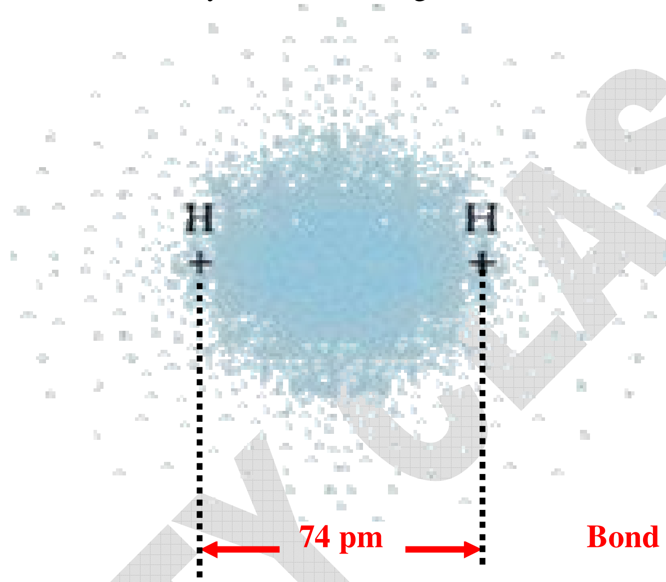
THE COVALENT BOND

- A covalent bond is a chemical bond formed by the sharing of a pair of electrons between atoms. It holds atoms together in a molecule

- Consider the formation of the H_2 molecule from two H atoms:
  - ➢ As two H atoms approach each other, the single 1s electron on each atom begins to feel the attraction of both nuclei.
  - ➢ The electron density shifts to the region between the nuclei:



H_2

$1s^2$ or $\uparrow\downarrow$ 1s

Bond Length = 74 pm

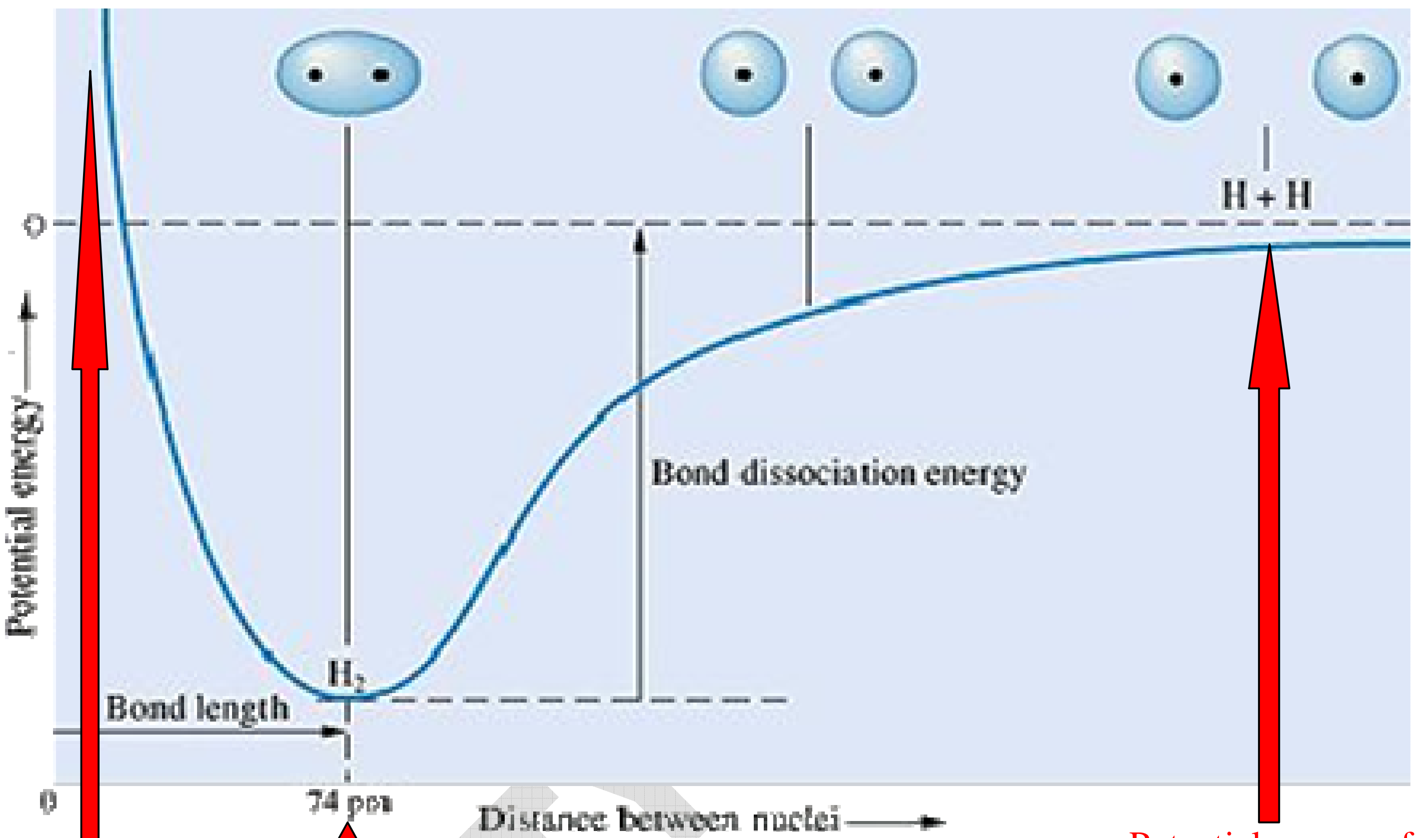
- The two electrons are shared by both atoms and serve as a sort of glue cementing the atoms together

- At a distance of 75pm between the nuclei:

The attraction of the two electrons for both nuclei	← balances out →	The repulsion between the nuclei

Result:
- ➢ The Potential Energy is at a minimum
- ➢ The molecule is stable

Energy Diagram for the formation of H_2 from two H atoms



Potential energy of
2 isolated H atoms

Potential Energy is at a minimum (attractions and repulsions are balanced)

Potential Energy rises steeply
(nuclei get closer and start to repel)

COVALENT BOND TERMINOLOGY

BONDDISSOCIATIONENERGY (or simply Bond Energy)

- The Energy that must be supplied to separate atoms from molecules

  Example: For H_2 the Bond Energy is 435 kJ/mol)

BONDLENGTH (or simply Bond Distance)

- The distance between the nuclei of the atoms involved in a covalent bond when the energy is at a minimum.

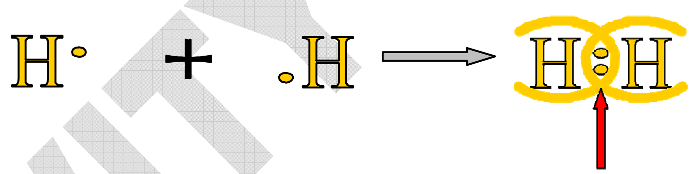
  Example: For H_2, the Bond Length is 74 pm

The Formation of the H_2 molecule can be represented in abbreviated form:

1. By writing out the electron configurations of the atoms:

$$\underset{1s^1}{H} + \underset{1s^1}{H} \longrightarrow \underset{1s^2\ [He]}{H_2} \quad \text{(stable doublet)}$$

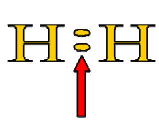
2. By Lewis electron-dot formulas:



one pair of shared electrons
that belongs to both atoms
(stable doublet)

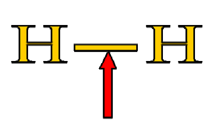
- One pair of shared electrons is commonly represented by a dash. The dash stands for One Covalent Bond

ElectronDotFormula



One pair of shared electrons

StructuralFormula

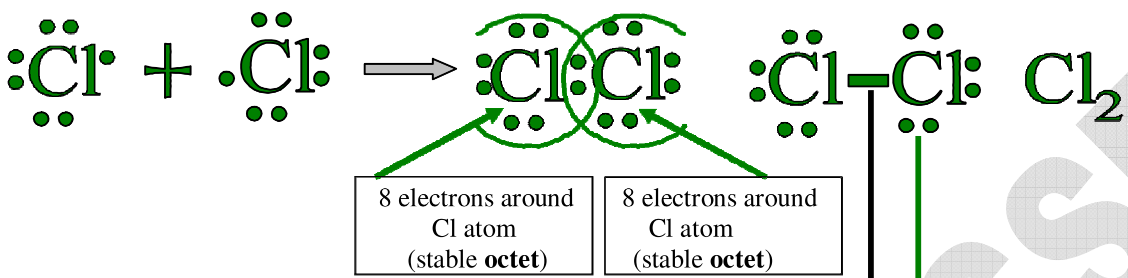


One Covalent Bond

MolecularFormula

COVALENT BONDS BETWEEN IDENTICAL ATOMS (Nonmetals)

Electron-Dot Formula | **Structural Formula** | **Molecular Formula**



– = one pair of bonding electrons (shared electrons)

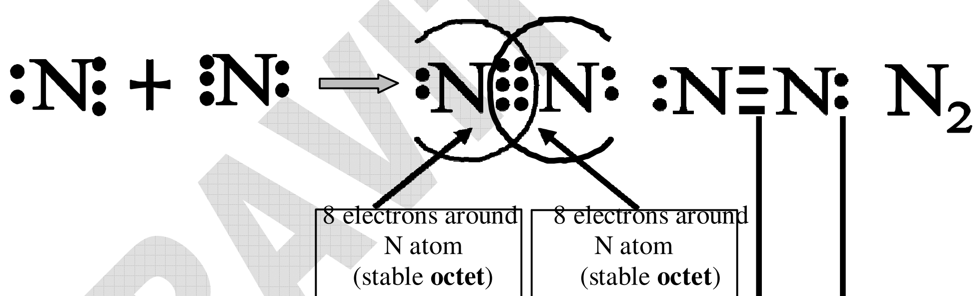
•• = **one pair of non-bonding electrons (lone pair)**

NOTE: There are 3 non-bonding electron pairs (lone pairs) around each Cl atom.

Similar formulas can be written for the following molecules:

F_2, Br_2, I_2 (same group, same number of valence electrons)

Electron-Dot Formula | **Structural Formula** | **Molecular Formula**



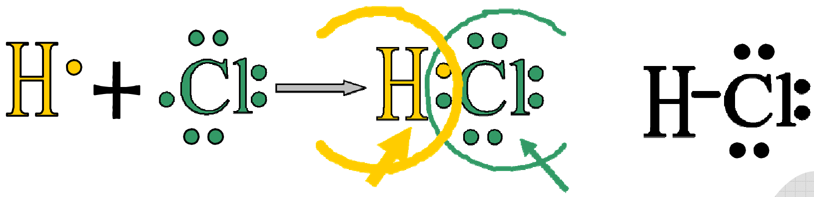
≡ triple covalent bond
three pairs of bonding electrons (shared electrons)

•• = one pair of non-bonding electrons (lone pair)

NOTE: There is one non-bonding electron pair (lone pair) on each N atom.

COVALENT BONDS BETWEEN UNLIKE ATOMS (Nonmetals only)

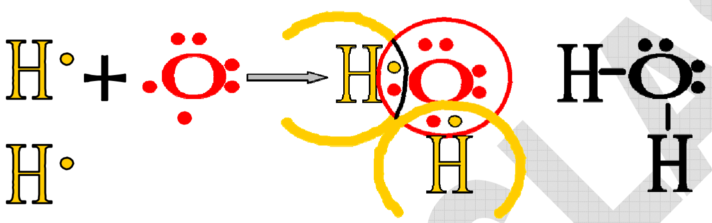
	Electron Dot Formula	**Structural Formula**	**Molecular Formula**



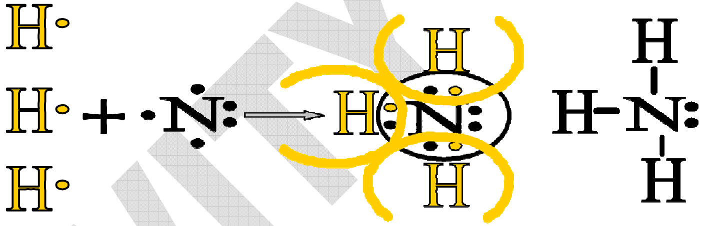
HCl

stable doublet around H atom

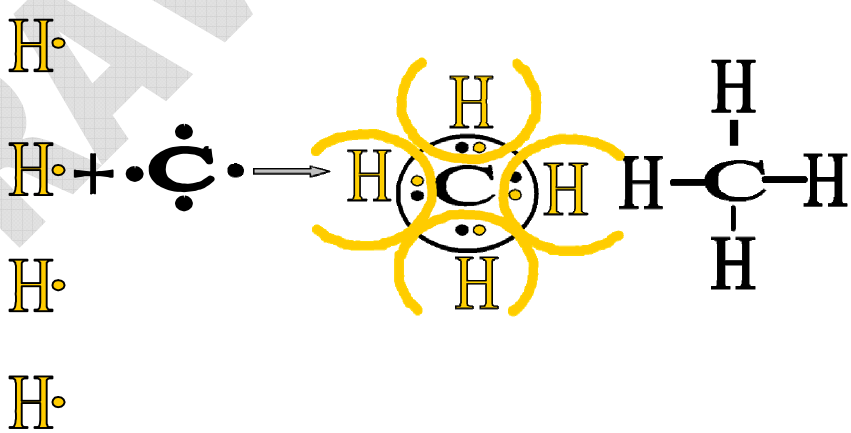
stable octet around Cl atom



H_2O

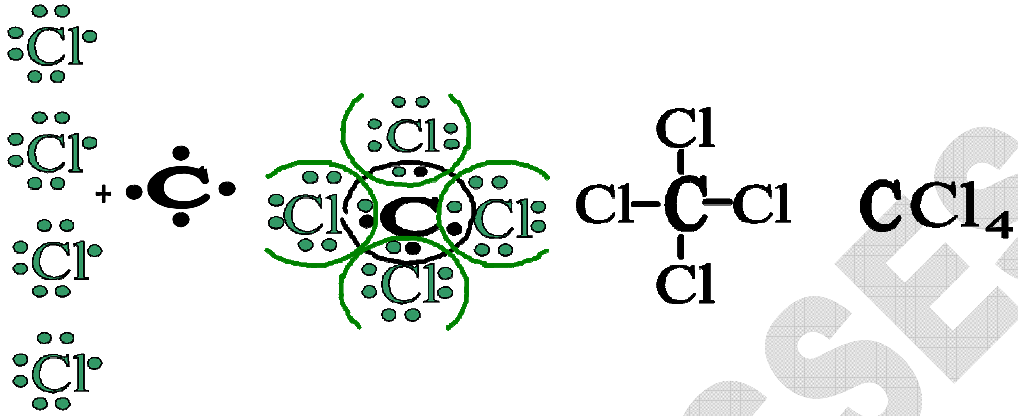


NH_3



CH_4

ElectronDot Formula | **Structural Formula** | **Molecular Formula**



NOTE:

1. In sharing electrons, atoms obtain a Noble Gas Configuration (ns^2 np^6 or $1s^2$)
   This is referred to as the "**OCTETRULE**"

The OCTET RULE is the tendency of atoms in molecules to have 8 electrons in their valence shell

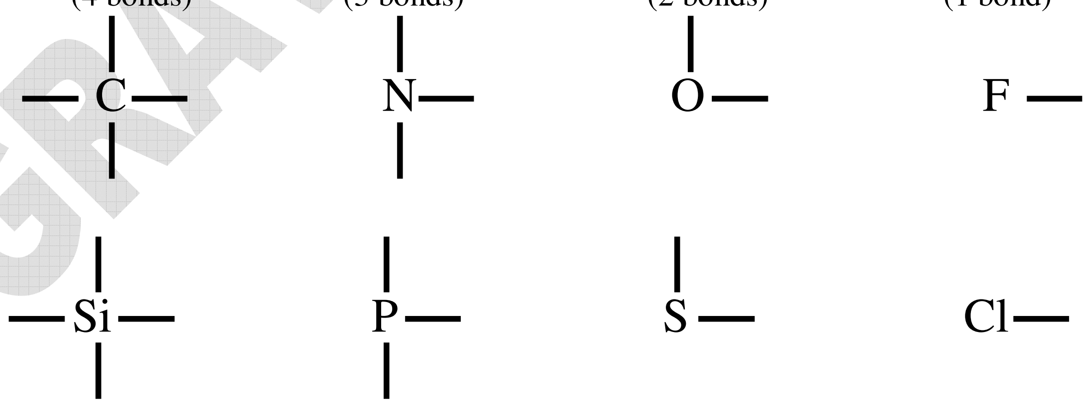
H is an exception since it has only one shell; **H obeys THE DOUBLET RULE**

2. | The number of covalent bonds an atom forms | = | 8 – Group Number |

NOTE: H always forms only one bond (2 – Group Number): H—

This is a useful "Rule of Thumb" that works for many (not all) elements

IVA (4 bonds)	VA (3 bonds)	VIA (2 bonds)	VIIA (1 bond)



DRAWING LEWIS STRUCTURES

Not all Lewis Structures can be easily determined.
For Example: Draw a Lewis Structure for the molecule of CO_2
A systematic approach is needed:

Step1: **Countallthevalenceelectronsofallatoms**

CO_2

$4\ e^-$ $\quad$ $2 \times 6\ e^-$

$4\ e^- + 12\ e^- =$ **16valenceelectrons (16 dots may be used)**

Step2: Drawaskeletonstructure, keeping in mind that:

- The most symmetrical arrangement is the most likely,
- H cannot be a central atom (forms only one bond)

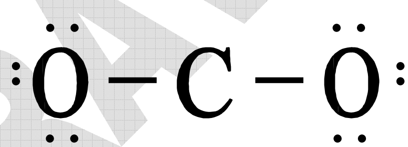
O C O

Step3: Connectallatomswithonebond (place one pair of electrons in each bond)

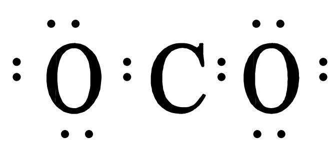
O— C— O or O : C : O

Note: 4 electrons of the available 16 have been used (12 remain available)

Step4: Attempttocompletetheoctetsofallatoms by using the available electrons
(Recall that 12 electrons are still available)

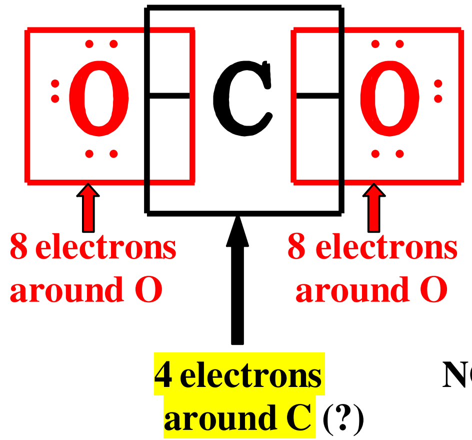


or



Step5:Checkifalloctets(doubletforH)aresatisfied.

(A) If octets (respectively doublet) are satisfied, the Lewis structure is correct.



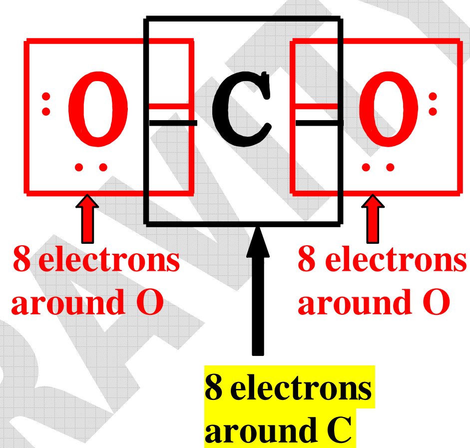
NOTE: TheoctetofCisnotsatisfied!

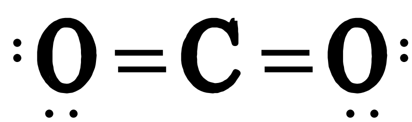
(B) If the octets are not satisfied:

- **Place any additional electrons on the central atom in pairs,**
  In this case there are no additional electrons (all 16 have been used)

OR

- **Form multiple bonds by rearranging electrons, so that each atom has an octet**



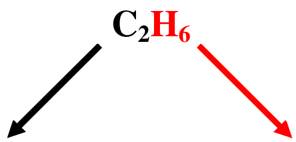


NOTE: TheoctetofCissatisfied!

ExamplesofLewisStructures

1. DrawtheLewisStructureforC_2H_6 (ethane)

Step 1: Countallthevalenceelectrons of all atoms



2 x 4 e^- — 8 electrons + **6 x 1 e^-** — 6 electrons = **14valenceelectrons**

Step2: Drawaskeletonstructure, keeping in mind that:

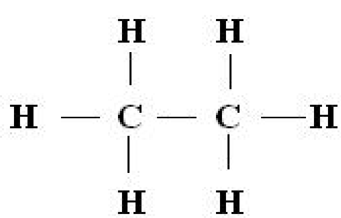
- The most symmetrical arrangement is the most likely,
- H cannot be a central atom (forms only one bond)

H H

H C C H

H H

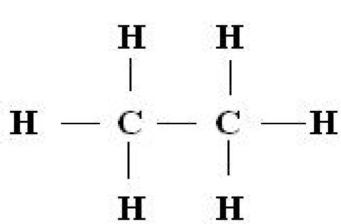
Step3: Connectallatomswithonebond (place one pair of electrons in each bond)



NOTE: All 14 electrons have been used
(7 bonds x 2 electrons/bond = 14 electrons)

Step4: Attempttocompletetheoctetsofallatoms by using the available electrons
This step will be skipped since there are no available electrons

Step5:Checkifalloctets(doubletforH)aresatisfied.



NOTE: The octets of both C's are satisfied
The doublets of all 6 H's are satisfied

Hence: **TheLewisstructureiscorrect**

2. <u>DrawtheLewisStructureforC_2H_4 (ethene)</u>

Step 1: Count all the valence electrons of all atoms

C_2H_4

2 x 4 e^-		**4 x 1 e^-**		
8 electrons	+	4 electrons	=	**12valenceelectrons**

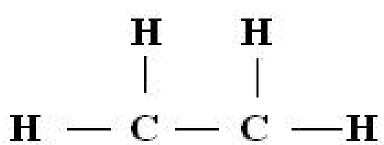
<u>Step2</u>: Drawaskeletonstructure, keeping in mind that:

- The most symmetrical arrangement is the most likely,
- H cannot be a central atom (forms only one bond)

H H

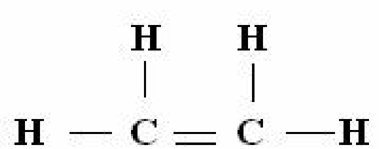
H C C H

<u>Step3:</u> Connectallatomswithonebond (place one pair of electrons in each bond)



<u>NOTE:</u> 10 electrons (5 bonds) have been used (2 electrons remain available)

<u>Step4</u>: Attempttocompletetheoctetsofallatoms by using the available electrons
(Recall that 2 electrons (. .) are still available)



<u>Step5:</u>Checkifalloctets(doubletsforH's)aresatisfied.

<u>NOTE:</u>

- The octets for both C's are satisfied (4 bonds = 8 electrons surround both C's)
- The doublets for all 4 H's are satisfied (each H attached by 1 bond = 2 electrons)

TheLewisStructureiscorrectaswritten

3. DrawtheLewisStructureforC_2H_2 (acetylene)

Step 1: Count all the valence electrons of all atoms

C_2H_2

2 x 4 e⁻ — 8 electrons + **2 x 1 e⁻** — 2 electrons = **10valenceelectrons**

Step2: Drawaskeletonstructure, keeping in mind that:

- The most symmetrical arrangement is the most likely,
- H cannot be a central atom (forms only one bond)

H C C H

Step3: Connectallatomswithonebond (place one pair of electrons in each bond)

H — C — C — H

NOTE: 6 electrons (3 bonds) have been used (4 electrons remain available)

Step4: Attempttocompletetheoctetsofallatoms by using the available electrons

(Recall that 4 electrons (**::**) are still available)

H — C ≡ C — H

Step5:Checkifalloctets(doubletsforH's)aresatisfied:

NOTE:

- The octets for both C's are satisfied (4 bonds = 8 electrons surround both C's)
- The doublets for all 4 H's are satisfied (each H attached by 1 bond = 2 electrons)

TheLewisStructureiscorrectaswritten

LEWIS STRUCTURE OF POLYATOMIC IONS

- Polyatomic Ions are ions consisting of two or more atoms bonded together by covalent bonds and carrying an electric charge.

- Examples: NH_4^+ (ammonium), SO_4^{2-} (sulfate), NO_3^-(nitrate), OH^- (hydroxide)
- Recall: Positive ions are short of electrons
  Negative ions have excess electrons.

Write Lewis structure for the following Polyatomic Ions:

I. TheNH_4^+ (ammonium) ion

Step1: Count all the valence electrons of all atoms.
Subtract 1 electron since the ion has a charge of +1:

N	=	$5\ e^-$
4 H	=	$4\ e^-$
(+1) Charge	=	$-1\ e^-$
Total:	=	$8\ e^-$

→ **8dotsareavailable**

Step2: Drawaskeletonstructure, keeping in mind that:

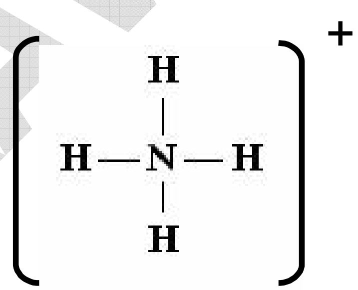
- The most symmetrical arrangement is the most likely
- H cannot be a central atom (forms only one bond)

H

H N H

H

Step3: Connectallatomswithonebond (place one pair of electrons in each bond)



Step4: Checkifalloctets(doubletforH)aresatisfied.

- The octet of N is satisfied (4 bonds x 2electrons/bond = 8 electrons)
- The doublets of all 4 H's are satisfied (1 bond = 2 electrons)

Hence: **TheLewisstructureiscorrect**

II. TheSO_4^{2-} (sulfate) ion

Step1: Count all the valence electrons of all atoms.
Add 2 electrons since the ion has a charge of −2:

S	=	1 x 6 e^-	=	6 e^-
4 O	=	4 x 6 e^-	=	24 e^-
(2 –) Charge	=	+ 2 e^-	=	2 e
		Total:	=	32 e^-

→ 32dotsareavailable

Step2: Drawaskeletonstructure, keeping in mind that:

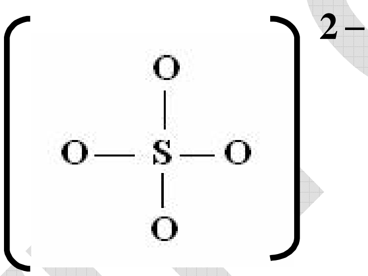
- The most symmetrical arrangement is the most likely.

O

O **S** **O**

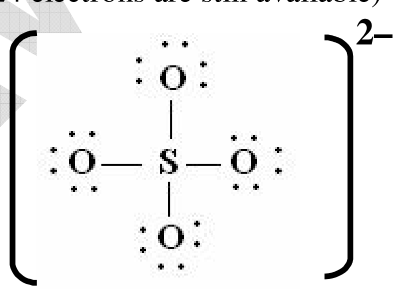
O

Step3: Connectallatomswithonebond (place one pair of electrons in each bond)



Note: 8 electrons have been used (4 bonds)
Available electrons : 32 – 8 = **24**

Step4: Attempttocompletetheoctetsofallatoms by using the available electrons
(Recall that 24 electrons are still available)



Step5: Checkifalloctetsaresatisfied.

- The octet of **S** is satisfied (4 bonds x 2electrons/bond = 8electrons)
- The octets of all 4 **O**'s are satisfied : 1 bond = 2 electrons
  3 lone pairs = 6 electrons
  Total electrons surrounding O = **8electrons**

Hence: **TheLewisStructureiscorrect**

EXCEPTIONS TO THE OCTET RULE

I. Molecules with atoms that are surrounded by less than an octet

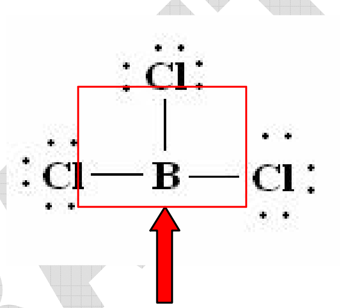
- **Be** and **B** compounds are typical examples

BeH_2	1 Be	=	1 x 2 electrons	= 2 electrons
	2 H	=	2 x 1 electron	= 2 electrons
			Total number of electrons	= **4electrons**

H — Be — H

Be does not have an octet (only **4electronssurroundBe**)
Be is "electron deficient"

BCl_3	1 B	=	1 x 3 electrons	= 3 electrons
	3 Cl	=	3 x 7 electrons	= 21 electrons
	Total			= **24electrons**



B does not have an octet (only **6electronssurroundB**)
B is "electron deficient"
B cannot form double or triple bonds
(Reason will be given later)

EXCEPTIONS TO THE OCTET RULE

II. Molecules with atoms that are surrounded by more than an octet

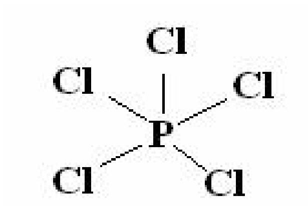
- This occurs if the molecule contains atoms with **available "d" orbitals**
- This implies:
  - these atoms must have at least 3 energy levels
  - these **atoms** must be in **Periods3,4,5,6,or7**
  - these atoms cannot be: - in Period 1 (H) or
    - in Period 2 (B, C, N, O, Cl)

Examples:

1. PCl_5

1 P	=	1 x 5 electrons	= 5 electrons
5 Cl	=	5 x 7 electrons	= 35 electrons
Total number of electrons:			= 40 electrons

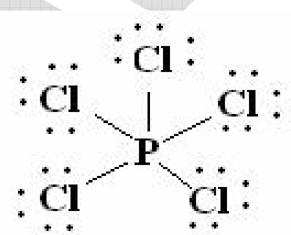
- Most symmetrical arrangement:



Note: 10 electrons have been used (5 bonds)
Available electrons : 40 – 10 = **30**

- Connect all atoms with one bond

- Attempt to complete the octets of all atoms by using the available electrons (Recall that **30electronsarestillavailable**)



Adding 6 electrons to each of the 5 Cl atoms (6 x 5 = 30 electrons) will complete the octets of the Cl atoms.

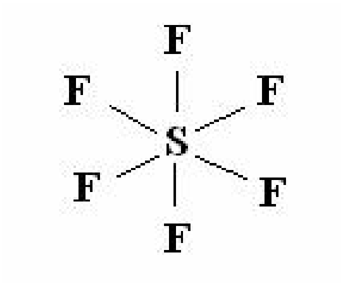
- Check if all atoms have at least an octet.
  NOTE: The octets of all 5 of the **Cl** atoms are satisfied
- Total electrons surrounding Cl = **8 electrons**
- The **P** atom is surrounded by **10 electrons**
- Recall that P has 3 shells (3d subshell available)
  Therefore: P can have up to 18 electrons since additional electrons can be accommodated on the 3d subshell

2. SF_6

1 S	=	1 x 6 electrons	= 6 electrons
6 F	=	6 x 7 electrons	= 42 electrons

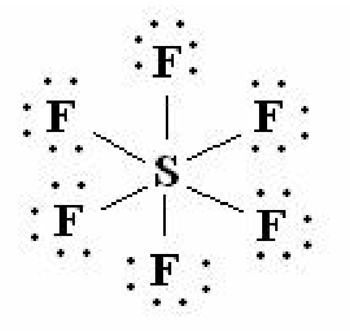
Total number of electrons: = 48 electrons

- Most symmetrical arrangement, connecting all atoms with one bond:



Note: 12 electrons have been used (6 bonds)
Available electrons : 48 – 12 = **36**

- Attempt to complete the octets of all atoms by using the available electrons (Recall that **36electronsarestillavailable**)



Adding 6 electrons to each of the 6 F atoms (6 x 6 = 36 electrons) will complete the octets of the F atoms

- Check if all atoms have at least an octet:
  NOTE: The octets of all 6 of the **F** atoms are satisfied

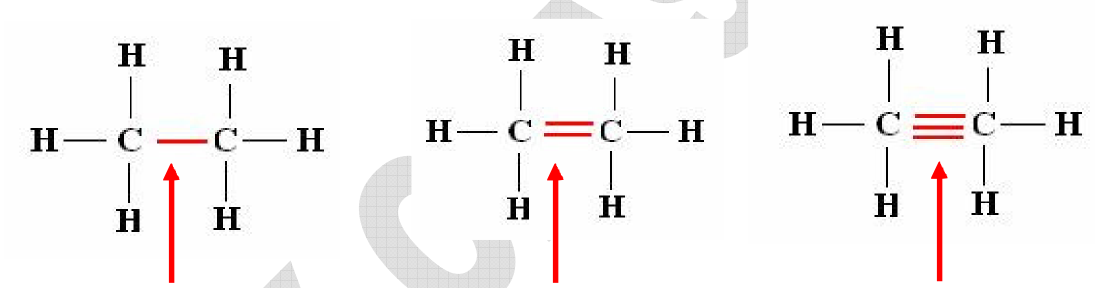
- The **S** atom is surrounded by **12electrons**
- Recall that **S** has 3 shells (3d subshell available)

Therefore: **S** can have up to 18 electrons since additional electrons can be accommodated on the 3d subshell.

BOND PROPERTIES

- **<u>BondLength</u>**
  - is the distance between the nuclei of the atoms forming a covalent bond.
  - is determined experimentally by X-ray diffraction, a method that locates the nuclei of the atoms involved in a covalent bond.
  - is the sum of the covalent radii of the atoms joined in a bond.

- **<u>BondOrder</u>**
  - is the number of electron pairs that form a covalent bond



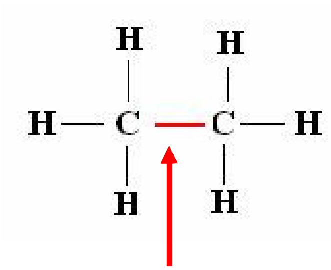
C – C Bond Length	**154 pm**	**137 pm**	**120 pm**
C – C Bond Order	**1**	**2**	**3**

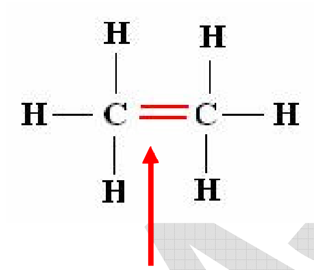
<u>NOTE</u>: **AstheBondOrderincreases,theBondLengthdecreases** Reason:
As the Bond Order increases, electron density increases. Hence:
the higher electron density pulls the atoms closer together.

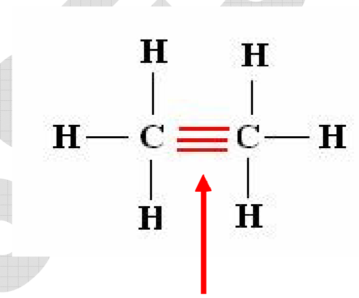
BOND ENERGIES

- Bond energy is the energy required to break a covalent bond
- It is a measure of the strength of the bond:

THEHIGHERTHEBONDENERGY,THESTRONGERTHEBOND







C – C Bond Length	**154 pm**	**137 pm**	**120 pm**
C – C Bond Order	**1**	**2**	**3**
BondEnergy: (kJ/mol)	**+346**	**+602**	**+835**

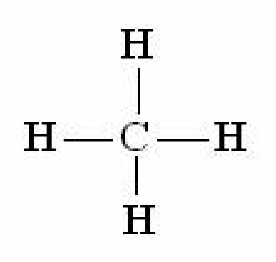
NOTE:

- Bond Energies are always positive (it takes energy to break a bond)
- Conversely: Formation of a bond is an exothermic process (Bond Energy is released)
- The higher the Bond Energy, the shorter the Bond Length, the stronger the bond

HighBondEnergy → **ShortBondLength** → **StrongBond**

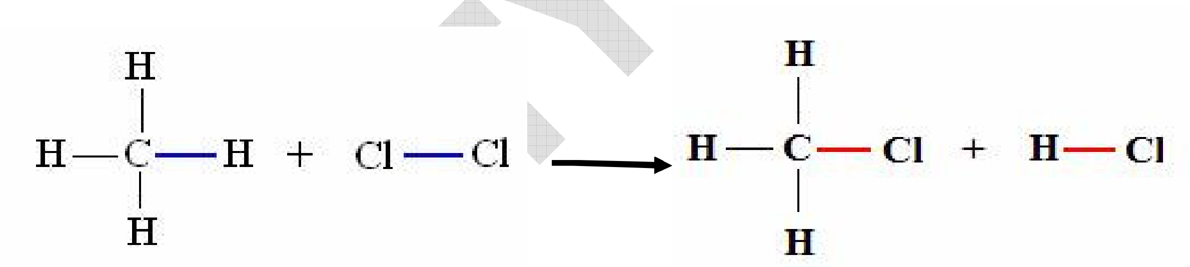
Thermochemical Definition of BOND ENERGY

- Bond energies can be defined as the Average Enthalpy change for the breaking of a covalent bond in a molecule in gas phase


(g) ⟶ **C(g) +4 H (g)** **ΔH = + 1644 kJ/mol**

$$\textbf{Bond Energy for the C—H bond} = \frac{+1644\ \text{kJ/mol}}{4} = +411\ \text{kJ/mol}$$

- It follows that Heats of Reactions (Enthalpy Changes) can be calculated from known values of Bond Energies.
- Consider the following reaction:


ΔH=?

Bonds broken are shown in Blue **Bonds formed are shown in Red**

Bond Energies (kJ/mol) for Single Bonds

C—H	Cl—Cl	C—Cl	H—Cl
411	240	327	428

- Consider the steps:

$$CH_3 - H \longrightarrow CH_3 + H \qquad \Delta H = +411 \text{ kJ/mol (bond breaking)}$$

$$Cl - Cl \longrightarrow Cl + Cl \qquad \Delta H = +240 \text{ kJ/mol (bond breaking)}$$

$$CH_3 + Cl \longrightarrow CH_3Cl \qquad \Delta H = -327 \text{ kJ/mol (bond formation)}$$

$$H + Cl \longrightarrow HCl \qquad \Delta H = -428 \text{ kJ/mol (bond formation)}$$

- **According to Hess's Law:**

ΔH= (+ 411 kJ) + (+ 240 kJ) + (–327 kJ) + (–428 kJ) = –104kJ/mol Exothermic!

(+ 411 kJ) + (+ 240 kJ): Energy used for bond breaking

(–327 kJ) + (–428 kJ): Energy released by bond formation

- In General:

ΔHofReaction = **[Sum of Bond Energies required for Bond Breaking]** — **[Sum of Bond Energies given off by Bond Formation]**

- What makes a Reaction **Exothermic ($\Delta H < 0$)** or **Endothermic ($\Delta H > 0$)** ?

Exothermic:

Energy given off by Bond Formation > Energy required to Break Bonds

Meaning:WeakBondsarereplacedStrongBonds

Endothermic:

Energy given off by Bond Formation < Energy required to Break Bonds

Meaning:StrongBondsarereplacedbyWeakBonds

Examples:

1. Calculate the Enthalpy of Reaction for the following Reaction:

$$2\,H_2\,(g) \quad + \quad O_2\,(g) \longrightarrow 2H_2O\,(g) \qquad \Delta H=?$$

Is the Reaction Exothermic or Endothermic ?

Bond Energies (kJ/mol)

H—H	O=O	H—O
432	142	459

ΔHofReaction = [**Sum of Bond Energies required for Bond Breaking**] — [**Sum of Bond Energies given off by Bond Formation**]

ΔHofReaction = **[2 (+432 kJ) + (142 kJ)]** — **[4 (–459 kJ)]** = **–830kJ**

- **The Reaction is strongly exothermic!**

2. Use bond energies in Table 9.5 in your textbook to determine ΔH for the reaction shown below:

$$2\,NCl_3 \rightarrow N_2 + 3\,Cl_2$$