

# Forces between particles and what they decide

AP Chemistry · Lesson

**Quick answer:** Intermolecular forces are the attractions between separate particles of a substance. London dispersion forces act between all particles, dipole-dipole forces between polar molecules, hydrogen bonds between molecules with O-H, N-H or F-H bonds, and ion-dipole forces between ions and polar solvents. Stronger attractions give higher boiling points, lower vapour pressure and higher viscosity.

**Level:** AP Chemistry · **Curriculum:** AP Chem Unit 3

## What are intermolecular forces?

### Definition

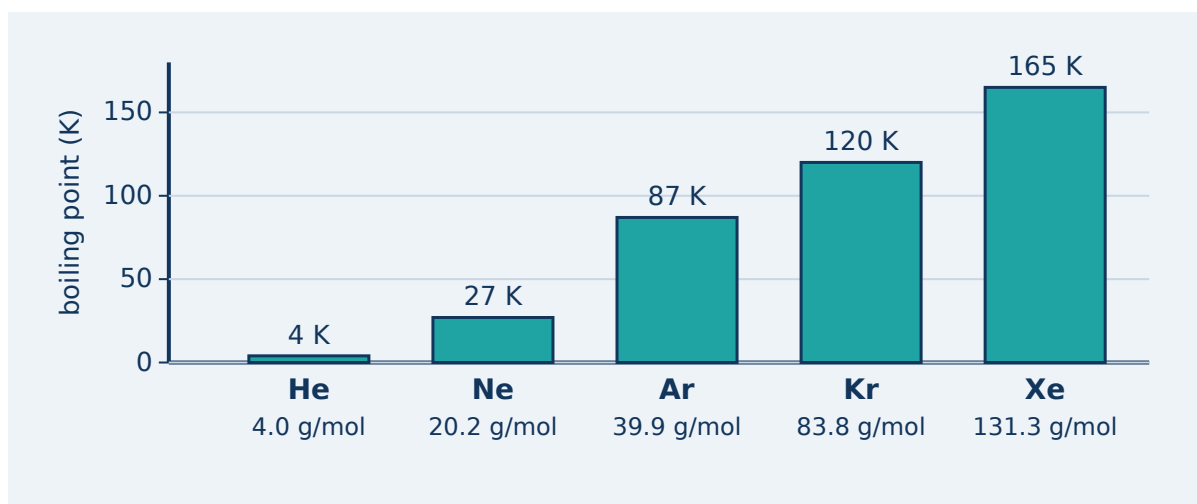
**Intermolecular forces** (IMFs) are the electrostatic attractions between separate molecules, atoms or ions in a substance. They are far weaker than the covalent bonds *inside* a molecule, so melting, boiling and dissolving change how particles are arranged without breaking the molecules themselves.

A covalent bond such as O-H in water needs roughly 460 kJ/mol to break. The attraction between two water molecules is only about 20 kJ/mol. That gap explains why steam is still H<sub>2</sub>O.

| Force             | Acts between                                               | Typical strength      | Example                                |
|-------------------|------------------------------------------------------------|-----------------------|----------------------------------------|
| London dispersion | all particles, from temporary dipoles                      | 0.05 to 40 kJ/mol     | Ar, CH <sub>4</sub> , I <sub>2</sub>   |
| Dipole-dipole     | permanent dipoles of polar molecules                       | 5 to 25 kJ/mol        | HCl, CH <sub>3</sub> COCH <sub>3</sub> |
| Hydrogen bonding  | H bonded to N, O or F, and a lone pair on N, O or F nearby | 10 to 40 kJ/mol       | H <sub>2</sub> O, NH <sub>3</sub> , HF |
| Ion-dipole        | an ion and a polar molecule                                | often above 40 kJ/mol | Na <sup>+</sup> in water               |

## How does molecular size affect London dispersion forces?

Electrons move constantly, so at any instant one side of an atom may hold slightly more charge. This temporary dipole induces a matching dipole in a neighbour and the two attract. A large electron cloud is easier to distort, which chemists call high **polarisability**. More electrons and a larger cloud therefore mean stronger dispersion forces.

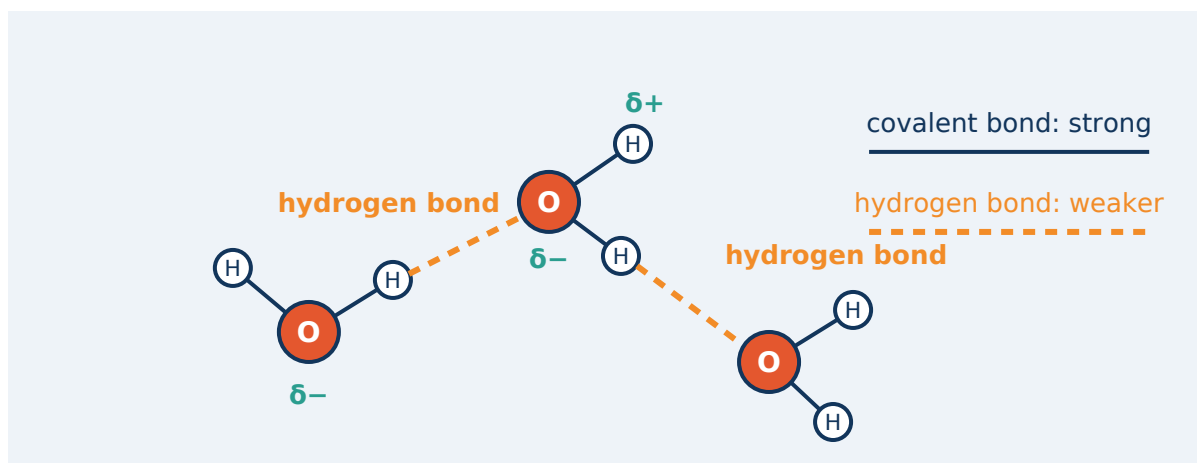


Boiling points of the noble gases rise as atoms get larger, because larger electron clouds are more polarisable.

Shape matters as well. Long, straight molecules touch along their whole length, while compact, branched molecules touch at fewer points. Pentane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) boils at  $36^\circ\text{C}$  but its branched isomer neopentane,  $\text{C}(\text{CH}_3)_4$ , boils at only  $9.5^\circ\text{C}$ .

## What is hydrogen bonding and why is water special?

When hydrogen is bonded to a very electronegative atom (N, O or F), the bond is strongly polar and the hydrogen carries a large partial positive charge,  $\delta+$ . It is attracted to a lone pair on a neighbouring N, O or F atom. This is a **hydrogen bond**, the strongest of the three molecular forces. Water, with two O-H bonds and two lone pairs on each oxygen, forms a network that raises its boiling point to  $100^\circ\text{C}$ , while  $\text{H}_2\text{S}$ , a heavier molecule with no hydrogen bonds, boils at  $-60^\circ\text{C}$ .



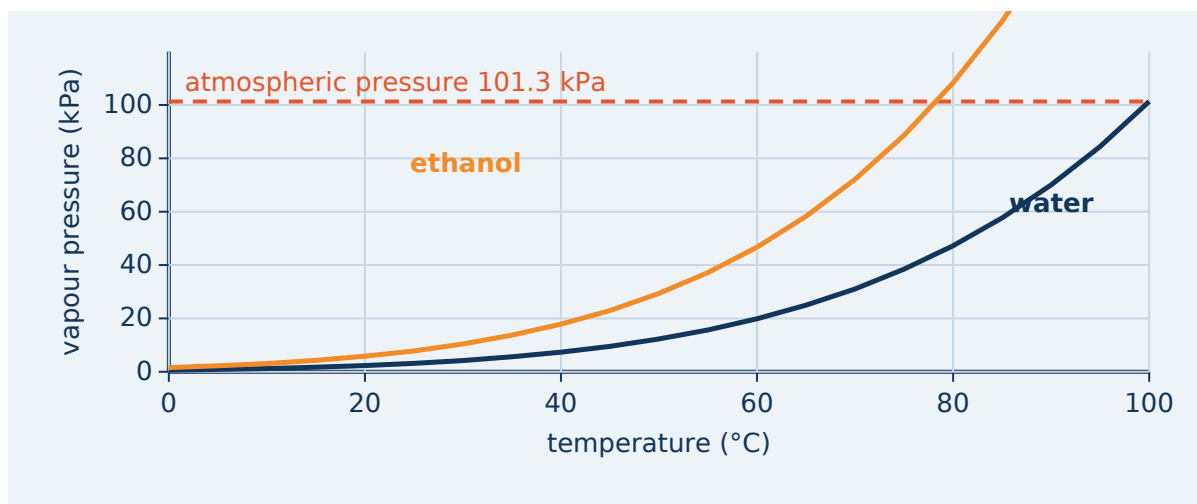
Hydrogen bonds (dashed) link the slightly positive hydrogen of one molecule to a lone pair on the oxygen of a neighbour.

### Key law

The stronger the intermolecular forces, the higher the boiling point, melting point, enthalpy of vaporisation, viscosity and surface tension, and the lower the vapour pressure at a given temperature.

## How does vapour pressure depend on temperature?

A liquid in a closed container reaches dynamic equilibrium when the rate of evaporation equals the rate of condensation. The pressure of the vapour then is the **equilibrium vapour pressure**. Hotter liquids have more molecules able to escape, so the pressure climbs steeply. The **normal boiling point** is the temperature at which vapour pressure equals 101.3 kPa.



Vapour pressure rises steeply with temperature. A liquid boils when its curve meets the external pressure.

### Formula

$$\ln(P_2/P_1) = (\Delta H_{\text{vap}}/R) \times (1/T_1 - 1/T_2)$$

$P$  = vapour pressure (any unit, same for both),  $\Delta H_{\text{vap}}$  = enthalpy of vaporisation (J/mol),  $R$  = 8.314 J/(mol·K),  $T$  = temperature (K).

### Worked example 1

Rank propane,  $\text{CH}_3\text{CH}_2\text{CH}_3$  (44 g/mol), methoxymethane,  $\text{CH}_3\text{OCH}_3$  (46 g/mol), and ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$  (46 g/mol), by boiling point.

Masses are almost equal, so dispersion forces are similar. Propane is nonpolar and has only dispersion forces. Methoxymethane is polar, adding dipole-dipole forces. Ethanol has an O-H bond, so it forms hydrogen bonds.

**Order: propane (−42 °C) < methoxymethane (−24 °C) < ethanol (78 °C).**

### Worked example 2

Water has  $\Delta H_{\text{vap}} = 40.7$  kJ/mol and boils at 373.15 K under 101.3 kPa. Find its vapour pressure at 80.0 °C (353.15 K).

$$\ln(P_2/101.3) = (40\,700/8.314) \times (1/373.15 - 1/353.15) = 4895.3 \times (-1.5177 \times 10^{-4}) = -0.7430$$

$$P_2 = 101.3 \times e^{-0.7430} = 101.3 \times 0.4757$$

$$\mathbf{P_2 = 48.2\ kPa}$$

## How do the four types of solid differ?

| Type             | Particles and attraction                            | Melting point                              | Conducts electricity?         | Example                       |
|------------------|-----------------------------------------------------|--------------------------------------------|-------------------------------|-------------------------------|
| Ionic            | cations and anions, strong electrostatic attraction | high (NaCl 801 °C)                         | only when molten or dissolved | NaCl, MgO                     |
| Metallic         | cations in a sea of delocalised electrons           | varies (Cu 1085 °C)                        | yes, as solid and liquid      | Cu, Fe                        |
| Molecular        | molecules held by IMFs                              | low (ice 0 °C)                             | no                            | I <sub>2</sub> , ice, sucrose |
| Covalent network | atoms joined by covalent bonds throughout           | very high (SiO <sub>2</sub> about 1710 °C) | usually no                    | diamond, quartz               |

### Common mistake

Do not say that boiling water breaks O-H bonds. Boiling overcomes hydrogen bonds between molecules. The molecules stay intact, which is why steam is still H<sub>2</sub>O. Only in a network solid or an ionic solid do the bonds that melt the substance coincide with the bonds that hold it together.

### Lina's tip

Before ranking boiling points, ask in order: is it ionic or a network? Does it have O-H, N-H or F-H? Is it polar? Then compare sizes. The first yes decides the group.

### Key points to remember

- Strength order for molecules of similar size: dispersion, then dipole-dipole, then hydrogen bonding.
- Larger, more polarisable electron clouds give stronger London dispersion forces; branching weakens them.
- Normal boiling point: vapour pressure equals 101.3 kPa.
- $\ln(P_2/P_1) = (\Delta H_{\text{vap}}/R)(1/T_1 - 1/T_2)$ , with  $R = 8.314 \text{ J/(mol}\cdot\text{K)}$  and  $T$  in kelvin.
- Ionic and network solids melt at high temperature; molecular solids melt at low temperature.

## Forces between particles and what they decide: frequently asked questions

### Why is hydrogen bonding stronger than ordinary dipole-dipole attraction?

Hydrogen is very small and carries a large partial positive charge when bonded to N, O or F. It can approach a lone pair on a neighbouring atom very closely, and the attraction rises sharply with a smaller distance.

**Do nonpolar molecules have intermolecular forces?**

Yes. All particles have London dispersion forces, because electrons move and create temporary dipoles. Nonpolar molecules such as methane and iodine have only these forces, which is why they are gases or soft solids.

**Why does evaporation cool a liquid?**

The fastest molecules escape first, so the average kinetic energy of those left behind falls. The energy to overcome the intermolecular forces also comes from the liquid. This is how sweating cools the body.

**Why do liquids boil at lower temperature on a mountain?**

A liquid boils when its vapour pressure equals the external pressure. At altitude the air pressure is lower, so the vapour pressure reaches it at a lower temperature.

**How can I tell if a bond is intramolecular or intermolecular in a diagram?**

Intramolecular bonds join atoms inside one molecule and are drawn as solid lines. Intermolecular forces connect different molecules and are usually drawn as dashed lines, as in the hydrogen bonds in water.