

Focus 2 notes

2-1

Atoms/Molecules (Background)

- Atom size: quite small $\sim 10^{-10}$ m
nucleus size $\sim 10^{-15}$ m
- majority of the volume of an atom is vacuum
 - Pauli exclusion property prevents atoms from getting too close
 - can now observe their image and move single atoms on a surface in a controlled manner.

(1989)

<https://phys.org/news/2009-09-16m-celebrates-30th-anniversary-atoms.html>

\sim 300 years ago, chemistry became a scientific study based on observations that predicted the existence of atoms and molecules

- Antoine Lavoisier (1743-1794) used return on investments in a private tax-collecting agency of King Louis XVI to equip a private lab and finance his research. Back ground as an accountant led him to apply principles of the balance sheet to everything, including chemical reactions. As a royal tax

collector, he was迫害 by the leaders of the French Revolution & was beheaded on a guillotine.

- Now called the "father" of modern chemistry

Law of conservation of mass

- the total mass remains constant during a chemical reaction
- Joseph Proust (1754-1826) decomposed compounds into elements that form them

Law of constant composition (Law of Definite Proportions)

All samples of a compound have the same composition; i.e., all samples have the same proportions by mass of the elements present

- a compound not only has constant or fixed composition, but it also has fixed properties

- physical & chemical properties of chemical substances depend on their composition, they are not a matter of chance!

- John Dalton (1766 - 1844) was not an experimenter but he used results of others to formulate his atomic theory. But first, another scientific law was developed.

Law of multiple proportions

When two or more different compounds of the same two elements are compared, the masses of one element that combine with a fixed mass of the second element are in the ratio of small whole numbers.

Example: Carbon dioxide (respiration, burning of fuels) 2 elements combine in a ratio of 8.0g O to 3.0g C. In carbon monoxide the poisonous gas formed when fuel is burned in limited air, the elements combine in the ratio of 4.0g O to 3.0g C.

	CO_2	CO
elements	3 g C 8 g O	3 g C 4 g O
Compound	11 g CO_2	7 g CO
O to C	8.0 g O	4.0 g O
mass ratio	3.0 g C	3.0 g C

$$\frac{\text{mass ratio } \text{CO}_2}{\text{mass ratio CO}} = \frac{8\text{g O}/3\text{g C}}{4\text{g O}/3\text{g C}} = \frac{8\text{g O}}{4\text{g O}} = 2:1$$

limited air, the elements combine in the ratio of
4.0 g oxygen to 3.0 g carbon

	carbon dioxide	carbon monoxide
elements	3.0 g C + 8.0 g O	3.0 g C 4.0 g O
compound	17.0 g carbon dioxide	7.0 g carbon monoxide
oxygen to carbon mass ratio	<u>8.0 g oxygen</u> <u>3.0 g carbon</u>	<u>4.0 g oxygen</u> <u>3.0 g carbon</u>

Mass ratio CO_2 : $\frac{\underline{8.0 \text{ g O}}}{\underline{3.0 \text{ g C}}} = \frac{8.0 \cancel{\text{g O}}}{3.0 \cancel{\text{g C}}} = 2:1$

Mass ratio CO: $\frac{\underline{4.0 \text{ g O}}}{\underline{3.0 \text{ g C}}} = \frac{4.0 \cancel{\text{g O}}}{3.0 \cancel{\text{g C}}} = 4:3$

Dalton's Atomic Theory: atomic model explained the laws of chemical combination:

- all matter is composed of extremely small, indivisible particles called atoms
- all atoms of a given element are alike, in mass and other properties, but atoms of one element differ from the atoms of every other element

Dalton's Atomic Theory; atomic model explained the laws of chemical combination

- all matter is composed of extremely small, indivisible particles called atoms
- all atoms of a given element are alike in mass and other properties, but atoms of one element differ from atoms of every other element
- compounds are formed when atoms of different elements unite in fixed proportions
(es, AB , A_2B , A_3B , A_3B_2 , ...)
- a chemical rxn involves a rearrangement of atoms. No atoms are created, destroyed, or broken apart in a chemical rxn.

Can restate Law of Conservation of Mass:

Atoms can neither be created nor destroyed in a chemical rxn, and as a consequence, the total mass remains unchanged.

Atoms: concept of atom used by Dalton, originated ~440 BC by Leucippus & Milesius, who with his student, Democritus, refined the concept. Their original

writings are lost, known now primarily through quotes from the texts of other writers of the time, such as Epicurus (341 - 270 BC) and Lucretius (99 BC - 55 BC), who wrote "On the Nature of Things" (lost until rediscovered in a monastery in 1417). This ancient text shows:

- 1) a developed atomic theory, resembling the proposed by Dalton & even ours today.
- 2) clearly defined the laws of conservation of matter & energy, in a manner similar to ours today.
- 3) Presented a concept of parts at the molecular level, which is analogous to the concept of molecular attraction & combination. He missed the concept of electrical charges, but this was only developed w/ atoms in 1904 by Thomson.
- 4) Also discussed concept of biological mutations & selection of the fittest to survive.

Leucippus & Democritus argued that all matter is composed of atoms (which are too small to be seen). Atoms cannot be further split into

smaller parts (which we now know to be incorrect). The word atom was meant to imply that there is an upper limit to the division of matter & the term meant they the smallest part could not be divided.

In Greek, the prefix "a" means "not" and the word "toma" means cut, & is meant to indicate that atoms are uncuttable.

www.physlink.com/education/askexperts/aredd2.cfm

The origin of Dalton's theory of the chemical atom remains a contested episode in the history of science. Whether Dalton knew of Lucretius' work is not directly established, but some evidence suggests he did.

philarchive.org/archive/JOHPT

Divisible Atom

Dalton's concept of indivisible atom failed scientific work for the 1800's but new experiments probed the nature of the atom & found the concept needed to be changed.

(recall experiments about protons, neutrons, & electrons.)

Summary: Dalton's belief that all atoms of a given element have the same mass isn't quite accurate

- atomic mass number is the sum of protons + neutrons
- type of atom governed by # protons in the nucleus, that # Z defines the element
- any atoms that have the same Z but different # neutrons are called isotopes
- cannot determine mass of atom by adding the masses of Z and neutrons + electrons because forming nucleus from Z + n causes a small amount of mass to be released as a quantity of energy called the nuclear binding energy ($E=mc^2$).

Periodic Table + electron shells:

$$n=1$$

$1s^1$ H: hydrogen atom - reactive

$1s^2$ He: not reactive, $2e^-$ offers stability
assume based on observation "quota" has been filled
"quota" is a shell of e^- , or a collection of subset used to describe the organization of an atom

$n=2$ $1s^2$ $1e^-$ beyond He filled shell
 $Z=3$ core valence shell valence e^- available for chemical combination.
 Li both H^- and Li^- each have 1 valence e^-

$Z=4$ "Be" not like He, as 2 valence e⁻ are reactive

$Z=5$ • B • 3 valence electrons

$Z=6$ • C. 4 valence e⁻

$Z = 7$ N. 5 valence e⁻

$Z = 8$: 6 valence e⁻

$Z = 9$ \rightarrow Fluorine e-

$Z = 10$: Ne: 8 valence-

$n=2$ $2s, 2p_x, 2p_y, 2p_z$

8 electrons (valence) \rightarrow $1s^2$ filled e^-
core core e^-

$n=3$ $Z=11$ Na - new shell, reactive like H, Li.

$Z=12$ "Mg" 2 valence e^-

$Z=13$ "Al" 3 valence e⁻ core is [Ar]s²p⁶ or [Ne]

$Z=18$: Ar: 18 total e⁻, $2+8+\frac{8}{16}$ inert

pattern recurs with

$$Z = 19 \text{ Hart}$$

$$Z = 20 \text{ "Ca"}$$

then a new pattern of 10 elements
 (transition metals) $\text{Sc} \rightarrow \text{Zn}$ before
 6 more to end at Kr $Z=36$

$$\hookrightarrow 2 + 8 + 8 + 10 + 8$$

Pattern based on physical & reactivity
 properties was used by Dimitri Mendeleev
 (1834-1907) to develop a systematic
 listing/grouping of chemical elements.
 First version 1869

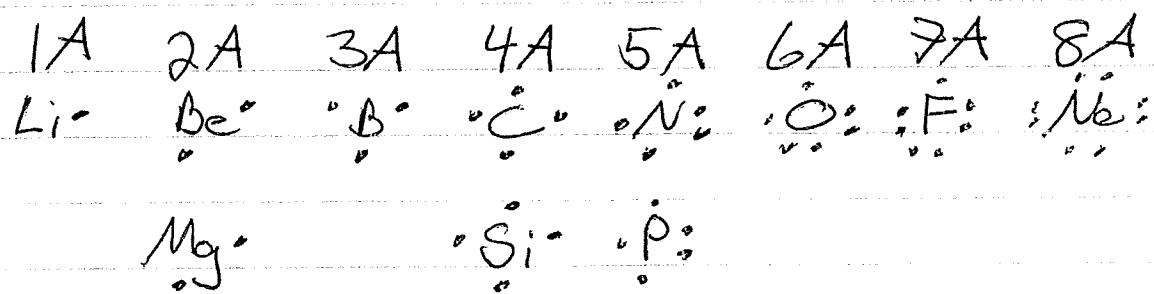
Chemical Combination

Atoms combine to form molecules - they
 combine because this process of sharing e^-
 density lowers the total energy of the system, i.e.,
 it is more favorable.

- When atoms combine, they form bonds
- e^- , particularly valence e^- play a fundamental role in chemical bonding
- if valence electrons are transferred between different types of atoms,
 then they form cations and anions
 & electrostatic forces of attraction
 between the ions give rise to ionic bonds.

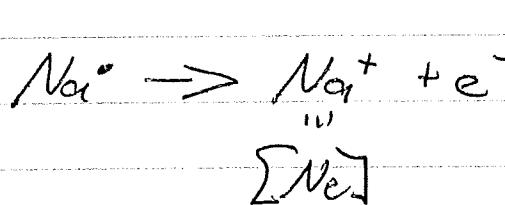
- In other combinations, one or more pairs of valence e^- are shared between the bonded atoms, producing covalent bonds
- In losing, gaining, or sharing e^- 's to form chemical bonds, atoms tend to acquire the electron configuration of noble gases (noble gas or octet rule)
 - H, Li, Be tend to acquire a He $1s^2$ configuration, the duet rule
 - Other atoms (main group) tend to acquire an e^- configuration like the other noble gases $8e^-$ in a $(ns^2 np^6)$ octet rule
 - Transition metal compounds do not follow the octet rule

Lewis Symbols: uses the chemical symbol for an atom to represent the nucleus & core electrons & dots around the symbol to represent the valence electrons.

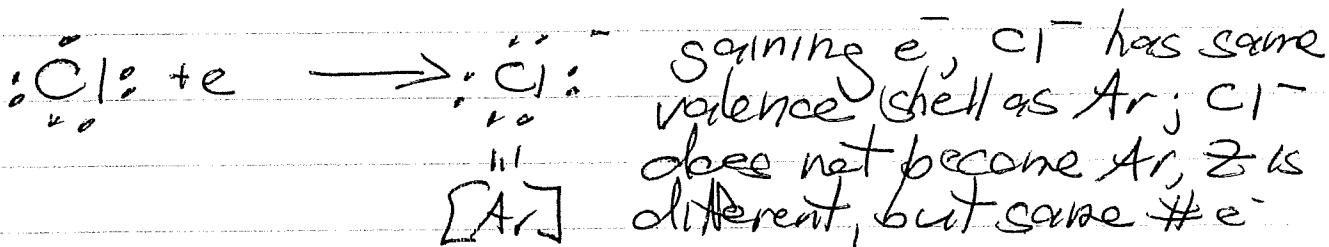


Ionic Bonding

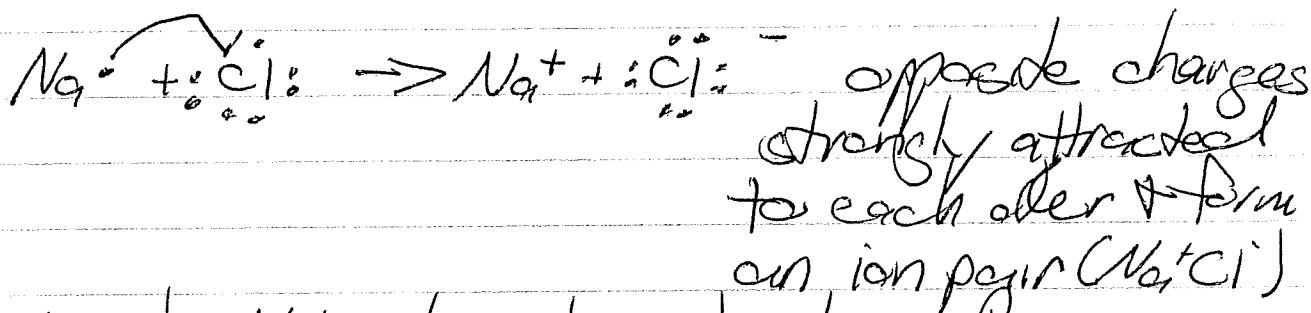
electron configurations of Na & Cl



losing e^- , Na^+ has same valence shell as Ne ; Na^+ does not become Ne , Z is different, but same # e^-



gaining e^- , Cl^- has same valence shell as Ar ; Cl^- does not become Ar , Z is different, but same # e^-

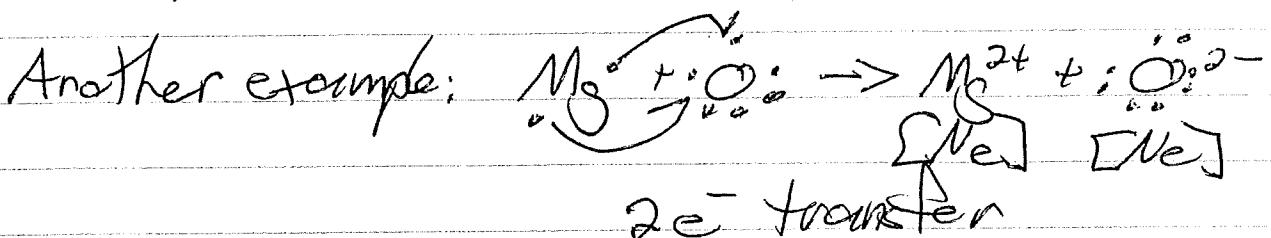


opposite charges
strongly attracted
to each other & form
an ion pair (Na^+, Cl^-)

Each Na^+ interacts not only with one Cl^- but the six neighbouring Cl^- in the solid lattice. Each Cl^- is attracted to six neighbouring Na^+ ions as well. Longer range (weaker) attractions also exist. So do repulsive forces.

Attractive & repulsive forces counteract one another to some extent, but net effect is to produce a regular arrangement of ions arranged in a regular pattern of alternating cations & anions.

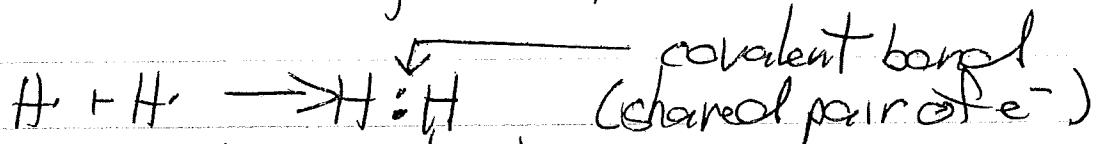
- net attractive electrostatic forces hold cations & anions together are ionic bonds & the cluster of ions is called an ionic crystal



Covalent Bonding

Consider $H^{+} + H^{+} \rightarrow H_2$ hydrogen gas bond cannot be ionic; one H^{+} cannot accept an e^{-} from another H^{+} because all H^{+} have same (egual) electron affinity. Also, as we shall see, loss of e^{-} requires a significant amount of energy.

G.N. Lewis (1875-1946) proposed that a chemical bond is a pair of e^{-} shared between the bonded atoms; it is a covalent bond



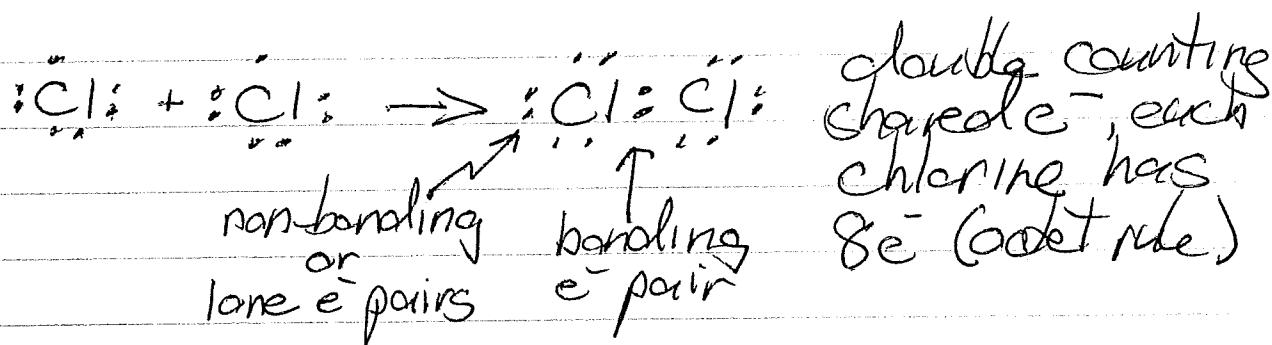
Lewis structure

\hookrightarrow combination of Lewis symbols that represent the formation of covalent bonds between atoms

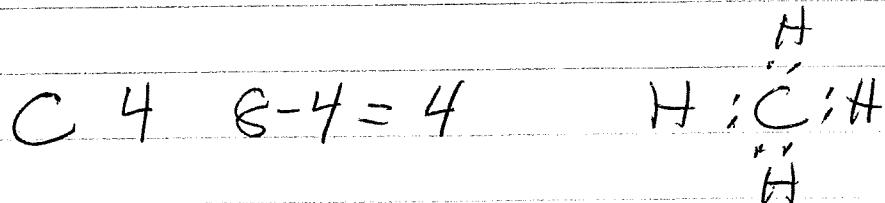
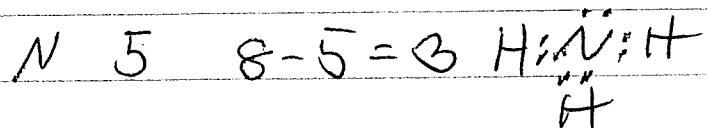
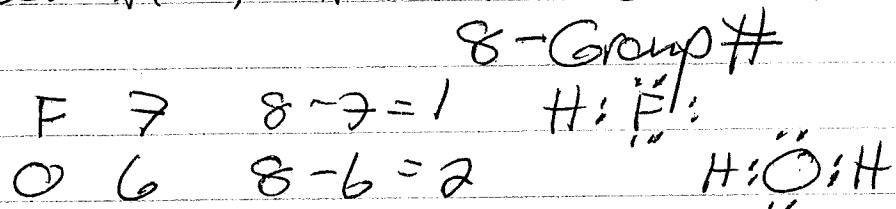
Lewis Structures

- Indicate proportions in which atoms combine
- Show that the bonded atoms typically acquire the e^- configuration of a noble gas, i.e., the octet rule holds (H obeys the duet rule)

$H:H$ double counting | tells us that each shared e^- | H atom has $2e^-$,
conf of He



Observation: # covalent bonds to H:

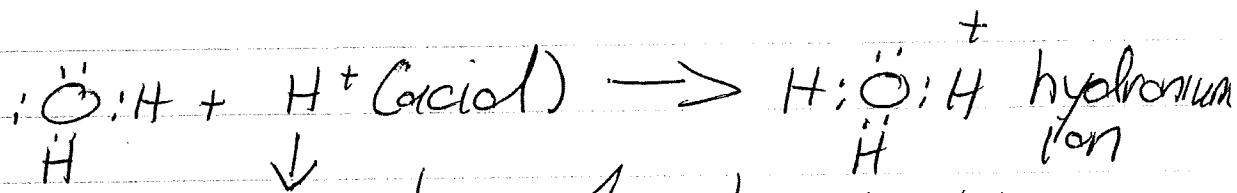


* Note: Lewis structures do not predict molecular shapes

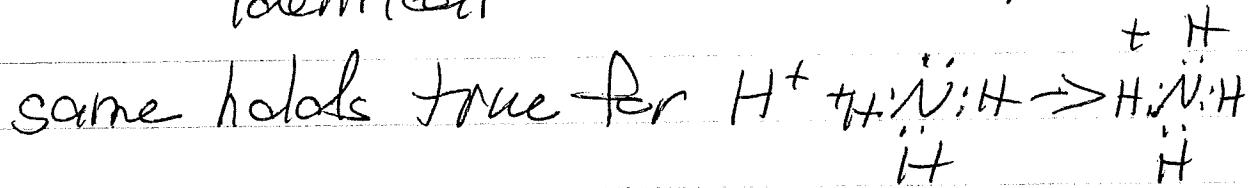
- Molecules considered: H_2 , Cl_2 , HF , H_2O , NH_3 , CH_4

- each of the bonded atoms contributes $1e^-$ to a shared pair of bonding electrons

Sometimes, one atom can provide both electrons of the shared pair to form a coordinate covalent bond



associates with entire H_3O^+ ion / once formed, cannot distinguish among the 3 O-H bonds, they are identical



Multiple Covalent Bonds

so far, covalent bonds share 1 pair of e^- , or bond type called a single bond

two atoms can also share more than one pair of e^- between them, resulting in a multiple bond.

double bond: bonded atoms share 2 pairs of e^-

triple bond: bonded atoms share 3 pairs of e^-



shift 4 unpaired e^-
into regions between
 C & O & we overcome
repulsion

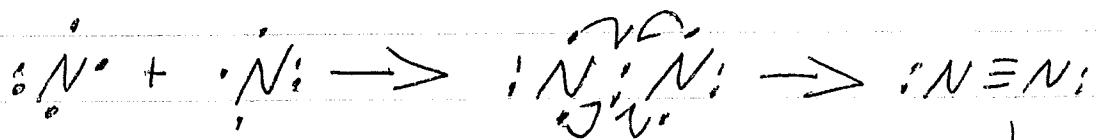
unsatisfactory, none of
the atoms has acquired
a valence shell octet

solid line (bond)
represents 2 e^-



octet rule satisfied

each O atom joined to C atom by
double bond



incorrect
not octet

each N has
8 e^- , correct

2-16

Note: $\ddot{\text{O}} = \ddot{\text{O}}$: Lewis structure for O_2 fits the rules but not consistent with experiment

O_2 known to consist of unpaired e⁻'s
ground-state structure of O_2 does not match Lewis structure

Lewis structures not true solutions unless they fit experimental evidence

See: www.youtube.com/watch?v=Lt4P6ctf8E
"paramagnetism of O_2 "

Polar Covalent Bonds + Electronegativity

Consider the following:



Lewis structure does not show whether the atoms share the e⁻'s equally

\uparrow - the more inclined an atom is to return its e⁻'s, the greater its ionization energy

\downarrow - the more an atom is inclined to acquire an additional e⁻, the greater (more

negative) its electron affinity

summarized by electronegativity: the ability of an atom to attract bonding e⁻'s to itself

- the greater the electronegativity of an atom in a molecule, the more strongly it attracts the electrons in a covalent bond

within a period, electronegativity generally
↑ from left to right

within a group, electronegativity generally
↑ from bottom to top

Difference in electronegativity of bonded atoms is relevant to chemical bonding

- 2 identical atoms have the same electronegativity share a bonding pair of electrons equally. Bonding e⁻'s not any closer to one atom & the pair than the other

Non-polar bond



→ very similar

2-18

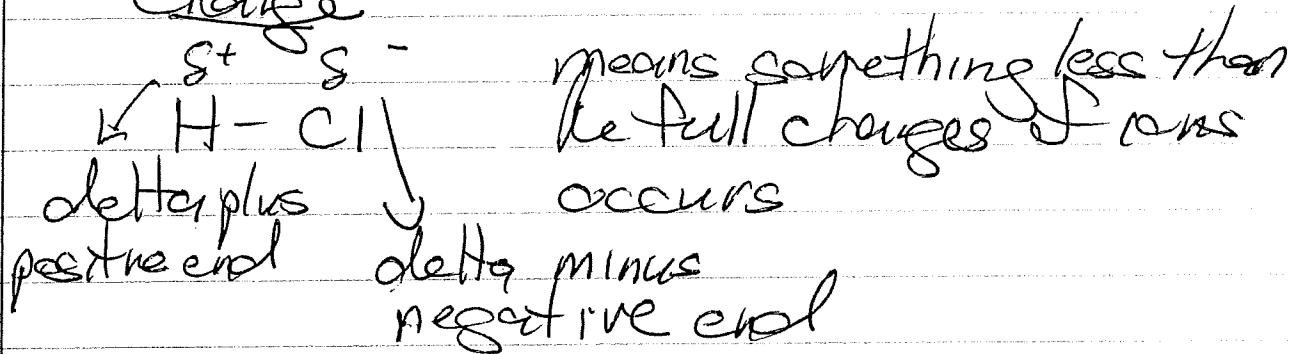
Covalent bonds between atoms with larger electronegativity differences:

- electron pairs are shared unequally
- pair drawn closer to the atom of higher electroneg.

Polar bond H - Cl:



Depict these differences by using Greek letter delta (δ) to indicate partial charge



Another depiction is $\xrightarrow{\text{H}-\text{Cl}}$

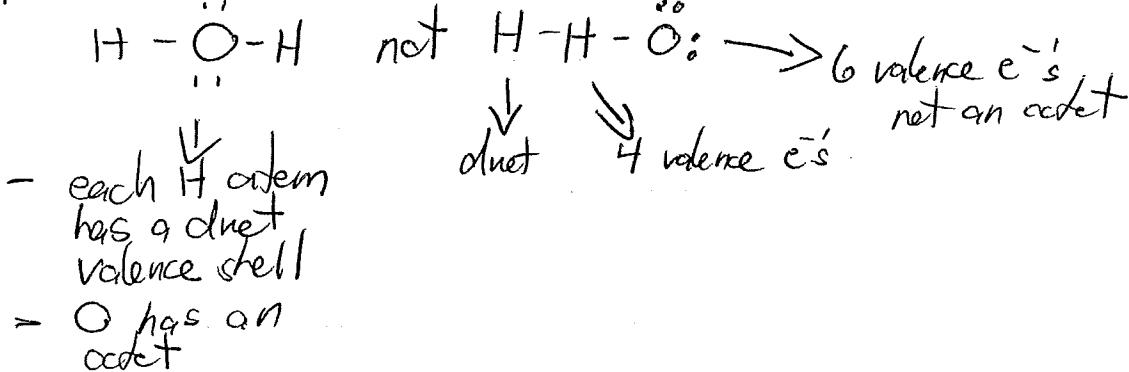
Gilbert N Lewis: The atom & the molecule 2-20

JACS 1916 38 762-785
 French deft German in war Battle of Verdun water created here
 Einstein's theory of general relativity presented in Chicago 1921 → 1922
 Wrigley Field in Chicago open

Strategies for Writing Lewis Structures

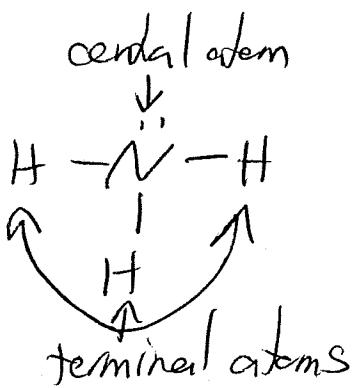
use ke duet & octet rules to write lewis structures

H_2O : correct incorrect



Not always this simple: need a strategy:

arrangement of atoms within a molecule or skeletal structure
 rous order in which atoms are attached to one another
 consists of 1 or more central atoms & terminal atoms



bonded to 2 or
more atoms in
the structure

bonded to only
one other atom

must attach every atom to the
structure by at least 1 bond

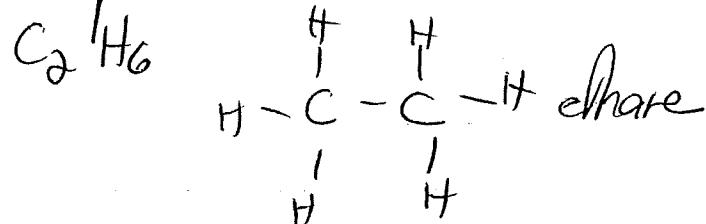
do so by joining bonded atoms
by single line; no attempt to
account for all valence e^-

skeletal structure
is NOT a lewis structure

first step in
deducing plausible lewis structure

1) H atoms are terminal atoms.

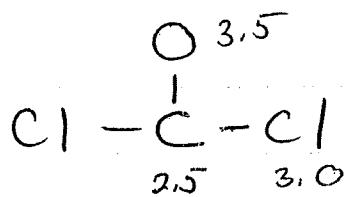
bonded H can only have 2 e⁻'s & form 1 bond
exceptions rare & will not encounter you



2) Central atoms of a structure usually have the lowest electronegativity, & terminal atoms generally have higher electronegativity.

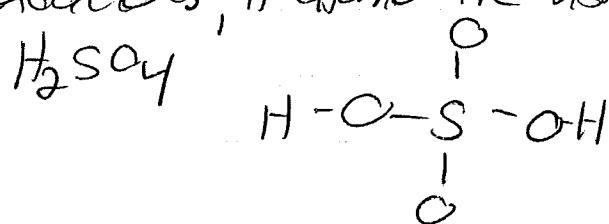
- H exception as it must be terminal (H_2C , NH_3 , CH_3O)
 - F has a higher electronegativity than any other element & is expected to be terminal atom/position

es phosgene COCl_2 (plastics)

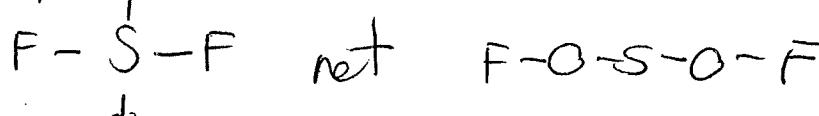


3)

In stocks, H atoms are usually bonded to O atoms



4) Molecules & polyatomic ions usually have compact symmetrical structures : SO_2F_2



Method for Writing Lewis Structures

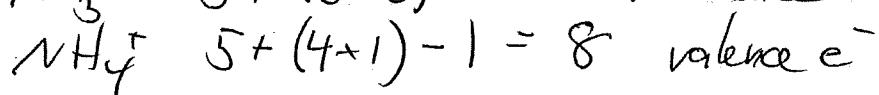
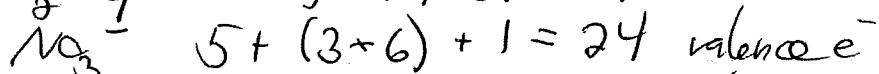
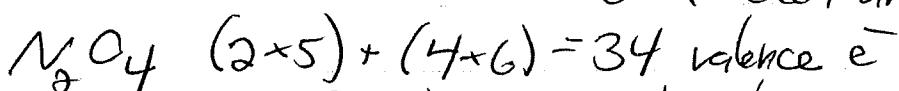
5 step procedure

- Determine total # of valence e⁻; these & no other e⁻ must appear in Lewis structure

total # e⁻ in Lewis structure: sum valence e⁻ each atom

polyatomic: add to the sum of valence e⁻ 1 anions e⁻ for each unit of negative charge

polyatomic: subtract from the sum of valence e⁻ 1 cations e⁻ for each unit of positive charge



- Use previous ideas to write a skeletal structure - connect the bonded atoms by single covalent bonds

- Place pair of e⁻ as lone pairs around terminal atoms of give each (except H) an octet

- Assign any remaining e⁻ as lone pairs around central atom(s)

- If necessary, move one or more lone pairs of e⁻ from a terminal atom(s) to form a multiple bond & a central atom(s)

if # valence e⁻ is sufficient so that all atoms in structure in step 4 have an octet (but for H) structure has only single bonds

If not enough e^- to form octets, necessary to form one or more multiple bonds

atoms most commonly involved in double bonds
C, N, O & S

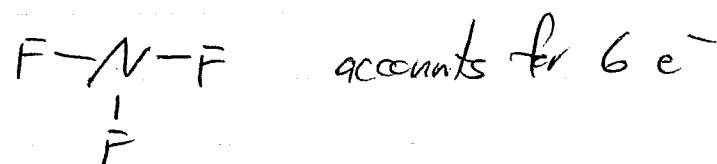
triple bonds

C, N

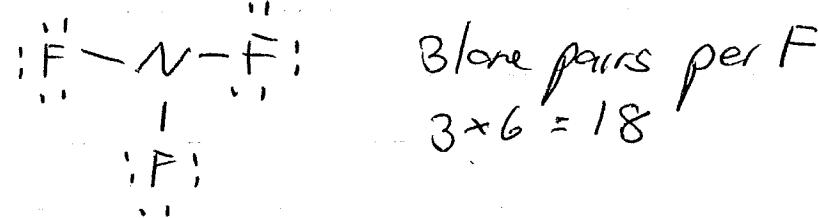
Lewis structure for nitrogen trifluoride NF_3

1) # valence e^- : $(5+1) + (7+3) = 26$
 $N \quad 3F$

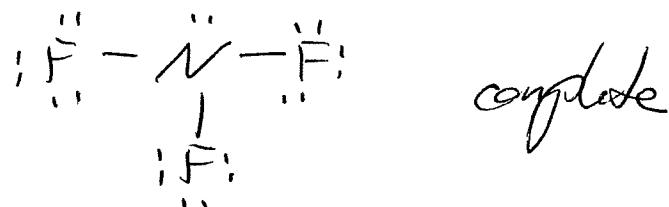
2) skeletal structure: electroneg: $F > N$



3) Complete octets of terminal atoms:



4) Assign lone pairs to central atoms: $6+18=24$
 2 on N

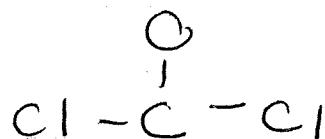


Γ phosgene COCl_2

1) # valence e⁻: $(1 \times 4) + (1 \times 6) + (2 \times 7) = 24$

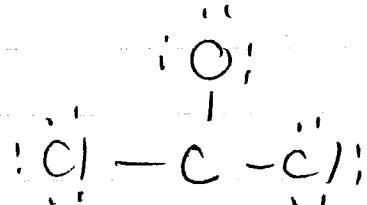


2) skeletal structure:
electroneg
 $\text{O} > \text{Cl} > \text{C}$



6 valence C^-

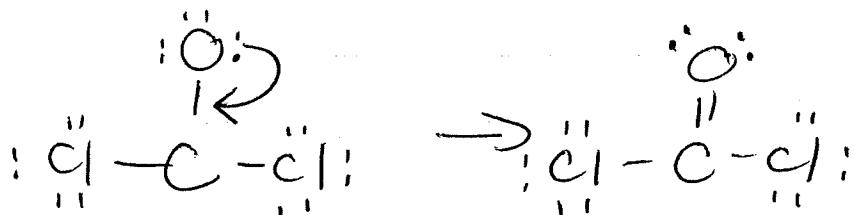
3) complete octet of terminal atoms

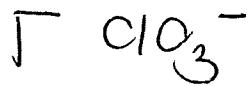


3 pairs, 6 each
18 total

4) Assign lone pairs to central atom(s) $6 + 18 = 24$
accounts for all valence electrons
none available to complete C octet

5) form multiple bonds to complete octet about central atom
complete octet of C by shifting lone pair O^-
from O to form $\text{C}=\text{O}$



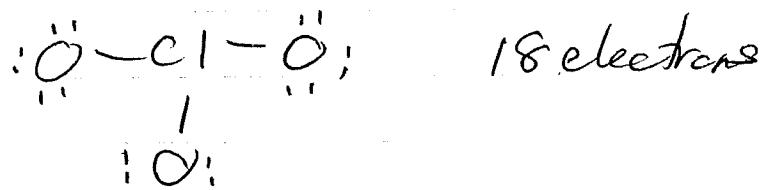


1) # valence e⁻: $(1 \times 7) + (3 \times 6) + 1 = 26$

2) skeletal structure: $\begin{array}{c} \text{Cl} & \text{O}^- \\ | & | \\ \text{O}-\text{Cl}-\text{O} \end{array}$ electron pair O>Cl



3) Complete octets of terminal atoms



4) lone pair skeletal atoms: $6+18=24 \neq 26$
last 2 on Cl



2-26

Formal charge:

When Leached at H_3O^+ , Mg^+ coordinate covalent bond

How do you recognize coord. coval. bond when writing lewis structure?

why atom lowest electron in center?

In $COCl_2$, one double bond - why C & not Cl?

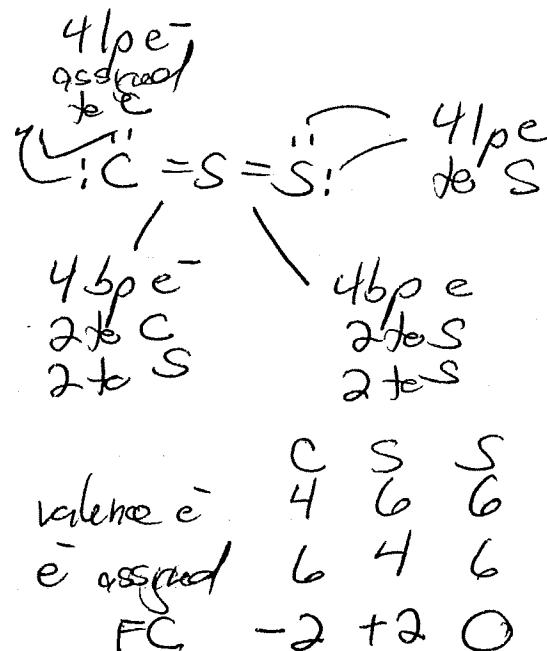
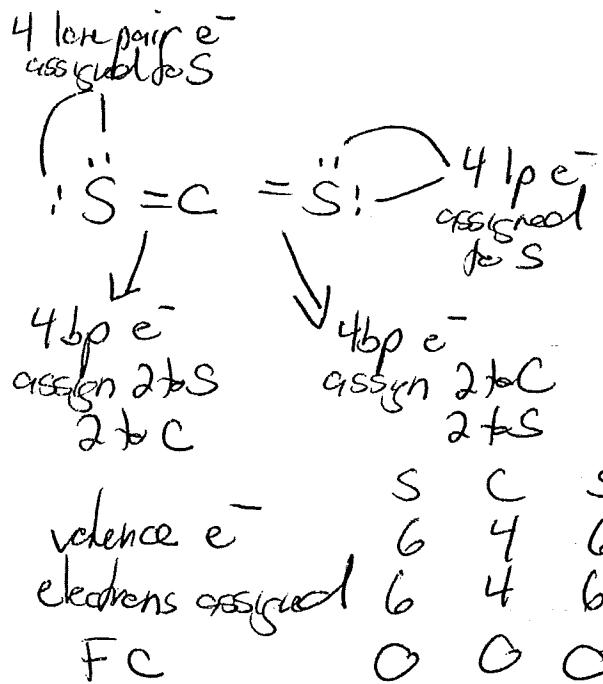
Electron, bond keeping beyond total # valence e^- in lewis structure
 Formal charge: difference between # valence e^- in free (uncombined) atom & # e^- assigned to that atom when bond is written in lewis structure

$$FC = \left(\begin{matrix} \# \text{ valence } e^- \\ \text{in uncombined atom} \end{matrix} \right) - \left(\begin{matrix} \# \text{ valence } e^- \\ \text{assigned to bond atom in lewis structure} \end{matrix} \right)$$

\uparrow
easy to determine

- \downarrow to get this value
- all lone pair e^- are assigned to atom
 - e^- in bond are assigned equally to be 2 bond atoms; half to each atom

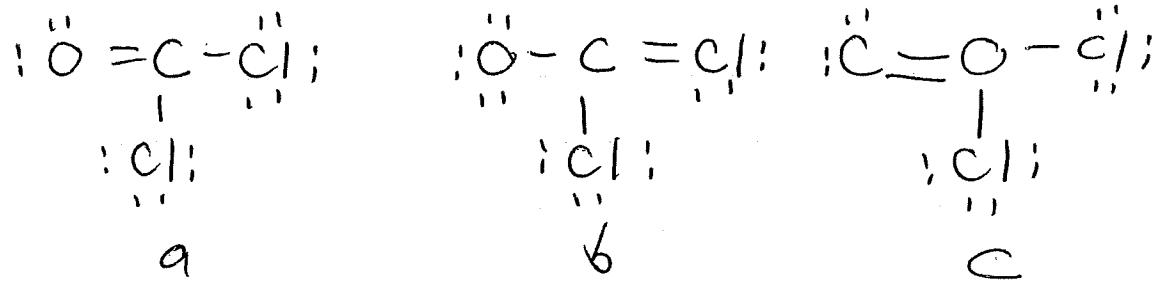
$$FC = \left(\begin{matrix} \# \text{ valence } e^- \\ \text{in uncomb. atom} \end{matrix} \right) - \left(\begin{matrix} \# \text{ lone pair } e^- \\ \text{on bond atom} \end{matrix} \right) - \frac{1}{2} \left(\begin{matrix} \# e^- \text{ in bonds} \\ \text{from atom} \end{matrix} \right)$$



(a) more plausible than (b); no formal charge

FC are hypothetical, atoms do not in a covalent molecule carry these charges

- * ↗ one or more FC indicate presence of coordinate covalent bonds
- usually most plausible Lewis structure is one with no FC (ie zero on all atoms)
- where FC are required, as small as possible, negative FC should appear on most electronegative atoms
- adjacent atoms in structure should not carry formal charges of the same sign
- total FC on atoms in Lewis structure must be zero for a neutral molecule & most equal net charge for a polyatomic ion.



$$FC = \left(\begin{matrix} \# \text{ valence } e^- \\ \text{in uncomb. atoms} \end{matrix} \right) - \left(\begin{matrix} \# p e^- \\ \text{on bound atom} \end{matrix} \right) - \frac{1}{2} \left(\begin{matrix} \# e^- \\ \text{in ligand atoms} \end{matrix} \right)$$

a) O: $FC = 6 - 4 - \frac{1}{2}(4) = 0$
 C: $FC = 4 - 0 - \frac{1}{2}(8) = 0$ plausible
 Cl: $FC = 7 - 6 - \frac{1}{2}(2) = 0$

b) O: $FC = 6 - 6 - \frac{1}{2}(2) = -1$
 C: $FC = 4 - 0 - \frac{1}{2}(8) = 0$ Cl +/ even higher
 -Cl: $FC = 7 - 6 - \frac{1}{2}(2) = 0$ more delocalized than C
 =Cl: $FC = 7 - 4 - \frac{1}{2}(4) = +1$ no formal charge

c) O: $FC = 6 - 0 - \frac{1}{2}(8) = +2$
 C: $FC = 4 - 4 - \frac{1}{2}(4) = -2$ least plausible
 Cl: $FC = 7 - 6 - \frac{1}{2}(2) = 0$

(a) is best

Resonance: Delocalized Bonding

Ozone: Lewis Structure

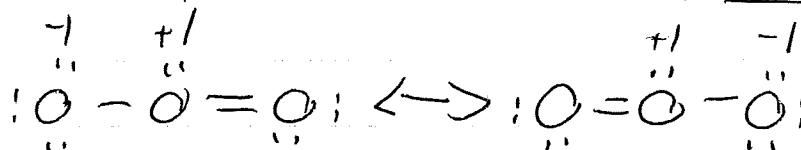
$\ddot{\text{:O}}-\overset{+!}{\text{O}}=\ddot{\text{O}}:$ structure implies 1 O-O bond is single
and the other is double

expt. both are equal/identical
intermediate between single & double bond

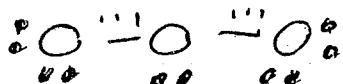
Whenever molecule/ion can be represented by 2 or more plausible Lewis structures, but differ only in the distribution of electrons, the true structure is a composite of hybrid form.

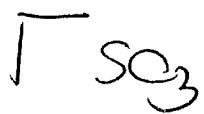
different plausible structures: resonance structures
atoms located in same place in each res. str.
only diff. is distrib. δ^-

actual molecule is then called a resonance hybrid



\Downarrow \swarrow res. bond

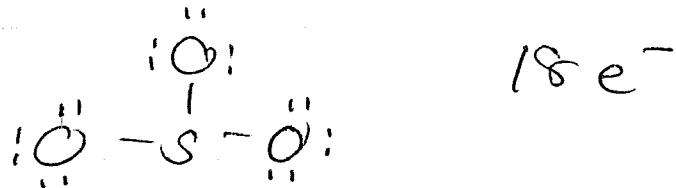




1) # valence e^- : $(1 \times 6) + (3 \times 6) = 24$ valence e^-

2) Skeletal structure: $\begin{array}{c} \text{O} \\ | \\ \text{O}-\text{S}-\text{O} \end{array}$ elect. $\text{S} \leq \text{O}$
 $6 e^-$

3) Cyclic octet:



4) Assign $lp e^-$ to central atom ($6+18=24$)

no $lp e^-$ on
central atom

5) Form multiple bonds & cyclic octet on central atom:

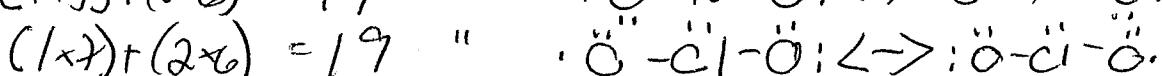
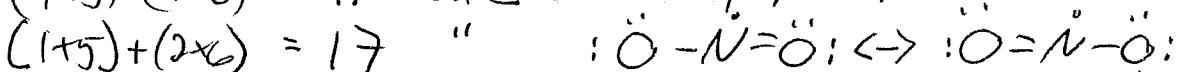


resonance structures

Molecules that do Not follow the Octet Rule

Lewis structures with odd # valence e^- , not possible to

have all e^- in pairs nor satisfy octet rule



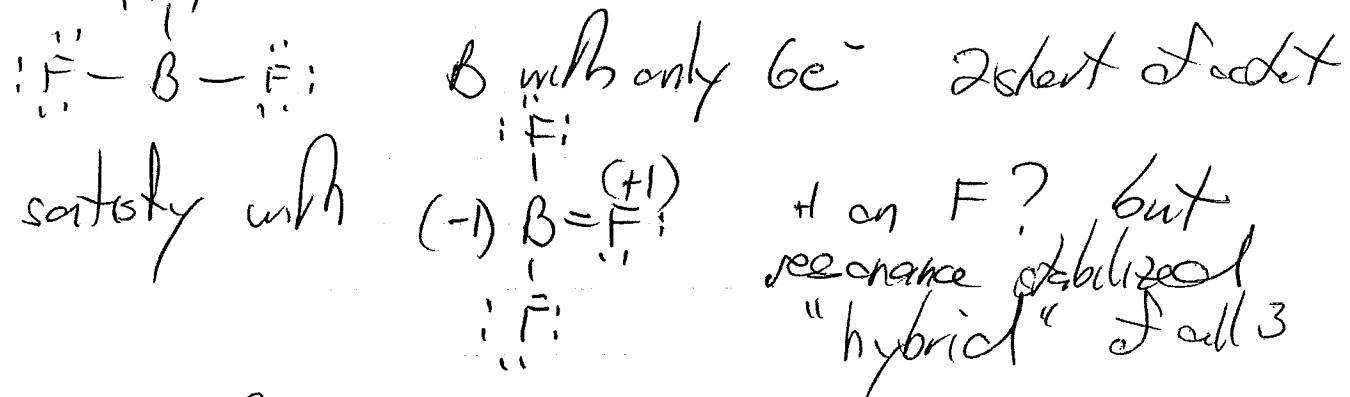
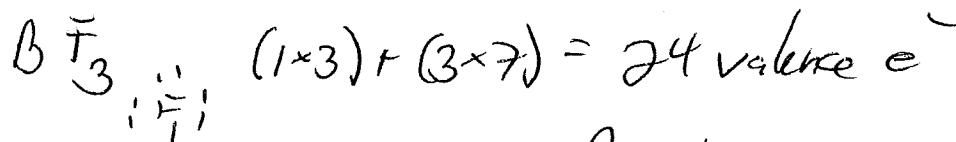
"free radicals"

nitric oxide NO
 dinitrogen pentoxide NO_2
 chlorine trifluoride ClF_3
 chlorine heptoxide ClO_7

Molecules with Incomplete Octets

not enough e^- to give every atom a valence shell octet
 e^- deficient molecules often unusual bonding & are
 reactive

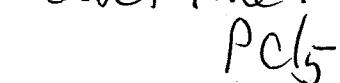
central atom Be, B or Al, not many others



Molecules with expanded Valence Shells

2nd period elements C, N, O, F typically obey
 octet rule

e^- deficient & odd electron exceptions are obvious
 3rd row & higher: can hold up to 18 e^-
 octet rule: 4 bonds but:

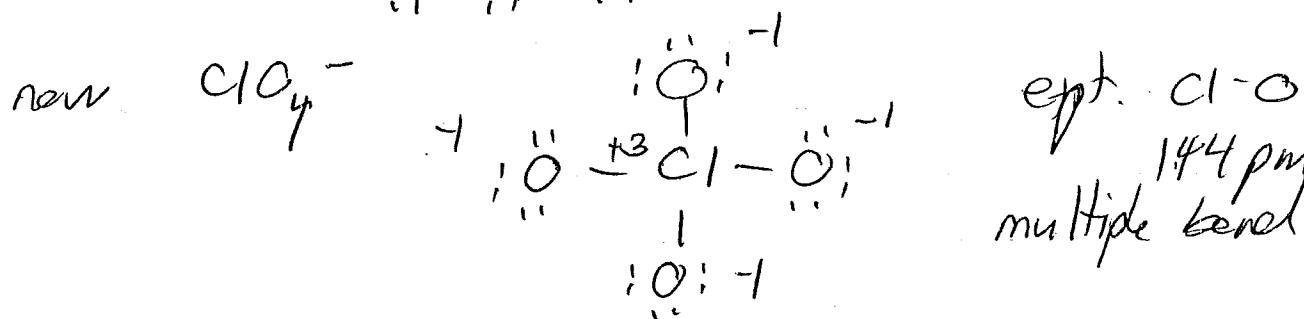
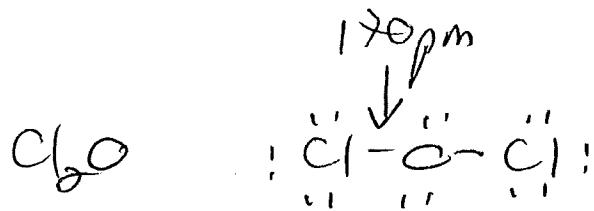


5 bonds
 10 e^-



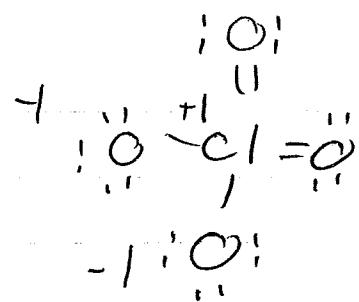
6 bonds
 12 e^-

require expanded
 valence shells



opt. $\text{Cl}-\text{O}$
144 pm
multiple bond character

real & expand octet:



formal charge for Cl lower
bond length shorter

resonance hybrid
structure

Molecular Geometry

The properties (physical) and reactivity chemistry exhibited by molecules is heavily influenced and dependent on the molecular geometry

- molecular geometry = 3D shape of the molecule
 - diatomics (having 2 nuclei) are linear
 - triatomics : linear + bent (angular)
- these molecular geometries arise from the fixed positions of atoms relative to each other
- atoms interact with each other to form molecules
 - atoms interact via bonding interactions
 - ionic interactions are not typically responsible for fixed geometries found in molecules
 - we will therefore focus on the dominant covalent interactions between atoms that give rise to molecular structures & their subsequent physical + electronic properties

Covalent Bond Theories

- 1) VSEPR (valence shell electron pair repulsion model)

A set of empirical rules for predicting a molecular geometry using a correct Lewis Dot representation

2) Valence Bond theory

A more advanced description of orbitals in molecules. We will focus primarily on one part of this theory, namely hybrid atomic orbitals. These work especially well for organic molecules.

3) Molecular Orbital theory

The most modern & powerful theory of bonding. Based on QM.

G.N. Lewis tried to develop a geometrical model for atoms & chemical bonds, but failed.

VSEPR theory (1957) is a simple qualitative model useful for predicting the shapes of individual molecules based on their extent of electron-pair electrostatics (repulsive), but are determined using steric numbers.

Theory also called Gillespie-Nyholm theory (Ronald Gillespie / Ronald Nyholm, Univ College London 1957) after the two main developers.

Premise of VSEPR:

- use a constructed Lewis structure to show all lone pairs & electrons alongside bonds to predict the geometric shape + lone pair behavior of the compound via considering the total coordination #

VSEPR theory:

- based on idea that the geometry for molecule or polyatomic ion is determined primarily by repulsions among the pairs of electrons associated with a central atom.
- electron pairs (groups) may be bonding or nonbonding
- only valence electrons of the central atom influences the molecular shape to a first approximation

Basic assumptions:

- 1) Pairs of electrons in the valence shell of a central atom repel each other
- 2) These e^- pairs try to occupy positions in space that minimize repulsions + maximize the distance of separation between them. This minimizes the overall energy of the system + gives rise to the most stable geometry/structure.
- 3) The valence shell is viewed as a sphere with e^- pairs localizing on the spherical surface but maintaining distance/position relative to each other.
- 4) A multiple bond is treated as one e^- pair (group) + the two or three pairs of a multiple bond are treated as one group.
- 5) Where two or more resonance structures

can be drawn for a molecule. So VSEPR model is applicable to any of them. You will get the same result.

3 types of repulsions occur between electrons for molecule.

- ↓ - lone pair - lone pair lp/lp
- lone pair - bonding pair lp/bp
- bonding pair - bonding pair bp/bp

You will minimize these repulsions to find / predict most likely structure. Search for the weaker repulsion or set of repulsions.

$$lp/lp > lp/bp > bp/bp$$

VSEPR is not part of valence bond theory, which addresses molecular shape through orbitals that are energetically accessible for bonding.

Valence bond theory deals with the formation of σ and π bonds.

Molecular orbital theory is a more fundamental approach for understanding how atoms & electrons are assembled into molecules & polyatomic ions.

Molecular Geometry

molecular geometry = three dimensional shape of molecule
 diatomics (having two nuclei) are linear
 triatomics: linear \pm bent (angular)

Valence-shell electron-pair repulsion (VSEPR)

valence e^- in bonded atoms repel one another
 - mutual repulsion pushes e^- pairs as far from one another as possible - lowest total energy

Predict shapes of molecules & polyatomic ions by VSEPR method:

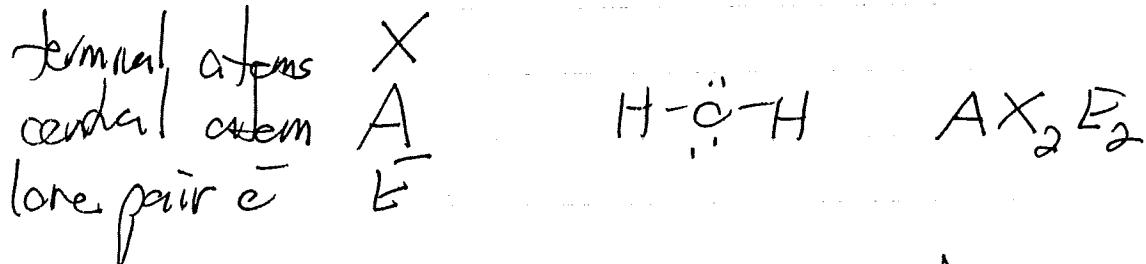
repulsions: involves groups. valence e^- rather than just pairs
 electron group = collection of valence e^- localized in region around central atom but exerts repulsions on other groups of valence e^-

electron groups: single unpaired e^-
 lone pair of e^-

one bonding pair of e^- in single covalent bond
 2 sp^2 or cf in double covalent bond
 3 sp^3 in triple covalent bond

Most common 2, 3, 4, 5 or 6 e⁻ groups about central atom
 mutual repulsion among e⁻ groups lead to an increase
 of groups behind e⁻ group symmetry

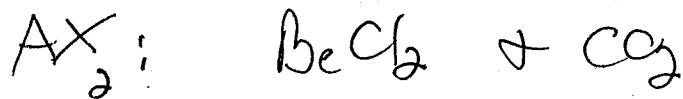
- 2 e⁻ groups: linear
- 3 e⁻ groups: trigonal planar
- 4 " tetrahedral
- 5 " trigonal bipyramidal
- 6 " octahedral
- (7 " pentagonal bipyramidal)

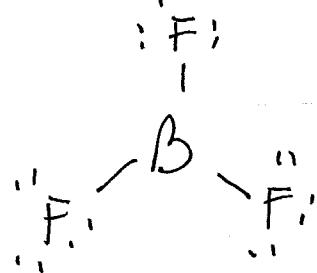


electron group: lone pairs & valence e⁻ are
 geometry/ arranged

molecular geometry: how bonded atoms are arranged

For no lone pairs: AX_n, molecular & electron group
 geometry are the same

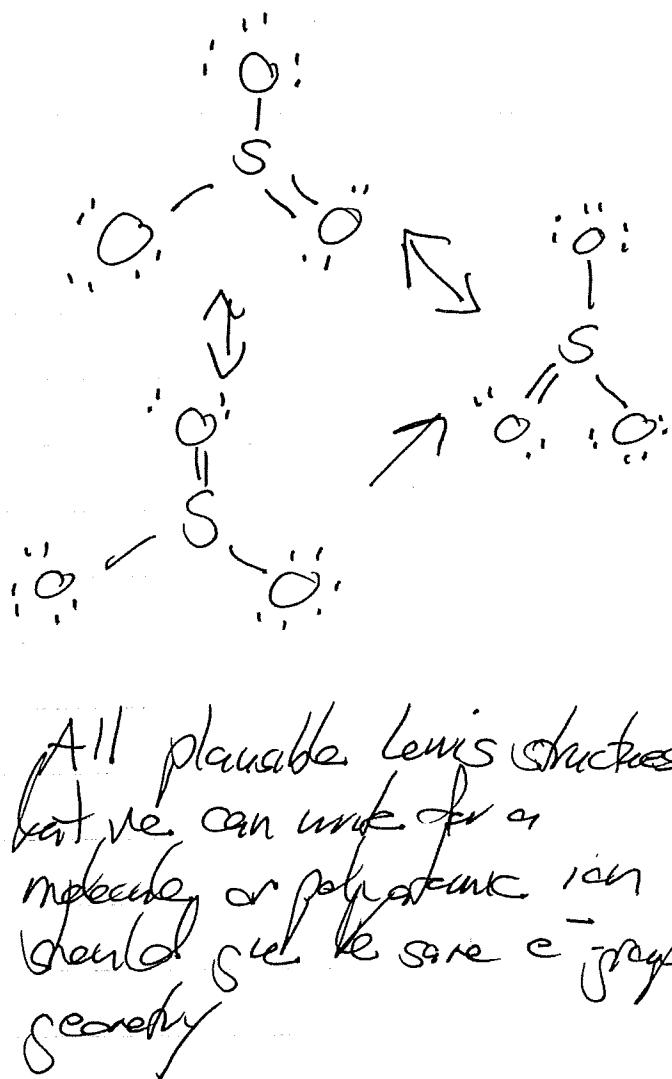
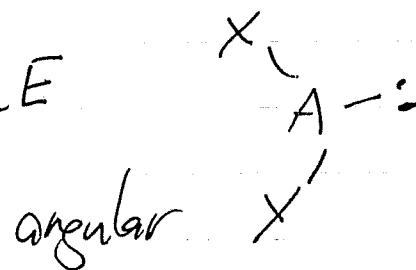




trigonal planar
3 e⁻ groups
3 pairs et in bonds

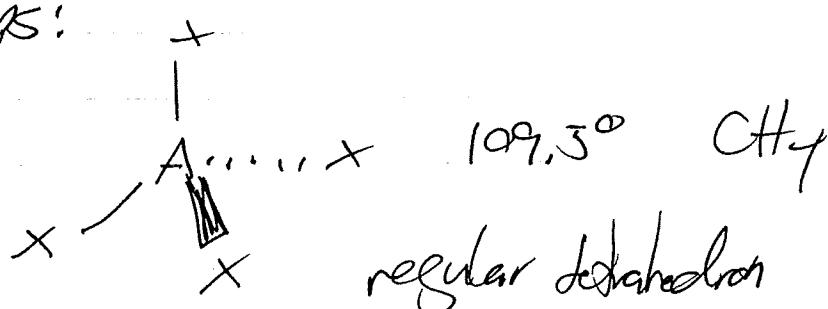
trigonal planar: 3 atoms
in plane; 120°

Now: AXE

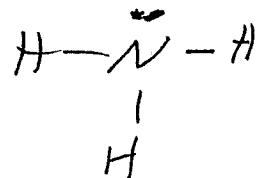
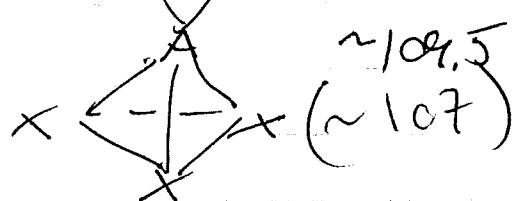


4 Electron Groups:

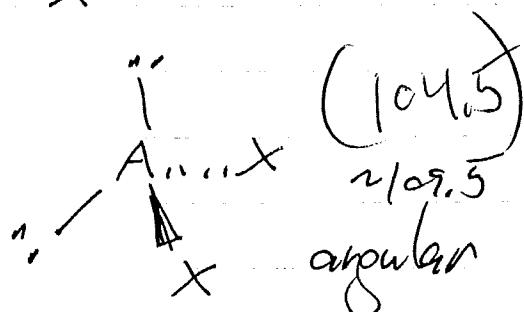
AX_4
no electrons
as lone pairs



AX_3E trigonal pyramidal

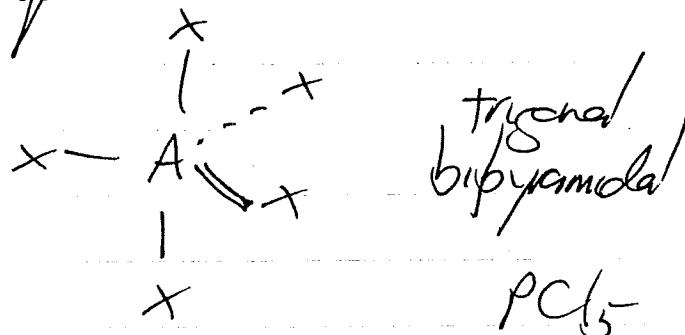


AX_2E_2

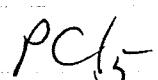


5 electron groups

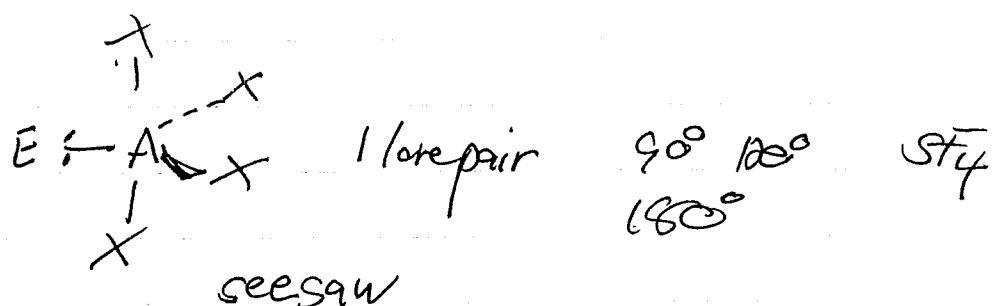
AX_5



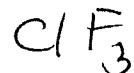
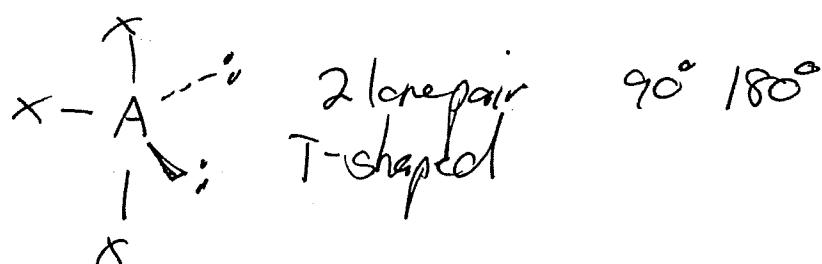
$90^\circ, 120^\circ, 180^\circ$



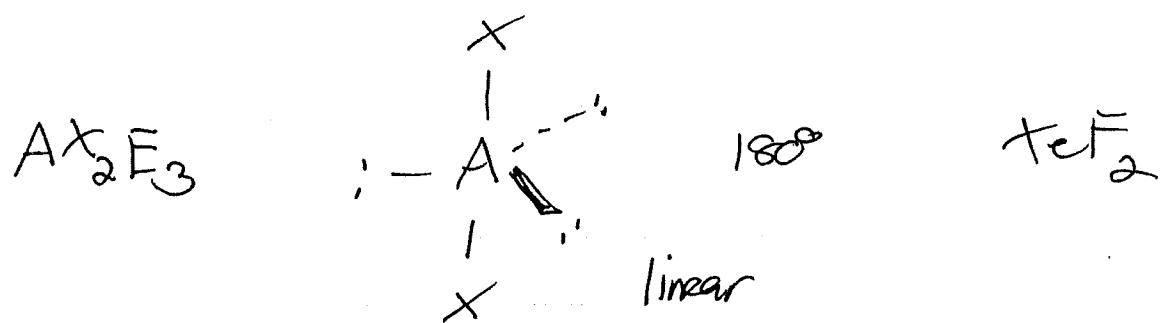
AX_4E



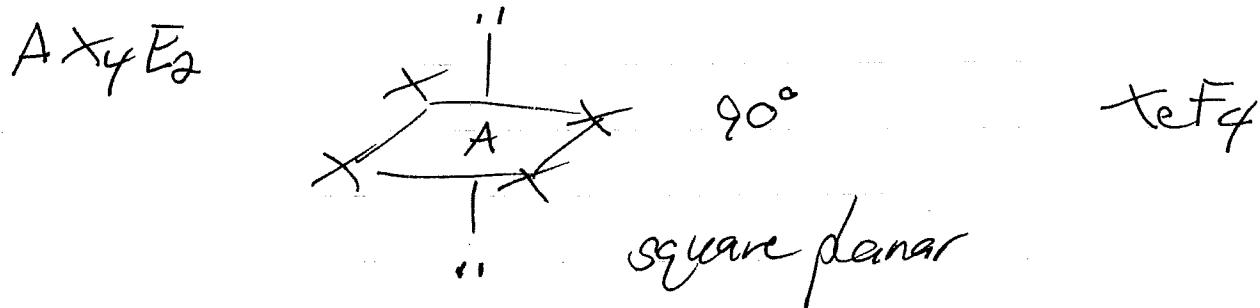
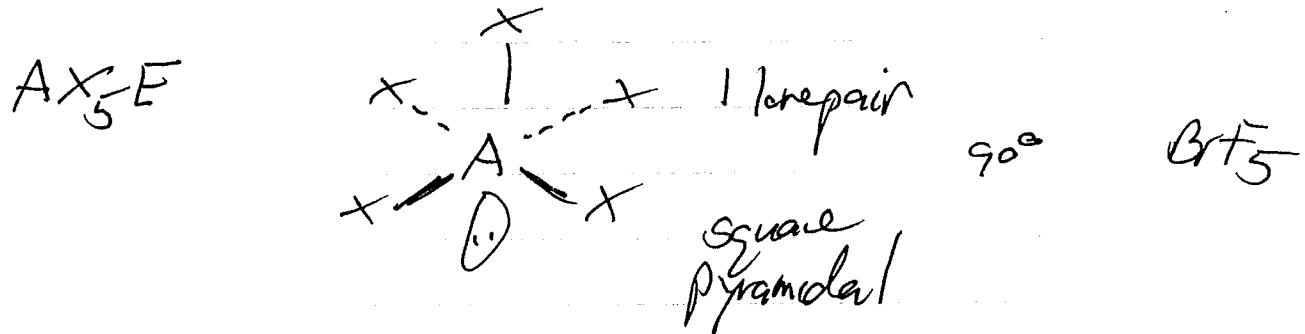
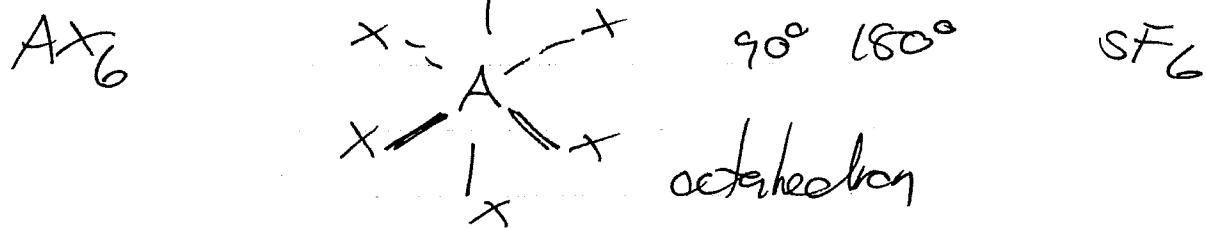
AX_3E_2



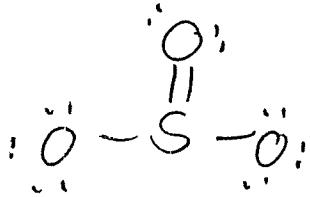
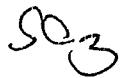
2-51



6-electron groups



4-pt strategy:



1) Draw Lewis structure. It ~~can~~ may be planar, not necessarily the best, if it may have formal charges & be only one of several resonance structures \leftrightarrow a resonance hybrid

2) Determine the e⁻ groups around central atom & identify each as either a bonding S⁺ or a lone pair S⁻
 - bonding group can be either a double or triple bond

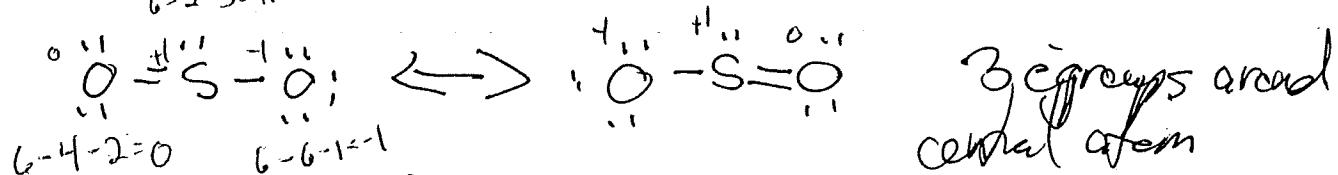
trigonal planar 3) Establish e⁻ group geometry

AX₃
 trigonal planar
 S in center
 $\Rightarrow 120^\circ$ O-S-O

4) Describe molecular geometry based on position around central atom. Vertices occupied by other atoms (not lone-pair electrons)

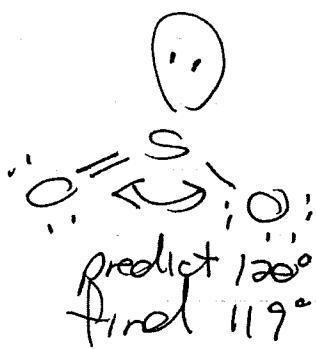
Structures with lone-pair e⁻ AX_nE_m

AX₃E: SO₂: 2 resonance structures



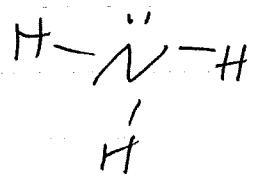
electron group geometry:
 \Rightarrow trigonal planar $\begin{matrix} \text{o atoms at 2 positions} \\ \text{of c + third} \end{matrix}$

molecular geometry based on ~~atoms~~
 \Rightarrow angular or bent



AX_3E : NH_3

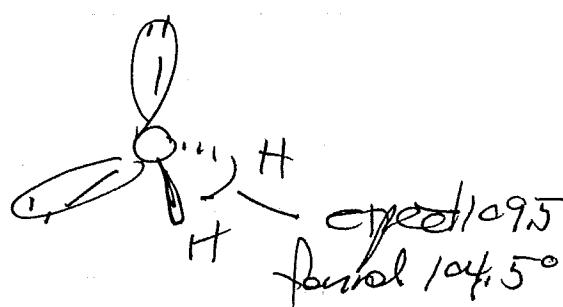
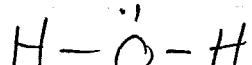
electron group Total
molecular geometry: trigonal pyramidal



predict 109.5°
find 107°

AX_2E_2 : H_2O

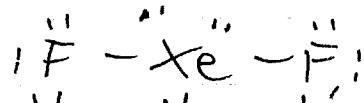
electron group second Total
molecular geometry: bent



- the closer together 2 groups get, the stronger the repulsion between them
 - force of repulsion between 2 groups ↑ dramatically as groups are forced very close together
 - repulsion between 2 groups & bond length decreases significantly when a bond angle is reduced from 180° to 120° to 90°
 - $1p$ electrons spread out more than do $6p$ electrons
 $6p$ & attached to 2 nuclei, e cloud associated with them is pulled, & compact shape.
 $1p$ associated with just 1 nucleus, cloud is more spread out.
- \Rightarrow repulsion of $1p$ & e^- is greater than repulsion between 2 bonds per pair.
- $1p/1p$ repulsions $>$ $1p/6p$ repulsions $>$ $6p/6p$ repulsions



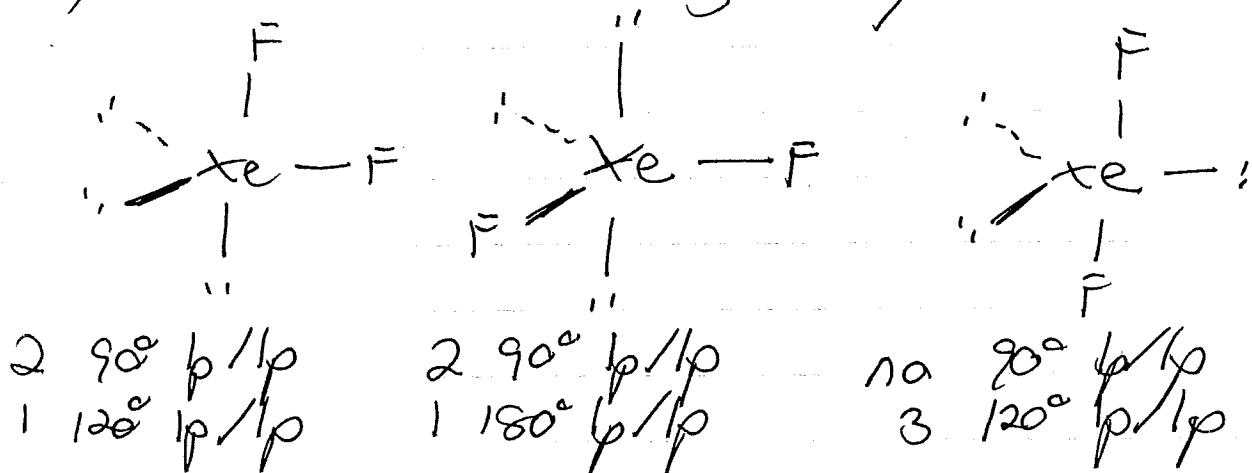
1) Lewis Structure: $8 + (2 \times 7) = 22$ valence e⁻



2) determine # e-groups: 5 e⁻ groups around Xe
2 bonds, 3 lone pair
 AX_2E_3

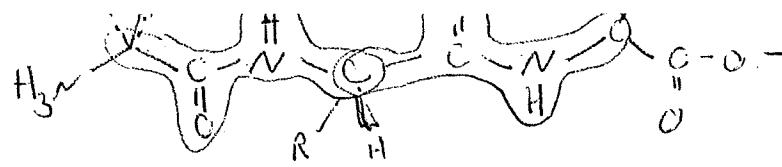
3) e-group geometry: trigonal bipyramidal

4) Describe molecular geometry



based on: $90^\circ > 120^\circ > 180^\circ$, structure 3 represents lowest energy configuration

linear geometry: observed experimentally



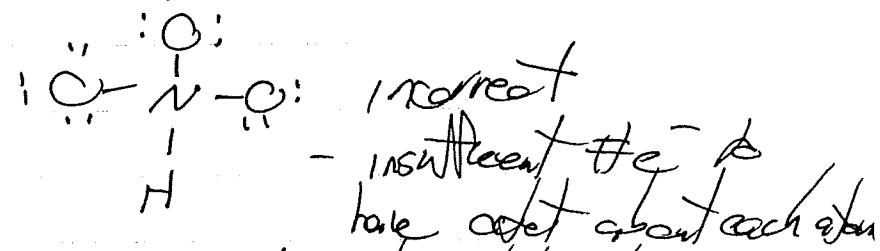
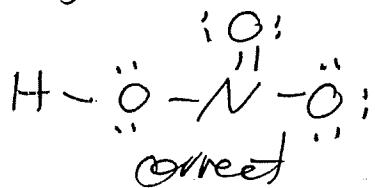
2-56

VSEPR Treatment of Substances with More than 1 Central Atom:

Next: out-of-plane orientation of groups or groups of atoms around each central atom & how compare the results to give an overall description of the molecular geometry.



1) Plausible Lewis structure: $1+5+(3+6)=24$ valence



2) Determine # electron groups around each central atom.
central N: 3 electron groups

2 single bonds, 1 double bond

central O: 4 electron groups

2 bp / 2 lp AX_2E_2

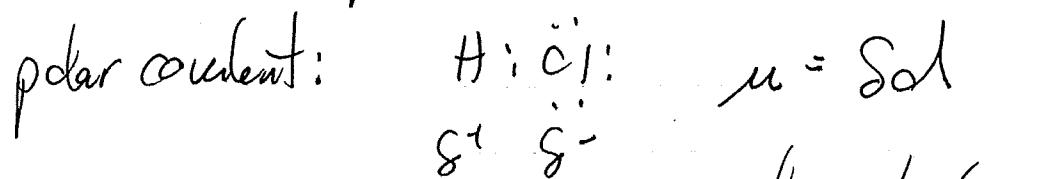
3) N: trigonal planar
O: tetrahedral

bent



Polar Molecules & Dipole Moments

electric charge \times distance
between centers



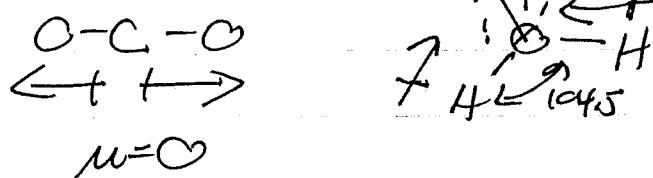
non-polar molecule: $\mu = 0$

polar molecules; non-zero
dipole moment

Bond Dipoles & Molecular Dipoles

Debye: $3.34 \times 10^{-3} \text{ C m}$

$$\mu_{HCl} = 1.07 \text{ D}$$



Molecular Shapes & Dipole Moments

- 1) use electrones. to predict bond dipoles
- 2) VSEPR to predict molecular shape
- 3) molecular shape, determine whether bond dipoles cancel to give a non-polar molecule or combine to produce a resultant dipole moment for molecule

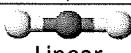
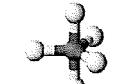
CCl_4 $CHCl_3$ examples

AXE Method

The "AXE method" of electron counting is commonly used when applying the VSEPR theory. The *A* represents the central atom and always has an implied subscript one. The *X* represents how many sigma bonds are formed between the central atoms and outside atoms. Multiple covalent bonds (double, triple, etc) count as one *X*. The *E* represents the number of lone electron pairs present outside of the central atom. The sum of *X* and *E*, sometimes known as the steric number, is also associated with the total number of hybridised orbitals used by valence bond theory.

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs
1	 linear			
2	 linear	 Linear		
3	 trigonal planar	 bent	 Trigonal Planar	
4	 tetrahedral	 trigonal pyramid	 bent	 linear
5	 trigonal bipyramidal	 seesaw (chemistry)	 T-shaped (chemistry)	 linear
6	 octahedral	 square pyramid	 square planar	
7	 Pentagonal bipyramidal	 pentagonal pyramid		

Table 1: VSEPR Geometries and Shapes

Steric Number on Central Atom	Geometry or Template	Idealized Bond Angles	# Bonded Atoms on Central Atom	# Lone Pairs on Central Atom	Formula	Shape
2	 Linear	180°	2	0	AX ₂	Linear
3	 Trigonal Planar	120°	3	0	AX ₃	Trigonal Planar
			2	1	AX ₂ E	Bent
			1	2	AXE ₂	Linear
4	 Tetrahedral	109.5°	4	0	AX ₄	Tetrahedral
			3	1	AX ₃ E	Trigonal Pyramidal
			2	2	AX ₂ E ₂	Bent
5	 Trigonal Bipyramidal	$X_{ax}-A-X_{eq} = 90^\circ$ $X_{eq}-A-X_{eq} = 120^\circ$	5	0	AX ₅	Trigonal Bipyramidal
			4	1	AX ₄ E	See-saw
			3	2	AX ₃ E ₂	"T" Shape
			2	3	AX ₂ E ₃	Linear
6	 Octahedral	90°	6	0	AX ₆	Octahedron
			5	1	AX ₅ E	Square Pyramidal
			4	2	AX ₄ E ₂	Square Planar