SUPPLEMENTARY TOPIC 4
INTERMOLECULAR FORCES.

Previous Topics dealt with the strong bonding forces associated with ionic bonds, covalent bonds and metallic bonds. These forces are typically in the range of hundreds of kJ per mole of bonds. Also examined in earlier Topics were forces known as hydrogen bonds - much weaker forces than the previously cited bonds but which have considerable influence on chemical properties. Hydrogen bonds are about 5% of the strength of a typical covalent bond. They can operate between molecules such as seen in water (INTERMOLECULAR HYDROGEN BONDING) but can also operate between atoms within the same molecule e.g. in proteins and DNA (INTRAMOLECULAR HYDROGEN BONDING). However hydrogen bonding is usually classed as one of the group of forces collectively called INTERMOLECULAR FORCES - forces operating between atoms on different molecules. Hydrogen bonding is limited to molecules containing H atoms along with O, N or F atoms. Atoms from lower in the Periodic Table such as P, S and Cl are too large to form a significantly concentrated polarity difference to enter into hydrogen bonding. Hydrogen bonding occurs in species like water, alcohols and nitrogen based groups such as amines found in proteins and in molecules containing F atoms such as hydrogen fluoride.

More about polar molecules.
In Topic 6, the concept of polarity associated with covalent bonds was introduced and it was shown how two polar O – H bonds in each water molecule can combine to provide an overall DIPOLE on the H₂O molecule due to its molecular shape. This unequal sharing of electrons by the pair of atoms in a covalent bond results from the greater attracting power for the bonding electrons by one of the two atoms, so displacing the bonding electrons towards that atom. This electron attracting power can be expressed in terms of the electronegativity of each element. Electronegativity is a function of the effective nuclear charge (see Topic 12) and the radius of the atom. The greater the effective nuclear charge and the smaller the atomic radius, the greater is the electron attracting power of that atom. Hence the most electronegative elements are those located to the top right hand part of the Periodic Table, excluding all the noble gases. The most electronegative element is fluorine followed by oxygen and then chlorine. However, there is normally at least a small electronegativity associated with the atoms of all elements so any covalent bond between atoms of different elements is expected to have at least a small electronegativity difference and hence some polarity. For a covalent bond between two atoms of identical elements, there will be no polarity difference and so the bond will be non-polar. This is illustrated in the following diagrams which show the non-polar Cl₂ molecule where the bonding electrons are shared equally between both Cl atoms, the polar HCl molecule in which
the more electronegative Cl atom attracts more than its share of the bonding electrons and the non-polar CO$_2$ molecule. Note that although the CO$_2$ molecule has two polar C=O bonds, the molecule overall is non-polar because the magnitude and direction of the two bond dipoles exactly cancel out.

Ion/dipole forces.

Apart from hydrogen bonding encountered in earlier Topics, another type of intermolecular force was previously seen to account for the dissolution of the typically very stable crystal lattice in ionic solids. Recall that the main source of the energy needed to extract cations and anions from the three dimensional crystal lattice of the solid is supplied by the attraction between the polar water molecules and the ions near to the crystal surface, resulting in ions leaving the crystal, each surrounded by a sheath of water molecules. The attractive forces operating here are between the slightly positive charge on the H atoms of the water molecule and the negative charge of the anion, or, in the case of the cations, between the slightly negative charge of the O atoms of the water molecules and the positive charge on the cation. Recall that this non-uniform distribution of charge on water molecules was described in terms of a dipole in which the H end and the O end of each H$_2$O molecule represent a slight charge separation. This type of interaction between the dipolar water molecule and the cations and anions is called **ION-DIPOLE INTERACTION**. As ions are not molecules, this is not strictly an intermolecular force.
Other interactions involving dipoles.

There are two other much weaker versions of intermolecular force which involve dipoles - **DIPOLE/DIPOLE INTERACTIONS** and **DIPOLE/INDUCED DIPOLE INTERACTIONS**. The former arise from the dipole of one molecule interacting with the dipole of another molecule. The dipole/induced dipole type of interaction arises when a dipolar molecule approaches a non-polar molecule sufficiently closely to cause a small dipole to be induced in the latter and then interact with it.

For example, dipole/dipole forces would be experienced between molecules of polar species such as hydrogen chloride, HCl, in which the more electronegative Cl atom attracts a greater share of the bonding electrons from the H atom. This force enhances the boiling point of hydrogen chloride but it is still much lower than the boiling point of hydrogen fluoride which experiences the far more significant hydrogen bonding as well as dipole/dipole attractions.

Dipole/induced dipole forces do have observable effects in mixtures containing both polar and non-polar species. The close approach of a polar molecule such as H$_2$O can induce the electrons in a non-polar species such a noble gas to temporarily form an induced dipole which can then interact with the polar molecule. An example of this type of interaction is seen in the greater than expected solubility of the noble gas xenon and others of the group in water. The following diagram illustrates the polar HCl molecule inducing a temporary dipole in the non-polar Br$_2$ molecule when the two approach closely.
However dipole/dipole and dipole/induced dipole interactions generally play only a relatively minor role in intermolecular interactions.

Dispersion forces.
Apart from hydrogen bonding and ion-dipole forces, the most significant type of intermolecular force is known as the **DISPERSION FORCE**. It is typically weaker than hydrogen bonding or ion-dipole forces. This residual force operates between all molecules regardless of whether they are polar or non-polar. Although usually weaker than hydrogen bonding or ion/dipole forces, dispersion forces can play a significant role in determining the physical state of a species. For example, consider the halogen series fluorine, chlorine, bromine and iodine. At room conditions these elements are respectively gas, gas, liquid and solid yet each element consists of simple diatomic, non-polar covalent molecules. The explanation is that the more electrons that are present in a molecule, the stronger are the dispersion forces between molecules, leading to closer approach between the molecules down the series. For the gases, the dispersion forces are insufficient to overcome the kinetic energy of the F₂ and the Cl₂ molecules so these elements remain in the gaseous state. In the case of bromine, the larger number of electrons in the molecules leads to increased intermolecular forces and the attraction is enough to overcome the kinetic energy of the Br₂ molecules and cause them to become sufficiently close to exist as a liquid. For iodine, again the increased number of electrons causes even greater attractions between I₂ molecules leading to their being able to condense to the solid state.

What is the basis for dispersion forces?
For a collection of non-polar molecules, hydrogen bonding and any type of interaction involving dipoles is not possible. However, transient, mutually induced dipoles are set up between closely adjacent species whereby the motion of electrons in one of them induces electrons to move to the opposite side in the other. The result is an overall short lived, fleeting attraction between the two arising from these temporary induced dipoles. Similar interactions occur simultaneously with other nearby molecules or atoms, setting up a network of attractions throughout the medium. The following diagram illustrates dispersion forces acting on a network of H₂ molecules leading to temporary complementary induced dipoles in molecules when they approach closely.
It is because of dispersion forces that noble gases can be liquefied and non-polar substances can exist not just as gases but in the liquid and solid phases as well. To illustrate the increase in the force as the number of electrons increases, consider the boiling point of the noble gases given in the table.

<table>
<thead>
<tr>
<th>Element</th>
<th>BP (K)</th>
<th>Molar mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>helium</td>
<td>4.2</td>
<td>4.0</td>
</tr>
<tr>
<td>neon</td>
<td>27.1</td>
<td>20.2</td>
</tr>
<tr>
<td>argon</td>
<td>87.3</td>
<td>40.0</td>
</tr>
<tr>
<td>krypton</td>
<td>120</td>
<td>83.8</td>
</tr>
<tr>
<td>xenon</td>
<td>165</td>
<td>131.3</td>
</tr>
</tbody>
</table>

As indicated by the increasing boiling point, the amount of energy needed for the atoms to escape from the liquid phase increases down the series as the molar mass (and therefore the number of electrons) increases. Note that it is the increasing number of electrons and not the heavier mass of the atoms that leads to the increase in strength of the dispersion force and the boiling point. The following diagram illustrates the operation of dispersion forces in atoms of the noble gas argon when they are sufficiently close. High pressure forces the atoms closer and allows the dispersion forces to overcome the kinetic energy of the moving atoms to the point where ultimately the gas phase atoms convert to the liquid phase.

An unusual but telling example of the comparative strengths of dispersion forces and hydrogen bonding is seen in the following. If a vat of fat is heated to a temperature below its boiling point but above that of water, and chips are then put into the liquid fat, one observes violent spitting from the chips. This is due to water in the chips boiling and turning to vapour due to the temperature exceeding its boiling point. The fat is not boiling because there has not been enough energy supplied to overcome the dispersion forces between the long molecules of fat and so they remain as a liquid but the water is boiling because at the same temperature, hydrogen bonding is not strong enough to keep water in the liquid phase. This shows that caution is needed in using blanket descriptions of the relative strengths of the intermolecular forces acting in a
system of species and that dispersion forces are not necessarily very small as often implied in texts.

Check your understanding of this section:

Define the terms polar bond, electronegativity, hydrogen bonding, ion/dipole force, dispersion force.

Fluorine is the most electronegative element yet the F₂ molecule is non-polar. Explain why.

Objectives of this Topic.

1. Understand the concepts associated with polarity of covalent bonds and the role of electronegativity.

2. Understand that although intermolecular forces are typically much smaller than bonding forces, they determine many important properties of molecules.

3. Be familiar with the range of intermolecular forces, especially hydrogen bonding, ion-dipole forces and dispersion forces.

4. Recognise the importance of dispersion forces in determining the physical state of non-polar substances.

SUMMARY.

While weaker than the usual bonding forces, intermolecular forces play an important role in determining the properties of matter and especially their physical states. One component of most of the various types of intermolecular force is polarity associated with covalent bonds between atoms of different elements. Due to the differing electron attracting power of each element, the electrons in any covalent bond are only shared uniformly between the two bonded atoms if they are the same element. Otherwise, due to the differing electronegativity of the elements involved, covalent bonds usually have some asymmetry in their charge distribution and the bonds are said to be polar. For a symmetric molecule, the bond dipoles resulting cancel out and the molecule overall is non-polar - for example, the carbon dioxide molecule. In a non-symmetric molecule, the addition of all the polar bonds may lead to an overall polar molecule such as the water molecule.
Interactions between polar molecules such as water and ionic solids such as sodium chloride provide the energy for the crystal to dissolve in the solvent, releasing the ions into solution surrounded by a number of polar water molecules in an interaction called the ion/dipole force.

Another type of intermolecular force, hydrogen bonding, accounts for the mixing of polar liquids and the elevated boiling points of hydrogen bonded liquids such as water and ethanol as well as conformations of proteins and DNA. Hydrogen bonding requires participating molecules to have H atoms and N, O or F atoms - the small size of these atoms allows a significant polarity difference to exist between them and the H atoms.

Apart from their involvement in hydrogen bonding and ion/dipole interactions, polar species can interact with each other through dipole/dipole forces and with non-polar species through dipole/induced dipole forces. These interactions are relatively small but can influence properties such as boiling point and solubility. Separate from hydrogen bonding and ion/dipole interactions, the principal intermolecular force operating is the dispersion force which is present between all species. It is especially important in molecules that cannot hydrogen bond. Consequently the dispersion force accounts for why non-polar covalent species can be liquefied or solidified even though stronger intermolecular forces are absent. Examples include the ability to liquefy the noble gases despite their existing as individual atoms.

The dispersion force arises when two atoms come sufficiently close for the electrons on one of them to distort temporarily the electron cloud on the other so as to induce a momentary dipole in each. These two temporary dipoles can provide a brief period of attraction before collapsing and reforming with each other or with other nearby atoms. In this way, a network of temporary induced dipoles interact to provide an overall attractive force - the dispersion force. The strength of these forces depends on how many electrons surround each of the atoms - the more electrons there are, the greater the scope for the dispersion force to operate. This is illustrated nicely in the halogen series from fluorine and chlorine (both gases), bromine (liquid) to iodine (solid) at room conditions. As the number of electrons on the halogen atoms increase, the dispersion forces between the halogen molecules also increases allowing them to condense closer together to undergo the relevant phase change.
TUTORIAL QUESTIONS - SUPPLEMENTARY TOPIC 4.

1. The boiling point of methanol, CH₃OH, is lower than that of ethanol, CH₃CH₂OH, even though both have extensive hydrogen bonding present throughout the liquid. Explain why.

2. What would you expect to be the main type of intermolecular force operating between molecules of the following compounds. Draw a diagram to illustrate the forces described.

(a) hydrogen fluoride

(b) methane

3. Explain why the boiling point of CCl₄ (350 K) is greater than the boiling point of CH₄ (111 K).

4. List the following substances in order of increasing normal boiling point: HBr, HCl, HF, HI. Explain your reasons.

5. Dry ice is solid carbon dioxide and at room conditions, it undergoes sublimation, the heat absorbed can be used for refrigerating. Normal ice from water under the same conditions does not sublime but instead melts even though carbon dioxide has a molar mass twice as large as water. Explain these observations.
6. Iodine solid deposited in a sealed container has a purple colour but after a period of time, brown deposits are seen around the inside of the container and even around the outside of the lid. Sodium iodide crystals in a similar container show no changes. Explain these observations.

7. If 1.00 L of water is mixed with 1.00 L of ethanol, the final volume is 1.92 L. How can this loss of volume be explained?

**ANSWERS TO TUTORIAL SUPPLEMENTARY TOPIC 4**

1. Methanol and ethanol both exhibit hydrogen bonding between their component molecules but ethanol has an additional -CH₂- group in its molecule and therefore has more electrons able to participate in dispersion forces. The extra contribution from the additional dispersion forces accounts for the greater energy needed to separate ethanol molecules from the liquid to the gas phase and thus its higher boiling point.

2. (a) Hydrogen fluoride molecules contain both H atoms and F atoms which allow hydrogen bonds to be established between the molecules. Hydrogen bonding is typically the strongest of the intermolecular forces.

   (b) Methane consists of a tetrahedral arrangement of C – H bonds and due to the symmetry resulting, is molecules are non-polar. The only intermolecular force able to operate between non-polar molecules is the dispersion force.
3. CCl$_4$ would be expected to have a higher boiling point than CH$_4$ since it possesses more electrons than CH$_4$. Thus the magnitude of the dispersion forces present between CCl$_4$ molecules is greater than that between CH$_4$ molecules, and this is the main reason for the higher boiling point. Note that the increased molar mass of CCl$_4$ contributes only very slightly to the higher boiling point. The dominant factor is the increased dispersion force.

4. In order of increasing boiling point: HCl, HBr, HI, HF. The trend is determined by strength of dispersion force which is related to the number of electrons, except for HF, which exhibits hydrogen bonding sufficiently strongly to more than compensate for the smaller number of electrons in the HF molecule. This results in a boiling point higher than even the most electron rich hydrogen halide, HI.

5. When ice formed from water melts, there is extensive hydrogen bonding present between the H$_2$O molecules in the liquid phase. To escape from the liquid phase, enough energy is required to break these hydrogen bonds. In dry ice, the component CO$_2$ molecules are held together in the solid state by dispersion forces alone. Breaking the dispersion forces when energy is supplied to the dry ice allows the molecules to escape directly into the gaseous phase and bypass the liquid state as the dispersion forces are too weak to hold CO$_2$ molecules together sufficiently closely to liquefy at atmospheric pressure.

6. Iodine consists of I–I molecules which are necessarily non-polar. Consequently the only force operating to hold the molecules together in the solid phase is the dispersion force. After being sealed in a container, the outer molecules of the crystals are able to absorb energy and some escape directly into the gaseous phase and condense on the inside of the container as brown deposits of I$_2$ molecules. Some are even able to escape from the lid of the container if not sealed tightly and can be seen as brown deposits on the outside. Sodium iodide solid consists of sodium and iodide ions held in the crystal lattice by strong ionic bonds. High temperatures are needed even to melt ionic crystals as the energy required for the solid to liquid phase change is considerable and even greater for the transition to the gaseous state. [The greater strength of ionic bonds compared with hydrogen bonds is seen when all the water from a solution of a salt is boiled away, leaving the solid ionic crystal.]

7. Water and ethanol both have extensive hydrogen bonding forces operating between their component molecules. When the two liquids are mixed, the network of bonded H$_2$O and C$_2$H$_5$OH molecules makes even more efficient use of the volume and due to the closer proximity of all the molecules in the mixture, has a smaller final volume than the sum of the initial volumes.