CHAPTER 7
Chemical Bonding and Molecular Geometry

7

summary page from 1412 review

$$\Delta H_{rxn} = \sum BE_{(broken)} - \sum BE_{(formed)}$$
$$= \sum BE_{(reactants)} - \sum BE_{(products)}$$

```
run an experiment
```

```
Bond Energy
—bond level—
```

```
Calc
ΔH, ΔG, ΔS
```

```
ΔH(formation)
—molecule level—
```

$$\Delta H_{rxn} = \sum \Delta H_{f(reactants)} - \sum \Delta H_{f(products)}$$

```
ΔG = ΔH + TΔS
```

```
Hess' Law
—equation level—
```

$\underline{\Delta H^{\circ}_{298}}$

① $C_{(s)} + O_2{(g)} \rightarrow CO_2{(g)}$ -394 kJ

② $C_{(s)} + \frac{1}{2}O_2{(g)} \rightarrow CO{(g)}$ -111

③ $CO{(g)} + \frac{1}{2}O_2{(g)} \rightarrow CO_2{(g)}$ -283

                                   -394 kJ

2+3=1 $C_{(s)} + O_2{(g)} \rightarrow CO_2{(g)}$
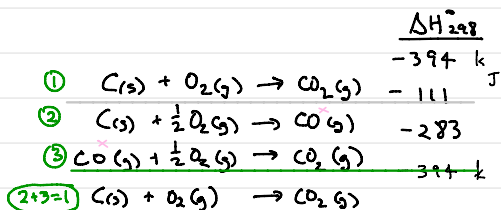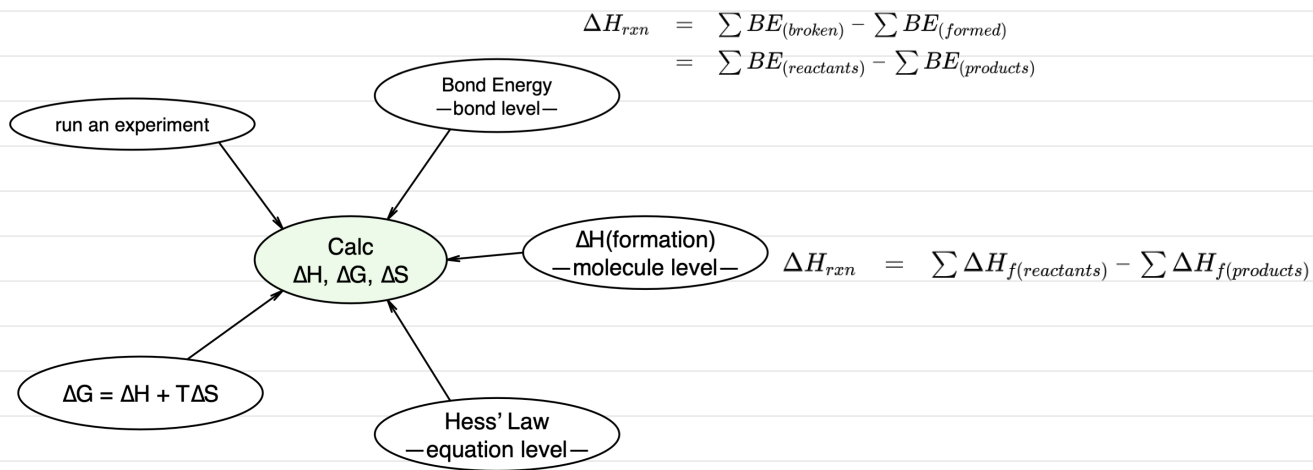
Chapter 7.5: Bond Strength

Ionic Bonding [7.1]

ionic bond — ⊕ ᴍᴜᴄ ⊖
    ↳ opposites attract
      ↳ vs. COVALENT.. <u>no electrons</u> shared in IONIC

The Formation of Ionic Compounds

↳ Combine to make CHARGE NEUTRAL compound
↳ eg. $Al\,O \longrightarrow Al^{3+}\,O^{2-} \xrightarrow{\;x\text{-multiply}\;} Al_2O_3$
↳ Technically $\}$ ✗ ionic "MOLECULE"
           ✓ "UNIT" or "FORMULA UNIT"
↳ Tell-Tell $\}$ ① Metal + Non-metal
    Sign   ② Opposite sides of PC

Electronic Structures of Cations

Main Group Elements

↳ Isoelectric w closest Noble Gas

↳ But, _Exception_ for select heavier Representative element ...

    ... INERT PAIR EFFECT — atypically low energy of valence s- electron pair

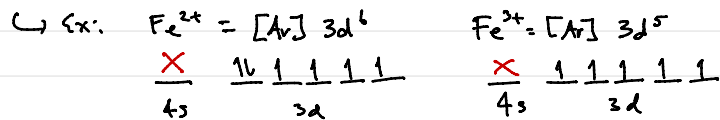↳ _Exception 2_: Mercury forms diatomic ion Hg_2^{2+}, in add'n to monatomic Hg^{2+}

Transition Elements

↳ Most have 2+ or 3+ : loss of outermost "s" electrons, any maybe 1 or 2 "d" electrons

↳ Filling (AUFBAU) vs. Loss Order
- "s" orbits : <u>FIFO</u> (first in, first out)
- "s" orbits fill before "d" orbitals, but are lost before them, →

↳ Ex: Fe^{2+} = [Ar] $3d^6$ Fe^{3+} = [Ar] $3d^5$

    ✗   ⇅ ↑ ↑ ↑ ↑   ✗   ↑ ↑ ↑ ↑ ↑

   4s   3d   4s   3d
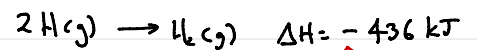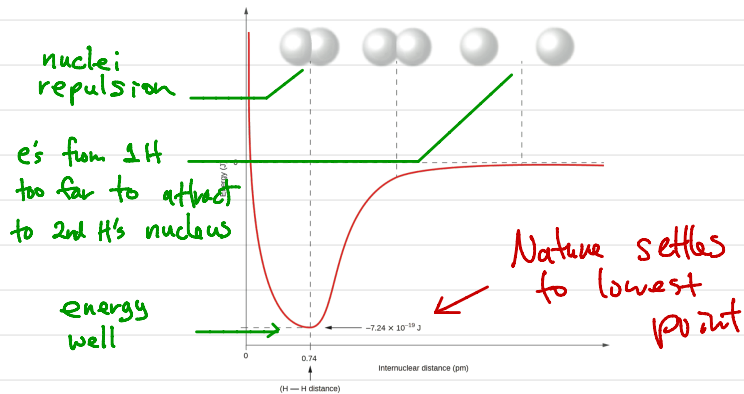
↳ Form when: neutral NON-metal gains electrons to fill its "s" and "p" valence subshells.
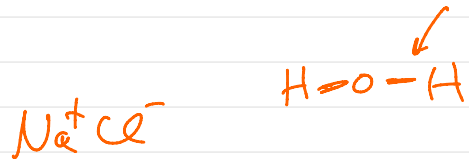
covalent bond — SHARE electrons

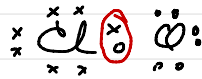↳ comprising elements lay in p-block (+ Hydrogen)

Formation of Covalent Bonds

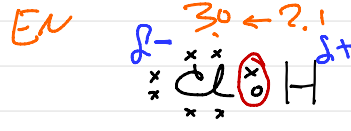↳ Form b/c ΔE (after bonding) < ΔE (before bonding)
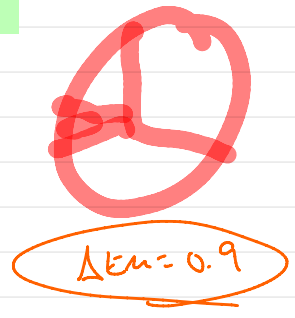
nuclei
repulsion

e's from 1H
too far to attract
to 2nd H's nucleus

energy
well

Nature settles
to lowest
point

$2H(g) \longrightarrow H_2(g)$ $\Delta H = -436 \text{ kJ}$

EXO
favorable

$Na^+ Cl^-$

$H-O-H$

Pure vs. Polar Covalent Bonds

EN

δ- $3.0 \leftarrow ?.1$ δ+

$\ddot{Cl} \ddot{O} H$

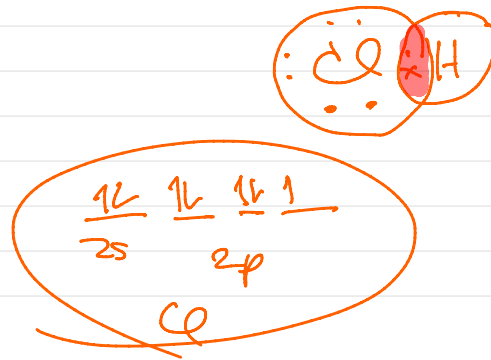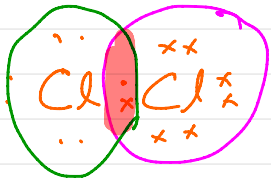Cl — Cl
PURE
COVALENT
(equal sharing)

vs.

$3.0 \leftarrow + 2.1$

Cl — H
POLAR
COVALENT
(UNequal sharing)

$\Delta EN = 0.9$

Both atoms have same EN

One atom (Cl) has a greater
EN than the other atom (H)

$\frac{\uparrow\downarrow}{2s} \quad \frac{\uparrow\downarrow}{} \frac{\uparrow\downarrow}{2p} \frac{\uparrow}{}$

Cl

Electronegativity

electronegativity — measure of unequal sharing
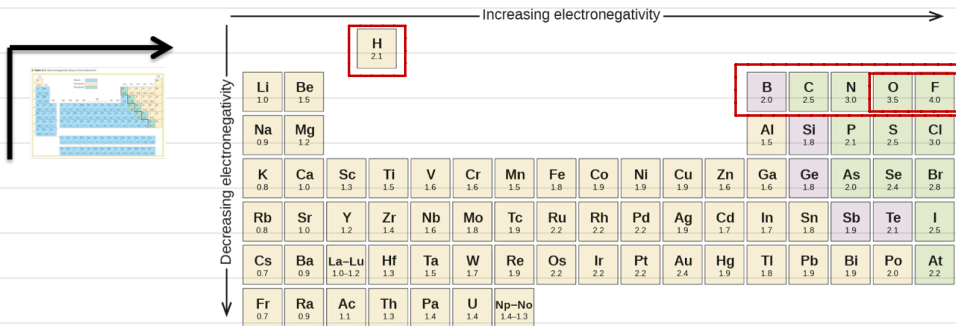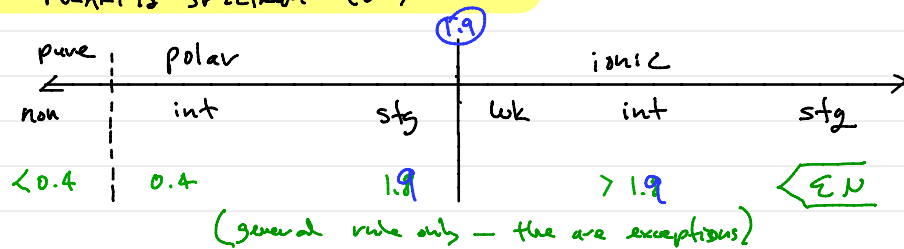

Electronegativity versus Electron Affinity

• ELECTRON AFFINITY of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol.
• ELECTRONEGATIVITY describes how tightly an atom attracts electrons in a bond... It is a dimensionless quantity that is calculated, NOT measured.
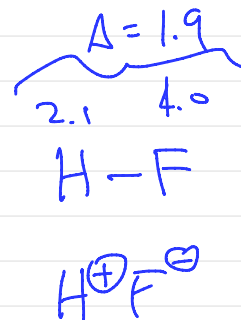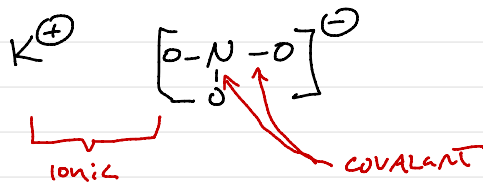
↳ ΔEN = estimate of Polarity

ex: H–H (0), H–Cl (0.9, polar), NaCl (2.1, ionic)

"POLARITY SPECTRUM" (wks)

pure	polar		ionic		
non	int	stg	wk	int	stg
<0.4	0.4	1.9		>1.9	EN

(general rule only — there are exceptions)

Mixed Compounds

KNO_3 = $K^{\oplus}$ $\left[O–N–O \right]^{\ominus}$
                              |
                              O

ionic   COVALENT

$\Delta = 1.9$

2.1   4.0

H–F

$H^{\oplus} F^{\ominus}$
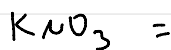
√ trend

Se, Ba, Si, Sc   < F

Ba < Sc < Si, Se   < F → | Ba < Sc < Si < Se < F |

1.8 ↗   ↖ 2.4
need table

↑EN

↓EN

(EX) Direction of Polarity
¿Place an arrow to identify the direction of polarity in each of the chemical species below?

2.5 2.1   3.0 2.1   2.5 3.5   3.5 2.1
C — H   N — H   C — O   O — H
←┬   ←———┬   ┬——→   ←———

←┬   ←┬   ┬——→   ←┬
C — Cl   N — H   C — O   O — H

<CAVEAT: sections [7.3] and [7.6] will be taught together>

<CAVEAT: sections [7.3] and [7.6] will be taught together>

Molecular Structure and Polarity [7.6]

Lewis Symbols   [P345/353]

Lewis symbol   —   Valence electrons

ex: ·Ca·   :Ö:

Lewis Structures   [P 347/355]

└─ The Octet Rule   [P 347]

└─ Double and Triple Bonds   [P 348]

Writing Lewis Structures with the Octet Rule   [P348/356]

Exceptions to the Octet Rule   [P353/361]

└─ Odd-electron Molecules   [P353]

└─ Electron-deficient Molecules   [P353]

└─ Hypervalent Molecules   [P354]

VSEPR Theory

└─ Electron-pair Geometry versus Molecular Structure   [P368]

└─ Predicting Electron Pair Geometry and Molecular Structure   [P371]

└─ Molecular Structure for Multicenter Molecules   [P376]
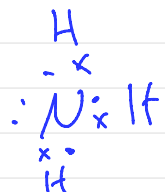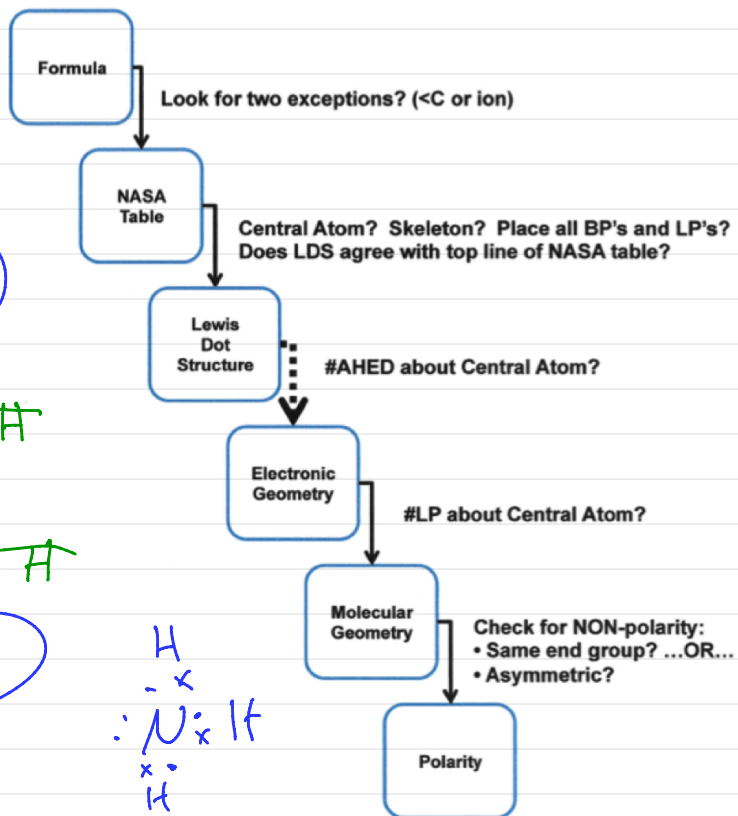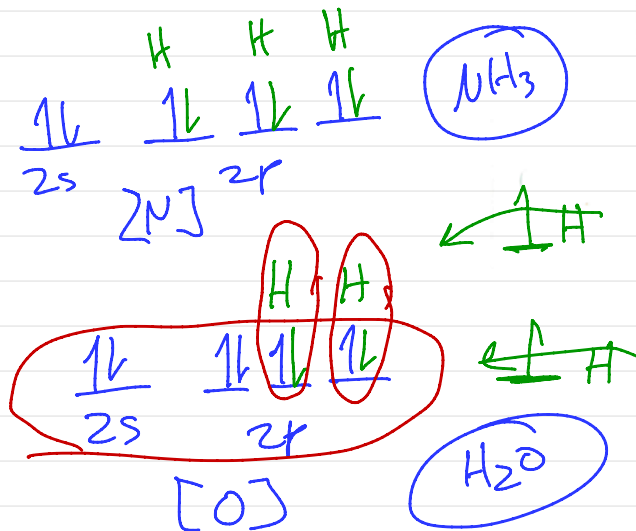
Molecular Polarity and Dipole Moment   [P 378/386]

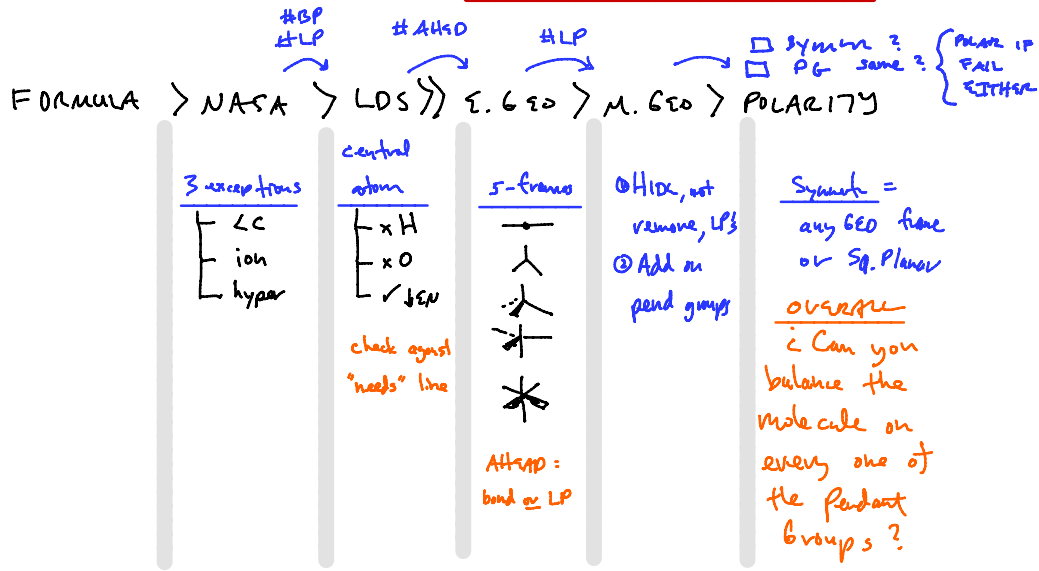└─ Properties of Polar Molecules   [P 380]

The NASA Protocol

NOTE:

This is a study aid I invented from surveying the work of others…
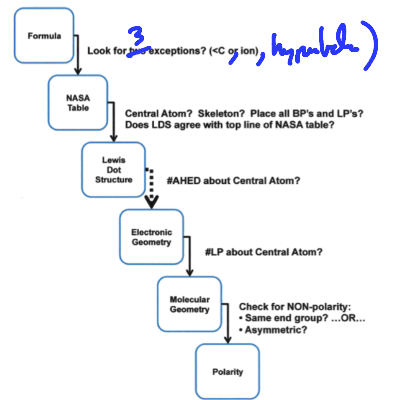it is NOT found in textbooks

H   H   H
⇂↾   ⇂↾ ⇂↾ ⇂↾
2s   2p
$[N]$ NH_3

H H
⇂↾   ⇂↾ ⇂↾ ⇂↾
2s   2p
$[O]$ H_2O

⇽ $\overline{IH}$

⇽ $\underline{IH}$

H
$:\ddot{N}\!\!\times\! H$
H

Formula

Look for two exceptions? (<C or ion)

NASA Table

Central Atom? Skeleton? Place all BP's and LP's?
Does LDS agree with top line of NASA table?

Lewis Dot Structure

#AHED about Central Atom?

Electronic Geometry

#LP about Central Atom?

Molecular Geometry

Check for NON-polarity:
• Same end group? …OR…
• Asymmetric?

Polarity

[7.3]   **[7.6]**

#BP
#LP   #AHED   #LP   □ Symm ?   POLAR IF
                                          □ PG Same ?   FAIL
                                                             EITHER

FORMULA > NASA > LDS >> E. GEO > M. GEO > POLARITY

3 exceptions
- <C
- ion
- hyper

central atom
- x H
- x O
- ✓ δEN

check agnst
"needs" line

5-frames
—•—
人
．人
⫠
✳

ATTMD:
bond or LP

① HIDE, not
remove, LP's
② Add on
pend groups

Symmetry =
any GEO frame
or Sq. Planar

OVERRIDE
¿ Can you
balance the
molecule on
every one of
the Pendant
Groups ?

CHECKLIST: PROTOCOL FOR THE DETERMINATION OF
ELECTRONIC & MOLECULAR CONFIGURATIONS

Formula
Look for **3** exceptions? (<C or ion), hyperhalo)

NASA
Table
Central Atom? Skeleton? Place all BP's and LP's?
Does LDS agree with top line of NASA table?

Lewis
Dot
Structure   #AHED about Central Atom?

Electronic
Geometry   #LP about Central Atom?

Molecular
Geometry   Check for NON-polarity:
                  • Same end group? ...OR...
                  • Asymmetric?

Polarity

Molecular shapes determined by bond angles between atoms

↳ bond angle
↳ bond distance

118°

Bond angle

H

H

Bond length (Å)
(center to center)

C ══════ O

1.21Å
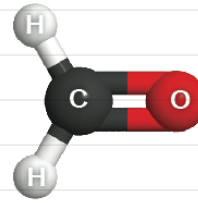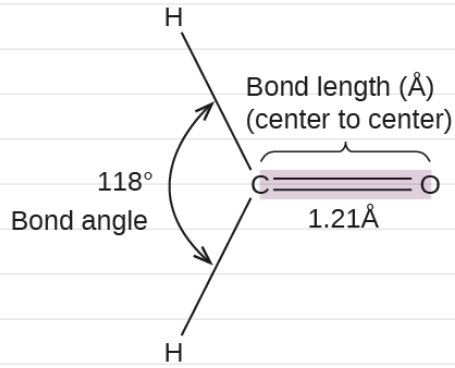
VSEPR Theory: Valence shell electron-pair repulsion theory

5-Electronic Geometries

AH₂D

linear
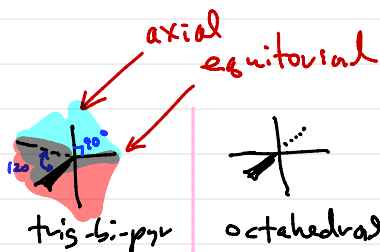①

trig-planer
②
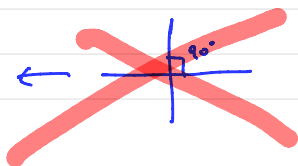
tetra
③

axial
equitorial

120° 90°

trig-bi-pyr
④

octahedral
⑤

Electronic Geometry versus Molecular Structure

trig-planer ②	tetra ③	trig-bi-pyr ④	octahedral ⑤
bent 120	trig pyr	see saw	sg. pyramid
	bent 109	T-shape	sg. planar
		linear	T-shape
			linear
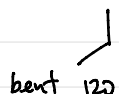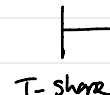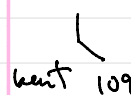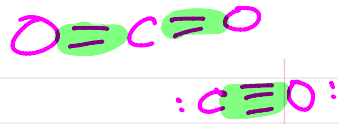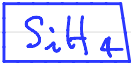
Tue, Nov 5

O≡C≡O

:C≡O:

SiH₄

$N = 1(8) + 4(2) = 16$
$A = 1(4) + 4(1) = 8$
$S = [8 \ OF]$ 8
$A' = [0 \ LP]$ 0

LDS

H—Si—H (with H above and below)

H
|
H — Si — H
|
H

has 8, needs 8

4 ATOMS

0 LP

Polar If
Fail Symm
Fail PG   :OR:

☑ Symm
☑ EG
⋮ NONPOLAR

e's → pairs → bond

4 flow

AHED

area   density
high
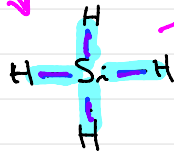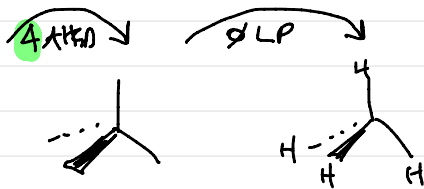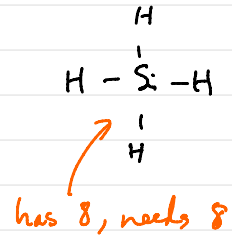
MG
① single bond
② dbl bond
③ triple bond
④ lone pair

EG

AtbED

$\#es \xrightarrow{NKA} pars \xrightarrow{LOS} bond$

#es	pars	bond
2	1	—
4	2	=
6	3	≡

MG

EG

EG only they

CHO_2^-

CHO_2^-

$N = 1(1) + 1(4) + 2(6) = 26$

$A = 1(4) + 1(1) + 2(6) + 1 = 18$

$S = [C + DP] \leftarrow 8$

$A' = [S \, LP] \leftarrow 10$

$\left[H - C = \ddot{O} \right]^-$

$\left[H - \overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} - \ddot{O} \right]^-$

has 6, needs 8

3 AHdD   Ø LP   ☑ Symm
                          ☒ PG

                          ∴ POLAR

H—C(=O)(O)

MG
tvy planer

← Hole
  #
  LP
  Ø

EG
trig planar

#
AHdD
= 3
∴ tvj μ
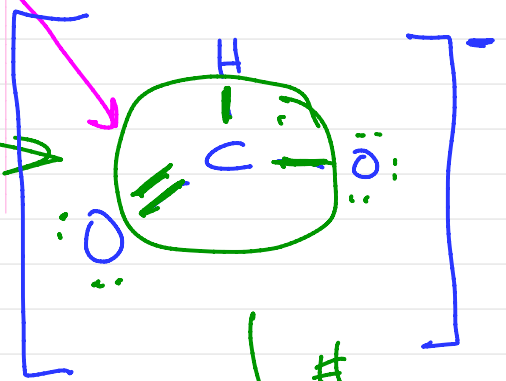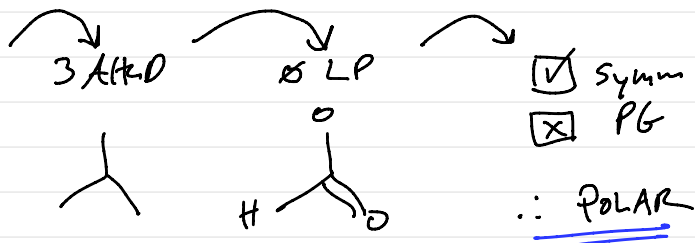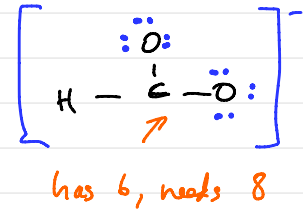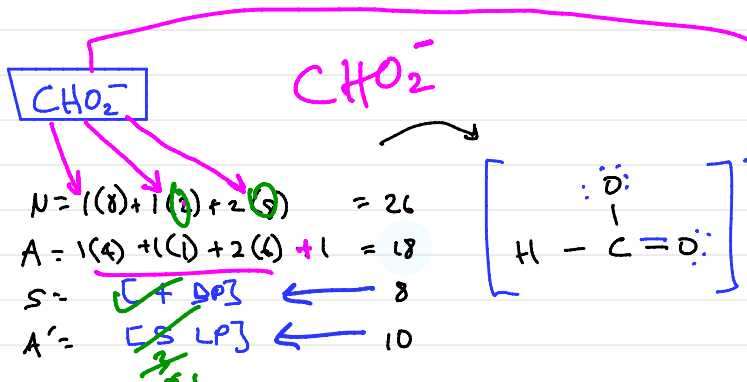
NO^+

$N = 1(8) + 1(8) = 16$

$A = 1(5) + 1(6) - 1 = 10$

$S = [3 \, BP] \quad 6$

$A' = [2 \, LP] \quad 4$
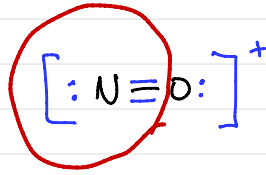
$$\left[\; : N \equiv O : \; \right]^+$$

$$\left[\; : N - \overset{..}{\underset{..}{O}} : \; \right]^+$$

has 4, needs 8

2 ATTeD

1 LP

$\longleftarrow \bullet$

$: \longleftarrow \bullet \longrightarrow O$

☑ SYMM

☒ PG

∴ POLAR

OF_2
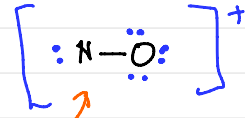
$N = 1(8) + 2(8) = 24$
$A = 1(6) + 2(7) = 20$
$S = [2\ BP] \quad 4$
$A = [8\ LP] \quad 16$
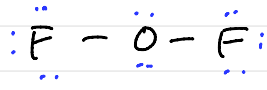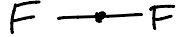
:F — O — F:

2 Atk O

F —•— F

☑ SYMM
☑ PG

∴ NON·POLAR

:F—O—F:

has 8, needs 8

H —Ö— H

Three Exceptions

↳ Work as above, except there will be one UNPAIRED
electron
↳ Place it on the least electronegative element, if possible.
↳ ex:

$$:N = \ddot{O}: \qquad \text{not} \qquad \ddot{N} = \ddot{O}.$$

$$
\begin{array}{llll}
H = hi = & \text{Group 1} & \rightarrow & \text{has 1, needs 2} \\
Be = & \text{Group 2} & \rightarrow & 2 \qquad 4 \\
B = & \text{Group 3} & \rightarrow & 3 \qquad 6
\end{array}
$$

(e' → pair → bonds)

$x - A - x$
$x = A$
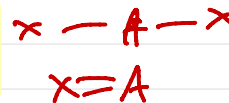
↳ Greater - than - octet : 10 e's or 12 e's
↳ _Textbook method_ : place all left-over e's on CTRL ATOM
↳ _NASA Protocol_ : convert LP to BP
↳ ex: XeF_4

(1a)
(1b)
(2)

Xe   F
$N = 1(8) + 4(8) = 40$
$A = 1(8) + 4(7) = 36$
S   2 BP → 4   4   2
A   16 BP → 14   32   16
$\frac{-12}{2}$

e's pairs

:F̈ — Xë — F̈: (with F above and below)

6 AHRD

→ 2 LP

F —⧸— F (with F, F around)

:F̈ — Xe⊕ — F̈: (cross structure with F above and below)

F̈
F : X : F̈
F̈ (crossed out in blue)
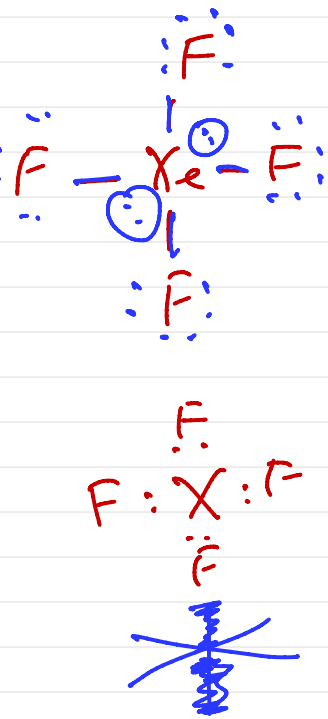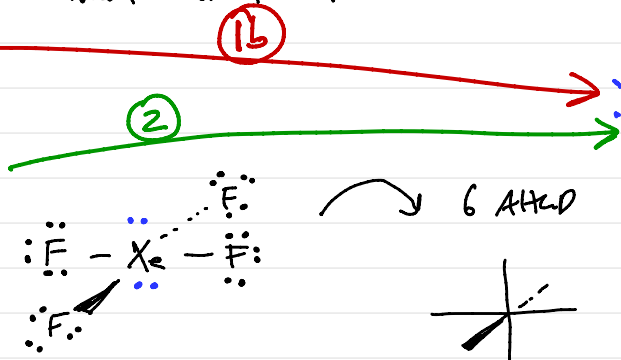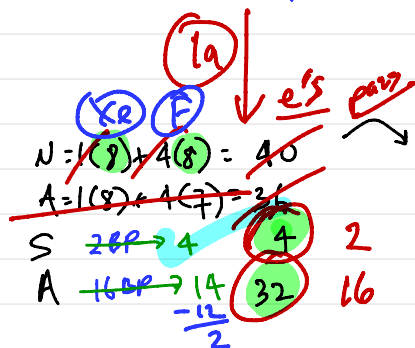
XeF_6
$N = 1(8) + 6(8) = 56$
$A = 1(8) + 6(7) = 50$
$S = [3 or] 6 \quad 6$
$A' = [22 \, LP] \quad ^{19} \quad 44$

☑ SYMM
☑ PL
∴ NON-POLAR
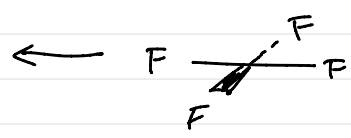
Fine-tuning bond angles

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

lone pair > triple bond > double bond > single bond
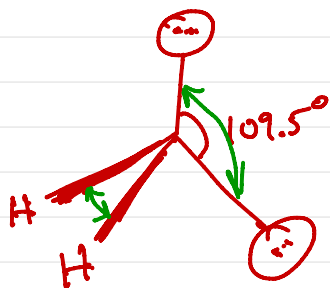
Molecular Polarity and Dipole Moments in Bonds and Molecules

Bond

$$\mu = Qr$$

$$\underline{\text{bond dipole moment}} = (\Delta EN)(\text{dist between charges})$$

$$\text{bond} = \Sigma (\text{vectors})$$

H—O
      \
       H

O=C=O

O=C=S
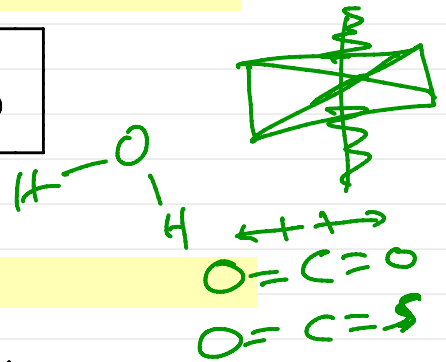
Whole Molecule

polar molecule — dipole (or else, its "nonpolar")

dipole moment — measure extent of CHG SEPARATION

non polar   polar

☑ Amp   ☒ Symmetry ?
☑   or ☒ pendant group same ?
} def'n POLAR vs. NONPOLAR

☒ or ☒   ☑ ☑ Symmetry ?
          are both all
          pendant gr.?
          (% same ?)

non polar

polar, if each is false.

Properties of Polar Molecules

└ Polar molecules align in electric field

⊕⊕⊕⊕ ⊖ → ⊕ ⊖⊖⊖⊖

Thursday, Nov 7

Calculating Formal Charge

↪ eq: FC = (# Valence e's) − (#LP e's) − (# BP)

↪ alt· homo-cleave LDS bonds, then compare to "A"-value

: in neutral atom, as in PC

(EX) ¿What is the formal charge of each atom of the ion CHO_2^-?

CHO_2^- (earlier example) →

The (−) chg is on an oxygen

=or=

FC   H: $1 - 0 - 1 = 0$
     O: $6 - 6 - 1 = -1$
     O: $6 - 4 - 2 = 0$
     C: $4 - 0 - 4 = 0$

$$:C \equiv O: \quad \longrightarrow \quad \overset{-1}{:C:} \overset{+1}{:O:}$$

$$Na^{+} Cl^{-}$$

FC C: 4 −2 −3 = −1
    O: 6 −2 −3 = +1
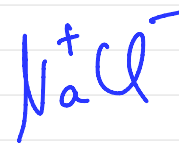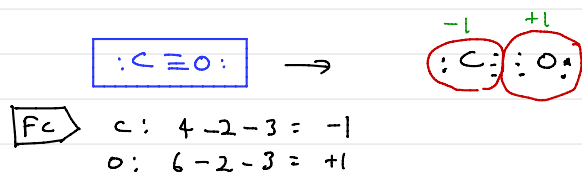
PROCESS SUMMARY FOR DETERMINING FORMAL CHARGE

① Draw LDS, using all "dots"
② Homolytically cleave each bonding pair, giving one electron to each of the associated atoms
③ Count up the total number of electron associated with each atom, and compare that to the atom's group number
④ • award a -1 for each electron greater than the group number
  ↳ eg, a Group 6 element with 8 'formal' valence electrons would be assigned a formal charge of –2
  ↳ as in: O_2^-
  • award a +1 for each electron less than the group number
  ↳ eg, a Group 5 element with 4 'formal' valence electrons is assigned a formal charge of +1
  ↳ as in: N^+

Using Formal Charge to Predict the Most Stable of Possible Structures

↳ Indicates most stable structure
(i) "∅" Formal Chg preferred
(ii) Closest to "∅" charge
(iii) adjacent formal Charges are "∅" or "Opposite SIGN"
(iv) ↳ Chg on more EN element

NO_2^-

$$\ddot{N} = O - \ddot{\ddot{O}}:$$

$$:\ddot{O} = N - \ddot{\ddot{O}}:$$
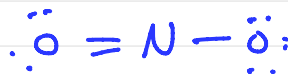
(EX) Formal Charge
¿Write the most stable structure for nitrite ion?

$$\left[:\ddot{N} = \ddot{O} - \ddot{\ddot{O}}: \right]^-$$
$$\quad -1 \quad +1 \quad -1$$

$\underline{or}$

$$\left[:\ddot{O} = \ddot{N} - \ddot{\ddot{O}}: \right]^-$$
$$\quad ∅ \quad ∅ \quad -1$$
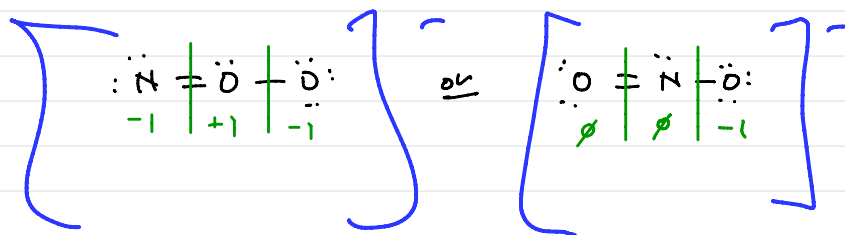
↪ " shifting " dbl & triple bonds
↪ get same structure when have chones of where
   to add Bonding Pair

$$\left[\ :\ddot{\overset{\ominus}{O}}\ -\ \dot{\ddot{N}}\ =\ \ddot{O}\ :\ \right]^{-} \longleftrightarrow \left[\ :\ddot{O}\ =\ \dot{\ddot{N}}\ \ominus\ddot{O}\ :\ \right]^{-} \equiv \left[\ :O\ =\!=\ N\ =\!=\ O\ :\ \right]^{-}$$

resonance   structures
(windshield   wipers)

$$:\ddot{O}\ -\ \dot{\ddot{N}}\ \ominus\ddot{O}\ : \longrightarrow \ddot{O}\ =\ N\ -\ \ddot{O}\ : \qquad :\ddot{O}\ =\!=\!=\ N\ =\!=\!=\ \ddot{O}\ :$$
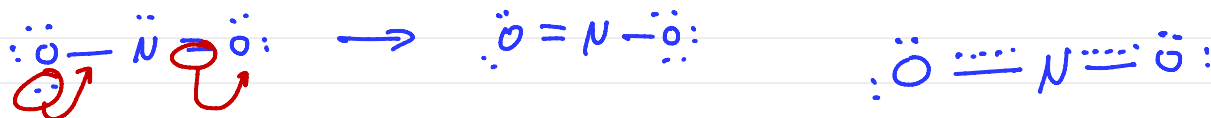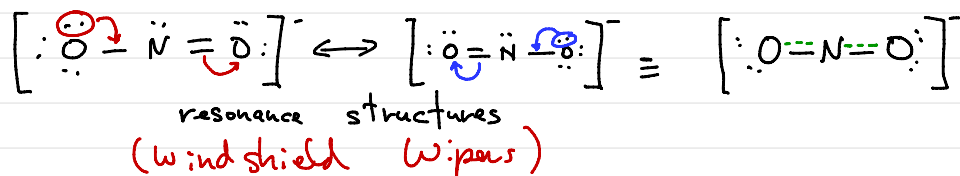
Bond Strength: Covalent Bonds

↳ bond energy (endo) $XY_{(g)} \longrightarrow X_{(g)} + Y_{(g)}$ ΔH°_{be}
↳ energy needed to break bond

$$\cancel{C=C}$$

$$\cancel{C=C}$$

$$\boxed{C \equiv C}$$

Average Bond Energy

$$H - \underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}} - H \longrightarrow 1C + 4H \qquad \Delta H^\circ_{RXN} = 1660 \, kJ$$

methane
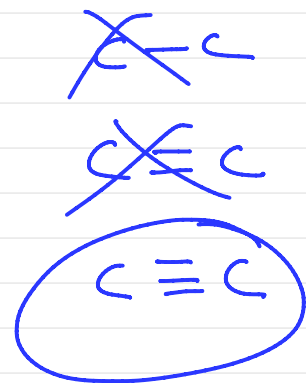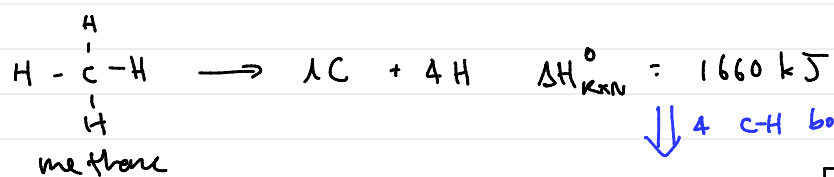
$$\Downarrow \; 4 \; C\text{-}H \; \text{bonds broken}$$

$$BE \, (C\text{-}H) = \frac{1660 \, kJ}{4 \, bonds} = \boxed{415 \, kJ/bond}$$

Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	N = N	418	Si–Cl	359
H–P	320	N ≡ N	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
C = C	611	O–O	140	P–I	215
C ≡ C	837	O = O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C = N	615	O–Si	370	S–Br	215
C ≡ N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C = O	741	O–I	200	Cl–I	210
C ≡ O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table 7.2

Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C = C	1.34	611
C ≡ C	1.20	837
C–N	1.43	290
C = N	1.38	615
C ≡ N	1.16	891
C–O	1.43	350
C = O	1.23	741
C ≡ O	1.13	1080

Table 7.3

C — C   C — N   C — O
1.54 Å   1.47 Å   1.43 Å
346 = BE ↖ 1 BP   305 = BE   358 = BE

C = C
1.34 Å   ↖ 2 BP
602

C ≡ C   ↑ EN →
1.21 Å   ↖ 3 BP   ↓ ↑ # BP
835
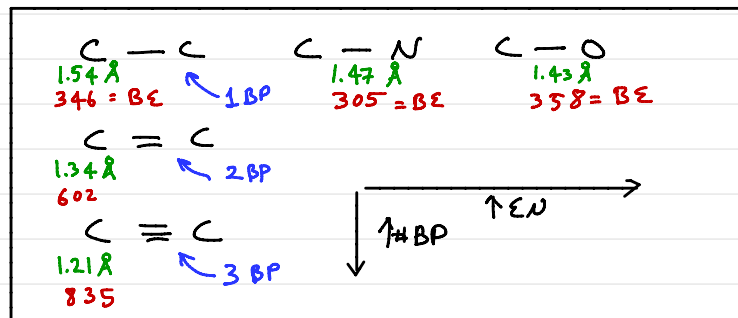
__TREND__ :   Stronger bond; greater BE; shorter Length

Calculation of ΔHrxn from Bond Energies

$$\Delta H_{RXN} = \Sigma BE_{(broken)} - \Sigma BE_{(formed)}$$
$$= \Sigma BE_{(REACTANTS)} - \Sigma BE_{(PRODUCTS)} \quad *unusual$$

(EX) Calculate ΔHrxn from Bond energies   [ex 7.9b]
¿Ethyl alcohol, CH 3 CH 2 OH, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:
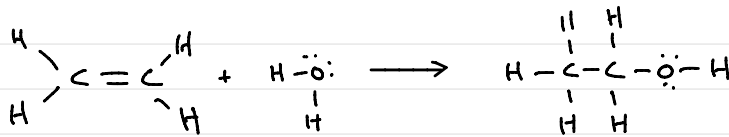
$$4(C-H) + 1(C=C) + 2(O-H) \longrightarrow 5(C-H) + 1(C-C) + 1(C-O) + 1(O-H)$$

$$[1(611) + 1(464)] - [1(415) + 1(345) + 1(350) + 1]$$

$$1075 \quad - \quad 1110$$

$$\boxed{-35\ kJ}$$

↳ lattice energy — energy needed to place component ions of an ionic solid into the gas phase:

$$MX_{(s)} \xrightarrow{\Delta E} M^{n+}_{(g)} + X^{n-}_{(g)} \qquad \Delta H_{LATTICE}$$
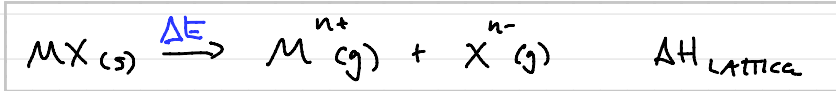
↳ always ENDO

$$\Delta H_{Lattice} = \frac{C(z^+)(z^-)}{R_0}$$

constant = f(crystal type) ← ionic charge

↖ inter-ionic distance

↳ In terms of Force: $\dfrac{(q^+)(q^-)}{d^2}$

↳ Analogous to covalent: $\mu = Qr$

$$Li \quad O \qquad Na \quad Cl \qquad \Rightarrow$$

$$R_0 \quad < \quad R_0$$
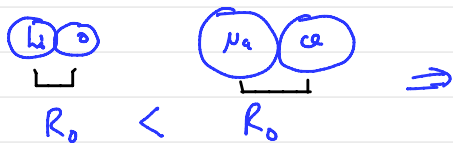
(i) charges are identical
(ii) $R_0(Li_2O) < R_0(NaCl)$
$\therefore \Delta H_{Lattice}$ is greater

$\begin{array}{|l|}\hline mp \ (Li_2O) = 1700 °C \\ mp \ (NaCl) = 801 °C \\ \hline \end{array}$ ⟵ Li_2O more strongly ionic
eg., BP

The "Polarity Spectrum"

Covalent		Ionic
Non-Polar — Polar	Weakly Ionic — Strongly Ionic

POLARITY SPECTRUM

Covalent → Non-polar | Polar

Ionic → Weak Ionic | Strong Ionic

pure ← | polar $\Delta E \cdot \cdot 1.9$ $Na^+ Cl^-$ $Ca^{2+} O^{2-}$ $Ca^{2+} PO_3^{3-}$

non | int   stg $H-F$ | $H^+ F^-$ ionic

< 0.4 | 0.4 1.8 wk   int   stg

                              > 1.8 $\langle EN$

incr charge / decr distance
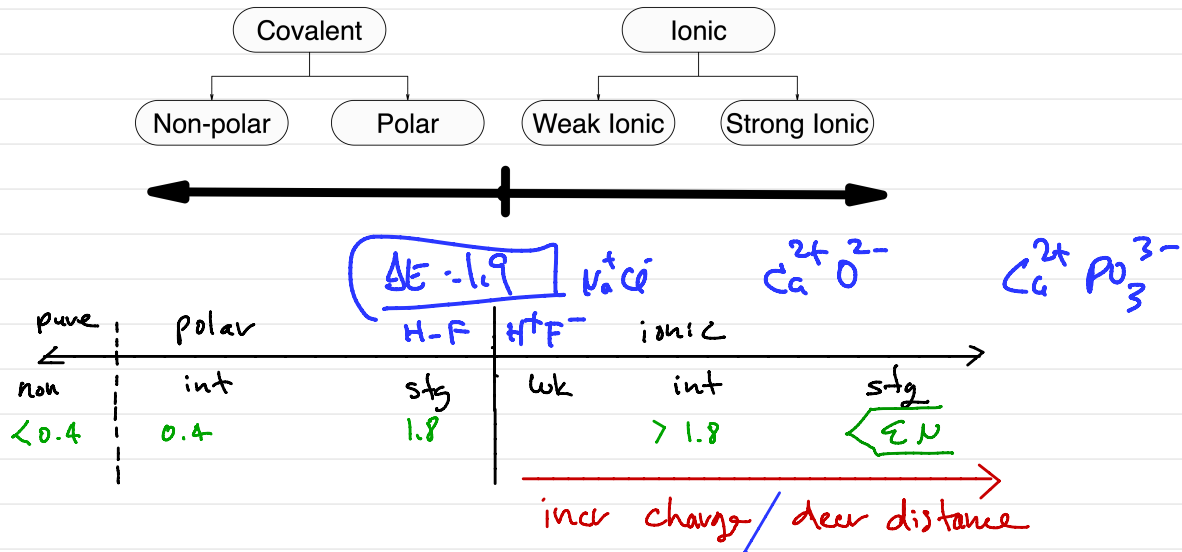
○ Shows relationship between enthalpies of various steps,
and enthalpy of formation.

Cs$^+$(g) + F(g)

BE (F–F)
↑ Cs$^+$(g) + $\frac{1}{2}$F$_2$(g)

$\frac{1}{2}D = 79.4$ kJ/mol

+ e$^-$

EA = –328.2 kJ/mol

Cs$^+$(g) + F$^-$(g)

IE = 375.7 kJ/mol

– 1e$^-$

H increasing

Cs(g) + $\frac{1}{2}$F$_2$(g)

$\rightarrow$ ↑

Cs(s) + $\frac{1}{2}$F$_2$(g)

$\Delta H_s^\circ = 76.5$ kJ/mol

Overall change

$\Delta H_f^\circ =$
–553.5 kJ/mol

Condense
gas ions
into
solid salt

$-\Delta H_{lattice} = -756.9$ kJ/mol

CsF(s)