Chem Factsheet
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Intermolecular Forces

Intermolecular forces are the **weak** forces of attraction **between** covalent molecules. They are distinct from other, stronger attractive forces that occur in chemistry. When covalent molecules melt or boil, it is the intermolecular forces that are disrupted.

Weak Attractive Forces:	**Strong Attractive Forces:**
1. Van der Waals' forces: a. London dispersion forces. b. Permanent dipole-permanent dipole interactions.	1. Ionic bonds: electrostatic attraction between oppositely charged ions in ionic compounds.
2. Hydrogen bonds.	2. Covalent bonds: electrostatic attraction between electron pairs and two nuclei in a molecule.
3. Ion-dipole interactions – strictly speaking not inter**molecular**.	3. Metallic bonds: electrostatic attraction between delocalised electrons and positive metal ions in metals and alloys.

Intermolecular forces are important to study because they influence the physical properties of a molecule. Properties that are affected include melting points, boiling points, solubility and vapour pressure.

London (Dispersion) Forces
These forces are alternatively known as temporary or instantaneous dipole-induced dipole interactions. They exist between all molecules whether those molecules exhibit other, stronger intermolecular forces of attraction or not. London forces are the principal forces of attraction between non-polar molecules.

What is a Dipole?
A dipole is a region of space in which one area has slightly more negative charge (δ^-) than the area opposite it (δ^+); thus creating two oppositely charged poles. Typically, dipoles exist where atoms with different electronegativities are covalently bonded to each other (see Fig 1A) or where electrons are unevenly distributed at an instant in time across individual atoms or molecules (see Fig 1B).

Fig. 1 A

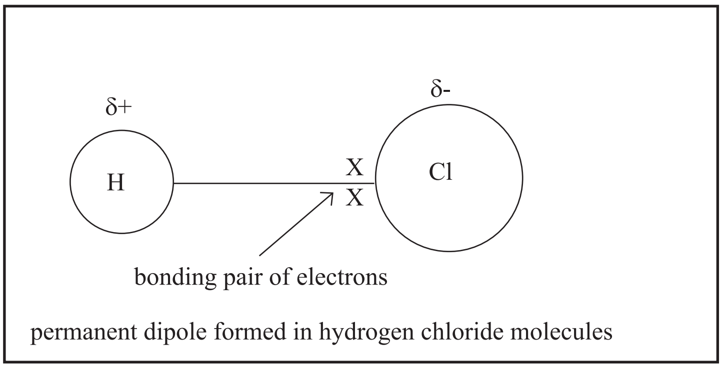
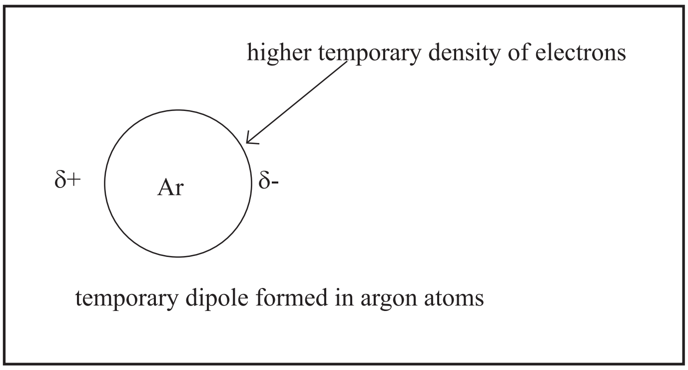
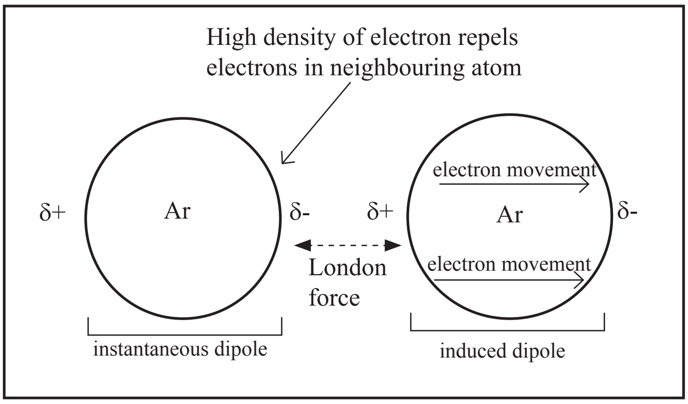


Fig. 1 B



How London Forces Arise:
1. The random distribution of electrons in an atom or molecule causes one side of the particle to become slightly more negatively charged than the other at any particular instant in time. This is termed an instantaneous dipole.
3. The slightly more negative region of this particle repels electrons in a neighbouring particle creating an induced dipole. It is said to polarise it.
3. This creates an attractive force between the negative pole of one particle and the positive pole of the neighbouring one as shown in Fig. 2.

Fig. 2 The formation of a London force between adjacent argon atoms.



This attractive force lasts only for that "instant" and is, therefore, very weak. However, they are continually forming and dispersing and, thus, exist throughout the material when particles come close together.

Strength of London forces

1. Effect of Electron Number

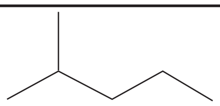
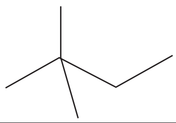
In lighter atoms and smaller molecules, where the number of electrons is low, London forces are extremely weak. The strength of London forces increase as atoms become heavier and therefore contain more electrons which makes the atoms easier to polarise. This effect is most clearly demonstrated by studying the boiling points of the halogens or noble gases.

Halogen	Boiling point /K	Noble Gas	Boiling point /K
F_2	85	He	4.4
Cl_2	239	Ne	27.3
Br_2	332	Ar	87.4
I_2	457	Kr	121.5

As the number of electrons in the halogen atom (and therefore molecule) increases (F<Cl<Br<I), the strength of the London forces between the molecules increases. The boiling point therefore increases as a result of the extra energy required to break the stronger forces. The noble gases show a similar trend as a result of the increasing number of electrons in the noble gas atoms (He<Ne<Ar<Kr).

2. Effect of surface area contact

London forces exist only over very short distances. This means molecules need to be extremely close to each other to induce dipoles. The greater the surface area over which molecules make contact with one another the greater the strength of the London forces between them. This effect is best shown by comparing the boiling points of isomers of an alkane such as hexane.

Isomer	Structure	Boiling point /K
Hexane		342
2-methylpentane		333
2,2-dimethylbutane		323

As the extent of branching of the isomer increases, the surface area over which the molecules can make contact decreases. This makes induction of dipoles less likely, resulting in a decrease in the strength of London forces and a decrease in boiling point.

Permanent dipole-permanent dipole interactions

Permanent dipole-permanent dipole interactions exist between polar molecules.

Polarity

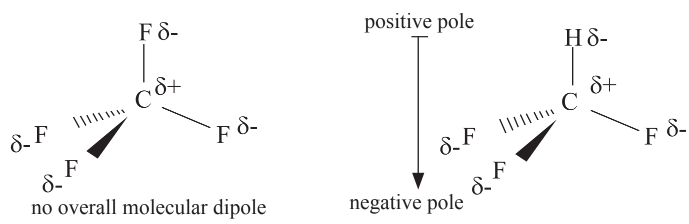
To determine if a molecule is polar or not, both the polarity of the individual covalent bonds and the shape of the molecule must be taken into account. For a molecule to be polar it must contain one or more polar bonds **and** the dipoles of those bonds must **not** cancel each other. In other words the molecule must not be a symmetrical shape.

A covalent bond will be polar if the two atoms are of different elements as they will then have different electronegativities. On average, the pair of electrons within the bond exists closer to the more electronegative atom, giving it a slightly more negative charge (δ^-) than the other atom (δ^+).

For example, in hydrogen chloride, the bonding electrons lie closer to the chlorine atom as it is the more electronegative element (see Fig. 1). This polarises the H—Cl bond as shown and, as there is no other dipole to cancel it out, the molecule overall is polar.

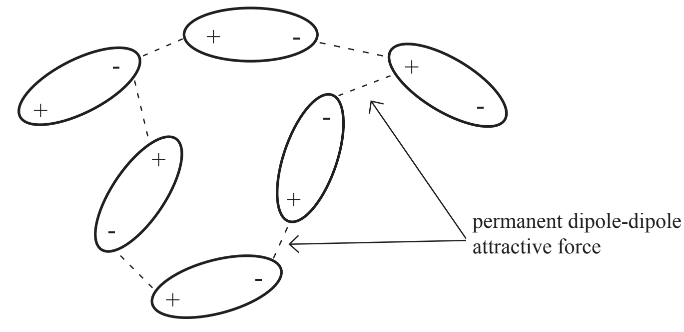
As shown in Fig. 3, in CF_4, each C—F bond is polar. However, the symmetry of the tetrahedral arrangement of the fluorine atoms means that the four dipoles cancel each other and, overall, the molecule is non-polar. Replacing one fluorine atom with a hydrogen atom means the dipoles do not cancel (as H is much less electronegative than F) and so CHF_3 is polar.

Fig. 3 Dipoles in CF_4 and CHF_3 showing the origin of a molecular dipole moment in CHF_3

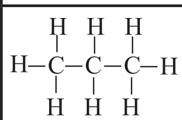
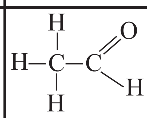


Polar molecules have one end with a slight negative charge (δ^-) and the opposite end has a slight positive charge (δ^+). Permanent dipole-permanent dipole attractions exist between the δ^- end of one molecule and the δ^+ end of a neighbouring molecule.

Fig. 4 The formation of permanent dipole-permanent dipole attractions between opposite poles of adjacent polar molecules



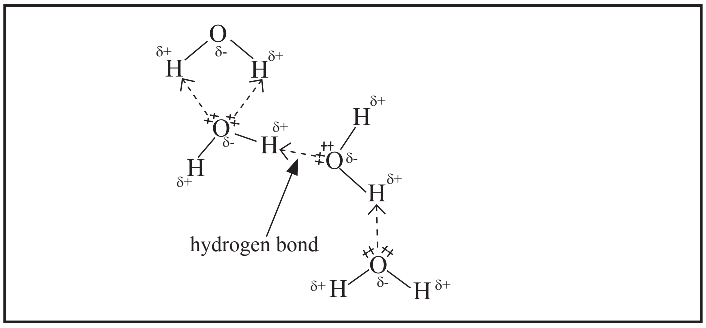
Due to the permanent nature of the dipoles, these forces are typically stronger than London forces in molecules with similar molecular mass and number of electrons.

Molecule	Propane	Ethanal
Structure		
Polar/non-polar	Non-polar	Polar
Molar mass /g mol^{-1}	44.10	44.05
Boiling point /K	231	293

Propane and ethanal both have a molecular mass of 44, yet their boiling points differ by 62 K. Propane is a non-polar molecule whereas the presence of a single oxygen atom in ethanal makes it polar, meaning stronger permanent dipole-permanent dipole interactions exist between ethanal molecules (in addition to London forces). Propane only exhibits weaker London forces between its molecules.

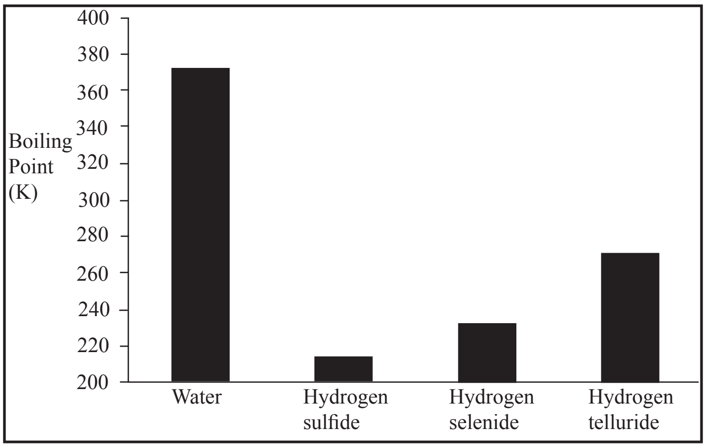
Hydrogen bonds
Hydrogen bonds are typically the strongest of the three common types of intermolecular force. They only form under specific circumstances. A hydrogen bond is a directional attraction between a lone pair of electrons on a δ^- atom and a δ^+ hydrogen atom attached to a nitrogen, oxygen or fluorine atom. This is illustrated in fig. 5 for water.

Fig. 5 Hydrogen bonds between water molecules forming between lone pairs on oxygen in one molecule and δ^+ hydrogen atoms attached to oxygen atoms in another



Hydrogen bonding has a significant impact on the boiling point of a molecule. This effect is most evident when comparing the boiling points of the Group 16 (old group VI) hydrides as shown in fig. 6.

Fig. 6 Boiling point variations for the group 16 hydrides, H_2O, H_2S, H_2Se and H_2Te



The hydrides of sulphur, selenium and tellurium have a non-symmetrical bent shape (V-shape) and moderately polar bonds. This makes them polar molecules overall. Their molecules are held to one another through permanent dipole-permanent dipole interactions and London forces. The boiling point increases as the number of electrons in the Group 16 element increases and the London forces between the molecules get stronger. However, hydrogen bonds are able to form between water molecules and this increases the boiling point enormously.

Comparing melting and boiling points
When comparing the relative boiling points of two compounds the three key factors to consider are:
1. Do the principal intermolecular forces differ?
2. Is there a significant difference in molecular mass/number of electrons?
3. When both molecules can hydrogen bond, how many hydrogen bonds can form per molecule?

For compounds that have a similar molecular mass/number of electrons then the relative boiling points can be predicted by determining the intermolecular forces present, e.g., propane vs ethanal.

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London forces < Permanent dipole-dipole < Hydrogen bonding

If the compounds exhibit the same type of intermolecular force then the one with the higher molecular mass/number of electrons will tend to have the higher boiling point, e.g., Group 16 hydrides (H_2S, H_2Se, H_2Te).

When two compounds are capable of hydrogen bonding then the number of hydrogen bonds formed per molecule is very important. Both water and ethanol (CH_3CH_2OH) demonstrate hydrogen bonding. However, water has two hydrogen atoms and two lone pairs on the oxygen atom which are capable of hydrogen bonding but ethanol has only one appropriate hydrogen atom. Water is capable of forming double the number of hydrogen bonds per mole and therefore has a higher boiling point despite being having a significantly lower molecular mass than ethanol.

Solubility
The saying "**like dissolves like**" is very helpful when trying to determine suitable solvents for a variety of compounds. Essentially, if compounds have the same principal intermolecular force then they will probably dissolve in each other and be miscible. For example, non-polar molecules such as bromine, Br_2, will preferentially dissolve in non-polar solvents such as alkanes, e.g., hexane. Compounds which exhibit significant hydrogen bonding, e.g., methanol have low solubility in non-polar solvents but are fully miscible with water which also exhibits hydrogen bonding. Molecules such as propanone (CH_3COCH_3) are good at dissolving a wide variety of compounds as they have both non-polar methyl groups, which form London forces with non-polar molecules, and a polar carbonyl group, which is able to form permanent dipole-permanent dipole interactions and hydrogen bonds with the appropriate polar molecules.

Questions
1. Determine whether each of the following molecules is polar or non-polar:
   a. BF_3 b. CF_2Cl_2 c. PF_5 d. SCl_2 e. CO_2 f. BrF_3
2. State the principal type of intermolecular force present between molecules in:
   a. ethanol b. methane c. SF_4 d. CH_3OCH_3 e. CH_3CH_2F f. $BeCl_2$
3. For each of the following pairs of molecules, state and explain which molecule is expected to have the higher boiling point.
   a. P_4 and S_8 b. HF and HCl c. HCl and HBr
   d. H_2O and NH_3 e. CH_3OCH_3 and $CH_3CH_2CH_3$
4. For each of the following compounds, suggest, with a reason, which of hexane, dichloromethane (CH_2Cl_2) and water would be the best solvent.
   a. PCl_3 b. BH_3 c. I_2 d. C_2H_4 e. N_2H_4 f. CH_3COOH

Answers

1. a. non-polar because of symmetrical trigonal planar shape
   b. polar
   c. non-polar because of symmetrical trigonal bipyramid shape
   d. polar because of non-symmetrical see-saw shape
   e. non-polar because of symmetrical linear shape
   f. polar because of non-symmetrical T- shape

2. a. Hydrogen bonding
   b. London forces
   c. permanent dipole-permanent dipole interactions seesaw shape
   d. permanent dipole-permanent dipole interactions v shape
   e. permanent dipole-permanent dipole interactions
   f. London forces

3. a. S_8 is higher; both non-polar molecules; S_8 has higher M_r/number of electrons so stronger London forces.
   b. HF is higher; HF exhibits hydrogen bonding but HCl exhibits permanent dipole-permanent dipole interactions which are weaker.
   c. HBr is higher; both molecules exhibit permanent dipole-permanent dipole interactions but HBr has higher M_r/number of electrons so stronger London forces.
   d. H_2O is higher; both molecules exhibit hydrogen bonding; H_2O can form two hydrogen bonds per molecule but ammonia can form only one.
   e. CH_3OCH_3 is higher; CH_3OCH_3 is polar and exhibits permanent dipole-permanent dipole interactions; $CH_3CH_2CH_3$ is non-polar and exhibits London forces which are weaker.

4. a. CH_2Cl_2; both exhibit permanent dipole-permanent dipole interactions.
   b. Hexane; both are non-polar held by London forces only.
   c. Hexane; both are non-polar held by London forces only.
   d. Hexane; both are non-polar held by London forces only.
   e. H_2O; both form hydrogen bonds
   f. H_2O; both form hydrogen bonds

Acknowledgements: *This Factsheet was researched and written by Dr Chris Martin.*
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