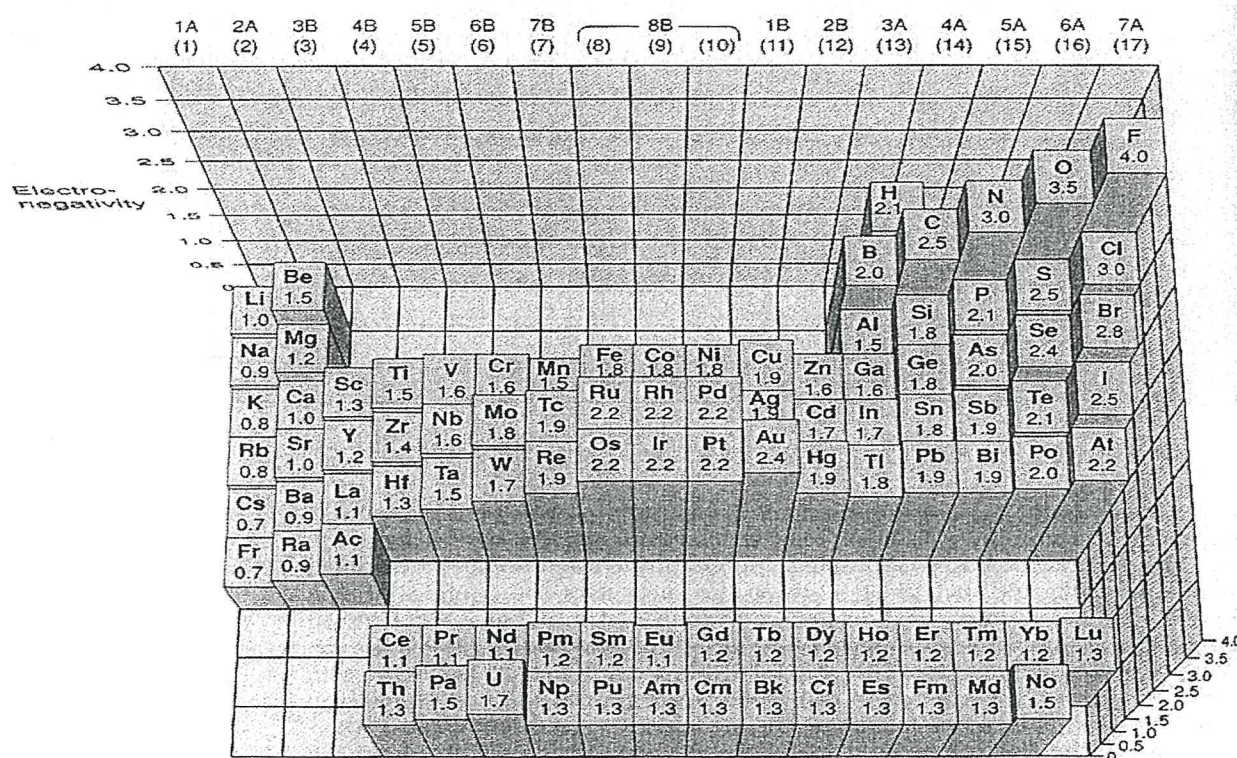


## ELECTRONEGATIVITY & BOND POLARITY

**ELECTRONEGATIVITY (EN):** The relative ability of a bonded atom to attract the shared electrons is one of the most important concepts in chemical bonding.

Linus Pauling, (American Chemist and dual Nobel Prize winner, Chemistry 1954 and Peace 1962) developed the most common scale of relative electronegativity values for the elements. The values themselves are not measured quantities but are based on an assigned value of 4.0 for fluorine, the element with the highest electronegativity.

In general, an atom's electronegativity is inversely proportional to its size i.e. in general, an element with a smaller atomic size has a higher electronegativity. Because the nucleus of a smaller atom is closer to the shared pair than that of a larger atom, it attracts bonding electrons more strongly. Therefore, *electronegativity generally increases up a group and across a period. Non-metals are more electronegative than metals.*



**FIGURE 9.16** The Pauling electronegativity (EN) scale. The EN is shown by the height of the post (the value appears in the element box). In the main groups, EN generally *increases* from left to right and bottom to top. The noble gases are not shown because, except in a few cases, they do not form bonds. The transition and inner transition elements show relatively little change in EN. Hydrogen is shown near elements of similar EN to point out that its value is much higher than those of the Group 1A(1) metals.

The most electronegative element is fluorine, with oxygen a close second. Both elements form compounds with almost every other element. Thus, except when it bonds with fluorine, oxygen always pulls bonding electrons towards itself. The *least* electronegative element (also referred to the most *electropositive*) is francium, in the lower left corner of the periodic table, but for all practical purposes we consider caesium the most electropositive.



You can see from a discussion of the bonding in  $\text{H} - \text{F}$ , with different electronegativities ( $\text{H}$ ; 2.1 and  $\text{F}$ ; 4.0), the bonding pair is not equally shared and so the bond has partially negative and positive poles. This type of bond is called a **polar covalent bond** and is depicted by  $\delta^+$  and  $\delta^-$ .

In  $\text{H} - \text{H}$  or  $\text{F} - \text{F}$ , the bonded atoms are identical, so the bonding pair is shared equally, and the bond is called a **nonpolar covalent bond**. Thus, by knowing the EN values of the atoms in a bond, you can determine the direction of the bond polarity.

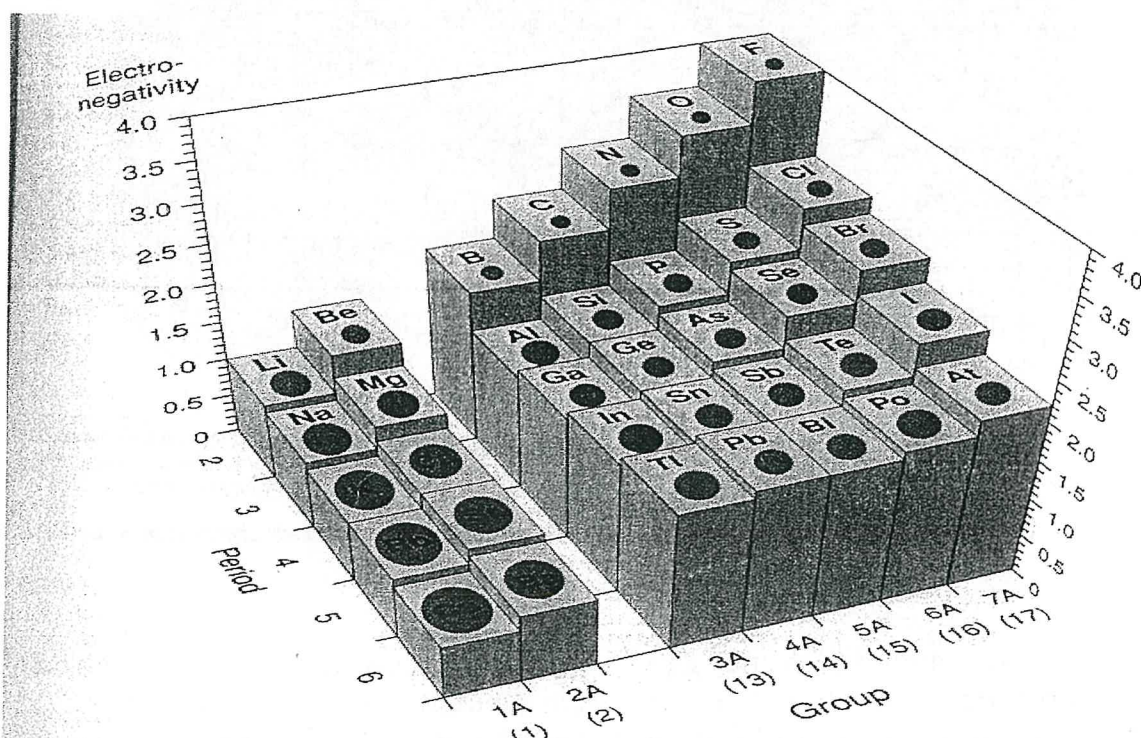
If you ask whether a bond is ionic or covalent, the answer in almost every case is "Both!" A better question is "How ionic or covalent is the bond?" The existence of partial charges means that a polar covalent bond behaves as if it were partially ionic. The **partial ionic character** of a bond is related to the **electronegativity difference ( $\Delta\text{EN}$ )**, the difference between the EN values of the bonded atoms:

*A greater  $\Delta\text{EN}$  results in larger partial charges and a higher partial ionic character.*

For example,  $\Delta\text{EN}$  in  $\text{LiF}_{(\text{g})}$  is  $4.0 - 1.0 = 3.0$   
 $\Delta\text{EN}$  in  $\text{HF}_{(\text{g})}$  is  $4.0 - 2.1 = 1.9$   
 $\Delta\text{EN}$  in  $\text{F}_{2(\text{g})}$  is  $4.0 - 4.0 = 0$

Thus the bond in  $\text{LiF}$  has more ionic character than the  $\text{H} - \text{F}$  bond, which has more than the  $\text{F} - \text{F}$  bond.

$\Delta\text{EN}$	IONIC CHARACTER
$> 1.8$	Mostly ionic
$0.4 - 1.8$	Polar covalent
$< 0.4$	Mostly covalent
0	Nonpolar covalent



**FIGURE 9.17** Electronegativity and atomic size in the main-group elements. The electronegativities of the main-group elements from Periods 2 to 6 (excluding noble gases) are shown as posts of different heights. On top of each post is a circle showing the relative atomic size. Note that, in general, an element with smaller atomic size has a higher electronegativity.

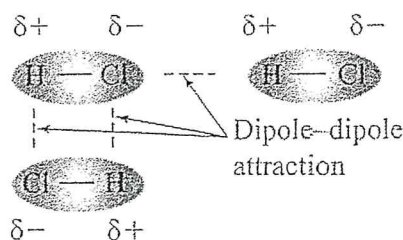
# Intermolecular Forces

The melting and boiling points of covalent molecular substances are much lower than those of ionic and metallic substances. This implies that the forces of attraction between the molecules in a molecular crystal are relatively weak. The weak forces between molecules in molecular solids and liquids are called van der Waals forces after the Dutch scientist who first attempted to explain them. Although all intermolecular forces are referred to as van der Waals forces they can be further classified as dipole-dipole forces, dispersion forces and hydrogen bonds.

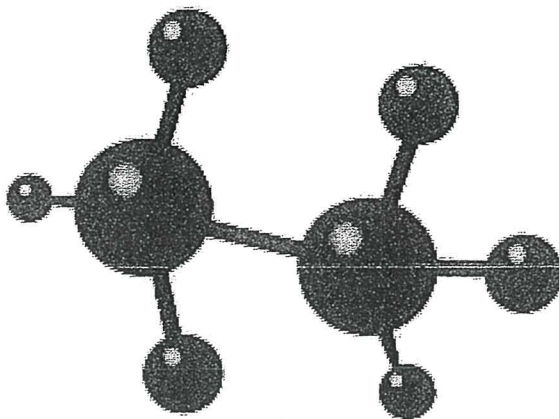
## Dipole – Dipole Forces

If two polar molecules such as HCl approach they will tend to orient themselves in such a way that the positive end of one molecule is close to the negative end of another molecule, as shown in Figure . This orientation leads to a lower potential energy.

The force of attraction between the oppositely charged ends of neighbouring polar molecules is called dipole-dipole attraction. The ordered structure illustrated in Figure is most pronounced in the solid state. In the liquid state the molecules are not as ordered due to their higher kinetic energy.



The charged ends of a dipole have a relatively small charge compared with the charges of ions in ionic substances. Consequently, dipole-dipole attractive forces are relatively weak compared with the attractive forces between oppositely charged ions. Thus solid HCl, a polar molecular crystal, melts at  $-114^\circ\text{C}$  whereas NaCl, an ionic crystal, melts at  $801^\circ\text{C}$ .

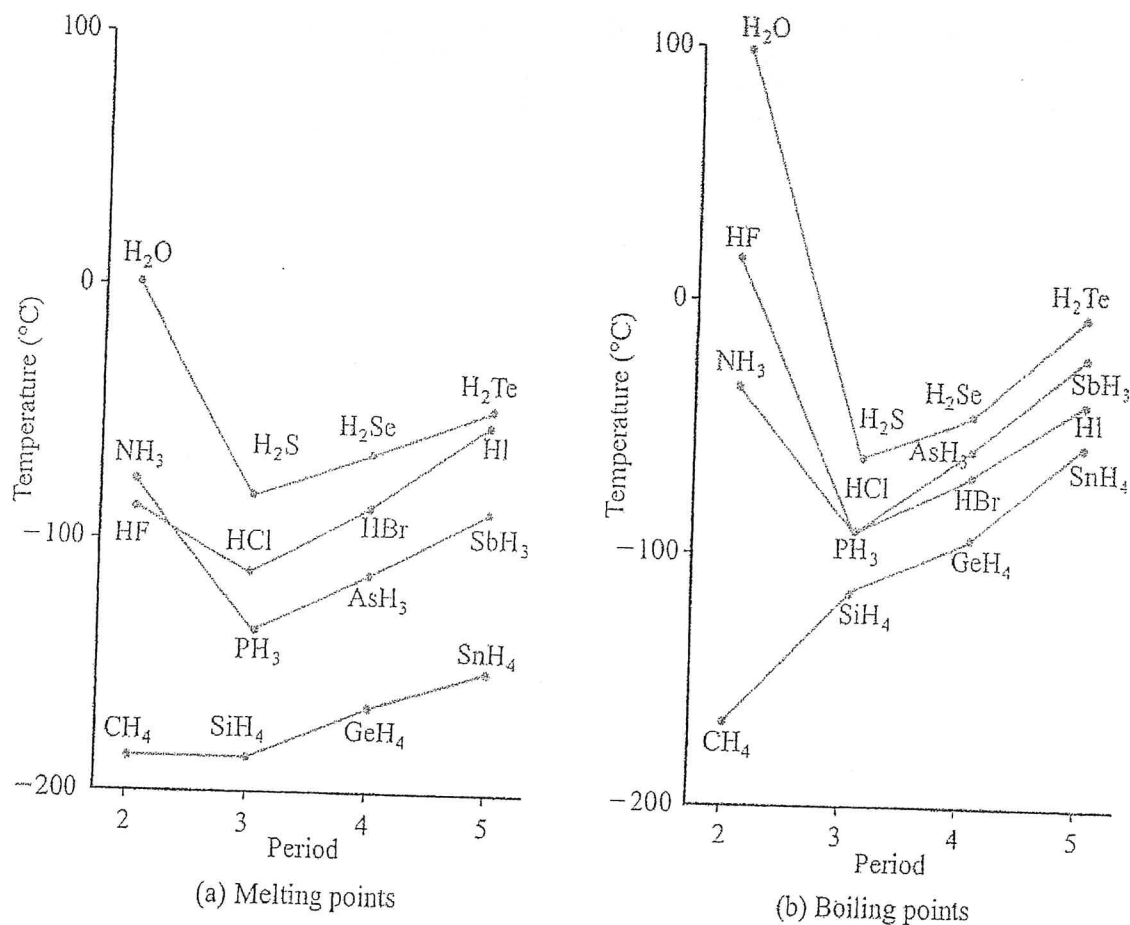




# Hydrogen Bonding Forces

The graphs in Figure show the melting points and boiling points of the hydrides of the group IV, V, VI and VII elements. There is a general increase in melting and boiling points with increasing molecular mass for the hydrides of the group IV elements.

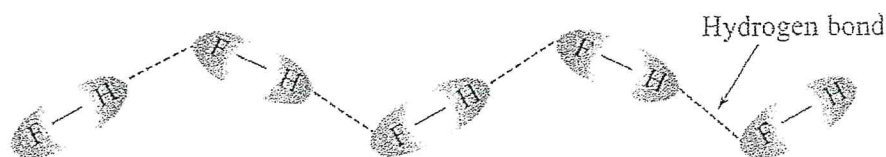
The regular increase in melting and boiling points also occurs for the compounds  $\text{H}_2\text{S}$  through  $\text{H}_2\text{Se}$  to  $\text{H}_2\text{Te}$ , but  $\text{H}_2\text{O}$  has a higher melting and boiling point than expected. A similar pattern occurs with the hydrides of groups V and VII, where



$\text{NH}_3$  and  $\text{HF}$  have higher melting and boiling points than the trends would suggest. The higher melting and boiling points for  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  indicate that there must be unusually strong intermolecular forces between the molecules of these substances.

$\text{HF}$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  are all highly polar since they contain the three most electronegative elements, fluorine, oxygen and nitrogen, bonded to hydrogen which has a relatively low electronegativity. This results in very polar molecules and much stronger intermolecular forces than expected for dipole-dipole interactions. These particularly strong intermolecular forces are referred to as hydrogen bonds.

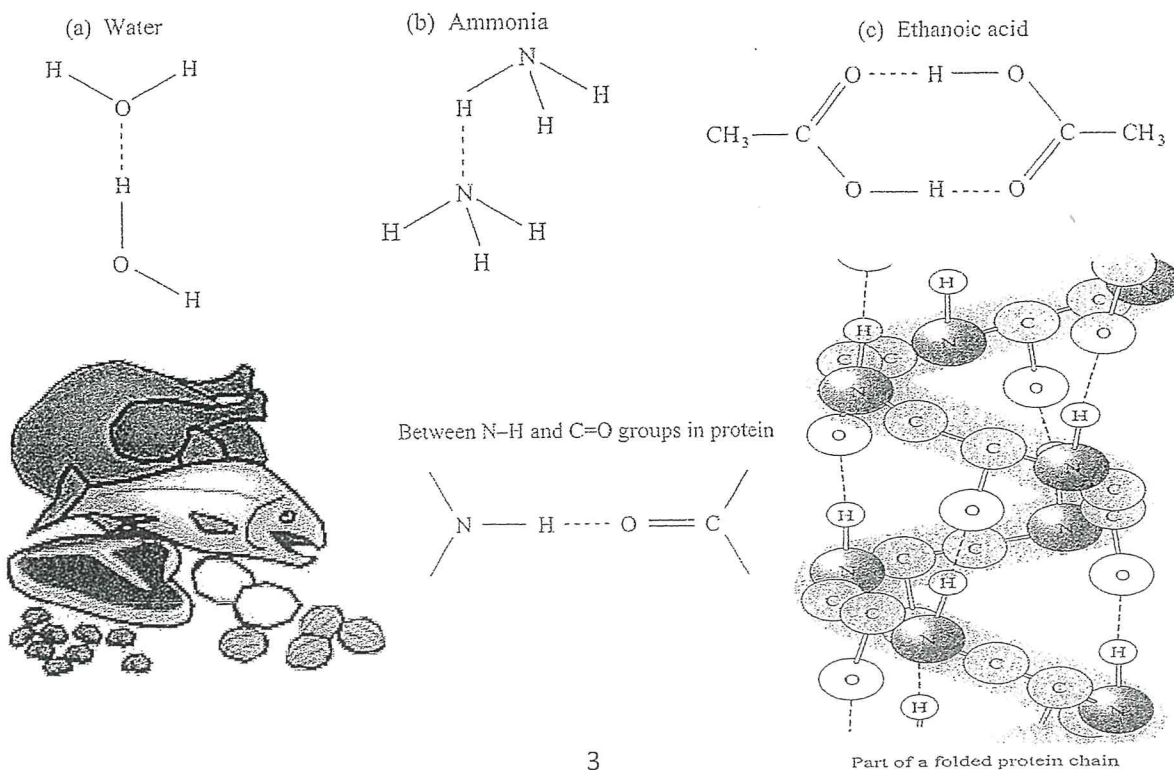
Hydrogen bonding is a special form of dipole-dipole attraction. It is found in systems where a hydrogen atom is bonded to an atom of oxygen, nitrogen or fluorine. When hydrogen is bonded to the highly electronegative fluorine, oxygen or nitrogen atoms, the resulting bond is very polar and the shared electrons are strongly attracted towards the more electronegative atom. Since the hydrogen atom in these circumstances has an appreciable partial positive charge, it experiences a strong attractive force with lone pairs of electrons on oxygen, nitrogen or fluorine atoms of nearby molecules. Hydrogen bonding is particularly strong in solid HF which consists of long chains of HF molecules, shown in Figure 7.16.



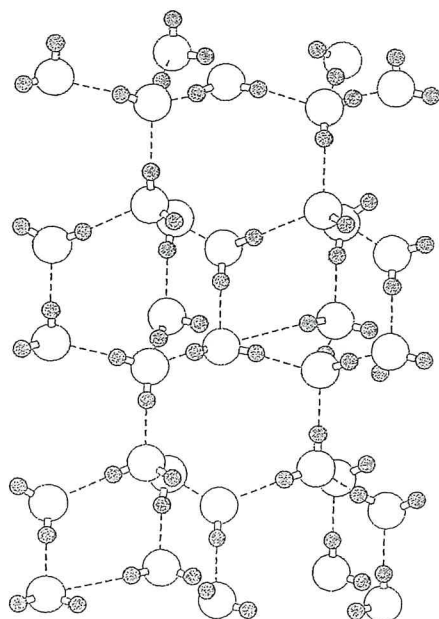
The essential requirements for hydrogen bonding are as follows.

- 1 A hydrogen atom bonded to N, O or F so that the hydrogen atom has an appreciable partial positive charge due to the unequal sharing of the pair of electrons in the covalent bond.
- 2 An unshared pair of electrons on a neighbouring N, O or F atom which can attract the partially positive hydrogen atom.

The strength of hydrogen bonds are in general about ten times those of dipole-dipole forces but about one-tenth those of ionic or covalent bonds. Hydrogen bonding is important in many chemical systems. Some examples are included in Figure 7.17. These include the formation of hydrogen bonds between simple molecules such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{CH}_3\text{COOH}$ . Figure 7.17 also illustrates the formation of hydrogen bonds between N-H and C=O groups. Hydrogen bonds such as these are extremely important in biological systems and play a critical role in determining the structure of proteins and the double helix of DNA.



The presence of hydrogen bonding accounts for many of the unique properties of water. For example, the arrangement of water molecules in ice creates a very open structure which causes the density of ice to be less than that of liquid water. Figure 7.18 illustrates the arrangement of water molecules in ice. When ice melts, the regular lattice breaks up and the water molecules can pack more closely to form a liquid of somewhat higher density. Without hydrogen bonding, ice would sink to the bottom of oceans and lakes, a process that in cold climates would cause the death of fish and other aquatic life.



#### Hydrogen bonding



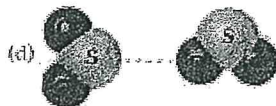
#### London dispersion forces



#### Ion-dipole forces



#### Dipole-dipole forces





# Dispersion Forces

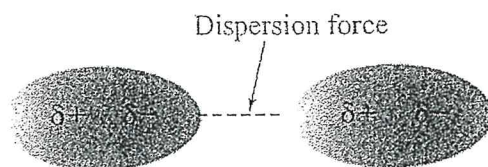
If there were no intermolecular forces between the molecules of some substances then these substances would exist only as gases, because there would be no forces to attract the molecules together. However, every substance can be condensed to a liquid and finally to a solid if it is cooled to a low enough temperature. Thus some form of intermolecular force must exist in every substance, even when the molecules consist of identical atoms as in  $O_2$  or  $N_2$  and do not possess a permanent dipole.

Intermolecular forces between non-polar molecules arise from the fact that at any instant a molecule may have a temporary dipole. The temporary dipole occurs at any moment when the electrons in an atom or molecule are not symmetrically distributed. This means that the electron charge cloud will not be symmetrical, as indicated in Figure



Temporary Dipole due to unsymmetrical electron charge distribution

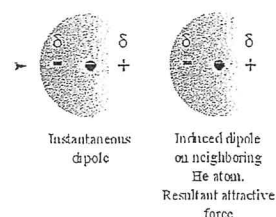
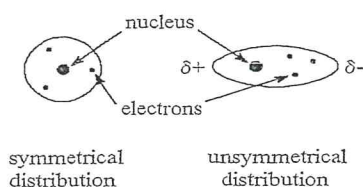
When an atom or molecule with a temporary dipole is near another atom it influences the charge distribution in the second atom. The temporary dipole is said to induce a dipole in the neighbouring atom. The two species then attract each other as shown in Figure



Attraction between two species with temporary dipoles.

The weak forces of attraction between atoms or molecules arising from such temporary dipoles are known as dispersion forces. Dispersion forces are the weakest kind of intermolecular forces. It should be noted that any particular temporary dipole exists only for an instant of time because the distribution of electrons changes constantly. Elements that form molecular crystals held together by dispersion forces include hydrogen and the non-metals on the right-hand side of the periodic table

Dispersion forces between molecules increase in strength with the number of electrons present in the molecules. The number of electrons is greater in larger molecules so that dispersion forces are also related to molecular size and mass. This is illustrated by examining the melting point trends of the noble gases and halogens shown in



## Melting Points of the Noble Gases and Halogens

Noble gas	Atomic mass	Number of electrons	Melting point (°C)	Halogen	Molecular mass	Number of electrons	Melting point (°C)
He	4	2	-272	F <sub>2</sub>	38	18	-220
Ne	20	10	-249	Cl <sub>2</sub>	71	34	-101
Ar	40	18	-189	Br <sub>2</sub>	160	70	-7
Kr	84	36	-157	I <sub>2</sub>	254	106	114
Xe	131	54	-112				

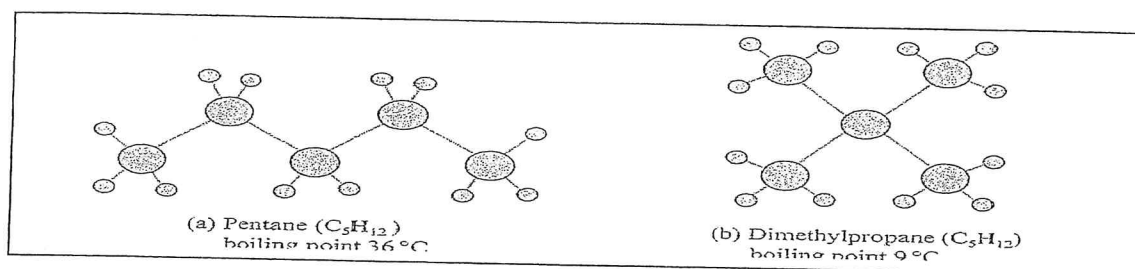
It should be noted that dispersion forces contribute to the attractive forces between all molecules. However, in the case of highly polar molecules, the dipole-dipole forces are much stronger and the effect of the dispersion forces is not as significant. Between molecules that are non-polar or only slightly polar, dispersion forces are the main intermolecular forces acting. Consider the melting points of the compounds HCl, HBr, and HI shown

Melting points of HCl, HBr and HI

Substance	Molecular mass	Melting point (°C)
HCl	36.5	-114
HBr	81	-87
HI	128	-51

Although the HCl molecule is the most polar of the series, HI has the highest melting point. In this series of compounds the increase in dispersion forces more than compensates for the decrease in dipole-dipole forces as the electronegativity of the halogen element decreases.

The shapes of molecules also influence the strength of dispersion forces. To determine the effect of shape consider the two substances pentane and dimethylpropane that exist as non-polar molecules with the same molecular formula, C<sub>5</sub>H<sub>12</sub>, but differ in shape. The shapes of the two molecules are shown



The overall attraction between molecules is greater in the case of pentane, a linear chain-like molecule with a zig-zag structure, because there can be relatively large surface contact over the entire length of the molecule. In the case of dimethylpropane, less contact is possible between molecules, thus the dispersion forces are weaker and its boiling point is lower.



# The Chemistry of Bonding

## An Outline of Intermolecular Forces



There are three types of intermolecular forces that exist between atomic and molecular elements or covalent compounds that contain discrete molecules.

All are forms of **Van der Waals** forces

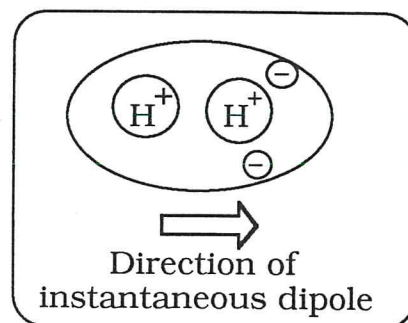
### Dispersion Forces

These exist between all molecules but are the only forces existing between non-polar molecules such as Hydrogen gas or atoms, as in a Noble gas. (Diagram at right)

Individually, they are in general, weak forces.

They are formed when the electrons in a molecule, by the nature of random motion, are found on the same side of a molecule or atom. This causes the formation of a temporary dipole. These temporary dipoles interact with neighbouring molecules and form similar temporary dipoles. The weakness of these forces is indicated by the low melting and boiling points of substances that exhibit these forces exclusively. Examples include the diatomic gases (eg;  $O_2$ ,  $N_2$ , and  $Cl_2$ ), the Noble gases (He, Ar, Ne, and Kr), discrete covalent molecules (eg;  $P_4$  and  $S_8$ ) and many Polymers (eg; polyethene and polytetrafluoroethene (PTFE)).

Note: Although generally weak forces, their significance increases with increasing atomic and molecular mass.

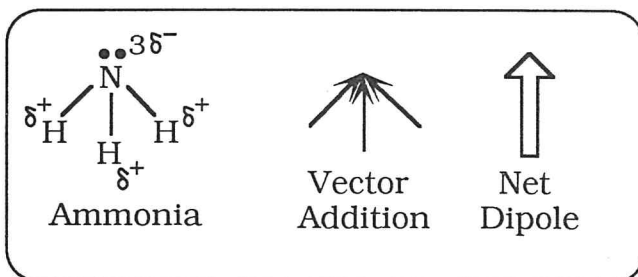
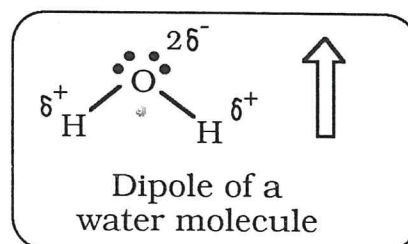


### Dipole - Dipole Forces

These occur when;

1. molecular covalent compounds contain elements with different electronegativities which give rise to polar bonds.
2. the vector sum of the polar bonds result in a net permanent dipole.

The molecular dipoles of adjacent molecules attract each other via electrostatic forces.



An example of the formation of a molecular dipole, using ammonia, is shown at left.

1. Each bond is polar.
2. The vector sum of the bond dipoles is not zero.
3. There is a net dipole vector.

### Hydrogen Bonding

This occurs between the non-bonding pairs of electrons on the atoms of **fluorine, oxygen or nitrogen** and a hydrogen atom which is covalently bonded to F, O or N on an adjacent molecule.

Hydrogen bond strength is  $F\cdots H > O\cdots H > N\cdots H$ .

For molecules of a similar size, it is the strongest of the intermolecular forces.

