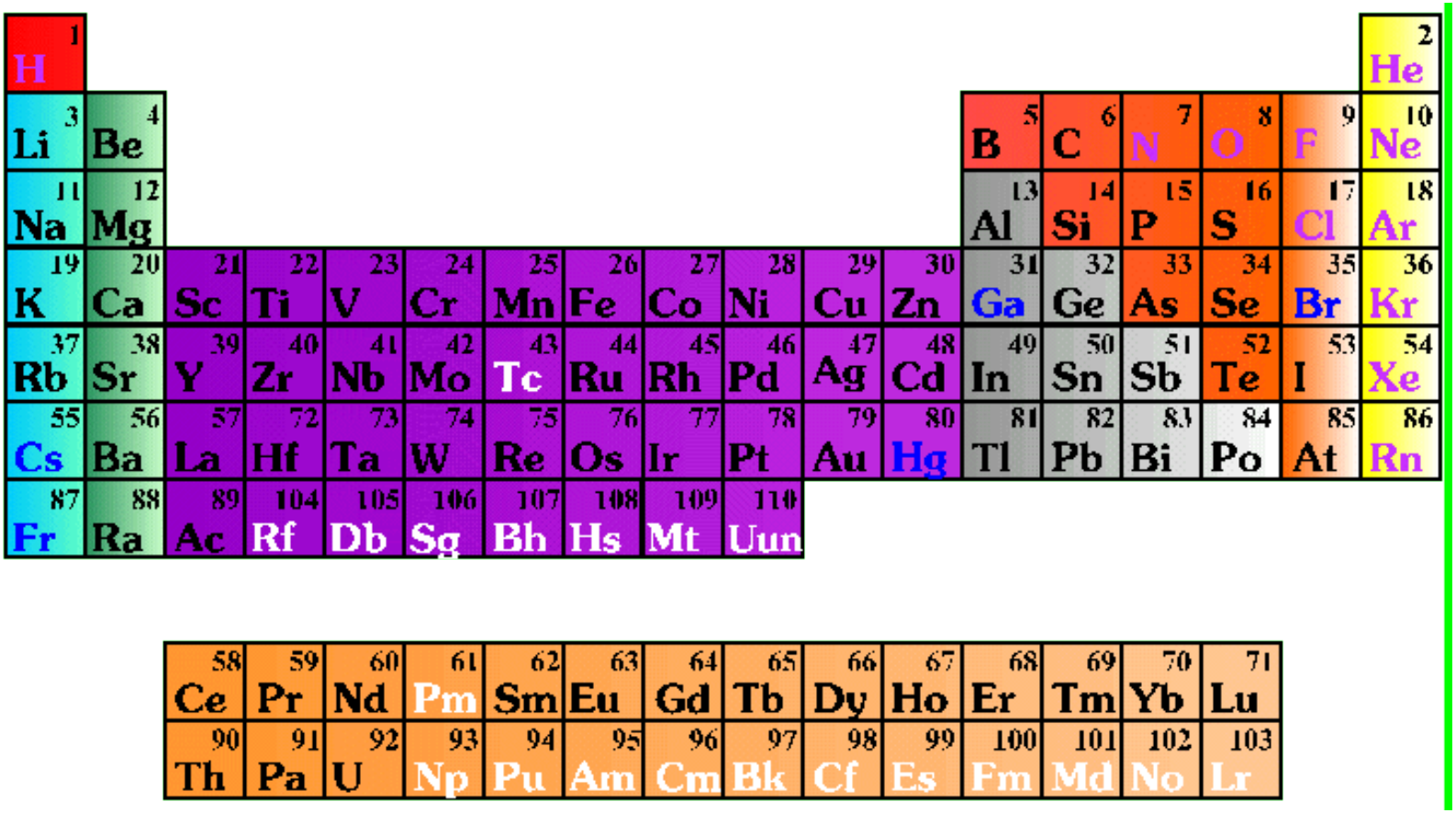
Bonding,
Molecular Shape & Structure

By
Dr. Fawaz Aldabbagh

http://www.nuigalway.ie/chem/Fawaz/fawaz.htm

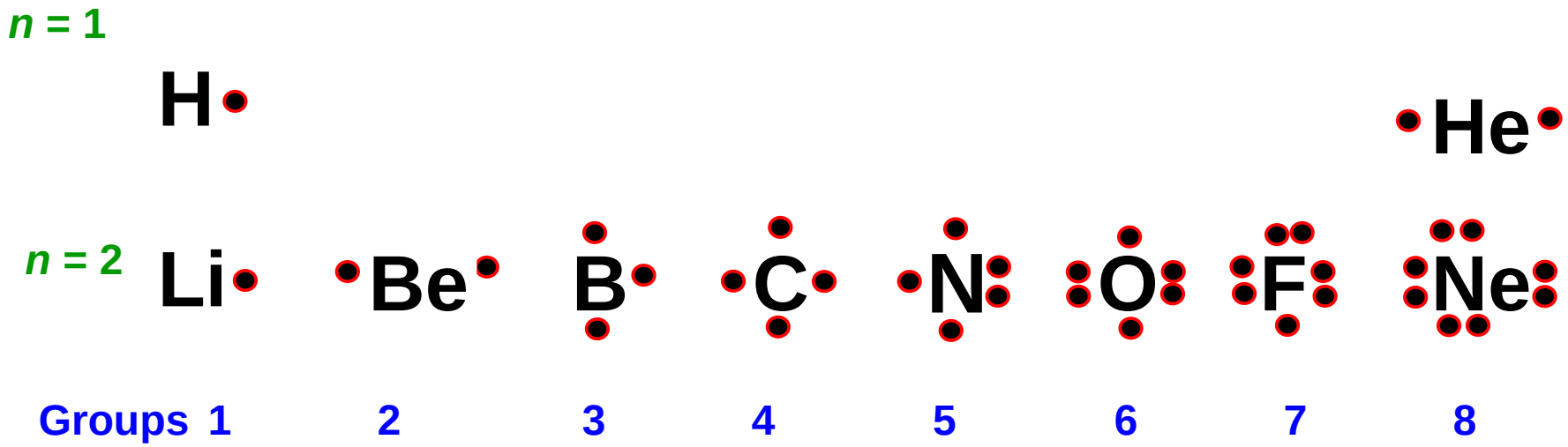
The Periodic Table



Lewis Symbols

Represent the number of valence electrons as dots

Valence number is the same as the Periodic Table Group Number



For example,

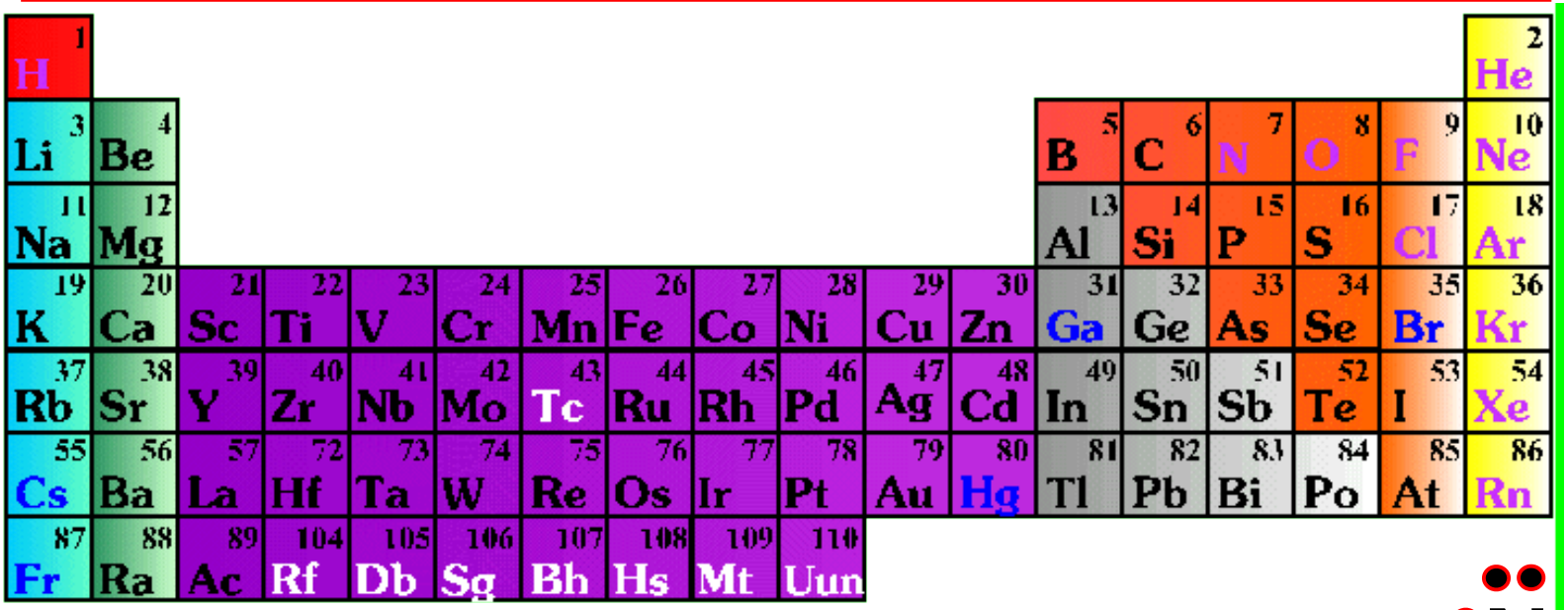
Na; $1s^2, 2s^2, 2p^6, 3s^1$ = [Ne] $3s^1$

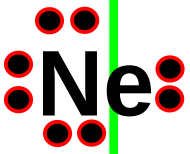
Lewis Structure = 

Elements want to achieve the stable electron configuration of the nearest noble gas

n = 2

n = 3





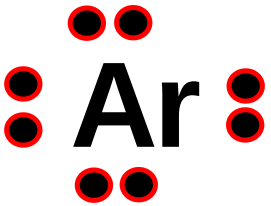
Atoms tend to gain, lose or share electrons until they are surrounded by 8 electrons

Octet Rule

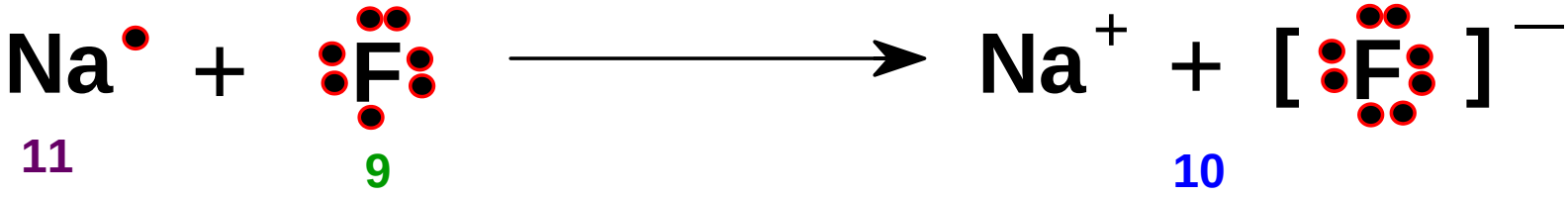
Nobel Gas Has a Stable Electron Configuration

Ne; $1s^2, 2s^2, 2p^6$

Ar; [Ne] $3s^2, 3p^6$



Example of Ionic Bonding



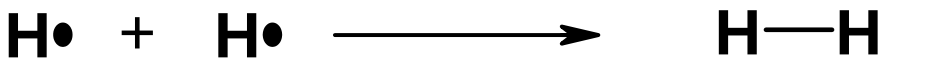
Electronic *configuration* of Neon achieved in both cases

There are two types of bonding;

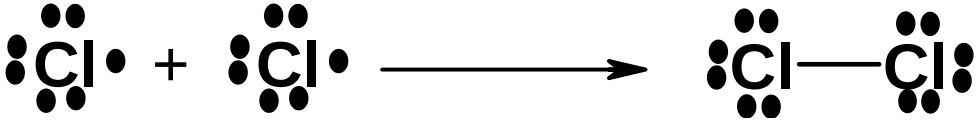
Ionic Bonding refers to electrostatic forces between ions, usually a metal cation and a non-metal anion

Covalent Bonding results from the sharing of two electrons between two atoms (usually non-metals) resulting in molecules

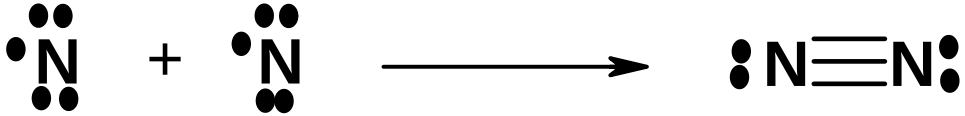
Octet Rule applies



number of electrons around each atom = He



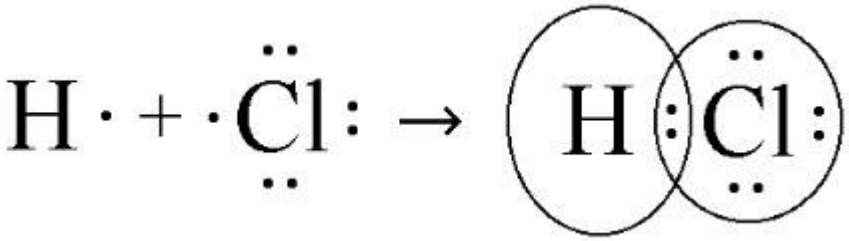
number of electrons around each atom = Ar



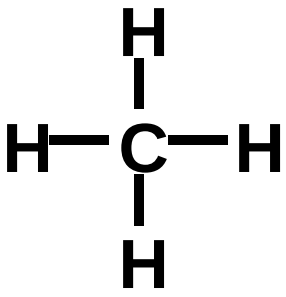
Triple bond

number of electrons around each atom = Ne

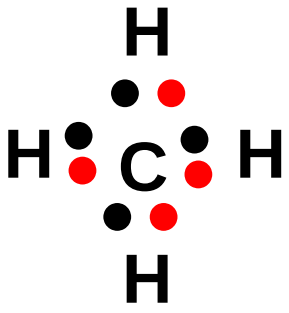
Each Covalent Bond contains two electrons

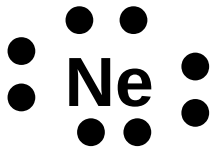


Carbon has 4 valence electrons

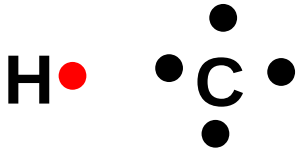


methane





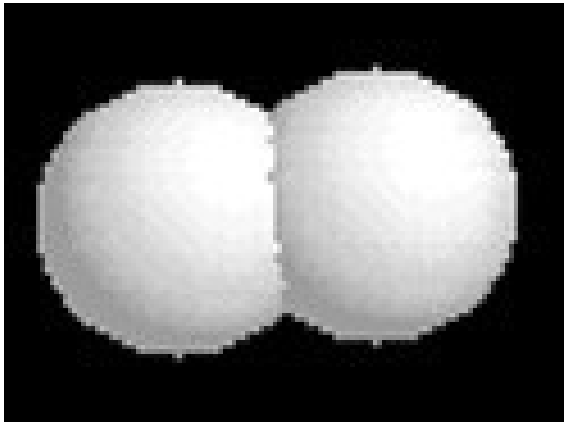
Neon



Stable Octet required

Covalent Bonding – Atoms Share Electrons

Hydrogen molecule, H_2



Concentration of negative charge between two nuclei occurs in a covalent bond

7A elements (e.g. F) have one valence electron for covalent bonding, so to achieve octet

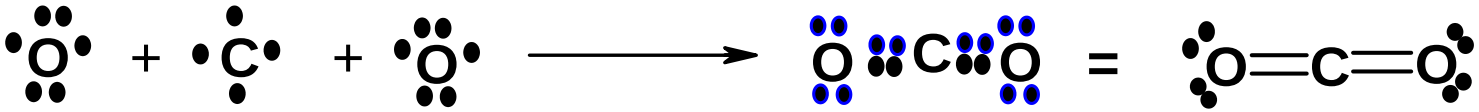
6A elements (e.g. O) use two valence electrons for covalent bonding, so to achieve octet

5A elements (e.g. N) use three valence electrons for covalent bonding, so to achieve octet

4A elements (e.g. C) use four valence electrons for covalent bonding, so to achieve octet

Carbon dioxide, CO_2

Total Number of valence electrons = 4 + (2 x 6) = 16

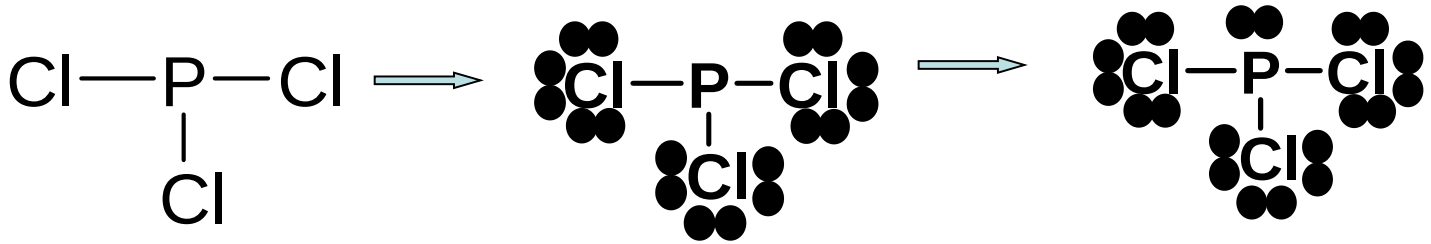


Double bonds

Rules for Drawing Lewis Structures

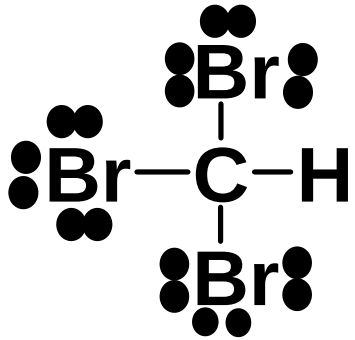
- ***First sum the number of valence electrons from each atom***
- ***The central atom is usually written first in the formula***
- ***Complete the octets of atoms bonded to the central atom (remember that H can only have two electrons)***
- ***Place any left over electrons on the central atom, even if doing so it results in more than an octet***
- ***If there are not enough electrons to give the central atom an octet , try multiple bonds***

E.g. 1. PCl_3 **Total Number of valence electrons = 5 + (3 x 7) = 26**



E.g. 2; $CHBr_3$

Total Number of valence electrons = 4 + 1 + (3 x 7) = 26



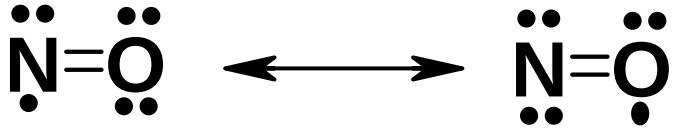
Exceptions to the Octet Rule in Covalent Bonding

1. **Molecules with an odd number of electrons**
2. **Other Natural Radicals, which do not obey Lewis Structures (e.g. O_2)**
2. **Molecules in which an atom has less than an octet**
3. **Molecules in which an atom has more than an octet**

1. Odd Number of Electrons

NO

Number of valence electrons = 11



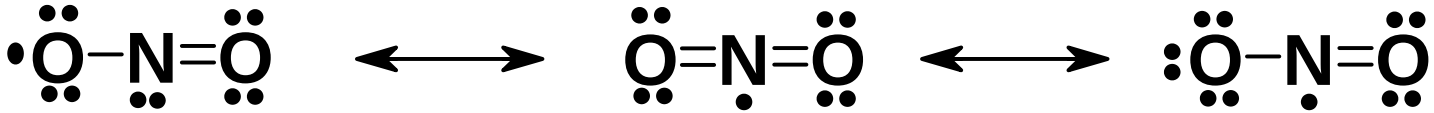


Resonace Arrows

***Resonance* occurs when more than one valid Lewis structure can be written for a particular molecule (i.e. rearrange electrons)**

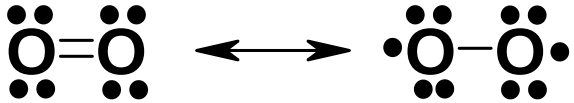
NO_2

Number of valence electrons = 17



Molecules and atoms which are neutral (contain no formal charge) and with an unpaired electron are called Radicals

O_2

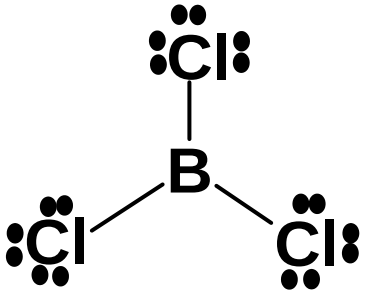


Oxygen is a ground state "diradical"

2. Less than an Octet

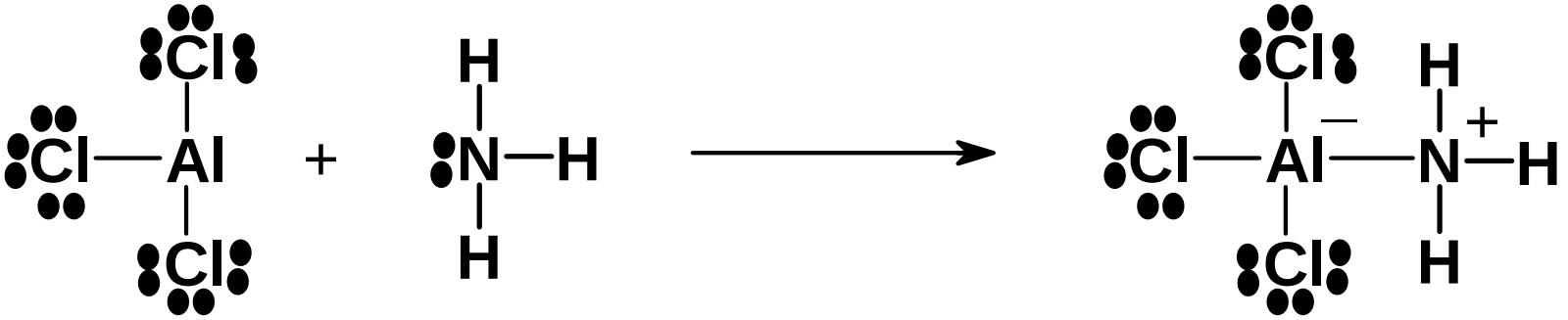
Includes Lewis acids such as halides of B, Al and compounds of Be

BCl_3



Group 3A atom only has six electrons around it

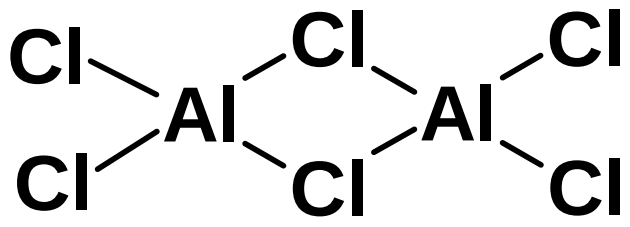
However, Lewis acids "accept" a pair of electrons readily from Lewis bases to establish a stable octet



Lewis acid **Lewis base** **salt**

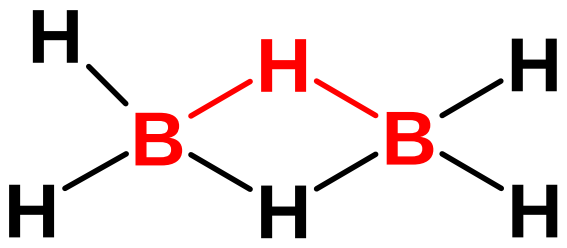
AlX_3

Aluminium chloride is an ionic solid in which Al^{3+} is surrounded by six Cl^-. However, it sublimes at 192 °C to vapour Al_2Cl_6 molecules



B_2H_6

A Lewis structure cannot be written for diborane.
This is explained by a three-centre bond – single electron is delocalized over a B-H-B



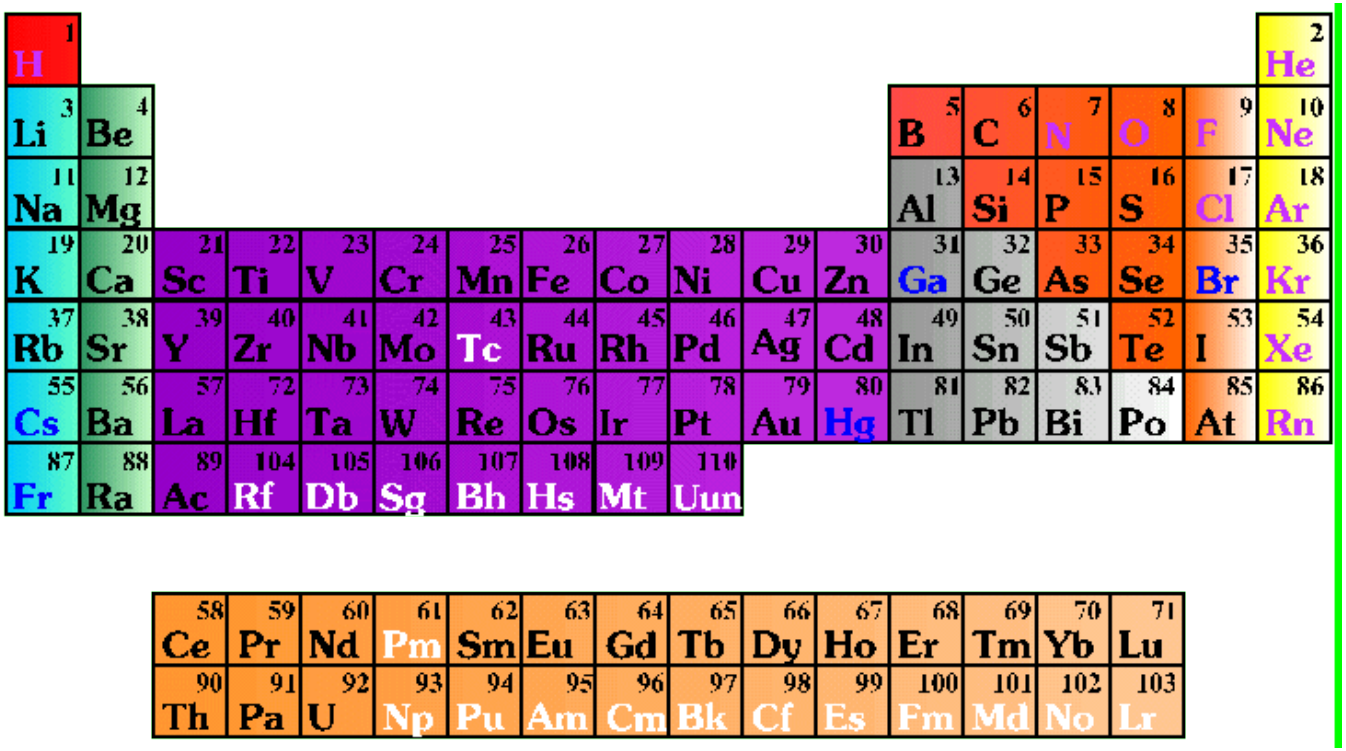
Octet Rule Always Applies to the Second Period = n^2 ; number of orbitals

$2s$, $2p_x$, $2p_y$, $2p_z$ ---orbitals cannot hold more than two electrons

Ne [He]; $2s^2$, $2p_x^2$, $2p_y^2$, $2p_z^2$

n = 2

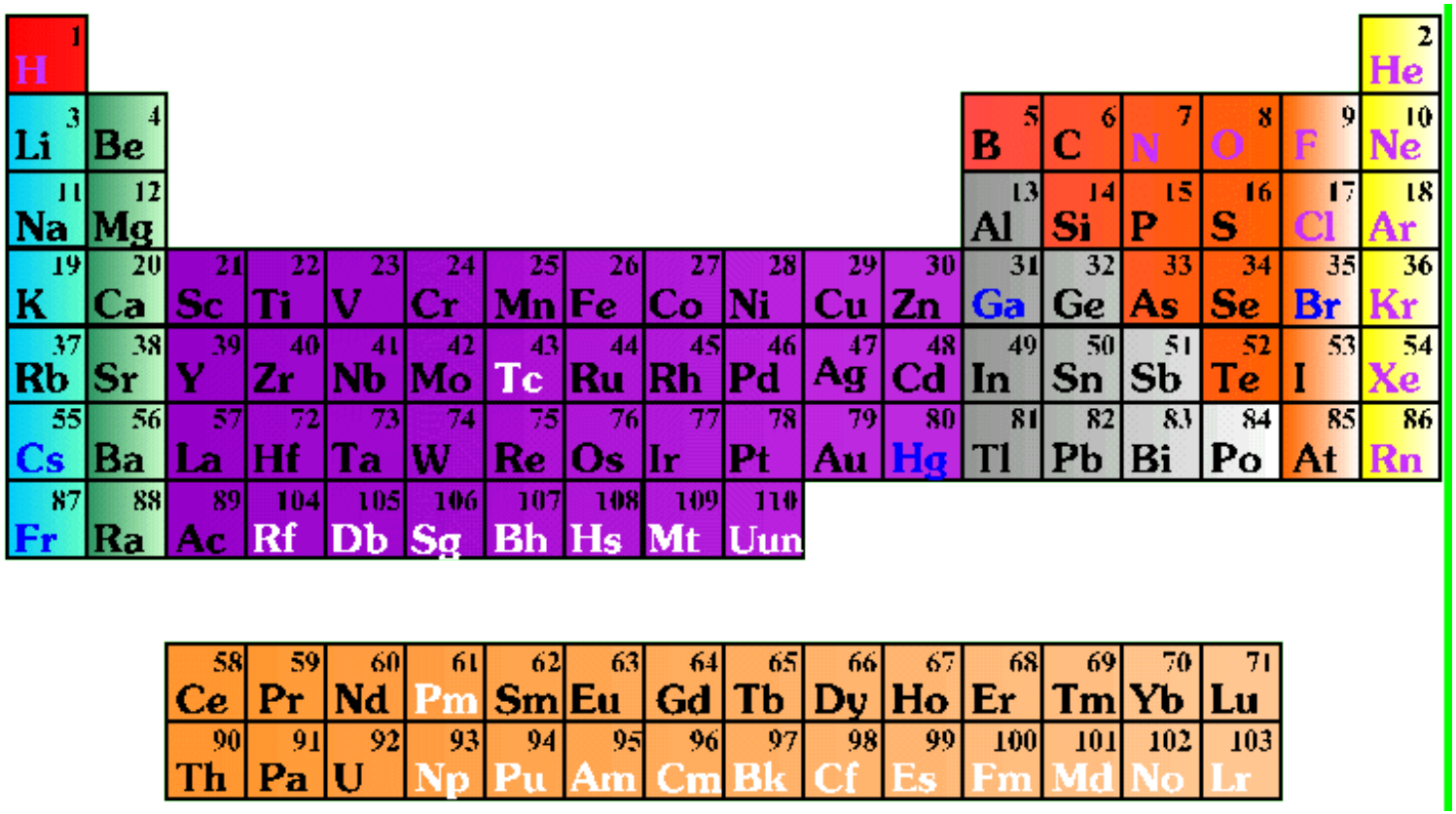
n = 3



Third Period ; $n^2 = 32 = 9$ orbitals

Ar [Ne]; $3s^2$, $3p_x^2$, $3p_y^2$, $3p_z^2$ $3d^0$ $3d^0$ $3d^0$ $3d^0$ $3d^0$

n = 3



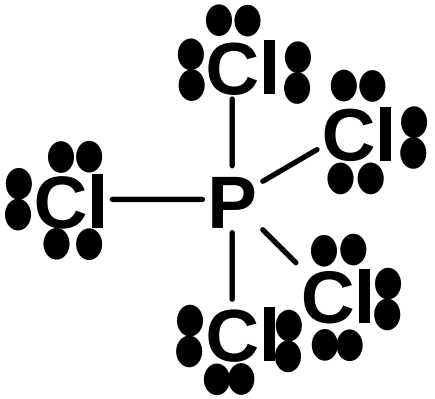
3. More than an Octet

Elements from the third Period and beyond, have *n*s, *n*p and unfilled *n*d orbitals which can be used in bonding

PCl_5

P : (Ne) $3s^2$ $3p^3$ $3d^0$

Number of valence electrons = 5 + (5 x 7) = 40

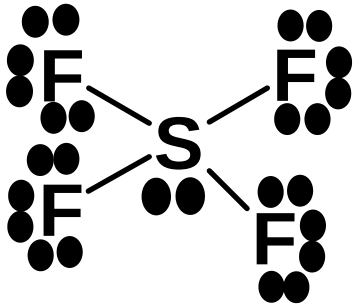


10 electrons around the phosphorus

SF_4

S : (Ne) $3s^2$ $3p^4$ $3d^0$

Number of valence electrons = 6 + (4 x 7) = 34



The Larger the central atom, the more atoms you can bond to it – usually small atoms such as F, Cl and O allow central atoms such as P and S to expand their valency.

Electronegativity **is defined as the ability of an atom in a molecule to attract electrons to itself**

Electronegativity **is a function of two properties of isolated atoms;**
The atom's ionization energy (how strongly an atom holds onto its own electrons)
The atom's electron affinity (how strongly the atom attracts other electrons)



Prof. Linus Pauling
Nobel Prize for Chemistry 1954
Nobel Prize for Peace 1962

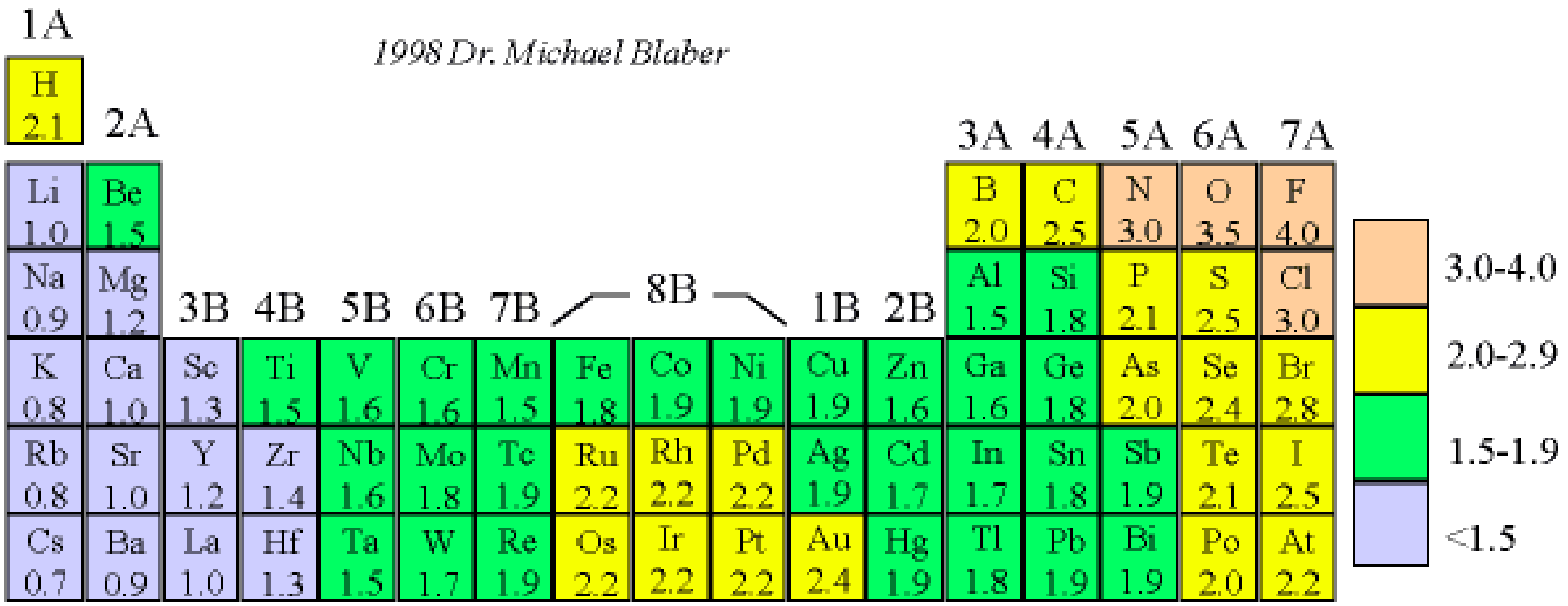
For example, an element which has:
A large (negative) electron affinity
A high ionization (always endothermic, or positive for neutral atoms)

Will: Attract electrons from other atoms and Resist having electrons attracted away

Such atoms will be highly electronegative

Pauling scale of electronegativity;

Electronegativities of the Elements

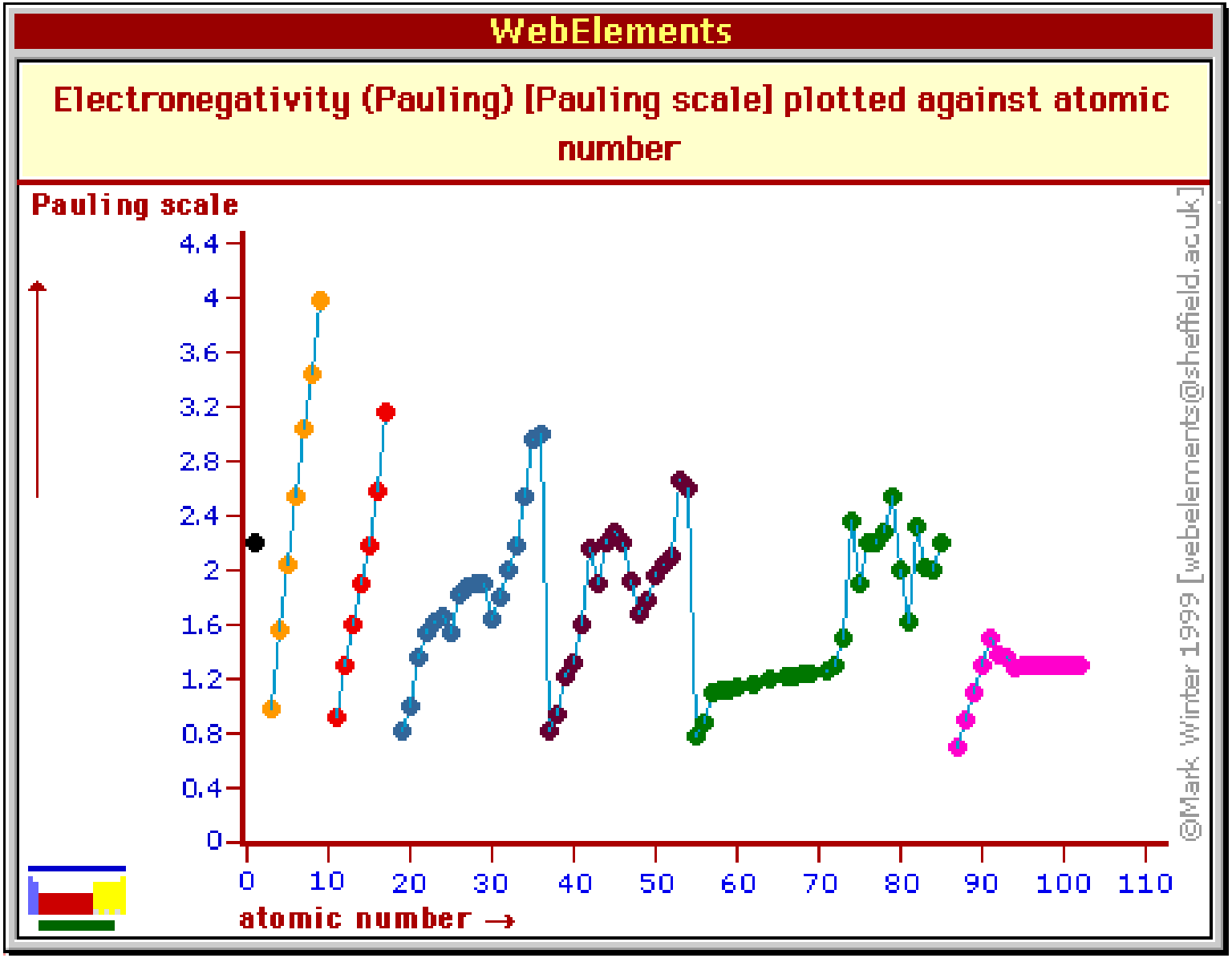


Fluorine is the most electronegative element followed by O and N, Cl are equal third. Cs is least.

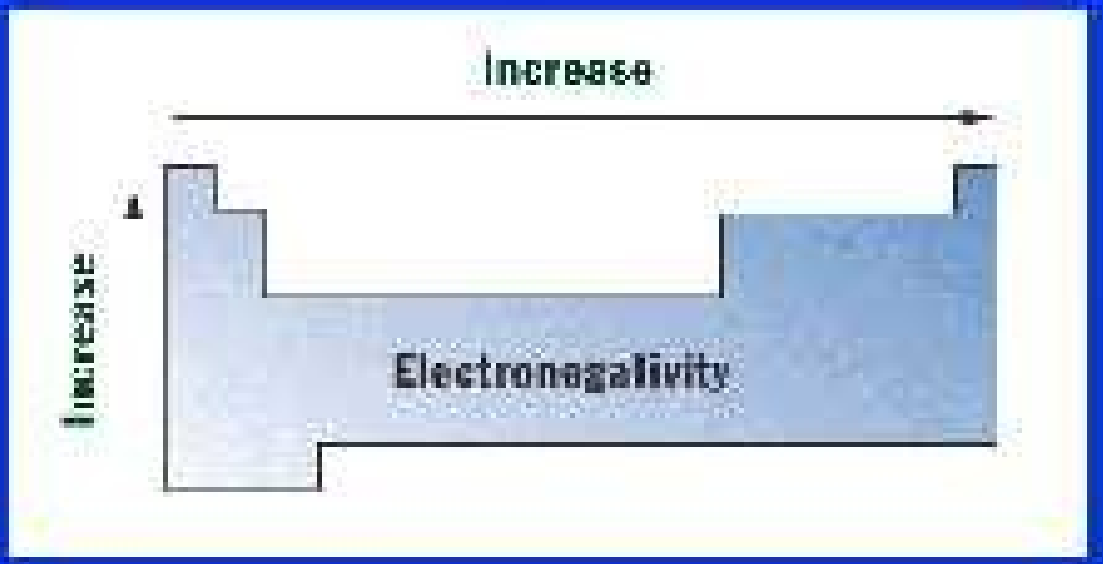
Electronegativity *increases from left to right* along the Periodic Table.

For the representative elements (s & p block), the *electronegativity decreases as you go down a group*.

No trend in the transition metals.


WebElements
Electronegativity (Pauling) [Pauling scale] plotted against atomic number
Pauling scale
4.4
4
3.6
3.2
2.8
2.4
2
1.6
1.2
0.8
0.4
0
0
10
20
30
40
50
60
70
80
90
100
110
atomic number →
©Mark Winter 1999 [webelements@sheffield.ac.uk]

Electronegativity Trends



Electronegativity is dictated by

- The number of protons in the nucleus

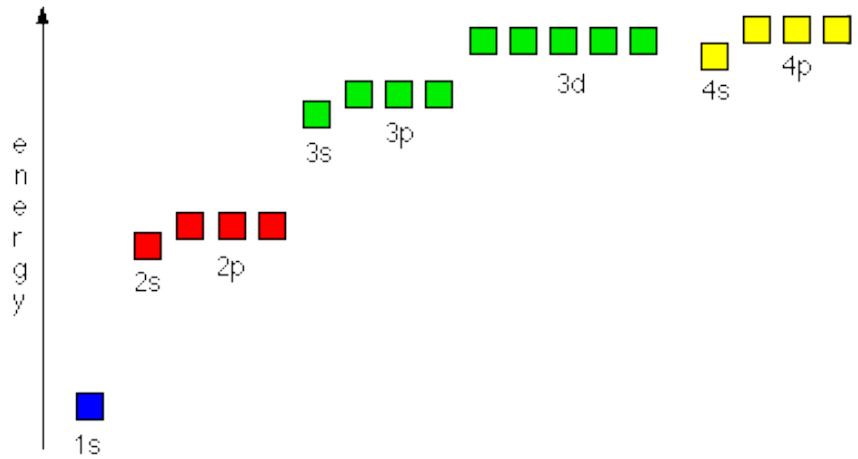
across a period you are increasing the number of protons, but filling electrons in the same Bohr quantized energy level. You are only filling sub-shells, so electronegativity increases from left to right

- The distance from the nucleus

down groups, you are placing electrons into new quantized energy levels, so moving further away from the attractive power of the nucleus. Outer shell becomes further away from the nucleus.

- The amount of screening by the inner electrons

level of screening upon bonding electrons increases down groups, and adds to the reduction in electronegativity. Screening is caused by repulsion of electrons for each other.



In hydrogen atom, energy of orbital depends on the principle quantum number, *n*.
But in many electron atoms, electron-repulsions cause different sub-shells to have different energies,
Sub-shell energy increases (with increasing *l*)
s < p < d

The three major types of intramolecular bond can be described by the electronegativity difference:

Non-Polar Covalent – Bonds which occur between atoms with little or no electronegativity difference (less than 0.5).

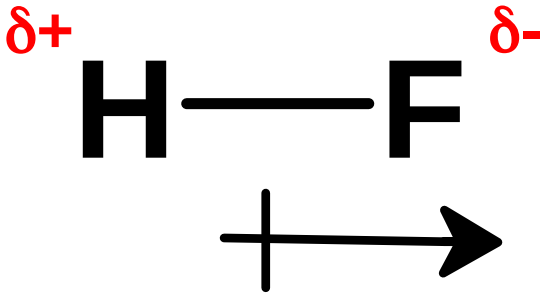
Polar Covalent – Bonds which occur between atoms with a definite electronegativity difference (between 0.5 and 2.0).

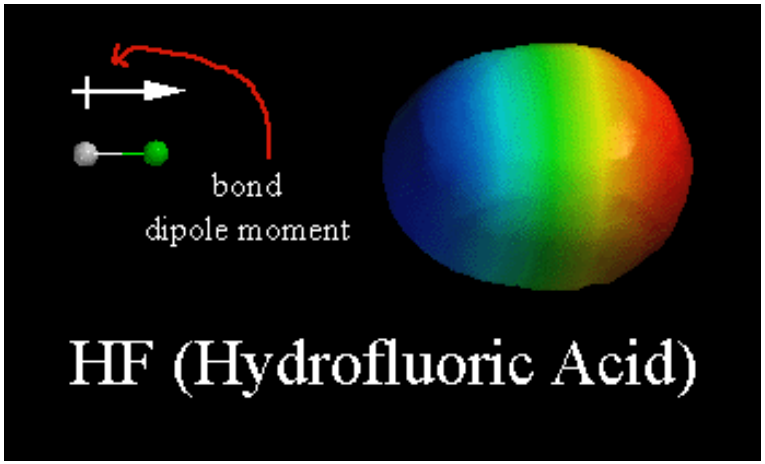
Ionic – Bonds which occur between atoms with a large electronegativity difference (2.0 or greater), where electron transfer can occur.

E.g. **F-F (4.0 – 4.0 = 0) is *non-polar covalent***

H-F (4.0 – 2.1 = 1.9) is *polar covalent*

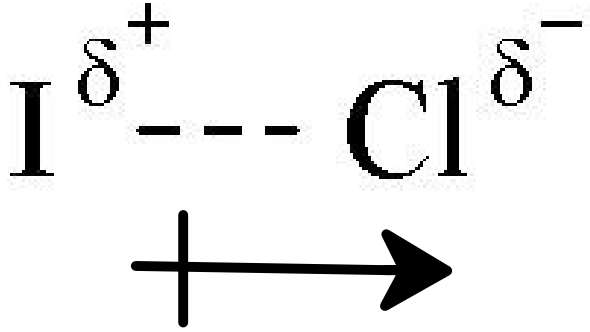
LiF (4.0 – 1.0 = 3.0) is ionic





The Relationship between Electronegativity and Bond Type

Electronegativity difference between the bonding atoms	Bond type	Covalent character	Ionic character
zero ↓ intermediate ↓ large	covalent ↓ polar covalent ↓ ionic	Increases	Increases



Dipole Moment occurs in any polar covalent bond, because of an unequal sharing of the electron pair between two atoms

E.g. Which of the following bonds is most polar: S-Cl, S-Br, Se-Cl or Se-Br?
S-Cl (3.0 – 2.5) = 0.5
S-Br (2.8-2.5) = 0.3
Se-Cl (3.0-2.4) = 0.6
Se-Br (2.8-2.4) = 0.4
Therefore, Se-Cl is the most polar!

We should be able to reach the same conclusion using the Periodic Table,
Cl is furthest to the right and to the top of the Periodic Table, so is the most electronegative. Se is furthest to the left ('metallic like') and towards the bottom. Therefore, difference in electronegativity should be the greatest!

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
H-F	0.92	1.9	1.82
H-Cl	1.27	0.9	1.08
H-Br	1.41	0.7	0.82
H-I	1.61	0.4	0.44

Electronegativity difference decreases as bond length increases

Dipole Moment: $\mu = Qr$



Prof. Peter Debye
Noble Prize 1936

Dipole moment is defined as the magnitude of charge (*Q*) multiplied by the distance between the charges;
units are D (Debye) = 3.36 x 10^{30} C.m

When proton & electron 100 pm apart, the dipole moment is 4.80 D

4.8 D is a key reference value! It represents a pure charge of +1 and -1, which are 100 pm (100pm = 1Å) apart. The bond is said to be 100% ionic!

H-F; *μ = 1.82 D (measured)* *bond length = 0.92 Å*
If 100% ionic,
μ = 92/100 (4.8 D) = 4.42 D
% ionic = 1.82/4.42 x 100 = 41 % ionic

H-Cl; *μ = 1.08 D (measured)* *bond length = 1.27 Å*
If 100% ionic,
μ = 127/100 (4.8 D) = 6.10 D
% ionic = 1.08/6.10 x 100 = 18 % ionic

H-Br; *μ = 0.82 D (measured)* *bond length = 1.41 Å*
If 100% ionic,
μ = 141/100 (4.8 D) = 6.77 D
% ionic = 0.82/6.77 x 100 = 12 % ionic

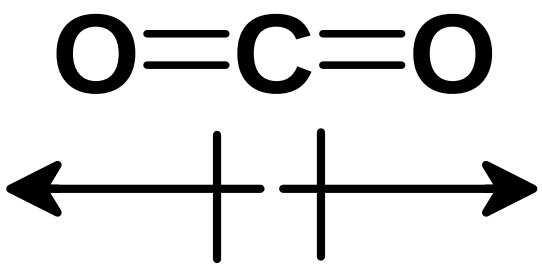
Polar Molecules = Molecules with permanent dipole moments

HCl has only one covalent bond (which is polar). Therefore, its dipole moment = H-Cl bond dipole

In a molecule with two or more polar bonds, each bond has a dipole moment contribution = bond dipole

Net dipole moment = vector sum of its bond dipoles

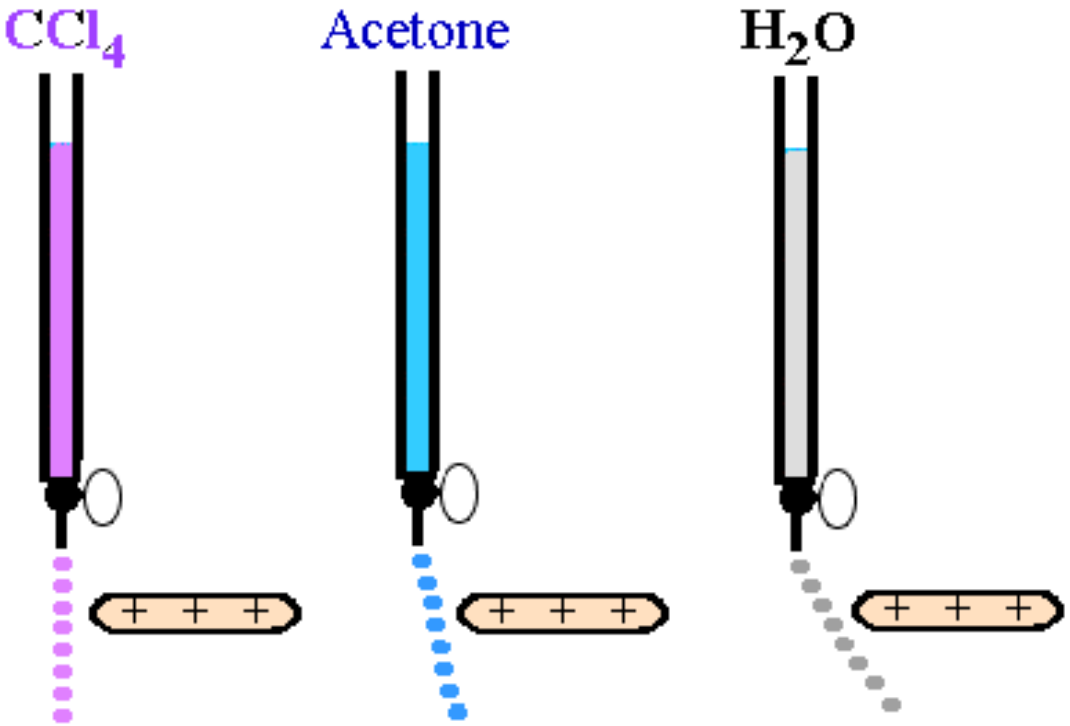
Linear Molecules: CO_2 is Non-polar



Net dipole = 0

Because CO_2 dipoles are orientated in opposite directions. The dipoles have equal magnitudes; they cancel

Symmetrical molecules (e.g. CCl_4, CH_4) are **non-polar**. The four dipoles are of equal magnitude and neutralize one another at the center of a tetrahedron



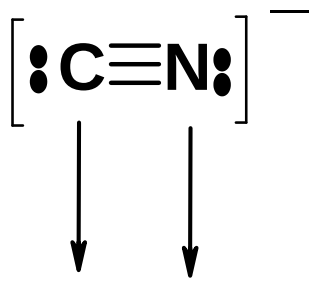
Non-symmetrical molecules (e.g. $CHCl_3$, $CO(CH_3)_2$, H_2O) are **Polar**.

The dipoles are not all equal or in opposite directions (partial charges and bond lengths are all different in C-Cl, C-H, C=O, C-H)

(H_2O is a bent molecule not linear, see later notes)

Formal Charges: the number of valence electrons in the isolated atom minus the number of electrons assigned to the atom in the Lewis structure. These are not real charges, but help with keeping count of electrons in Lewis structures.

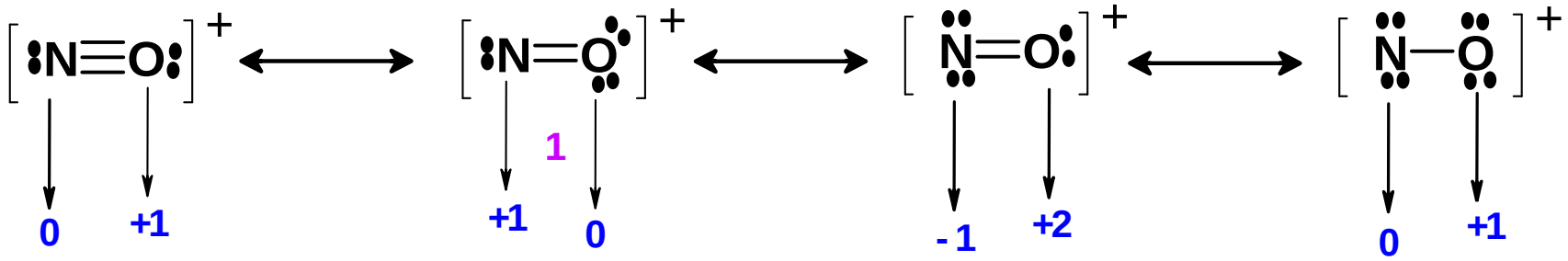
E.g. CN^-



Number of valence electrons = 9 + 1 =10

Question: Draw the Lewis structures of NO^+ and determine the formal charges of the atoms. Which Lewis structure is the preferred one?

Number of valence electrons = 11 - 1 = 10

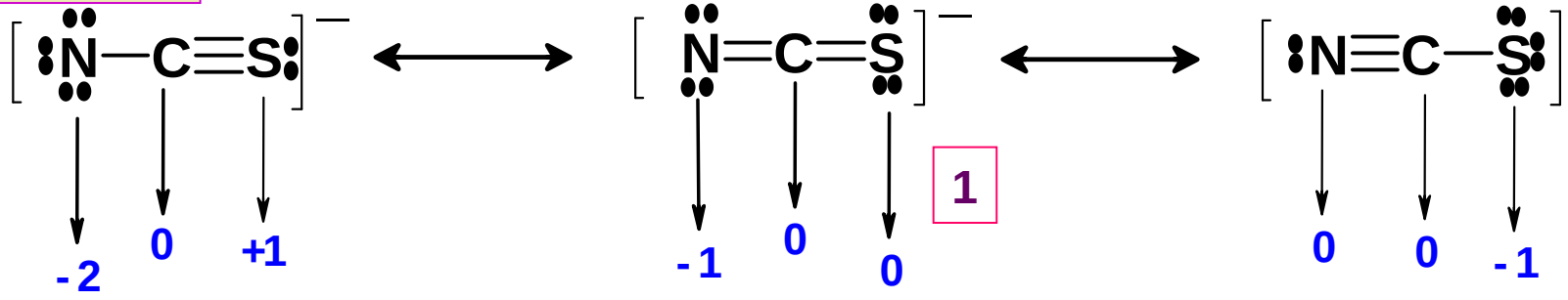


Structure 1 is preferred because the positive charge is on the least electronegative atom.

Lewis structures of Charged Molecules: Predict the most likely structure!

E.g. NCS^-

Number of valence electrons = 15 + 1 =16



Structure 1 is preferred because the negative charge is on the most electronegative atom with the lowest formal charge.

Tutorial Questions:

1. **Use the electronegativities of C (2.5) and Cl (3.0) to describe the character of the C-Cl bond in CCl_4, and explain why CCl_4 is a non-polar molecule.**
2. **$CHCl_3$ has a C-Cl bond of 178 pm, and measurements reveal 1.87 D. Calculate the percentage ionic character. Is this a polar molecule?**
3. **Draw the most plausible Lewis Structure for NO_2^+, H_2SO_4 and SO_4^{2-}**
4. **Describe the molecule $(ClO_2)^-$ using three possible Lewis structures, which is the most important?**

Shapes of Molecules

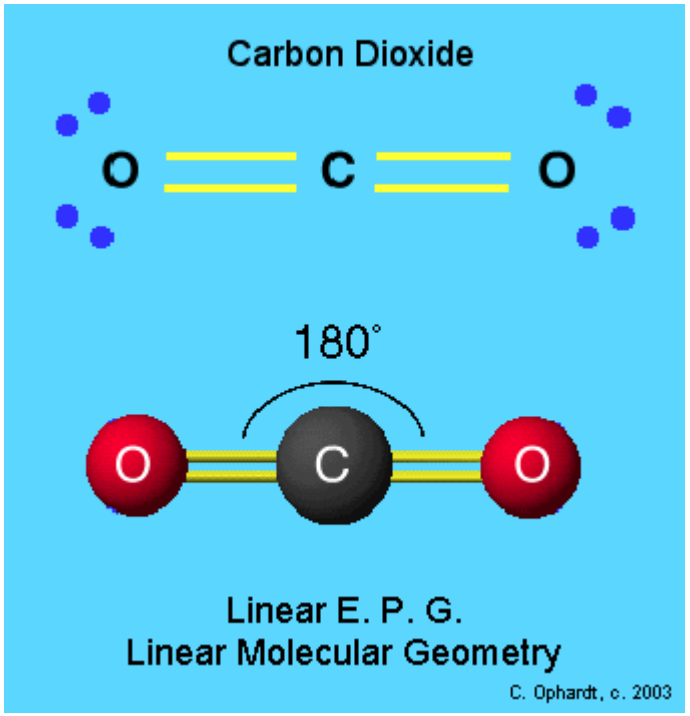
We use Lewis structures to account for formula of covalent compounds.
Lewis structures also account for the number of covalent bonds.

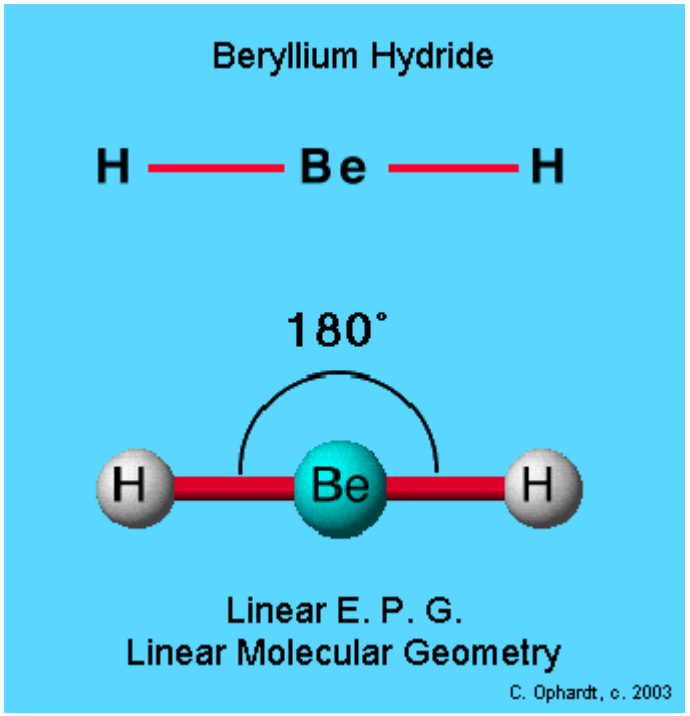
Lewis structures however do *not* account for the shapes of molecules.

Molecules of AB_n have shapes dependent on the value of *n*

AB_2 must be either linear or bent:

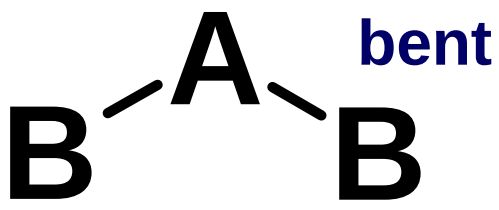
Examples of Linear molecules





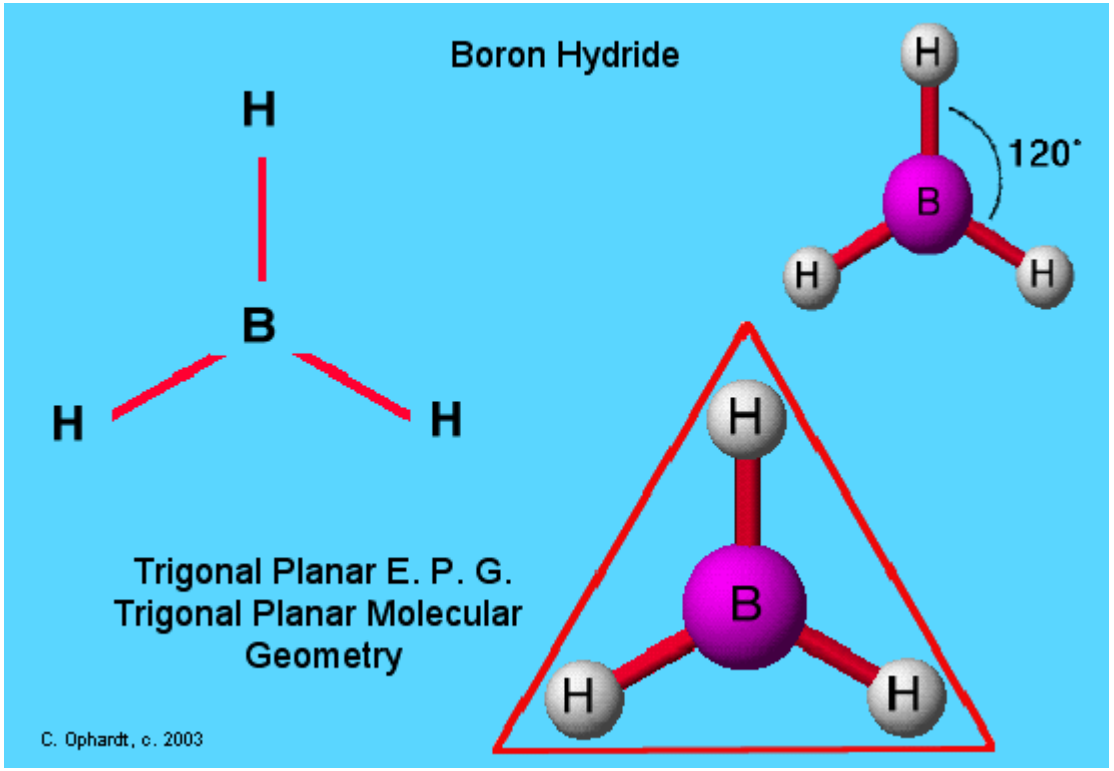
Linear - No non-bonding electrons

Linear Molecules have a bond angle = 180°
Bent molecules have a bond angle ≠ 180°



AB_3 most common shapes place the B atoms at the corners of an equilateral triangle:

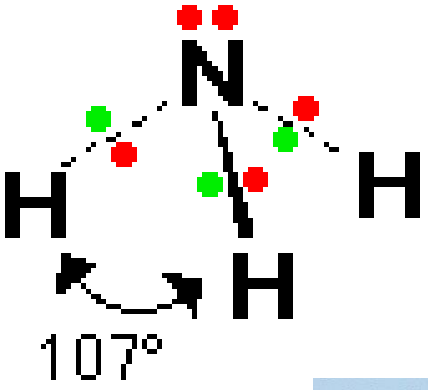
Trigonal Planar



The A atom lies in the *same plane* as the B atoms (Flat)

Bond angle = 120°

No non-bonding electrons

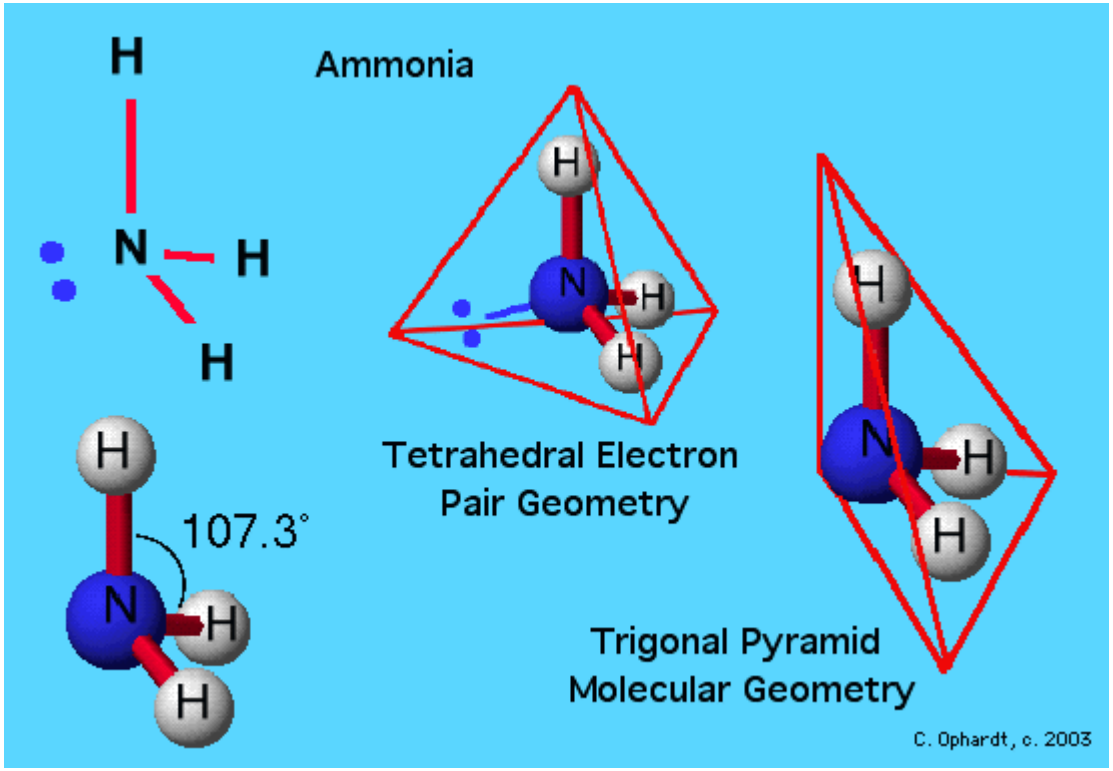


Trigonal Pyramidal

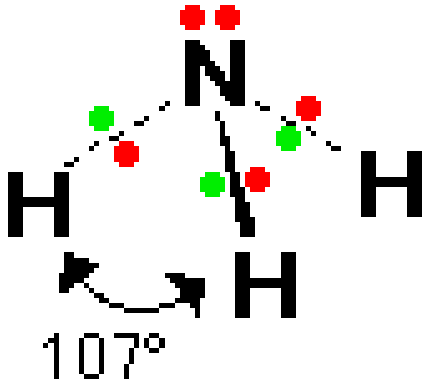
The A atom lies above the plane of the B atom.
Pyramid with an equilateral triangle as the base.



The ideal tetrahedron has a bond angle = 109.5°



VSEPR model explains distortions of molecules

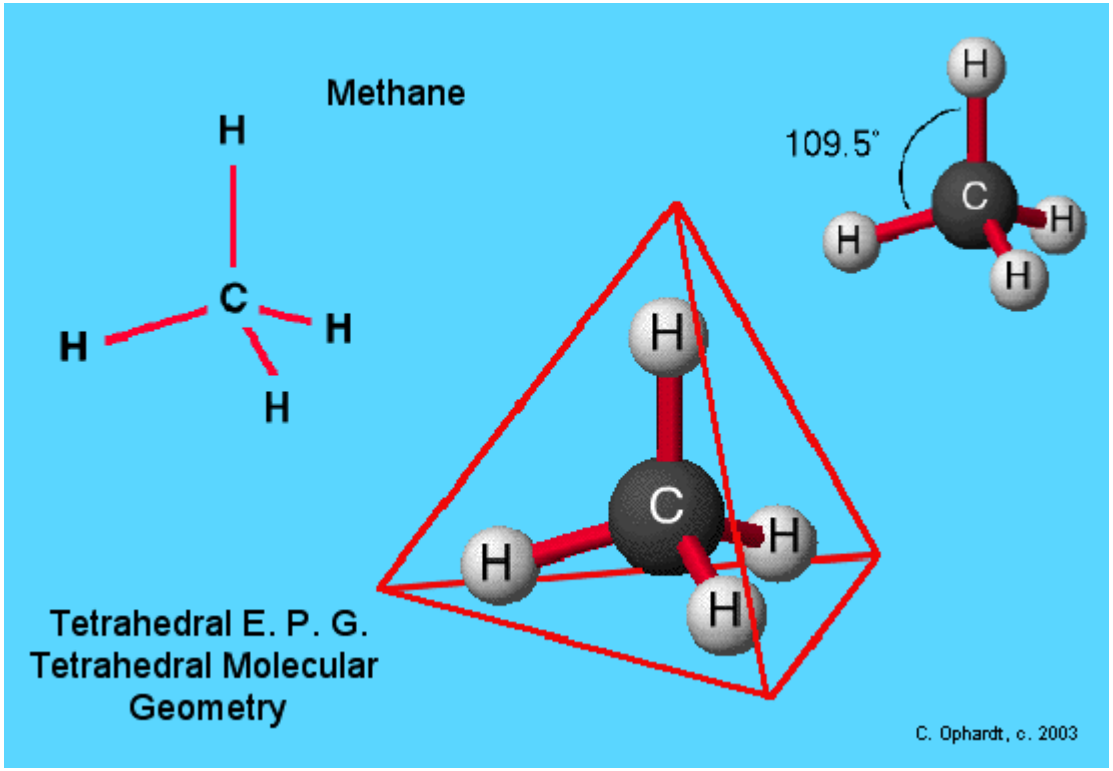


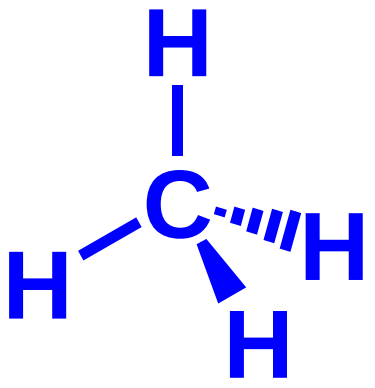
The lone electron pair exerts a little extra repulsion on the three bonding hydrogen atoms to create a slight compression to a 107° bond angle.

Less repulsion is exerted by a bonding pair of electrons because they feel attraction from two nuclei, while a non-bonding pair feels attraction from only one nucleus.

***Non-bonding pairs spread out more*!**

AB_4 is Tetrahedral





The carbon has 4 valence electrons and thus needs 4 more electrons from four hydrogen atoms to complete its octet. The hydrogen atoms are as far apart as possible at 109° bond angle. This is tetrahedral geometry. The molecule is three dimensional.

Valence-Shell Electron-Pair Repulsion Theory (VSEPR)

In molecules there are 2 types of electron
1. Bonding Pairs
2. Non-bonding or lone pairs

The combinations of these determine the shape of the molecule

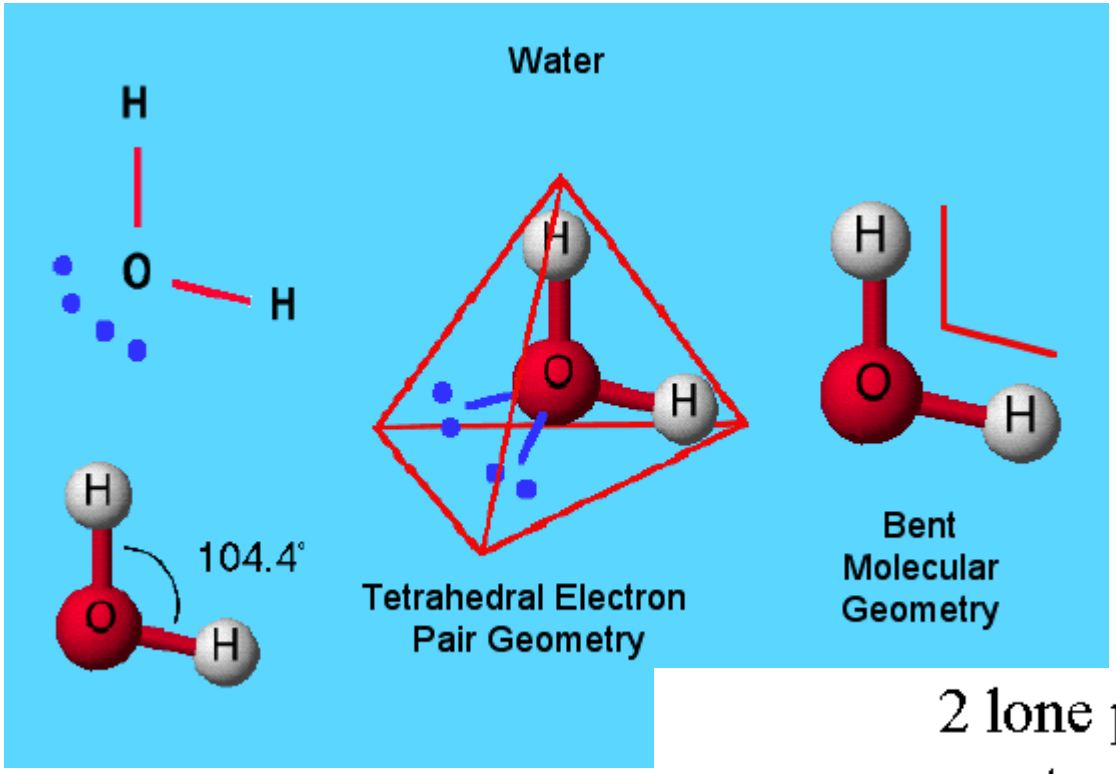
Single bonds have a big impact on shape, double bonds have little effect

The outer pairs of electrons around a covalently bonded atom minimize repulsions between them by moving as far apart as possible

Bonding pair	–	Bonding pair	Increasing repulsion ↓
Bonding pair	–	Non-bonding pair	
Non-bonding pair	–	Non-bonding pair	

Water is a bent molecule with bond angles of 104.5°

Notice – the bond angle decreases as the number of non-bonding pairs increases



H_2O

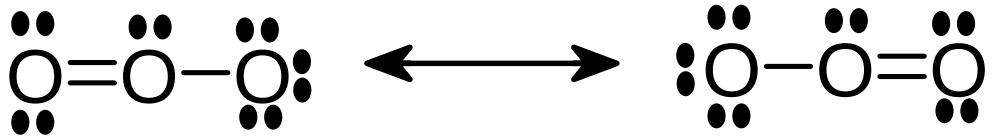
AB_2 - classification

2 lone pairs on the oxygen create a repulsion, *bending* the molecule

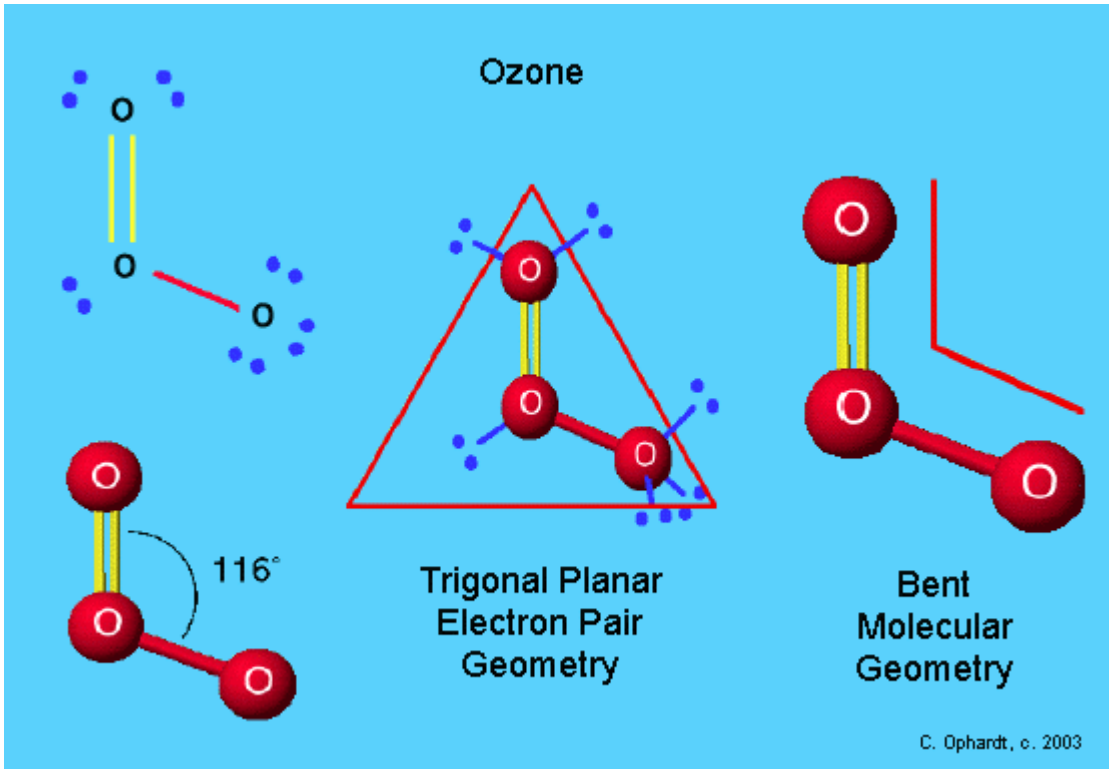


Ozone

O_3 ; number of valence electrons = 18 electrons



Resonance structures



AB_3 - classification

Valence Shell Electron-Pair Repulsion Theory (VSEPR)

Procedure

1. Sum the total Number of Valence Electrons

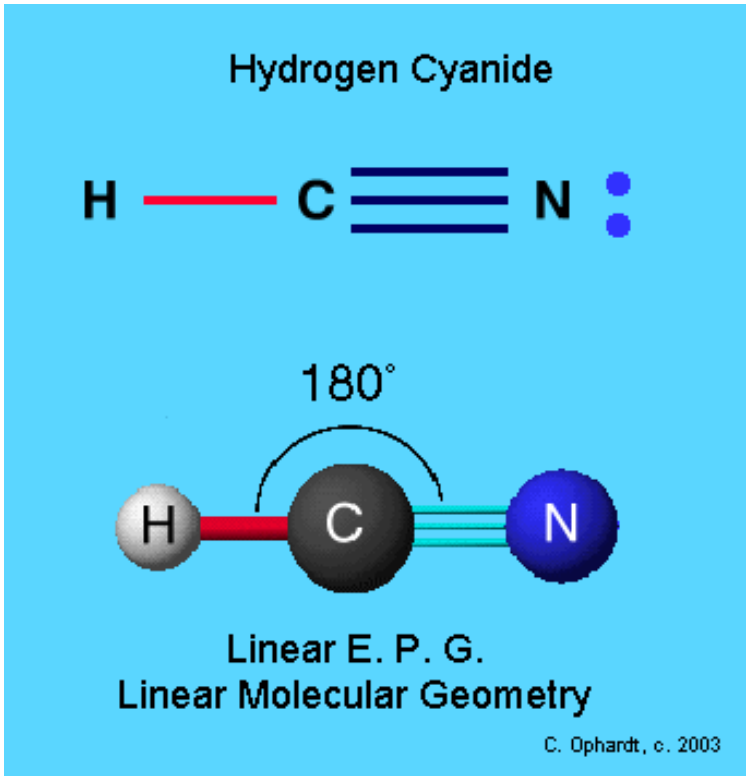
Drawing the Lewis Structure

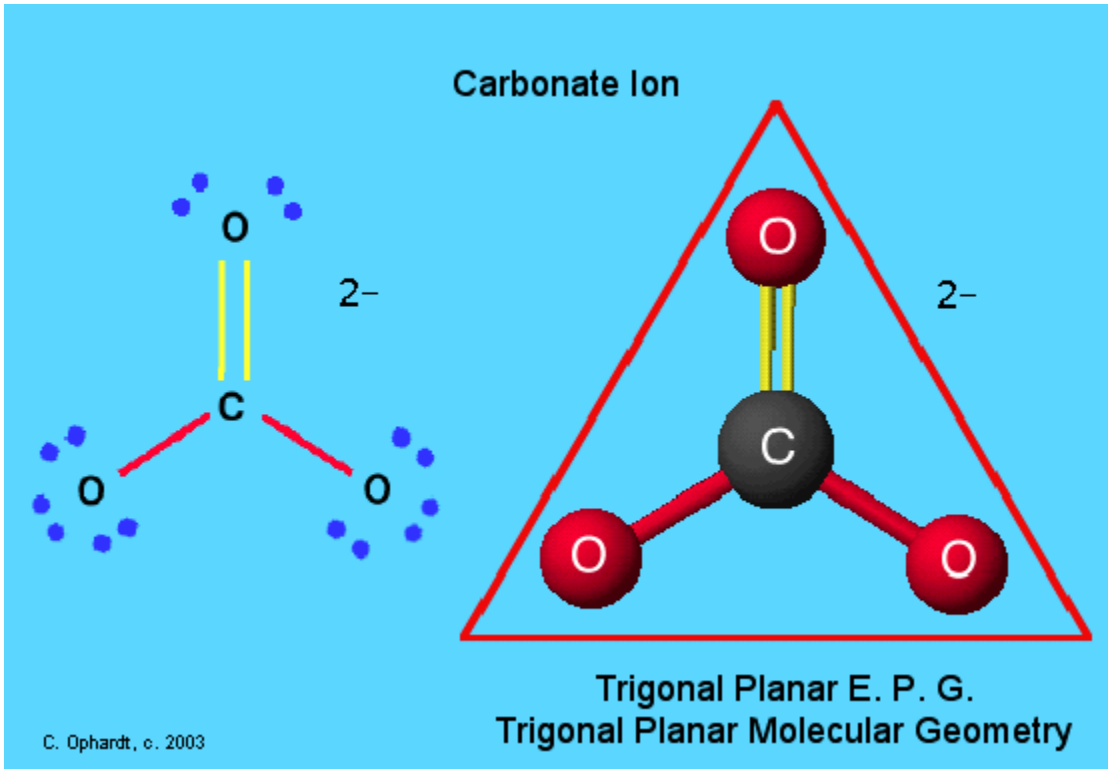
2. The atom usually written first in the chemical formula is the Central atom in the Lewis structure
3. Complete the octet bonded to the Central atom. However, elements in the third row have empty d-orbitals which can be used for bonding.
4. If there are not enough electrons to give the central atom an octet try multiple bonds.

Predicting the Shape of the Molecule

5. Sum the Number of Electron Domains around the Central Atom in the Lewis Structure; Single = Double = Triple Bonds = Non-Bonding Lone Pair of Electrons = One Electron Domain
6. From the Total Number of Electron Domains, Predict the Geometry and Bond Angle(s); 2 (Linear = 180º); 3 (Trigonal Planar = 120º); 4 (Tetrahedral = 109.5º); 5 (Trigonal Bipyramidal = 120º and 90º); 6 (Octahedral = 90º)
7. Lone Pair Electron Domains exert a greater repulsive force than Bonding Domains. Electron Domains of Multiple Bonds exert a greater repulsive force than Single Bonds. Thus they tend to compress the bond angle.

Further Examples:





Tutorial Questions :

Draw Lewis structures and the molecular geometry of the following molecules:

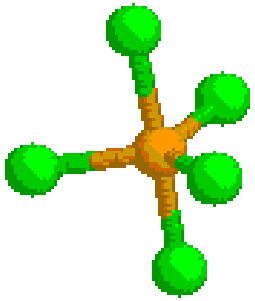
H_3O^+, NH_4^+, CS_2, SCl_2

Shape	Bonding-pairs	Non-bonding pairs	Bond angle /°	Examples
Linear	2	0	180	$BeCl_2$, CO_2, HCN, C_2H_2
Trigonal planar	3	0	120	BF_3, SO_3, NO_3^-, CO_3^{2-}, C_2H_4
Tetrahedral	4	0	109.5	NH_4^+, SO_4^{2-}, PO_4^{3-}, $Ni(CO)_4$, CH_4
Trigonal pyramidal	3	1	107	PH_3, SO_3^{2-}, NH_3
Non-linear (Crooked)	2	2	105	H_2S, SO_2, H_2O

Molecules with Expanded Valence Shells

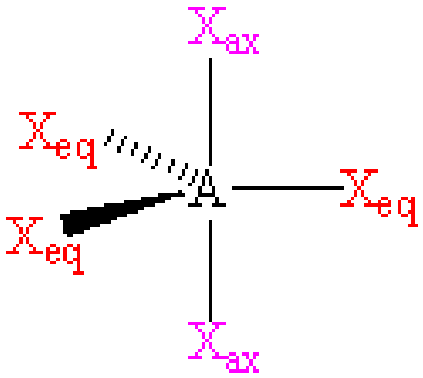
When the central atom of a molecule is from the third period of the Periodic Table and beyond, that atom may have more than four pairs of electrons around it

Five pairs of electrons around the central atom are based on the Trigonal Bipyramidal structure.



AB_5: e.g. PCl_5

Three pairs define an Equatorial Triangle (Equatorial electrons)
Two pairs lie above and below the triangle plane (Axial electrons)



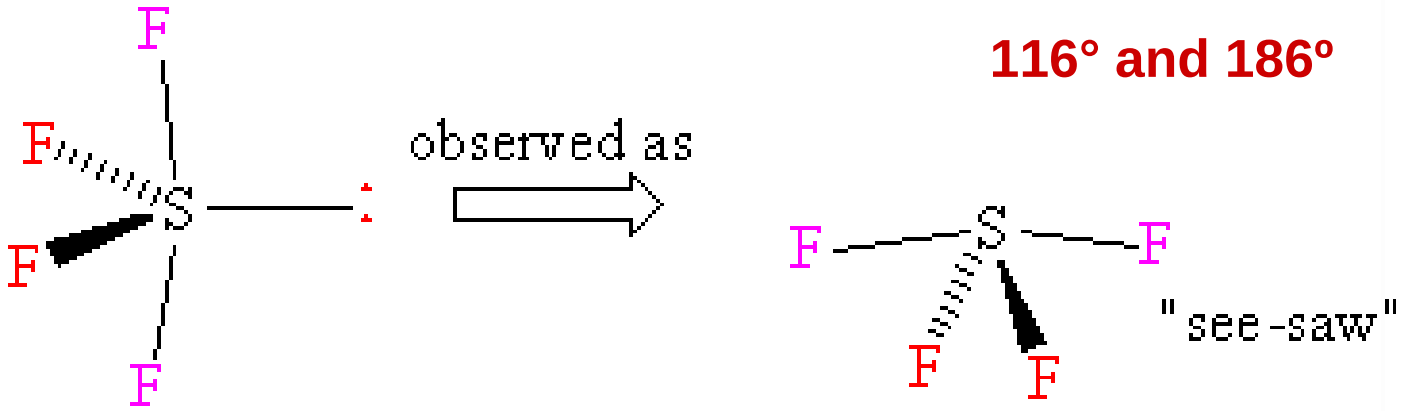
axial positions are 90° from 3 equatorial positions

equatorial positions are 90° from 2 axial positions

The repulsion between pairs located 90° apart are *much* greater than for those 120° apart:

Because repulsion is greater for non-bonding than for bonding electron pairs, then non-bonding pairs occupy equatorial positions on the Trigonal Bipyramidal structure

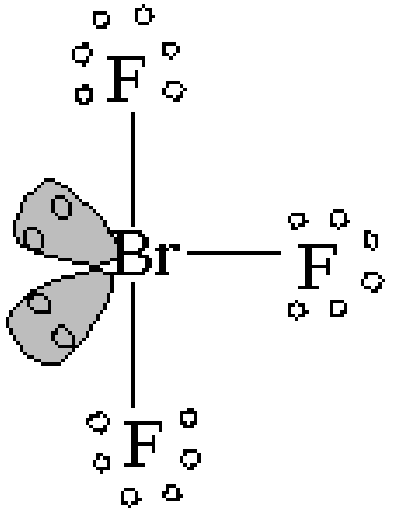
SF_4 :



116° and 186°

The non-bonding pair occupies an equatorial position. The axial and equatorial S-F bonds are slightly bent back because of the larger repulsive effect of the lone pair.

BrF_3 : T-shaped

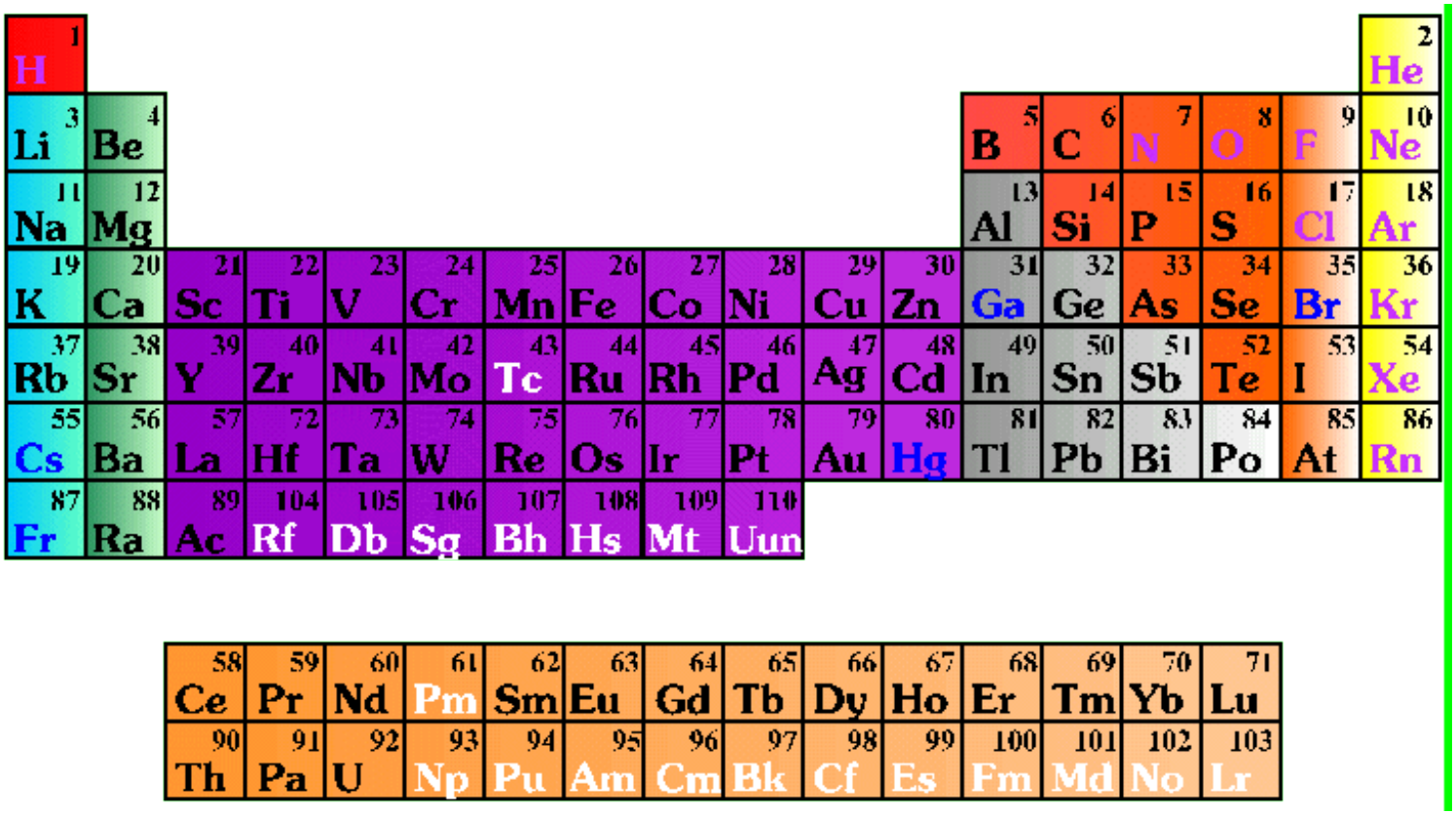


90°

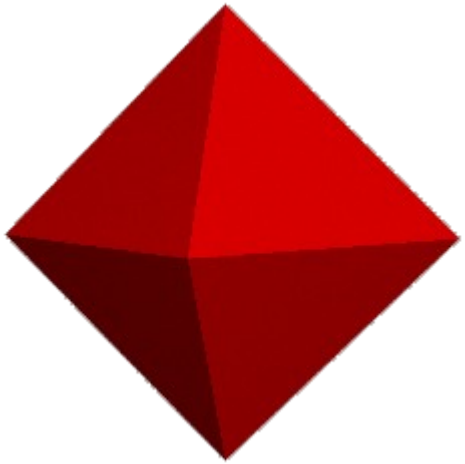
Third Period ; $n^2 = 3^2 = 9$ orbitals

Ar [Ne]; $3s^2$, $3p_x^2$, $3p_y^2$, $3p_z^2$ $3d^0$ $3d^0$ $3d^0$ $3d^0$ $3d^0$

n = 3

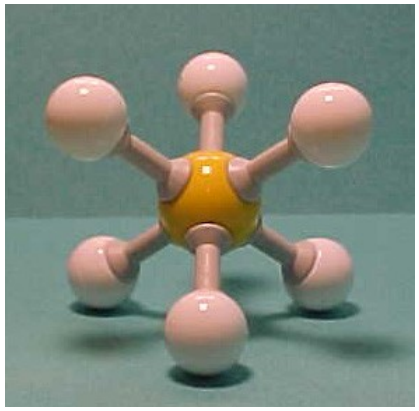


Six pairs of electrons around the central atom are based on the Octahedron structure.



AB_6 : e.g. SF_6

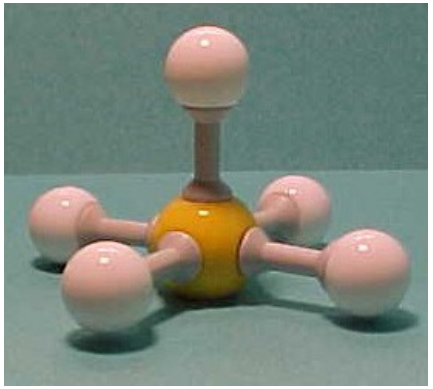
The central atom can be visualized as being at the centre of an octahedron, with the six electrons pointing to the six vertices – all bond angles are 90°



Octahedral

90°

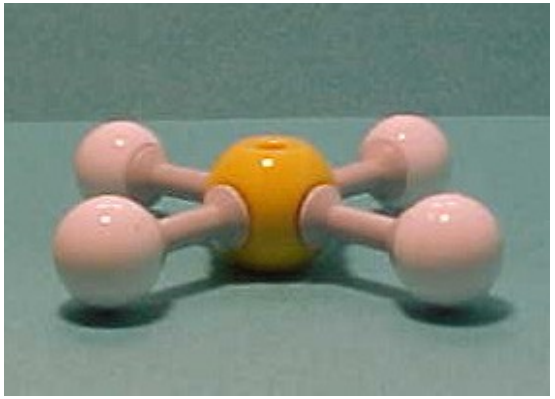
E.g. BrF_5



Square Pyramidal

Should be less than 90º

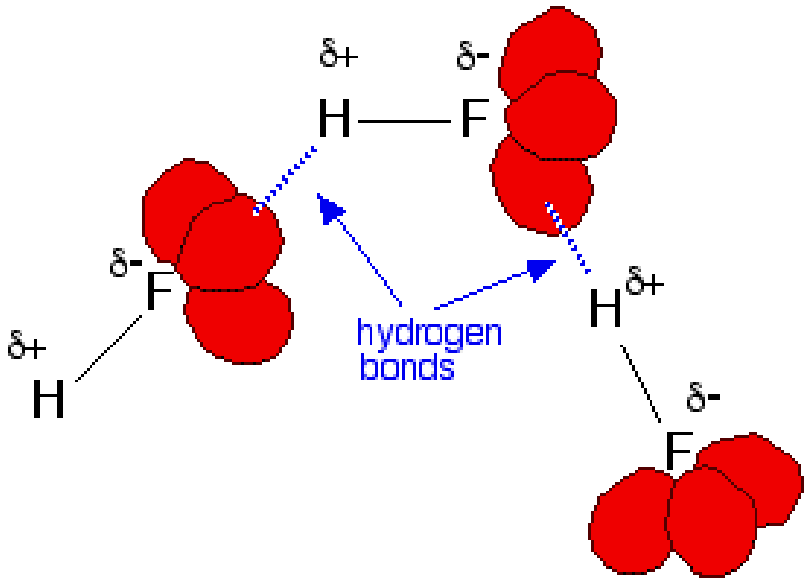
E.g. XeF_4



Square Planar

Intermolecular Forces: are generally much weaker than covalent or ionic bonds. Less energy is thus required to vaporize a liquid or melt a solid. Boiling points can be used to reflect the strengths of intermolecular forces (the higher the Bpt, the stronger the forces)

Hydrogen Bonding : ***the attractive force between hydrogen in a polar bond (particularly H-F, H-O, H-N bond) and an unshared electron pair on a nearby small electronegative atom or ion***



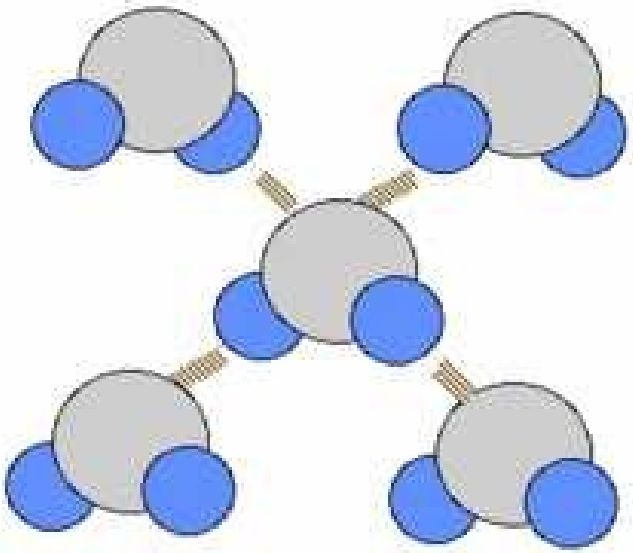
Very polar bond in H-F.
The other hydrogen halides don't form hydrogen bonds, since H-X bond is less polar. As well as that, their lone pairs are at higher energy levels. That makes the lone pairs bigger, and so they don't carry such an intensely concentrated negative charge for the hydrogens to be attracted to.

Hydrogen Bonding & Water

Hydrogen bonding

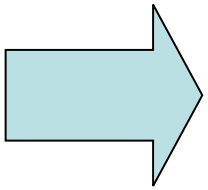
The small size of hydrogen along with the shape and polarity of the water molecule all add up to a relatively strong attraction between water molecules.

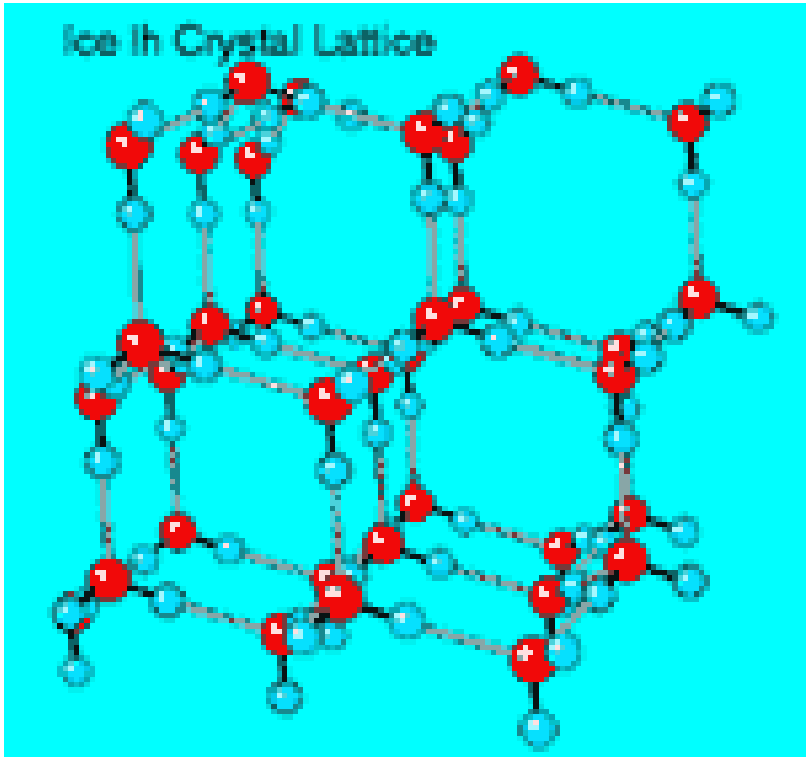
Hydrogen bonding is the strongest of the intermolecular forces.



One of the most remarkable consequences of H-bonding is found in the lower density of ice in comparison to liquid water, so ice floats on water. In most substances the molecules in the solid are more densely packed than in the liquid. A given mass of ice occupies a greater volume than that of liquid water. This is because of an ordered open H-bonding arrangement in the solid (ice) in comparison to continual forming & breaking H-bonds as a liquid.

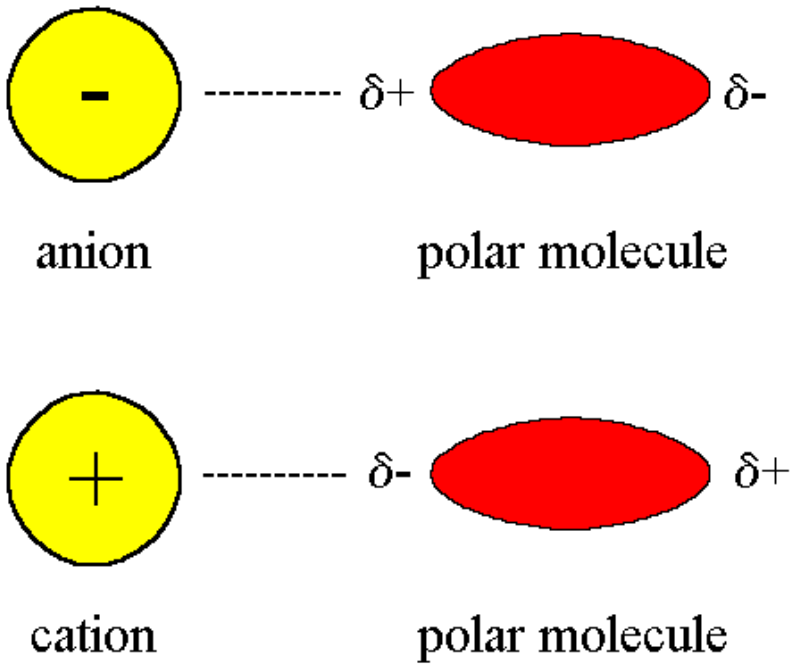






Weaker Intermolecular Forces

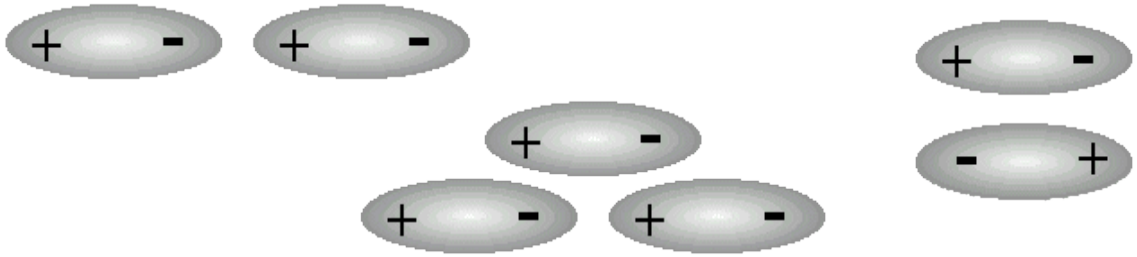
Ion-Dipole Forces



An ion-dipole force is an attractive force that results from the electrostatic attraction between an ion and a neutral molecule that has a dipole.
Most commonly found in solutions.
Especially important for solutions of ionic compounds in polar liquids.
A positive ion (cation) attracts the partially negative end of a neutral polar molecule.
A negative ion (anion) attracts the partially positive end of a neutral polar molecule.

Ion-dipole attractions become stronger as either the charge on the ion increases, or as the magnitude of the dipole of the polar molecule increases.

Dipole-dipole Attractive Forces



Attractive Dipole-Dipole Interactions

A dipole-dipole force exists between neutral polar molecules
Polar molecules attract one another when the partial positive charge on one molecule is near the partial negative charge on the other molecule
The polar molecules must be in close proximity for the dipole-dipole forces to be significant
Dipole-dipole forces are characteristically weaker than ion-dipole forces
Dipole-dipole forces increase with an increase in the polarity of the molecule

Boiling points increase for polar molecules of similar mass, but increasing dipole:

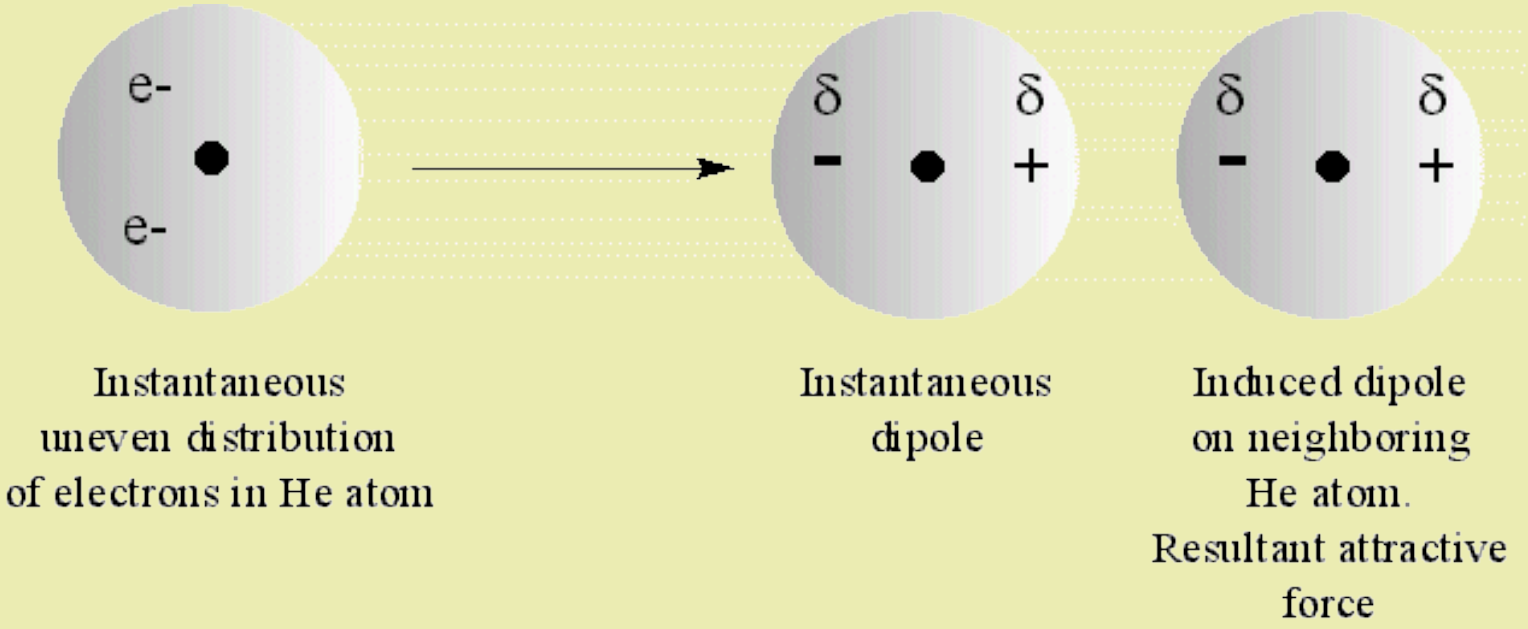
Substance	Molecular Mass (amu)	Dipole moment, *u* (D)	Boiling Point (°K)
Propane	**44**	**0.1**	**231**
Dimethyl ether	**46**	**1.3**	**248**
Methyl chloride	**50**	**2.0**	**249**
Acetaldehyde	**44**	**2.7**	**294**
Acetonitrile	**41**	**3.9**	**355**

London Dispersion Forces –
significant only when molecules are close to each other



Due to electron repulsion, a temporary dipole on one atom can induce a similar dipole on a neighboring atom

Prof. Fritz London



The ease with which an external electric field can induce a dipole (alter the electron distribution) with a molecule is referred to as the "polarizability" of that molecule

The greater the polarizability of a molecule the easier it is to induce a momentary dipole and the stronger the dispersion forces

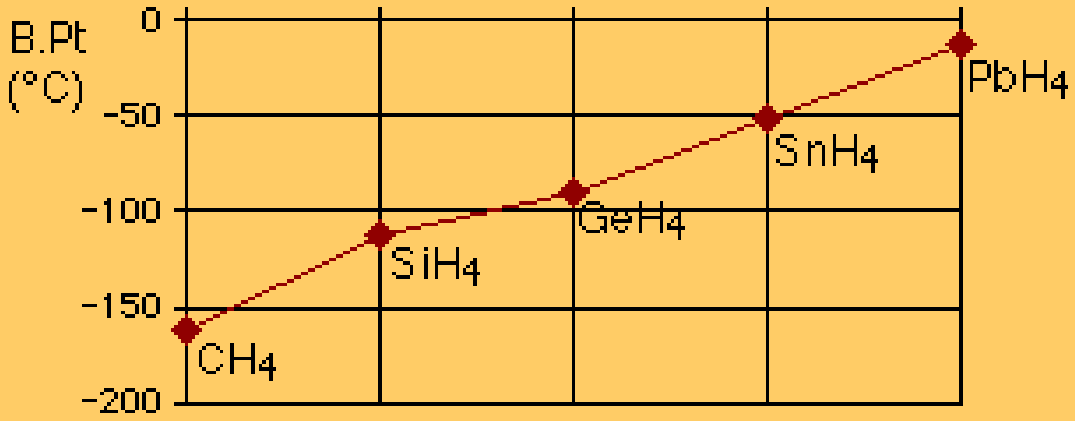
Larger molecules tend to have greater polarizability

- **Their electrons are further away from the nucleus (any asymmetric distribution produces a larger dipole due to larger charge separation)**
- **The number of electrons is greater (higher probability of asymmetric distribution)**

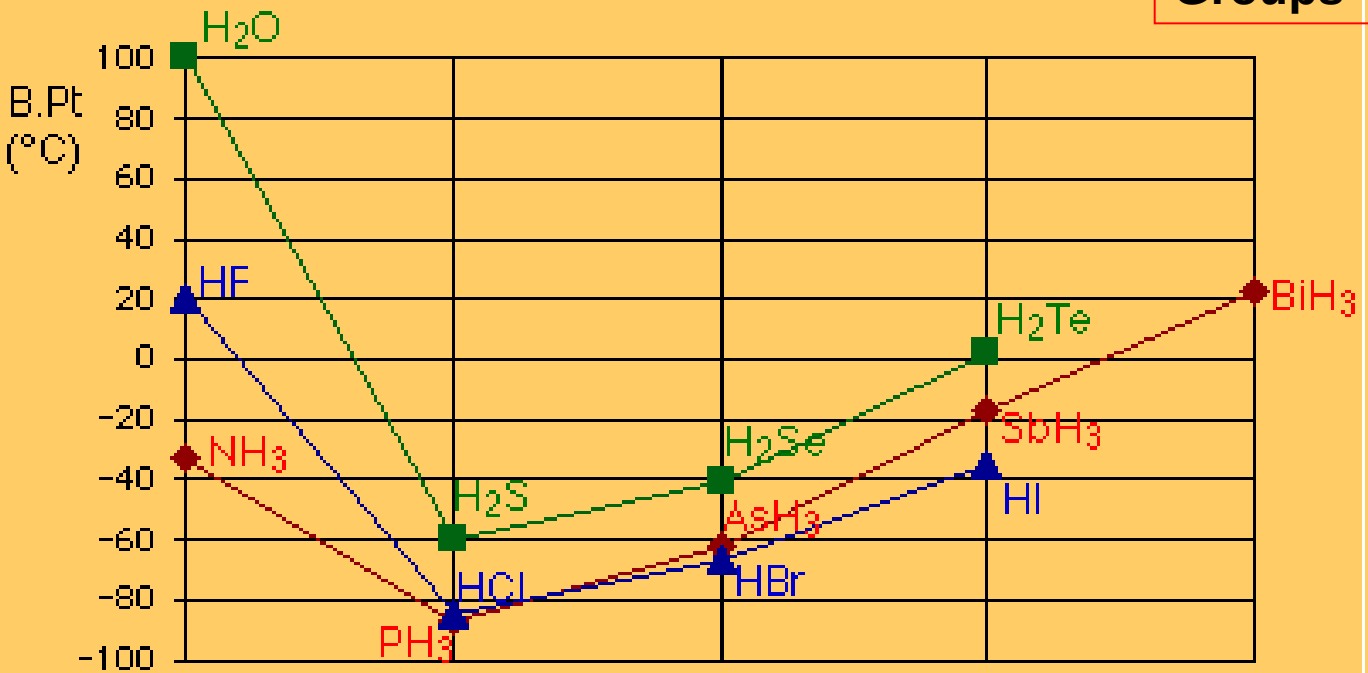
thus, dispersion forces tend to increase with increasing molecular mass

- **Dispersion forces are also present between polar/non-polar and polar/polar molecules (i.e. between all molecules)**

Van der Waals forces are made of dipole-dipole and London dispersion forces



Group 4A hydrides



Groups 4, 5, 6A hydrides