

# INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

Dr. Rajvir Kaur  
Chemistry

## SYLLABUS

(4 Lecturers)

Ionic, dipolar and van Der Waals interactions. Equations of state of real gases and critical phenomena. Potential energy surfaces of  $H_3^+$ ,  $H_2F$  and  $HCN$  and trajectories on these surfaces.

### 3.1 INTRODUCTION

The forces present between the molecules of the substances are called *intermolecular forces*. These forces are present in all kinds of molecules. These weak attractive forces are present for all the states of matter and determine their structural and physical properties. These forces are present in even non-polar substances such as  $H_2$ ,  $Cl_2$ ,  $CH_4$ , etc., since all these substances can be liquified. Even the inert gases such as He, Ne, Ar, etc possess intermolecular force because they can also be liquified. and some weak forces must be operative among the molecules.

The existence of these forces among the non-polar molecules in their liquid and solid states was first proposed by the Dutch scientist J.D Van der Waals. Interaction between various molecules leads to *intra-molecular forces*, which affect the physical as well as chemical properties of the compounds. Along with intermolecular forces, we shall take up the study of potential energy surfaces in this chapter.

### 3.2 TYPES OF INTERACTION FORCES

It is completely established that forces of attraction exist between polar as well as non-polar molecules. These intermolecular forces called *Cohesive forces* or *Van der Waals forces* originate from two types of interactions, namely (i) Dipole – Dipole Interactions and (ii) Induced Dipole – Induced Dipole Interactions.

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The following types of intermolecular forces exist between the molecules of different substances:

1. Dipole-dipole interaction
2. Induced dipole-induced dipole
3. Ion-dipole
4. Ion-induced dipole
5. Instantaneous dipole-instantaneous induced dipole forces (or dispersion forces)

It may be noted that the term Van der Waals forces refer to *dipole-dipole, dipole-induced dipole and dispersion forces*.

**1. Dipole-dipole interaction:** These are second strongest intermolecular forces. These forces exist between permanent dipoles. The dipoles tend to align with oppositely charged ends directed at each other. As permanent dipoles exist only in polar compounds, so these interactions occur only in polar compounds, e.g. acetone and dichloromethane. These forces weaken even more rapidly as the distance increases as compared to an ion-dipole interaction.

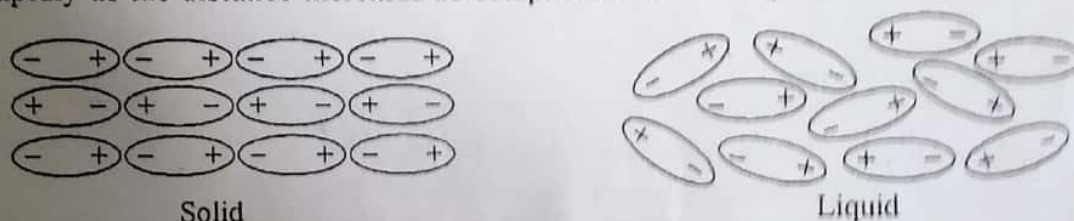


Fig. 3.1

These forces are also called *Keesom forces* as these were first studied by Keesom (1912). He termed this effect as *orientation effect*.

**2. Induced dipole-Induced dipole Interaction. (London Forces or Dispersion Forces):** As we know, the Van der Waals forces exist even in nonpolar molecules such as  $O_2$  and  $N_2$  and also in inert gases such as He, Ne, Ar, etc. This attraction is clear from the condensation of these gases into liquids at sufficiently high pressures and low temperatures.

In 1930, F. London provided a satisfactory explanation for the existence of forces of attraction between non-polar molecules on the basis of quantum mechanics. According to him, electrons of a neutral molecule keep on oscillating with respect to the nuclei of the atoms. As a result, at a given instant, positive charge may be concentrated in one space and negative charge in another space of the same molecule. Thus, a non-polar molecule may become polarised for a little while, this polarised molecule may induce a dipole moment in a neighbouring molecule with anti-parallel orientation, as shown in Fig. 3.2.

The electrostatic forces of attraction between induced dipoles and the original dipoles (due to electron oscillation) are known as the *London forces*. These forces

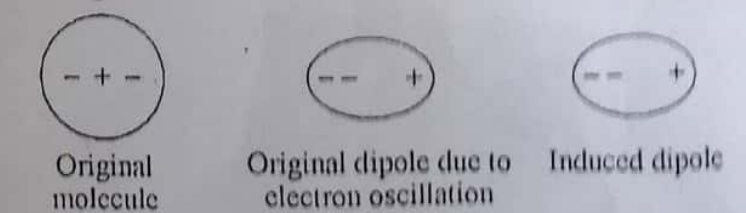


Fig. 3.2. Origin of cohesive forces in non-polar molecule



are also called *dispersion forces* because the well known phenomenon of dispersion of light is also related with these dipoles. The *Van der Waal's attraction* in nonpolar molecules is thus exclusively due to the London forces.

The average interaction energy in this case is given by

$$\text{Interaction energy, } \phi(r) = -\frac{C}{r^6}$$

where  $C$  is a constant, depending upon the ionisation energy of the two molecules.

### Nature of the Van der Waals Interactions.

Though the Van der Waals constants  $a$  and  $b$  take into consideration the effect of attractive interactions in gaseous molecules, the exact nature of these interactions has to be understood. Since molecules are composed of positively charged nuclei and negatively charged electrons, whenever any two molecules come closer, interactions occur between the charge clouds of the nuclei and the electrons of the two molecules. At relatively large intermolecular distances, the attractive forces originating from attraction between electrons and atomic nuclei operate between the two molecules. At very small distances, however, the molecules strongly repel each other, the repulsion arising from the interaction between the similarly charged electron clouds. Thus, we expect the intermolecular potential energy to be composed of the long range *attractive term* and the short range *repulsive term*.

**3. Ion-dipole forces:** These are the strongest inter-nuclear forces. These occur between the ions formed by dissolving the ionic compound in polar solvents. The polar solvent is generally water but it can also include organic salts dissolved in polar organic compound, e.g.  $[\text{Et}_4\text{N}]\text{Br}$  in acetone. The negative end of the dipole will be attracted to positive ions and vice versa.

The magnitude of the interaction between these dipoles and ions depends upon the ionic charges and size of dipoles. These forces sharply decrease with increasing distance. Thus, they act over very short distance only.

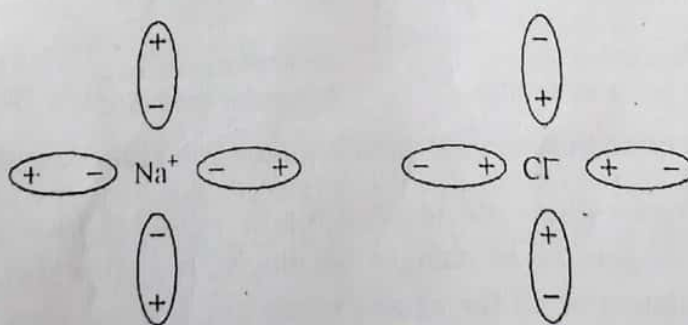


Fig. 3.3

**4. Ion-induced dipole interactions:** These interactions occur between an ion and the induced dipole, for example dissolving benzene in acetone. This occurs when the ion approaches towards non-polar molecule, the symmetrical distribution of non-polar molecule

gets distorted because the electrons on the non-polar molecules are attracted to the positive end of the dipole and repelled by the negative end of the dipole. The interaction lasts as long as the polar molecule is near the non-polar molecule. The formation of induced dipole depends upon the charge on the ion and polarizability of the atom or molecule. As a result, these forces are weak forces and effective only at short range.

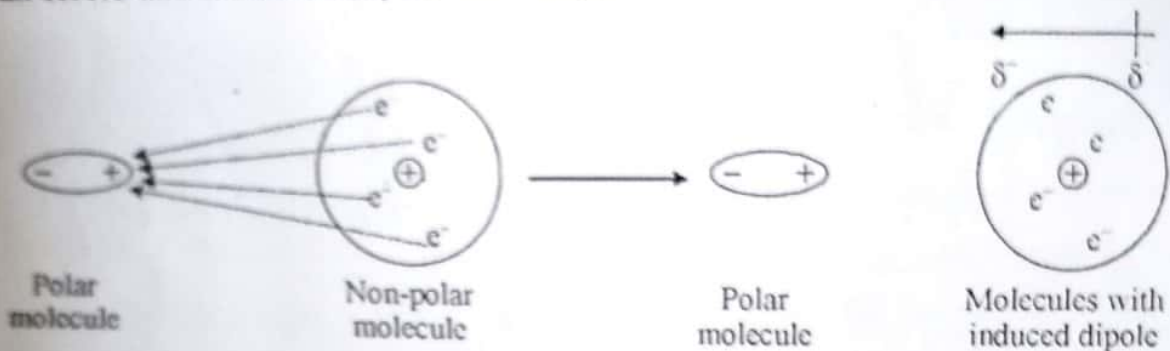


Fig. 3.4

**5. Instantaneous dipole- instantaneous induced dipole forces:** Let us try to understand the formation of instantaneous dipole. When two noble gas atoms are very close to each other, each atom is uncharged because the electron distribution around the nucleus is symmetrical. However, due to motion of electrons, it is possible that for the fraction of time, electron distribution is not symmetrical because of the distortion of the electron cloud. As a result, a small temporary dipole is formed called *induced or instantaneous dipole*. The instant or induced dipole further distorts the electron cloud of neighbouring atom as shown below in Fig. 3.5.

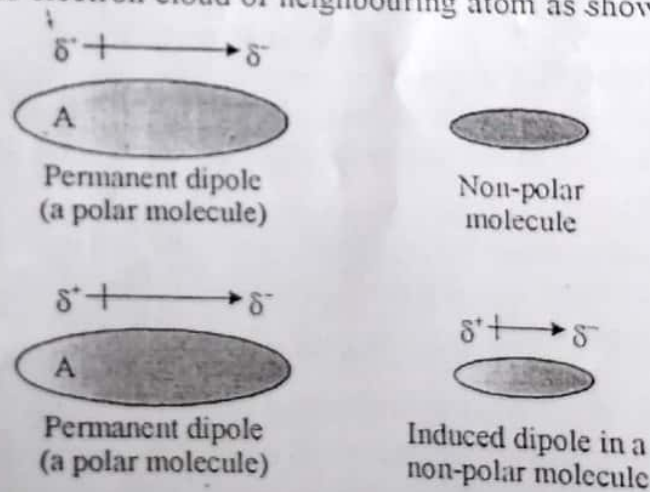


Fig. 3.5. Interaction between permanent dipole and induced dipole.

The attraction that occurs between induced dipole is called *induced dipole-induced dipole interaction*. As the magnitude of charges developed is very small, these forces can operate over the shortest distance of all forces and hence are weakest forces. The strength of these forces depends upon

- (i) size of molecule, i.e. its molecular mass,
- (i) number of electrons present in the molecule, and
- (iii) molecular structure.



The larger the size, the higher the number of electrons present in the molecule or an atom more easily, the atom can be polarized (i.e. easily undergo distortion of electron cloud) and greater will be the strength of these forces. So, larger the size of the molecule of an atom, greater will be the strength of these forces and vice versa.

### 3.3 IDEAL AND REAL GASES

#### 1. Ideal Gases

Gases which obey gas equation  $PV = RT$  rigidly for all values of temperature  $T$  and pressure  $P$  are called ideal or perfect gases. Thus an ideal or perfect gas is one which rigidly obeys Boyle's and Charles law at all values of temperature and pressure.

*Characteristics of an ideal gas may be summarised as:*

- (i) The product of pressure and volume of a given mass of an ideal gas at constant temperature should be constant, i.e., if product  $PV$  is plotted against pressure  $P$  at constant temperature, the curve obtained should be a straight line parallel to the pressure axis (Boyle's law).
- (ii) The compressibility factor  $\left(Z = \frac{PV}{RT}\right)$  of an ideal gas should be unity i.e.  $PV = nRT$  (Gas equation).
- (iii) If at a constant pressure, the temperature is reduced, the volume should get reduced uniformly and become zero at  $-273^\circ\text{C}$  or zero Kelvin (Charles Law).
- (iv) If a gas is allowed to expand without doing any external work, it should show no thermal effect (No force of attraction between the molecules).
- (v) At constant temperature if pressure is doubled, the volume should reduce to half (Boyle's law).
- (vi) According to Avogadro's law, one mole of every gas should occupy 22.4 litres at N.T.P. ( $0^\circ\text{C}$  and 1 atm). Experiments show that this is true only approximately because the actual value for different gases does not come out to be the same (Avogadro's law).

If we study, however, the actual behaviour of the gases, we notice that no gas is ideal or perfect in this sense although some gases approach perfection as the temperature rises above their boiling points.

Thus, an ideal or perfect gas is only hypothetical. It has been observed that at high pressures and low temperatures gases do not obey the gas laws. However, at low pressures and high temperatures they obey the gas laws to a fair degree of approximation. Such gases are, therefore, known as real gases.

#### 2. Real Gases

Real gas is one which obeys the gas laws fairly well under low pressure and high temperature. It means all gases are real gases, but they show deviation from ideal behaviour. The deviations are more pronounced as the pressure is increased or the temperature is decreased. Further in case of real gases it is not possible to reduce uniformly the volume of a gas to zero



at  $-273^{\circ}\text{C}$ , as all real gases liquefy when sufficiently cooled. Real gases like  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ , etc., which are difficult to be liquefied differ from an ideal gas to a greater extent than like  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{CO}_2$  etc., which can be easily liquefied. Helium shows an ideal gas behaviour to some extent.

We know that no gas is ideal or perfect, the gas equation is obeyed as an approximation by a real gas at low pressure and high temperature, while at high pressure and low temperature there is much deviation from this ideal behaviour.

### 3.4 DEVIATIONS OF REAL GASES FROM GAS LAW (BOYLE'S LAW)

#### 1. Effect of Pressure

The plots of  $PV$  versus  $P$  for various gases at  $0^{\circ}\text{C}$  are depicted in Fig. 3.6. For an ideal gas, the plot should be a straight line parallel to pressure axis. Such a plot is indicated by a dotted line. It is clear from the various plots that all gases deviate considerably from the ideal gas behaviour and the product  $PV$  does not remain constant with increasing pressure. Only in the limit of zero pressure, all gases are behaving ideally.

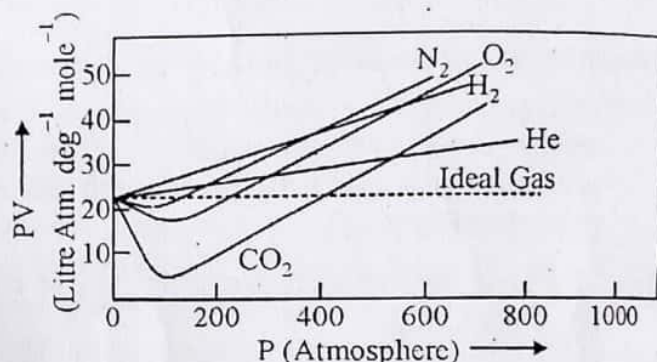


Fig. 3.6.  $PV$  Vs  $P$  plot (variation of  $PV$  with  $P$ ) for various gases at  $0^{\circ}\text{C}$

A close examination of Fig. 3.6 reveals that all the curves can be classified into two types:

**Type 1:** Here the curves start ascending at once from the value of  $PV$  and the value of  $PV$  increases continuously with increasing pressure. This is true in case of gases having smaller molecules, e.g.,  $\text{H}_2$ ,  $\text{He}$ , etc.

**Type 2:** Here the curves show a decrease in  $PV$  in the beginning, passes through a minimum and then begins to increase with increasing pressure. This is true in case of gases having larger molecules e.g.,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$  etc.

Above 400 atmospheres, the product of  $PV$  increases with the increase in pressure for all gases.

#### Compressibility Factor

To show both the deviations more clearly, a quantity, called compressibility factor ( $Z$ ) is used which, is defined as:

$$Z = \frac{PV}{RT}$$

where  $V$  is the volume occupied by one mole of the gas at a given temperature  $T$  and pressure  $P$ .

For an ideal gas,  $Z=1$  and is independent of pressure and temperature.

For a real gas,  $Z$  is a function of both temperature and pressure and its value varies.

The amount by which the actual factor differs from a value of unity gives measure of deviation from the ideal behaviour.

$$\text{Since } (PV)_{\text{ideal}} = RT$$

$$\therefore Z = \frac{PV}{RT} = \frac{PV}{(PV)_{\text{ideal}}}$$

So compressibility factor is a measure of deviation from ideality.

Fig. 3.7 shows a plot of  $Z$  versus  $P$  for some gases at  $0^\circ\text{C}$ . For  $\text{H}_2$ , the value of  $Z$  continuously increases but for  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{CO}_2$ ,  $Z$  first decreases and then increases quite rapidly with increasing pressure.

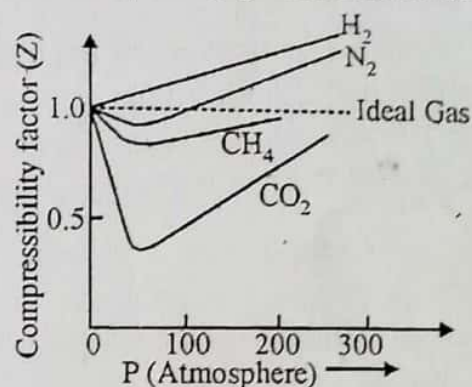


Fig. 3.7  $Z$  vs.  $P$  curves for various gases at  $0^\circ\text{C}$

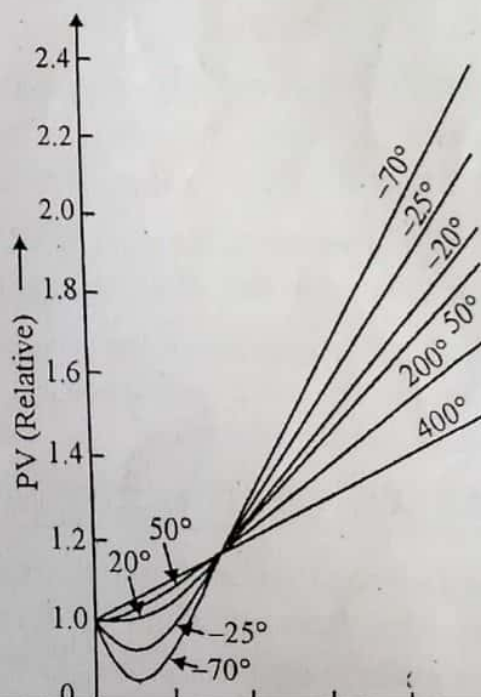
It has been found that for those gases which can be easily liquefied,  $Z$  decreases sharply below the value of unity at low pressure. Since carbon dioxide is a gas which can be more easily liquefied than nitrogen and methane, therefore, the dip in value of  $Z$  is much more pronounced in carbon dioxide and, persists over a range of pressures. But as hydrogen gas cannot be easily liquefied, its curve does not show any dip in the value of  $Z$  with increasing pressure.

### Effect of temperature

If a plot of  $Z$  (compressibility) or relative  $PV$  versus  $P$  is constructed for a gas at several temperatures, it is found that as the temperature decreases, the dip in the curve is more pronounced.

Fig. 3.8 shows various curves of  $Z$  (or relative  $PV$ ) versus  $P$  for nitrogen at various temperatures.

All the curves start with  $Z = 1$  at  $P = 0$  and value of  $Z$  varies from unity as pressure increases in a manner dependent on temperature. As the temperature increases, the minimum in the curve (dip) becomes smaller and shifts towards lower pressure.





It is seen that in case of nitrogen when PV values are plotted against pressure at different temperatures, the shape of PV curve changes with temperature. In general the deviations are greater at higher pressures and near the temperature of liquefaction. Further it is also observed that nitrogen gas behaves like hydrogen gas at higher temperatures whereas at lower temperatures it behaves like  $\text{CO}_2$ .

An examination of the Fig. 3.8 also reveals that at  $50^\circ\text{C}$  the value of PV remains constant and is close to the value of the ideal gas for an appreciable range of pressure. In fact upto 100 atmospheres pressure, the compressibility factor (Z), changes from 1.0 to 1.02. Beyond 100 atm. the value of Z increases rapidly and attains values much greater than 1.

The temperature at which a real gas obeys the ideal gas law over an appreciable range of pressure is known as the *Boyle's temperature or the Boyle point*. It is so named because at this temperature Boyle's law is obeyed over a range of pressures. Obviously about the Boyle's temperature, a gas shows positive deviation only.

For every gas when the temperature is below the Boyle's temperature, the value of Z or PV will first decrease with increasing pressure, pass through a minimum and then increase continuously. But if the temperature is above the Boyle's point, Z or PV increases sharply, with increasing pressure and the values of Z are higher than unity.

The Boyle's temperature is different for different gases. Boyle's temperature for hydrogen and helium are  $-165^\circ\text{C}$  and  $-240^\circ\text{C}$  respectively. Hydrogen gas obeys Boyle's law at  $-165^\circ\text{C}$  for an appreciable range of pressure. Below this temperature plot of PV versus P will first show a fall and then a rise with the increase of pressure. Obviously, above the Boyle's temperature all gases show positive deviations.

From the above observations the following three points are evident:

- (i) **At low pressures**, the values of PV for all gases except hydrogen, helium and neon, are lower than those expected of an ideal gas.
- (ii) **At high pressures**, the value of PV for all gases including  $\text{H}_2$ , He, Ne, etc., are higher than those expected of an ideal gas.
- (iii) **Effect of temperature**: At a particular pressure the deviation of a gas from ideal behaviour is more pronounced at low temperature. The lower the temperature, the greater are the deviations.

### 3.5 CAUSES OF THE DERIVATIONS FROM IDEAL BEHAVIOUR

The failure of the ideal gas equation  $PV=RT$  over an extensive range of temperatures and pressures has been explained by Van der Waal's to be due to the following two faulty assumptions made in the kinetic theory:

- (i) The actual volume occupied by the gas molecules is negligible as compared to the total volume of the gas.
- (ii) The molecules exert no inter-molecular attraction among themselves.



Both these assumptions are not true, particularly at low temperature and high pressure. So, necessary correction to the ideal gas equation should be made.

### 3.6 VAN DER WAALS' EQUATION (REDUCED EQUATION OF STATE) (EQUATION OF STATE FOR REAL GASES)

Van der Waals' deduced a modified gas equation by making following necessary corrections to the gas equation  $PV = RT$ .

#### 1. Volume correction

The assumption that actual volume of the molecules is negligible, does not introduce any appreciable error at low pressures. At high pressure when the molecules are quite close together, the volume occupied by the molecules themselves becomes considerable fraction of the total volume occupied by the gas.

According to Van der Waal the actual free space available inside the vessel for the movement of the molecules is not  $V$ , the volume of the container, but  $(V-b)$ , where ' $b$ ' is the effective volume of the molecules. It can easily be shown that effective volume of molecules in motion is equal to about 4 times the actual volume of molecules at rest. The effective volume ( $b$ ) is also called *co-volume* or *excluded volume*.

Let us consider two molecules approaching each other. Let  $\delta$  and  $r$  represent the diameter and the radius of each molecule. The molecules cannot approach more closely than the distance  $\delta$  as shown in Fig. 3.9. It is because the molecules are impenetrable. It is clear from the figure that within a sphere of radius  $\delta$  ( $=2r$ ), no volume will be occupied by this pair of molecules. Thus:

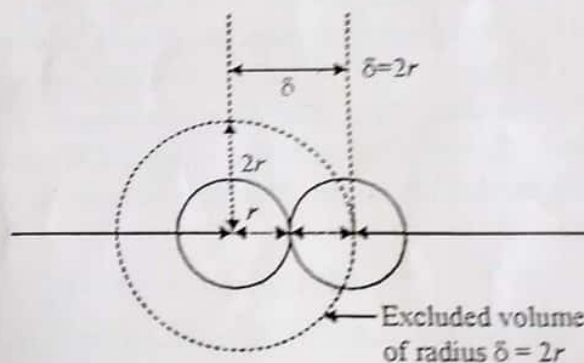


Fig. 3.9 Excluded volume of a pair of molecule

$$\text{The excluded volume per pair of molecules} = \frac{4}{3} \pi (2r)^3 = 8 \left( \frac{4}{3} \pi r^3 \right)$$

$$\text{So excluded volume for a single molecule} = \frac{8}{2} \left( \frac{4}{3} \pi r^3 \right) = 4 V_m$$

where  $V_m$  is the volume occupied by a single molecule.

Thus the excluded volume ( $b$ ) for a mole of a gas is given as :

$$b = 4 \left( \frac{4}{3} \pi r^3 \right) \times N = 4 V_m N$$

where  $N$  being the Avogadro's number.

Hence, the corrected volume =  $(V-b)$

where  $b$  is the volume to be excluded which is four times the actual volume of the molecules and it is a characteristic constant for each gas.

## 2. Attraction correction – Pressure correction

The assumption that molecules exert no appreciable intermolecular attraction is not justified especially at high pressure when the molecules are quite close together.

Consider particles A and B in the gas Fig. 3.10. The net force of intermolecular attraction on particle 'A' situated in the interior of the gas is nil, because it is surrounded by molecules which are equally distributed in opposite directions, thereby the attractions on all sides are mutually cancelled.

However, molecule 'B' just near the boundary which is about to strike the wall, is subjected to a net inward force of attraction or pull due to the interior molecules. So, when a molecule is about to strike the wall, this inward pull act, so as to reduce the force exerted by the impact and consequently the measured pressure  $P$  is less than the ideal pressure, i.e. when no attraction were there. The observed pressure is thus less than that would be expected from the Kinetic theory. This will tend to make  $PV$  less than  $RT$  and so will tend to cause a negative or under perfect deviation. Hence, a correction term  $p_a$  should be added to  $P$  to get ideal pressure.

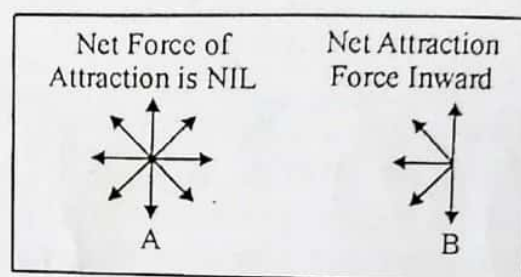


Fig. 3.10. Molecular attraction

$$\text{Ideal pressure} = P + p_a$$

The inward force,  $p_a$  exerted on molecules about to strike the walls of the vessel is proportional to:

- (i) The number of molecules striking the wall at any given instant, which is proportional to the density of the gas.
- (ii) The number of molecules in the interior which are attracting the striking molecules, which is also proportion to the density of the gas.

$$\therefore p_a \propto d^2$$

$$\text{But density} \propto \frac{1}{\text{volume}}$$

$$\therefore p_a \propto \frac{1}{V^2}$$



$$\therefore P_a = \frac{a}{V^2}$$

where 'a' is a proportionality constant, called *co-efficient of attraction*.

$$\text{Hence, ideal pressure} = \left( P + \frac{a}{V^2} \right)$$

Incorporating the volume correction and attraction correction (or pressure correction) in the gas equation, we get:

$$(V-b) \left( P + \frac{a}{V^2} \right) = RT \quad \dots(3.1)$$

This modified gas equation is called the Van der Waals' Equation of state as it was first established by J.D. Van der Waals' - a Dutch chemist in 1873. It represents the behaviour of real gases over a wide range of temperature and pressure for one mole of gases.

If there are  $n$  moles of the gas occupying volume  $V$ , then the effective volume of the molecules is given by  $nb$  and the actual free space available inside the vessel for the movement of the molecules is then  $V-nb$ .

The pressure correction  $P_a \propto n^2 d^2$

$$\propto n^2 \frac{1}{V^2}$$

$$P_a = \frac{n^2 a}{V^2}$$

Therefore, the Van der Waal's equation for  $n$  moles of a gas will be

$$\left( P + \frac{n^2 a}{V^2} \right) (V-nb) = nRT \quad \dots(3.2)$$

### 3.6.1 Units of Van der Waals' Constants

The units for Van der Waals' constants  $a$  and  $b$  depends on the units in which  $P$  and  $V$  are expressed.

$$\text{From equation } P_a = \frac{an^2}{V^2}$$

$$\therefore a = \frac{P_a V^2}{n^2}$$

$$\text{or } a = \frac{\text{Pressure} \times (\text{Volume})^2}{(\text{moles})^2}$$

If pressure is expressed in atmospheres and volume in litres,  $a$  will be expressed in atm. litre<sup>2</sup> mole<sup>-2</sup>.

In SI Units: Now volume correction for  $n$  moles of a gas is  $nb$

$$\text{Volume correction} = nb$$

$$\therefore b = \frac{\text{Volume}}{n}$$

In SI Units: If volume is expressed in litres, the units of  $b$  are litre  $\text{mol}^{-1}$ .

### 3.6.2 Significance of Van der Waals' Constant

The gases such as  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{HCl}$  which can be easily liquefied, have high values of Van der Waals' constant  $a$  and  $b$  and show maximum departure from the ideal gas equation.

The Van der Waals' constant ' $a$ ' is a measure of strength of the Van der Waals' force between the molecules of the gas. Greater the magnitude of  $a$ , stronger are the Van der Waals' forces. The greater the magnitude of these, forces, i.e.,  $a$ , greater is the ease with which gas can be liquefied.

The Van der Waals' constant ' $b$ ' represents effective volume of gas molecules. It has been observed that its value remains constant over a wide range of temperature and pressure for a gas. This shows that gas molecules are incompressible.

### 3.7 EXPLANATION OF BEHAVIOUR OF REAL GASES ON THE BASIS OF VAN DER WAALS' EQUATION

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \quad \dots \text{Van der Waals' equation of state.}$$

$$\text{or} \quad PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

Neglecting  $\frac{ab}{V^2}$ , a product of two very small quantities, we get

$$\text{or} \quad PV - Pb + \frac{a}{V} = RT = P'V' \quad \dots(3.3)$$

where  $P'$  and  $V'$  are the ideal pressure and ideal volume of the gas respectively.

(i) **At low pressure:** At lower pressure the gas has a large volume and volume taken up by the molecules is relatively unimportant. Small addition of pressure due to mutual attraction plays an important part while  $b$  is negligible as compared to the large total volume  $V$ . The factor

$$\frac{a}{V}, \text{ therefore, overweight } Pb \text{ i.e. } \frac{a}{V} > Pb$$

$$\text{Let} \quad \frac{a}{V} - Pb = Z, \text{ positive quantity}$$

From equation (3.1), we get



$$PV - Z = RT = P' V'$$

$$PV = RT - Z = P' V' - Z$$

i.e., the observed  $PV$  is less than  $P' V'$ .

The observed product  $PV$  at low pressure is less than  $P' V'$ , product of pressure and volume if the gases were ideal. Thus the intermolecular attractive forces cause a *negative or under perfect deviation*.

At low pressures, therefore,  $PV$  decreases with increase in pressure in case of  $N_2$ ,  $O_2$  and  $CO_2$ , etc.

(ii) **At high pressure:** When the pressure is high, the volume is small and small volume occupied by molecules themselves cannot be neglected, whereas in comparison with the high pressure, small addition of pressure due to mutual attraction is negligible. Hence  $Pb$  over weights

$$\frac{a}{V}, \text{ i.e. } Pb > \frac{a}{V}$$

$$\text{i.e. } \frac{a}{V} - Pb = -y, \text{ a negative quantity}$$

$$PV + (-y) = P' V' \quad \text{or} \quad PV - y = P' V'$$

$$PV = P' V' + y$$

i.e., the observed  $PV$  is greater than the value expected from an ideal gas. The volume occupied by the gas molecules cause a *positive or over perfect deviation*.

This explains the fact that  $PV$ , after reaching a minimum, increases with further increase in pressure.

(iii) **At extremely low pressures and high temperatures:** When  $P$  is very small,  $V$  will be very large. In this case both the correction terms  $\frac{a}{V^2}$  and  $b$ , in the Van der Waals' equation are negligibly small in comparison to  $P$  and  $V$  and the equation reduces to  $PV = RT$  the equation for an ideal gas. Similarly, when the temperature is very high,  $V$  will be very large (since volume  $\propto$  temperature) or  $P$  will be very small and again  $PV = RT$  is obtained. Thus, at extremely low pressures and high temperatures, all real gases obey the ideal gas laws.

(iv) **At ordinary (medium) pressure:** We have seen that at ordinary temperature, the factor  $\frac{a}{V^2}$  predominates at low pressure, whereas the factor  $Pb$  predominates at high pressures.

Therefore, these two factors will balance each other at some intermediate range of pressures in which the gas will show the ideal behaviour.

$$\text{Thus at medium pressure, } Pb = \frac{a}{V}$$

The equation (3.3) is reduced to  $PV = RT = P' V'$

and the gas behaves like an ideal gas.

(v) **At high temperature:** At high temperatures,  $V$  is very large and hence both  $Pb$

and  $\frac{a}{V}$  will be negligibly small, so that we have  $PV = RT = P' V'$

i.e., at high temperatures the behaviour of a real gas nearly agrees with that expected for ideal gas.

(vi) **At low temperature:** Both  $P$  and  $V$  are small, hence, both pressure (attraction) and volume corrections are appreciable, with the result that the deviations are more pronounced.

(vii) **Exceptional behaviour of hydrogen and helium:** The molecules of these gases are of very small mass and consequently the force of attraction between the molecules is always negligible.

Thus neglecting the term  $\frac{a}{V}$  the equation (3.3) is reduced to

$$PV - Pb = RT = P' V'$$

$$PV = P' V' + Pb.$$

i.e., the product  $PV$  is greater than  $P' V'$  even at low pressures.

### Solved Numerical Problems

**Example 1.** Using Van der Waal's equation, calculate the pressure exerted by one mole of carbon dioxide. When it occupies a volume of 0.05 litre at  $100^\circ\text{C}$ , given that  $a = 3.592$ ,  $b = 0.0426$  and  $R = 0.0821$  litre atmosphere/ degree mole.

**Solution.** It is given that,  $n = \text{one mole}$ ,  $V = 0.05$  litre

$$a = 3.592 \text{ atms. litre}^2 / \text{mole}^{-2},$$

$$b = 0.0426 \text{ litre/ mole}$$

$$R = 0.0821 \text{ litre atmosphere/ degree / mole}$$

$$T = 100^\circ\text{C} + 273 = 373^\circ\text{A}$$

Van der Waal's equation, for one mole

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P + \frac{a}{V^2} = \frac{RT}{V - b}$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$



and is, therefore, called *isotherm*. The curves should be rectangular hyperbolas like that expected for an ideal gas. It is quite clear that  $\text{CO}_2$  does not give rectangular hyperbolas although with increasing temperature the curves approximate to one. Let us consider the various isotherms separately.

- (i) **Isotherm at  $0^\circ\text{C}$ :** The isotherm shows that carbon dioxide is entirely gaseous at low pressures and the volume decreases with increasing pressure in the normal fashion.

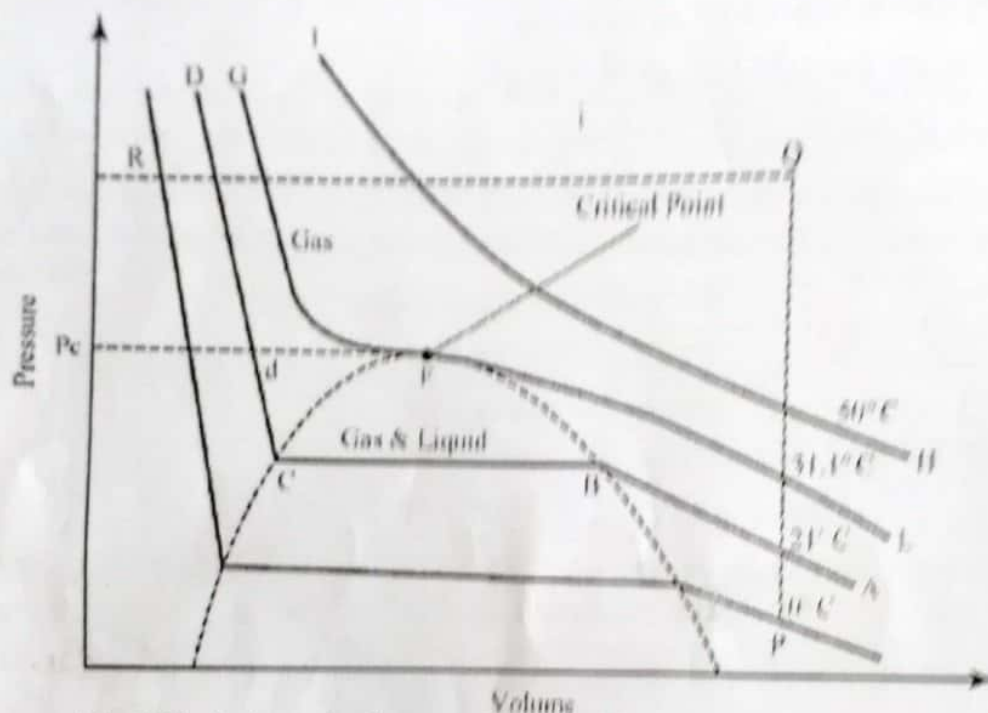


Fig. 3.11. Andrews isotherms of  $\text{CO}_2$  at different temperatures

- (ii) **Isotherm below  $31^\circ\text{C}$ :** The isotherm below  $31^\circ\text{C}$  is not continuous. For example, in the isotherm of  $21^\circ\text{C}$ , the point A corresponds to gaseous  $\text{CO}_2$  occupying a certain pressure. At low pressures, if the pressure is increased, the volume decrease as indicated by the curve AB.

At B liquefaction commences; vapour is converted into liquid of very much greater density and the decrease suddenly as the volume occupied by a liquid is much less than that of BC is approximately parallel to the volume axis indicating the sudden decrease in volume taking place at the same pressure.

Liquefaction is complete at C and CD shows the small effect of pressure on a liquid. The steep line CD which is almost vertical represents the compressibility of a liquid and shows that the liquids are much less compressible, i.e., increase in pressure produces a very small decrease in volume.

To summarize, along curve AB there is only vapour, along CD only liquid and along BC liquid and vapour co-exists. Since BC is parallel to the volume axis, there can be only one pressure at which liquid and vapour co-exists. This pressure is called vapour pressure of the gas.

(iii) Isotherm at  $31^{\circ}\text{C}$ : As the temperature is raised, this horizontal portion becomes less and less till at  $31.1^{\circ}\text{C}$ ; it reduces almost to a point F. Above this temperature, there is no trace of horizontal portion, i.e., beyond  $31.1^{\circ}\text{C}$ , there is no indication of liquefaction at all. Point F is the critical point for  $\text{CO}_2$ . The distinction between liquid and vapour state disappears at this point and  $\text{CO}_2$  exists in a state called the *critical state*. The isotherm passing through critical point is called the *critical isotherm*.

(iv) Isotherm above  $31^{\circ}\text{C}$ : If the temperature was beyond  $31.1^{\circ}\text{C}$ ,  $\text{CO}_2$  could not be liquefied. Yet Andrews applied a pressure of 300-400 atm. However, at  $21^{\circ}\text{C}$ , only a pressure of 75 atm was quite sufficient to liquefy  $\text{CO}_2$ .

From the experiment, Andrews concluded that if the temperature of  $\text{CO}_2$  is above  $31.1^{\circ}\text{C}$ , it cannot be liquefied no matter how high the pressure may be. This maximum temperature ( $31.1^{\circ}\text{C}$ ) at which liquefaction can be brought about is called critical temperature. The pressure required to liquefy a gas at the critical temperature is known as the critical pressure. If the temperature happens to be below the critical temperature, the gas will liquefy at a somewhat lower pressure. All other gases have been found to behave similarly. The critical phenomenon observed by Andrews for  $\text{CO}_2$  may be observed for any gas.

### 3.9 PRINCIPLE OF CONTINUITY OF STATES

Let us refer back to the isotherms plotted in Fig. 3.11. The dome-shaped curve shown by the dashed line connects the end points of the horizontal portions of the isotherms. Since a horizontal portion represents two phases in equilibrium, all points inside the dome correspond to equilibrium between liquid and vapour. For such points, it is always possible to draw any sharp distinction between liquid and vapour, since there is a definite boundary surface between the two phases. For points lying outside the dome, only one phase (liquid or vapour) is present, and here it is not possible to draw any sharp distinction between liquid and vapour.

Actually there is no dividing line between the liquid and the gaseous states and there is a gradual transition from gas to liquid and vice versa without any abrupt change in state. The fact that it is not possible to make distinction between a gas and a liquid is known as the *principle of continuity of state*. The distinction between gas and liquid is possible only within the dome area when both are present in equilibrium and there is boundary surface. In the absence of this boundary, no fundamental distinction between gas and liquid is possible.

When a gas is compressed at a temperature below its critical temperature, its volume is decreased, i.e., the free space between the molecules is decreased and the inter-molecular forces are increased. Consequently, the gaseous state changes to the liquid state. Therefore, the liquid state is only a continuation of the gaseous state into a region of low volume and high inter-molecular forces of attraction. Below the critical temperature whenever gaseous state is changed to liquid state, we have to pass through a stage when both the liquid and the gaseous states change into liquid state and vice versa without passing through a stage in which both the phases are present together.

In this transition, the continuity of state is said to be maintained. This can be done as follows. Consider a certain volume of  $\text{CO}_2$  gas represented by a first point P on the isotherm.



Let us increase the pressure of the gas at constant volume from point P to point Q by increasing the temperature. After arriving at point Q, the volume is decreased at constant pressure along the line QR by decreasing the temperature. At R, the temperature is again  $31.1^{\circ}\text{C}$ , but  $\text{CO}_2$  exists as liquid; there has never been more than one phase present at any time. The volume of the gas decreases gradually, as the temperature is decreased from Q to R. Ultimately, the molecules are so close that the inter-molecular forces of attraction become strong enough to cause their condensation into the liquid state. Thus, it is not always possible to distinguish a gas from a liquid and the conversion of gas to liquid or vice-versa is continuous. *Therefore, the liquid state may be taken as highly compressed gaseous state.*

### 3.10 CRITICAL CONSTANTS

- (i) **Critical temperature of a gas ( $T_c$ )** is the minimum temperature which must be reached before the gas can be liquefied by the application of pressure. A gas cannot be liquefied by pressure above its critical temperature, no matter how high the applied pressure may be. Each gas has a definite critical temperature, e.g.,  $T_c$  of  $\text{CO}_2$  is  $31.1^{\circ}\text{C}$  or  $304.1\text{ K}$ .
- (ii) **Critical pressure of gas ( $P_c$ )** is the minimum pressure necessary for the liquefaction of a gas at critical temperature, e.g.,  $P_c$  for  $\text{CO}_2$  is  $72.9\text{ atm}$ .
- (iii) **Critical volume of a gas ( $V_c$ )** is the volume occupied by one mole of the gas or liquid under critical pressure and under critical temperature e.g.,  $V_c$  for  $\text{CO}_2$  is  $95.65\text{ ml}$ .

From Andrews experiment, very useful conditions for the liquefaction of a gas may be stated as:

- (a) *The temperature must be at or below the critical temperature.*
- (b) *A suitable pressure must be applied equal to the critical pressure if the temperature is at the critical temperature but becoming less if the temperature is reduced below this value.*

#### 3.10.1 Relations Between van der Waals' Constants and Critical Constants

A very good confirmation of the general character of Van der Waals' equation is furnished by its application to critical phenomenon.

The Van der Waals' equation is

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \quad (\text{putting } n=1)$$

Alternatively,  $PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$

Multiplying throughout by  $V^2$ , we get

$$PV^3 + aV - PbV^2 - ab = RTV^2$$

$$PV^3 + aV - PbV^2 - RTV^2 = 0$$

Arranging in descending powers of V

$$PV^3 - PbV^2 - RTV^2 + aV - ab = 0$$

Dividing by P, we get

$$V^3 - bV^2 - \frac{RTV^2}{P} + \frac{aV}{P} - \frac{ab}{P} = 0$$

$$V^3 - V^2 \left( b + \frac{RT}{P} \right) + \frac{aV}{P} - \frac{ab}{P} = 0 \quad \dots(3.4)$$

This is a third-degree equation in terms of V (cubic equation in V) and below a certain value of temperature T, the equation can have three real roots. With the rise of temperature, these roots approach one another and become identical ultimately. This can be easily understood if we plot a theoretical P - V graph from the Van der Waals' equation. The curves obtained are of the type ABLMNCD as shown in the Fig. 3.12.

The three real unequal roots correspond to point B, M and C. The points B and C represent saturated vapour and liquid, respectively, but M has no physical significance. As the temperature rises, the S-shaped dotted portion of the curve gets reduced to a point. The values for the volume of liquid and gas approach each other until at this point, the three values of V become identical. This point corresponds to the critical temperature and the volume V. At the critical point, then the three roots of the Van der Waals' equation become identical and equal to V.

Since this is the value of the three roots of the Van der Waals' equation at the critical point,

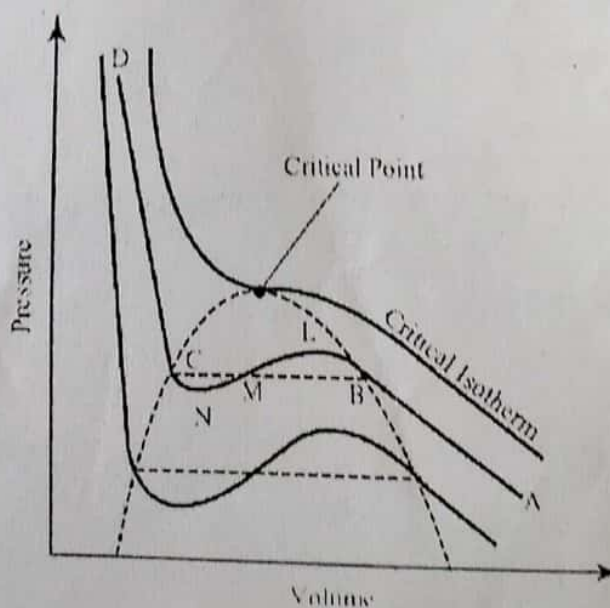


Fig. 3.12. Isotherms of  $\text{CO}_2$  from Van der Waals' equation



$$(V - V_c)^3 = 0$$

$$\text{or } V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad \dots(3.5)$$

Under critical conditions,  $T = T_c$  and  $P = P_c$ .

Substituting these values in equation (3.4),

$$V^3 - V^2 \left( b + \frac{RT_c}{P_c} \right) + \frac{V_a}{P_c} - \frac{ab}{P_c} = 0 \quad \dots(3.6)$$

As both the (3.5) and (3.6) are identical, then, the coefficients of the equal powers of  $V$  in the two equations may be equated as

$$3V_c = b + \frac{RT_c}{P_c} \quad \dots(3.7)$$

$$3V_c^2 = \frac{a}{P_c} \quad \dots(3.8)$$

$$V_c^2 = \frac{ab}{P_c} \quad \dots(3.9)$$

Dividing equation (3.9) by equation (3.8), we get

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} \times \frac{P_c}{a} \quad \text{or} \quad \frac{V_c}{3} = b$$

$$\text{or } \boxed{V_c = 3b} \quad \dots(3.10)$$

Substituting the value of  $V$  from equation (3.4) in equation (3.2), we get

$$\frac{a}{P} = 3 \times (3b)^2 = 27b^2$$

$$\text{or } \boxed{P = \frac{a}{27b^2}} \quad \dots(3.11)$$

Substituting the values of  $V_c$  and  $P_c$  in equation (3.1), we get

$$3 \times 3b = b + RT_c \times \frac{27b^2}{a} \quad \text{or} \quad 9b = b + RT_c \times \frac{27b^2}{a}$$

$$\text{or } 8b = RT_c \times \frac{27b^2}{a} \quad \text{or} \quad T_c = 8b \times \frac{a}{27b^2} \times \frac{1}{R}$$

$$\text{Alternatively, } \boxed{T_c = \frac{8a}{27bR}} \quad \dots(3.12)$$

$$(V - V_c)^3 = 0$$

$$\text{or } V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad \dots(3.5)$$

Under critical conditions,  $T = T_c$  and  $P = P_c$ .

Substituting these values in equation (3.4),

$$V^3 - V^2 \left( b + \frac{RT_c}{P_c} \right) + \frac{V_c}{P_c} - \frac{ab}{P_c} = 0 \quad \dots(3.6)$$

As both the (3.5) and (3.6) are identical, then, the coefficients of the equal powers of  $V$  in the two equations may be equated as

$$3V_c = b + \frac{RT_c}{P_c} \quad \dots(3.7)$$

$$3V_c^2 = \frac{a}{P_c} \quad \dots(3.8)$$

$$V_c^2 = \frac{ab}{P_c} \quad \dots(3.9)$$

Dividing equation (3.9) by equation (3.8), we get

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} \times \frac{P_c}{a} \quad \text{or} \quad \frac{V_c}{3} = b$$

$$\text{or } \boxed{V_c = 3b} \quad \dots(3.10)$$

Substituting the value of  $V$  from equation (3.4) in equation (3.2), we get

$$\frac{a}{P} = 3 \times (3b)^2 = 27b^2$$

$$\text{or } \boxed{P = \frac{a}{27b^2}} \quad \dots(3.11)$$

Substituting the values of  $V_c$  and  $P_c$  in equation (3.1), we get

$$3 \times 3b = b + RT_c \times \frac{27b^2}{a} \quad \text{or} \quad 9b = b + RT_c \times \frac{27b^2}{a}$$

$$\text{or } 8b = RT_c \times \frac{27b^2}{a} \quad \text{or} \quad T_c = 8b \times \frac{a}{27b^2} \times \frac{1}{R}$$

$$\text{Alternatively, } \boxed{T_c = \frac{8a}{27bR}} \quad \dots(3.12)$$



### 3.10.2 Derivation of $P_c V_c = \frac{3}{8} RT_c$ from Van der Waal's Equation

From Van der Waal's equation, we have

$$V^3 - V^2 \left( b + \frac{RT_c}{P_c} \right) + V \frac{a}{P_c} - \frac{ab}{P_c} = 0 \quad \dots(3.13)$$

In addition,  $V_3 - 3 V_c V^2 + 3 V_c^2 V - V_c^3 = 0 \quad \dots(3.14)$

Equating the coefficients of equation (3.13) and (3.14), we get

$$3 V_c = \frac{RT_c}{P_c} + b \quad \dots(3.15)$$

$$3 V_c^2 = \frac{a}{P_c} \quad \dots(3.16)$$

$$V_c^2 = \frac{ab}{P_c} \quad \dots(3.17)$$

Dividing equation (3.17) by (3.16), we get

$$V_c = 3b \quad \text{or} \quad b = \frac{1}{3} V_c \quad \dots(3.18)$$

Substituting the values of  $b$  in equation (3.15), we get

$$3 V_c = \frac{RT_c}{P_c} + \frac{V_c}{3} \quad \text{or} \quad 3 V_c - \frac{V_c}{3} = \frac{RT_c}{P_c}$$

$$\text{or} \quad \frac{9 V_c - V_c}{3} = \frac{RT_c}{P_c} \quad \text{or} \quad \frac{8}{3} V_c = \frac{RT_c}{P_c}$$

$$\text{or} \quad \boxed{P_c V_c = \frac{3}{8} RT_c} \quad \dots(3.19)$$

### 3.10.3 Calculation of Van der Waal's Constants in terms of $T_c$ and $P_c$

Rearranging equation (3.19), we get

$$V_c = \frac{3}{8} \times \frac{RT_c}{P_c}$$

Squaring, we get

$$V_c^2 = \frac{9}{64} \times \frac{R^2 T_c^2}{P_c^2} \quad \dots(3.20)$$

Substituting the value of  $V_c^2 = \frac{a}{3P_c}$  from equation (3.16) in equation (3.20), we get

$$\frac{a}{3P_c} = \frac{9}{64} \times \frac{R^3 T_c^2}{P_c}$$

$$a = \frac{27 R^3 T_c^2}{64 P_c}$$

....(3.21)

Substituting the value of  $V_c = 3b$  in equation (3.15), we get

$$9b = \frac{R T_c}{P_c} + b \quad \text{or} \quad 8b = \frac{R T_c}{P_c}$$

or

$$b = \frac{R T_c}{8 P_c}$$

....(3.22)

### 3.11 POTENTIAL ENERGY SURFACE