

Chapter 4: Bonding

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Ionic bonding → an ionic bond is the electrostatic attraction between 2 oppositely charged ions

- Ionic compounds are formed when electrons are transferred from one atom to another to form atoms with complete outer shells of electrons
- Example (formation of NaCl) → formed when Na burns in chlorine, the energy from the heat breaks the bonds in the Cl_2 molecule to give Cl atoms. Each sodium atom then transfers one electron to each chlorine atom to form Na^+ and Cl^-

Polyatomic ions

- | | |
|--------------------------------------|---|
| 1) hydroxide, OH^- | 6) carbonate, CO_3^{2-} |
| 2) Nitrate, NO_3^- | 7) hydrogencarbonate, HCO_3^- |
| 3) Nitrite, NO_2^- | 8) ethanoate, CH_3COO^- |
| 4) sulfate, SO_4^{2-} | 9) Phosphate, PO_4^{3-} |
| 5) hydrogensulfate, HSO_4^- | |

Ionic bonds form due to high electronegativity differences (>1.8)

Properties

- 1) Exist in a crystal lattice structure
- 2) High m.p and b.p → due to strong electrostatic forces of attractions between ions, hence large amounts of energy are required to melt ionic compounds
- 3) Low volatility → ionic compounds have low odours, because of high lattice enthalpies
- 4) Soluble in polar compounds - The δ^- part of a polar molecule attracts the cations in a ionic lattice and the δ^+ part attracts the anions. This causes the ions to separate from the lattice and become surrounded by polar molecules. If water is the polar compound, the ions have been hydrated, otherwise, they have been solvated
- 5) Conduct electricity in liquid and aq form → In solid state, comp ions are held in place within the lattice and cannot move to carry a charge. In liquid and aq forms, the ions are free to move and carry a charge
- 6) Brittle - Movement of ions within the lattice places ions of the same charge alongside one another, hence the repulsive forces cause them to split.

Octet Rule: Atoms tend to get valence shell of 8 electrons, exception include Be and B

1 Covalent Bond: Electrostatic attraction between a shared pair of electrons and positive nuclei

Covalent Bonding

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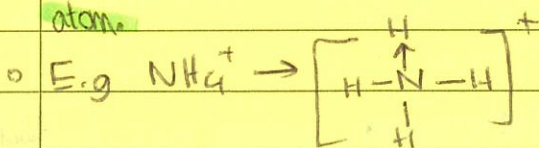
- sharing of one or more pairs of electrons so each atom involved achieves noble gas configuration
- The formation of a covalent bond stabilises the atoms, so energy is released as the bond forms
- tendency of atoms to form a stable arrangement of 8 outer electrons is called the octet rule
- double and triple bonds can be formed e.g. $O=O$ and $N\equiv N$
- If you have more bonds (double bond vs triple bond), the bond length is shorter and the bond is stronger

Shorter the bond, the more powerful it is.

- Multiple bonds have a greater number of shared electrons and so have a stronger force of electrostatic attraction between bonded nuclei
- Hence, there is a greater pulling force on the nuclei, bringing them closer together

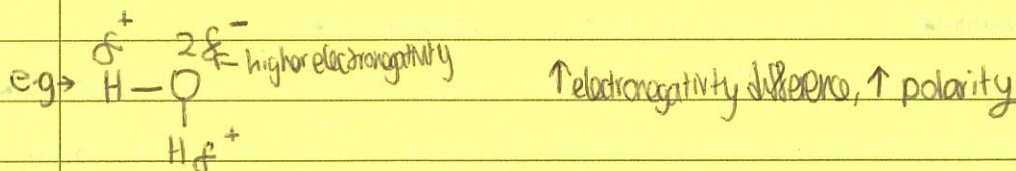
Coordinate (dative) covalent bonds

- a covalent bond in which both electrons in the covalent pair originate from the same atom.



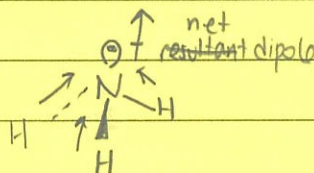
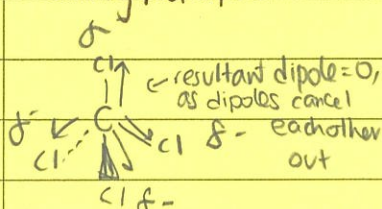
Polar Covalent Bonds

- polar bonds result from unequal sharing of electrons
- The more electronegative atom exerts a greater pulling power on the shared electrons, hence it holds the electrons more than the other, but now electron distribution is unsymmetrical.
- This is because one end of the molecule becomes more electron rich than the other.



- The more electronegative atom has the greatest electron density when bonded

Determining Net Dipole



Van Der Waals Forces = collective term
for LDF, permanent \rightarrow instantaneous dipole,
and p-dipole \rightarrow p-dipole 3

Intermolecular Forces

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London dispersal forces [LDF]

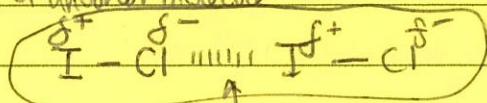
In non polar molecules, electrons are unevenly spread throughout the molecule but can be concentrated in at the sides of the molecule, producing a temporary instantaneous dipoles. These dipoles can ~~also~~ induce another dipole in a neighbouring particle, resulting in weak attraction between the particles. (by way of polarising the other molecule)

Factors affecting LDF

- 1) $\uparrow e^-$, \uparrow LDF because more electrons produce stronger dipoles
- 2) \uparrow RM, \uparrow LDF because larger ~~to~~ instantaneous dipoles created
- 3)

Dipole - Dipole Forces

Polar molecules are attracted to each other because the more electronegative elements attract the least electronegative elements. Positive end of one molecule attracts the negative end of another molecule.



dashed line represent weak intermolecular forces

Hydrogen bonding [H]

- \rightarrow occurs when H is bonded to a small, highly electronegative element (e.g. O, N, F)
 is attracted
- \rightarrow The electron pair ~~moves~~ more to the electronegative element, leaving a single proton in the hydrogen
- \rightarrow The proton then attracts a non-bonding pair of electrons from the highly electronegative element, creating a stronger dipole-dipole attraction.

Proof of hydrogen bonding

A graph of hydrogen compounds against temperature shows that if you go down a group, the b.p increases because more electrons are used in forming dipole-dipole forces. However the first element hydrogen bonds with in a period, its compound has an ~~thus~~ unusually high b.p, showing that additional intermolecular forces of attraction are present, forces that require more energy to break

Intermolecular forces in terms of bond strength

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




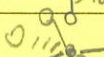





valent \rightarrow hydrogen bonding $>$ dipole-dipole $>$ LDF
 The weaker the intermolecular forces, the lower the boiling point.

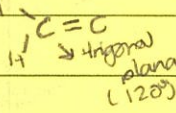
reading at the end

* Valence Shell Electron Pair Repulsion (VSEPR) theory

\rightarrow theory states that pairs of electrons arrange themselves around the central atom such that they are as far apart as possible, minimising forces of repulsion between pairs

\rightarrow Repulsive forces \rightarrow l.p-l.p $>$ b.p-l.p $>$ b.p-b.p (b.p = bonded pair) (l.p = lone pair)

Total no. of e ⁻ Pairs	b.pairs	l.pairs	shape + example
2	2	0	 linear, e.g. BeCl ₂ , 180°
3	3	0	 trigonal planar, e.g. BF ₃ , 120°
	2	1	 bent, e.g. SO ₂ , 118°
	4	0	 tetrahedral, e.g. CH ₄ , 109.5°
4	3	1	 trigonal pyramidal, e.g. NH ₃ , 107°
	2	2	 bent, e.g. H ₂ O, 104.5°
5	5	0	 trigonal bipyramidal, e.g. PF ₅ , 180°, 90°, 120°
	4	1	 distorted tetrahedral, 118°, 89°
	3	2	 Trigonal Planar or T-shape e.g. ICl ₃
6	6	0	 octahedral, 90°, SF ₆
	5	1	 distorted square pyramidal, 89°, IF ₅
	4	2	 square planar, 90°, XeF ₄

For molecules like CH₄, look at only one C atom
 e.g.  trigonal planar (120°)

Note: Electron Domain Geometry (EDG) describes shape formed by total number of electron domains. Molecular geometry is actual shape formed

Explaining how VSEPR gives a shape

- \rightarrow Shape is created because it minimises the repulsive forces between the X lone pairs/and Y bonded pairs, and which pairs repel most
- \rightarrow E.g. H₂O has a bent linear shape because it minimises the repulsive forces between the 2 lone and 2 bonded electron pairs. The lone pairs repel each other more than the bonded pairs do. Lone-lone pair equal repulsion



Allotropes of Carbon

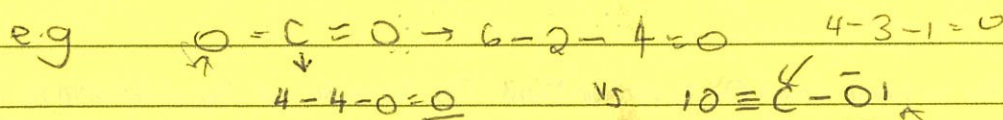
- Allotropes occur when an element can occur in different crystalline forms
- Diamond is a strong form of carbon as each C is covalently bonded to 4 other Cs, forming a macromolecule. All electrons are localised, so it cannot carry a charge.
- In graphite, each C has 3 strong covalent bonds to 3 other C atoms to give layers of hexagonal rings. The layers can slide over each other, hence graphite is a good lubricant. Because the electrons are delocalised, graphite can conduct electricity.
- Graphene is 1 atom thick graphite that is a semiconductor, light and is 200x stronger than steel
- C₆₀ - Buckminsterfullerene → football looking structure → sp² hybridisation; semiconductor because only a small number of delocalised electrons

Resonance Structures [e.g. C₆H₆, CO₃²⁻, O₃]

- Sometimes, a molecule can have many potential Lewis structures, and if none of them are stable, the molecule must keep moving between the potential structures because it moves the negative charges around stabilising itself in the process.
- Eg in a double bond, (2 O and 1 C) each have a p orbital with one electron left after σ bonds have been formed. Instead of just forming one double bond (C=O), the electrons delocalise over all 3 atoms, something that is more energetically favourable than forming a single double bond, hence the double bond can be in a variety of positions.
- electrons from the π bonds [p electrons] delocalise + spread evenly over possible bonding sites, shared across different bonding zones

Formal Charge

- assumes all atoms have same electronegativity
- FC = VE - BE (of the atom) - LE (lone electrons)



- The structures that are most likely are those that have the least charge transfer (lowest charge per atom), hence it is the most stable arrangement

- More stable if negative charges on most electronegative element

Ozone


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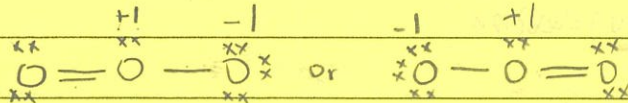
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$\overset{\times\times}{\underset{\times\times}{\text{O}}} = \overset{\times\times}{\underset{\times\times}{\text{O}}} - \overset{\times\times}{\underset{\times\times}{\text{O}}} \leftrightarrow \overset{\times\times}{\underset{\times\times}{\text{O}}} - \overset{\times\times}{\underset{\times\times}{\text{O}}} = \overset{\times\times}{\underset{\times\times}{\text{O}}}$ → The central O atom has an electron domain geometry of 4, but its molecular geometry is bent (117°) due to the presence of a lone pair.

Because there are a total of 3 pairs of electrons employed in bonding, the bond order of ozone is 1.5.

$\text{O} \begin{array}{c} \text{---} \sigma \\ \text{---} \sigma \end{array} \text{O} - \sigma \text{O}$. The electrons in the π bond are not held tightly and are delocalised, giving rise to resonance structures. ‡

Its true structure is a resonance hybrid.  Ozone is also polar, despite the fact that it is made of only of O atoms. This can be explained using formal charge

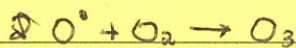


The uneven distribution of electrons through the molecule, as illustrated by formal charge, results in a net dipole across the molecule, making it polar.

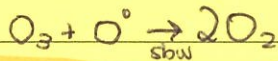
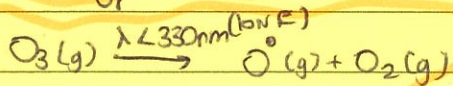
The Ozone Layer (in the lower stratosphere)

- contains 90% of the atmosphere's ozone
- A cycle is used to maintain ozone levels, involving the formation and breakdown of ozone and oxygen

‡ $\text{O}_2(\text{g}) \xrightarrow{\lambda < 242 \text{ nm (high E)}} 2 \text{O}^\bullet(\text{g})$ = oxygen radicals are produced, atoms that are highly reactive, due to the presence of an unpaired electron.



or



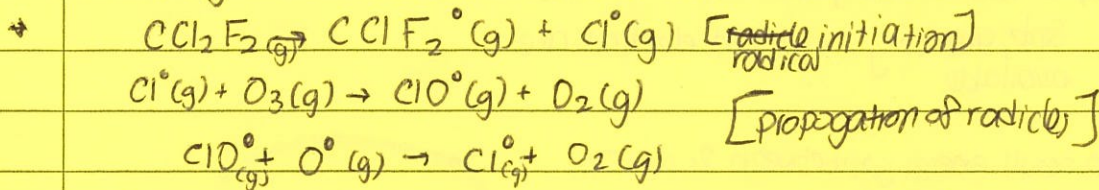
The energy needed to break down O_2 is higher than O_3 because of the difference in bond enthalpies (bond order 2.0 vs 1.5). Ozone absorbs radiation between 200nm to 315nm, such as UV-B and UV-C rays that can damage tissue. This absorption of radiation is also a major source of heat in the stratosphere, hence \uparrow °C with increasing stratospheric height.

Catalysis + Ozone destruction by CFCs and NO_x

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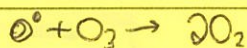
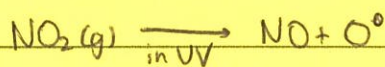
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- high energy UV rays results in the homolytic fission of the C-Cl bond to produce Cl[•].
- C-F bond cannot be broken by UV rays but C-Cl can because the bond enthalpy is lower
- Cl[•] break down O₃ and regenerate more radicals in the process, such that ozone can be continuously broken down until the radicals escape or terminate ()

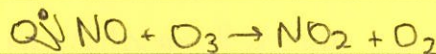


Evidence that supports this mechanism of reactions → ↑ ClO concentration, ↓ O₃ concentration

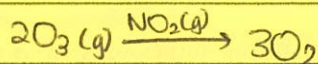
NO₂'s ability to break down O₃



The catalyst can then be regenerated



Overall



Molecular Orbitals

- formed when 2 atomic orbitals, each containing one electron overlap, forming a molecular orbital that is at a lower energy level.
- σ (sigma) bonds are formed when s and s overlap, s and p overlap, hybrid orbital and s overlap, hybrid orbitals and hybrid orbitals and when 2 p orbitals overlap head on on the internuclear axis
- π bonds are formed when 2 p orbitals overlap sideways on. This bond only forms alongside the formation of a σ bond, it also occurs above and below the internuclear axis

Double + Triple Bonds

Double bonds consist of a σ and π bond, the atoms involved have been sp² hybridized

Triple bonds consist of 2 π bonds and 1 σ bond, indicating sp hybridization.

The π bond overlap is not as strong as the σ bond because as evidenced by the debromination of bromine by ethene (breaking the π bond in C=C)

Hybridization: merging of atomic orbitals within the same atom

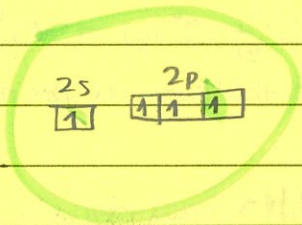
Degenerate orbitals

sp^3

Carbon as an example

$2s$ $\uparrow\downarrow$ $2p$ \uparrow \uparrow \uparrow → carbon can only form 2 bonds in this state, since only 2 unpaired electrons are available

Since there is a small energy gap between $2s$ and $2p$, energy can be provided from the C atom to promote an e^- from $2s$ into the vacant $2p_z$ orbital! Now



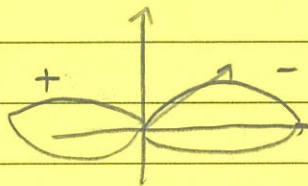
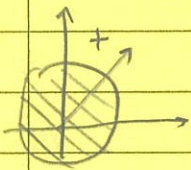
C can form 4 bonds! This is energetically favourable as when bonds are made later, energy will be released and the system will stabilise.

5 there are 4 unpaired electrons

s orbital

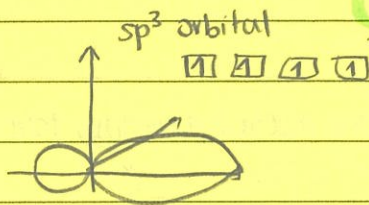
p orbital (p_x)

→ merging of 3 p orbitals and one s orbital



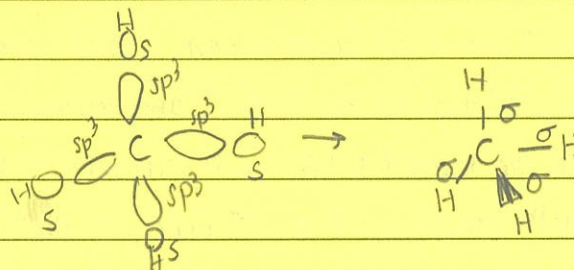
→ The positive s attracts the negative part of p, forming an sp^3 orbital (4 variants)

→ The orbitals arrange themselves in a manner such that repulsion between them is minimised



→ formed when ~~molecule~~ electron domain geometry = 4, Tetrahedral shape (109.5°)

CH_4



$sp^3 \rightarrow$ bonds that have no double
 $sp^2 \rightarrow$ must have a double bond
 $sp \rightarrow$ 2 double bonds or a triple bond

sp^2

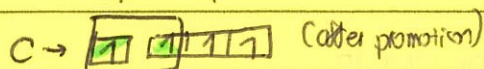
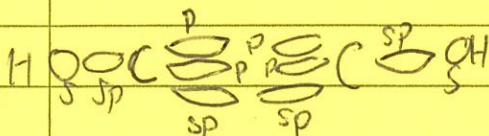
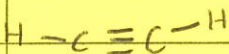
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sp^3

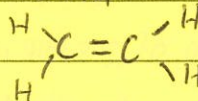
\rightarrow when EOG = 3 domains

C_2H_2

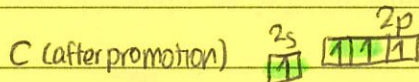


\downarrow
 these 2 orbitals merge
 to form 2 sp orbitals
 2 σ bonds are formed and
 1 sigma bond is formed between
 the Cs.

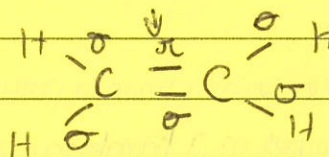
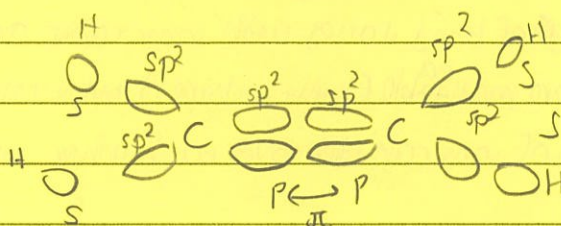
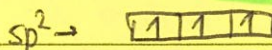
C_2H_4



\rightarrow EOG = 3 domains



Only 2 of the p orbitals merge with the s, to form 3 sp^2 orbitals



Predicting bonding through hybridization

The extra p orbitals overlap sideways to form a π bond.

Carbon

Graphite

Diamond

C60

Structure

Each C is sp^2 hybridized, hexagonal rings, held by LDF, 120°
 1 e⁻ delocalised per C atom, hence can carry charge

Each C is sp^3 hybridized, 109.5°, tetrahedral
 No delocalised charged particles

sp^2 hybridized, football-like structure
 Some e⁻ mobility, semiconductor

Conductivity [e⁻]

slippery because layers can slide over each other

Very hard, high m.p

low m.p, very light + strong

Special properties

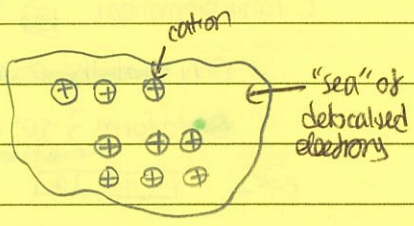
Alloys: added metals have different charge and radius, distort structure of original metal such that non directional bonding occurs.
 → less ductile + malleable, due to distorted structure
 → e.g solder alloy melts at lower temp, suitable for welding
 tin + lead

Metallic Bonding

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In a metal, valence electrons delocalise from individual atoms, such that metals consist of a closely packed lattice of positive ions surrounded by delocalised electrons.

A metallic bond is the attraction that 2 neighbouring cations have for the delocalised electrons between them.

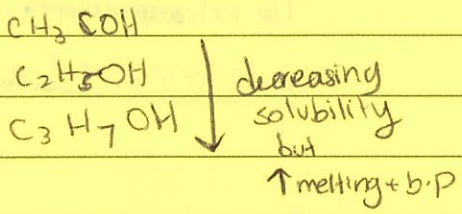


Strength of bond varies with ionic radius and ion charge

They are malleable (can be reshaped) and ductile (can be drawn into wires) because the layers of ions can slide over each other without breaking more bonds than are made.

Solubility

Organic molecules usually have a polar head and a non polar carbon chain. As the carbon chain length increases in a homologous series, the solubility decreases



Non-polar substances dissolve in the other non polar substances easily because of the formation of LDFs between solute and solvent

M.P and B.P

- H-bonding > D-D > LDF
- ↑ Mr, ↑ strength of LDF and D-D
- Mr m creates greater change than replacing with electronegative element

