



◆ COVALENT BONDS

The **covalent bond** is the electrostatic forces of attraction of the **positively charged nuclei** of each bonding atom for the **shared pair of electrons**.

A covalent bond forms due to the sharing of a pair of electrons between two atoms with similar electronegativity.



Dative / Co-ordinate Bonding

A **co-ordinate (dative covalent) bond** is formed when both electrons in a covalent bond come from only one of the bonding atoms.

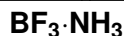
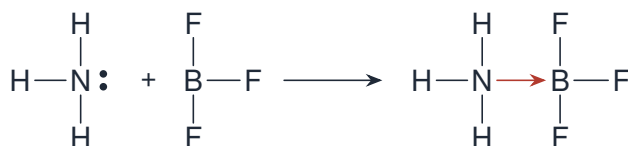
The bonding atom that **provides a lone pair of electrons** is called the **donor atom**.

The bonding atom that **contains a low-lying vacant orbital** that readily accepts the lone pair of electrons is called the **acceptor atom**.

The dative bond is denoted by an arrow ($\rightarrow$) drawn from the donor atom to the acceptor atom.

A dative bond is equal in strength and length to a single covalent bond.

Common Examples



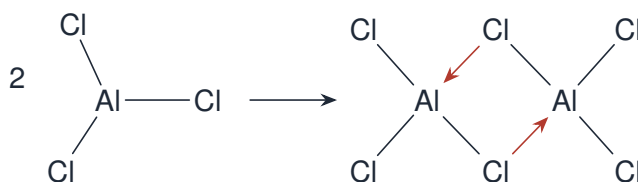
In BF_3 , the B atom has a low-lying vacant 2p orbital that can readily accept a lone pair of electrons. Hence, it is an **acceptor atom**.

In NH_3 , the N atom has a lone pair of electrons that is readily available to be donated. Hence, it is a **donor atom**.

◆ **Note.** For Answering Technique, it is very important to establish who is your donor atom and acceptor atom while explaining its role.



Al_2Cl_6



In AlCl_3 , the **Al atom** has a low-lying vacant 3p orbital that can readily accept a lone pair of electrons. Hence, it is an **acceptor atom**.

In AlCl_3 , the **Cl atom** has a lone pair of electrons that is readily available to be donated. Hence, it is a **donor atom**.

Types of Covalent Bonds

Sigma (σ) Bond

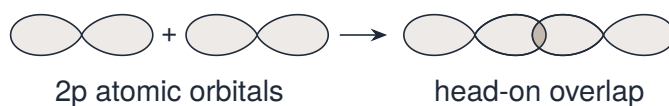
σ bond is formed by **head-on overlap** of two atomic orbitals.

There can only be ONE sigma bond between any two atoms.

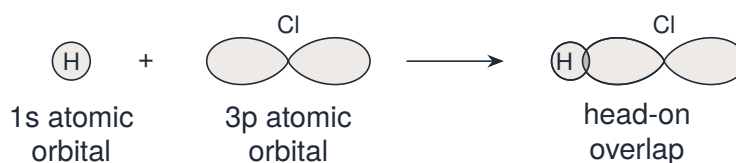
- s-s overlap (e.g. H_2)



- p-p overlap (e.g. F_2)



- s-p overlap (e.g. HCl)



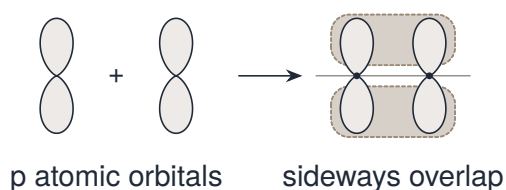
Pi (π) Bond

π bond is formed by **sideways overlap** of two p atomic orbitals.

Electron density is concentrated above and below the internuclear axis.

A π bond is formed only after a σ bond is formed.

Therefore, π bonds are present only in multiple bonds (double or triple).





Sigma (σ) vs Pi (π) bonds

A single bond = 1 σ
A double bond = 1 σ + 1 π
A triple bond = 1 σ + 2 π

Head-on overlap is more effective than sideways overlap, so a sigma bond is stronger than a pi bond.

This can be proven by looking at the bond energy values of C–C vs. C=C

Type of Bond	C–C (σ)	C=C ($\sigma + \pi$)	π bond in C=C
Bond Energy / kJ mol^{-1}	350	610	260

Covalent Bond Strength and Bond Length

Bond energy is the energy required to break **one mole** of a specified covalent bond between atoms in a **gaseous molecule**.

Bond length is the distance between the nuclei of the two atoms that are covalently bonded.

The stronger the covalent bond, the shorter its bond length.

Factors Affecting Covalent Bond Strength

Bond Order

Bond order refers to the number of covalent bonds between two atoms.

The higher the bond order, the greater the number of orbitals overlapped (by head-on or sideways overlap), hence greater electron density between the bonding atoms, greater attraction between nuclei and shared electrons which results in a stronger covalent bond.

Bond	Bond Energy (kJ mol^{-1})	Bond	Bond Energy (kJ mol^{-1})
C–C	350	C–O	360
C=C	610	C=O	740
C $\equiv$ C	840	C $\equiv$ O	1077

Effectiveness of Orbital Overlap

In general, **more effective orbital overlap** results in a stronger covalent bond.

Larger atoms have larger, more diffuse orbitals that undergo less effective orbital overlap, resulting in a weaker covalent bond.

Bond	Cl–Cl	Br–Br	I–I
Bond Energy (kJ mol^{-1})	244	193	151
Relative orbital overlap effectiveness	Highest	Medium	Lowest

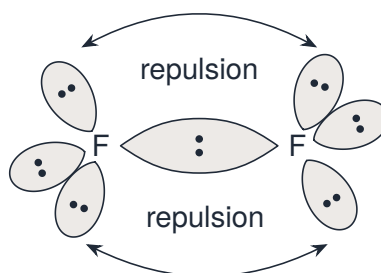


There are however, exceptions.

Bond	F – F	Cl – Cl
Bond Energy (kJ mol^{-1})	158	244

F atoms, being of smaller atomic size, should have a more effective and stronger covalent bond as compared to Cl.

However, because F atoms are small, the lone pairs of electrons on the two bonded F atoms are close together and repel each other strongly. This weakens the F–F bond.



Physical Properties of Covalent Substances

Simple Molecular Structure

Consists of simple discrete molecules held together by weak intermolecular forces.

- **Low melting and boiling points**

Only small amounts of energy are needed to overcome the weak intermolecular forces between molecules. The covalent bonds remain intact.

- **Usually soluble in non-polar solvents such as CCl_4 .**

Polar covalent molecules have greater solubility in polar solvents such as H_2O .

- **Usually non-electrical conductors**

This is due to the absence of mobile charge carriers. However, simple covalent molecules with acidic or basic properties react with water to form ions such as H_3O^+ or OH^- . Their aqueous solutions conduct electricity because the free-moving ions act as mobile charge carriers.

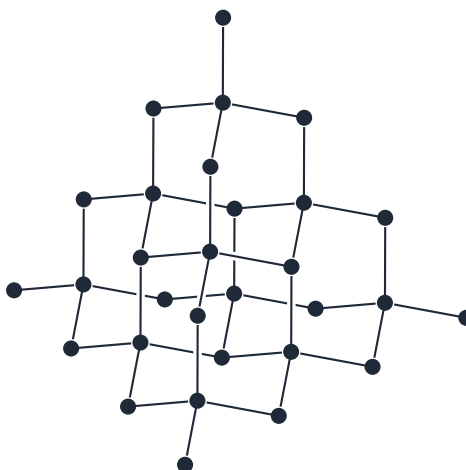


Giant Molecular Lattice Structure

Atoms are held by strong covalent bonds throughout the lattice.

Diamond

SiO₂ has the same tetrahedral arrangement. Every Si atom is bonded to 4 O atoms and every O atom is bonded to 2 Si atoms.



In diamond, each carbon atom is **sp³ hybridised**. Each **sp³ hybridised** carbon atom forms strong covalent bonds with **4 other carbon atoms** in a 3-dimensional tetrahedral arrangement.

- **Very high melting point**

A large amount of energy is required to break all the strong covalent bonds throughout the giant molecular structure.

- **Non-electrical conductor**

Absence of mobile charge carriers as all the valence electrons in C are used for bonding.

- **Hard**

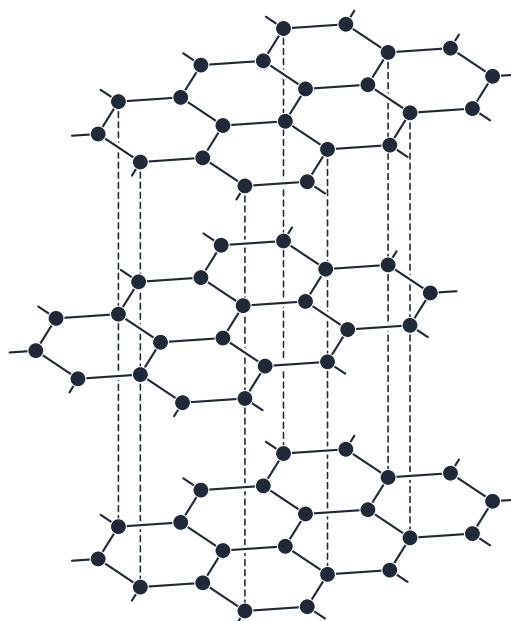
Atoms are held in fixed positions by strong covalent bonds.

- **Insoluble in all solvents**

Energy released in forming interactions between diamond and solvent is insufficient to overcome the strong covalent bonds between the C atoms.



Graphite



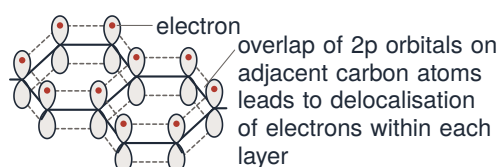
In graphite, each carbon atom is **sp^2 hybridised**.

Each sp^2 hybridised carbon atom forms strong covalent bonds with **3 other carbon atoms** in a 2-dimensional layer of hexagonal carbon rings.

The unhybridised p orbital on each sp^2 C atom is perpendicular to the layer plane.

- **Good electrical conductor**

The unhybridised p orbitals overlap sideways continuously across each layer. The resulting π electrons are delocalised above and below each layer and act as mobile charge carriers, so electricity is conducted along the layers.



- **High melting point**

Large amounts of energy are needed to break the strong covalent bonds in graphite.

- **Slippery and lubricating**

There are weak *id-id* interactions between the graphene layers, allowing layers to slide over each other easily.

- **Insoluble in all solvents**

Energy released in forming interactions between graphite and solvent is insufficient to overcome the strong covalent bonds between the C atoms.

Each layer in graphite is called graphene.



◆ DOT-AND-CROSS DIAGRAMS

In a dot-and-cross diagram, electrons from different atoms are distinguished using dots (•) and crosses (×).

This shows the arrangement of valence electrons and types of bonds around each atom.

Steps to Draw a Dot-and-Cross Diagram

Step 1:

Identify the central atom. This is usually the atom that can form the most covalent bonds, which is often the least electronegative atom. H is never the central atom because it forms only one bond.

Step 2:

Count the total valence electrons for all atoms. This follows group number.

Step 3:

Draw the bonds between the central atom and terminal atoms to form a Lewis structure first.

Step 4:

Arrange the remaining electrons as lone pairs, completing the octets of the terminal atoms first (duplet for H).

Step 5:

Check the total electron count on the central atom (bond pairs + lone pairs).

- If Period 2 central atom and total electron count > 8
Replace a double bond with a dative bond, with both electrons donated from the central atom to a terminal atom.
- If Period 3+ central atom and total electron count > 8
Verify expanded octet is within capacity. If so, the structure is correct.
If not, **replace a double bond with a dative bond** donated from the central atom.
- If the central atom has fewer than 8 electrons and an octet is not possible
Leave it as close to an octet as possible (for example BeCl_2 , BH_3 and AlCl_3).

Step 6:

Replace each bond and lone pair in the Lewis structure with dots and crosses.

For molecules containing charges:

For an anion, add electron(s) to the more electronegative atom.

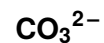
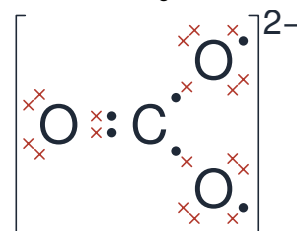
For a cation, remove electron(s) from the less electronegative atom.



Neutral Molecules



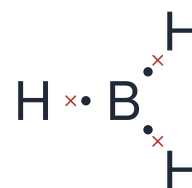
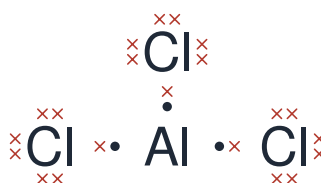
Cations and Anions



Electron-Deficient Molecules: Groups 2 and 13

These central atoms have fewer than 8 valence electrons.

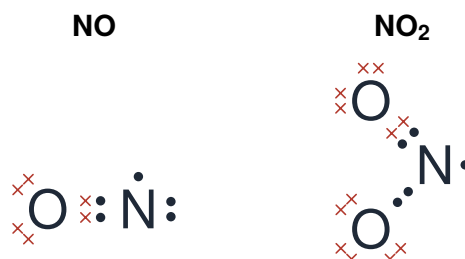
They may achieve a full octet by accepting a dative bond but are stable without.





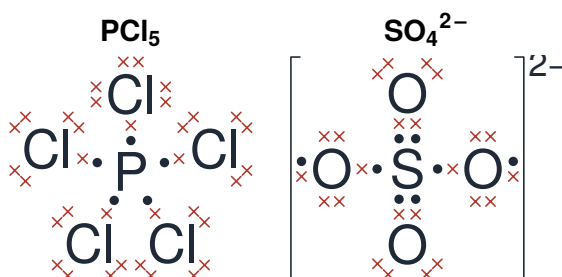
Odd-Electron Species (Radicals)

Species with an odd number of valence electrons cannot satisfy the octet rule, and the central atom has an odd number of electrons.



Expanded Octet: Period 3 Elements and Beyond

Only Period 3+ elements can accommodate more than 8 electrons, using vacant *d* orbitals.



Dative Covalent Bonds

A dative bond forms when both electrons come from the same atom.

Used in Step 5 to fix the Period 2 octet violation, and in cation formation when H⁺ accepts a lone pair.

