CHEM 3.1 CHEMICAL BONDING 1

Lewis electron-dot model, Bond types, Polarity.

(Molecular structure, **intra**- and **inter**- molecular bonding)

INTER-ATOMIC BONDING also termed **INTRAMOLECULAR bonding** (between atoms joined in a molecule or ion)

Electronegativity (EN)

EN = the power of an atom to attract electrons

The larger the value, the greater the electron attracting ability.

For two atoms bonded together:

Largest difference between largest EN **F** (3.98) and smallest EN **Cs** (0.79): $\mathbf{Cs^+F^-}$ ΔEN = 3.19

Gives rise to an **ionic (polar)** material.

Smallest difference = 0, for two identical atoms which gives rise to a **covalent** (shared electrons)bond which is **non-polar.**

Inter-atomic Bond types:

Ionic $Na^+ C\ell^-$ (complete electron transfer from one atom to the other)

When there is a large difference in EN (> ≈ 2.0) we have an ionic compound ;

Usually between an s-block element and a p-block element

$\mathbf{Na^+ C\ell^-}$ ΔEN = 0.93 – 3.16 = 2.23 : $\mathbf{Cs^+F^-}$ ΔEN = 3.19 $\quad$ $Na\bullet \curvearrowright \bullet \ddot{\underset{\cdot\cdot}{Cl}}\!:$ $\rightarrow$ $Na^+ \; :\ddot{\underset{\cdot\cdot}{Cl}}^-\!:$

Covalent Br-Br (sharing of two electrons, creates a single, sigma(σ) covalent bond)

ΔEN(Br/Br) = 2.96 – 2.96 = 0

Smallest difference ΔEN = 0 (termed **non-polar** molecule) **A ↑** **↓ B** → **A ↑↓ B** = **A-B**

Usually between elements within the p-block

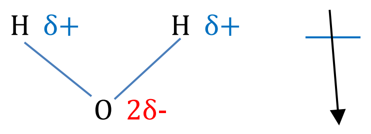
C-H ΔEN(C-H) = 2.55 – 2.20 = 0.35 (This turns out to be small enough that the C-H bond behaves as if it is **non-polar**, with no significant charge separation)

Polar covalent **H-F** ΔEN = 2.20 – 3.98 = 1.78 (uneven sharing of two electrons creates a single, sigma(σ) covalent bond, but with a significant 'ionic component' due to the difference in electronegativity which results in a distorted "polarized" molecular electron cloud)

So, **H-F** = (δ+)H—F(δ-) (the **polar molecule** now possesses a **dipole moment, symbol μ**, designated , since it contains both a positive electric 'pole' (δ+) and a negative electric 'pole' (δ-), the symbol δ 'delta' means a 'small amount') .

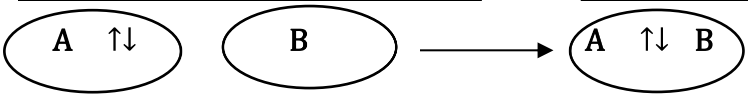
This will be the case, to a greater or lesser extent, for all bonds consisting of different atoms.

Water **H-O-H** ΔEN(O-H) = 3.44 – 2.20 = 1.24



So, **water is** described as **a polar molecule, μ > 0.**

<u>Donor Covalent or Co-ordinate Bond :</u> When <u>one atom donates both electrons</u> to the bond:



denoted **A:→ B or A^{+}—B^{-}**

$\ddot{}$
H_2O **:** → H^+ = H_3O^+ H_3N: → H^+ = NH_4^+ CH_3N : → Cu^{2+}
H_2

Chemical Bonding: LEWIS ELECTRON-DOT STRUCTURES as models of chemical bonding (and their use to assign oxidation numbers)

The model is based on the fact that all atoms combine to give compounds in which each atom (or ion) achieves the inert gas valence electron configuration of 's^2p^6' (or s^2 for H) in its outer shell, as this is the most stable configuration.

Eg H x • O • x H   : F • x H

• C •   • N •   • O •   : F •

Can form 4 bonds	3 bonds	2 bonds	1 bond
No unshared pairs	1 unshared pair	2 unshared pairs	3 unshared pairs

<u>BONDING, SINGLE & DOUBLE BONDS, SHAPE & POLARITY</u>

CARBON DIOXIDE CO_2 SULPHUR DIOXIDE SO_2

O = C = O   O = S = O
••

Single & Double bonds

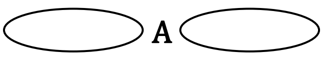
When 2 electrons are shared between 2 atoms we describe the bond as a single, **SIGMA-bond**, and when a further 2 electrons are shared between the same 2 atoms we describe the additional bond as a **PI-bond**, and the combination of the sigma & pi-bonds as a double bond.

<u>SHAPE</u> from Valence Shell Electron Pair Repulsion Theory = VSEPR theory

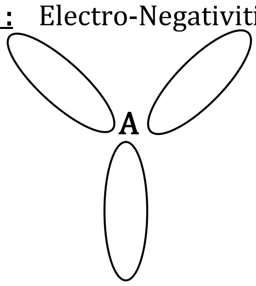
How many electron domains (groups of electrons) surround the central atom?

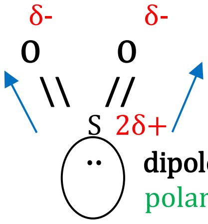
2 electron clouds = linear   3 electron clouds = trigonal planar = triangular

<u>Shapes</u> of CO_2 and SO_2 molecules and their <u>Polarity</u> : Electro-Negativities: C = 2.5, O = 3.5, S = 2.5



δ- 2δ+ δ-
O = C = O **dipoles cancel**
← →
so non-polar μ=0

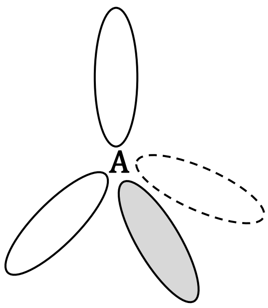




dipoles add – so a
polar molecule μ>0

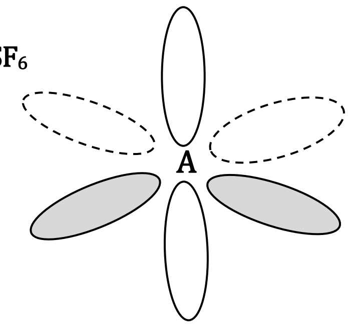
4 electron clouds = tetrahedral

eg. CH_4



6 electron clouds = octahedral

eg. SF_6



INTERMOLECULAR bonding forces (between separate molecules)

IONIC

A <u>Strong inter-particle electrostatic attraction</u> between oppositely charged ions which usually gives rise to hard, solid materials due to their regular giant 'lattice' structure, with an almost infinite number of 3-D ionic attractions.

Eg. Na^+Cl^- K^+ $H_2PO_4^-$ Mg^{2+}/Ca^{2+} CO_3^{2-}

Can also get <u>isolated</u> ionic interactions such as an ionic "salt bridge" in a protein structure, when proton from -COOH is transferred to $-NH_2$ group :

/\/\/\/\/-NH_2 HOOC-/\/\/\/\ $\longrightarrow$ /\/\/\/\/-NH_3^+ ····· $^-$OOC-/\/\/\/\

COVALENT (or DONOR-COVALENT)

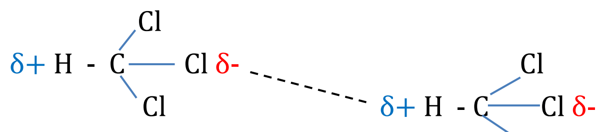
(A <u>Strong bond</u> arising from electron sharing)

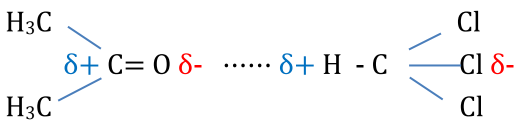
C-C C-O C-N C-H N-H

DIPOLE / DIPOLE (Polar covalent)

(An <u>Intermediate strength bond</u> in solids & liquids arising from attractions between partially charged atoms)

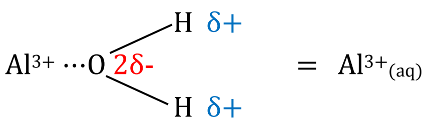
δ+ δ- δ+ δ-
>C= O ······· >C= O

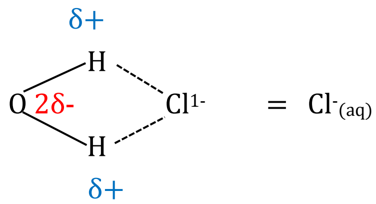




Can lead to molecules associating in solution

ION/DIPOLE

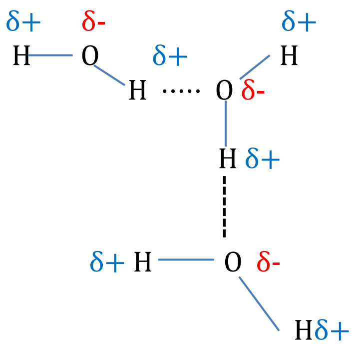




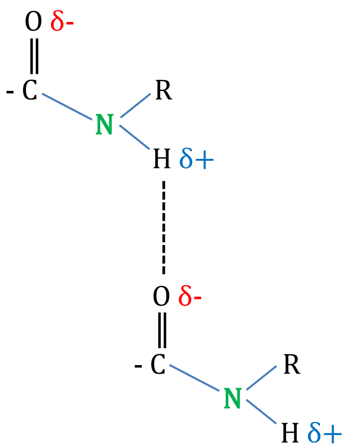
HYDROGEN-BONDING

(An <u>Intermediate strength bond</u> arising from a partially charged hydrogen atom ($H^{\delta+}$) bridging between partially charged negative atoms)

In water



In a protein

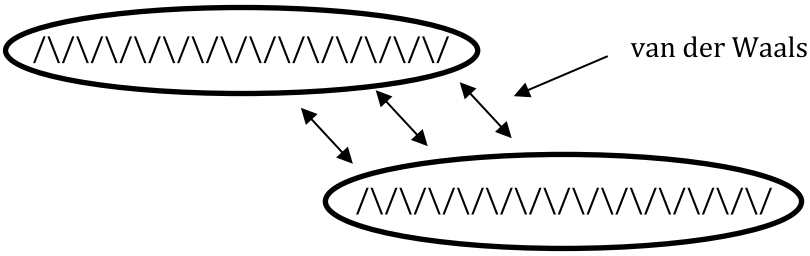


Van Der WAALS (DISPERSION) (also called **Hydrophobic Bonding**)

This very weak interaction is always present between molecules, and atoms, and arises when there are no permanent dipoles in a molecule, we then get **very weak inter-particle bonding** arising from transient distortions in the electron distribution in the atom or molecule. As a consequence, the compounds are usually liquids or gases.

Eg. Consider two **long hydrocarbon chains**, as in a fat/oil

The only covalent bonds present are C-C and C-H, which are both non-polar (due to the similarity in the electronegativities of C & H), which means the only inter-molecular (inter-particle) interactions are the very weak van der Waals forces acting between the separate molecules.

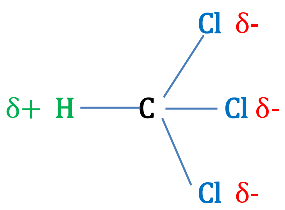


van der Waals (dispersion) forces

Eg. C_8H_{18} (liquid)	$H_3C(CH_2)_{10}CH_3$ (liquid)	$H_3C(CH_2)_{14}CH_3$ (solid, melting point =18^oC)
Octane	dodecane	hexadecane

Note the **effect of molecular symmetry** in the following examples:

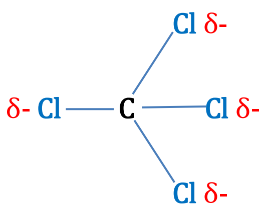
Chloroform = $CHCl_3$



A POLAR molecule

Here the bond dipoles add in a 3-D manner about the tetrahedral C-atom to give a resultant dipole $\mu > 0$.

Carbon Tetrachloride = CCl_4



A NON - POLAR molecule

Here the bond dipoles add in a 3-D manner about the tetrahedral C-atom to give a zero dipole, $\mu = 0$.