CH-110 Advanced General Chemistry I

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Overview: Topic 3D Intermolecular Forces

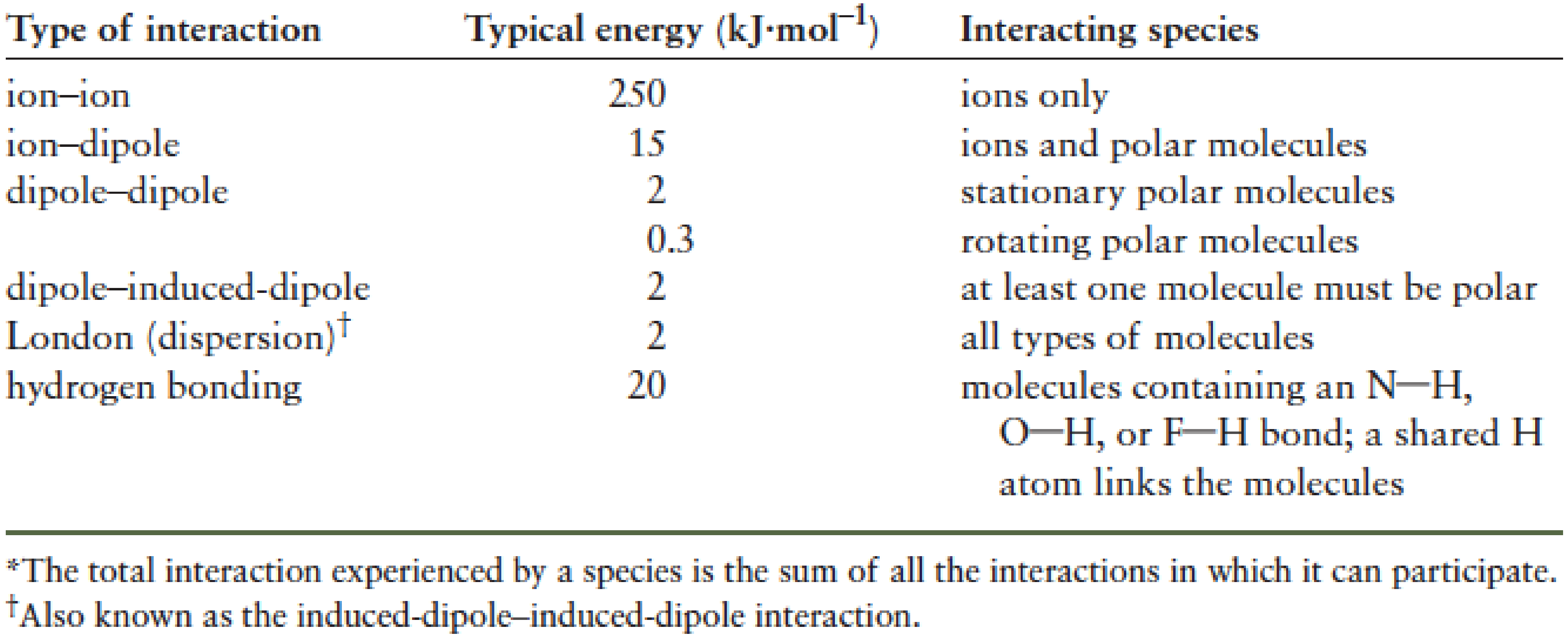
- Origin of intermolecular forces
- Ion-dipole interactions
- Dipole-dipole interactions
- London interactions
- Hydrogen bonding
- Repulsions

Introduction and background

- Intermolecular forces are the **attractions and repulsiond between molecules**. Their strengths vary with the separation of the molecules and depend on the type of interactions involved → responsible for the existence of the different phases and matter
- A phase is a form of matter that is uniform throughout in both chemical composition and physical state.
- In the gas state, molecules are far apart for most of the time, so molecules interact only weakly and deviations from ideal behaviour are only slight (treated previously)
- The molecules of **condensed phases**, the collective name for liquids and solids, are close together. Consequently, the forces that hold these molecules together are of greater importance and control their physical properties The strongest forces are the interionic forces, they are responsible for the rigidity of ionic solids (treated previously)
- Here we focus on the **interactions between uncharged molecules**.

Interactions between ions and molecules

Interionic and intermolecular interactions*



Type of interaction	Typical energy (kJ·mol^{-1})	Interacting species
ion–ion	250	ions only
ion–dipole	15	ions and polar molecules
dipole–dipole	2	stationary polar molecules
	0.3	rotating polar molecules
dipole–induced-dipole	2	at least one molecule must be polar
London (dispersion)†	2	all types of molecules
hydrogen bonding	20	molecules containing an N—H, O—H, or F—H bond; a shared H atom links the molecules

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*The total interaction experienced by a species is the sum of all the interactions in which it can participate.

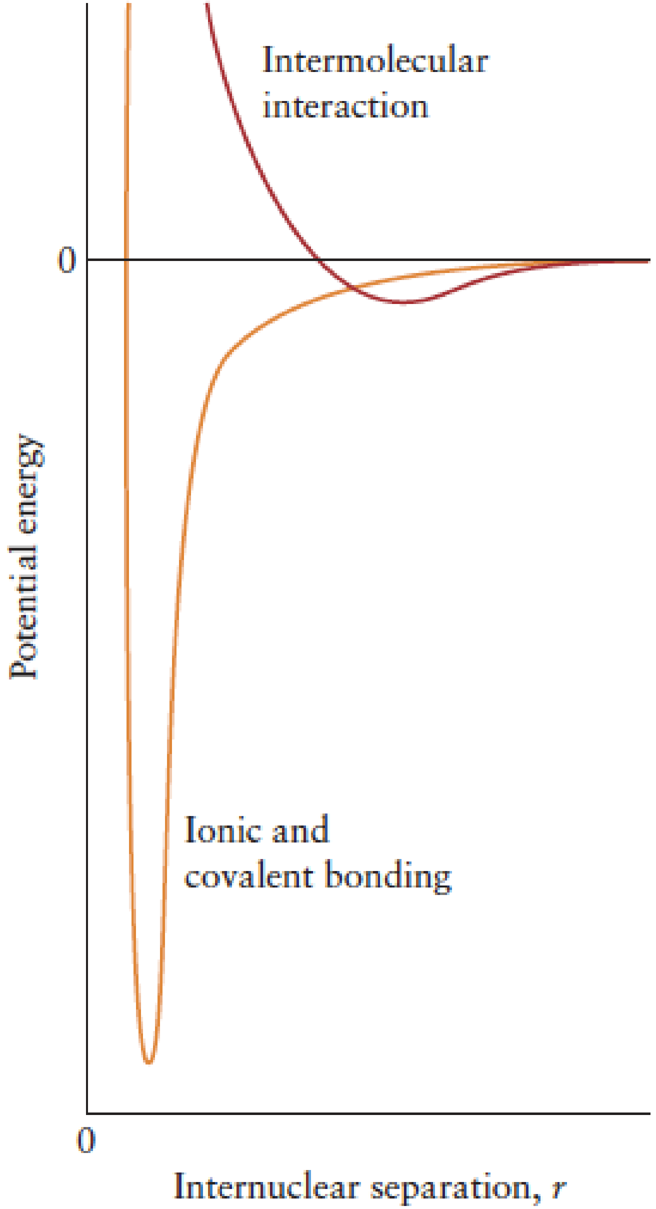
†Also known as the induced-dipole–induced-dipole interaction.

The origin of intermolecular forces

All molecules **attract each other** when they are close together, but, provided they do not react, they **repel one another** when their electron clouds come into contact.

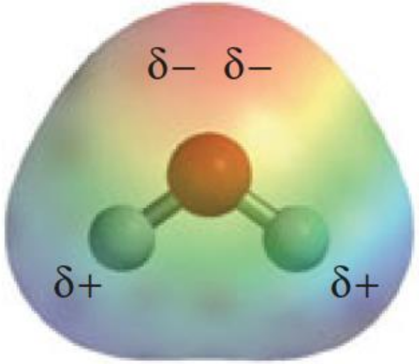
All interionic and almost all intermolecular interactions can be traced to the **coulombic interaction between charges**, the expression for the potential energy EP of two charges Q1 and Q2 separated by a distance r:

$$E_P = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$



Ion-dipole forces

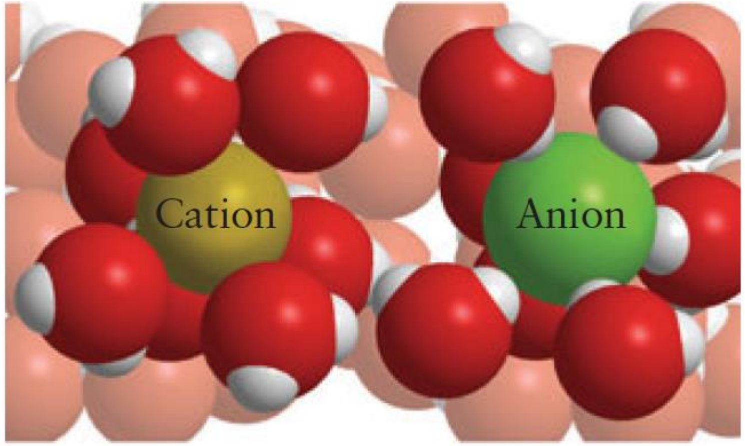
Ionic solids dissolve in water when a number of water molecules become attached to each ion and separate it from the other ions → **hydration**



Hydration of ions is due to the polar character of the H_2O molecule.

The partial **negative charge on the O atom is attracted to the cation**, and the partial **positive charges of the H atoms are repelled** by it.

The water molecules can be expected to cluster around the **cation** with a lone pair of electrons on each O atom pointing inward and the H atoms pointing outward.



We expect the **reverse arrangement around an anion**

Hydration is an example of ion-dipole interactions (interaction between an ion and a partial charge of a polar molecule)

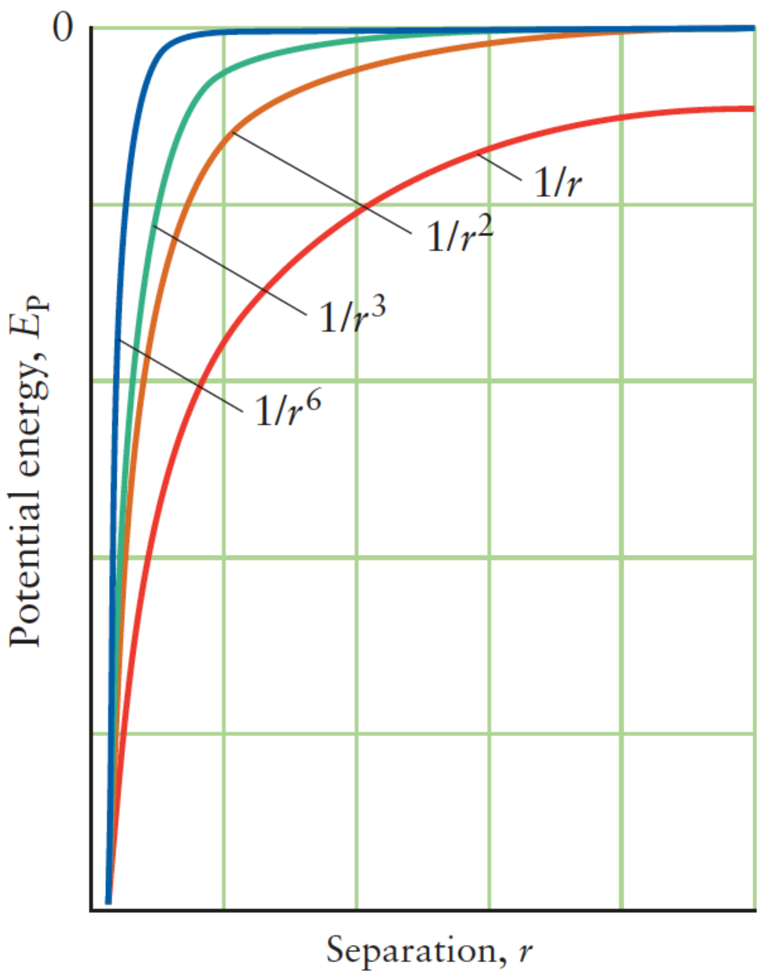
Ion-dipole forces

The **potential energy** of the interaction between the full charge of an ion and the two partial charges of a polar molecule is:

$$E_{\mathrm{p}} \propto -\frac{|z|\mu}{r^2}$$

Here z is the charge number of the ion and μ is the electric dipole moment of the polar molecule.

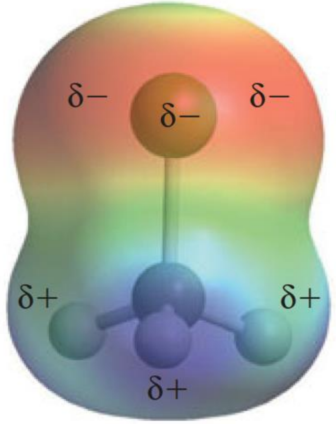
Ion-dipole interactions are **strong for small, highly charged ions**; one consequence is that small, highly charged cations are often hydrated in compounds.



The **distance dependence** of the potential energy of the interaction between ions (red, lowest line), ions and dipoles (brown), stationary dipoles (green), and rotating dipoles (blue, uppermost line).

Dipole-dipole forces (solids)

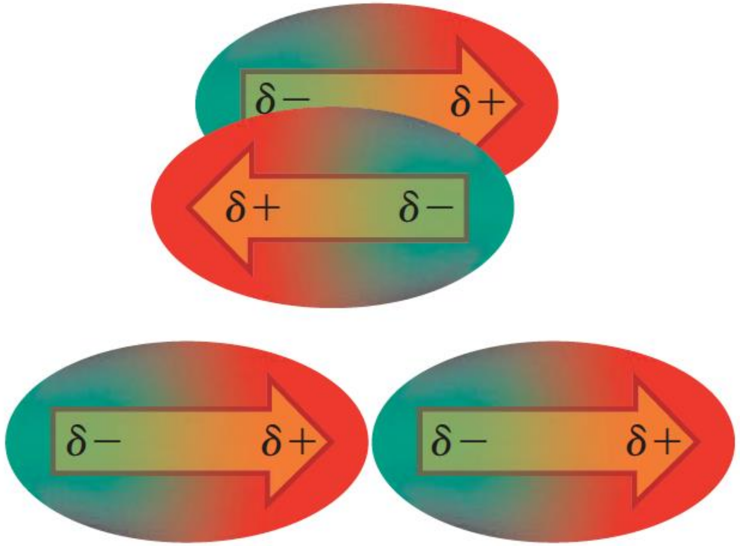
An example of a polar molecule is chloromethane, CH_3Cl, with the **partial negative charge** on the Cl atom and the **partial positive charge** spread over the H atoms



The interaction between dipoles is called the dipole-dipole interaction, and the resulting potential energy for solids is:

$$E_\mathrm{p} \propto -\frac{\mu_1\mu_2}{r^3}$$

Here, μ1 and μ2 are the dipole moments of two interacting molecules (for a solid composed of identical molecules). The greater the polarity of the molecules, the stronger are the interactions.



Dipole-dipole forces (gases)

For perfectly free rotation there should be no net interaction. However, in reality **the rotating neighbours linger slightly** in energetically favourable orientations → there is a **weak net attraction** between rotating polar molecules in the gas phase

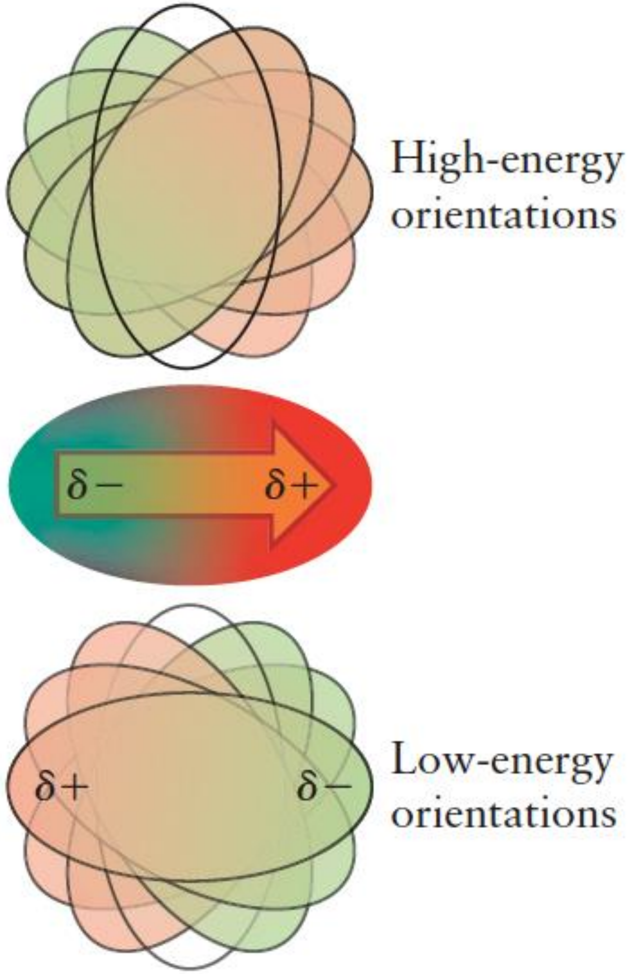
In a gas, the potential energy is:

$$E_\mathrm{p} \propto -\frac{\mu_1\mu_2}{r^6}$$

so dipole-dipole interactions between rotating molecules have a **significant effect only when the molecules are very close**

The equation also describes attractions between **rotating molecules in a liquid** → molecules are closer than in the gas phase and therefore the **dipole-dipole interactions are much stronger**

Polar molecules take part in dipole-dipole interactions, the attraction between the partial charges of their molecules. Dipole-dipole interactions are weaker than forces between ions and fall off rapidly with distance, especially in the liquid and gas phases, where the molecules rotate



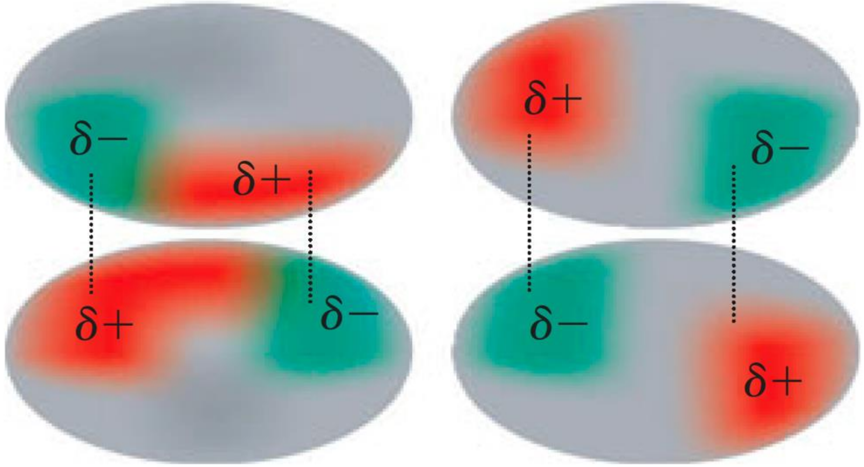
The London Interactions

Attractive interactions are found even between **nonpolar molecules**

In a nonpolar molecule or a single atom, the electrons appear to be symmetrically distributed (average values) → at any instant, the **electron clouds of atoms and molecules are not uniform**.

Even a nonpolar molecule may have an **instantaneous, fleeting dipole moment** → An instantaneous dipole moment on one molecule distorts the electron cloud on a neighbouring molecule and gives rise to a dipole moment on that molecule: the two **instantaneous dipoles attract each other.**

This attractive interaction is called the London interaction

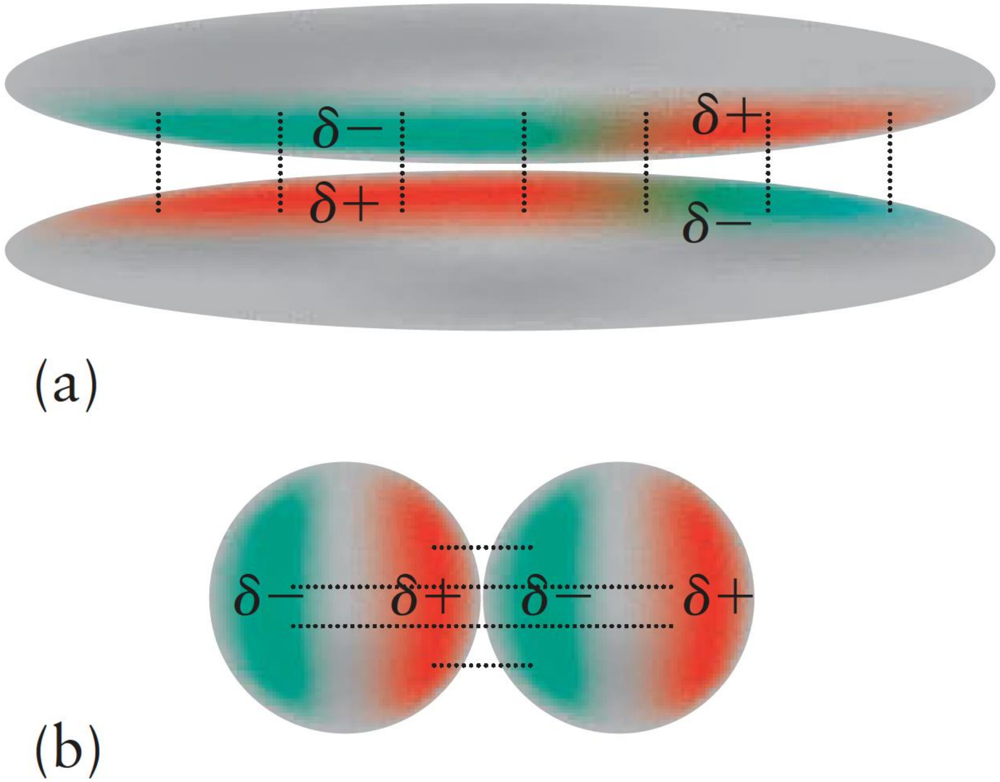


The London Interactions

The strength of the London interaction depends on the **polarizability α, of the molecules, the ease with which their electron clouds can be distorted**.

$$E_\mathrm{p} \propto -\frac{\alpha_1\alpha_2}{r^6}$$

London forces also depends on the **shapes of molecules** → the London interactions between rod-shaped molecules are more effective than those between spherical molecules with the same number of electrons



The London Interactions

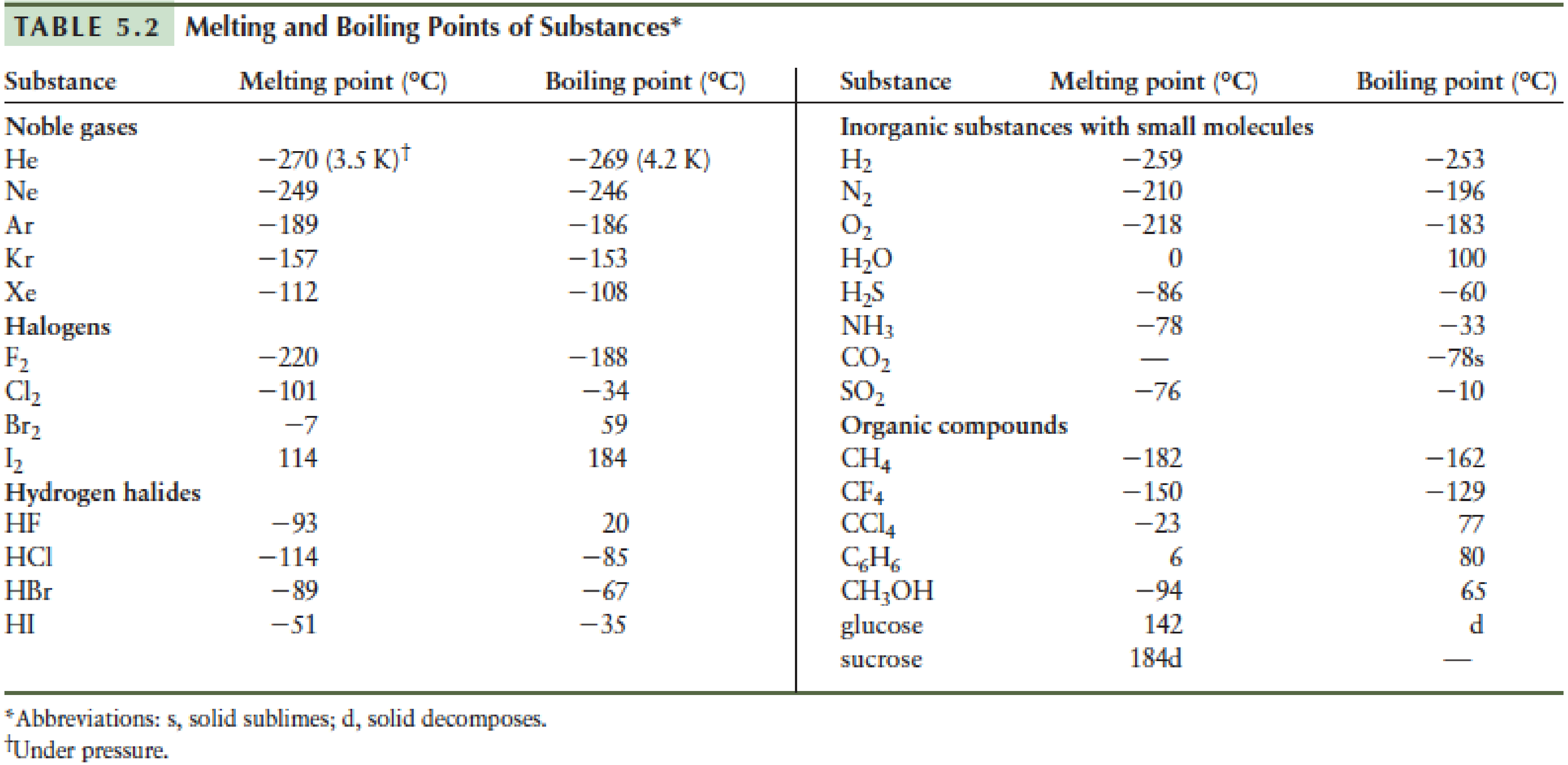


TABLE 5.2 **Melting and Boiling Points of Substances***

Substance	Melting point (°C)	Boiling point (°C)	Substance	Melting point (°C)	Boiling point (°C)
Noble gases			**Inorganic substances with small molecules**		
He	−270 (3.5 K)†	−269 (4.2 K)	H_2	−259	−253
Ne	−249	−246	N_2	−210	−196
Ar	−189	−186	O_2	−218	−183
Kr	−157	−153	H_2O	0	100
Xe	−112	−108	H_2S	−86	−60
Halogens			NH_3	−78	−33
F_2	−220	−188	CO_2	—	−78s
Cl_2	−101	−34	SO_2	−76	−10
Br_2	−7	59	**Organic compounds**		
I_2	114	184	CH_4	−182	−162
Hydrogen halides			CF_4	−150	−129
HF	−93	20	CCl_4	−23	77
HCl	−114	−85	C_6H_6	6	80
HBr	−89	−67	CH_3OH	−94	65
HI	−51	−35	glucose	142	d
			sucrose	184d	—

*Abbreviations: s, solid sublimes; d, solid decomposes.

†Under pressure.

Dipole-induced-dipole interaction

Closely related to the London interaction (for example, when oxygen dissolves in water).

Like the London interaction, the dipole-induced-dipole interaction arises from the ability of one molecule to induce a dipole moment in the other → **but here the molecule that induces the dipole moment has a permanent dipole moment**

$$E_{\mathrm{p}} \propto -\frac{\mu_1{}^2\alpha_2}{r^6}$$

Intermolecular interactions that depend on the inverse **sixth power of the separation** are known collectively as **van der Waals interactions**

The London interaction arises from the attraction between instantaneous electric dipoles on neighbouring molecules and acts between all types of molecules; its strength increases with the number of electrons and occurs in addition to any dipole-dipole interactions. Polar molecules also attract nonpolar molecules by weak dipole-induced-dipole interactions.

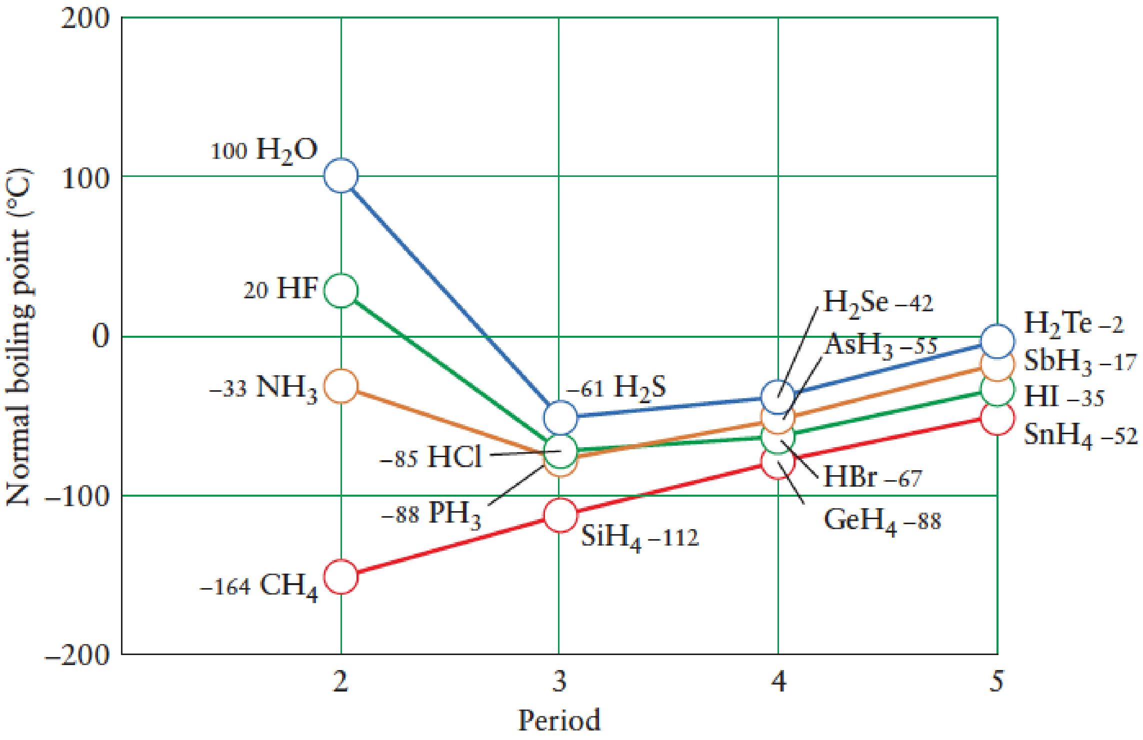
Hydrogen Bonding

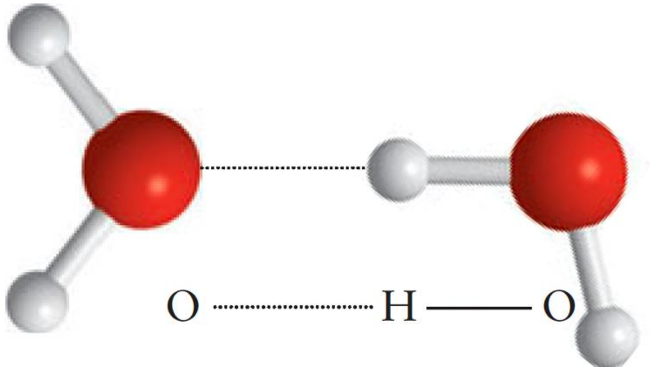
The strong interaction responsible for the high boiling points of these substances and certain others is **the hydrogen bond, an intermolecular attraction in which a hydrogen atom bonded to a small, strongly electronegative atom**, specifically N, O, or F, is attracted to a lone pair of electrons on another N, O, or F atom

Each O-H bond is polar. The electronegative O atom exerts a **strong pull on the electrons in the bond**, and the proton of the H atom is almost completely unshielded.

A hydrogen bond is denoted by a dotted line, so the hydrogen bond between two O atoms is denoted O-H···O. The O-H bond length is 101 pm and the H···O distance is somewhat longer; in ice it is 175 pm.

Hydrogen bonding, which occurs when hydrogen atoms are bonded to oxygen, nitrogen, or fluorine atoms, is the strongest type of intermolecular interaction.





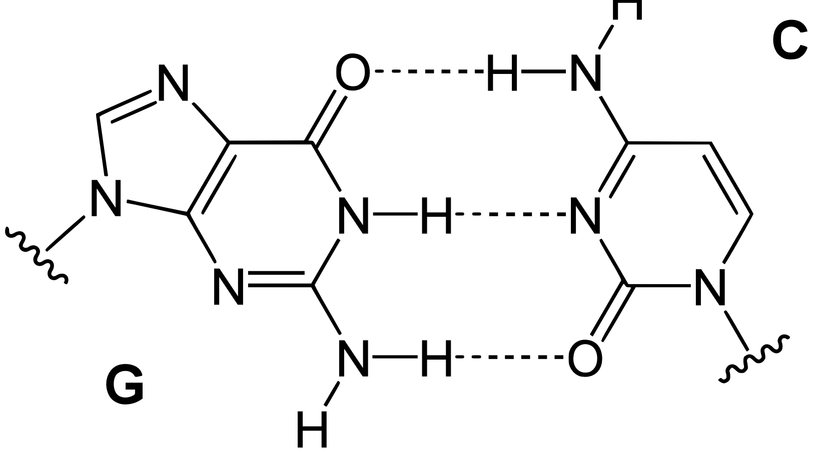
Hydrogen Bonding and Biomolecules: DNA

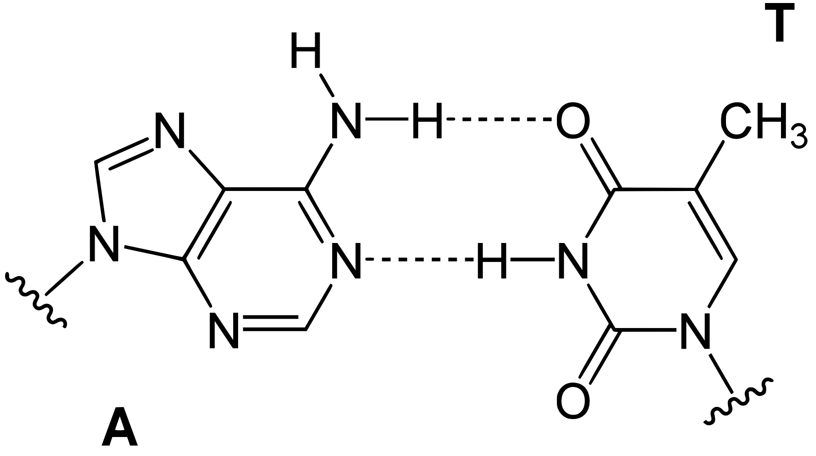
Hydrogen bonds provide the right balance of stability and flexibility in biomolecules, supporting complex structures and dynamic interactions. This balance is essential for the integrity and adaptability of life at the molecular level.

Stabilizing DNA Structure

In DNA, hydrogen bonds hold the two strands together in a double helix by linking complementary base pairs (adenine with thymine and guanine with cytosine).

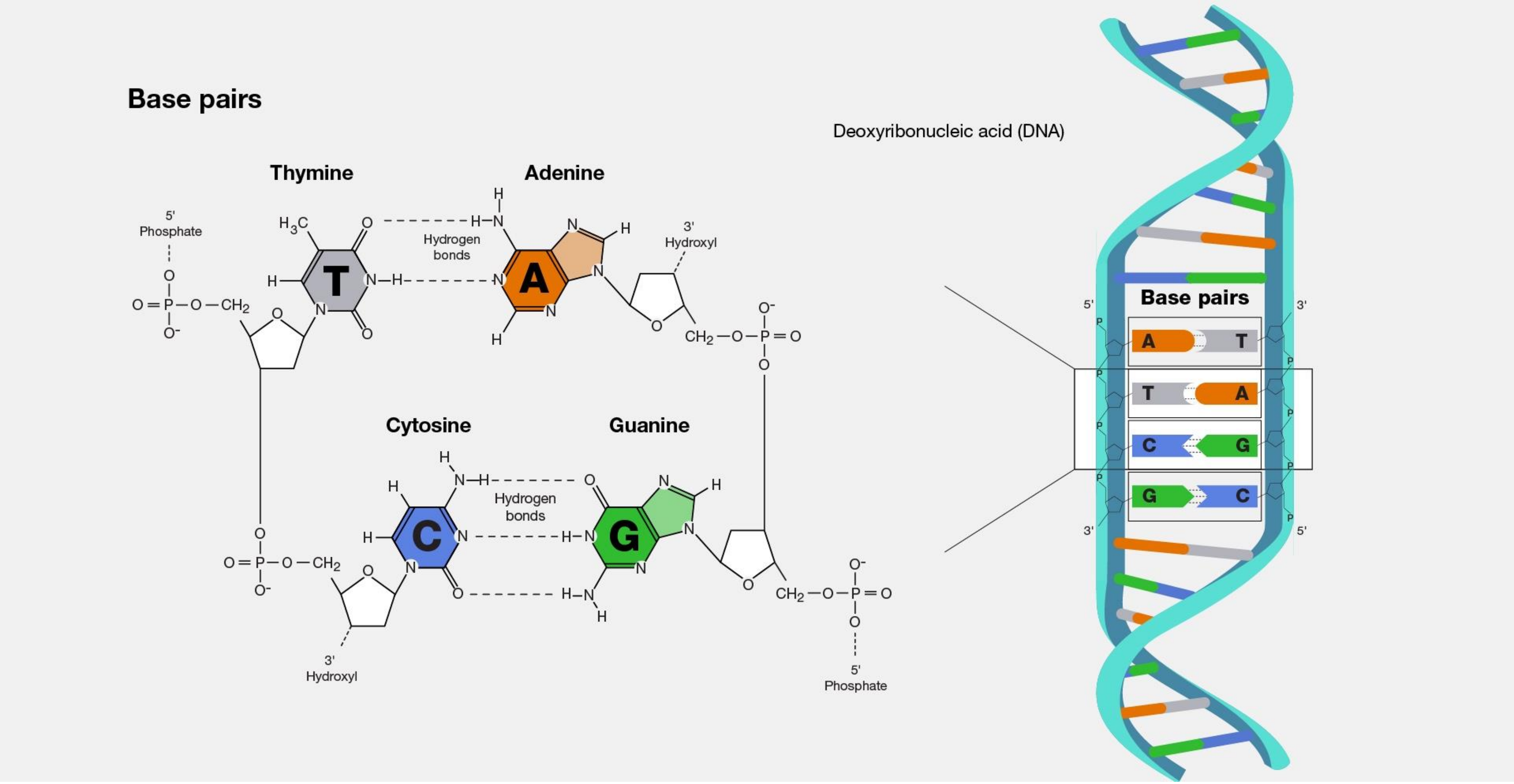
These bonds provide enough stability to maintain the DNA structure, yet are weak enough to allow the strands to separate during replication and transcription.





Source: Wikipedia

Hydrogen Bonding and Biomolecules: DNA



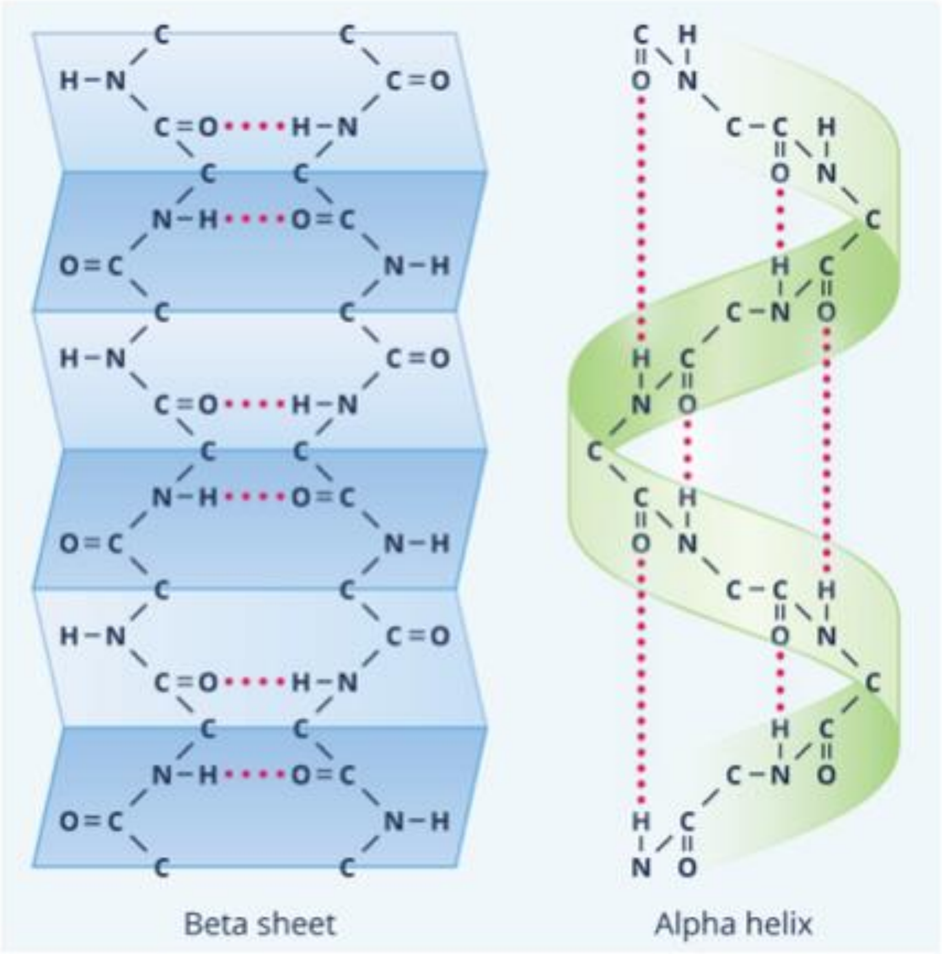
Source: Wikipedia

Hydrogen Bonding and Biomolecules: Proteins

Protein Folding and Structure

In proteins, hydrogen bonds contribute to the formation of **secondary structures like alpha-helices and beta-sheets**, which are fundamental to a protein’s 3D shape.

The overall **stability and functional conformation** of proteins largely depend on hydrogen bonding among amino acid side chains and backbone atoms.



Source: https://studymind.co.uk

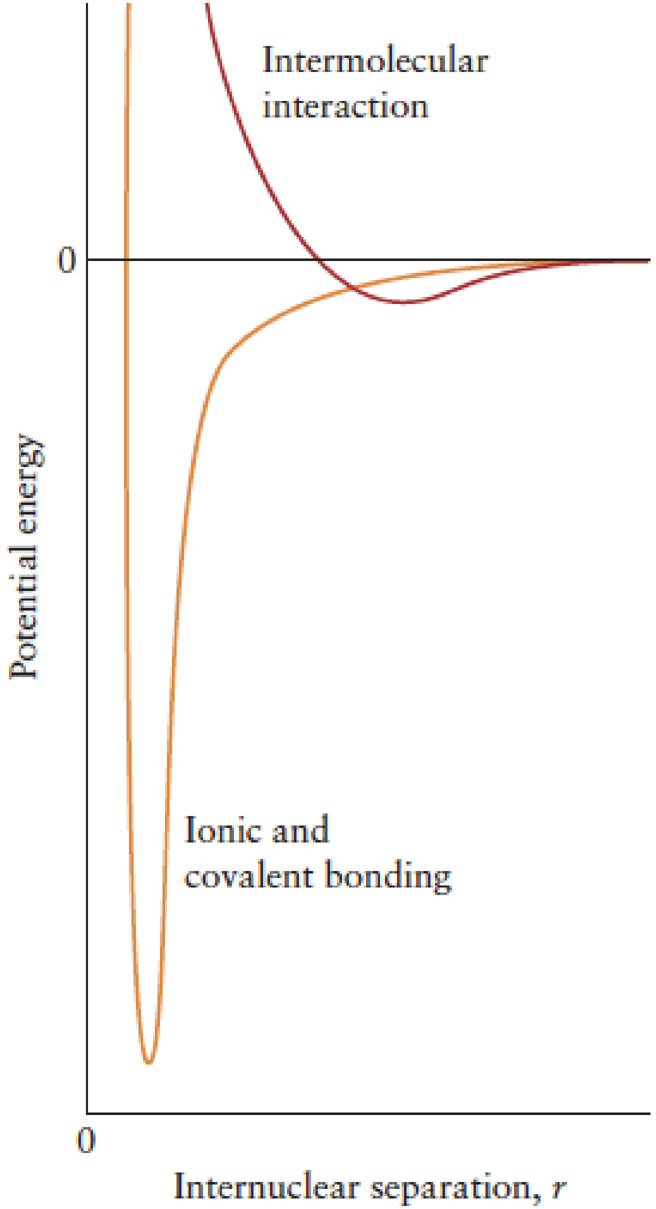
Repulsions

When molecules (or atoms that do not form bonds) are very close together, they repel one another → This repulsion can be traced to the **Pauli exclusion principle**

Reminder: The Pauli Exclusion Principle states that no two electrons can occupy the same quantum state simultaneously, which is essential for the structure and stability of atoms and matter.

The effect **increases sharply as the distance decreases** because the **overlap between the atomic orbitals increases** very rapidly as they approach.

Intermolecular repulsions arise from the overlap of orbitals on neighbouring molecules and the requirements of the Pauli exclusion principle.



The skills you have mastered are the ability to…

... predict the relative strength of ion-dipole and dipole-dipole interactions

… explain how London interactions arise and how they vary with the polarizability of the atom and the size and shape of the molecule

… predict the relative order of boiling points of two substances from the strengths of their intermolecular forces

… identify molecules that can take part in hydrogen bonding