

## Intermolecular Forces

Intermolecular forces are the forces of attraction between molecules which cause liquids and solids to form. The origin of intermolecular forces varies depending on the structure and functional groups of the molecules involved. They are considerably weaker than a covalent or ionic bond.

**Dipole-Dipole Forces:** Polar molecules with permanent dipole moments. The positive end of the dipole of one molecule will be attracted to the negative end of another. Strengths are typically between 1 and 25 kJ/mole. It is a short range force as the strength falls off with  $1/r^4$  (where  $r$  is the distance between dipoles). It is a much weaker force than the electrostatic forces of an ionic bond. For example, for NaCl, the strength is 786 kJ/mol and falls off with  $1/r^2$ .

**Hydrogen Bonding:** Is an exceptionally strong dipole-dipole force, one of the three most electronegative elements, F, O or N must be covalently bonded to a hydrogen (such as HF, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>3</sub>OH and CH<sub>3</sub>NH<sub>2</sub>). Strengths of H-bonds are typically between 13 and 40 kJ/mole.

**London Dispersion Forces (induced dipole forces):** The only attractive force for nonpolar molecules. At any point in time there can be instantaneous asymmetry in the electronic charge distribution on an atom or molecule, which will lead to an instantaneous dipole moment. Over time, these small fluctuations in charge will average out, but these fluctuating charge distributions tend to polarize the electron clouds of neighbouring atoms or molecules. A molecule or atom that is temporarily polarized is said to have an induced dipole. These small temporary induced dipoles tend to polarize neighbouring atoms or molecules. The strength of the London force depends on the magnitude of the induced dipole, which in turn depends on how easily the electron cloud is polarized. **It is generally true that the more electrons in a molecule or atom, the more easily it is polarized and the greater the strength of the London force.** Small atoms and molecules with the electrons tightly bound to the nucleus are not easy to polarize. The London force is a short range force and its strength falls off with  $1/r^7$ . **London Forces exist in all molecules.**

The halogens increase in size and number of electrons from chlorine to bromine to iodine and so the London force increases. As the intermolecular forces increase, higher energy is needed to separate the molecules in the liquid state so that they can form a gas. Thus the boiling points will increase as the London Forces increase and this is shown in the following table.

Comparison of Size with Boiling Point for the Halogens				
Halogen	Formula	Atomic radii of Atom (pm)	Boiling Point (°C)	Physical State at 25°C
chlorine	Cl <sub>2</sub>	99	-35	gas
bromine	Br <sub>2</sub>	114	-7	liquid
iodine	I <sub>2</sub>	133	114	solid

The intermolecular forces (dipole-dipole, hydrogen bonding and London) are all dipole-dipole, whether temporary or permanent.

The table below compares the magnitudes of the various contributions to the total energy of interactions in a group of simple molecules. It shows the permanent dipole moments (measured), the estimated permanent dipole-dipole energy (including hydrogen bonding for ammonia and water), the estimated London energy and the total energy. The molar heat of vapourization,  $\Delta H_{\text{vap}}$  is the energy required to convert one mole of the liquid into a gas, in other words the energy required to overcome the intermolecular forces in the liquid. Note that the London energy is substantial in all cases for these small molecules and is the same order as the energy of hydrogen bonding in ammonia. Only in the water molecule does the hydrogen bonding energy exceed the London energy.

Approximate Contributions To The Total Energy Of Interaction Between Molecules (kJ/mol)					
Molecule	Permanent Dipole Moment (D)	Permanent Dipole-Dipole Energy	London Energy	Total Energy	Molar Heat of Vapourization (kJ/mol)
Ar	0	0	8.5	8.5	6.7
CO	0.1	~0	8.7	8.7	8.0
HCl	1.03	3.3	17.8	21	16.2
NH <sub>3</sub>	1.5	13*	16.3	29	27.4
H <sub>2</sub> O	1.8	36*	10.9	47	40.7

Larger molecules generally exhibit lower vapor pressures since the summation of attractions is directly related to their size (or total number of electrons). In the figure below, each additional increment in size for a homologous series of n-alkanes causes  $P^\circ$  to decrease (or  $\Delta H_{\text{vap}}$  to increase) concomitantly.

Vapour pressure at 25°C of n-alkanes as a function of chain length.

