11/22/2019

back to ch 10!

Exceptions to the octet rule

1. Odd e^- species (radicals)

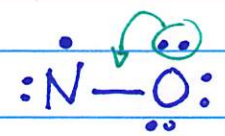
ex: NO

$5+6=11$

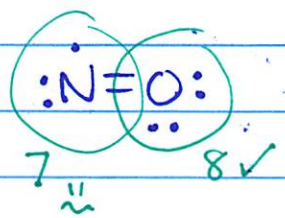
-2

9

$-6/3/3/0//$



center outer

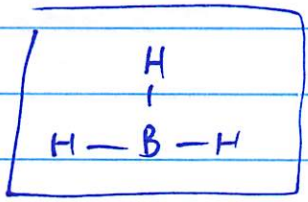


2. Electron deficient / incomplete octets.

Be (4)
B (6)

ex: BeH_2 H — Be — H

BH_3



BF_3

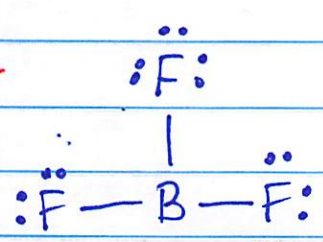
$3+ \rightarrow 7\times3=24e^-$

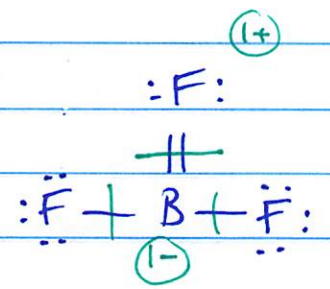
-6

18

-18

0





XPT: BF is ~single bond in length!

Expanded octets

$8e^-$ max (2^{nd} period)

2^{nd} period: $2s^2 2p^6$ — OCTET rule!

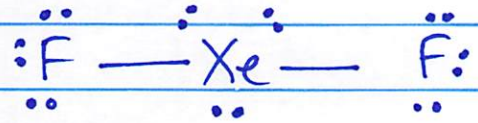
3^{rd} period (or beyond): $3s^2 3p^6 3d^{10}$ → $18e^-$ max!

ex: XeF_2 — xenon difluoride

$8 + 7 \times 2 = 22e^-$

$-4/18$

$-12/6/6/0//$



$10e^-$! ARGH!!

$\geq 3^{rd}$ period

s, p, d

2 : 6 : ~~8~~ 10 } 18 max

Bond energies + ΔH_{rxn}

- When we break bonds
- When we make bonds

ATP = ADP – P_i

H_2O = HO – H

$ATP + H_2O \rightarrow ADP + P_i$

$ADP \gtrless P_i \longrightarrow ADP - OH$ (made)

$H \gtrless OH \longrightarrow P_i - H$ (made)

BREAK (+) costs E

made releases E

Average Bond Energies

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
H—H	436	N—N	163	Br—F	237
H—C	414	N=N	418	Br—Cl	218
H—N	389	N≡N	946	Br—Br	193
H—O	464	N—O	222	I—Cl	208
H—S	368	N=O	590	I—Br	175
H—F	565	N—F	272	I—I	151
H—Cl	431	N—Cl	200	Si—H	323
H—Br	364	N—Br	243	Si—Si	226
H—I	297	N—I	159	Si—C	301
C—C	347	O—O	142	S—O	265
C= C	611	O=O	498	Si=O	368
C≡C	837	O—F	190	S=O	523
C—N	305	O—Cl	203	Si—Cl	464
C=N	615	O—I	234	S=S	418
C≡N	891	F—F	159	S—F	327
C—O	360	Cl—F	253	S—Cl	253
C=O	736*	Cl—Cl	243	S—Br	218
C≡O	1072			S—S	266
C—Cl	339				

*799 in CO_2

Pearson

88

Using Bond Energies to Estimate ΔH°_{rxn}

- The actual bond energy depends on the surrounding atoms and other factors.
- We often use **average bond energies** to estimate the ΔH_{rxn}.
  - Works best when all reactants and products in gas state
- Bond breaking is endothermic, ΔH(breaking) = +.
- Bond making is exothermic, ΔH(making) = −.

$$\Delta H_{rxn} = \underbrace{\sum(\Delta H\text{'s bonds broken})}_{\text{Positive}} + \underbrace{\sum(\Delta H\text{'s bonds formed})}_{\text{Negative}}$$

Pearson

89

(average)

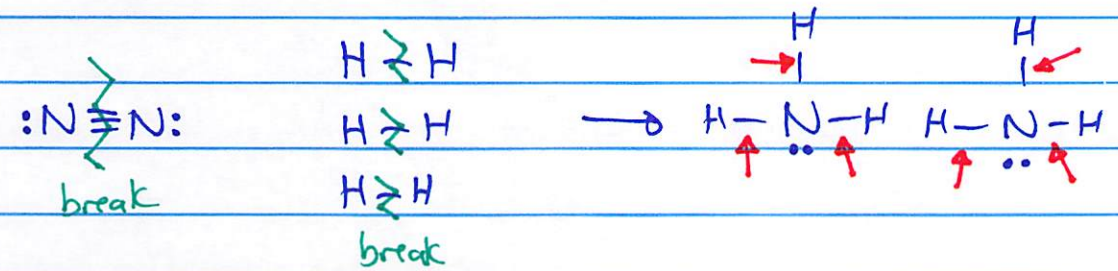
Bond	Bond "energy" (ΔH, KJ/mol)
C – C	347
C = C	611
N ≡ N	946
N – H	389
H – H	436

Can use to predict ΔH_{rxn}

How? $\Delta H_{rxn} = \sum$ Bonds broken $\oplus$ $\ominus \sum$ bonds made

endothermic (+) exothermic (−)

ex: $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H_{rxn} = ??$



$$\Delta H_{rxn} = \left[1 \text{ mol} \times N\equiv N + 3 \text{ mol} \times H-H \right] - \left[6 \text{ mol} \times N-H \right]$$

$$= \left[946 \text{ KJ} + 3 \text{ mol} \times 436 \frac{\text{KJ}}{\text{mol}} \right] - \left[6 \text{ mol} \times 389 \frac{\text{KJ}}{\text{mol}} \right]$$

$$= -80. \text{ KJ}$$ (xpt: −92 KJ, 13% error)

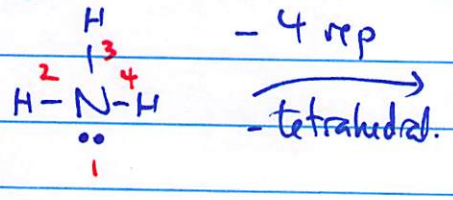
ch 11

the effect of lp upon geom.

ex:

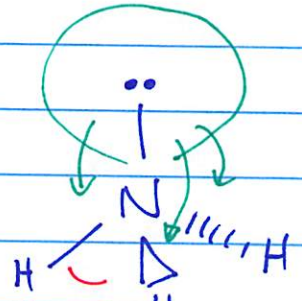
NH_3

Lewis



– 4 rep

– tetrahedral.



ideal: 109.5°

real: 107°

e⁻ pair geom: tetrahedral

molecular geom: trigonal pyramidal

(where the atoms are)