

Module-3: Intermolecular forces

Module3 (1 of 5) -MKM

[Ionic, dipolar and van Der Waals interactions. Measurement of non-covalent interaction, Hydrogen bond, Equations of state of real gases and critical phenomena.]

Intermolecular forces are forces of attraction or repulsion which act between neighboring particles (atoms, ions or molecule).

Intermolecular forces are weak compared to the intramolecular forces (the forces which keep a molecule together)

Table: Relative Approximate strength of forces

Forces	Bond Type	Dissociation Energy (KJ/mol)
Intramolecular	Covalent	400
Intermolecular	Van der Waals' forces	<1
Intermolecular	Dipole-dipole	0.5-2
Intermolecular	Hydrogen bond	12-16

Ionic Interactions:

Transfer of one or more electrons from one atom to the other between a metal and non-metal atom results in the formation of ionic bonds. The metallic atoms loses its electrons present in its valence shell and converts into a cation (positive ion), whereas a non-metallic atom gains electrons and converts into anion (negative ion). The electrostatic force of attraction holds the oppositely charged ions together. The ionic bond refers to the electrostatic force of attraction that hold the oppositely charged ions together.

The number of electrons that an atom gains or loses while forming an ionic bond is called its electrovalency. The atom losing electrons is called electropositive atom, whereas the atom gaining electrons is called electronegative atom.

e.g. Formation of NaCl

Factors on which formation of ionic bond depends:

- (i) The ionization energy of atom forming the cation should be low.
e.g.: alkali and alkaline earth metals
- (ii) The electron affinity of atom forming the anion should be high
e.g.: halogens and oxygen
- (iii) Lattice energy should be high or size of ions should be small and their charge should be large.

Properties of Ionic compounds:

- (i) Ionic compounds are non-directional and cannot exhibit isomerism.
- (ii) They are non conductor in solid state. The ions are trapped in fixed places in the crystal lattice and as they cannot migrate, they cannot conduct electricity.
- (iii) They are conduction of electricity in molten state and in solution.
- (iv) They are soluble in polar solvents but insoluble in non-polar solvents like benzene.
- (v) They possess high melting point and boiling point because binding energy is very high. Ionic compounds are made up of + and – ions arranged in a regular way in a lattice. The attraction between ions is electrostatic and non-directional, extending equally in all directions.
- (vi) They give ionic reactions, which are very fast. For ionic reactions to occur, the reacting species are ions, and as these already exist, they only to collide with the other type of ions.
- (vii) Ionic compounds are brittle in the solid state.

Dipolar Interaction:

Substances having molecules with permanent dipole moments interact with one another due to electrostatic attraction between the negative end of one molecule and the positive end of another molecule or vice versa. The dipole-dipole interactions help to determine the melting and boiling points of polar substances.



The distance between the two dipoles and their orientation determine the dipole-dipole interaction. The dipoles having similar charges remain as far as possible. A favorable orientation of two dipoles leads to an attraction dipole-dipole attraction. A substance having same molecular weight and shape but lacking the presence of dipole moment has relatively lower melting or boiling point than polar molecule.

VAN DER WAAL'S FORCES:

Van der Waal's forces are the weak forces of attraction between two non-bonded atoms of all atoms, molecules or ions when they close to one another.

Van der Waal's forces are responsible for the condensation of chlorine, hydrogen and carbon monoxide and even the inert gases.

Strength of Van der Waal's forces depends on : (i) Size of the molecule (ii) number of electrons present in the molecule (iii) Molecular structure

Van der Waal's forces are mainly three types:

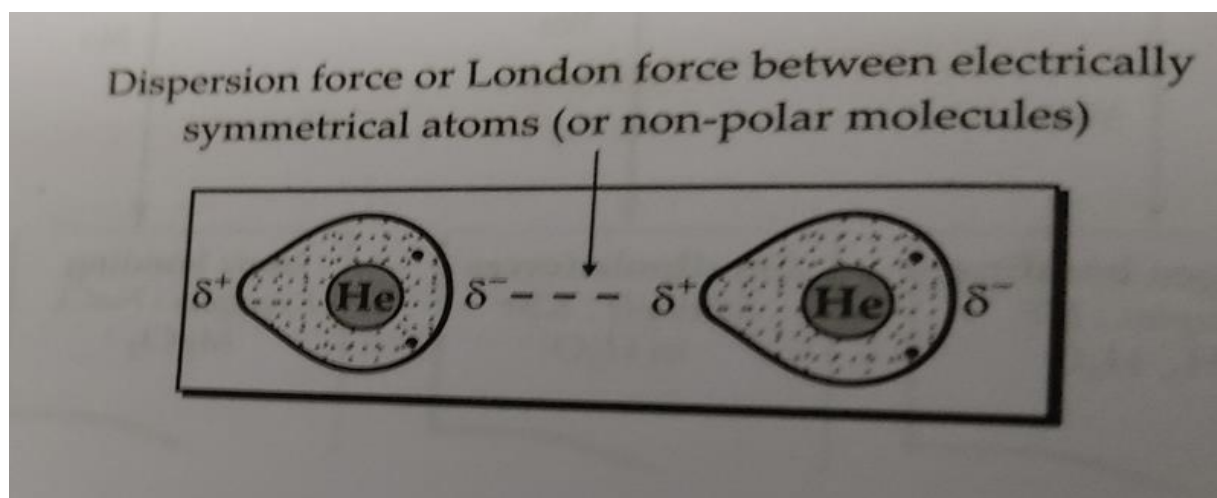
- (i) Induced dipole-induced dipole forces (between non-polar molecules)
- (ii) Dipole-dipole forces (between polar molecules)
- (iii) Dipole-induced dipole forces (between polar and non-polar molecules)

(i) Dispersion Forces **or** London Forces **or** Induced Dipole-induced Dipole Forces

The nucleus of one atom attracts electrons from the neighbouring atom. At the same time, the electrons in one particle repel the electrons in the neighbour and create a temporary charge imbalance. The force of attraction between two temporary dipole in nonpolar molecule is known as **London force** or **Dispersion force**.

London forces are always attraction and interaction energy (E) is inversely proportional to the sixth power of the distance between two interacting particle (i.e., $1/r^6$ where r is the distance between two particles). Thus, these forces are important only at short distances (approx 500pm)

The force of attraction between two temporary dipoles is known as London forces.



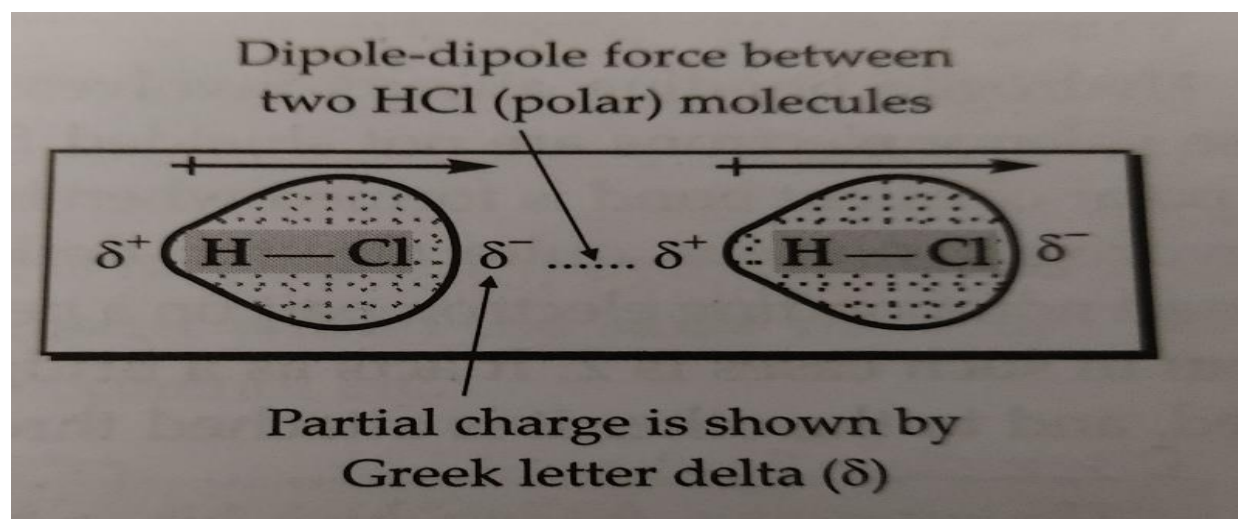
Question. Discuss in brief the origin of London forces between pair of helium atoms.

Answer: The liquefaction of inert gases cannot be explained by either dipole-dipole or dipole-induced dipole forces. For example, a helium atom is perfectly symmetrical. But movement of the electron around the nuclei of a pair of neighbouring He atoms can become synchronized so that each atom simultaneously obtains an induced dipole moment.

Induced dipole-induced dipole forces of attraction between pair of atoms are created by the constant fluctuation in electron density.

(ii) Dipole-dipole forces (between polar molecules)

These types of Van der Waal's forces are found in polar covalent molecules like HCl.



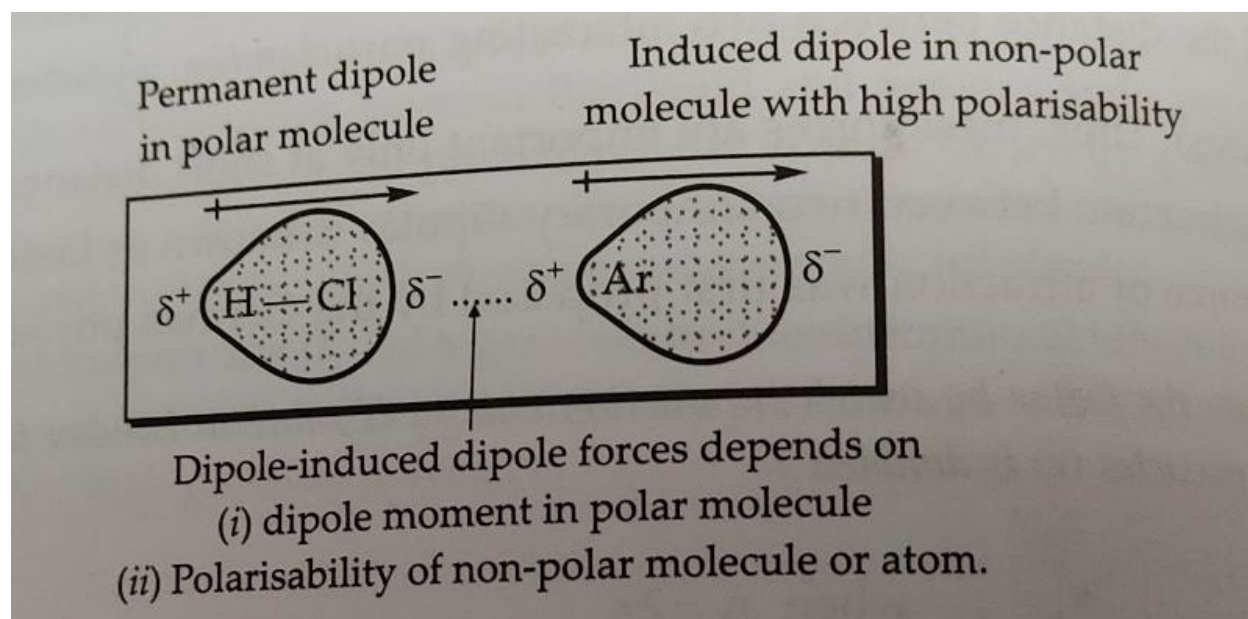
In these molecules, there are positive and negative ends, or poles, and the molecules are often said to have a dipole moment. Due to the difference between the electronegativities of the atoms, the hydrogen atom has a slight positive charge and chlorine atom has a slight negative charge in HCl molecule. Because of the force of attraction between oppositely charged particles, there is a small dipole-dipole force of attraction between adjacent HCl molecules.

Q. Why is boiling point of HCl low?

Ans: Compared to covalent bond, the dipole-dipole interaction is very weak. For example, the covalent bond between the H and Cl atoms in HCl is 130 times as strong as dipole-dipole interaction between HCl molecules. The force of attraction between HCl molecules is so small that hydrogen chloride boils at -85°C .

(iii) Dipole-induced dipole forces (between polar and non-polar molecules)

The electrons on an argon atom are distributed homogeneously around the nucleus of the atom. If we mix HCl with argon, and when an argon atom comes close to polar HCl molecules, the electrons can shift to one side of the nucleus to produce a very small dipole moment that lasts for only an instant.



A small dipole moment is induced on the argon atom by distortion of electron around it by the polar HCl molecule. This creates a weak dipole-induced dipole force of attraction between the HCl molecule and the Ar atom. This force is very weak with bond energy of about 1kJ/mole.

Q. Let A= Dipole-dipole interaction, B= London forces, C= Ion-ion interaction. Arrange the above forces in the order of their decreasing strength.

Solution: $C > A > B$

In ion-ion interaction, full charges are involved; in Dipole-dipole interaction, only partial charges are involved.

*Hydrogen bond is a special case of dipole-dipole interaction

Q. Predict which will have the higher boiling point: N_2 or CO . Explain your reasoning.

Solution: CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attraction. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attraction between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have higher boiling point.

Q. Order the following hydrocarbons from lowest to highest boiling point: C_2H_6 , C_3H_6 and C_4H_{10} .

Solution: $\text{C}_2\text{H}_6 < \text{C}_3\text{H}_6 < \text{C}_4\text{H}_{10}$. All these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore $\text{C}_2\text{H}_6 < \text{C}_3\text{H}_6 < \text{C}_4\text{H}_{10}$.

Measurement of non-covalent interaction

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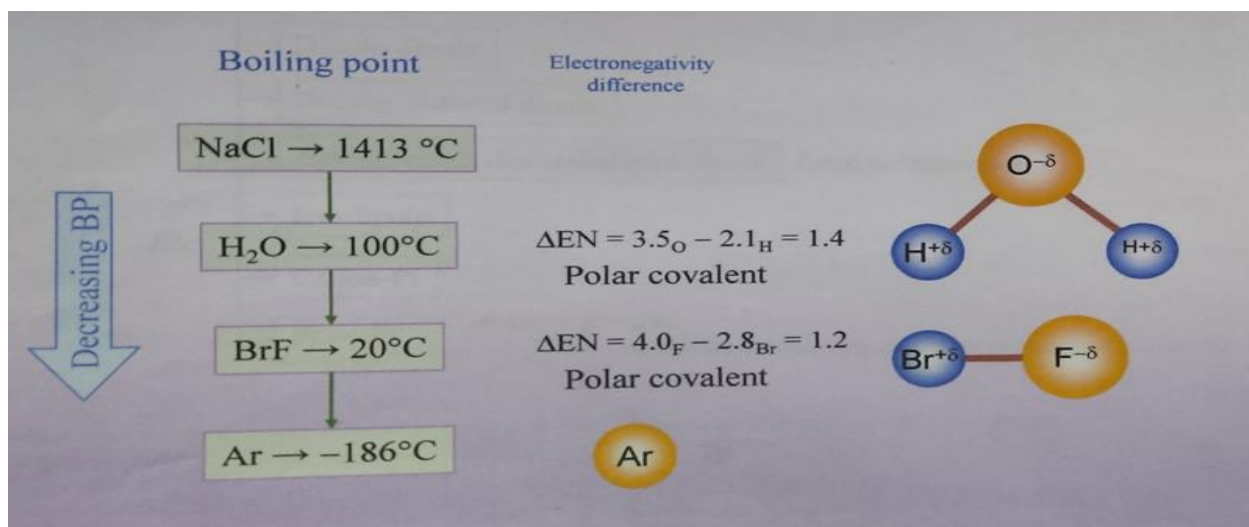
A non-covalent interaction differs from a covalent bond in that it does not involve the sharing of electrons, but rather involves more dispersed variations of electromagnetic interactions between molecules or within a molecule.

The chemical energy released in the formation of non-covalent interactions is typically on the order of 1–5 kcal/mol

Non-covalent interactions can be classified into different categories, such as electrostatic, π -effects, van der Waals forces, and hydrophobic effects.

How do we get a measure of non-covalent interaction?

- **Boiling point:** (being the temperature at which vapour pressure of substance equals the ambient pressure) is better measure of non-covalent forces compared to melting point (which not only influenced by attraction force but also the crystal lattice)



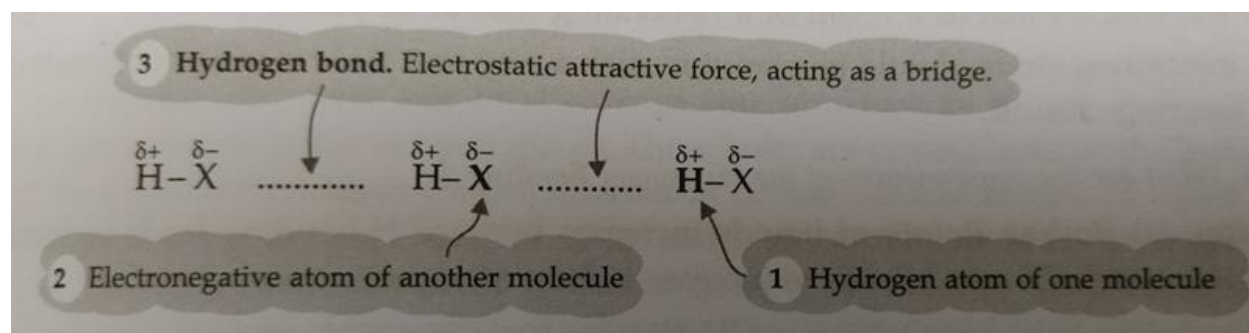
Hydrogen bonding:

Hydrogen bonding always involves hydrogen. It is only chemically reactive element whose valence electrons are not shielded from the nucleus by a layer of underlying electrons. A very polar covalent bond is formed when hydrogen bonds to an electronegative atom. This leaves the hydrogen nucleus quite electron – deficient. The hydrogen makes up for its deficiency by sharing a non-bonding electron pair on a nearby electronegative atom.

“The attraction force which binds hydrogen atom of one molecule with electronegative atom (F, O or N) of another molecule is known as **Hydrogen bond**.”

Causes of formation of Hydrogen Bond:

Consider a molecule H-X where X is strongly electronegative elements (F, O or N). The electron pair shared between H and X moves towards X due to its high electronegativity. Because there is displacement of electrons towards X, the hydrogen acquires fractional positive charge (δ^+) while X acquires fractional negative charge (δ^-). This results in the formation of a polar molecule. There are electrostatic forces of attraction between such molecules which can be represented as:



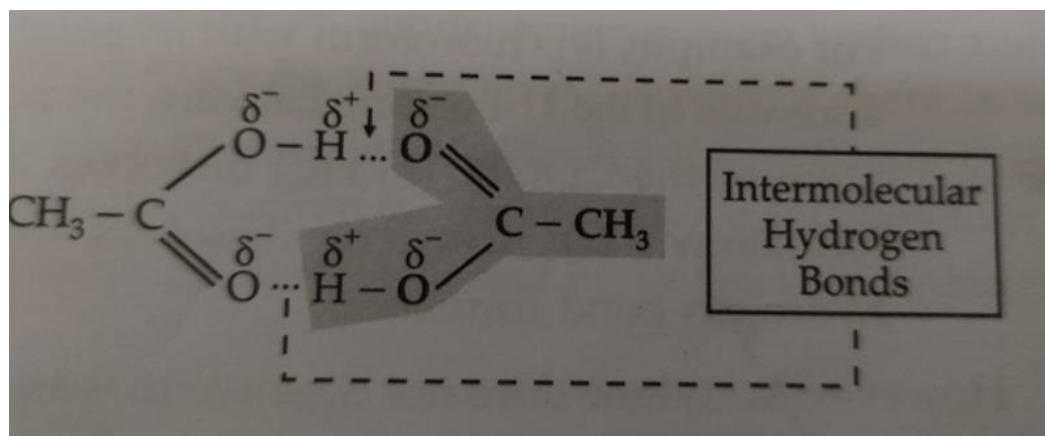
The weak electrostatic interaction leading to the hydrogen bond formation is shown by dotted lines. Thus $\text{X-H} \cdots \text{Y}$ represents H-bonding between H and Y atom.

Types of Hydrogen Bonds:

- (i) Intermolecular H-bond (between molecular)
- (ii) Intramolecular H-bond (within molecular)

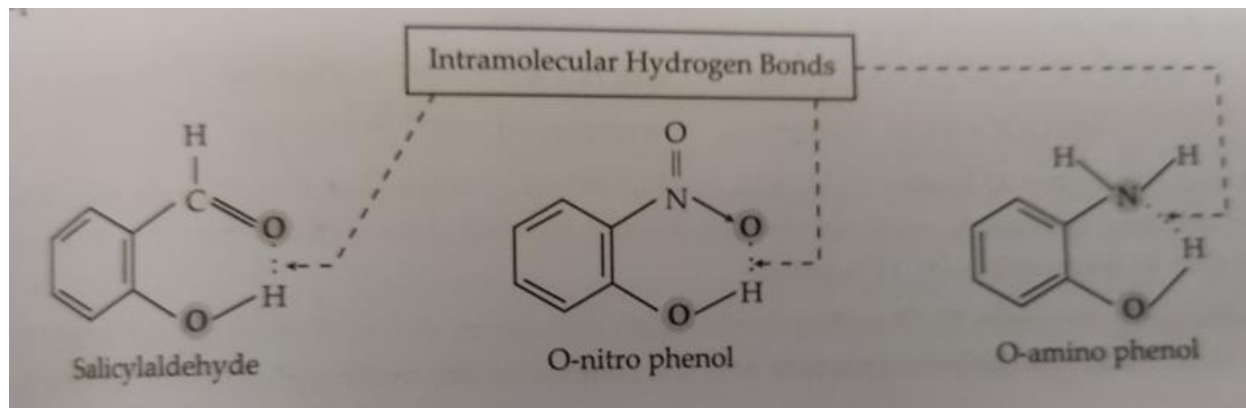
(i) Intermolecular H-bond (between molecular)

When hydrogen atom acts as a bridge between two different molecules of the same or different compounds. For example , H-bond in water, ammonia, hydrogen fluoride , acetic acid etc



(ii) Intramolecular H-bond (within molecular)

Where the hydrogen bond is formed when hydrogen atom is in between the two highly electronegative (F, O and N) atoms present within the same molecule. For example, H-bond in salicylic acid, O-nitrophenol, O- amino phenol



Effect of Hydrogen Bonding on Boiling Points:

Q. Consider the compounds dimethylether (CH_3OCH_3), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and propane ($\text{CH}_3\text{CH}_2\text{CH}_3$). Their boiling points not necessarily in order are -42.1°C , -24.8°C and 78.4°C .

Solution:

The VSEPR –predicted shapes of CH_3OCH_3 , $\text{C}_2\text{H}_5\text{OH}$, and $\text{CH}_3\text{CH}_2\text{CH}_3$ are similar, as their masses (46 g/mol, 46 g/mol and 44g/mol respectively), so they will exhibit similar dispersion forces. Since $\text{CH}_3\text{CH}_2\text{CH}_3$ is nonpolar, it may exhibit only dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, $\text{C}_2\text{H}_5\text{OH}$ has an $-\text{OH}$ group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of intermolecular forces (IMFs), and thus boiling points, is $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{C}_2\text{H}_5\text{OH}$. The boiling point of propane is -42.1°C , the boiling point of dimethylether is -24.8°C , and the boiling point of ethanol is 78.4°C .

Q. Ethane (CH_3CH_3) has a melting point -183°C and a boiling point of -89°C . Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Solution:

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an $-\text{NH}$ group and therefore may exhibit hydrogen bonding. This greatly increases its intermolecular forces (IMFs), and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of -93°C and a boiling point of -6°C .

Equations of state of real gases:

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IDEAL GAS AND REAL GAS

A gas which obeys Boyle's law, Charle's law etc under all condition of temperature and pressure is known as an **ideal gas** or a **perfect gas**.

Since the gas equation ($PV=nRT$) is obtained by combining Boyle's law and Charle's law, therefore, an ideal gas may also be defined as follows:

A gas which obeys the gas equation ($PV=nRT$) under all condition of temperatures and pressures is called an **ideal gas**. In fact, this is the reason that the gas equation ($PV=nRT$) is known as ideal gas equation.

A gas which obeys ideal gas equation or gas laws under low pressure or high temperature is known as **Real gas**. All gases are real gases. They show more and more deviation from the gas laws as the pressure is increased or the temperature is decreased.

Difference between Ideal and Real Gases:

S.No	Characteristics	Ideal Gas	Real Gas
1.	The attraction forces between gas molecules.	Not exists	Exists
2.	The actual volume of molecules in gas.	Negligible	Appreciable
3.	Molecular collision in a gas	Perfectly elastic	Non-elastic
4.	Confirms to the assumption of kinetic theory of gases.	Yes	No
5	Obeys the Boyle's law , Charle's law etc	Under all condition of temperature and pressure	Only at low pressure and high temperature
6	Existence of gas in reality	No(Only hypothetical)	Yes
7	Examples	None	H ₂ , O ₂ , N ₂ etc

Equations of state of real gases:

Van der Waal's in 1873 modified the ideal gas equation by incorporating correction terms, which took into account the volume of the gas molecules and the force of attraction between them.

Van der Waals equation modifies the kinetic theory of gases disproving the following points:

1. The force of attraction between gaseous molecules is negligible.
2. The volume of gaseous molecule is negligible as compared to the total volume of the gas.

The two corrections explained by Van der Waals are as follows :

(i) Correction for the volume

(ii) Correction for the force of attraction/Pressure correction

(i) Correction for the volume

Unlike volume of gas, volume of a molecule is not negligible.

Let us consider (n) moles of gas placed in a container of volume (V). If the volume occupied by the molecules themselves is negligible then the space in which the molecules are free to move is equal to (V), Fig.1 (i).

But in reality, the molecules have a finite size. Hence, the actual volume available to gas molecule for their free movement would be somewhat less than (V), Fig.1 (ii).

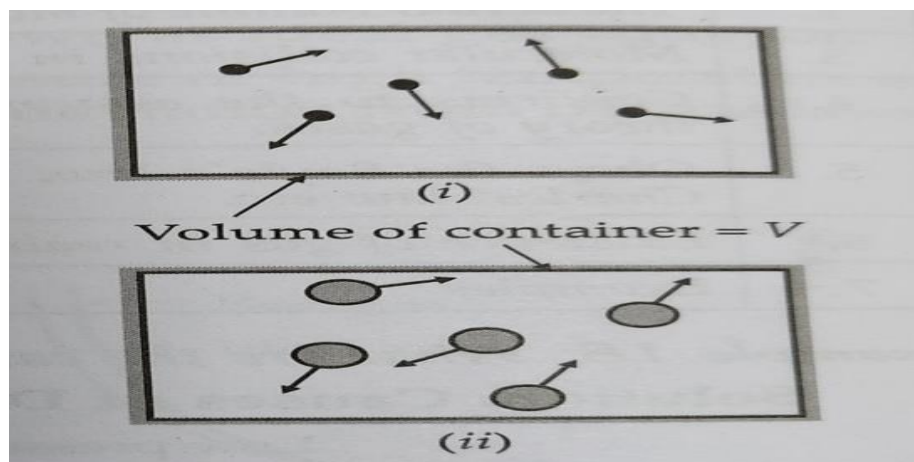


Fig1: Illustration of attraction forces between gas molecules

Let b = excluded volume or effective volume per mole of the gas
 n = number of moles of the gas

Hence, the actual volume for the free movement of gas molecule will be V_{ideal}

Ideal Volume $V_{\text{ideal}} = \text{Measured volume (V)} - \text{Volume correct term (nb)}$

$$V_{\text{ideal}} = V - nb \text{ -----(i)}$$

(ii) Correction for the force of attraction/Pressure correction

The force with which the molecules of the gas inside a container collide with the walls of the container is called the pressure of the gas. According to Van der Waals, the pressure of real gas is the combination of pressure developed due to collision of the molecules of gas with the walls of container and the pressure loss due to inward pull of adjacent molecules which makes the gas molecules striking the walls of the container experience some backward drag.

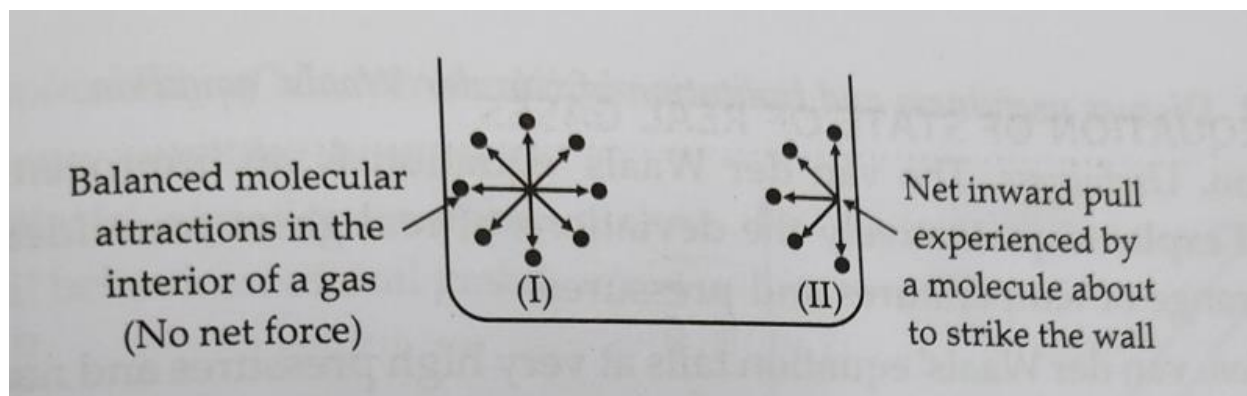


Fig 2: Illustration of attraction forces between gas molecules

Now consider the same gas molecule (A) moving towards the wall of the container. As it approaches the wall of the container, the uniform distribution of molecules around it is disturbed and it is attracted by molecules from the back side only. The molecule will thus experience a net inward force. Because of this, the molecule exerts less pressure as it is striking the wall of the container with lower velocity.

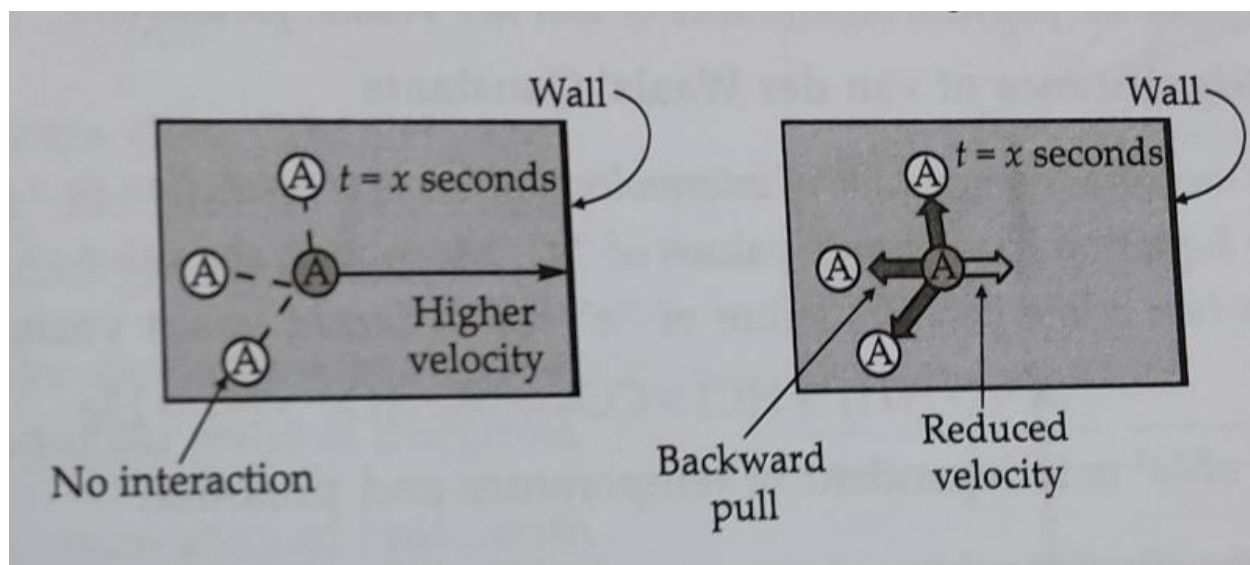


Fig3: The striking molecule is pulled inward (II) by other molecules which reduces its velocity and causes the decrease in pressure.

Hence, the measured pressure (p) is less than the ideal pressure. It is, therefore, necessary to add a correction term (p_o) to the measured pressure (p) in order to obtain the ideal pressure.

Hence, corrected (ideal pressure) $p_{\text{ideal}} = p + p_o$ ----- (ii)

The pressure depends on (i) frequency of collisions with the walls and (ii) force of each collision.

Both the above terms are reduced by the attraction forces, which act with a strength proportional to the molar concentration, n/V , of the molecule in the gas. Because, both the frequency and the force of collisions are reduced by the attraction forces, the pressure is reduced in proportion to the square of the concentration.

Hence, the correction term $p_o \propto \left(\frac{n}{V}\right)^2$

or $p_o = a \frac{n^2}{V^2}$ where a is the constant of proportionality.

Putting this value p_o in equation (ii), we get the corrected (ideal) pressure :

$$p_{\text{ideal}} = p + \frac{an^2}{V^2} \quad \text{(iii)}$$

measured pressure pressure correction factor to consider intermolecular forces

Since, the ideal gas equation is,

$$p_{\text{ideal}} V_{\text{ideal}} = nRT \quad \text{(iv)}$$

Substituting the values of p_{ideal} and V_{ideal} from equations (iii) and (i) respectively in equation (iv), we get improved ideal gas equation.

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad \dots(v)$$

This is known as the *van der Waals' equation* for n moles of the gas. The constants a and b are called van der Waals' constants.

For this work, Johannes van der Waals (the Dutch chemist) was awarded the Noble prize in Physics in 1910.

Q. Discuss usefulness and limitation of Van der Waal's equation.

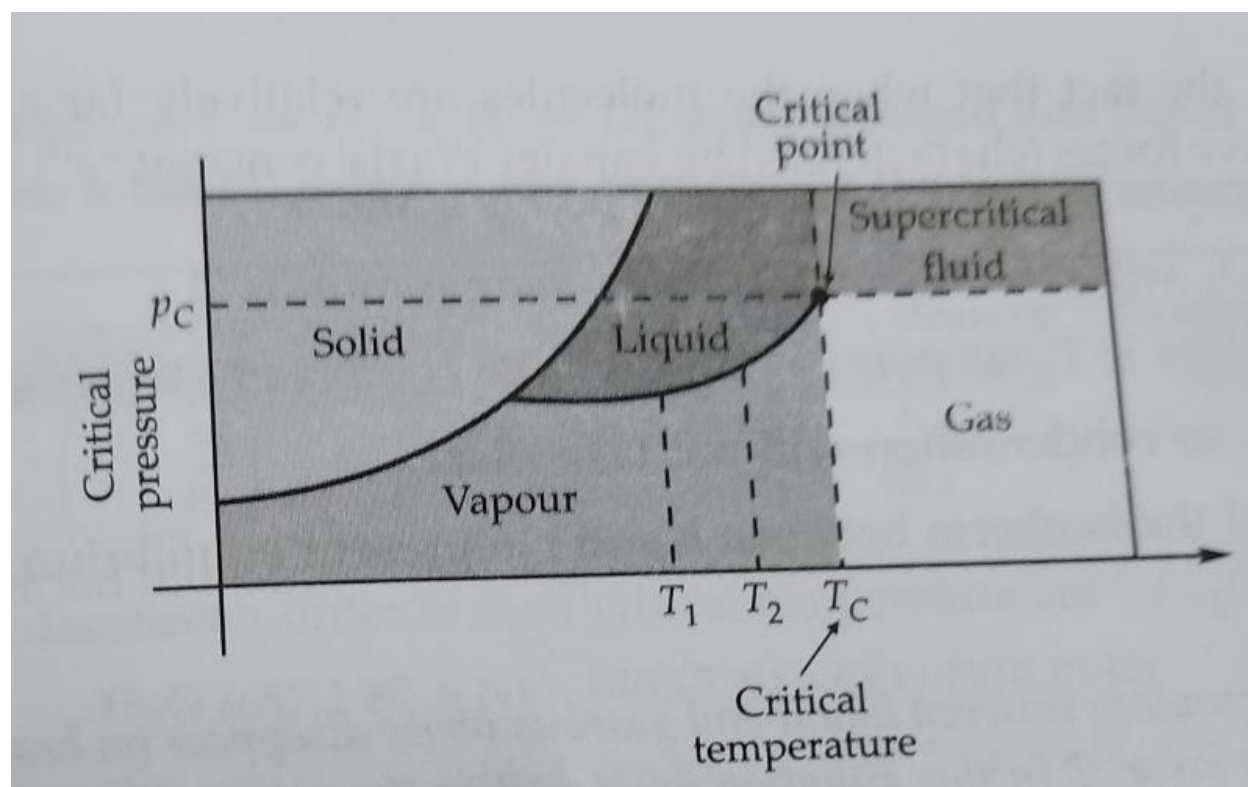
Answer: Usefulness: The Van der Waal's equation is an improvement over the ideal gas equation and explains qualitatively the deviation of real gases from ideal behaviour. It is valid over a wide range of temperature and pressure.

Limitation: Van der Wall's equation fails at very high pressure and near critical temperature.

Critical phenomena:

At the **critical point**, the densities of a substance in liquid and gaseous state are same. There is no distinction between the liquid and gaseous state and no second phase is formed irrespective of the pressure of the system. Generally gases below their critical temperature are called **vapours**. Fluids above the critical temperature are known as **super critical fluids**, which dissolve many organic substances.

Super critical fluids are used for speedy separation of a mixture into its components. For examples, carbon dioxide above 600 bar pressure and above 31.1°C (Which is T_c for CO_2) has a density around 1gm/cm^3 and used to remove caffeine from coffee beans, instead of using chlorofluorocarbons, which are not environmental friendly.



Critical temperature:

The temperature above which gas cannot be liquefied using only high pressure is called critical temperature. It is denoted by T_c . For every gas, there is a specific critical temperature.

$$T_c = 8a/27Rb$$

Critical Volume:

The volume which is occupied by one mole of a gas at critical temperature is called critical volume. It is denoted by V_c .

$$V_c = 3b$$

Critical Pressure:

The minimum pressure at which a gas can be liquefied at critical temperature is called critical pressure. It is denoted by P_c .

$$P_c = a/27b^2$$

$$P_c V_c = 3/8RT_c$$

Model Question:

Q.1.	Derive Vander waal's equation of state for n moles of gas. Write units of van der waals constant a and b and their physical significance. What are the limitations of this equation?
Q.2.	What are Vander Waal's forces? What are the Origin of Vander Waal's force
Q.3	Discuss the factors affecting the formation of ionic bond.
Q.4.	What is an ionic bond? Explain giving suitable examples why ions with three positive or three negative charges are rare.
Q.5	Write down Ideal gas equation and compare the same with real gas equation.
Q.6.	Predict which will have the higher boiling point: N ₂ or CO. Explain Your reasoning.
Q.7.	Define the following and give an example of each (a) dispersion forces (b) dipole-dipole attraction (c) hydrogen bond
Q.8	What do you mean by Critical temperature? What is the significance of Critical temperature of a gas?
Q.9.	Explain why beyond a certain temperature gases cannot be liquefied whatever the pressure may be.
Q.10	Define Critical Phenomena. Explain the terms Critical temperature, Critical pressure and Critical volume. Explain the significance of Critical temperature by giving a suitable example.

Q.1. Which of the following is a strongest bond ?

(a) **ionic bond** (b) covalent bond (c) hydrogen bond (d) dipole

Q.2. Which of the following is an intermolecular force ?

(a) ionic bond (b) covalent bond (c) **hydrogen bond** (d) none of this

Q.3. Which of the following having hydrogen bond ?

(a) **HF** (b) CCl_4 (c) NaCl (d) none of this

Q.4. Which of the following having intramolecular hydrogen bond ?

(a) HF (b) H_2O (c) NH_3 (d) **O-nitrophenol**

Q.5. Which of the following compound is covalent ?

(a) **NCl_3** (b) CaO (c) KCl (d) Na_2S

Q.6. NH_3 is a molecule

(a) Non polar (b) **Polar** (c) Ionic (d) none of this

Q.7. Which of the following term does not involve in ideal gas law ?

(a) Pressure (b) Volume (c) Temperature (d) **Time**

Q.8. Which of the following elements is least likely to participate in a hydrogen bond ?

(a) O (b) F (c) **S** (d) N

Q.9. What type of intermolecular forces are due to the attraction between temporary dipoles and their induced temporary dipoles ?

(a) Metallic bond (b) **London dispersion** (c) Hydrogen bond (d) Ionic bond

Q.10. The principle which excludes the possibility of presence of a third electron in an orbital is,

(a) Aufbau principle (b) Hund's rule (c) **Pauli exclusion principle** (d) none of these

Q.11. Which of the following is not a form of chemical bonding ?

(a) covalent bond (b) **hydrogen bond** (c) ionic bond (d) none of these

Q.12. Which one of the following pairs of atoms are most likely to form an ionic bond ?

(a) **Na and F** (b) C and F (c) N and F (d) O and F

Q.13. Which of the following has greatest covalent character ?

(a) NaCl (b) MgCl₂ (c) AlCl₃ **(d) SiCl₄**

Q.14. Which of the following compound does not contain an ionic bond ?

(a) NaOH **(b) HCl** (c) K₂S (d) LiH

Q.15. HCl is a gas but HF is a low boiling liquid, due to

(a) H-F bond is strong (b) H-F bond is weak **(c) molecules of HF form aggregate due to H-bonding** (d) HF is a weak base

Q.16. The correct sequence of increasing covalent character is represented by

(a) LiCl < NaCl < BeCl₂ (b) LiCl > NaCl > BeCl₂ **(c) NaCl < LiCl < BeCl₂** (d) NaCl > LiCl > BeCl₂

Q.17. Which of these is weakest?

(a) ionic bond (b) covalent bond (c) metallic bond **(d) Van der Waals forces**

Q.18. Real gases will approach the behaviour of ideal gas at

(a) low temperature and low pressure (b) low temperature and high pressure
(c) High temperature and high pressure **(d) High temperature and low pressure**

Q.19. Dipole-induced dipole interactions are present in which of the following pairs:

(a) H₂O and alcohol (b) Cl₂ and CCl₄ **(c) HCl and He atoms** (d) SiF₄ and He atoms

Q.20. Which type of intermolecular forces exist among the Cl₂ and CCl₄ molecule?

(a) Dipole-dipole interaction **(b) London dispersion forces**
(c) Hydrogen bonding (d) Dipole-induced dipole interaction

Q.21. Which one of the following gases has the highest Critical temperature?

(a) Nitrogen (b) Ammonia **(c) Water vapour** (d) Carbon dioxide

Q.22. The Critical temperature and reduced temperature of a gas are 150K and 3K respectively.

What is the temperature of the gas- (a) 150K (b) 147K (c) 153K **(d) 450K**

Q.23. Dispersion forces are present in -

(a) Ar and Ar atoms (b) HCl and He atoms (c) H₂O and alcohol (d) HCl and HCl

Q.24. Which of the hydrogen bonds is strongest:-

(a) O-H-----N **(b) F-H-----F** (c) O-H-----O (d) O-H-----F

Q.25. If 'Z' is compressibility factor, Van der-Waals equation at low pressure can be written as,

(a) $Z=1+RT/pb$ **(b) $Z=1-a/VRT$** (c) $Z=1-pb/RT$ (d) $Z=1+pb/RT$

Q.26. One of the followings represents the Boyle's Law

(a) $V \propto 1/P$ (b) $V \propto T$ (c) $V \propto n$ (d) none of this

Q.27. The intermolecular forces that exist between HF molecule in liquid state

(a) Dipole-dipole interaction (b) Hydrogen bonding

(c) both (a) and (b) (d) None of these

Q.28. Maximum deviation from ideal gas is expected from : (a) H₂ (b) N₂ (c) CH₄ **(d) NH₃**