

MOLECULAR STRUCTURE

Lecture 4



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OCTET / DUET RULE

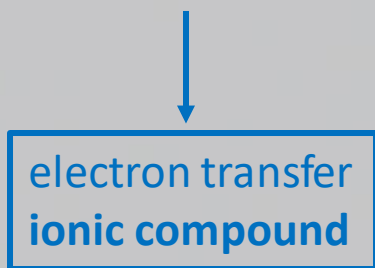
refers to the tendency of atoms to have two or eight electrons in the valence shell

1							8/0
s ¹							s ² p ⁶
H 1	2	3	4	5	6	7	He 2
s ²	s ²	s ² p ¹	s ² p ²	s ² p ³	s ² p ⁴	s ² p ⁵	
Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118

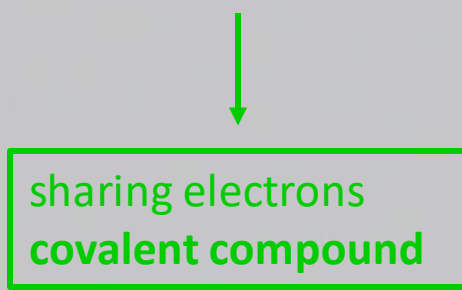
Metal atoms want 0 valence electrons

Non-metal/Metalloid atoms want 8 valence electrons (H wants 2)

Metal + Non-metal/Metalloid



Non-metal/Metalloid + Non-metal/Metalloid



COVALENT COMPOUNDS

- **binary covalent** - 2 different types of atoms
- **name in two parts** - each has prefix (if needed) then name of atom
- **first atom** is the one **further to the left** on PT
(H is above N)
If both are in the same group, it is the one lower down
- Use the atom name for this first atom
- Use **-ide** form of the name for the second atom
- **Prefix** – refers to how many of each type of atom

1 – mono, 2 – di, 3 – tri, 4 – tetra, 5 – penta,
6 – hexa, 7 – hepta, 8 – octa, 9 – nona, 10 – deka



Phosphorus sulfide
Tetraphosphorus hexasulfide



Silicone hydride
Disilicone hexahydride



Bromine chloride
Dibromine heptachloride



Nitrogen oxide
Dinitrogen monoxide
(laughing gas)

If there is only **one of the first atom**, omit the **'mono'**

If the prefix combined with the atom name puts **two vowels** in an awkward fashion, **omit the vowel on the prefix**

CO_2 is carbon dioxide **NOT** monocarbon dioxide

CO is carbon monoxide **NOT** carbon monoxide

LEWIS STRUCTURES

simplified representation of the valence shell electrons in a molecule

- Symbol and valence electrons (as dots)
- Top, bottom, left right – no set order
- Single until 4 of them, then pair up

Sodium atom	1 v.e.	Na•	Sodium cation	0 v.e.	[Na] ⁺
-------------	--------	-----	---------------	--------	---------------------

Carbon atom	4 v.e.	• • C • •
-------------	--------	-----------------

Nitrogen atom	4 v.e.	• • N • •
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Chlorine atom	7 v.e.	• • Cl • •	Chloride anion	8 v.e.	[: Cl :] ⁻
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COVALENT MOLECULES

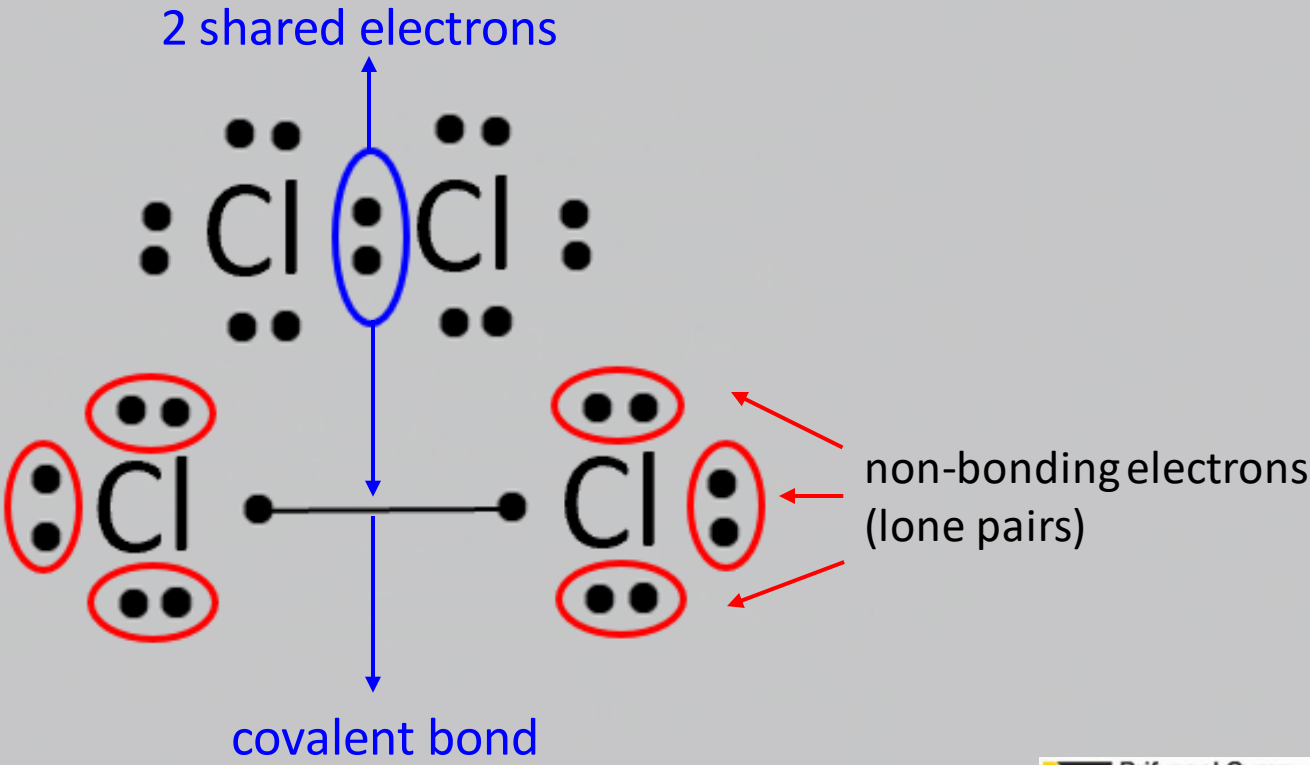


7 valence electrons
needs **one** more

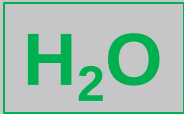


7 valence electrons
needs **one** more

Chlorine atom wants 1 electron to make one bond



COVALENT MOLECULES



1 valence electron
needs **one** more



1 valence electron
needs **one** more

6 valence electrons
needs **two** more

Hydrogen atom wants 1 electron to make one bond

Oxygen atom wants 2 electrons to make two bonds



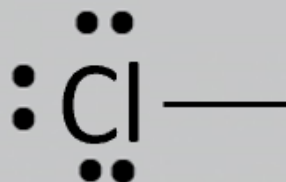
COVALENT MOLECULES

If an atom wants **X more electrons**, it will make **X bonds** (if sensible)

Cl

7 v.e.

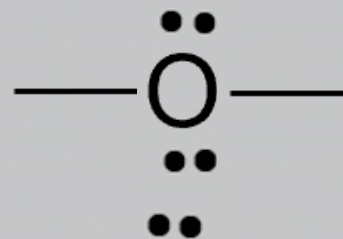
wants 1 more to make 1 bond



O

6 v.e.

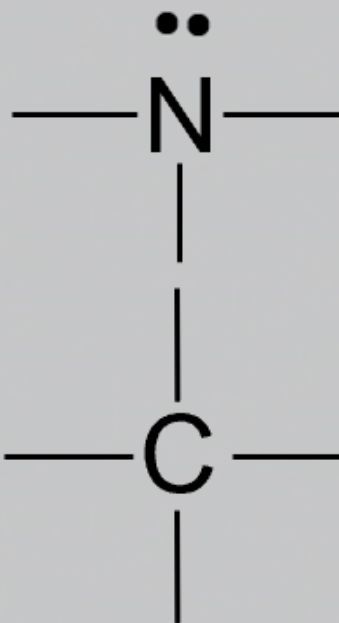
wants 2 more to make 2 bonds



N

5 v.e.

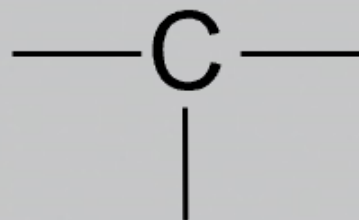
wants 3 more to make 3 bonds



C

4 v.e.

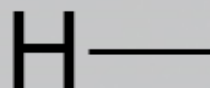
wants 4 more to make 4 bonds



H

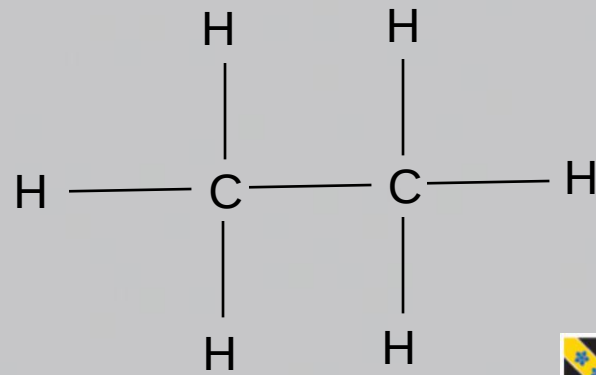
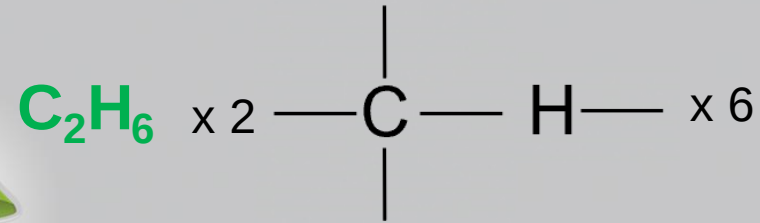
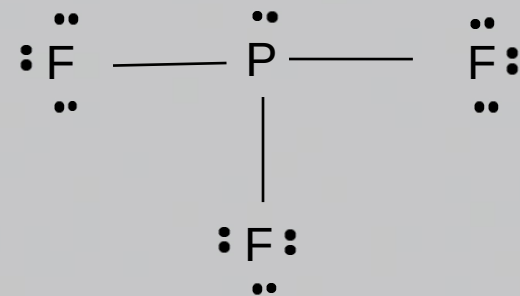
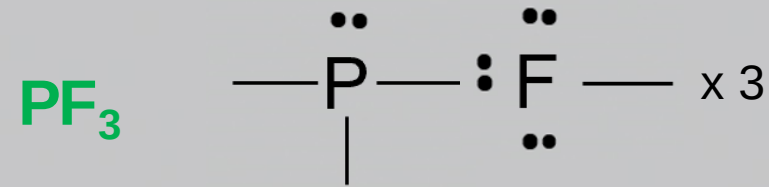
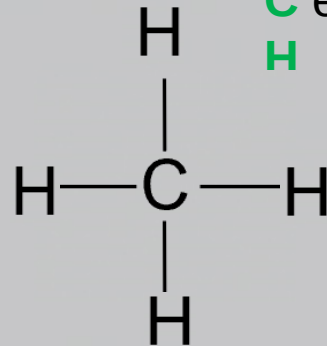
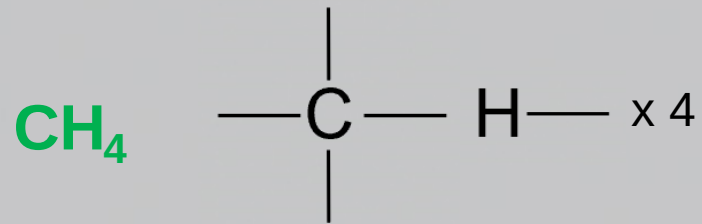
1 v.e.

wants 1 more to make 1 bond



COVALENT MOLECULES: single bonds

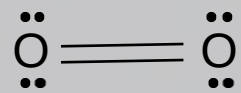
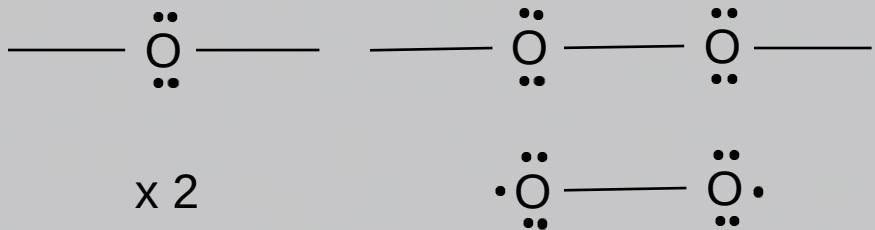
- F etc makes **1 bond**
- O etc makes **2 bonds**
- N etc makes **3 bonds**
- C etc makes **4 bonds**
- H makes **1 bond**



COVALENT MOLECULES: multiple bonds

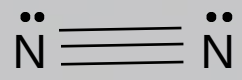
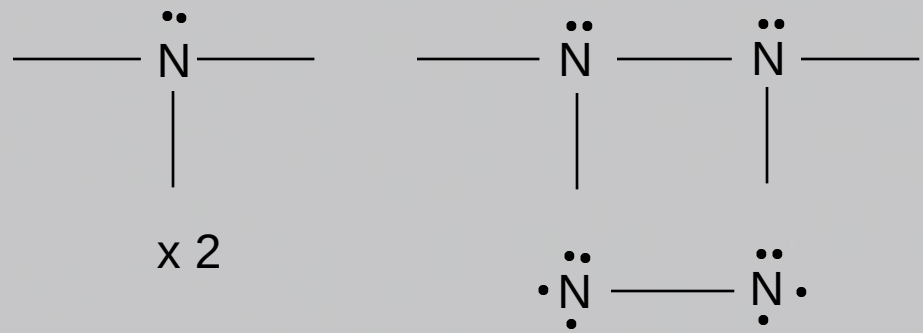
- F etc makes 1 bond
- O etc makes 2 bonds
- N etc makes 3 bonds
- C etc makes 4 bonds
- H makes 1 bond

O₂



4 shared electrons
DOUBLE BOND

N₂



6 shared electrons
TRIPLE BOND



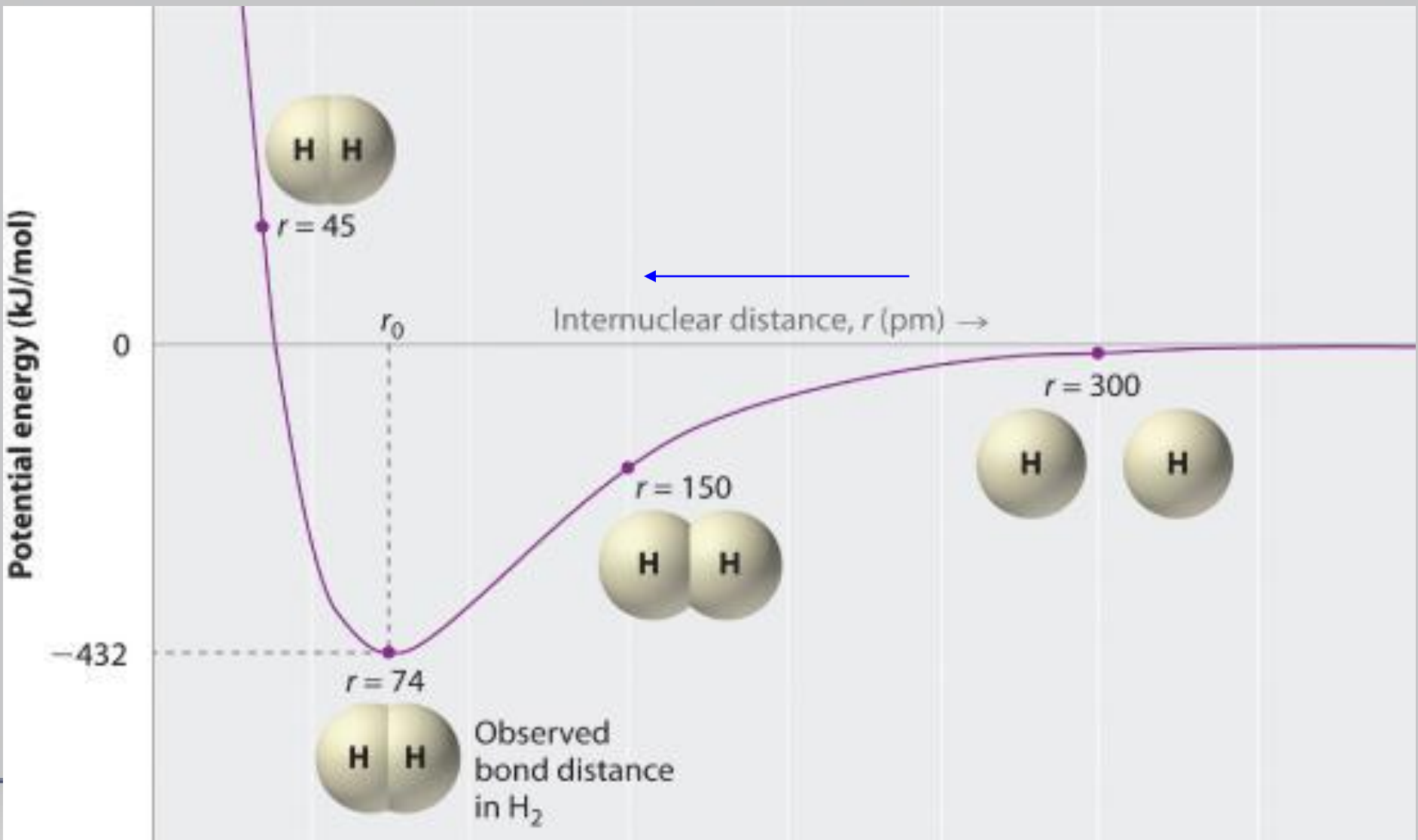
QUESTION 1: What is the name of the compound P_2N_7 ?

QUESTION 2: How many lone pairs will be present on a phosphorus atom when it obeys 'common sense' (i.e. achieves 8 valence electrons by making regular covalent bond(s))?

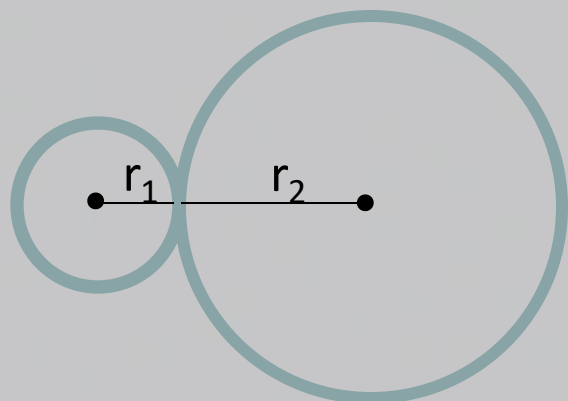
QUESTION 3: Draw the Lewis structure of C_2F_6 . How many lone pairs are there?



COVALENT BONDS



BOND LENGTHS (distance)



BOND LENGTH - sum of the atomic radii $r_1 + r_2$

X-Y	BL (pm)	X-Y	BL (pm)	X-Y	BL (pm)
C-H	109	N-H	101	O-H	96
C-Cl	177	N-Cl	191	Cl-H	127
C-Br	194	N-Br	214	Br-H	141
C-I	214	N-I	222	I-H	161

The bigger the atoms, the longer the bond

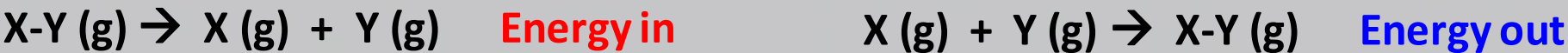
X-Y	BL (pm)	X-Y	BL (pm)	X-Y	BL (pm)
C-C	154	N-N	145	O-O	141
C=C	134	N=N	122	O=O	121
C $\equiv$ C	120	N $\equiv$ N	110	H-H	74

**Single bond longer than double;
double longer than triple**



BOND ENERGY (strength)

BOND ENERGY - energy that has to be put in to take two bonded atoms apart
OR energy that is given out when two atoms bond together



X-Y	D _{X-Y} (kJ/mol)	X-Y	D _{X-Y} (kJ/mol)	X-Y	D _{X-Y} (kJ/mol)
C-H	413	N-H	391	O-H	366
C-Cl	330	N-Cl	200	Cl-H	432
C-Br	228	N-Br	243	Br-H	366
C-I	214	N-I	159	I-H	298

In general, the longer the bond, the weaker the bond

X-Y	BE (kJ/mol)	X-Y	BE (kJ/mol)	X-Y	BE (kJ/mol)
C-C	348	N-N	170	O-O	145
C=C	614	N=N	418	O=O	498
C≡C	839	N≡N	945		

Single weaker than double;
double weaker than triple



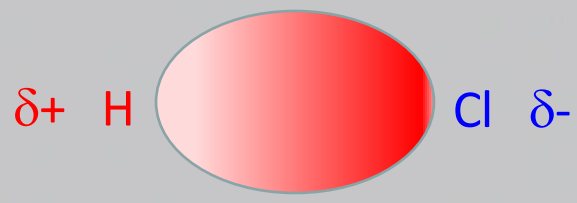
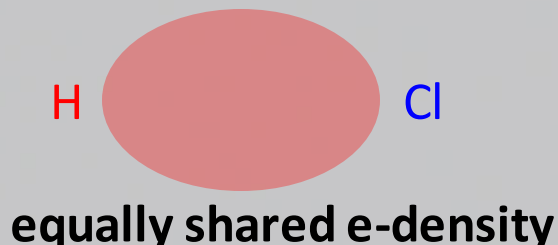
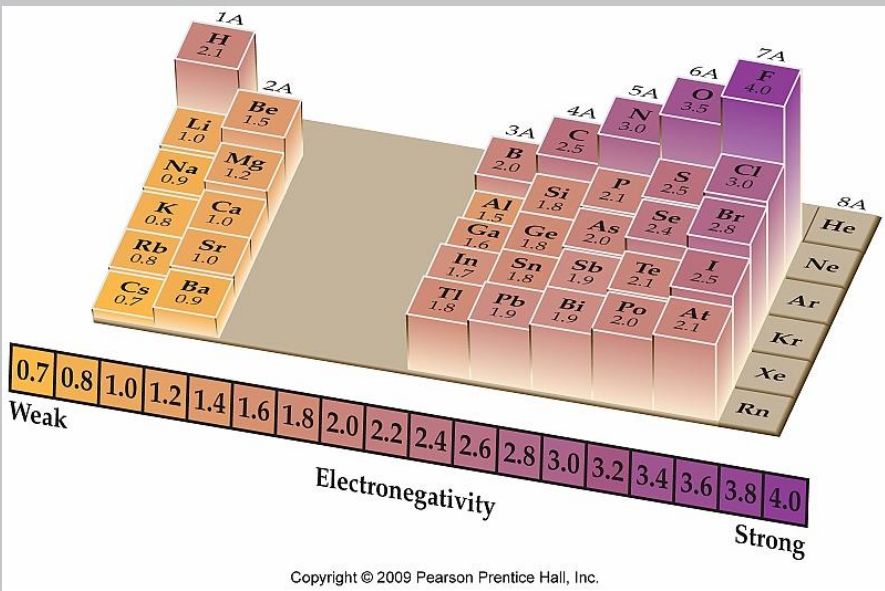
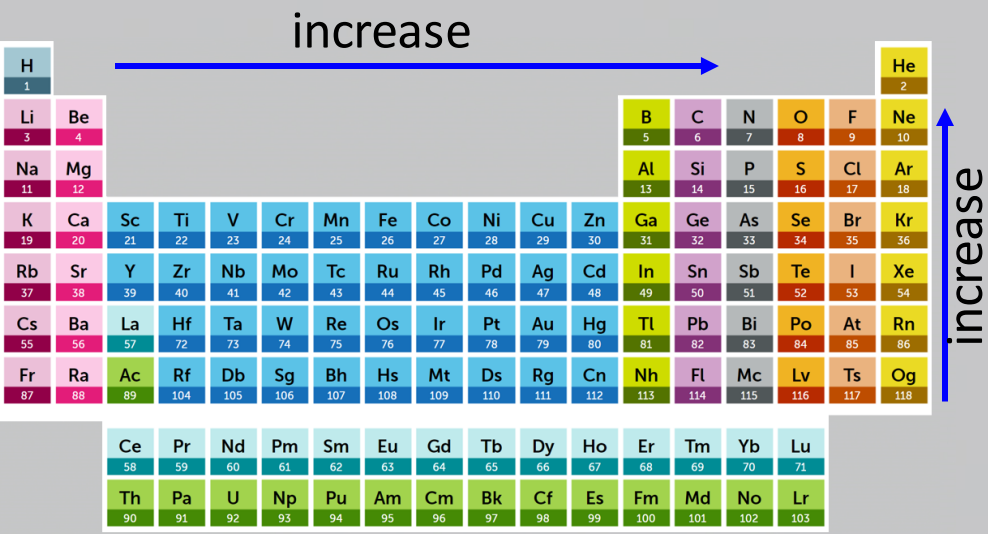
ELECTRONEGATIVITY

The measure of the extent to which an atom desires electrons in a shared bond X--Y

If Y is more electronegative than X, Y pulls electrons more.

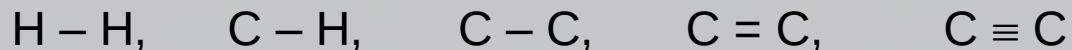
Unequal sharing electrons Partial 'ionic character'

Less electronegative atom gets a little more positive



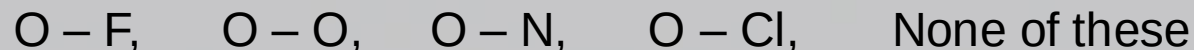
POLAR BOND

QUESTION 1: Predict which of the following bonds would be the longest?



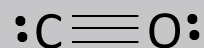
QUESTION 2: Which atom is more electronegative, oxygen or selenium?

QUESTION 3: In which of the following bonds would the oxygen atom would be the slightly positive one?



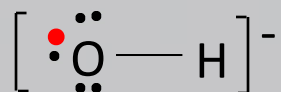
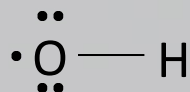
Species that violate common sense and/or octet rules

CO

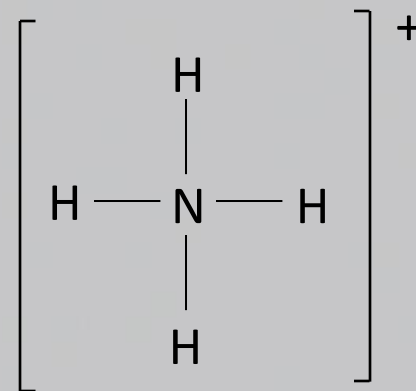
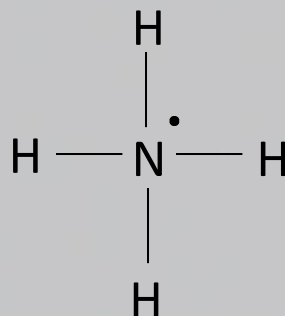
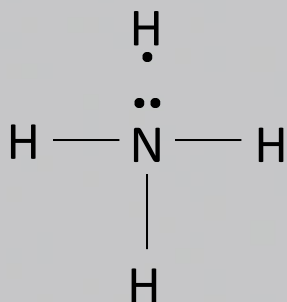


donor bond (all electrons
come from oxygen lone pair)

OH⁻



NH₄⁺



EXAMPLES

Hydroxide, OH⁻

Step 0:

Polyatomic ion – no common sense

Step 1:

O	6 v.e.
H	1 v.e.
e ⁻	1 v.e.

8 v.e.

Ammonium, NH₄⁺

Step 0:

Polyatomic ion – no common sense

Step 1:

N	5 v.e.
4 H	4 v.e.
+	-1 v.e.

8 v.e.



EXAMPLES

Sulphur dioxide, SO_2

Step 0:

All want 2 bonds – no common sense

Step 1:

S	6 v.e.
2 O	12 v.e.

18 v.e.

Sulphur Tetrafluoride, SF_4

Step 0:

S would have to have 4 bonds

Step 1:

S	6 v.e.
4 F	28 v.e.

34 v.e.



TOUGHER LEWIS STRUCTURES

Four steps:

Step 0:

Try common sense !!!

Step 1:

Count the number of valence electrons

Step 2:

Decide what atoms are bonded to what. Practice !!!

...

...

- a) H never has more than one bond
- b) Unless you have lots of carbons, no rings or chains of more than 3 non-hydrogen atoms
- c) Put the less electronegative atom(s) in the middle
- d) When in doubt, always make the more electronegative atoms 'happy' first



Sulfur dioxide, SO₂

Step 0:

All want 2 bonds – no common sense

Step 1:

S 6 v.e.
2 O 12 v.e.

18 v.e.

Step 2:

S is less electronegative than O, so in the middle



Sulfur Tetrafluoride, SF₄

Step 0:

S would have to have 4 bonds

Step 1:

S 6 v.e.
4 F 28 v.e.

34 v.e.

Step 2:

S is less electronegative than F, so in the middle



Step 3:

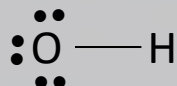
Add in dots.

Use single bonds and add enough 'lone pairs' to make every atom happy

Hydroxide, OH⁻

O H

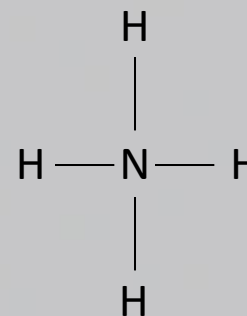
Step 3:



Ammonium, NH₄⁺

H
H N H
H

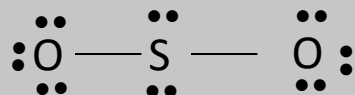
Step 3:



Sulfur dioxide, SO₂

O S O

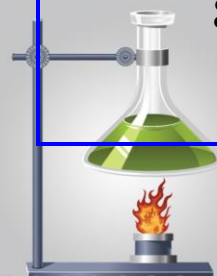
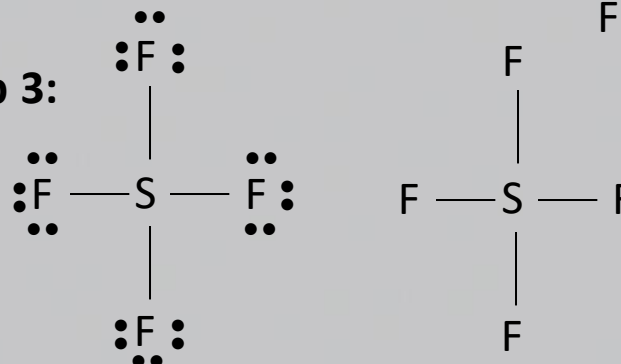
Step 3:



Sulfur Tetrafluoride, SF₄

F
F S F
F

Step 3:



TOUGHER LEWIS STRUCTURES

Step 3:

Add in dots.

Use single bonds and add enough 'lone pairs' to make every atom happy

Step 4:

Compare dots and numbers of v.e.:

- a) If equal, you are finished
- b) If dots > v.e., reduce dots but keep atoms still drawn happy
2 bonded atoms with lone pairs

Erase lone pairs from each and add bond

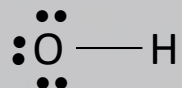
- c) If dots < v.e., need to add dots. Add to central atom as long as $Z > 10$. If not possible, a molecule not possible.



Hydroxide, OH⁻



Step 3:



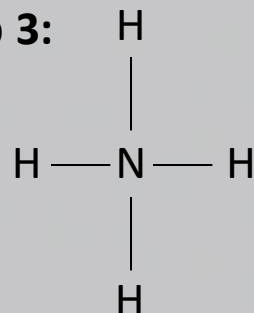
Step 4:

Dots = 8 = v.e.

Ammonium, NH₄⁺



Step 3:



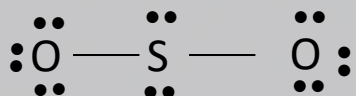
Step 4:

Dots = 8 = v.e.

Sulfur dioxide, SO₂

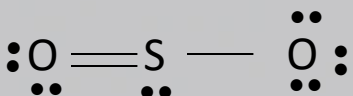
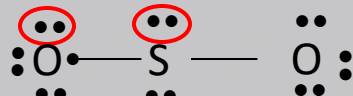
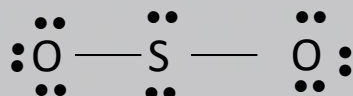


Step 3:



Step 4

Dots = 20 > v.e. (18)

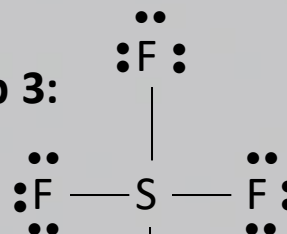


Dots = 18 = ve

Sulfur Tetrafluoride, SF₄



Step 3:

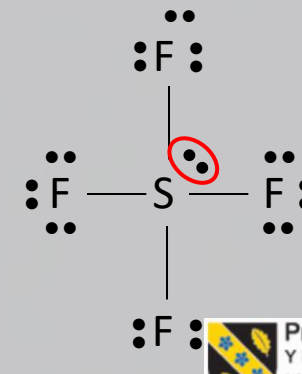
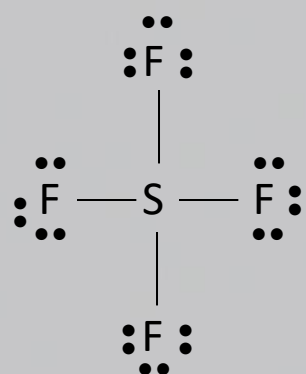


Step 4

Dots = 32 < v.e. (34)

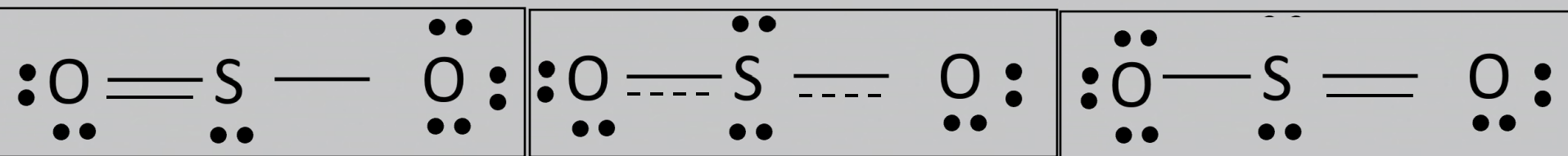
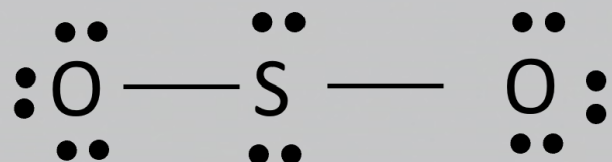
Put lone pair on S

Dots = 34 = ve



RESONANCE STRUCTURES

- average of more than one Lewis structure
- central atom same electronic structure
- terminal atoms vary with lone pairs
- cannot change connectivity
- bond order – average of bonds



From the Lewis Structure – expect 1 long and 1 short bond
 Reality – 2 equal length bonds BO = 1.5



FORMAL CHARGE

Artificial concept to distinguish which RSs are better

charge that would reside on the atom if all of the bonding electrons were shared equally

Applies to individual Lewis structures, not average

Assumes equal sharing of electrons in a bond

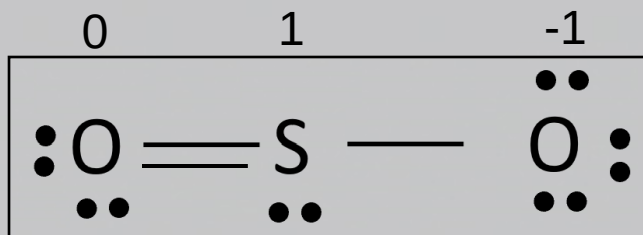
Sum of formal charges = overall charge

2 lone pairs (4e)
4 bonding electrons

4 x 1 electron
4 x ½ electrons

6 formal electrons
Started with 6

$$FC = 6 - 6 = 0$$



1 lone pairs (2e)
6 bonding electrons

2 x 1 electron
6 x ½ electrons

5 formal electrons
Started with 6

$$FC = 6 - 5 = +1$$

3 lone pairs (6e)
2 bonding electrons

6 x 1 electron
2 x ½ electrons

7 formal electrons
Started with 6

$$FC = 6 - 7 = -1$$



QUESTION 1: Draw the Lewis structure of the anion PF_6^- . How many single bonds are there?

QUESTION 2: Draw the Lewis structure of nitrite. How many single bonds are there?

QUESTION 2: Draw the Lewis structure of fulminate ion in $\text{Hg}(\text{CNO})_2$. How many resonance structures are there?

