Critical Phenomena

⇒ The essential condition for the liquefaction of the gas is described by the study of critical temperature (T_c), critical pressure (P_c) and critical volume (V_c) and their inter-relationship.

⇒ The most important property of gas is that their molecules lie far apart from one another and are in continuous rapid motion. Each molecule, therefore lead almost an independent existence. This is particularly so when temperature is high and pressure is low.

⇒ However as the temperature of gas is lowered, K.E of molecule ↓ses. At a sufficiently low temperature, some of the slow moving molecules ~~consist~~ cannot resist the force of attraction and they come closer & closer and ultimately the gas changes into liquid state. Thus liquefaction of gases result from ↓se of temperature. ↑se of pressure has also the effect of bringing the gaseous molecules closer & closer to one another due to ↓ee in Volume.

⇒ The effect of temperature however is more important than that of the pressure because for each gas there is a certain temperature above which it cannot be liquified, no matter

how high a prenure may be applied. This temperature is known as the critical temperature. Thus, the critical temperature of a gas may be defined as that temperature above which it cannot be liquified how so ever high prenure may be.

eg. T_c for CO_2 = 31.1°C

It is not posible to liquify CO_2 above 31.1°C by any means.

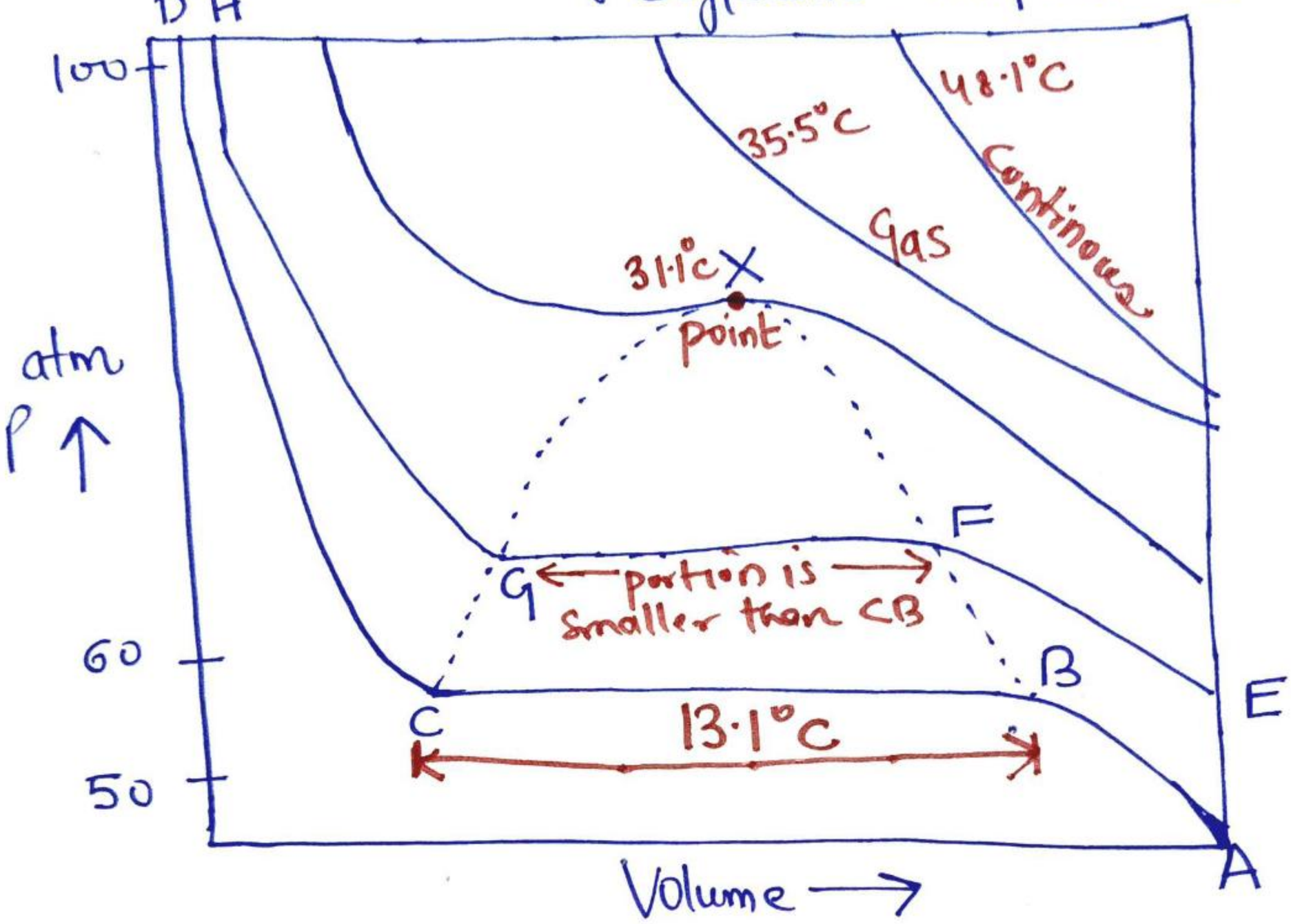
At the critical temperature, a certain prenure is needed to liquify the gas. This prenure is called the critical prenure.

The volume occupied by one mole of a gas at its critical temp. & critical prenure is known as the critical volume

P-V isotherm of CO_2
OR
Andrew Isotherm of CO_2

↓

To Study P-V relationship of CO_2 at different Temperature



Above shown is Experimental PV curve

First Isotherm at low temp = 13.1°C
↓ (ABCD)

(a line on a chart that represents changes of volume or pressure at constant Temp)

The point A represent CO_2 in gaseous state occupying a certain volume under a certain pressure. On increasing the pressure (as we move upward along the curve AB in graph), its volume ↓ses as is indicated by the curve AB.

At B, liquifaction of the gas starts and ∴, a rapid ↓se in the volume takes place at the same Pressure, as more and more of the gas is converted into the liquid state.

At C, the gas has been completely liquified. Now as the liquid is only slightly compressible, further ↑se of P produce only a very small ↓se in volume. This is shown by a steep line CD which is almost vertical

Along curve AB, CO_2 exists as gas

Along line BC, it exist partly as gas and partly as liquid

while along CD, entirely as liquid

A considerable decrease of volume (represented by BC) takes place when the gas changes into the liquid state at a constant P

Isotherm EFGH at 21.5°C shows similar behaviour except that now liquifaction starts at a higher ~~temi~~ pressure and horizontal portion FG, representing decrease in volume, becomes smaller.

At still higher temperature, the horizontal portion of the curve become shorter and shorter until at 31.1°C it reduces to a point (X). At this temp, ∴ the gas passes into liquid state gradually.

Above 31.1°C, the isotherm is continous. (no breakpoints)
There is no evidence of liquifaction at all.

Andrew concluded that if the temperature of CO_2 is above 31.1°C, it cannot be liquified, no matter how high the pressure may be.

31.1°C is the critical temp of CO_2

Calculation of critical constants (T_c, P_c, V_c) from vander Waals equation

first Start with vander Waals eq. i.e,

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

for $n = 1$ mol

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

{ V can be written as V_m molar volume } as we have considered $n = 1$

$$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT$$

$$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} - RT = 0$$

Multiply by V_m^2 and divide by P and rearrange in decreasing power of V_m

$$PV_m^3 - PbV_m^2 + aV_m - ab - RTV_m^2 = 0 \quad \{\times V_m^2\}.$$

$$V_m^3 - bV_m^2 + \frac{a}{P}V_m - \frac{ab}{P} - \frac{RT}{P}V_m^2 = 0 \quad \{/P\}.$$

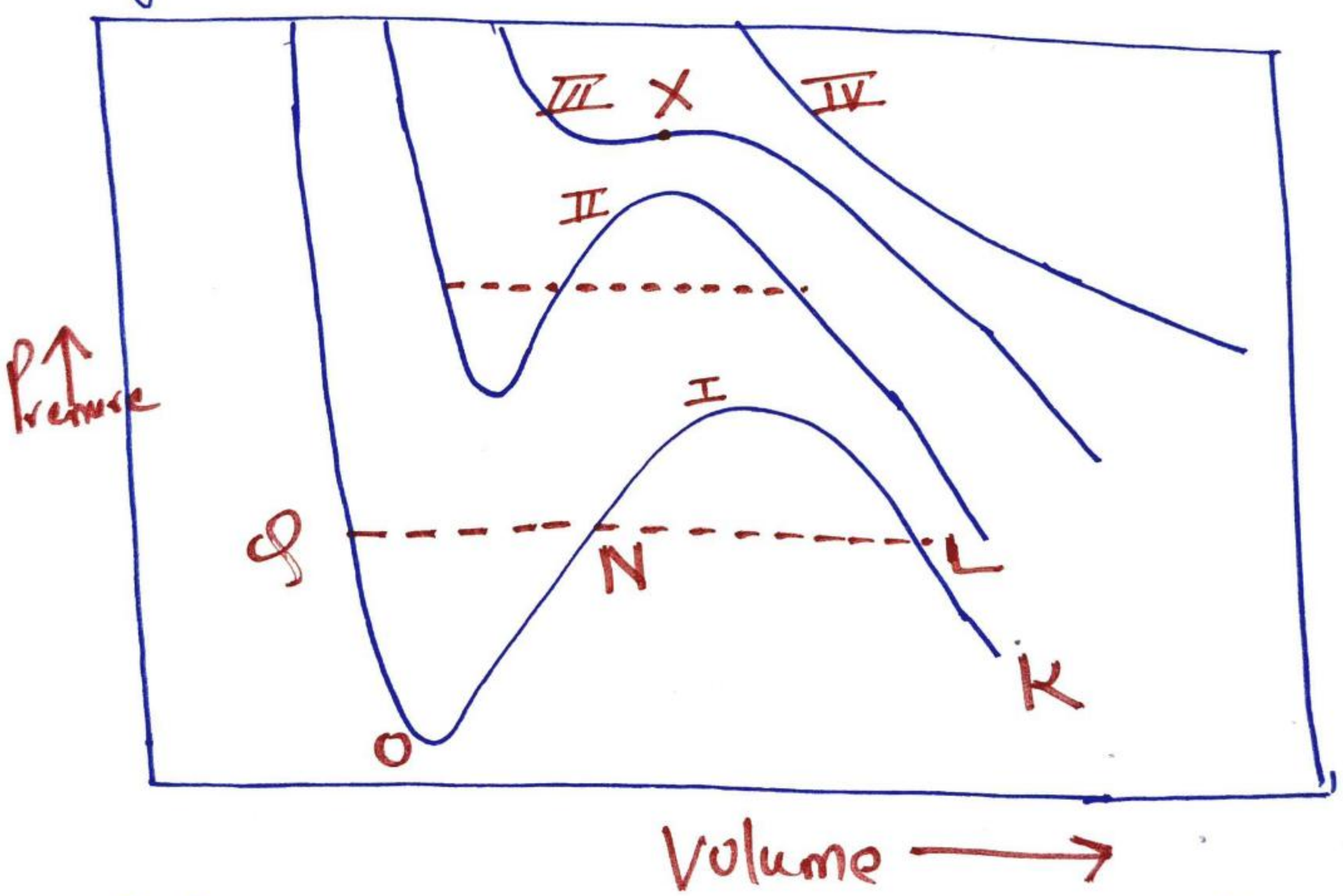
$$\left[V_m^3 - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{aV_m}{P} - \frac{ab}{P} = 0\right] \{\text{Rearrangement}\}$$

eq (1)

The equation 1 is cubic equation in V_m

For any single set of values of P and T, there should be three values of V_m - { all may be real / only one real & other two imaginary

If at constant temp, the values of P are plotted against V, then it will look like as



The above shown is theoretic P-V isotherm graph of CO_2 { based on theoretical calculation of V corresponding to different values of P }

Curve I for a certain pressure, three values of V → { L, N, Q } there are 3 pts shown in graph

As the temp ↑ses (isotherm II), three values of V get closer to one another (See dotted lines drawn is shorter in distance as compared to line drawn in Curve I)

At a certain higher temperature (isotherm III), three values of V become identical as shown by X.

At a still high temperature (IV curve), there is only one real value of V corresponding at a given pressure

As the temperature is raised, loops become smaller & smaller and at critical point X, three values of V become identical (single point)

Since the loop is now critical, value of V represents the critical volume of gas.

$\Rightarrow V_m = V_{m,c}$

(molar volume) (critical molar volume)

$$V_m - V_{m,c} = 0.$$

OR $$(V_m - V_{m,c})^3 = 0.$$

$$V_m^3 - 3V_{m,c}(V_m)^2 + 3(V_{m,c})^2 V_m - (V_{m,c})^3 = 0 \quad (2)$$

{ using $(a-b)^3 = a^3 - 3a^2b + 3ab^2 - b^3$ }

eq (1) and eq (2) must be identical at T_c and P_c

eq (1) rewritten as

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

On comparing coefficient of V_m in (2) & (3)

$$3V_{m,c} = b + \frac{RT_c}{P_c} \quad - \quad (i)$$

$$3(V_{m,c})^2 = \frac{a}{P_c} \quad - \quad (ii)$$

$$(V_{m,c})^3 = \frac{ab}{P_c}. \quad - \quad (iii)$$

On dividij (ii) & (iii)

$$\frac{3(V_{m,c})^2}{(V_{m,c})^3} = \frac{a}{P_c} \times \frac{P_c}{ab}$$

$$\frac{3}{V_{m,c}} = \frac{1}{b}$$

$$\boxed{V_{m,c} = 3b}$$ critical volume

Put $V_{m,c}$ value in (ii)

$$3(3b)^2 = \frac{a}{P_c}$$

$$\boxed{P_c = \frac{a}{27b^2}}$$ critical prenure

Put $V_{m,c}$ & P_c value in (1)

$$3(3b) = b + \frac{RT_c}{a/27b^2}$$

$$\boxed{T_c = \frac{8a}{27Rb}}$$ critical temperature