van der Waals Forces (Intermolecular Forces)

What are van der Waals Forces?

Till now we had been dealing with the forces or bonds between atoms 'leading to the formation of molecules. These are called inter-atomic or chemical forces.

A Dutch scientist, J van der Waals in 1873 pointed out that particles (atoms, molecules or ions) of substances (similar or different) exert attractive forces on each other, when they are brought near to each other. -These are physical forces (electrostatic in character) and much weaker than chemical forces i.e. ionic and "covalent bonds). These are named as van der Waals forces in honour of **J. van der Waals** who, for the first time, used the concept of these forces to explain the deviation of behaviour of gases at low temperature from that of the ideal gases.

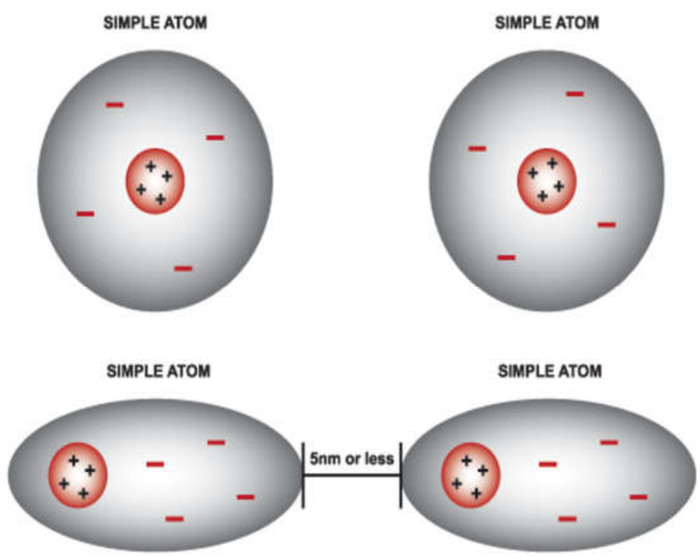


Fig 1. Van der Waals Forces

He proposed that particles of substances interact even if outer-shells of the atoms have acquired the noble gas configurations. Van der Waals forces can be defined as follows :

"van der Waals forces are very short-lived inter-molecular attractive forces which are believed to exist between all kinds of atoms, molecules and ions when they are sufficiently close to each other".

Unlike valence forces, van der Waals forces have nothing to do with valence electrons of the elements. They exist in neutral molecules, ions and atoms of inert gases or solid elements alike.

The atoms of the molecules like N_2, O_2, C_{12}, P_4, S_8 etc. in which the valence orbitals are either used in normal bonding or are occupied by non-bonding electrons, are rather firmly held together in the liquid or solid states by van der Waals forces or bonds. These forces are almost absent when the molecules of a gas are far apart and are in rapid kinetic motion. But as the atoms or molecules of the gas are brought nearer to each other by increasing the pressure and kinetic energy is withdrawn by cooling, van der Waals forces are capable of holding the molecules together to form the liquid or solid state. Thus a gas can be liquefied by allowing it to expand suddenly from high pressure. *During expansion the gas does work in overcoming intermolecular forces of attraction.* The energy required for this' purpose is obtained from the gas itself, thereby lowering the temperature and causing the liquefaction.

Types of van der Waals Forces

There are four types of van der Waals forces. The origin of each one of these has been explained by a different scientist. The name of scientist has been associated with that type to commemorate his contribution. The four types are:

1. Dipole-dipole interactions.

These forces are found in polar molecules having permanent polarity in them. We know that a polar molecule has separate centres of positive and negative charge and possess permanent dipole moment.

When polar molecules are brought nearer to each other, they orient themselves in such a way that the positive end of one dipole (polar molecule) attracts the negative end of another dipole and vice-versa as shown in Fig. 7.34. Due to this dipole-dipole interaction many molecules are held together. Dipole-dipole interactions between polar molecules are also called Keesom Forces and are the strongest of all other types of van der Waals forces. The intensity of these forces r is generally hampered by an increase 'in temperature."

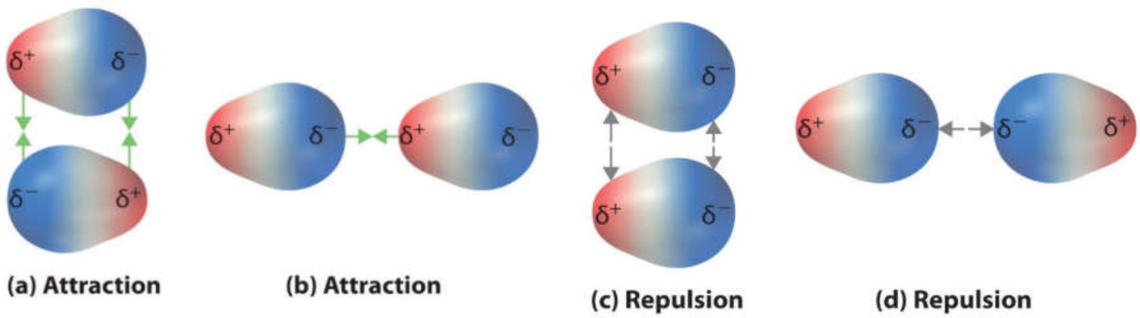
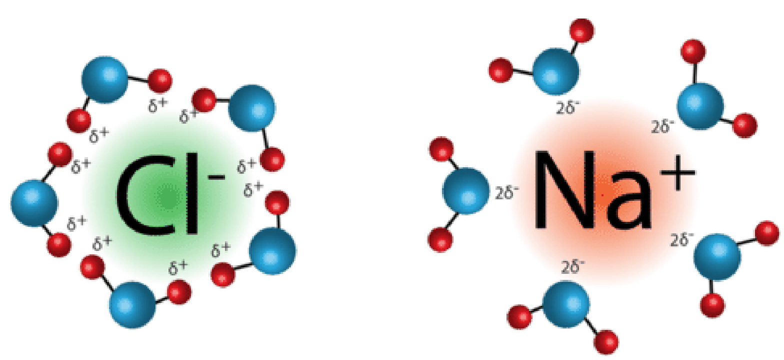


Fig 2. dipole-dipole interaction

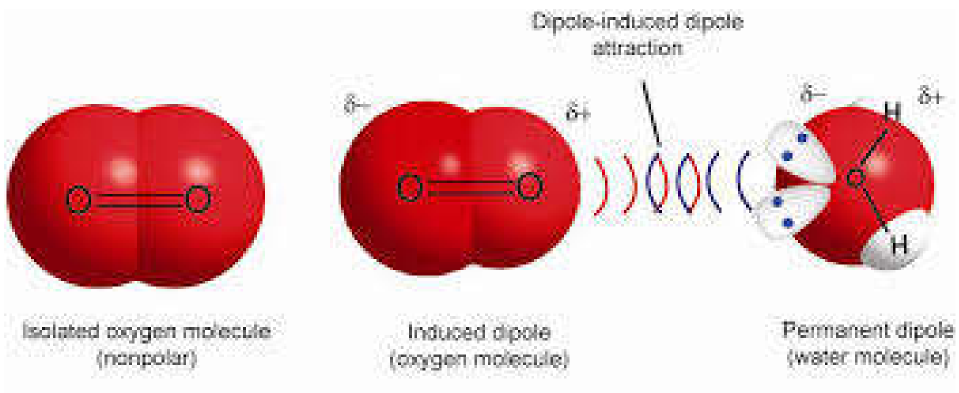
2. Ion-dipole interactions.

Polar molecules are attracted towards ions. The negative end of dipoles is attracted towards the cation while the positive end towards the anion (Fig. 7.35). This type of interaction is called ion-dipole interaction. Ion- dipole interactions have been used to explain the dissolution of NaCI in H20. When NaCl is put in H20, it dissolves in it since the negative ends of water molecule dipoles aggregate around Na" ions and the positive ends around CI- ions.



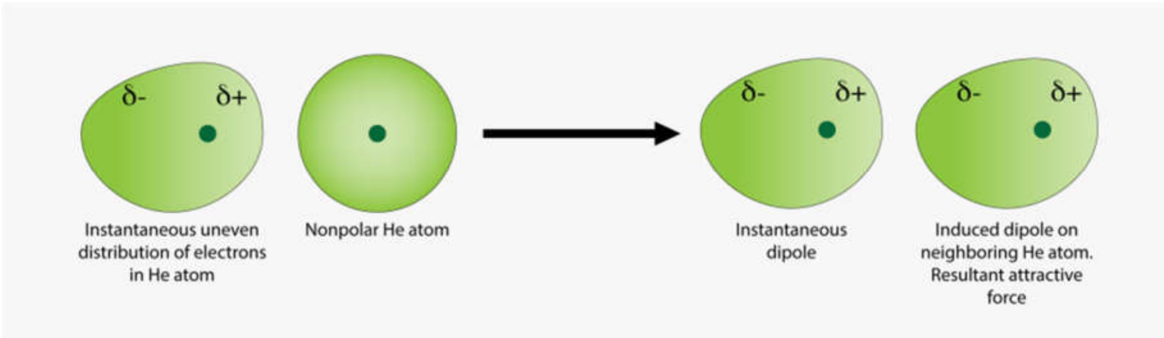
3. Dipole-induced dipole interactions.

This type of force is found in a mixture containing polar and non-polar molecules. When a non-polar molecule is brought near to a polar molecule, the positive end of the polar molecule attracts the mobile electrons of non-polar molecule and thus polarity is induced in non-polar molecule as shown in Fig. 7.36. Now both the molecules become dipoles and hence the positive end of the polar molecule attracts the displaced electron cloud of non-polar molecule. Thus the two types of molecules are held together by forces which are also called Debye Forces.



4. Instantaneous dipole-induced dipole interactions

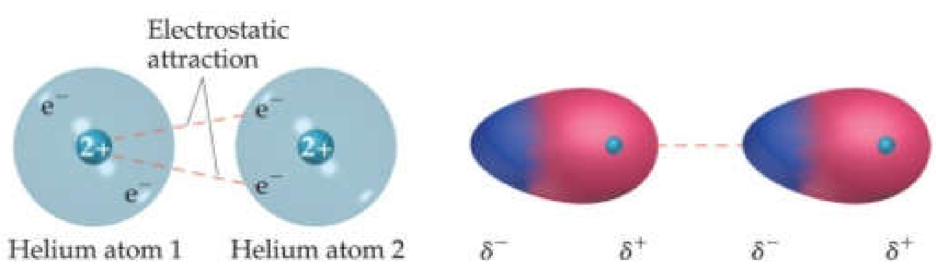
These forces are found in non-polar molecules such as di-atomic gases like H_2, O_2, C_{12} , N_2 etc. as well as mono-atomic noble gases like He, Ne, Ar etc. A non-polar atom or molecule may be visualised as a positive centre surrounded by asymmetrical negative electron colud. Both are in equilibrium. But as the electron cloud oscillates, the electron cloud becomes denser on one side of the molecule than on the other side and thus the equilibrium gets disturbed for a moment. The displacement of electron cloud creates an instantaneous dipole temporarily. Thus the non-polar molecule is momentarily self-polarized and becomes temporarily polar.



Now when the self-polarized (i.e. temporarily polar) molecule is brought near to a non-polar molecule, it polarizes the neighboring molecule by disturbing Its electronic distribution and an induced dipole is created in it, i.e. the non-polar molecule momentarily becomes polar.

In this way a large number of non-polar molecules become temporarily polar which are mutually attracted by weak attractive forces. Since the molecules are in ceaselessly rapid motion and are constantly departing from the site of temporary dipoles, the attractive forces acting between the polar molecules are very weak.

Since the electron cloud densities are continuously fluctuating, these attractive forces may be formed and broken quickly. According to **Frintz London (1930)** the instantaneous formation and subsequent decay of dipoles in a gas due to temporary distortion of electron cloud may be depicted as in Fig. 7.38



The weak inter molecular forces operating in gases due to instantaneous polarization of non-polar molecule are also called London Forces. These forces are very weak and are known to operate in all types of molecules. These forces are weaker in most cases than dipole-dipole or ion-dipole forces, but are responsible for bringing about condensation of gases, even of noble gases. These forces become stronger with the increase of number of electrons in molecules atoms. The forces become stronger with the increase in boiling points of the molecules as shown below

Nature of van der Waals Forces

van der Waals forces are much weaker than both ionic and covalent bonds, e.g. the energy needed to dissociate a Cl2 molecule (containing atoms bonded together by a covalent bond, Cl-Cl) into its atoms is 58.0 Kcal while that needed for sublimating crystalline chlorine (containing atoms bonded together by van der Waals forces) is only 6.02 Kcal.

These forces may also be present, to a lesser extent, in molecules which are partly polar and partly non-polar and even in those which are completely nonpolar.

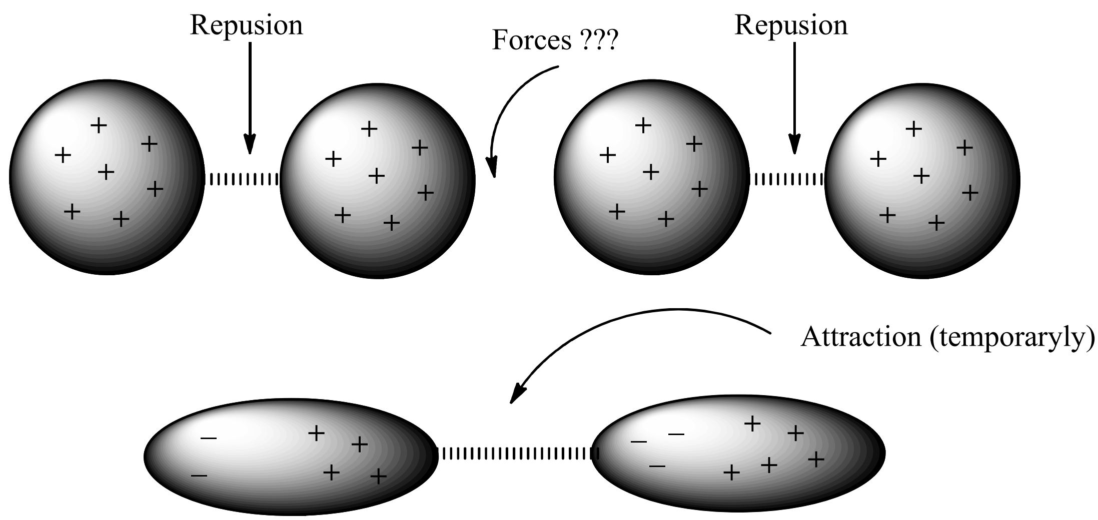


Fig X. Origin of van der Waals Forces

Origin of van der Waals Forces

When two atoms or molecules approach each other, both attractive and repulsive forces operate between their negative electrons and positive 'protons (nucleus) as shown in Fig. 7.39. Protons have been shown by + sign.

These forces are;

1. ***Attractive forces.*** *These forces act between the nucleus of a molecule and its own electrons, and between the nucleus of one molecule and electrons of the other molecule.*
2. ***Repulsive forces.*** *These forces act between the electrons of two different molecules, and between the nuclei of the two different molecules.*

The attractive and repulsive forces are in equilibrium at an inter-molecular distance which is, approximately equal to 4 A (1 A = 10^{-10} m). However, at intermolecular distance between 4 A to 10 A, attractive forces predominate. It is these attractive forces which are acting between the molecules and are called van der Waals forces.

Factors Affecting the Strength and Magnitude of van der Waals Forces

Following are the important factors that determine the strength and magnitude of van der Waals forces.

1. Large number of electrons in molecules.

With the increase in the number of electrons in a molecule, the magnitude of van der Waals forces between the molecules also increases. On account of larger number of electrons in a molecule, there is a greater diffusion of electron clouds. This results in a greater polarization and hence inter-molecular interactions (i.e. van der Waals forces) also increase.

Since the molecular weight is roughly proportional to the number of electrons in the molecule, the van der Waals forces increase with the increase in the molecular weight. The boiling point or melting point of a substance is taken as a measure of the magnitude of van der Waals forces. ,

With the increase of van der Waals forces the boiling point or melting point of a substance also increases. For inert gases the relationship between the number of electrons, molecular weight and boiling point, and magnitude of van der Waals forces is shown below :

2. **Large molecular size.**

   In large-sized molecules the electron clouds are more diffused and distorted. This brings about more and more polarization and more and more inter-molecular attraction, hence stronger van der Waals forces. Thus, larger molecules are held together by stronger van der Waals forces.

3. **Low temperature.**

   At low temperature, the random movements of molecules decrease and they come closer to each other and thus they interact more effectively. Hence, low temperature increases the strength and magnitude of van der Waals forces.

4. **High pressure.**

   At high pressures the molecules come closer and it results into strong inter-molecular interactions or van der Waals forces. Thus, higher the pressure, stronger will be the van der Waals forces.

Applications of van der Waals Forces

Although .van der Waals forces are weak, yet they have been used to explain many important phenomena. For example;

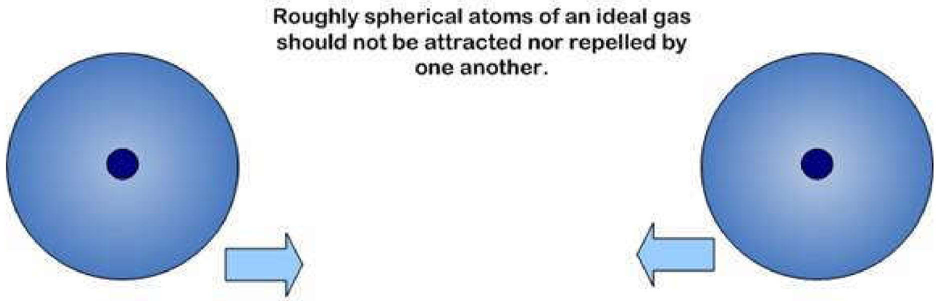
(i) It is the van der Waals forces between the molecules that cause substances like inert gases, halogens etc. to condense to liquids and to freeze into solids, when the temperature is considerably lowered. Thus these forces are responsible for bringing about condensation and crystallization (at low temperatures) in the noble gases and halogens.

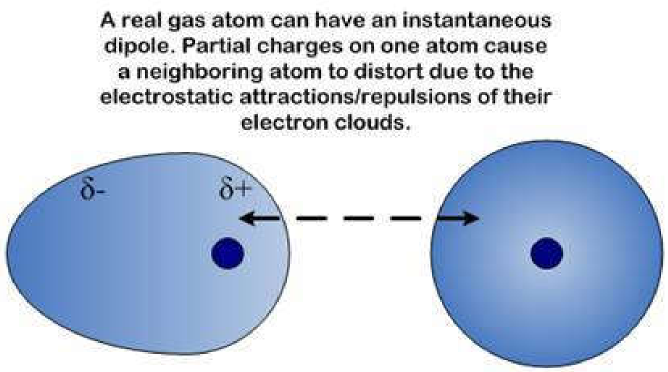
(ii) These forces account for varied hardness of certain solids. If the atoms or molecules in any crystal are united only by van der Waals forces, the crystals can be broken down easily. Such crystals will be soft and possess low melting points.

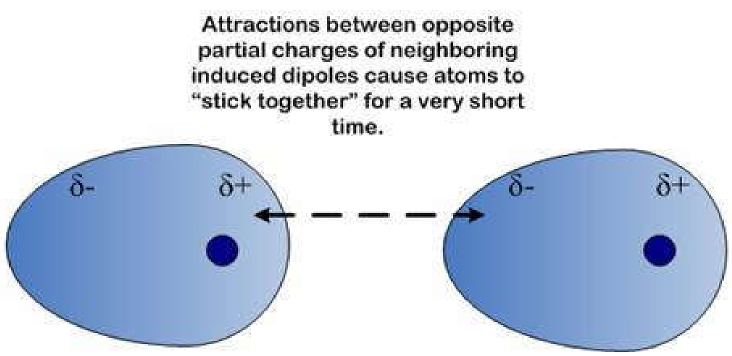
(iii) These forces, though extremely weak, can explain the deviation of the behaviour of gases at low temperature from that of the ideal gases.

Molecules/Atoms	:	He	H_2	Ne	N_2	O_2	Ar	F_2
No. of electrons	:	2	2	10	14	16	18	18
Boiling points (°C)	:	–269	–253	–246	–196	–183	–186	–186
Strength of London forces	:	——— Strength increasing ———→						

Inert gases	:	He	Ne	Ar	Kr	Xe	Rn
No. of electrons	:	2	10	18	36	54	86
Mol. wt.	:	4	20	40	83.7	131	222
Boiling point (°C)	:	–269	–246	–186	–152	–107	–62
Magnitude of van der Waals forces	:	——— Increasing ———→					


Roughly spherical atoms of an ideal gas should not be attracted nor repelled by one another.


A real gas atom can have an instantaneous dipole. Partial charges on one atom cause a neighboring atom to distort due to the electrostatic attractions/repulsions of their electron clouds.
δ-
δ+


Attractions between opposite partial charges of neighboring induced dipoles cause atoms to "stick together" for a very short time.
δ-
δ+
δ-
δ+