

# UNIT : KINETIC THEORY OF GASES - I (PHYSICS)

[B.Sc - 1st year] [Semester - II Ind]

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**(REMAINING TOPICS)**

## # VAN DER WAALS EQUATION OF STATE FOR REAL GASES

As we know, ideal gas equation is given by  
 $PV = RT$  (for one mole)

It is derived on the assumptions

① Size of molecules

is negligible as compared to the volume of gas

② force of attraction

between the molecules is negligible

Both the statements are true at low pressure and high temperature

Also obey Boyle's law & Ideal Gas eq<sup>n</sup> at low pressure & high temperature.

\* But at high pressure and low temperature

↓  
Volume of the Gas become small

↓  
molecules come closer to each other

↓  
molecular force become operative

Thus, size of molecules cannot be neglected.

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Now, to study the real behaviour of gases, we need some modification in ideal gas equation also assumptions should be revised.

Correction should be based on  $\rightarrow$  finite size of molecule  
 $\rightarrow$  Due to inter molecular forces

(a) Correction due to finite size of the molecule:-

Consider a real gas enclosed in a vessel ABCD shown in ~~graph~~ diagram of length  $l$ . Let a molecule move inside along the length.

Now, due to its finite mass it will travel from D to C at distance  $l-d$  (because  $d$  is the diameter of molecule & distance occupied by itself the molecule)

So, the effective volume of gas reduced. Let it be reduced by factor 'b'. (co-volume)

Thus effective volume of the gas is  $V-b$  (where  $V$  is the total volume in which gas is enclosed).

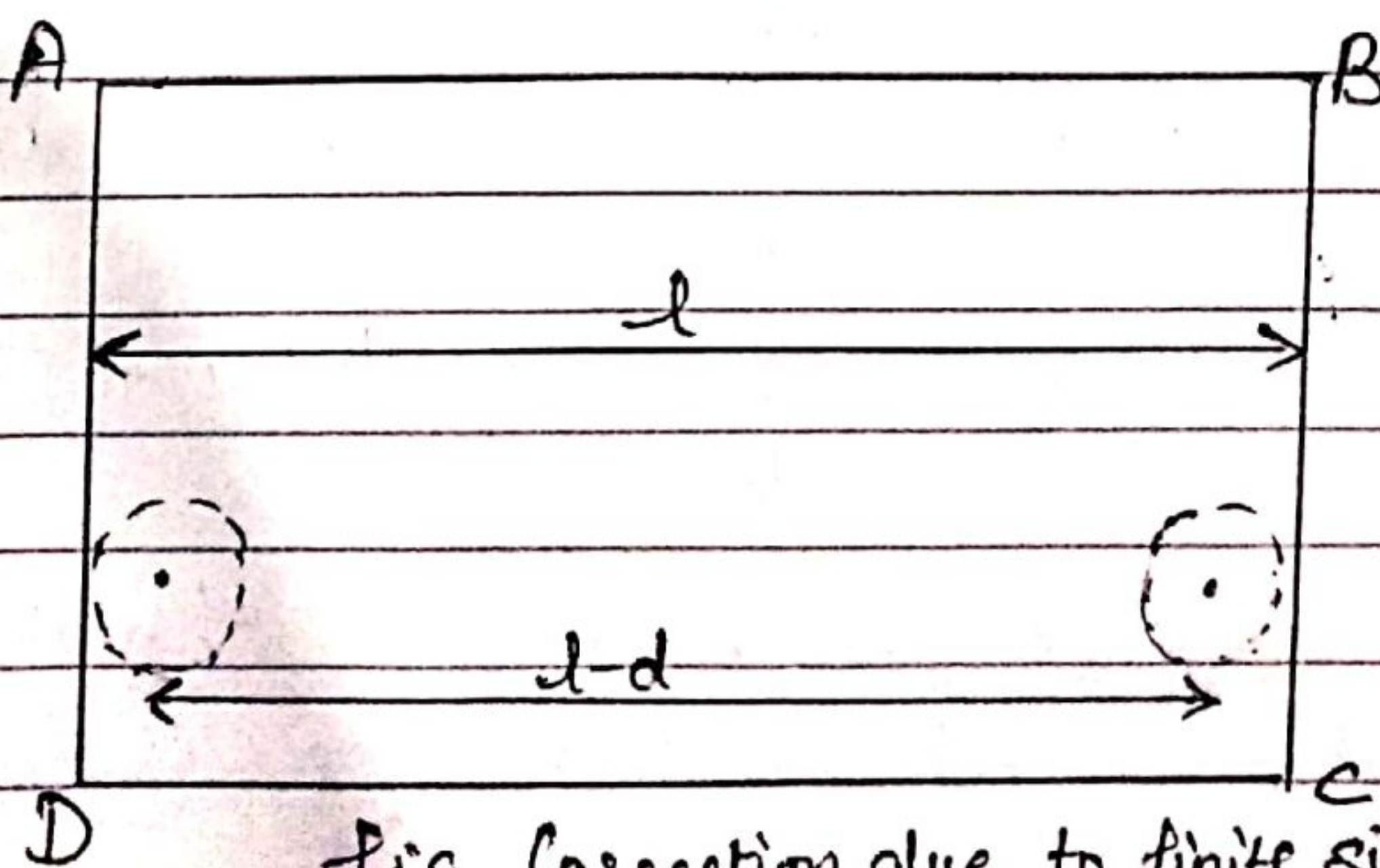


Fig. Correction due to finite size of molecule.

(b) Correction due to inter molecular forces :

Consider a molecule B (say) well within the gas. It is surrounded by other molecules in all possible directions. So, it is attracted equally by other molecules by equal forces. Thus cancelling each other, there is no net force on this molecule (we considered). But if we see a molecule N near the wall, it is experiencing unbalanced force away from the wall due to molecules present inside the vessel. Thus these unbalanced forces decrease its velocity & hence momentum with which it strikes the wall.

Now, as we know pressure on the wall due to is due to change in momentum.

Here momentum is decreasing hence pressure will also reduce.

Decrease in pressure depends on two factors

① Inward forces on molecules (due to other molecules)

thus, this factor depends on density of the gas

② Number of molecules striking per unit area of the wall per unit second. (It also depends on density of the gas)

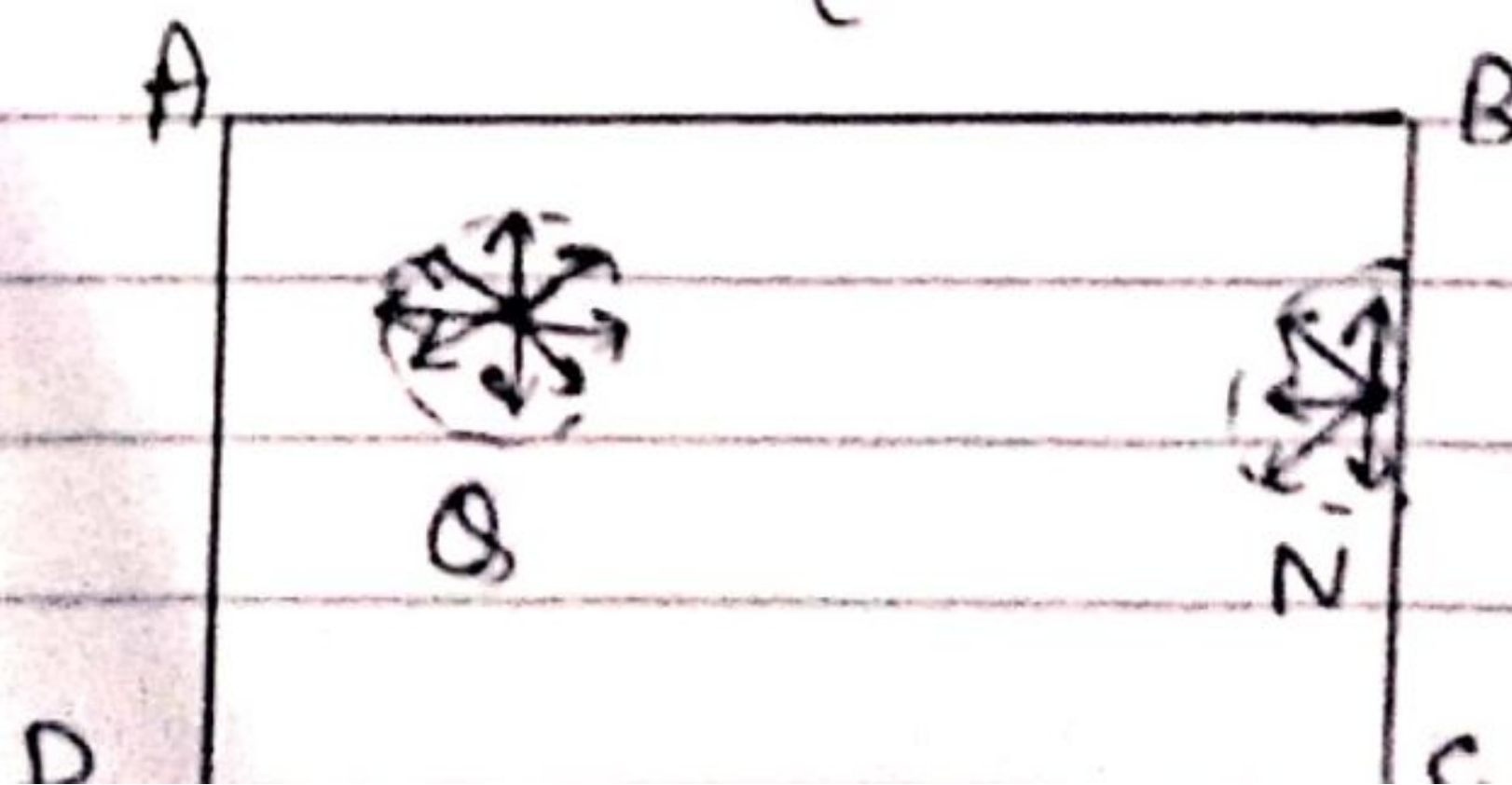


fig.

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Thus, decrease in pressure

$$p \propto \rho^2 \\ \propto \frac{M^2}{V^2} \quad \left( \because \rho = \frac{M}{V} \right)$$

$$\Rightarrow p \propto \frac{M^2}{V^2} \Rightarrow p = \frac{kM^2}{V^2} \quad (k = \text{any constant})$$

$$\Rightarrow p = \frac{a}{V^2} \quad (\text{where } a = kM^2)$$

'a' depends on mass and nature of Gas.

Thus in ideal Gas eq<sup>y</sup> P should be replaced by  $(P+p)$  or  $\left(P + \frac{a}{V^2}\right)$

Now, with both the correcting factors, eq<sup>y</sup>  $PV = RT$  for real Gas will become,

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

This is known as Vander Waal's equation of state for a real or actual Gas.

a & b are Vander waal's constants.

## RESULT OF ANDREW'S EXPERIMENT

Andrew carried out experiments on Carbon dioxide & lead to discovery of Critical temperature.

The Critical temperature of the Gas is the temperature below which a gas can be liquified by the increase of pressure alone and above it, the gas cannot be liquified by any amount of pressure.

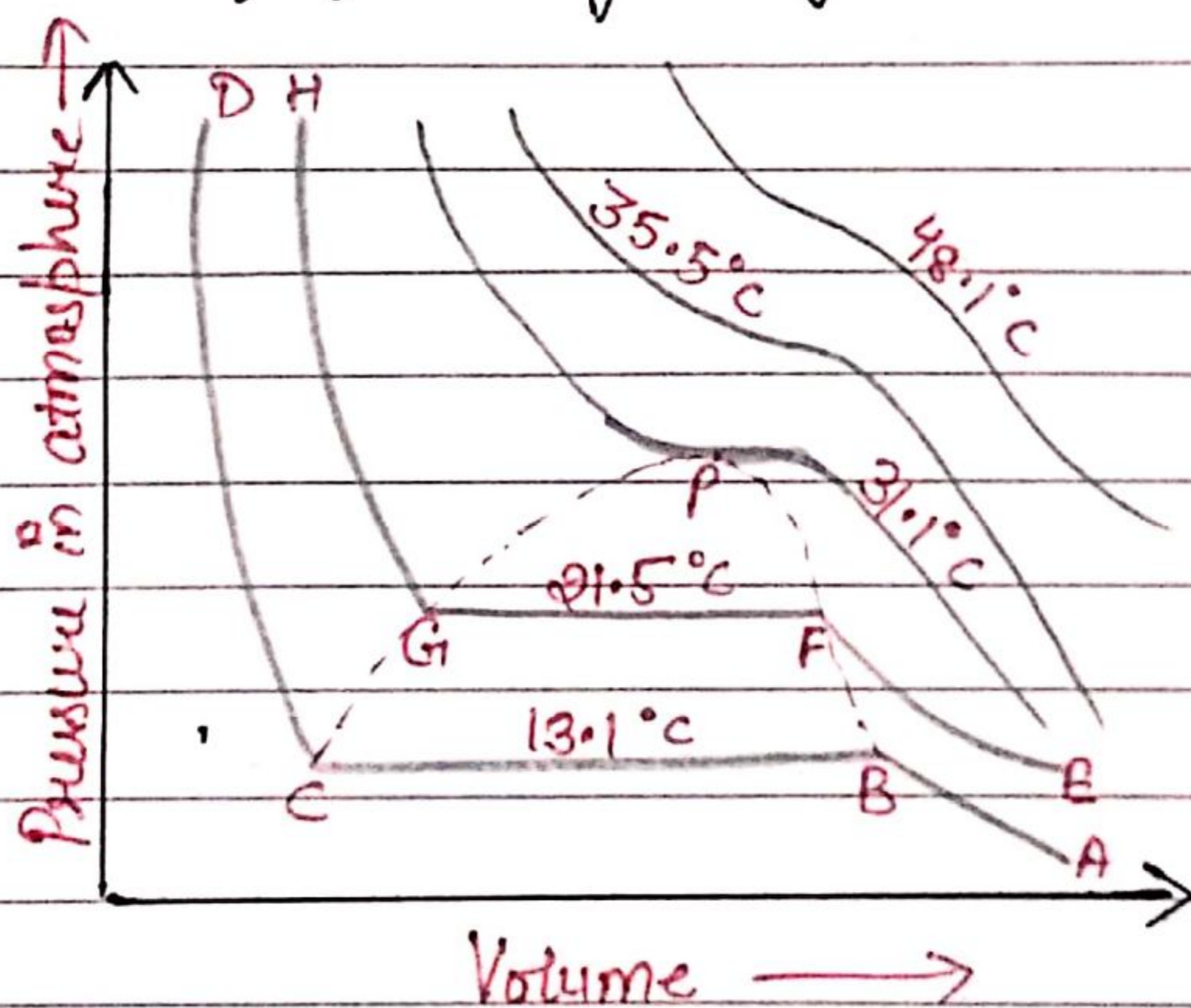


Fig → isothermals (P-V diagrams) at diff temperatures.

At 13.1°C → AB position → Gas (obey Boyle's law) upto B

At B → liquification of Gas starts.

BC → partly liquid + partly vapour state.

During BC [Saturated vapour pressure] = Constant.

At C → state of liquified (state of Boiling liquid)

(Graph is pressure axis parallel)

At 31.5°C → horizontal state (position) decreases.

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At  $31.1^\circ\text{C}$   $\rightarrow$  horizontal portion finally disappears  
 $\rightarrow$  This is called isothermal. & Here it is known as Critical isothermal.

Here, no horizontal portion shown above isothermal at temp greater than  $31.1^\circ\text{C}$ . This means Carbon dioxide cannot be liquefied above  $31.1^\circ\text{C}$ .

The dotted curve BFGC joining the extremities of the horizontal portions of isotherms & touches the Critical isotherm at P, known as Critical point.

Pressure & Volume corresponding to Critical point are called Critical Pressure ( $P_c$ ) and the Critical Volume ( $V_c$ )

Critical Pressure  $\rightarrow$  Pressure required to liquefy the gas just below the Critical temperature.

## # VAN DER WAAL'S ISOTHERMS

If we rearrange Van der Waal's equation, we can write it as

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

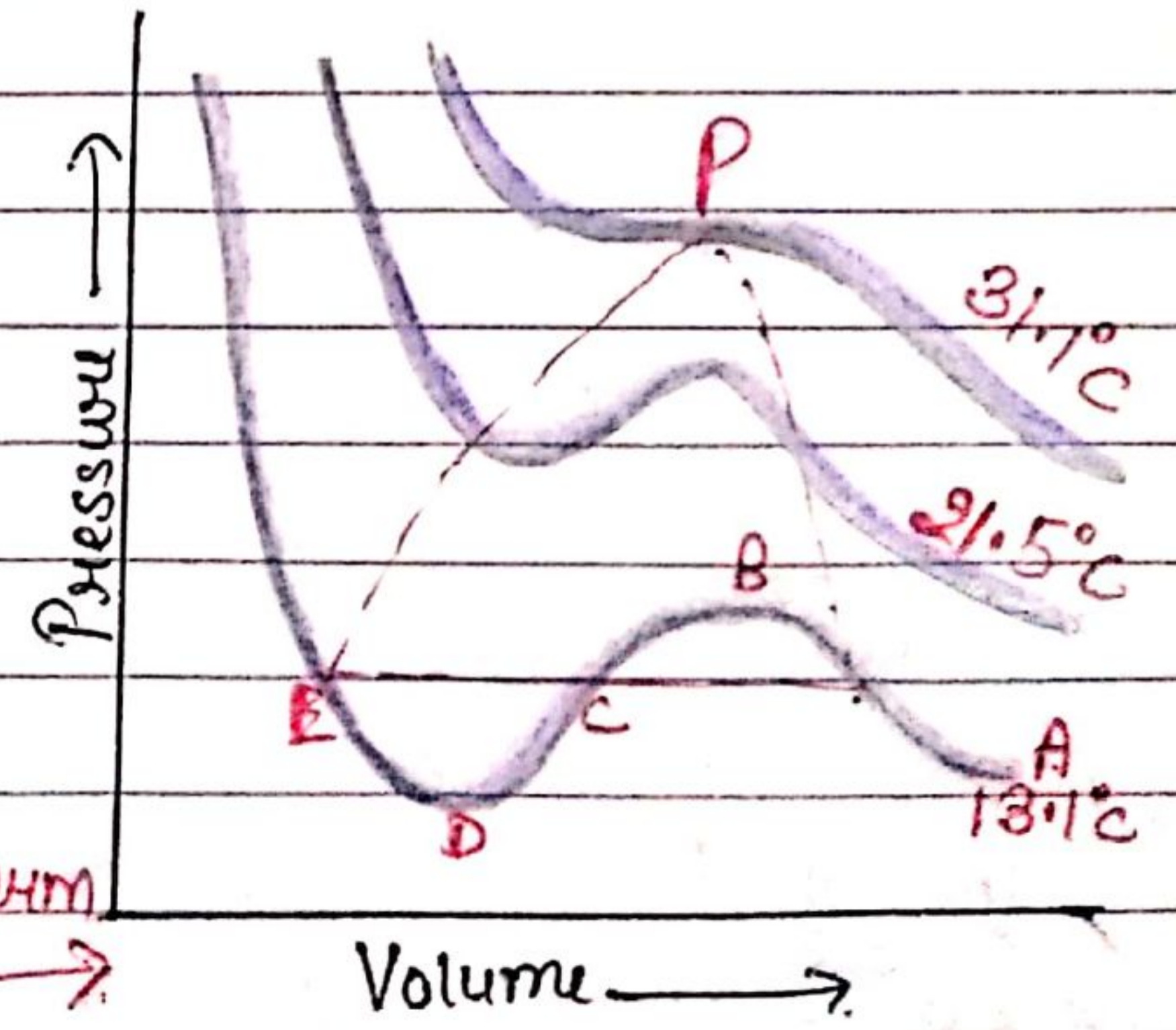


fig  $\rightarrow$  Vander Waal's isotherm

Above equation can be used to determine the pressure corresponding to any temperature and volume.

Here, in figure we have shown general isotherms obtained by van der waal's equation at various temperatures for Carbon dioxide.

Observation :- Here horizontal portion of Andrew's isotherms are absent

→ At  $13.1^{\circ}\text{C}$ , Curve obtained, contains portion ABCDE in which A refers to vapour state (explained due to super cooling of vapours)

Point E or portion DE is liquefied state and explained by super heating of liquid.

But BCD cannot be explained because here decrease in volume is due to decrease in pressure (unstable)

At higher temperature, isotherms are similar to Andrew's

## # CRITICAL CONSTANTS

There are three critical constants called Critical temperature, Critical pressure and Critical Volume

**Critical temperature** : Highest temperature of a gas at which gas can be liquefied by pressure alone, but above which the gas cannot be liquefied by the increase of pressure.

**Critical Pressure** : Pressure required to liquefy the gas just below at critical temperature

**Critical Volume** : The volume of unit mass of the gas at critical temperature and critical pressure is called critical volume.

**DERIVATION OF CRITICAL CONSTANT IN TERMS OF a and b :**

As Vander waal's equation is given by

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

P = Pressure & V = Volume & T = Temperature of Gas

a & b = Vander waal's constant.

Multiplying both brackets in d.H.S of eq<sup>n</sup> (1),

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

Multiplying  $V^2$  both sides,

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

$$\text{or } PV^3 - V^2(bP + RT) + aV - ab = 0$$

⇒ Divide P, we get

$$V^3 - V^2 \frac{(bP + RT)}{P} + \frac{aV}{P} - \frac{ab}{P} = 0$$



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

This is a cubic equation and has three roots for a given value of  $P$  and  $T$

But for a gas there is only one critical pressure, critical volume & critical temp.

Hence, the three roots must be equal.

Let  $x$  be the value of root i.e. critical volume

$$\boxed{V_c = x} \Rightarrow V = x \quad \text{or} \quad V - x = 0$$

$$\therefore (V - x)^3 = 0$$

$$\Rightarrow V^3 - V^2 3x + V 3x^2 - x^3 = 0 \quad \text{--- (3)}$$

Comparing equation (2) & (3), equating coefficients, we get

$$3x = b + \frac{RT}{P} \quad \text{--- (4)} \quad (\text{Coefficient of } V^2)$$

$$3x^2 = \frac{a}{P} \quad \text{--- (5)} \quad (\text{Coefficient of } V)$$

$$x^3 = \frac{ab}{P} \quad \text{--- (6)} \quad (\text{Constant term})$$

from (5) & (6), divide (6) by (5)

$$\frac{x^3}{3x^2} = \frac{ab/P}{a/P} \Rightarrow \boxed{x = 3b}$$

$$\Rightarrow \boxed{V_c = 3b} \quad \text{Critical Volume}$$

Putting value of  $x$  in (5)

$$3 \times 9b^2 = \frac{a}{P} \Rightarrow \boxed{P = \frac{a}{27b^2}}$$

$$\Rightarrow \boxed{P_c = \frac{a}{27b^2}} \quad \text{Critical Pressure}$$

Now, putting value of  $x$  in (4),

$$3 \times 3b = b + \frac{RT}{P}$$

$$\Rightarrow 9b - b = \frac{RT}{a} \cdot 27b^2 \quad (\text{Putting } P \text{ Value})$$

$$\Rightarrow 8b = \frac{RT}{a} \cdot 27b^2$$

$$\Rightarrow \boxed{T = \frac{8a}{27Rb}} \quad \text{Critical Temperature}$$

Critical Coefficient

from value of  $P_c, V_c$  &  $T_c$ ,

$$\frac{8a}{27Rb} \times \frac{27b^2}{a} \times \frac{1}{3b} = T_c \times \frac{1}{P_c} \times \frac{1}{V_c}$$

$$\Rightarrow \frac{T_c}{P_c V_c} = \frac{8}{3R}$$

$$\Rightarrow \frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.67 = \text{Constant}$$

(Same for all gases)

= Critical Coefficient

Determination of 'a' & 'b'

$$\text{Here, } \frac{T_c^2}{P_c} = \frac{\left(\frac{8a}{27bR}\right)^2}{\frac{a}{27b^2}} = \frac{64a}{27R^2}$$

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

$$\text{Also, } \frac{T_c}{P_c} = \frac{8b}{R}$$

$$\Rightarrow \boxed{b = \frac{RT_c}{8P_c}}$$