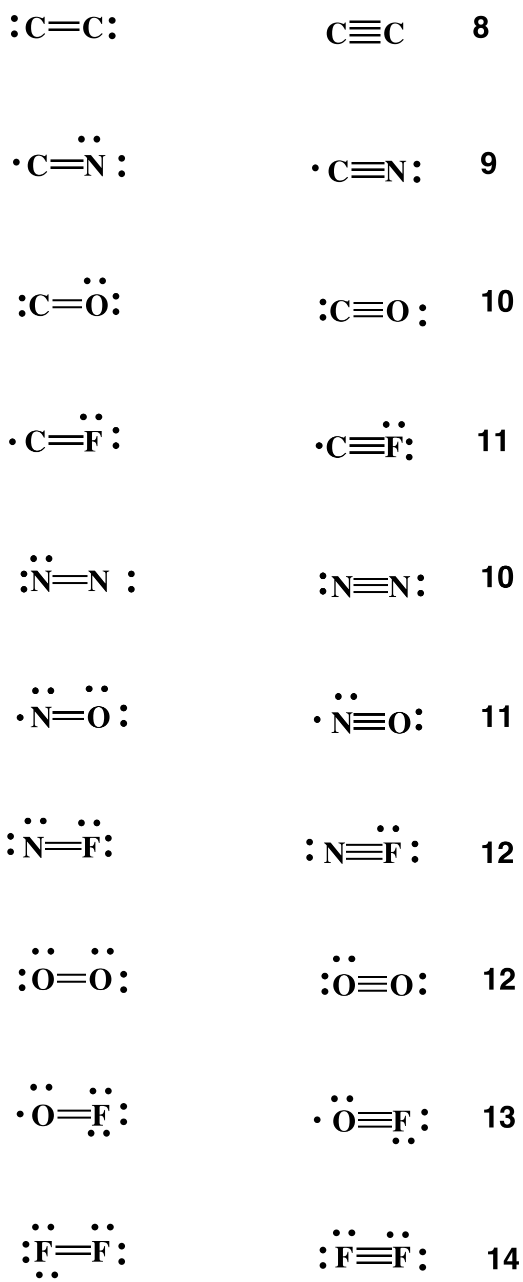
Rule for valid Lewis structures: First assign lone pairs to the outer atoms to give them octets as the first priority. If any valence electrons remain to be assigned, they are assigned to the central atom as lone pairs.

Example:

SF_6: S = 6 VE, 6F = 6 x 7 = 42 VE

Total = 48 VE





Rules:

(1) Must have the correct number of valence electrons.

(2) Must obey the octet rule except for an odd number of valence electrons.

(3) Best structures maximize bonding and obey the octet run

Other topics to be discussed in the lecture on Wed or next Monday (part of a separate ppt):

(1) Formal charge on atoms in covalent molecules

(2) Isomeric structures

(3) Resonance structures

(4) VSEPR theory of molecular shapes

(5) Polar and non-polar bonds

(6) Polar and non-polar molecules (dipole moment)