

12.3 Types of Intermolecular Forces (*IF*)

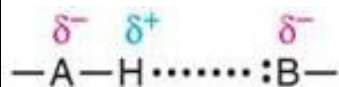
- ***IFs*** are based on electrostatic interactions between opposite charges, but they are much weaker than chemical bonds for two reasons:
 - Smaller el. charges are involved
 - The distances between the el. charges are longer
 - **Covalent radius** – $\frac{1}{2}$ the distance between two identical bonded atoms
 - **van der Waals radius** – $\frac{1}{2}$ the distance between two adjacent, identical (nonbonded) atoms from different molecules → *The van der Waals radius of an atom is always longer than its covalent radius*
- ***IFs*** are also called **van der Waals forces**
- Stronger ***IFs*** lead to higher T_b and T_m values

- **Ion-Dipole forces** – ***IFs*** between an ion and a nearby polar molecule (ionic compounds like NaCl dissolved in polar solvents like H₂O)
- **Dipole-Dipole forces** – ***IFs*** between two polar molecules (δ^+ of one molecule attracts δ^- of the other)
 - Increase with increasing the dipole moment

Example:

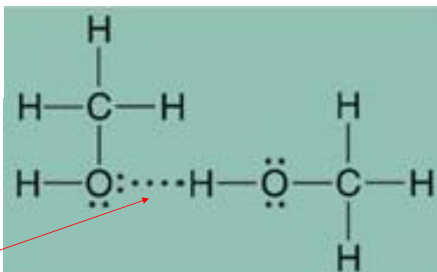
CH₃CH₂CH₃ and CH₃CN have almost the same molecular weight and size. Since CH₃CN is much more polar, its dipole-dipole forces are much stronger and its boiling and melting points, T_b and T_m , are much higher.

- **Hydrogen Bonding** – ***IF*** between molecules containing H-atoms connected to highly electronegative small atoms with lone pairs like F, O and N
 - Due to the very high polarity of the **H-F**, **H-O** and **H-N** bonds (the δ^+ of H is attracted to the δ^- of the lone pair of F, O or N)



Example:

CH₃OH has an O-H bond ⇒ H-bonding



- **Charge-Induced Dipole forces**
 - **Induced dipole** – a dipole induced in a particle through a distortion of its electron cloud by an electric field such as a nearby charge or another dipole
 - **Polarizability** – the ease with which the electron cloud of a particle can be distorted (increases with increasing the size of the electron cloud and therefore with the molar mass of the particle)
 - **Ion-Induced Dipole forces** – ***IFs*** between an ion and a dipole it induces in a nearby particle
 - **Dipole-Induced Dipole forces** – ***IFs*** between a dipole and a dipole it induces in a nearby particle

• **Dispersion (London) forces**

- **Instantaneous dipole** – a dipole that results from an instantaneous fluctuation of the electron cloud in a particle
- The instantaneous dipole can induce a dipole in a nearby particle and create an **induced dipole** in it
- **Dispersion (London) forces** – **IFs** between an **instantaneous dipole** and an **induced dipole** in a nearby particle
- Dispersion forces *exist between any particles*, but they are *the only type of IFs for non-polar molecules and atoms of noble gases*

Examples: CH₄, Cl₂, CO₂, Ar, Kr, Xe ... are all non-polar ⇒ only dispersion forces are present

– The **strength** of the dispersion forces depends on:

- The **polarizability** (size, molar mass) of the particles
↑size, molar mass ⇒ ↑dispersion forces
- The **shape** of the particles – dispersion forces between rod-shaped molecules are stronger compared to spherical molecules of the same size (rod-shapes provide more points of contact)

Example:

The boiling points of the noble gases increase down the group as the molar mass increases

Noble gases →	He	Ne	Ar	Kr	Xe
T_b (°C) →	-269	-246	-186	-153	-108
	Molar mass <u>↑ ⇒ Dispersion forces</u> <u>↑ ⇒ T_b ↑</u>				

	Force	Model	Energy (kJ/mol)	Example
Intermolecular	Ion-dipole		40–600	Na ⁺ ·····O
	H bond		10–40	
	Dipole-dipole		5–25	I–Cl·····I–Cl
	Ion-induced dipole		3–15	Fe ²⁺ ·····O ₂
	Dipole-induced dipole		2–10	H–Cl·····Cl–Cl
	Dispersion (London)		0.05–40	F–F·····F–F

	Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Intramolecular	Bonding				
	Ionic		Cation–anion	400–4000	NaCl
	Covalent		Nuclei–shared e ⁻ pair	150–1100	H–H
Metallic		Cations–delocalized electrons	75–1000	Fe	

- Comparing the different types of *IFs*
 - The most common *IFs* in substances are H-bonding, dipole-dipole and dispersion forces
 - Dispersion forces are typically more important than dipole-dipole forces, and if they have opposite trends, the dispersion forces dominate

Example:

H-halides →	HCl	HBr	HI
T_b (K) →	188	206	237
	$\text{Dipole moment } \downarrow \Rightarrow \text{Dipole-dipole forces } \downarrow$ <hr style="width: 50%; margin: 0 auto;"/> $\text{Molar mass } \uparrow \Rightarrow \text{Dispersion forces } \uparrow$		

The dispersion forces dominate the trend and $T_b \uparrow$

- Comparing the different types of *IFs*
 - H-bonding is typically much stronger than dipole-dipole and dispersion forces for particles of similar sizes

Example:

Hydrogen halides →	HF	HCl	HBr	HI
T_b (K) →	293	188	206	237
	$\text{Molar mass } \uparrow \Rightarrow \text{Dispersion forces } \uparrow$ <hr style="width: 50%; margin: 0 auto;"/>			

HF breaks the trend and has an anomalously high T_b due to the much stronger H-bonding forces which are not present in HCl, HBr and HI

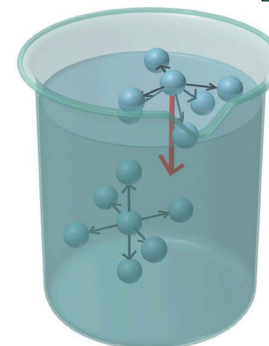
Example: Identify the types of *IFs* and rank the following substances in order of increasing boiling point, T_b :

CH_3CH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{-O-CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

$T_b \uparrow$	$\text{CH}_3\text{CH}_2\text{OH}$ → O-H bond → H-bonding → dispersion forces → polar → dipole-dipole forces
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ → non-polar → dispersion
	$\text{CH}_3\text{-O-CH}_3$ → no O-H bonds → dispersion → slightly polar → dipole-dipole
	CH_3CH_3 → non-polar → dispersion forces

12.3 Properties of Liquids

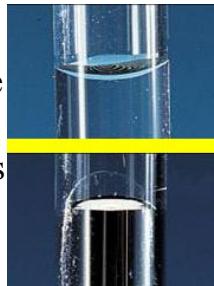
- **Surface tension** (σ) – the energy needed to increase the surface area of a liquid by a unit amount (units → J/m^2)
 - Surface molecules experience a **net inward force**
 - To create more surface (surface molecules), energy is needed to work against this inward force
- ⇒ Liquids tend to assume shapes that **minimize the surface area** (spherical drops)
- $\sigma \uparrow$ with increasing the strength of the *IFs*



- **Capillary action** – the rising of liquids in narrow tubes (capillaries) against the force of gravity (results from the competition of two types of forces)

- **Adhesive forces** – between the molecules of the liquid and the walls of the capillary
- **Cohesive forces** – between the molecules within the liquid (*IFs*)

Examples: The **H₂O** level rises inside a narrow glass tube → the adhesive forces are stronger; The **Hg** level drops inside a narrow glass tube → the cohesive forces are stronger



- **Viscosity (η)** – the resistance to flow
 - $\eta \uparrow$ with increasing the strength of the *IFs*
 - $\eta \downarrow$ with increasing the temperature (the kinetic energy of the molecules increases relative to the *IFs* of attraction between them)

Examples:

CH₃CH₂OH is more viscous than **CH₃CH₂CH₃**
H-bonding \uparrow London forces \uparrow

Oil and honey flow easier at higher **T**