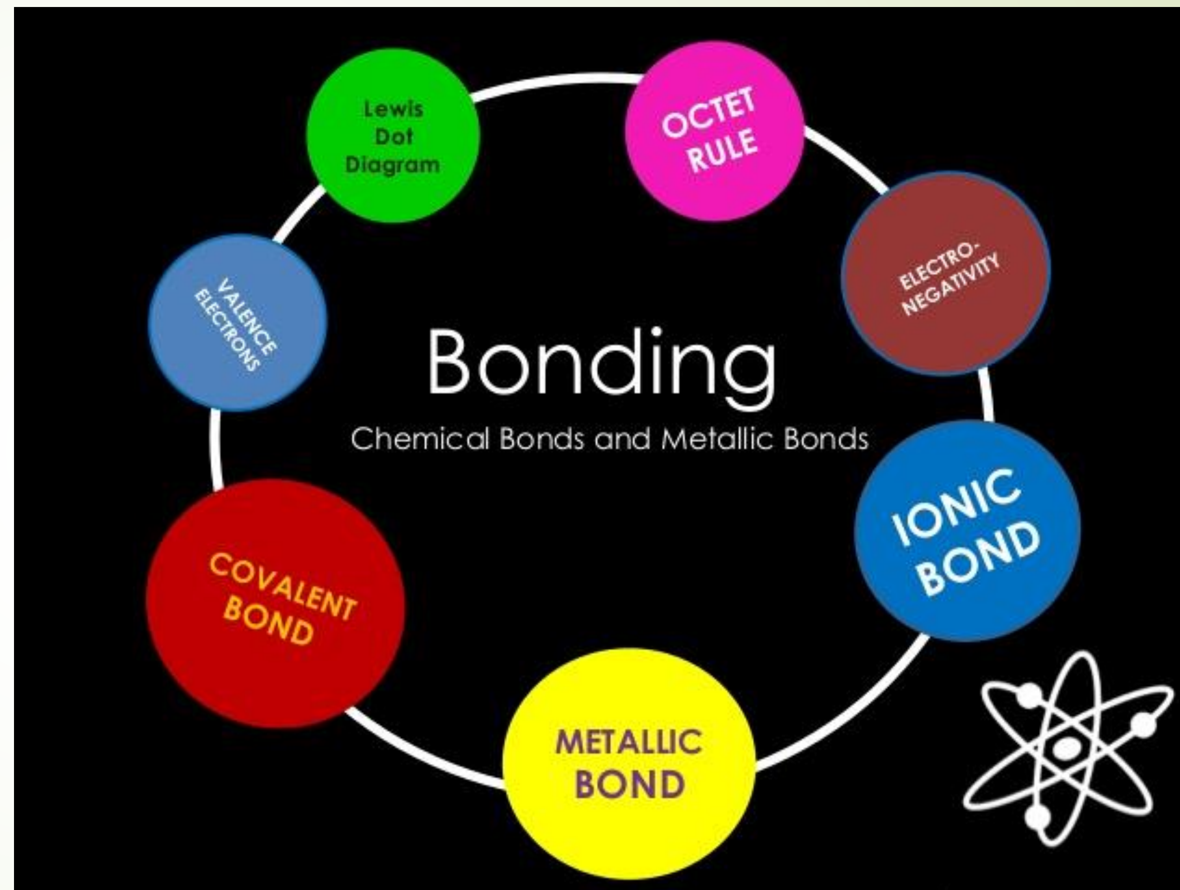
Bonding



Lewis Dot Diagram
OCTET RULE
ELECTRO-NEGATIVITY
VALENCE ELECTRONS
Bonding
Chemical Bonds and Metallic Bonds
IONIC BOND
COVALENT BOND
METALLIC BOND

Bonding

- Compounds can be divided into two main types of bonding:
  - Ionic – usually between a metal and a non-metal
  - Covalent – two or more non-metals

- Generally, elements that are close to each other on the periodic table form covalent compounds. Whereas, elements that are far apart form ionic compounds.

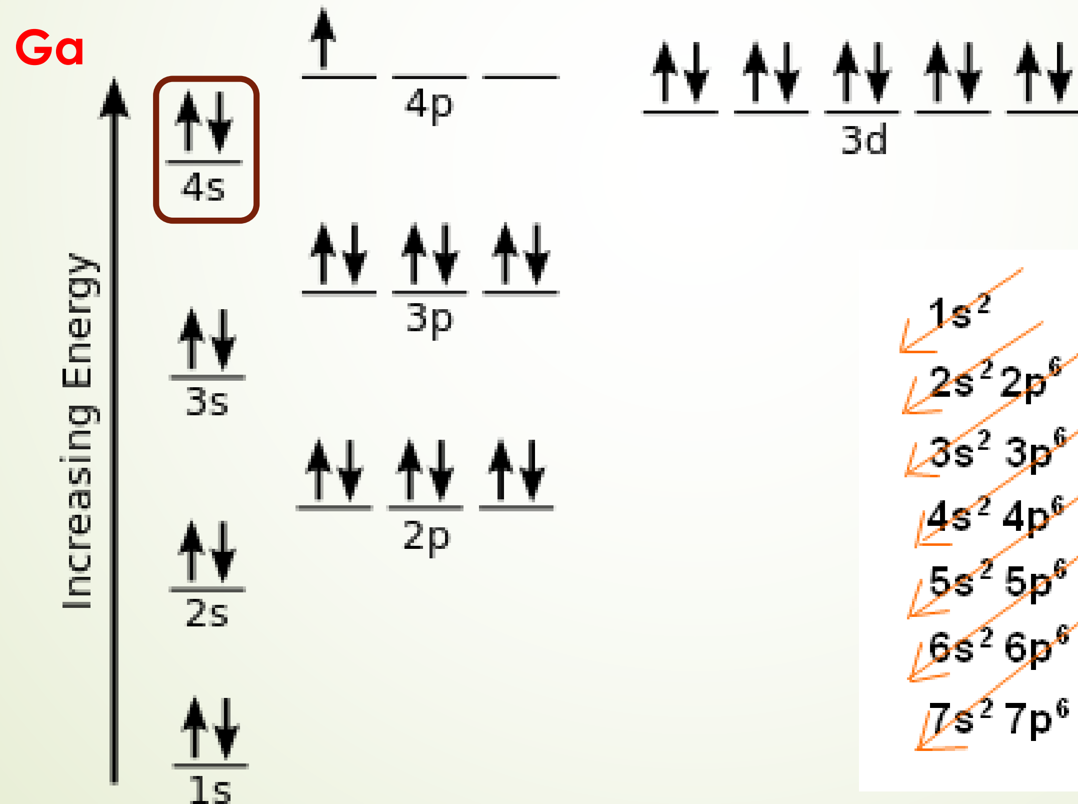
Ionic Bonding

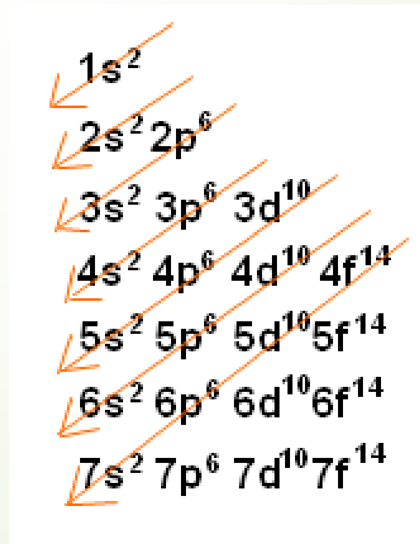
- Ionic bonding is the electrostatic attraction between oppositely charge ions
- Recall that ions are charge particles which are formed when atoms gain or lose electrons
- Positive ions (cations) are formed by metallic elements by the loss of electrons
    - Example – Magnesium, a group 2 element, loses 2 electrons from its valance shell to form a 2+ ion Negative ions are usually formed by non-metallic elements by gaining electrons
    - Example – Oxygen, a group 6 element, gains 2 electrons to fill its valance shell forming a 2− ion (anion)

- At the simplest level, elements in the main groups of the periodic table (1, 2, 3, 5, 6 and 7) gain or lose electrons to generate the electron configuration of the nearest noble gas.
- In other words, electrons are gained or lost to generate an ion that is **isoelectronic** with the nearest noble gas.
- Isoelectronic – same number of electrons

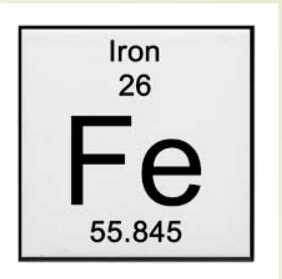
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr

- Another way of saying this is that electrons are gained or lost to generate a full valance shell. Although this is true for the first 20 elements, it is not generally true after that due to the existence of transition metals and d orbitals.
- Before we evaluate this we must be familiar with electron orbitals/configuration.





S – 2 electrons
P – 6 electrons
D – 10 electrons
F – 14 electrons



1s

2s

2p

3s

3p

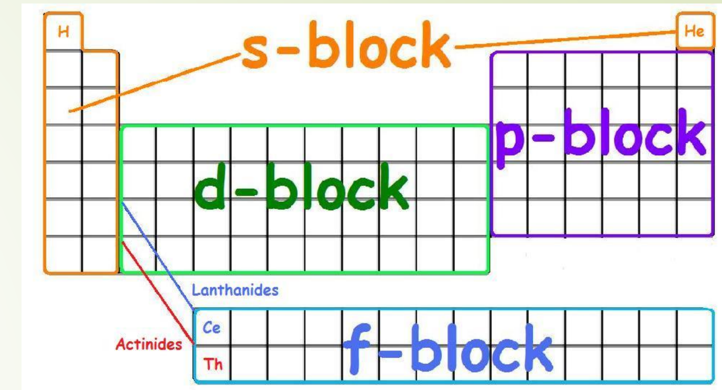
3d

4s

4p

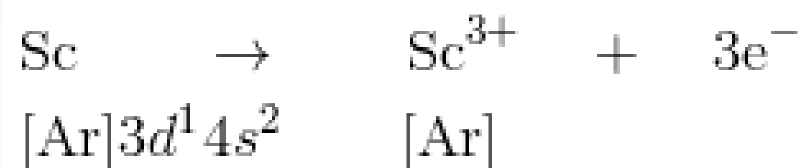
Transition Metals

"an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incomplete d sub-shell".

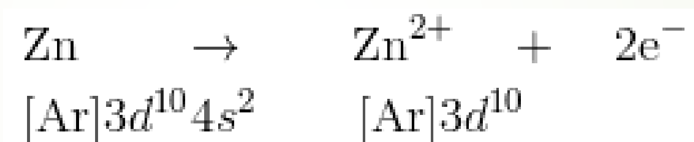


- Located in the '**d-block**'
- Can form more than one ion
  - For example, iron can form Fe^{2+} and Fe^{3+}
- Ionic formation for transition metals is complicated by the fact that these elements have <u>unfilled inner *d* shells</u>
- Electrons are removed from the s orbital before the d orbital. Ex. 4s before 3d
- The non-metal atoms determine their charge

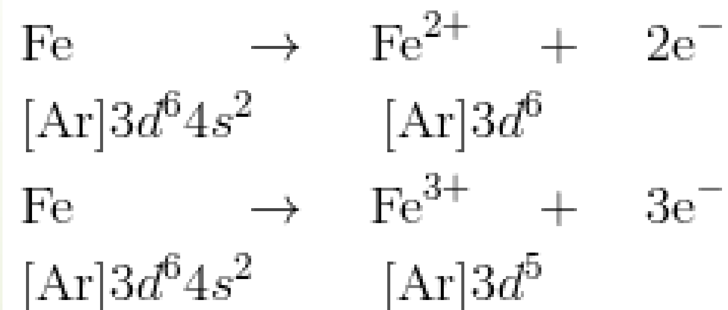
- Some transition metals, that have relatively few d electrons, may attain a noble-gas electron configuration. Scandium is an example.



- Others may attain configurations with a full *d* sublevel, such as zinc



- A half filled d level (d^5) is particularly stable, which is why iron loses a third electron

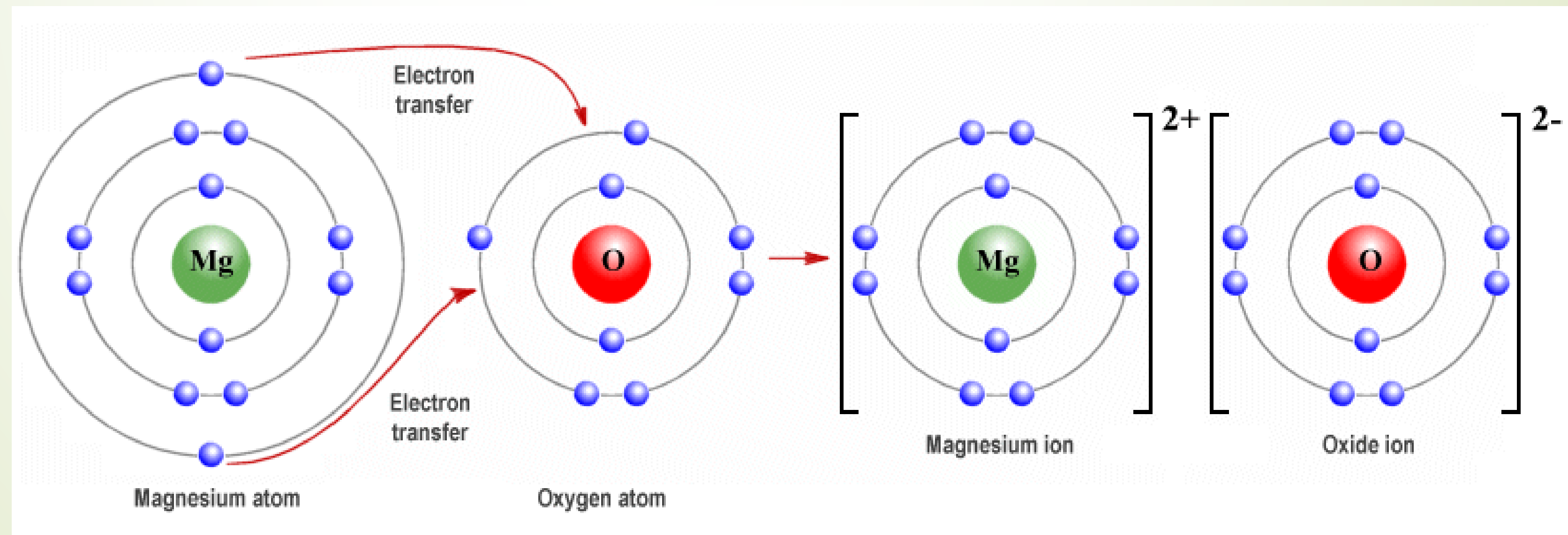


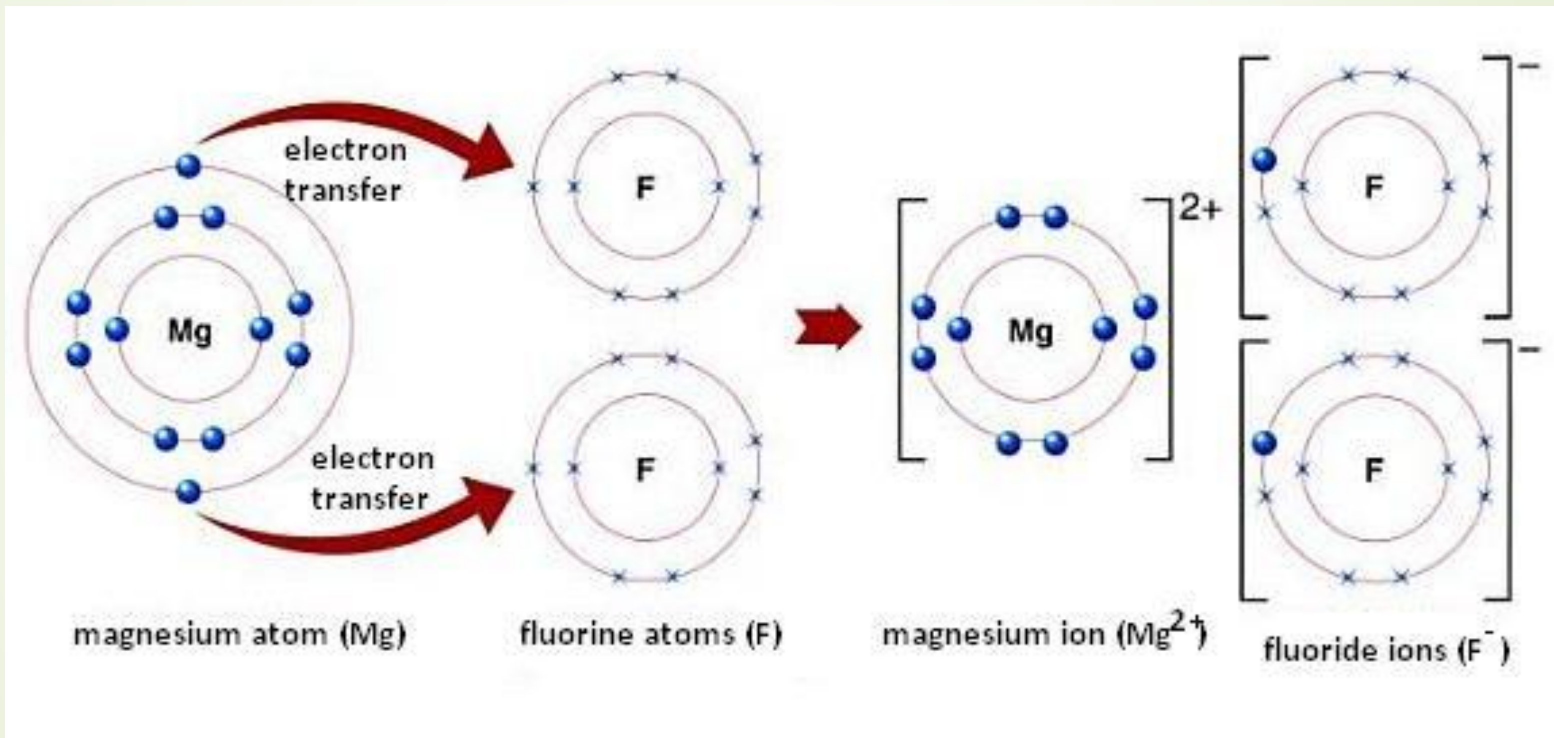
21 Sc [Ar]$3d^1 4s^2$	22 Ti [Ar]$3d^2 4s^2$	23 V [Ar]$3d^3 4s^2$	24 Cr [Ar] $3d^5 4s^1$	25 Mn [Ar]$3d^5 4s^2$	26 Fe [Ar]$3d^6 4s^2$	27 Co [Ar]$3d^7 4s^2$	28 N [Ar]$3d^8 4s^2$	29 Cu [Ar]$3d^{10} 4s^1$	30 Zn [Ar]$3d^{10} 4s^2$
39 Y [Kr]$4d^1 5s^2$	40 Zr [Kr]$4d^2 5s^2$	41 Nb [Kr]$4d^3 5s^2$	42 Mo [Kr]$4d^5 5s^1$	43 Tc [Kr]$4d^5 5s^2$	44 Ru [Kr]$4d^7 5s^1$	45 Rh [Kr]$4d^8 5s^1$	46 Pd [Kr]$4d^{10}$	47 Ag [Kr]$4d^{10} 5s^1$	48 Cd [Kr]$4d^{10} 5s^2$
57 La [Xe]$6s^2 5d^1$	72 Hf [Xe]$5d^2 6s^2$	73 Ta [Xe]$5d^3 6s^2$	74 W [Xe]$5d^4 6s^2$	75 Re [Xe]$5d^5 6s^2$	76 Os [Xe]$5d^6 6s^2$	77 Ir [Xe]$5d^7 6s^2$	78 Pt [Xe]$5d^9 6s^1$	79 Au [Xe]$5d^{10} 6s^1$	80 Hg [Xe]$5d^{10} 6s^2$

What is different for chromium (Cr) and copper (Cu)?

Ionic compound formation

- When an ionic compound is formed, electrons are transferred from one atom to another to form positive and negative ions.
- Electrons cannot be created or destroyed, therefore the total number of electrons lost must be equal to the total number gained .




electron
transfer
electron
transfer
Mg
F
F
Mg
2+
F
F
−
−
magnesium atom (Mg)
fluorine atoms (F)
magnesium ion (Mg2+)
fluoride ions (F-)

Ionic compound formulas

- To determine the formula of an ionic compound we must consider the electron configuration of the atoms involved.
- For example, determine the formula of aluminium fluoride
  - Aluminium is in group 3 – will form a 3+ ion by losing 3 electrons
  - Fluorine is in group 7 – will form a 1- ion to complete its valence shell
  - Aluminium will transfer 1 electron to 3 different fluorine atoms, therefore, the formula is AlF_3
- Determine the formula of the following ionic compounds:
  - Barium oxide
  - Chromium chloride
  - Silver oxide

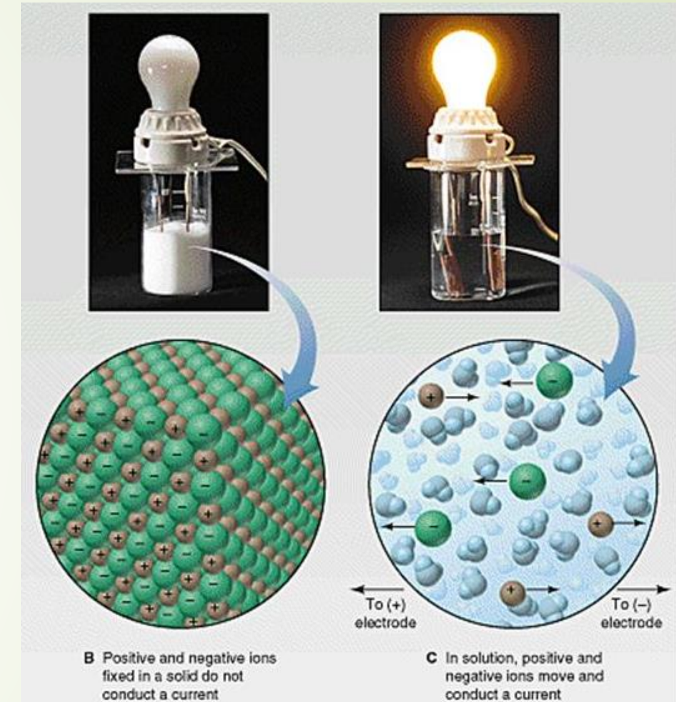
- Transition metal ions can have different charges, therefore, the oxidation number of the ion is usually given in the name.
- Oxidation number is equal to the charge on the ion
- Example – iron(II) sulphate
  - The roman numerals indicate the oxidation number of 2+
- Determine the formula of chromium(III) oxide

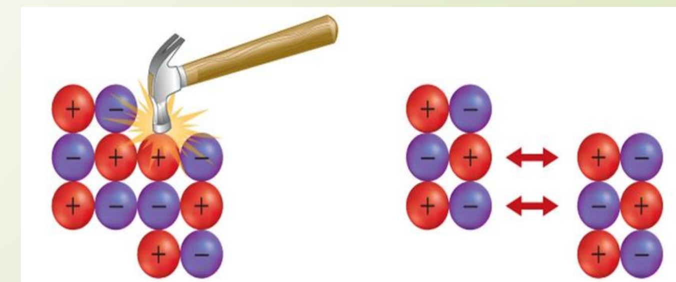
Ionic Crystals

- The **crystalline** form of Ionic Compounds.
- An **ionic crystal** consists of ions bound together by electrostatic attraction
- The arrangement of ions in a regular, geometric structure is called a **crystal lattice**.

Physical Properties of Ionic Compounds

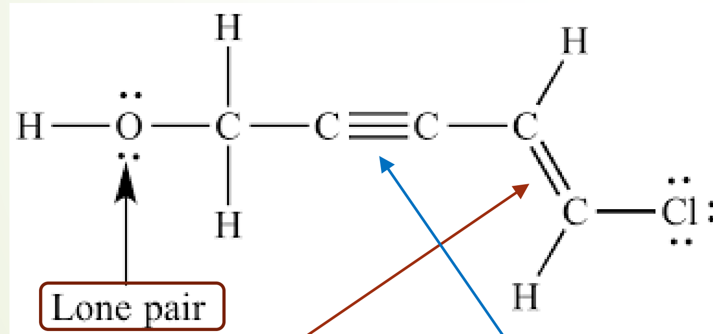
- Due to the strength of the electrostatic attractions throughout the lattice Ionic compounds have **high melting points and boiling points**.
  - The bonds must be broken which requires a lot of energy. E.g. magnesium oxide has a melting point of 2800°C and a boiling point of ~3600°C
- Ionic compounds are **soluble in polar substances**, such as water, but not in non-polar substances
- Ionic compounds do not conduct electricity when solid. They do, however, **conduct as aqueous solutions** when ions are free to move around
- Hardness – although ionic solids are hard (due to attractive forces), they are also **brittle**. A slight displacement of one layer of a crystal results in repulsive forces between the ions; breaking the crystal apart





Covalent Bonding

- Occurs when atoms share electrons
- A covalent bond is the electrostatic attraction between a shared pair of electrons and the nuclei of the atoms making up the bond.
- Covalent bonds can be illustrated through **Lewis structures**

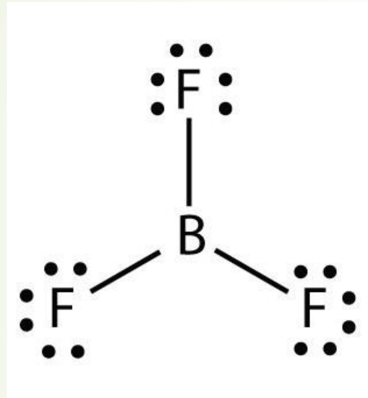


A lone pair is a pair of valance electrons that are not involved in covalent bonding

Double bond - two pairs of shared electrons

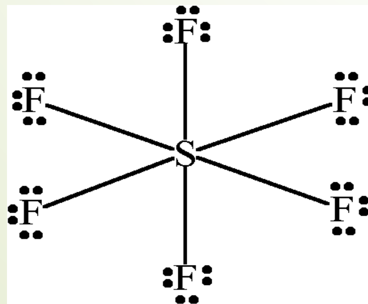
Triple bond - three pairs of shared electrons

- With the exception of hydrogen and noble gases, the first 20 elements tend to form covalent bonds to complete their **octet** (eight electrons in the valance shell).
- In some cases a noble gas configuration is not achieved



Boron, a group 3 element, only has 6 electrons in its covalent shell

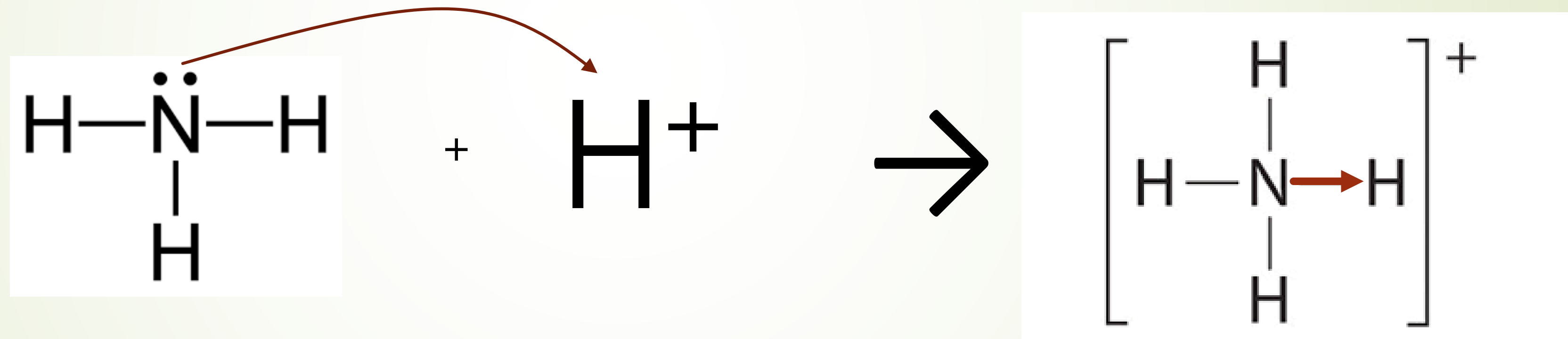
- In some cases an atom can have more than 8 electrons in its outer shell. This is called an **expanded octet**. Only elements in period 3 or higher can expand their octet



Elements, such as Sulphur, Phosphorous and Chlorine, can utilize the 3d-orbitals to 'expand their octet'

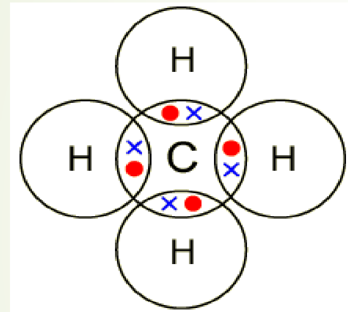
Dative Covalent Bonds

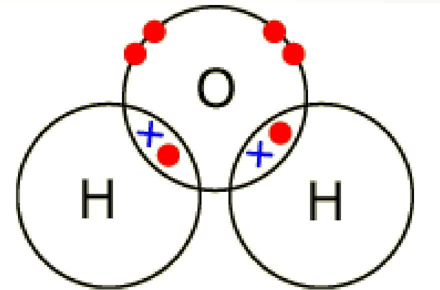
- Also known as a coordinate covalent bond, is a type of covalent bond wherein **both electrons come from the same atom**
- Consider the reaction between ammonia and H^+



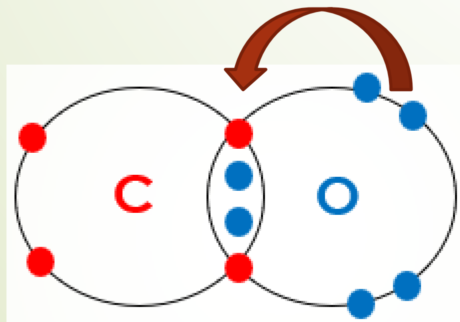
The lone pair (non-bonding electrons) of Nitrogen can be used to complete the valance of H^+

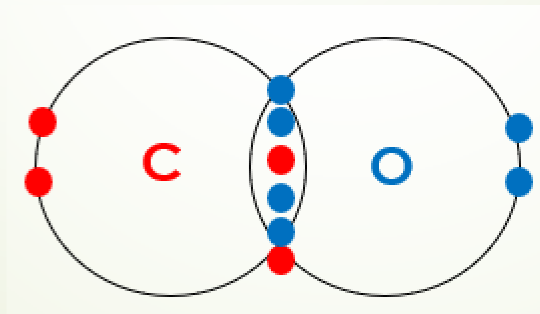
- Carbon, a group 4 element, normally shares 4 electrons to form 4 covalent bonds and complete its octet.
- Oxygen, a group 6 element, normally shares 2 electrons to form 2 covalent bonds and complete its octet.





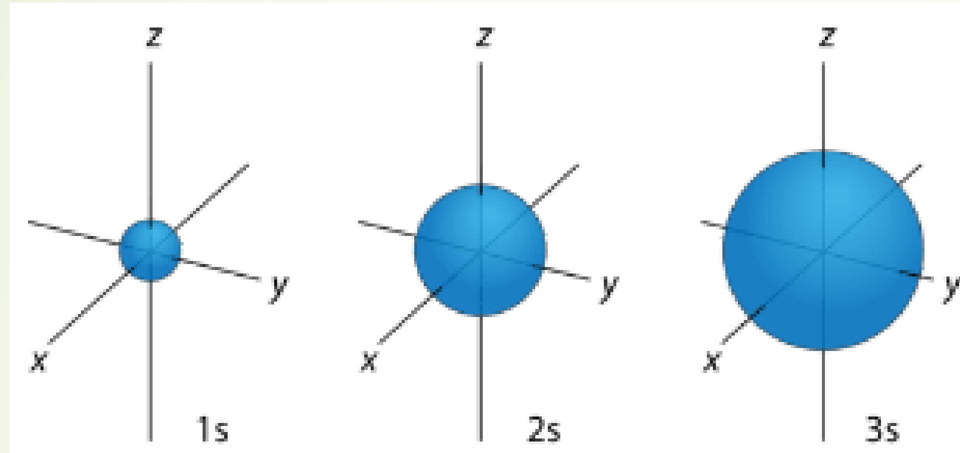
- How can carbon and oxygen in carbon monoxide (CO) covalently bond to complete their octets?



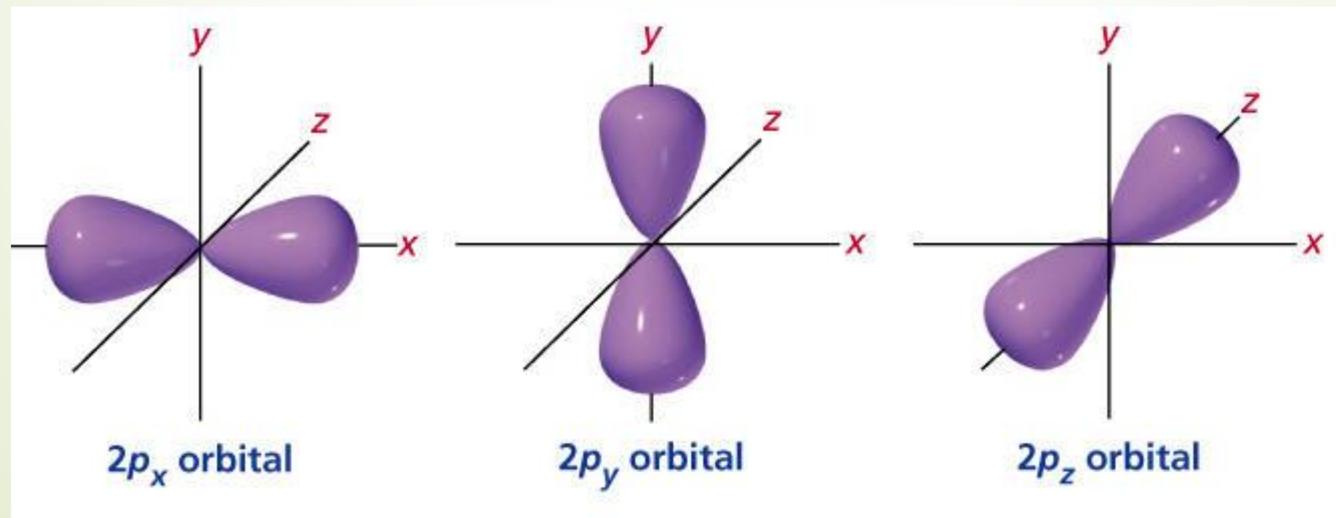


Both atoms can complete their octet if the oxygen atom donates a pair of electrons through a dative covalent bond

Covalent bonds in terms of orbitals

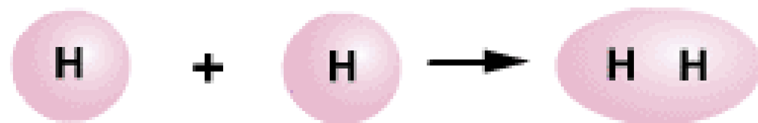


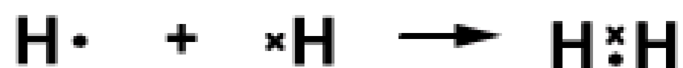
The s orbital has only one shape, which is spherical



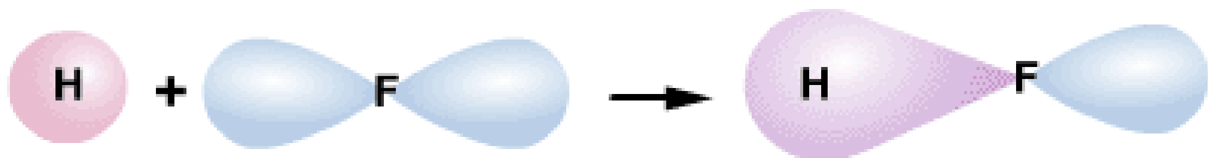
There are three p orbitals. They differ by orientation

A. *s* orbital + *s* orbital

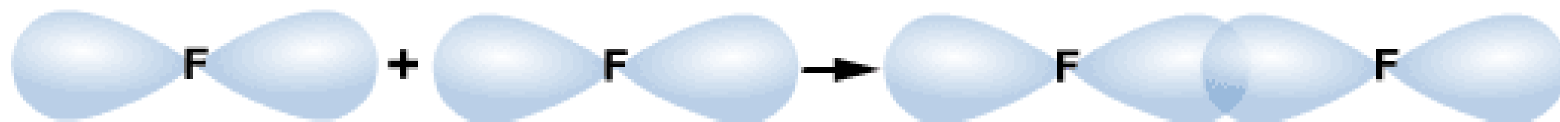




B. *s* orbital + *p* orbital

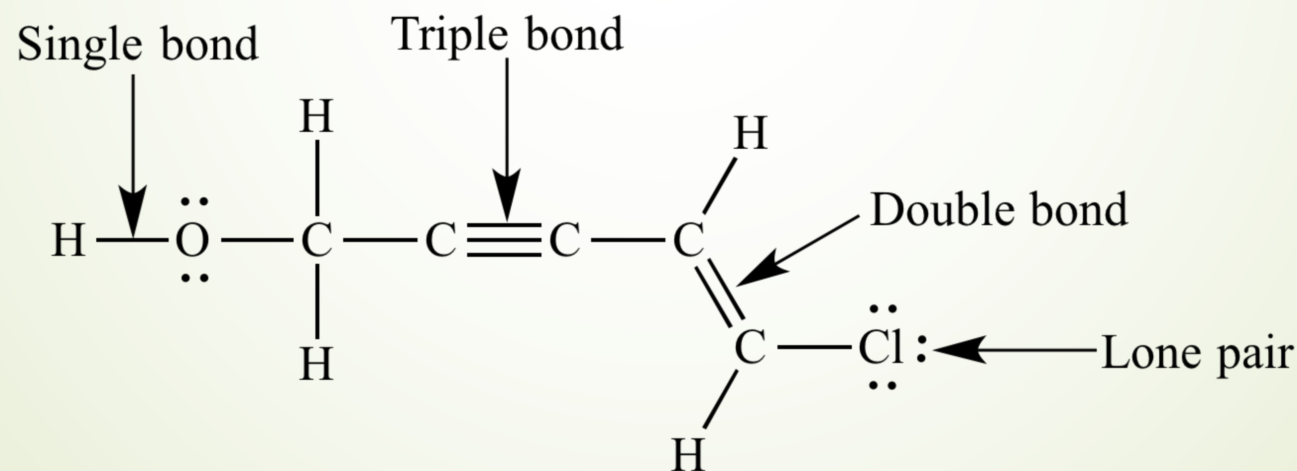


C. *p* orbital + *p* orbital ('head-on' overlap)



Lewis Structures

- Lewis structures are diagram showing all the valance electrons in a molecule.
- Typically, lines are used to show a pair of bonding electrons and dots are used to show non-bonding electrons



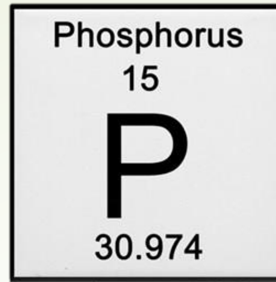
Drawing Lewis Structures

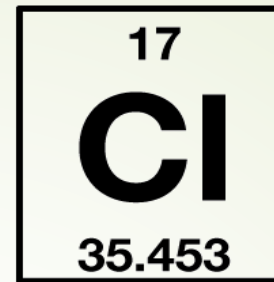
1. Determine the total number of valance electrons, for ions the charge must be taken into account.
2. Arrange the atoms so that the least electronegative occupies the central position.
3. Put 2 electrons (a line) between each atom to form a chemical bond
4. Add electrons on the outside of atoms to fill the valance shells (most electronegative atoms first)

   If there are not enough electrons, the least electronegative atom(s) are left short

   If there are too many electrons, the extra electrons are placed on the central atom
5. If the central atom does not have a complete valance shell move electrons from outer atoms to form double or triple bonds.

Example: **PCl_3**

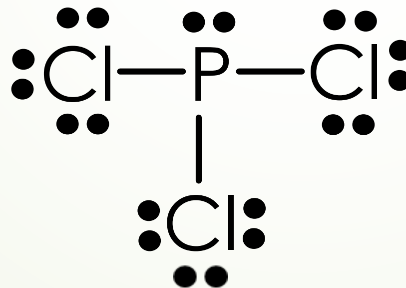




Group 5 Group 7

Total valance electrons = 5 + (7x3) = 26

Least electronegative = Phosphorus



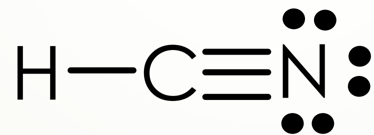
3 covalent bonds
= 6 electrons

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr

HCN

Total valance electrons = (1 + 4 + 5) = 10

Electronegativity = N>C>H



Two covalent bonds = 4 electrons

Carbon does not have a complete valance shell

ICl_3 CBr_4 SO_2^{2-} C_2H_4 HNO_3

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr

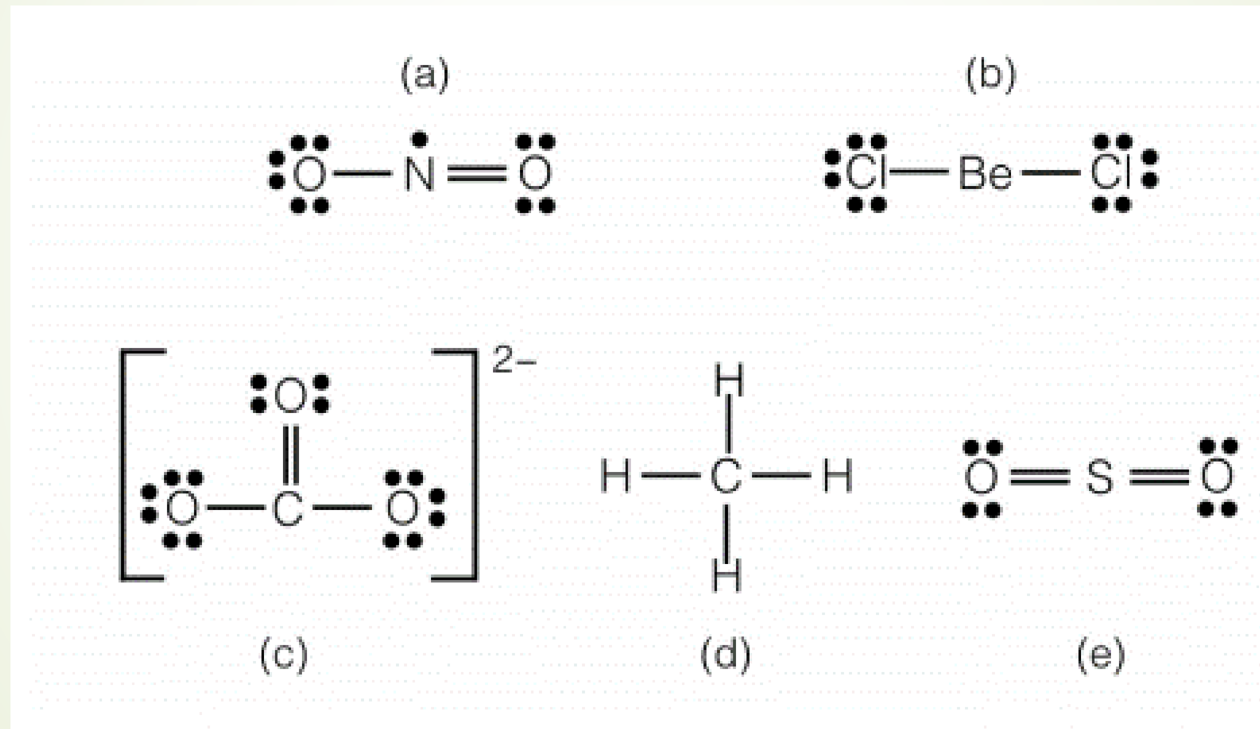
H 2,1																	He
Li 1,0	Be 1,6											B 2,0	C 2,5	N 3,0	O 3,5	F 4,0	Ne
Na 0,9	Mg 1,2											Al 1,5	Si 1,8	P 2,1	S 2,5	Cl 3,0	Ar
K 0,8	Ca 1,0	Sc 1,3	Ti 1,5	V 1,6	Cr 1,6	Mn 1,5	Fe 1,8	Co 1,9	Ni 1,9	Cu 1,9	Zn 1,6	Ga 1,6	Ge 1,8	As 2,0	Se 2,4	Br 2,8	Kr

Determining Formal Charge

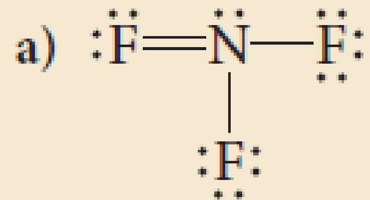
- Molecules can have more than one possible Lewis structure, known as resonance structures
- To determine which is the most likely we must determine the formal charge of each atom in the molecule
- The resonance structure with the lowest formal charge on each atom is the most stable and therefore the most likely to occur in nature

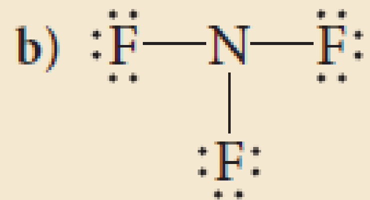
Formal Charge = Number of valence electrons – Number of non-bonding electrons – Number of bonding electrons divided by 2

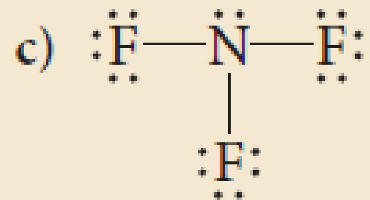
Formal Charge = Number of valence electrons – Number of non-bonding electrons – Number of bonding electrons divided by 2



Identify the most likely Lewis structure for NF_3 by determining the formal charges for each atom







Check list:

- ✓ Electrons
- ✓ Central atom
- ✓ Completed valance
- ✓ Formal charges

N = 5

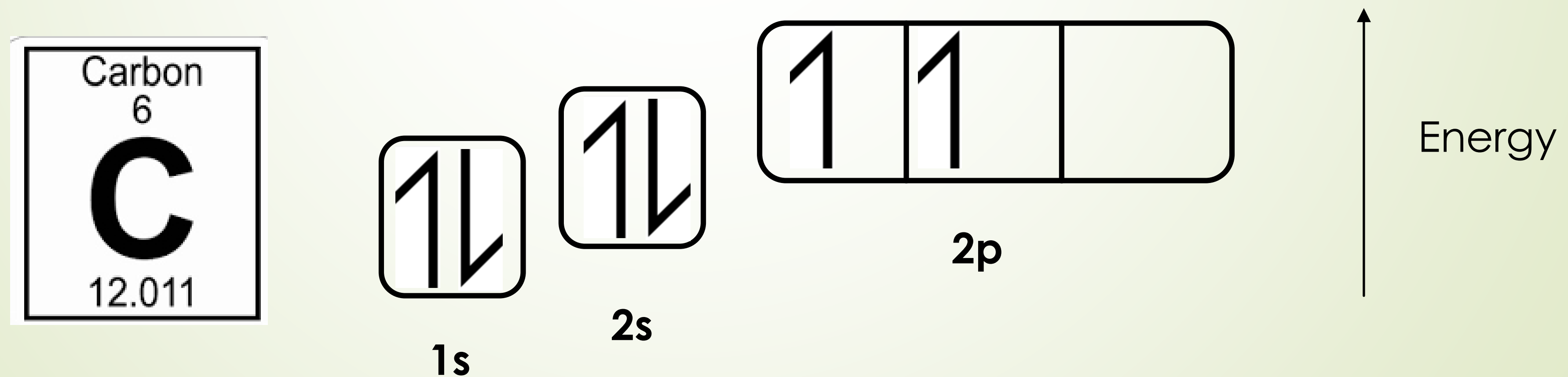
F = (7x3)

= 26 valence electrons

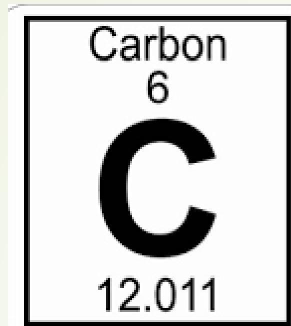
Hybridisation

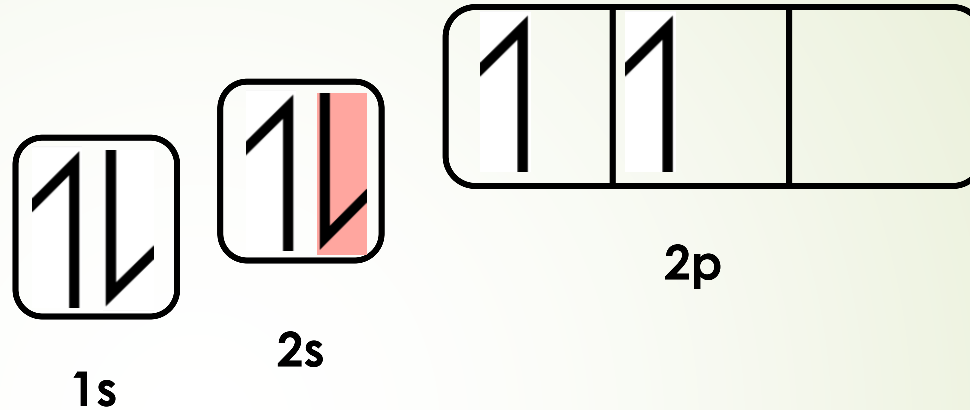
Valance orbitals only

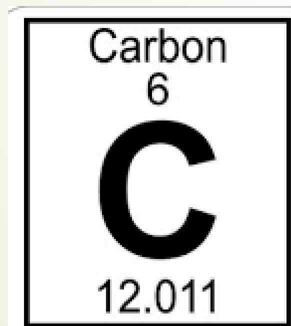
- Hybridisation is the mixing of atomic orbitals to produce a new set of orbitals that are better arranged in space for covalent bonding.
- Consider the electron configuration of a ‘ground state’ carbon atom
  - How many covalent bonds can it form?

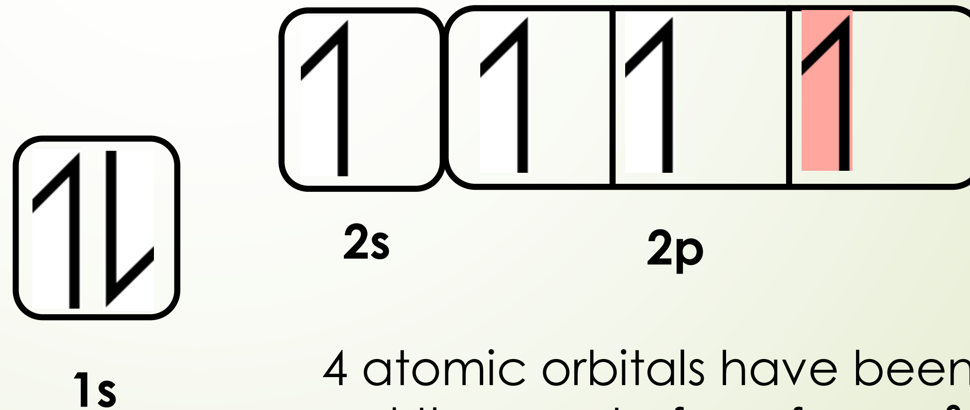


An electron can be 'promoted' from 2s to 2p.
Energy is required to do this



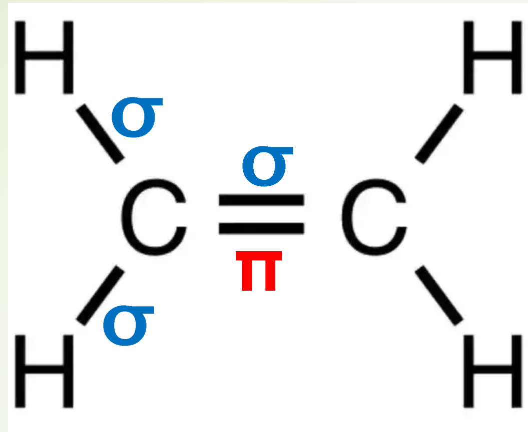




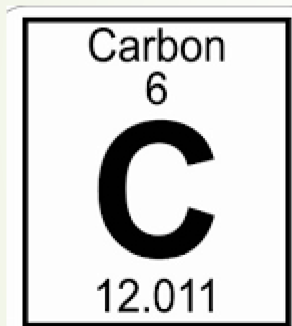


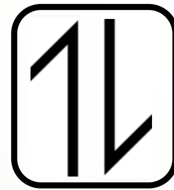
4 atomic orbitals have been mixed, one s and three p, to form four **sp^3** hybrid orbitals

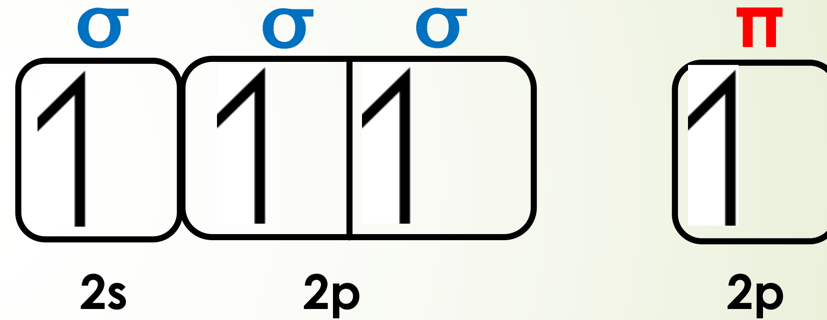
- sp hybridised orbitals can only form single bonds, known as sigma bonds (**σ**)
- The hybridisation of carbon depends on the number of sigma bonds it forms
- A double bond is made up of one sigma bond and one pi bond (**π**)
- A triple bond is made up of one sigma bond and two pi bonds
- Pi bonds are formed from overlapping unhybridized p orbitals
- Consider the structures of CH_4 , C_2H_4 and C_2H_2



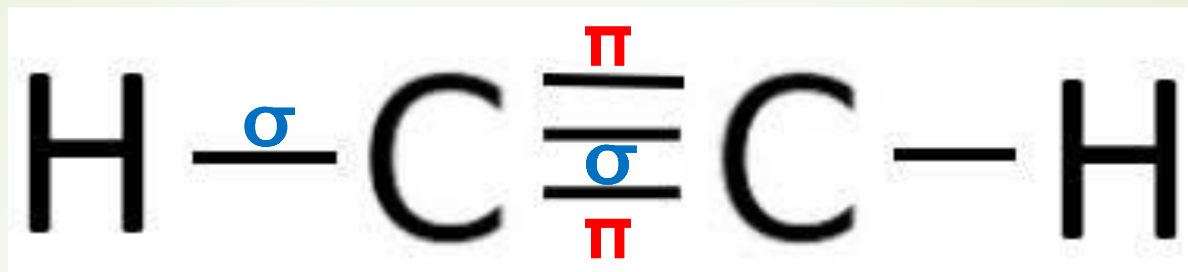
The unhybridized p orbital forms the pi bond between the two carbon atoms



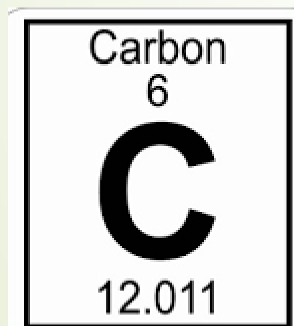


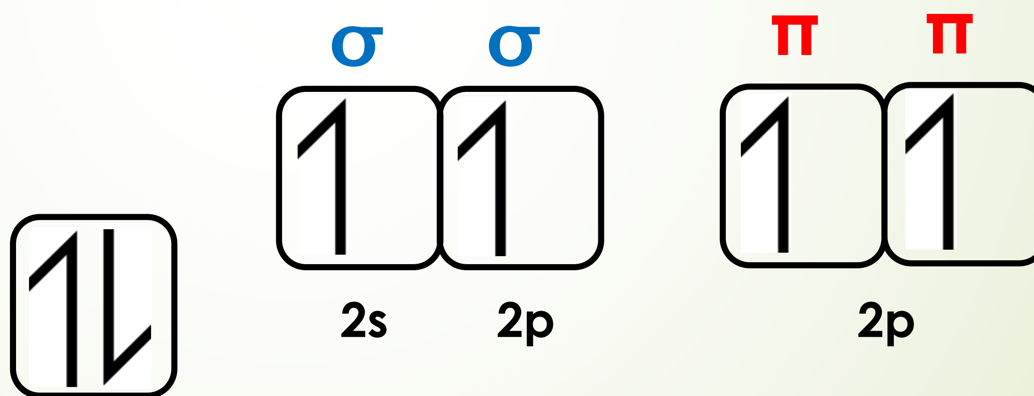


Mixing one s orbital and two p orbitals forms three **sp^2** orbitals



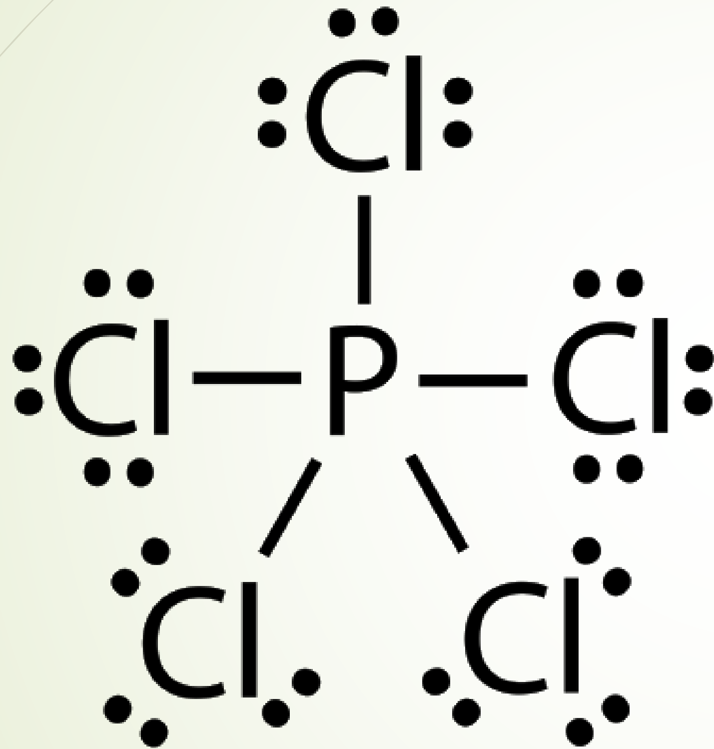
In order for a carbon atom to form a triple bond it must have two unhybridized p orbitals.

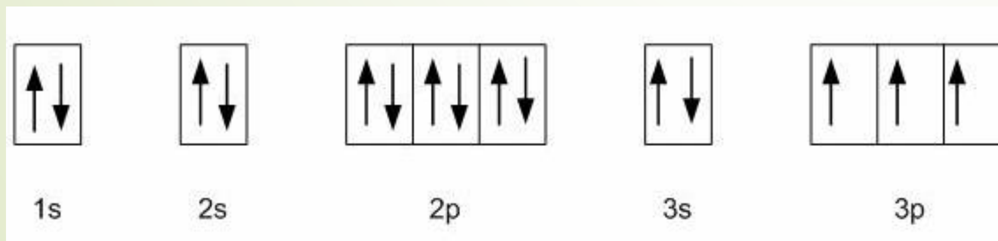




Mixing one s orbital with one p orbital forms two **sp** orbitals

Expanded Octet





- In order to have an expanded octet, the central atom of the molecule must have at least three shells of electrons in order to accommodate more than eight electrons in its valence shell.
- The ‘3d’ orbital and ‘4s’ orbital have a very similar energy level, however since ‘d’ orbitals can hold more electrons they are used for expanding octets.

Determine the hybridization for the atoms in the following molecules:

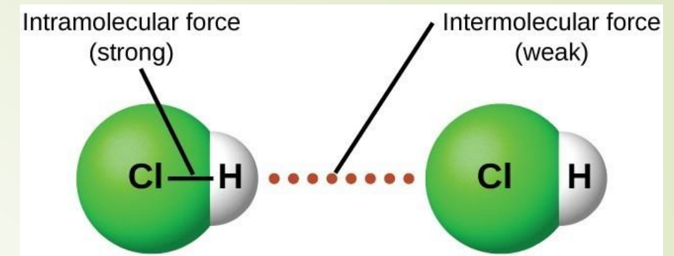
- N_2
- NO_2^-
- PCl_5
- ClF_3
- BF_3
- SO_3
- SO_4^{2-}

Recall that pi bonds require unhybridised orbitals (p or d)

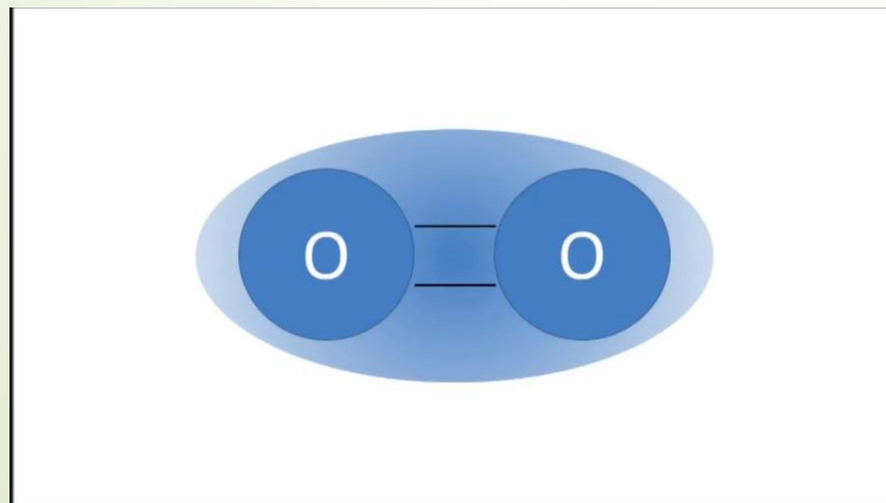
# of sigma bonds + # of lone pairs = x

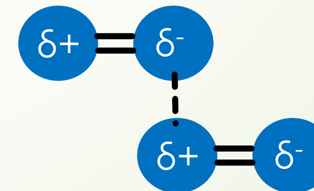
x = 2 = sp
x = 3 = sp^2
x = 4 = sp^3
x = 5 = sp^3d
x = 6 = sp^3d^2
....

Intermolecular Forces



- There are various types of intermolecular forces. The main type between non-polar atoms/molecules is the **Van der Waals'** force.
- Van der Waals' forces (also known as London dispersion forces)are the only attractive forces that occur between non-polar molecules.
- Van der Waals' forces arise as a result of constant electron motion. At any given time the electron distribution around the nucleus will not be symmetrical.
- This creates a temporary **dipole**, which induces an opposite dipole in a neighbouring atom.

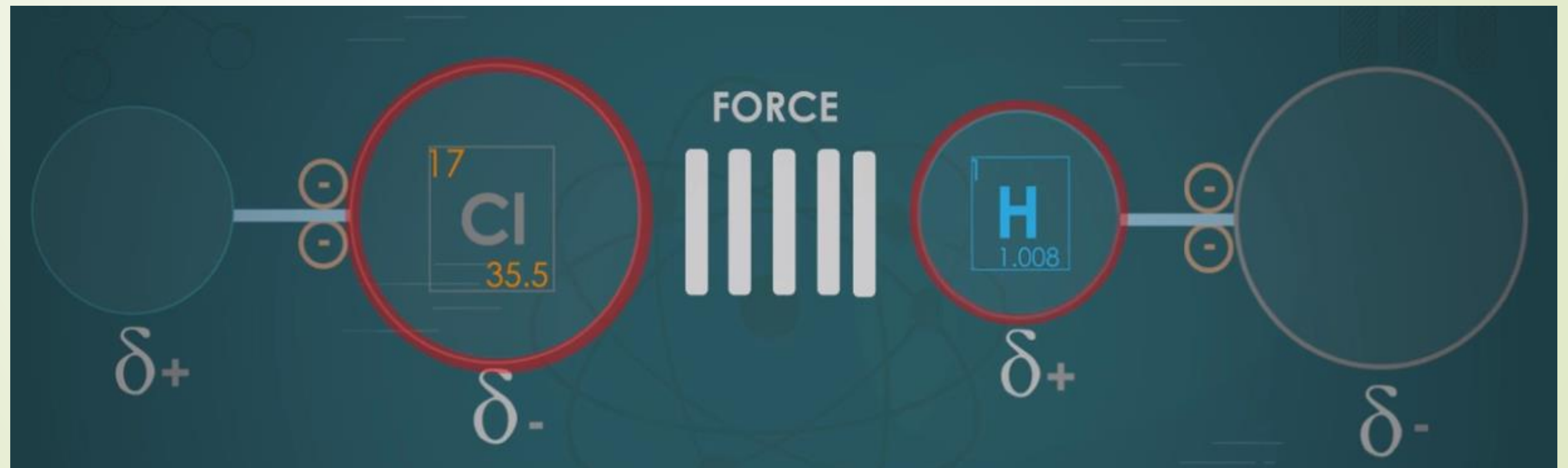




In general, van der Waals' forces get stronger as the number of electrons/molecular mass increases

Polar Molecules

- Van der Waals' forces are also present between polar molecules, such as HCl
- However, there are stronger forces present caused by the permanent dipoles produced by the difference in electronegativities.
- These forces are called **permanent dipole-permanent dipole** interactions, or usually just **dipole-dipole attractions**.

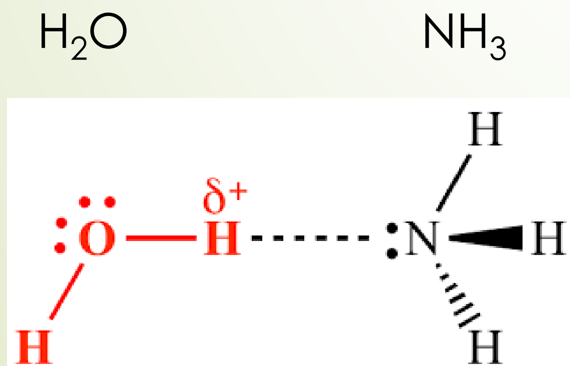


Hydrogen Bonding

Strongest of the intermolecular forces, but still much weaker than a covalent bond

- Hydrogen bonding occurs between molecules when a very electronegative atom (**N**, **O**, **F**) is bonded to a hydrogen atom in the molecule.
- The electronegative atom withdraws electron density from the hydrogen atom, polarising the bond.
- There is a strong electrostatic interaction between the δ− (N, O, F) and the δ+ H of another molecule.
- The electronegative atom must posses at least one lone pair for hydrogen bonding to occur.

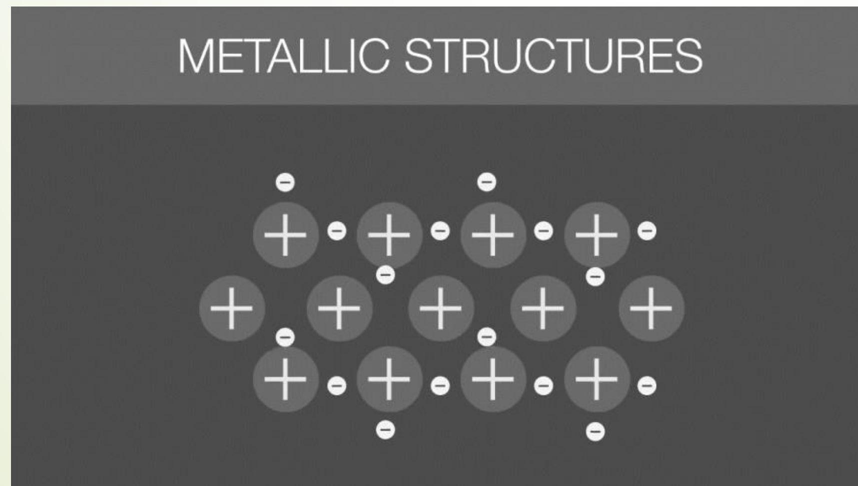
H_2O NH_3 HF



Element	Atomic Radius (picometers)
F	50
O	60
N	65
Cl	100

Metallic Bonding

- Metals form a lattice structure consisting of metal ions (+) and delocalized electrons (-).
- The electrostatic attraction between the metal cations and the electrons holds the lattice together.
- The greater the charge of the cation (e.g. Na^{+}, Mg^{2+}), and the smaller the atomic radius, the stronger the lattice.



Li^{+} (0.60) 60	Be^{2+} (0.31) 31	
Na^{+} (0.95) 95	Mg^{2+} (0.65) 65	Al^{3+} (0.50) 50
K^{+} (1.33) 133	Ca^{2+} (0.99) 99	Ga^{3+} (0.62) 62