

# DEVIATION FROM IDEAL GAS BEHAVIOR

A gas which obeys  $PV=nRT$  and all gas laws is called an ideal gas.

The gases which do not obey  $PV=nRT$  and gas laws strictly are called real gases.

Real gases show deviation from ideal behavior at low temperature and high pressure.

All gases are found to be real under certain conditions.

# WHY REAL GASES DEVIATE FROM IDEAL GAS BEHAVIOR?

Volume of Hydrogen gas at different pressure  
(Temperature remains constant):

Pressure (atm)	Volume (dm <sup>3</sup> )	PV
0.1	224.1	22.41
50	0.4634	23.71
1000	0.384	38.34

PV is not always constant. Boyle's law is not followed at high pressure.

# FAULTS IN KINETIC MOLECULAR THEORY

Van Der Waal attributed the deviation of real gases from ideal gas behavior to two faulty postulates of KMT.

## 1. Inter-Molecular forces of attraction:

There are no attractive or repulsive forces between molecules of an ideal gas.

## 2. Volume of molecules:

The volume of gas molecules is negligible as compared to the volume of the container.

## EXPLANATION OF DEVIATION

### 1. AT LOWER TEMPERATURE:

At higher temperature, Kinetic energy of molecules is also high. As a result the attractive forces are negligible.

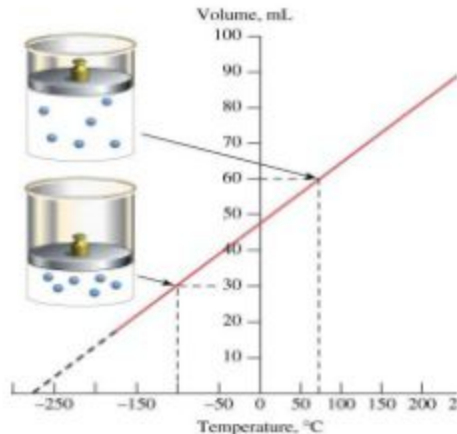
At lower temperature, kinetic energy of molecules is decreased.

Molecules come closer to each other. At certain low temperature gases change into liquid state.

The intermolecular forces become significant near liquefying temperature.

For example  $\text{SO}_2$  liquefies at  $10^\circ\text{C}$  and  $\text{H}_2$  liquefies at  $-252.7^\circ\text{C}$ .

$\text{SO}_2$  gas shows non ideal behavior at room temperature as compared to  $\text{H}_2$  gas.



## EXPLANATION OF DEVIATION

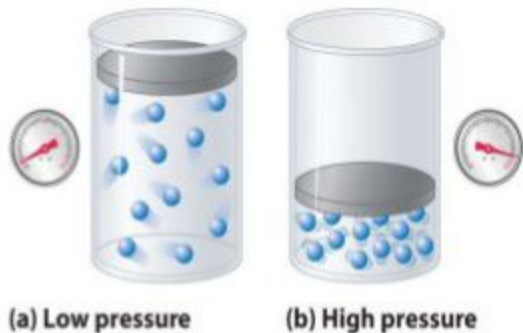
### 2. AT HIGH PRESSURE:

At low pressure, the actual volume of the gas molecule is very small as compared to the volume of container.

At high pressure this volume does not remain negligible.

At 1 atm pressure, individual volume of molecule say  $32 \text{ cm}^3$  is negligible as compared to total volume of gas  $22400 \text{ cm}^3$ .

At 100 atm pressure the volume of gas reduced to  $224 \text{ cm}^3$ , now the volume of individual molecule  $32 \text{ cm}^3$  is not negligible as compared to the total volume.



# COMPRESSIBILITY FACTOR

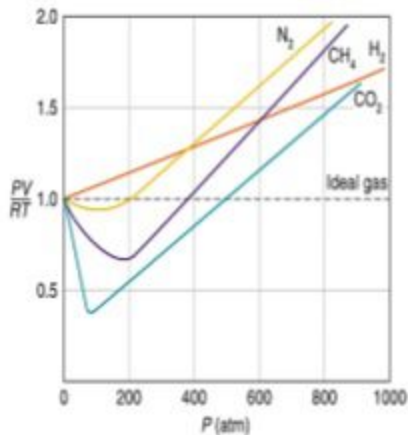
For 1 mol of a gas, if graph is plotted between  $PV/RT$  and pressure, then for an ideal gas, it must give a straight line. (The temperature remains 273 K)

Real gases do not produce a straight line on graph.

It is because when pressure is increased, it pushes the molecules closer and increase the intermolecular forces and the volume of gas shrinks. This will decrease the value of  $PV/RT$ .

$PV/RT$  is called Compressibility factor.

For ideal gas,  $PV/RT = 1$ .



# VAN DER WAALS EQUATION – CORRECTION FACTORS

J. D. Van Der Waals corrected the ideal gas equation in a simple, but useful way.

A equation that is applicable on real gases called Van Der Waals equation.

Van der Waals made corrections for Volume and pressure of the gases.



Johannes Diderik van der Waals

# VOLUME CORRECTION

When a gas is compressed, molecules are pushed so closer that repulsive forces operate between them. Further increase in pressure is opposed by the molecules themselves because molecules have definite volume.

Volume available to gas molecules =  $V = V_{\text{vessel}} - V_{\text{molecule}}$

V is "Free volume"

$$V_{\text{molecule}} = nb$$

Where n is the total no. of molecules and b is individual volume of one mole of the gas molecules.

So  $V = V_{\text{vessel}} - nb \dots\dots(i)$

b is not equal to actual volume of gas. It is in fact four times the actual volume of molecules

$$b = 4V_m$$



# PRESSURE CORRECTION

Each molecule in the middle of gas is attracted by all sides so the attraction forces are cancelled out.

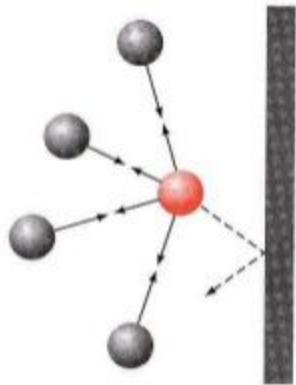
When a molecule is about to strike the wall of container, it experiences a force of attraction towards other molecules.

Pressure being observed on the walls of vessel is a less than ideal pressure.

$$P_{\text{observed}} = P_i - P'$$

Where  $P_i$  = ideal pressure and  $P'$  = Pressure lessened due to molecular attraction

$$P_i = P_{\text{observed}} + P' \dots (ii)$$



# PRESSURE CORRECTION

$P'$  is determined by attraction forces between molecules.

Suppose molecules A are striking walls of container and molecules B are pulling them inwards:

$$P' \propto C_A \cdot C_B$$

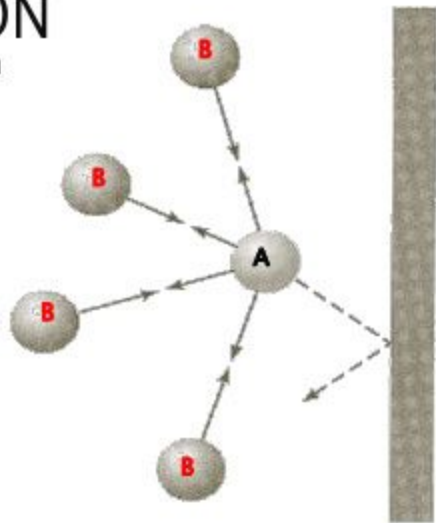
Let  $n$  = no. of moles of A and B and  $V$  = total volume.

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

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

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

Where  $a$  is called "Coefficient of attraction per unit volume". It has a constant value. Put value in equation (ii)



# VAN DER WAALS EQUATION

Ideal gas equation:  $PV = nRT$

Now put values from equation (i) and (iii):

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

For 1 mole of a gas  $n=1$

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

# UNITS OF VAN DER WAALS CONSTANTS

Units of  $a$

$$P + a \frac{n^2}{V^2}$$

$$a = \frac{PV^2}{n^2}$$

$$a = \frac{\text{atm. (dm}^3)^2}{(\text{mol})^2}$$

$$a = \text{atm. dm}^6 \cdot \text{mol}^{-2}$$

Units of  $b$

$$\text{dm}^3 \text{ mol}^{-1}$$

## LIQUEFACTION OF GASES – CRITICAL PHENOMENON

A gas can be liquefied by lowering the temperature and increasing the pressure. At lower temperature, the gas molecules lose kinetic energy. The slow moving molecules then aggregate due to attractions between them and are converted into liquid. The same effect is produced by the increase of pressure. The gas molecules come closer by compression and coalesce to form the liquid.

Andrews (1869) studied the P–T conditions of liquefaction of several gases. He established that for every gas there is a temperature below which the gas can be liquefied but above it the gas defies liquefaction. This temperature is called the critical temperature of the gas.

The **critical temperature,  $T_c$** , of a gas may be defined as that temperature above which it cannot be liquefied no matter how great the pressure applied.

The **critical pressure,  $P_c$** , is the minimum pressure required to liquefy the gas at its critical temperature.

The **critical volume,  $V_c$** , is the volume occupied by a mole of the gas at the critical temperature and critical pressure.

$T_c$ ,  $P_c$  and  $V_c$  are collectively called the **critical constants** of the gas. All real gases have characteristic critical constants.

At critical temperature and critical pressure, the gas becomes identical with its liquid and is said to be in **critical state**. The smooth merging of the gas with its liquid is referred to as the **critical phenomenon**.

**Table: The critical constants of some common gases**

Gas	Critical temperature (K)	Critical pressure (atm)	Critical volume (ml/mole)
Helium	5.3	2.26	57.8
Hydrogen	33.2	12.8	65.0
Nitrogen	126.0	33.5	90.1
Oxygen	154.3	50.1	74.4
Carbon dioxide	304.0	72.9	94.0
Ammonia	405.5	111.5	72.1
Chlorine	407.1	76.1	123.8

### **Methods of Liquefaction of Gases**

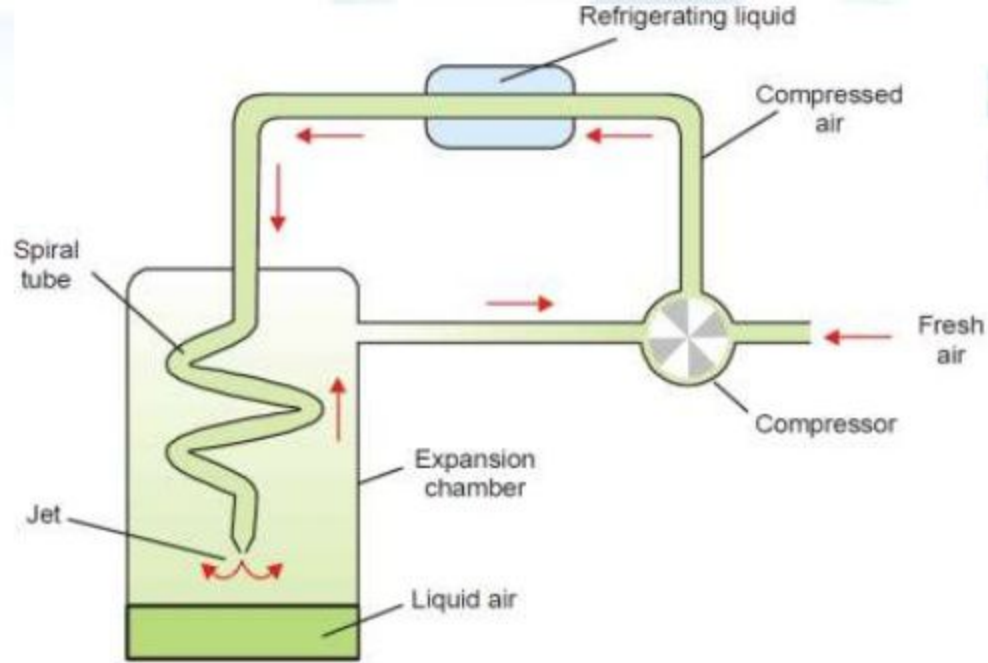
If a gas is cooled below its critical temperature and then subjected to adequate pressure, it liquefies. The various methods employed for the liquefaction of gases depend on the technique used to attain low temperature. The three important methods are:

- 1. Faraday's method in which cooling is done with a freezing mixture**
- 2. Linde's method in which a compressed gas is released at a narrow jet (Joule-Thomson effect)**
- 3. Claude's method in which a gas is allowed to do mechanical work**

## Linde's Method

Linde (1895) used Joule Thomson effect as the basis for the liquefaction of gases. **When a compressed gas is allowed to expand into vacuum or a region of low pressure, it produces intense cooling.** In a compressed gas the molecules are very close and the attractions between them are appreciable. As the gas expands, the molecules move apart. In doing so, the intermolecular attraction must be overcome. The energy for it is taken from the gas itself which is thereby cooled and become liquid.

Linde used an apparatus worked on the above principle for the liquefaction of air. Pure dry air is compressed to about 200 atmospheres. It is passed through a pipe cooled by a refrigerating liquid such as ammonia. Here, the heat of compression is removed. The compressed air is then passed into a spiral pipe with a jet at the lower end. The free expansion of air at the jet results in a considerable drop of temperature. The cooled air which is now at about one atmosphere pressure passed up the expansion chamber. It further cools the incoming air of the spiral tube and returns to the compressor. By repeating the process of compression and expansion, a temperature low enough to liquefy air is reached. The liquefied air is collected at the bottom of the expansion chamber.



### 1.9. MOLECULAR COLLISIONS ; -

It has been observed experimentally that the molecules in gases travel with velocities much smaller than those predicted from the kinetic theory. This discrepancy arises due to the involvement of the moving molecules into mutual collisions. These collisions make them to drift away from their normal path, thus resulting in a hindered motion. Therefore, molecular collision may be defined as a process in which a change in the direction of motion of the approaching molecules takes place. There are three types of the molecular collisions, as shown in Fig. 1.6.

- (i) **Glancing Collision.** In a glancing collision, the molecules move parallel to each other with average speed  $\bar{u}$ , but the relative speed of the molecules is very small i.e.,  $u_r \approx 0$ .
- (ii) **Head on Collision.** In a head on collision the approaching molecules retrace the straight line path in the reverse directions and the relative speed becomes  $2\bar{u}$ .
- (iii) **Right-angle Collision.** In a right angle collision, the approaching molecules move at right angles to each other at the instant of collision and the relative speed becomes  $\sqrt{2} \bar{u}$ .

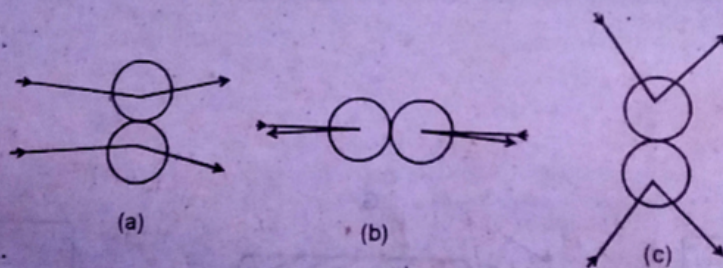


Fig. 1.6. Types of molecular collisions. Relative speed ( $u_r$ ) along the line of centers

(a)  $u_r = 0$  (b)  $u_r = 2\bar{u}$  and (c)  $u_r = \sqrt{2} \bar{u}$

As a result of molecular collisions, a change in the direction of movement and redistribution of energy takes place without any loss of their total energy. Such collisions between molecules in which there is no net loss or gain of energy are referred as elastic collisions. But when the collisions between the molecules result in the loss or gain of energy, then such collisions are known as inelastic collisions.

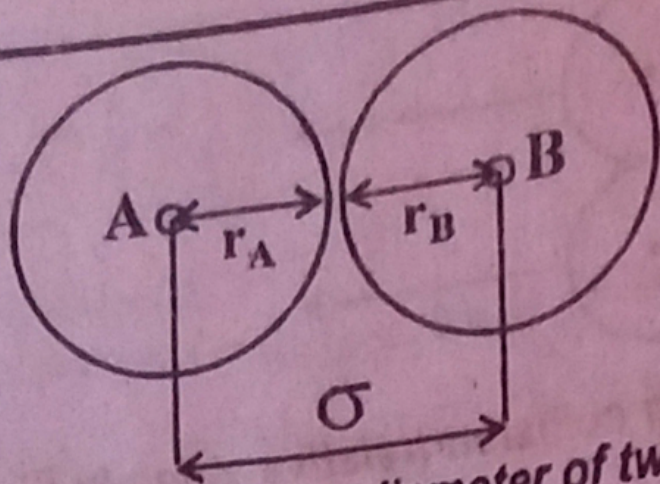


### 1.5.1 Collision Diameter:

In order to do the collision, the molecules approach each other. At the time of contact of the 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).

(کلر مارنے 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.



$$\sigma = r_A + r_B$$

Fig. (1.5) Collision diameter of two colliding molecules

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

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 فاصلے برابر نہیں ہوتے ان کا اوسط نکال لیں تو وہ  $\lambda$  کہلاتا ہے۔ جس کو 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)