9.3 The Covalent Bonding Model

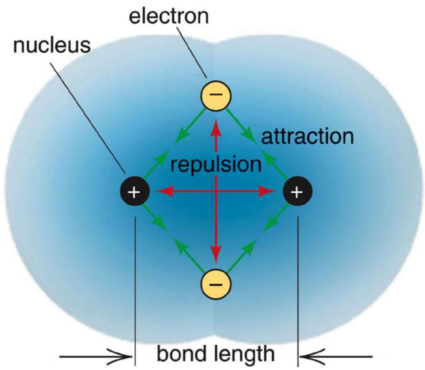
Formation of covalent bonds

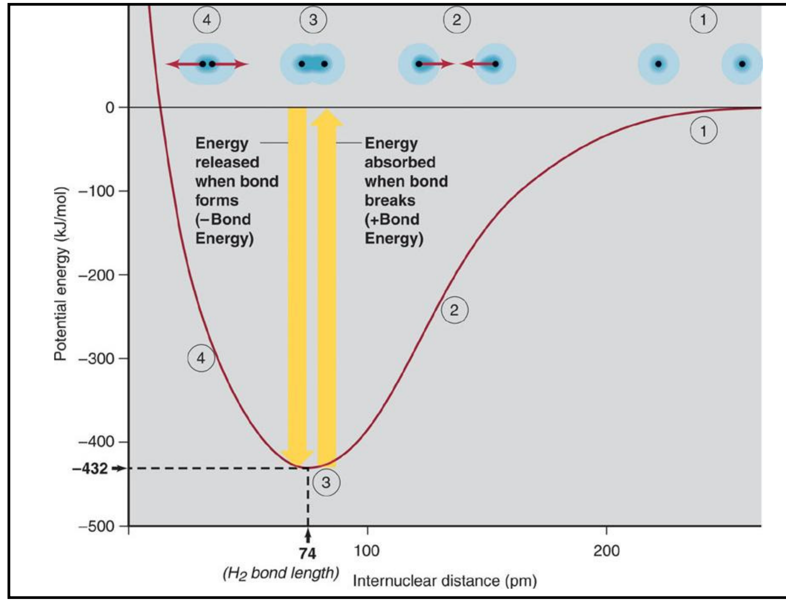
- **Covalent bond** – a result of atoms sharing a pair of electrons

H· + ·H → H:H

❖The electron density between the nuclei increases

❖The two positive nuclei are attracted to the negative charge of the shared pair of **e**$^-$

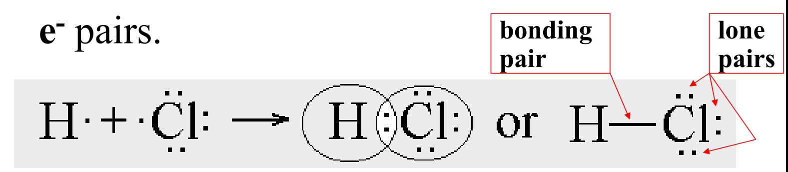




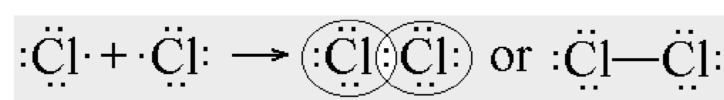
- **Octet rule** – in covalent bonding atoms share pairs of electrons until they reach **octet** (or **duplet**) configurations of noble gases
  - The number of shared **e**$^-$ pairs equals the number of electrons an atom needs in order to complete its octet (or duplet) structure
- **Lewis structures** – diagrams showing the distribution of electrons in a molecule
  - **Shared (bonding) e**$^-$ pairs – between the atoms (can be expressed as lines representing bonds)
  - **Lone e**$^-$ pairs – not involved in bonding (not shared)

Example:

Write the Lewis structures of HCl and Cl_2 and determine the number of shared and lone **e**$^-$ pairs.



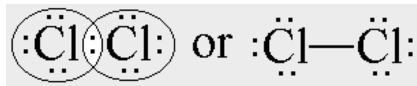
3 lone pairs at Cl and 1 bonding (shared) pair



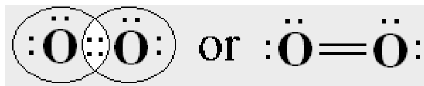
6 lone pairs at Cl and 1 bonding (shared) pair

- **Types of bonds**
  - **Single bond** – a single bonding (shared) pair
  - **Multiple bonds** – double or triple bonds (2 or 3 bonding pairs)
- **Bond order** – number of bonds linking two atoms

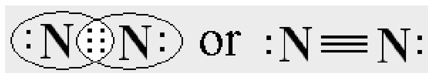
Single bond →



Double bond →



Triple bond →



Bond Energy (Enthalpy) and Bond Length

- **Bond enthalpy** (ΔH_B) – the enthalpy change for the dissociation of one mole bonds from molecules in the gas phase

$$\textbf{A-B(g)} \rightarrow \textbf{A(g) + B(g)} \qquad \Delta H_B > 0$$

- ΔH_B is a measure of the **strength** and stability of chemical bonds

Large $\Delta H_B \Leftrightarrow$ stronger bonds

  - The strength of the bond between a given pair of atoms varies slightly in different molecules
  - **Average bond enthalpies** (ΔH_B) – averaged over many compounds

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- Bond strength (ΔH_B) increases with increasing the bond order

:N≡N:	**945 kJ/mol**
:Ö=Ö:	**498 kJ/mol**
:F̤̈–F̤̈:	**159 kJ/mol**

- In general, bond strength (ΔH_B) increases with decreasing the size of the bonded atoms

H–F	**565 kJ/mol**
H–Cl	**427 kJ/mol**
H–Br	**363 kJ/mol**
H–I	**295 kJ/mol**

- **Bond length** – the distance between the nuclei of two bonded atoms
  - Bond lengths increase with decreasing the bond order

:N≡N:	**110 pm**
:Ö=Ö:	**121 pm**
:F̤̈–F̤̈:	**143 pm**

  - Bond lengths increase with increasing the size of the bonded atoms

Cl–Cl	**199 pm**
Br–Br	**228 pm**
I–I	**266 pm**

  - **Average bond lengths** – averaged over many comp.

- In general, a shorter bond is a stronger bond

Table 9.4 The Relation of Bond Order, Bond Length, and Bond Energy

Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C═O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C═C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N═N	2	122	418
N≡N	3	110	945

- **Covalent radii** of atoms – contributions of individual atoms to the lengths of covalent bonds (average values are tabulated and depend on the bond order)

Example:

Rank the following bonds by their strengths and lengths: **C–C, C=N, C≡N, C–S**

Bond strength: C≡N > C=N > C–C > C–S

Bond order **Atomic size**

Bond length: C–S > C–C > C=N > C≡N

The Properties of Covalent Compounds

- **Molecular compounds** – most covalent compounds consist of molecules (water, sugar, …)
  - Low melting and boiling points – the forces holding the molecules together are much weaker than the covalent bonds inside the molecules
  - Soft solids (often gases or liquids)
  - Poor electrical conductors in the solid state as well as when melted or dissolved (non-electrolytes)
- **Covalent network solids** – three-dimensional arrays of covalently bonded atoms (diamond, quartz, …)
  - Very high melting and boiling points– very strong covalent bonds hold the atoms together
  - Extremely hard
  - Poor electrical conductors