

## 1.5.0 COLLISION DIAMETER, COLLISION FREQUENCY, COLLISION NUMBER AND MEAN FREE PATH:

### Introduction:

In the kinetic molecular theory of gases, we come to know that the molecules of a gas are moving randomly, colliding among themselves and with the walls of the vessel. During the collisions, they suffer a change in their directions and also change their velocities. The time for which the two molecules are in contact at the time of collision is called compression time.

Since, we are going to discuss the frequency of the collisions and the free path in between the collisions, so first of all we should know about the nature of the collisions.

The collisions are of three types.

#### (i) Grazing Collision or Glancing Collision: (چھو کے گزرنے سے ٹکر)

"In these collisions, the molecules are moving just parallel to each other, with the average velocity ( $\bar{c}$ ) and their outer boundaries touch each other." The following diagram shows the grazing collisions. Fig. (1.4 a)

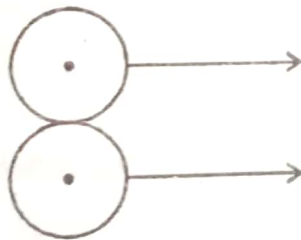


Fig. (1.4 a) Grazing collision (relative velocity  $\bar{c}$ ).

#### (ii) Head on Collision:

"When two molecules approach each other on a straight line, then they collide head to head and the collision is head on." The approaching molecules retrace the straight line path in the reverse direction. The relative speed becomes  $2\bar{c}$ . Following diagram (1.4 b) shows the head on collision.

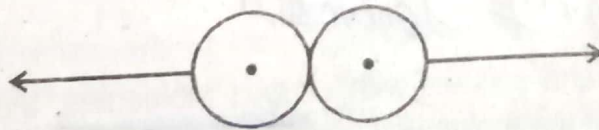


Fig. (1.4 b) Head on collision (relative velocity  $2\bar{c}$ ).

#### (iii) Right Angled Collision:

When two molecules approach each other and their approaching lines are approximately  $90^\circ$  to each other. Then the collision is right angled. The relative speed is ' $\sqrt{2}\bar{c}$ '. Following diagram (1.4 c) shows this collision

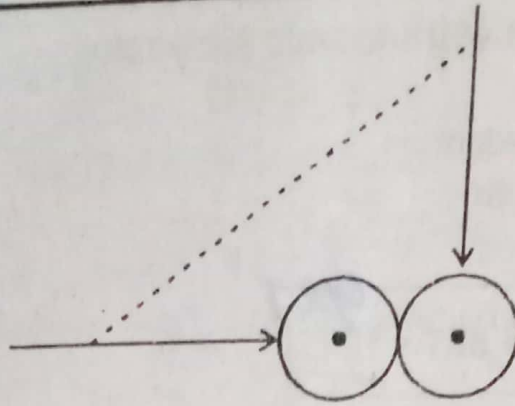


Fig. (1.4 c) Right-angled collision (relative velocity  $\sqrt{2c}$ )

**Elastic Collision (چک دار ٹکراؤ):**

During the collisions there happens a change in the direction of the motion but total energy remains the same. **The collisions in which there is no net loss or gain of energy are called elastic collisions.**

**1.5.1 Collision Diameter:**

In order to do the collision, the molecules approach each other. At the time of contact of their outer boundaries, there is a limit beyond which they cannot come close to each other. This is called the distance of closest approach. **"The closest distance between the centers of two molecules taking place during collision is called collision diameter."** Collision diameter is represented by  $\sigma$  Fig. (1.5)

(ٹکراؤ کے دوران دونوں مالیکیولز کے سنٹرز کا درمیانی فاصلہ  $\sigma$  سے ظاہر کیا جاتا ہے)

The following diagram shows that the collision diameter is equal to the sum of radii of the two particles.

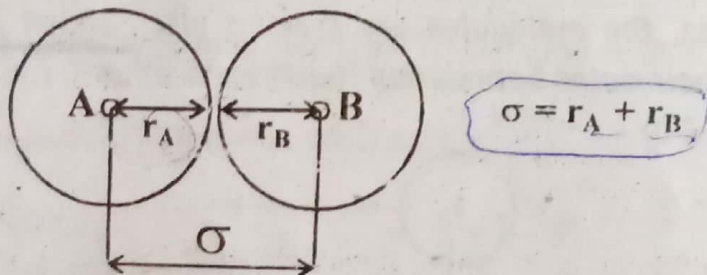


Fig. (1.5) Collision diameter of two colliding molecules

**1.5.2 Collision Frequency ( $Z_1$ ):**

"If we follow a single molecule in one  $cm^3$  of the gas, and want to observe that, how many collisions are being faced by this molecule in one second, then it will be collision frequency of that molecule." It is denoted by  $Z_1$ . Its value should depend upon the velocity of gas molecules, sizes of molecules and closeness of the molecules in the vessel.

Collision کو  $Z_1$  کہا جاتا ہے۔  $Z_1$  کے ساتھ جتنی ٹکرائیں مارتا ہے۔  $Z_1$  کہلاتا ہے۔

**1.5.3 Mean Free Path ( $\lambda$ ):**

frequency کہتے ہیں۔

When a molecule travels and collides with various molecules, then it travels free path in the vessel. Anyhow, all the free paths of the molecules are not equal. So, if we take the average of all these free paths, then we get the mean free path. **"Hence, mean free path is average distance covered by a molecule between two successive collisions."** It is denoted by ' $\lambda$ '.

ایک مالیکیول کے کوئی سے دو تصادم کے درمیان جو فاصلہ ہوتا ہے وہ آزاد فاصلہ کہلاتا ہے۔ اگر آپ بہت سے آزاد فاصلے ماپ لیں۔ وہ تمام فاصلوں کے اوسط (Average) ہے۔ اسے Mean free path کہتے ہیں۔

Mathematically, ' $\lambda$ ' is related to the mean distance travelled by the molecule in one second and its number of collisions per second.

$$\lambda = \frac{\text{mean velocity of molecule}}{\text{collision frequency}}$$

$$\lambda = \frac{\bar{c}}{Z_1}$$

..... (1)

#### 1.5.4 Collision Number ( $Z_{11}$ ):

"It is the number of collisions happening in all the molecules in  $1 \text{ cm}^3$  of the gas in one second." It is denoted by ' $Z_{11}$ '. Mathematically, we can say that,

' $nZ_1$ ', is divided by 2, so that each collision may not be counted twice.

ایک سی سی گیس کے اندر تمام مالیکیولز حرکت پذیر ہیں۔ لہذا سب تصادم کرنے میں مصروف ہیں۔ ایک سیکنڈ میں ان تمام تصادموں کو  $Z_{11}$  سے ظاہر کرتے ہیں۔  $Z_{11}$  کو Collision number کہتے ہیں۔

$$Z_{11} = \frac{nZ_1}{2}$$

..... (2)

#### 1.5.5 Derivation For the Expression of Collision Frequency ( $Z_1$ ):

Anyhow, it has been observed that the most common gases like  $H_2$ ,  $N_2$ , He,  $CO_2$  etc. do not follow the straight line as shown in the diagram (1.11). It means that the product of  $P$  and  $V$  does not remain constant, at constant temperature.

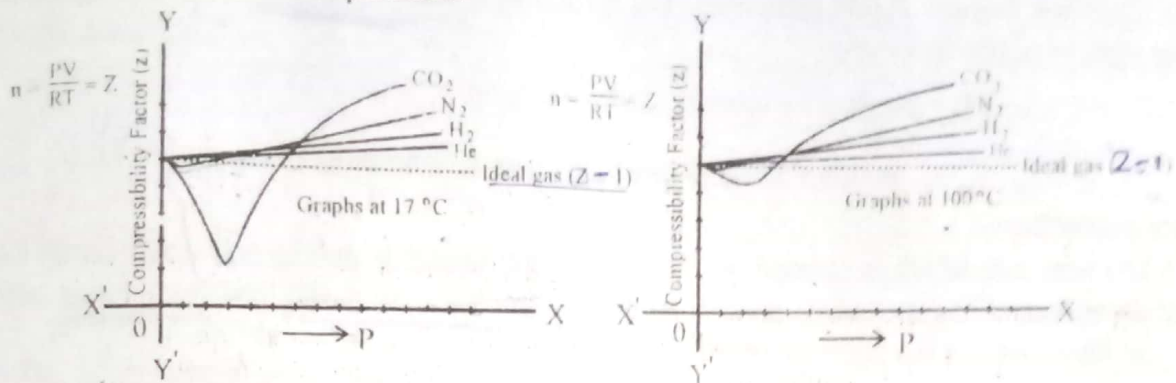


Fig. (1.11) Graphical explanation of effect of pressure and temperature on compressibility factor  $Z = \frac{PV}{RT}$

The graphs of the gases at  $17^\circ C$ , show more deviations from ideal behaviour than at  $100^\circ C$ . Moreover, the extent of deviation (انحراف کی حد) of these gases are more prominent (زیادہ نمایاں) at high pressures. We draw the important conclusion from the above graphs.

- (i) The gases are comparatively ideal at high temperature and low pressures.
- (ii) The gases become non-ideal at low temperature and high pressures.

1.7.1 Causes For Deviation From Ideality:

Kinetic theory is the foundation stone of all the gas laws and the general gas equation. There are two faulty assumptions (نقص دار مفروضے) in the kinetic theory of gases.

Let us recall these faulty assumptions and then try to find the remedy (تلافی) for them.

- (i) Actual volume of gas molecules is negligible (نظر انداز کرنے کے قابل) as compared to the volume of the vessel.
- (ii) There are no forces of attractions among the molecules of gases.

Both these postulates are correct, at low pressures and high temperatures and these postulates become wrong at low temperatures and high pressures. *molecules spread → volume negligible* (اس کا مطلب تو یہ ہوا کہ یہ مفروضے کبھی حقیقت کے قریب ہوتے ہیں اور کبھی دور ہوتے ہیں۔)

Actually, low temperature and high pressure become responsible (ذمہ دار) for creation of forces of attractions and moreover, actual volume does not remain negligible.

It is necessary to account for (حساب دینا) the actual volume and mutual attractions of molecules.

This job was done by Van der Waal.

1.7.2 Van der Waal's Equation:

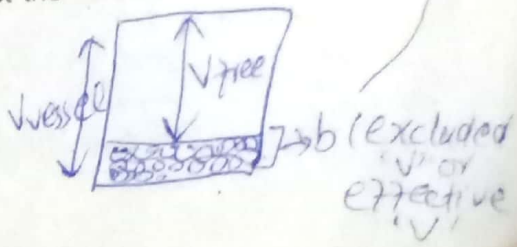
Van der Waal modified (ترمیم کرتا) the general gas equation and performed the corrections i.e., volume correction and pressure correction. *Volume occupied by gas molecules in highly compressed state but not in liquid state*

Volume correction:

Van der Waal thought that some of the volume of the vessel is occupied by the molecules of the gas and that volume is not available (میسر ہوتا) for the free movement of the molecules. Actually, we need the free volume of the gas and that is obtained when we subtract the volume of molecules from the volume of the vessel.

$$V_{free} = V_{vessel} - V_{molecule} / b$$

Let ' $V_{free}$ ' is ' $V$ ' and ' $V_{molecule}$ ' is ' $b$ ' for one mole of a real gas.



$$\text{So, } V = V_{\text{vessel}} - b \quad \dots \dots (1)$$

This 'b' is called **effective volume** (متاثر کرنے والی جسامت) of gas molecules. Keep it in mind that 'b' is not the actual volume of gas molecules, but is roughly equal to 4 times their molar volumes. If we have one mole of a gas, then

$$b = 4V_m$$

$V_m$  = actual volume of gas molecules for one mole of the gas.

### Pressure correction:

The pressure which is exerted on the walls of the vessel is due to collisions. Since there are attractive forces, so the molecules can not hit the walls of the vessel with that much force, with which they should have been in the absence of attractive forces.

گیس کے مالیکیولز اتنی قوت سے دیواروں کو ٹکریں نہیں مار سکتے جتنے گیس کی آئیڈیل حالت میں انہوں نے کرنا تھا۔

It means that the pressure being observed on the walls of the vessel is a little bit less than the ideal pressure.

$$P_{\text{observed}} = P_{\text{ideal}} - P_{\text{lessened}}$$

The pressure which is being lessened (کم ہو رہا ہے) is denoted by  $P'$ .

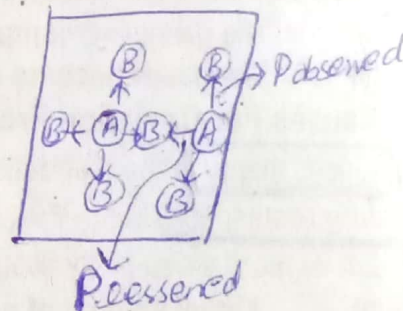
Let us say that  $P_{\text{observed}} = P$  and  $P_{\text{lessened}}$  is denoted by  $P'$ .

$$P = P_i - P'$$

$$P_i = P + P'$$

The value of  $P'$  given by Van der Waal is  $\frac{a}{V^2}$ .

$$P' = \frac{a}{V^2}$$



In order to estimate (اندازہ لگانا) the value of  $P'$  which is lessened (کم ہو گیا) pressure, we proceed as follows.

Suppose we have two types of molecules A and B. Let the concentrations of A and B type molecules are  $C_A$  and  $C_B$ . The force of attraction between A and B is proportional to  $C_A$  and  $C_B$ . So,

$$P' \propto C_A C_B$$

Now suppose that "n" is the number of moles of A and B separately. Hence  $\frac{n}{V}$  is the number of moles  $\text{dm}^{-3}$  of A and B separately. "V" is the volume of the vessel containing the gas. So,

$$P' \propto \frac{n}{V} \cdot \frac{n}{V}$$

$$P' \propto \frac{n^2}{V^2}$$

$$P' = \frac{an^2}{V^2}$$

where  $a$  = constant of proportionality

If the number of moles of gas is unity, then  $n = 1$

$$P' = \frac{a}{V^2}$$

Pressure of the ideal gas  $P_i = P + P'$

$$\text{So, } P_1 = P + \frac{a}{V^2} \quad \dots\dots (2)$$

'a' is the co-efficient of attraction. In other words, it is attraction per unit volume and is a constant for a particular real gas.


Introducing these corrections, the general gas equation is modified.

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

For 'n' moles of a gas,

$$\left( P + \frac{a n^2}{V^2} \right) (V - nb) = nRT \quad \dots\dots (4)$$

'a' and 'b' are called Van der Waal's constants.

Born	23 November 1837, Leiden, Netherlands	
Nationality	Netherlands	
Fields	Physics	
Institutions	University of Amsterdam	
Alma mater	University of Leiden	
Known for	Equation of state, intermolecular forces	
Notable awards	Nobel Prize for Physics (1910)	
Died	8 March 1923 (aged 85)	Johannes van der Waals

### 1.7.3 Nature of Van der Waal's Constants:

These constants 'a' and 'b' are the quantitative measurement (مقدار کے پیش نظر پیمائش) of non-ideality of the gases. They are usually determined experimentally by measuring the deviation from the real gas equation, under suitable conditions of temperature and pressures i.e., those conditions when the effects of molecular volume and mutual attractions predominate (باہمی کششوں کا غالب آنا).

The values of 'a' and 'b', depend upon the nature of the gas and the units of volume and temperature. Table (1.3)

Units of 'a' and 'b':

The units of Van der Waal's constant are derived as follows.

$$\text{Since, } P = \frac{a n^2}{V^2}$$

$$a = \frac{P V^2}{n^2} = \frac{\text{atm (dm}^3)^2}{\text{mol}^2} = \text{dm}^6 \text{ atm mol}^{-2}$$

In S.I. units

$$a = \frac{P V^2}{n^2} = \frac{\text{N m}^{-2} \times (\text{m}^3)^2}{\text{mol}^2} = \frac{\text{N m}^4}{\text{mol}^2} = \text{N m}^4 \text{ mol}^{-2}$$

'b' has the units of volume  $\text{mol}^{-1}$  so, it may be expressed as  $\text{dm}^3 \text{ mol}^{-1}$  or  $\text{m}^3$

$\text{mol}^{-1}$

Table (1.3) Van der Waal's Constants Alongwith their units

Gases	a	a	b	b
	dm <sup>6</sup> – atm mol <sup>-2</sup>	Nm <sup>4</sup> mol <sup>-2</sup>	dm <sup>3</sup> mol <sup>-1</sup>	m <sup>3</sup> mol <sup>-1</sup>
H <sub>2</sub>	0.244	24.72 × 10 <sup>-2</sup>	0.02661	26.61 × 10 <sup>-6</sup>
He	0.034	34.5 × 10 <sup>-3</sup>	0.02370	23.70 × 10 <sup>-6</sup>
O <sub>2</sub>	1.360	138 × 10 <sup>-2</sup>	0.03180	31.80 × 10 <sup>-6</sup>
N <sub>2</sub>	1.390	141 × 10 <sup>-2</sup>	0.03913	39.13 × 10 <sup>-6</sup>
CO <sub>2</sub>	3.592	346 × 10 <sup>-2</sup>	0.04267	42.67 × 10 <sup>-6</sup>
NH <sub>3</sub>	2.250	422 × 10 <sup>-2</sup>	0.03710	37.10 × 10 <sup>-6</sup>
CH <sub>4</sub>	2.250	228 × 10 <sup>-2</sup>	0.04280	42.80 × 10 <sup>-6</sup>

### Interconversion of Units:

$$\text{dm}^3 \text{ mol}^{-1} = 10^{-3} \text{ m}^3 \text{ mol}^{-1}$$

$$\text{dm}^6 \text{ atm mol}^{-2} = 10^{-6} \text{ m}^6 \times 101325 \text{ Nm}^{-2} \text{ mol}^{-2}$$

$$= 1.01325 \times 10^{-1} \text{ Nm}^4 \text{ mol}^{-2}$$

### 1.7.4 Van der Waal's Constants for Some Important Gases:

Since H<sub>2</sub> and He are non-polar gases so, their 'a' factors are sufficiently smaller than many other gases. CO<sub>2</sub> and NH<sub>3</sub> are big sized molecules and so their 'a' factors are sufficiently high. 'b' factor is the measurement of volume of gas molecules in closest possible positions of molecules. This factor is also significant for CO<sub>2</sub>, NH<sub>3</sub> and CH<sub>4</sub>.

When we say that, the value of the 'b' factor for H<sub>2</sub> is 0.02661 dm<sup>3</sup> mole<sup>-1</sup>, then it means that it is 26.61 cm<sup>3</sup> mol<sup>-1</sup>. In other words, we can say that, one mole of H<sub>2</sub>, i.e., 2.016 grams will occupy a volume of 26.61 cm<sup>3</sup> when the molecule are very very close to each other in the gaseous state. It means that, calculated volume of H<sub>2</sub> gas molecules is 26.61 cm<sup>3</sup>.

### 1.7.5 Prove That $b = 4V_m$ :

According to kinetic molecular theory of gases an individual molecule in a gas occupies no volume. But actually molecules of real gases have finite sizes. So the available free space for their motion may be less than the total volume of the container. The space which is occupied by a molecule at an instant will not be available to other molecules at the same instant for their motion. It means that every molecule excludes (باہر نکال دیتا) certain volume for all other molecules.

In order to illustrate it, suppose that a molecule of a gas is non-compressible (جس کو دبایا نہ جاسکے). It is a spherical particle of radius 'R'. When two molecules are at closest approach to each other, then their centres are separated by '2R', as shown in the following diagram (1.12).

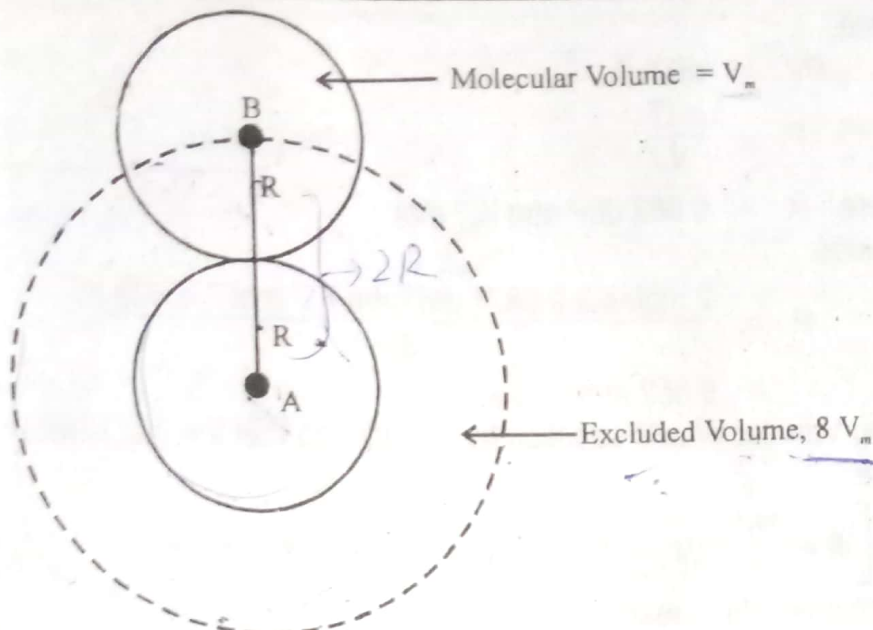


Fig. (1.12) Concept of excluded volume.

The molecule 'A' excludes the centre of the molecule 'B' to be present in a space equal to the volume of dotted sphere. The volume of this sphere with dotted lines is

$$\frac{4}{3} \cdot \pi (2R)^3 = 8 \times \frac{4}{3} \pi R^3 \quad \therefore V = \frac{4}{3} \pi r^3$$

In the same manner, the molecule B also excludes centre of the molecule 'A' from a space equal to  $8 \times \frac{4}{3} \pi R^3$ . When the two molecules are closest approach, then they mutually exclude a

volume  $8 \times \frac{4}{3} \pi R^3$ . *Volume excluded by two molecules*

The volume excluded by one molecule is half of this volume and that is  $4 \times \frac{4}{3} \pi R^3$ .

Since, the volume of one molecule is  $= \frac{4}{3} \cdot \pi \cdot R^3$ , so volume excluded by one molecule = four times the above volume. Now, if we have one mole of gas which has Avogadro's number of molecules, then

$$b = 4N_A \left( \frac{4}{3} \pi R^3 \right)$$

Now *molar*  $N_A \left( \frac{4}{3} \pi R^3 \right) = V_m$

Hence  $b = 4V_m$

This 'b' is called excluded volume, effective volume or vibratory volume/

Sample Problem (1.6)

... of 5 dm<sup>3</sup> at 27°C. Calculate the



$$V - nb = V^2$$

Substituting the values, we get

$$P = \frac{2 \times 0.0821 \times 300}{5 - 2 \times 0.0371} - \frac{4.17 \times (2)^2}{(5)^2}$$

$$= 9.98 - 0.67 = \boxed{9.31 \text{ atm.}} \quad \text{Ans.}$$

Ideal pressure is greater than pressure of the gas when it is non-ideal. In non-ideal gases molecules have forces of attractions and the pressure is less.

(اس کا مطلب یہ ہے کہ کوئی گیس نہ آئیڈیل ہے اور نہ ہی نا آئیڈیل ہے۔ اس کا درجہ حرارت اور باہر کا دباؤ اس کو اپنا رویہ بدلنے پر مجبور کر

### 1.7.6 Validity of Van der Waal's Equation:

While we have discussed the non-polar behaviour of gases by graphical explanation, it is

noticed that some of the gases have lower values of  $\frac{PV}{RT} = Z$ , than expectations at low pressures.

At high pressures the values of  $\frac{PV}{RT} = Z$  increases too much. We have to justify these trends of gases.

For this purpose, we change the shape of Van der Waal's equation.

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

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

$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2} \quad \dots\dots (5)$$

#### (i) At Low Pressure:

When the pressure is smaller then, volume will be larger. Hence, the term 'Pb' and  $\frac{ab}{V^2}$  in

equation (5) may be neglected in comparison to  $\frac{a}{V}$ . Actually  $\frac{a}{V}$  represents the effect of attractions between the molecules.

Hence, equation (5) becomes,

$$PV = RT - \frac{a}{V}$$

Divide this equation by 'RT' on both sides

$$\frac{PV}{RT} = \frac{RT}{RT} - \left( \frac{a}{RTV} \right)$$

$$\frac{PV}{RT} = 1 - \left( \frac{a}{RTV} \right) \quad \dots\dots (6)$$

$\frac{PV}{RT}$  is also called compressibility factor and is denoted by Z.

$$\text{Hence } Z = 1 - \frac{a}{RTV} \quad \dots\dots (7)$$

It means, at low pressures the compressibility factor is less than unity. It explains that, the graphs of  $N_2$  and  $CO_2$  lie below the ideal curve. When the pressure is increased, 'V' decreases and the value of 'Z' increases. It means that the curve should show the upward trend.

(ii) **At High Pressure:**

When the pressure is high then 'V' is small. In this case both the terms  $\frac{a}{V}$  and  $\frac{ab}{V^2}$  can be ignored,

Equation (5) is reduced to the following equation.

$$PV = RT + Pb$$

Dividing this equation with 'RT' on both sides,

$$\frac{PV}{RT} = \frac{RT}{RT} + \frac{Pb}{RT} = 1 + \frac{Pb}{RT}$$

$$Z = 1 + \frac{Pb}{RT} \quad \dots\dots (8)$$

It means that at high pressure 'Z' is greater than 1 and so the graph between 'Z' and 'P' lies above the ideal gas curve. When the pressure is increased the factor  $\frac{Pb}{RT}$  increases further and 'Z' becomes greater and greater.

(iii) **At Extremely Low Pressure:**

At very low pressure, we say that the pressure approaches to zero. In this way, 'V' becomes very large. Under these circumstances, the term  $Pb$ ,  $\frac{a}{V}$  and  $\frac{ab}{V^2}$  would become negligible and can be ignored relative to 'RT'. Thus equation (5) is converted to,

$$PV = RT$$

It means that at very very low pressures, the real gases behave ideally.

(iv) **At High Temperature:**

When the temperature of the real gas is very high, then volume would be very large. In other words, 'P' will be small. The terms like ' $Pb$ ',  $\frac{a}{V}$  and  $\frac{ab}{V^2}$  can be ignored. Equation (5) reduces to,

$$PV = RT$$

It means that at high temperature, the real gases behave ideally.

(v) Exceptional Behaviour of  $H_2$  and He:

$H_2$  and He are very small sized molecules and they are non-polar in nature. They have attractive forces. Their 'a' factor is very small, so  $\frac{a}{V}$  and  $\frac{ab}{V^2}$  in equation (5) can be ignored. Equation (5) can be written as

$$PV = RT + Pb$$

Dividing by 'RT'

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$Z = 1 + \frac{Pb}{RT}$$

It means 'Z' is always greater than 1. Graphs for  $H_2$  and He also show that the curves for hydrogen lie above the ideal curve.

### 1.8.0 CRITICAL PHENOMENON OF GASES

Boyle's law is for ideal gases. The graphs which are plotted between 'P' and 'V' at constant temperature are called isotherms. Isotherms are the parabolic curves and these curves go away from the axis, when they are plotted at higher temperature for a gas.

The idea of the study of critical phenomenon of gases was stated by Andrew (1869). He studied the isotherms of  $CO_2$  at different temperatures. The isotherms are shown in the diagram (1.13) and they are drawn at  $50^\circ C$ ,  $40^\circ C$ ,  $31.1^\circ C$ ,  $21.5^\circ C$  and  $13.1^\circ C$ . The graphs at  $50^\circ C$  and  $40^\circ C$  show that gas is never liquefied even at a very high pressures.

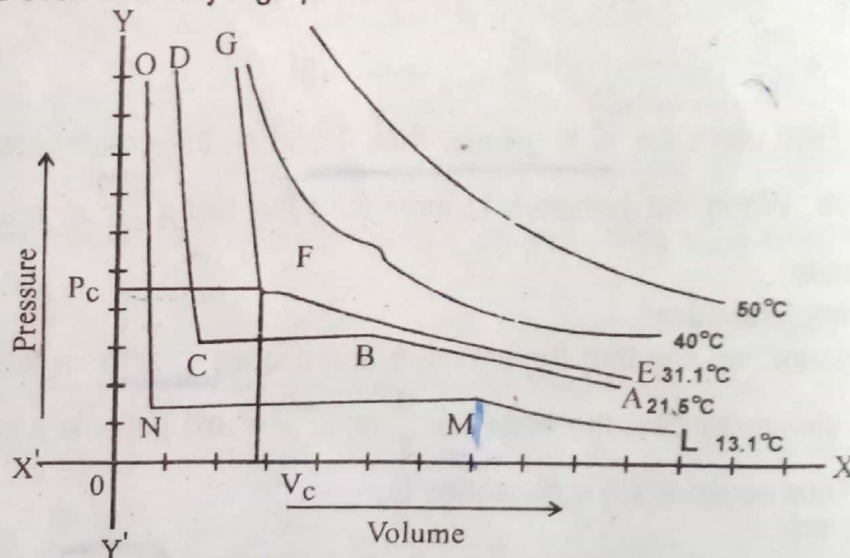


Fig. (1.13) Isotherms of one mole of  $CO_2$  at various temperatures and idea of critical temperature of gases.

Anyhow, when temperature is  $31.1^\circ C$ , then the isotherm EFG is obtained and the  $CO_2$  gas becomes liquid at the point F. If the temperature of  $CO_2$  is maintained above this temperature, then liquefaction never happens for  $CO_2$ . Hence  $31.1^\circ C$  is called critical temperature of  $CO_2$ . It is that temperature for a gas above which the gas can never be liquefied, how much the pressure is applied. It is denoted by ' $T_c$ '.

$31.1^\circ C$  کا درجہ حرارت  $CO_2$  کے لئے ایسا ہے کہ اس سے ذرا بھر بلند درجہ حرارت پر یہ گیس مائع میں تبدیل نہیں ہو سکتی۔ خواہ کتنا بھی دباؤ

لائے جائے۔ یہ درجہ حرارت اس کا critical درجہ حرارت کہلاتا ہے۔

The minimum pressure required to liquify a gas at its critical temperature is called critical pressure. It is denoted by ' $P_c$ '.

The volume occupied by one mole of a gas at its critical temperature and critical pressure is called critical volume. It is denoted by ' $V_c$ '.

' $P_c$ ', ' $V_c$ ', and ' $T_c$ ', of a gas are called the critical constants. The point F is called critical point of  $CO_2$  and the isotherm EFG is called critical isotherm.

The main conclusion which can be drawn from the above diagram are as follows.

- (i) When the temperature of  $CO_2$  is reasonably above the critical temperature, the **smooth hyperbolic curves** are obtained, as we get for other ideal gases.
- (ii) The isotherm in the range of  $32.5$ — $35.5^\circ C$ , do not obey the Boyle's law and smooth isotherms are not obtained.
- (iii) When the temperature is maintained at  $31.1^\circ C$  for one mole of  $CO_2$ , then a very **small horizontal portion** (چھوٹا متوازی حصہ) is developed near the point F. After that, it becomes parallel to the pressure axis.
- (iv) The isotherm at  $31.1^\circ C$ , shows that  $CO_2$  has become liquid at the point 'F' and if the temperature is more than  $31.1^\circ C$ , then there is no chance for such types of a curve.
- (v) Isotherm at  $21.5^\circ C$ , shows a **horizontal portion**. For this horizontal portion, vapours and liquid  $CO_2$  exists in equilibrium. After the point 'C' the curve becomes parallel to the pressure axis. It means that at this temperature, low pressure than the critical pressure is required to liquify  $CO_2$ .
- (vi) The isotherm at  $13.1^\circ C$  has horizontal portion even longer than that at  $25.5^\circ C$ . It means that, even low pressure is required to liquify the gas at  $13.1^\circ C$ .
- (vii) Closer the temperature to the critical temperature, shorter the horizontal portion of the curve and when the temperature reaches  $31.1^\circ C$ , then horizontal portion becomes a single point 'F'.
- (viii) The isotherm below critical temperature have three portions, the right portion is for gaseous  $CO_2$ , middle is for both phases and left is for liquid phase.

### 1.8.1 Application of Van der Waal's Equation to Critical Phenomenon:

In order to see, that whether the Van der Waal's equation can explain the isotherm of  $CO_2$  or

**Reason:-**

The molecules of the compressed gas are very close to each other and appreciable attractive forces are present among them. When a gas is allowed to undergo sudden expansion through the nozzle of a jet, then the molecules move apart. In this way energy is needed to overcome the intermolecular attractions. This energy is taken from the gas itself, which is cooled.

*Imp* Heat generated when air is compressed

**Linde's Method of Liquefaction of Gases**

*long* Linde has employed Joule-Thomson effect as the basis for liquefaction. The apparatus designed for this purpose is shown in the Fig (3.11).

For the liquefaction of air, it is compressed to about 200 atmospheres, and then passed through a water cooled pipe where the heat of compression is removed. It is then allowed to pass through a spiral pipe having a jet at the end. When the air comes out of the jet the expansion takes place from 200 atm. to 1 atm. In this way, considerable fall of temperature occurs. This cooled air goes up and cools the incoming compressed air. It returns to the compression pump. This process is repeated again and again. The liquid air is collected at the bottom of the expansion chamber.

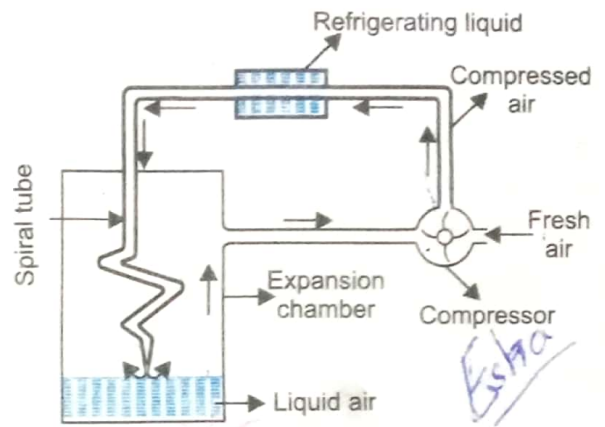


Fig (3.11) Linde's method for the liquefaction of air

**Limitation:-** All gases except  $H_2$  and He can be liquefied by the above procedure.

*Reason:-* Due to smaller size of  $H_2$  and He molecules

$$\gamma_l = 19.42 \times 10^{-3} \text{ Nm}^{-1} = \boxed{1.942 \times 10^{-2} \text{ Nm}^{-1}} \quad \text{Ans.}$$

### 2.3.0 THE PARACHOR

Macleod in 1923, gave the following mathematical relationship between the surface tension and the density of a liquid. His relationship is empirical (تجربی).

$$\gamma = C(D - d)^4 \quad \dots\dots (1)$$

- where,  $\gamma$  = surface tension of liquid  
 $D$  = density of liquid  
 $d$  = density of the vapours of liquid  
 $C$  = characteristic constant of the liquid.

This constant 'C' can give us a additive and constitutive property called parachor (پاراکور) which can be secured (حاصل کرتا) by rearranging the above equation (1).

$$\frac{\gamma}{C} = (D - d)^4$$

Taking 4th root on both sides

$$\left(\frac{\gamma}{C}\right)^{1/4} = (D - d)$$

Taking inverse of above equation

$$\left(\frac{C}{\gamma}\right)^{1/4} = \frac{1}{(D - d)}$$

Rearranging, to keep C on L.H.S

$$C^{1/4} = \frac{\gamma^{1/4}}{(D - d)} \quad \dots\dots (2)$$

In 1924, **Sudgen** obtained a relationship by multiplying equation(2) with the molar mass of the liquid. This constant obtained is called parachor.

$$M.C^{1/4} = \frac{M \gamma^{1/4}}{(D - d)} \quad \dots\dots (3)$$

Let us put [P] =  $MC^{1/4}$

$$\boxed{[P] = \frac{M \gamma^{1/4}}{(D - d)}} \quad \dots\dots (4)$$

Since, the values of 'd' is very less as compared to 'D', so it can be ignored. (Since volume of vapours is 1600 times greater than that of liquid so density of vapours is 1600 times less).

d جو بخارات کی کثافت اضافی ہے وہ مائع کی کثافت اضافی D سے تقریباً 1600 گنا کم ہوتی ہے۔ لہذا d کو D کے مقابلہ میں مساوات میں نظر انداز کیا جاسکتا ہے۔ بشرطیکہ d اور D ایک دوسرے میں جمع ہو رہی ہوں یا نفی ہو رہی ہوں۔ اگر آپس میں ضرب یا تقسیم کر رہی ہوں تو چھوٹی مقدار کو نظر انداز کرنے سے مساوات ختم ہو جاتی ہے۔

$$\boxed{[P] = \frac{M \gamma^{1/4}}{D}} \quad \dots\dots (5)$$

Since mass/volume is the density, so molar mass and density give molar volume

$$\frac{M}{D} = V_m \text{ (molar volume of liquid)} \quad \dots\dots (6)$$

$$\boxed{[P] = V_m \gamma^{1/4}}$$

So, the **parachor of a liquid is obtained from the surface tension and the molar volume of liquid**. If we manage the temperature of the liquid in such a way that its surface tension becomes unity, then

$$\boxed{[P] = V_m (1)^{1/4} = V_m} \quad \dots\dots (7)$$

Hence, the **parachor of a liquid is the molar volume of a liquid, when the surface tension of that liquid is unity.**

Parachor is an **additive and constitutive property**.

Each atom of a molecule has a definite value of the parachor and total parachor value of a simple molecule is the sum of parachor values of constituting atoms. The parachor values which are associated with the atoms are called atomic parachors. Similarly, we have **group parachors**.

The units of parachor can be derived by putting the units of M, D and  $\gamma^{\frac{1}{4}}$ .

#### SAMPLE PROBLEM (2.3)

The parachor values of  $C_2H_6$  and  $C_3H_8$  are 110.5 and 150.8 respectively. What values of parachor

$$\begin{aligned} \text{Experimental value of parachor, (P)} &= \frac{M\gamma^{1/4}}{D} \\ &= \frac{78 \times (29.3)^{1/4}}{0.878} = \boxed{206.7} \text{ Ans.} \end{aligned}$$

The experimental value agrees with the calculated value. Hence Kekule's structure is justified.

## 2.4.0 VISCOSITY

(چسبپاہٹ، لزوجت)

Thickness of fluid.

Resistance to flow

### 2.4.1 Introduction:

It is a common observation (مشاہدہ) that the thick liquids like honey and mobile oil, flow slowly than many organic liquids like benzene and toluene etc. It means that different rates of flow of liquids depend upon certain property and that is viscosity.

Viscosity is the property which opposes the relative motion of adjacent (ساتھ ساتھ) layers. In order to understand the viscosity. Let us consider the flow of a liquid as shown in the following diagram (2.9). Liquid is considered to be arranged in a large number of parallel (متوازی) layers. The layer adjacent to the walls of the tube is stationary (ساکن). When we move towards the centre of the tube, then the velocities of the successive (یکے بعد دیگرے) layers go on increasing.

When the steady flow (متوازن بہاؤ) is reached then velocity difference between any two layers becomes constant.

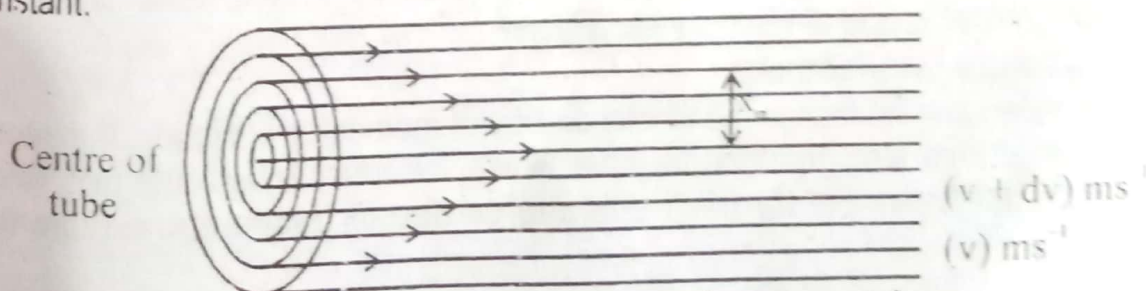


Fig. (2.9) Flow of a liquid through a narrow tube.

The force which is required to maintain the steady flow of liquid in direction of the force is directly proportional to the velocity gradient which is normal to the direction of flow. It is also proportional to the area of the contact 'A' between the moving layers of the liquids.

In C.G.S system, the unit of ' $\eta$ ' is expressed as  $\text{g cm}^{-1} \text{sec}^{-1}$  and it is called Poise.



A = Area of contact

$\frac{dv}{dx}$  = Velocity gradient (Rate of change of velocity w.r.t distance perpendicular to the layers)

$$F \propto -A \frac{dv}{dx}$$

$$\text{or } F = -\eta A \frac{dv}{dx} \quad \dots\dots (1)$$

$$\eta = -\frac{F}{A \cdot \frac{dv}{dx}} \quad \dots\dots (2)$$

$\eta$  = co-efficient of viscosity or simply called viscosity.

### 2.4.2 Definition and Units of Viscosity

*"It is the force per unit area, needed to maintain unit difference of velocity between two parallel layers of the liquid, unit distance apart."*

The units of viscosity ' $\eta$ ' can be derived from the equation (1)

$$\eta = \frac{F}{A} \times \frac{dx}{dv} = \frac{\text{force}}{\text{area}} \times \frac{\text{distance}}{\text{velocity}}$$

Since  $J = \text{kg ms}^{-2}$ , so, force = mass  $\times$  length  $\times$  time $^{-2}$

$$\eta = \frac{\text{mass} \times \text{length} \times \text{time}^{-2}}{(\text{length})^2} \times \frac{\text{length}}{\text{length/time}}$$

$$\eta = \text{mass} \times \text{length}^{-1} \times \text{time}^{-1}$$

In SI units  $\eta$  is in  $\text{kg m}^{-1} \text{s}^{-1}$

$$\boxed{1 \text{ poise} = 10^{-1} \text{ kg m}^{-1} \text{ s}^{-1} = 0.1 \text{ kg m}^{-1} \text{ s}^{-1}}$$

### Unit of viscosity "Poise":

*"When a force of one dyne per square cm is maintained, between two layers which are 1 cm apart and the difference of velocity between the two layers is 1 cm per second, then it is called poise."*

$$1 \text{ centipoise} = 10^{-2} \text{ poise}$$

$$1 \text{ millipoise} = 10^{-3} \text{ poise}$$

### Fluidity (بہہ نکلنے کی صلاحیت):

*"Fluidity is the reciprocal of viscosity."*

$$\phi = \frac{1}{\eta}$$

The units of fluidity are reciprocal of viscosity i.e.  $(\text{Poise})^{-1}$ .

### 2.4.3 Effect of Temperature on Viscosity:

The increase of temperature increases the kinetic energy of molecules of liquids. It means that a liquid starts flowing faster at high temperatures. In other words, viscosity of a liquid falls with the increase in temperature. It is estimated that for each one degree rise of temperature, there is 2% decrease of viscosity.

#### Mathematical Relationship:

Arrhenius has given the following relationship between viscosity and temperature

$$\eta = Ae^{B/RT} \quad \dots\dots (1)$$

A and B are the constants depending upon the nature of liquid. According to this equation,

and 'B' then we can convert it into the equation of a straight line by taking the natural log i.e. log to the base e. (It can be written as ln)

$$\ln \eta = \ln A + \frac{B}{RT} \quad \dots\dots (2)$$

$$\ln \eta = \frac{B}{R} \cdot \left(\frac{1}{T}\right) + \ln A \quad \dots\dots (3)$$

(یا  $\log_e \eta$  ایک ہی چیز ہے)

If we plot a graph between  $\frac{1}{T}$  on x-axis and  $\log_e \eta$  ( $\ln \eta$ ) on y-axis, then a straight line is obtained. From the slope of the straight line 'B' can be calculated and from the intercept of the straight line factor 'A' can be calculated.

The following graphs of Fig. (2.10) show that many of liquids show the straight lines. The anomalous (خلاف معمول ہے قائمہ) behaviour of  $H_2O$  is seen from the graph, because its hydrogen bonded structure is broken with the rise of temperature. The quantity 'B' is the activation of energy for the viscous flow. It is the energy barrier which must be overcome before the flow can occur. It means that a molecule of a liquid should gain sufficient energy to push aside (پرے دھکیانا) the surrounding molecules before it can take part in the liquid flow.

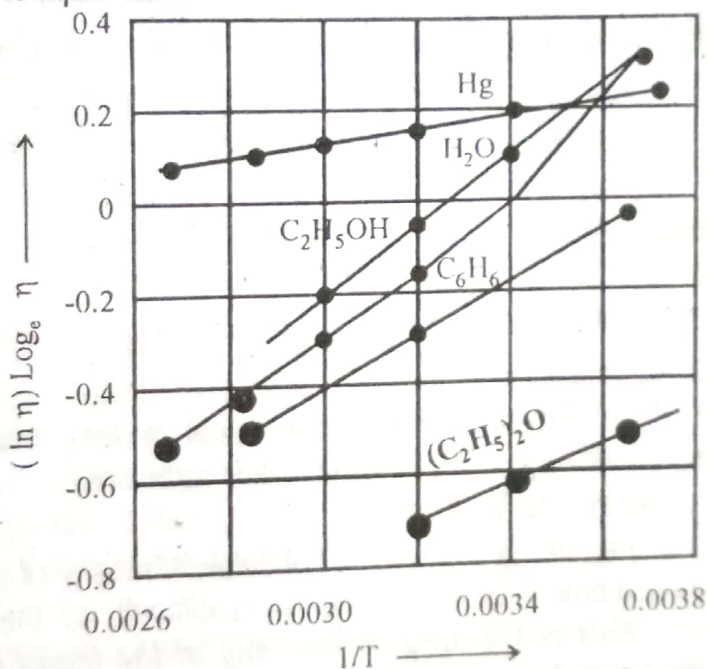


Fig. (2.10) The dependence of viscosity on temperature  $\log_e \eta$  versus  $1/T$ .

Viscosities of Some Important Liquids:

Table (2.3): Co-efficients of Viscosity of Liquids at 20°C in Poise and in SI Units ( $kg\ m^{-1}\ sec^{-1}$ ) Remember that 1 pouse =  $10^{-1}\ kg\ m^{-1}\ s^{-1}$

Liquid	Viscosity (C.G.S. units) poise	Viscosity (SI units) $kg\ m^{-1}\ s^{-1}$
Benzene	0.00652	0.000652
Carbon tetrachloride	0.00969	0.000969
Ethanol	0.01200	0.001200
Ether	0.00233	0.000233
Glycerin	14.9	1.49
Water	0.0101	0.00104