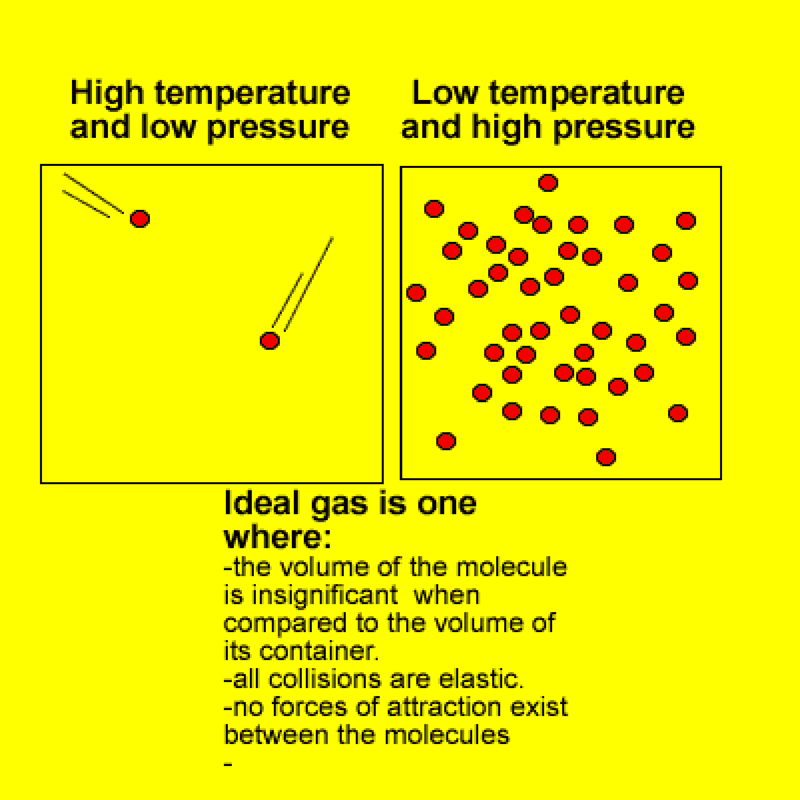
UNIT:II

Real Gases And Their Behavior



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Andrew's Experiment on CO_2

- **Principle :**

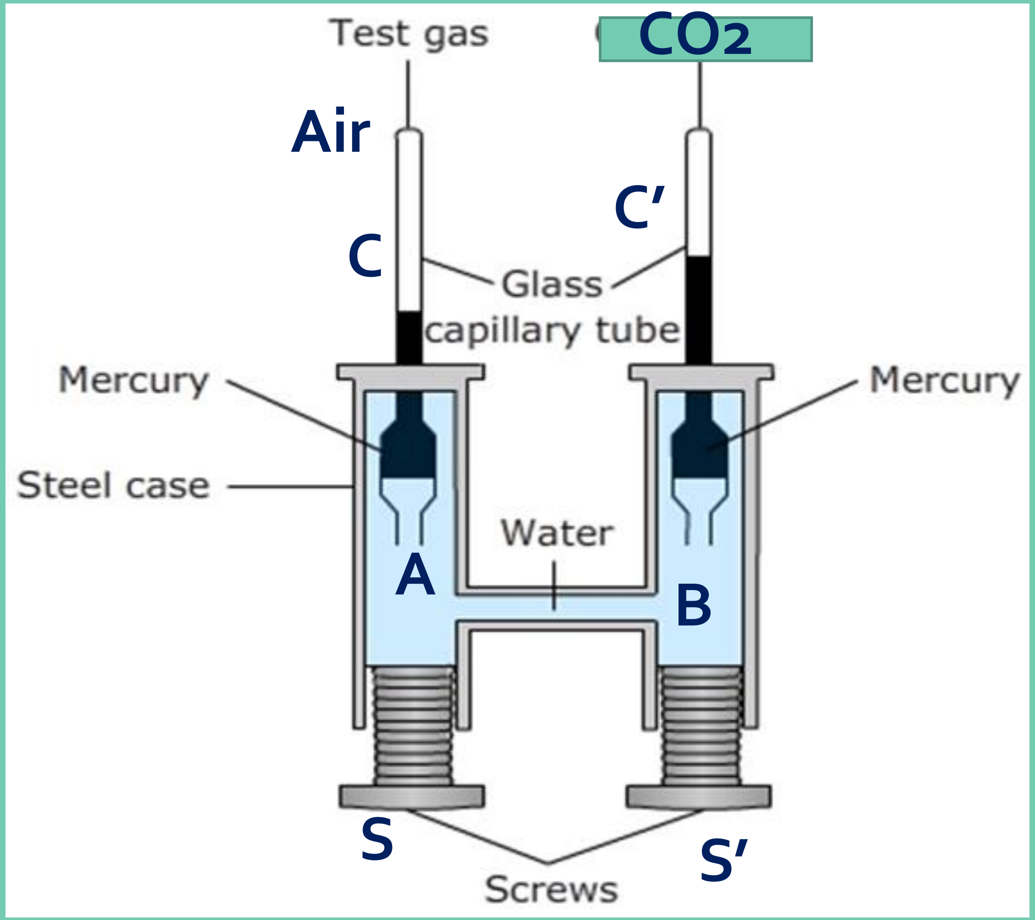
Measure volume of fixed mass of gas at various pressures at a given constant temperature and isothermals are drawn .Various isothermals for different fixed temperatures are obtained. The deviation from ideal gas law can be studied

Apparatus:

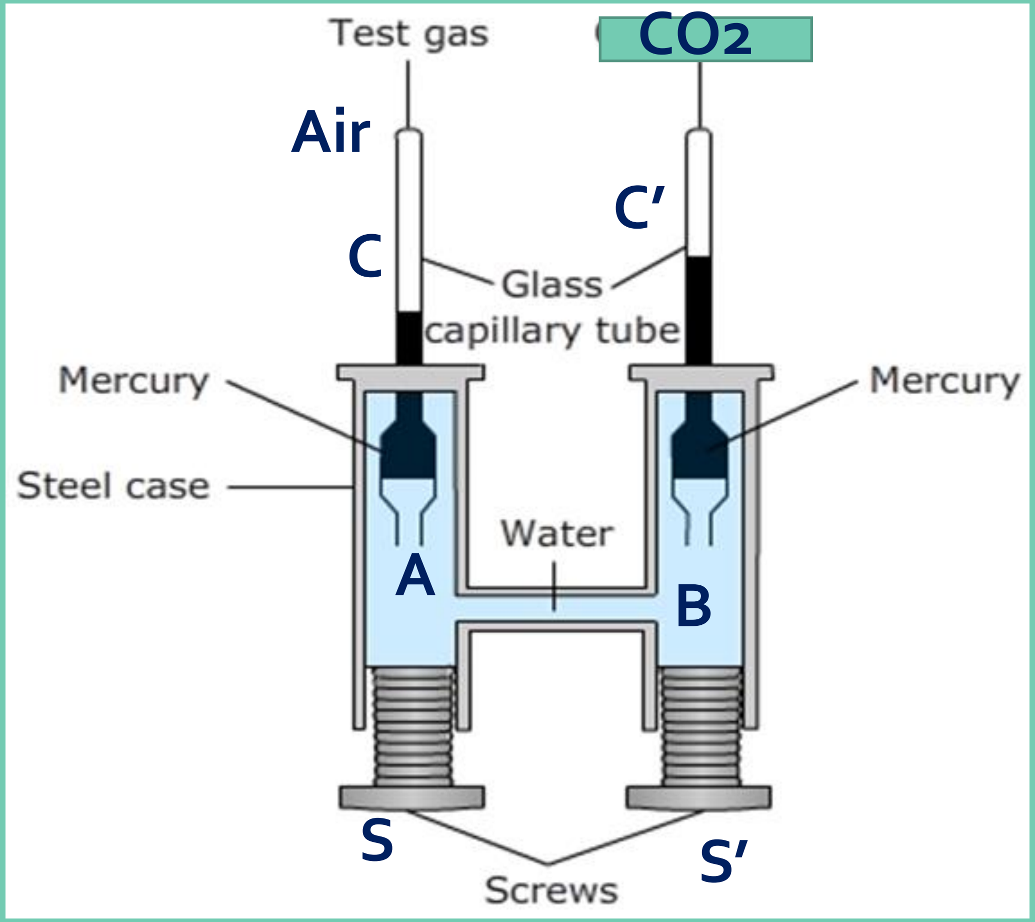
Two similar glass tubes A and B having capillary tubes C and C' at top

In tube A pure dry air is passed for long time and ends are sealed

In tube B experimental gas CO_2 is passed for long time and ends are sealed



Andrew's Experiment on CO_2



Lower ends of both tubes are immersed in mercury

Small pallets of mercury drawn in both tubes by alternately heating and cooling the tubes

Both tubes are fixed in H shaped copper vessel having stoppers S and S'

The vessel is filled with water

By screwing in plunger water is compressed and pressure up to 400 atmosphere can applied.

Since pressure on A and B are same ,from volume of air in A ,pressure of CO_2 can be calculated

Volume of B can read directly

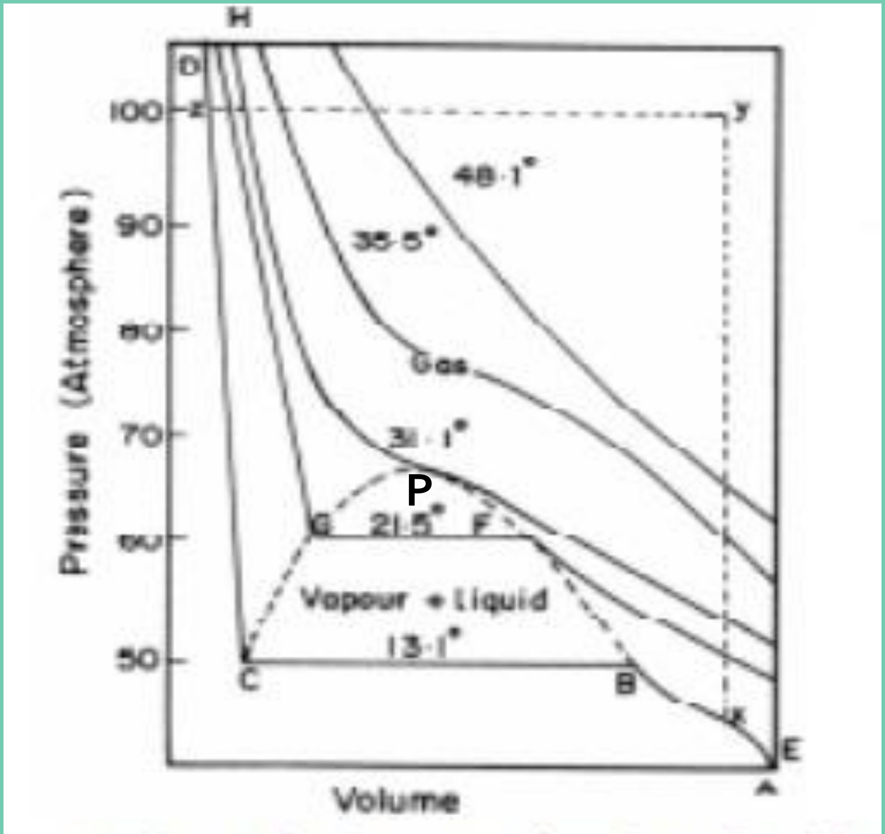
Temperature of CO_2 maintained at desire (0 to 100°C)

Andrew's Experiment on CO_2

Result:

Isothermals are drawn at various temperatures

1. At 13.1 °C AB represent gaseous state of CO_2 up to point B and obeys Boyles law.
2. From B to C it shows an enormous decrease in volume with slight increase in pressure.
3. BC represents change of CO_2 from gaseous to liquid state
4. At C gas has been completely liquefied and portion CD represent the liquid state of CO_2
5. At 21.5 oC the curve is similar , horizontal portion (FG) decreases



Andrews isotherms of carbondioxide

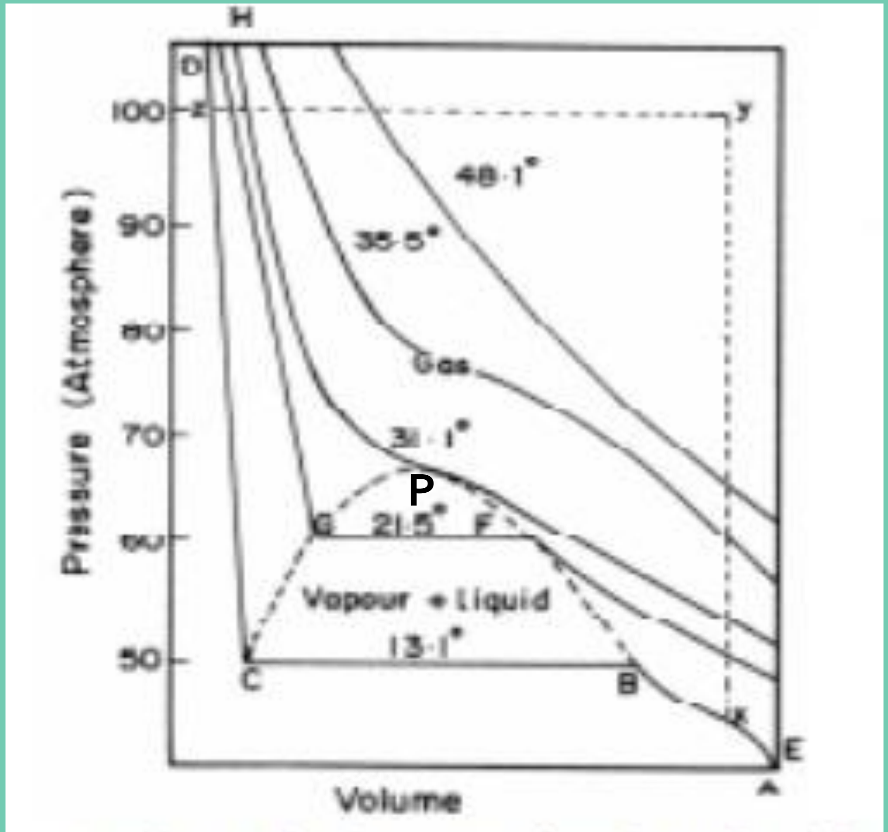
Andrew's Experiment on CO_2

Result:

At 31.1 oC Horizontal portion vanished called critical isothermal for CO_2

Above this temperature gas can not be liquified

At 35.50C and 48.1 oC no horizontal portion, gas can not liquified and Boyles law is obeyed from one end to other

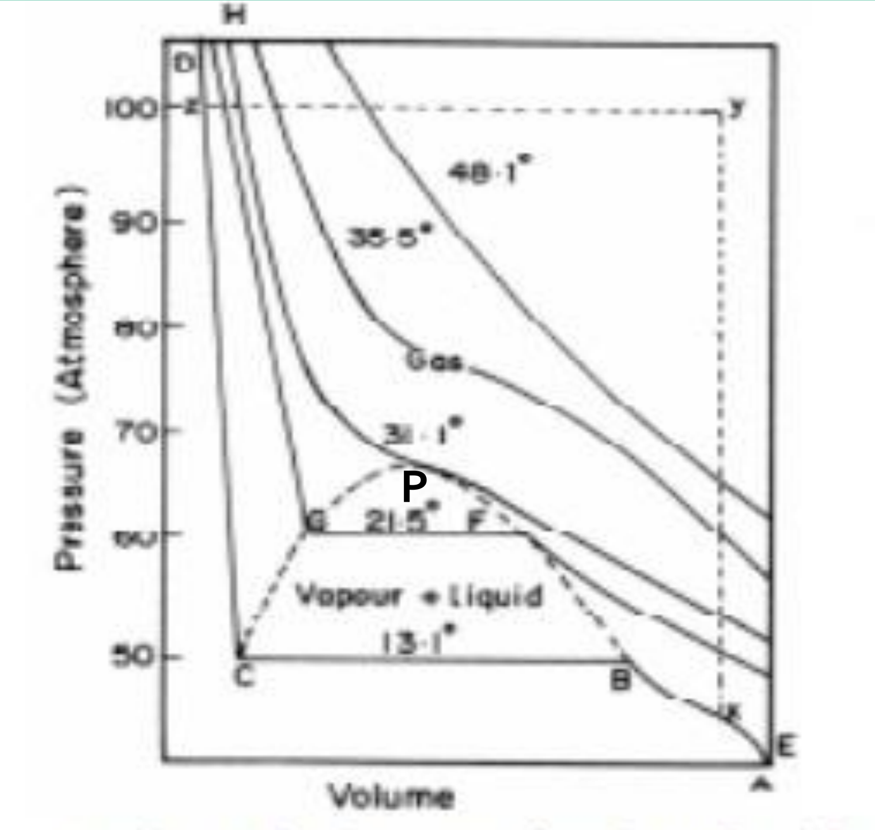


Andrews isotherms of carbondioxide

Andrew's Experiment on CO_2

Experimental Findings:

1. Andrew found liquification of CO_2 occurred only below 31.1 oC called critical temperature
2. There is no physical distinction between liquid and gas on horizontal portion of isothermal
3. Gas behaves almost as perfect above critical temperature
4. Density of liquid and vapour becomes equal at critical point

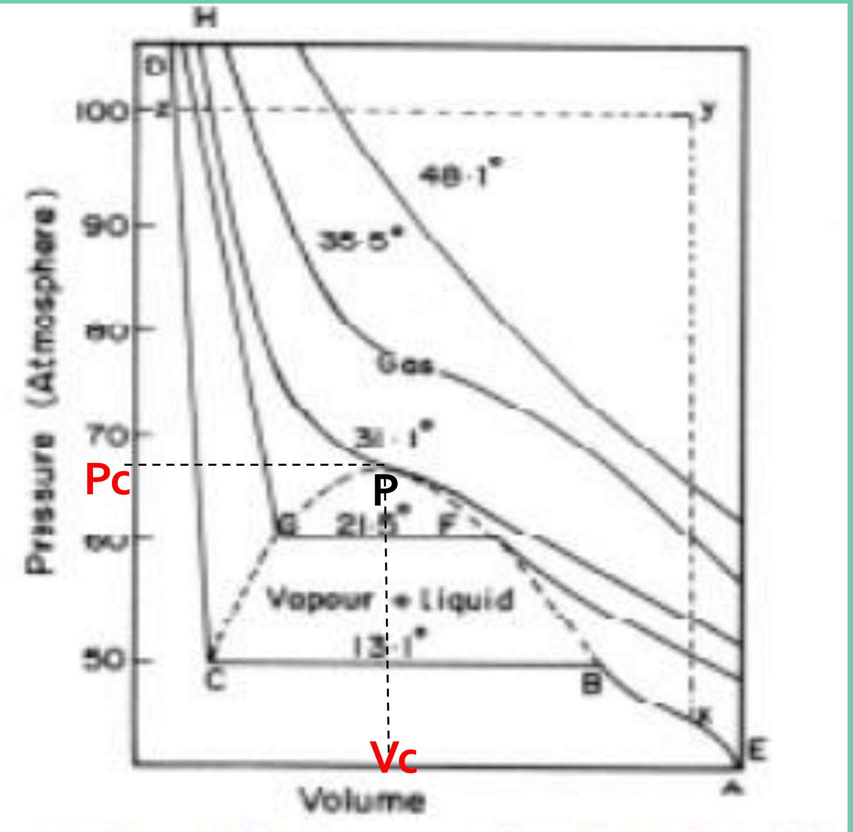


Andrews isotherms of carbondioxide

Andrew's Experiment on CO_2

Definitions:

1. **Critical point:** Point on isothermal at which gas is liquified
2. **Critical isothermal:** Isothermal corresponding to critical temperature
3. **Critical Temperature (Tc):** The highest temperature at which a gas can be liquified by increase of pressure alone
4. **Critical Pressure (Pc):** Pressure applied to gas at its critical temperature so that it get liquified
5. **Critical Volume (Vc):** The particular volume of gas at critical pressure and volume



Andrews isotherms of carbondioxide

Amagat's Experiment

Amagat performed series of experiments with hydrogen ,nitrogen and CO_2 to study their behavior at high pressure

Apparatus:

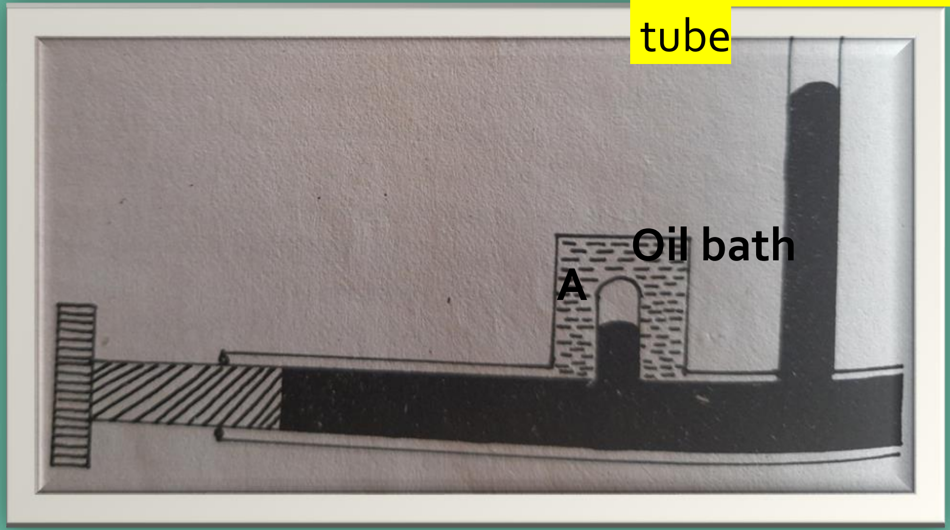
Large metallic cylinder of mercury having large screw plunger S fitted to end

Apparatus was arranged at base of mine 327 m deep subjecting about 423 atmospheric pressure

Long steel manometer about 1000 feet fixed along the shaft of coal mine and opened at top

Calibrated inverted tube A contains experimental gas

Oil bath surrounds the tube



Amagat's Experiment

Amagat plotted isothermal between PV and P

For Hydrogen Gas:

All isothermals are parallel

Product PV increases with increase of Pressure

Hydrogen is less compressible

Isothermals do not sag

For Nitrogen Gas:

PV first decreases with increase of P

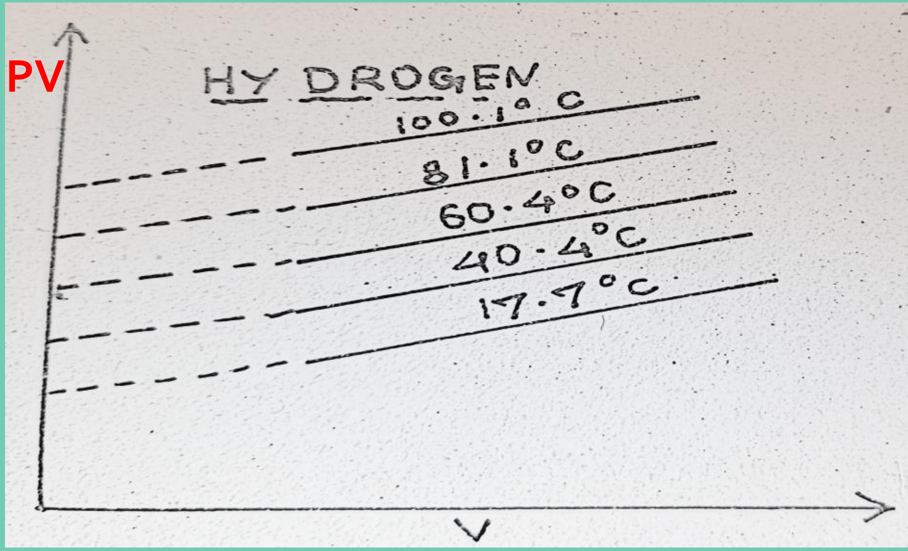
Attains minimum

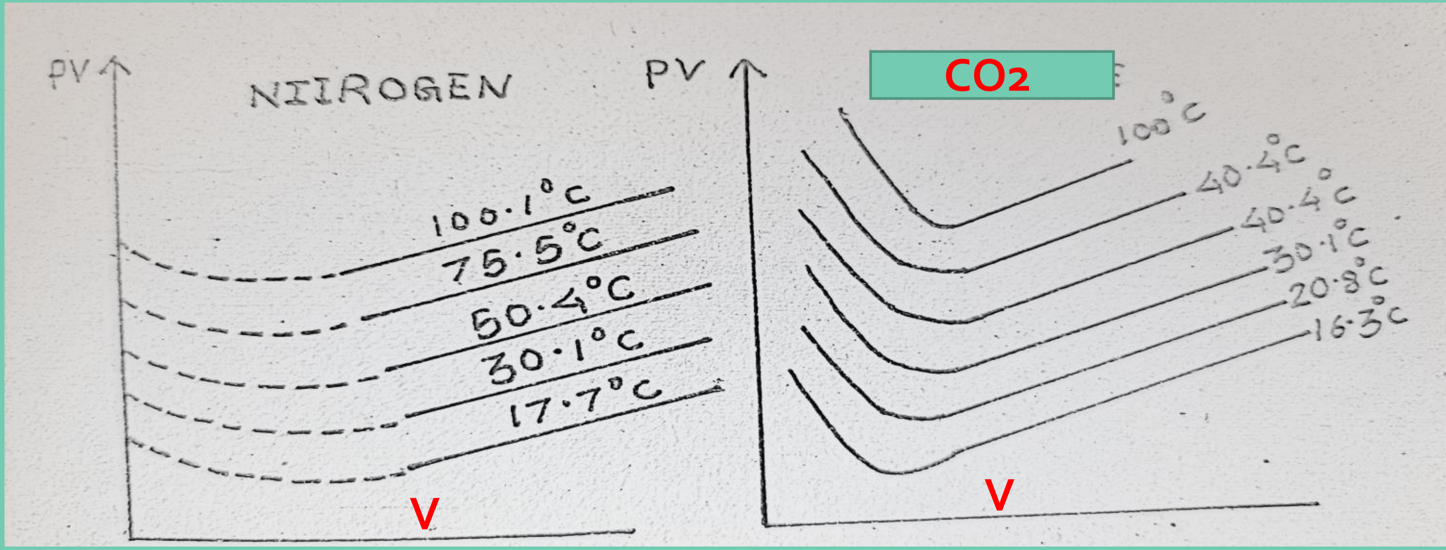
And increases slowly with pressure

Sag is found at lower temperature

For CO_2 Gas:

Minima is more pronounced





Amagat’s Experiment

Experimental findings:

No gas obeys Boyles law at higher pressure

All gases shows same pattern of deviation from Boyles law

Greater deviation from Boyles law is found near critical temperature

The gas which liquified easily shows more deviation from Boyles law

Behavior of gases at high pressure:

General nature of curves same for all gases

1. At high temp. PV increases with P
2. At low temp. PV decreases initially with increase in P attains minimum and then increases with P
3. Locus of minima shown by dotted curve A
4. At temp. below the critical temp. sudden decrease in PV with increase in P corresponds to change of state from gas to liquid
5. When liquification is complete, PV gradually increase with P
6. Shaded area represents region of liquification
7. Boyles law is obeyed at high temp and low pressure

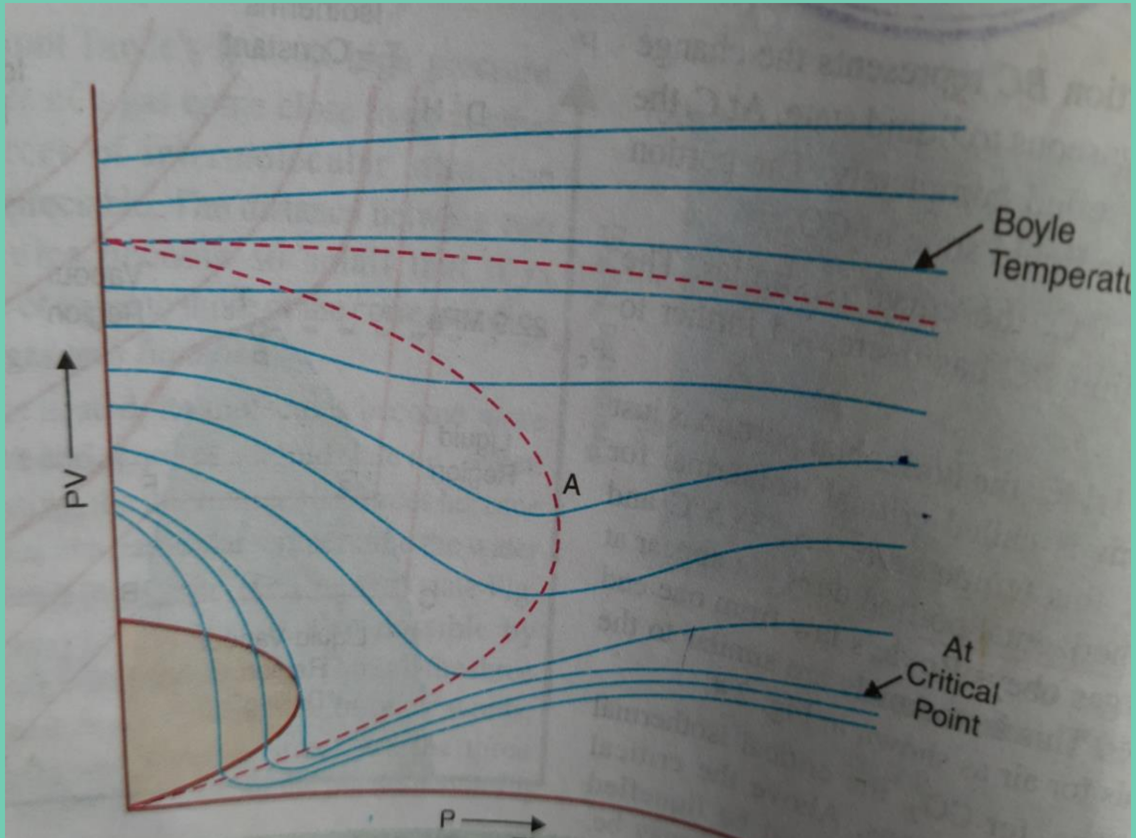


Fig. 2.5

POROUS PLUG EXPERIMENT:

Joule –Tomson Effect :

When a gas under constant pressure is allowed to pass through insulated porous plug to a region of constant lower pressure, the temperature of escaping gas changes.

Changes in temperature ∝ pressure difference on two sides

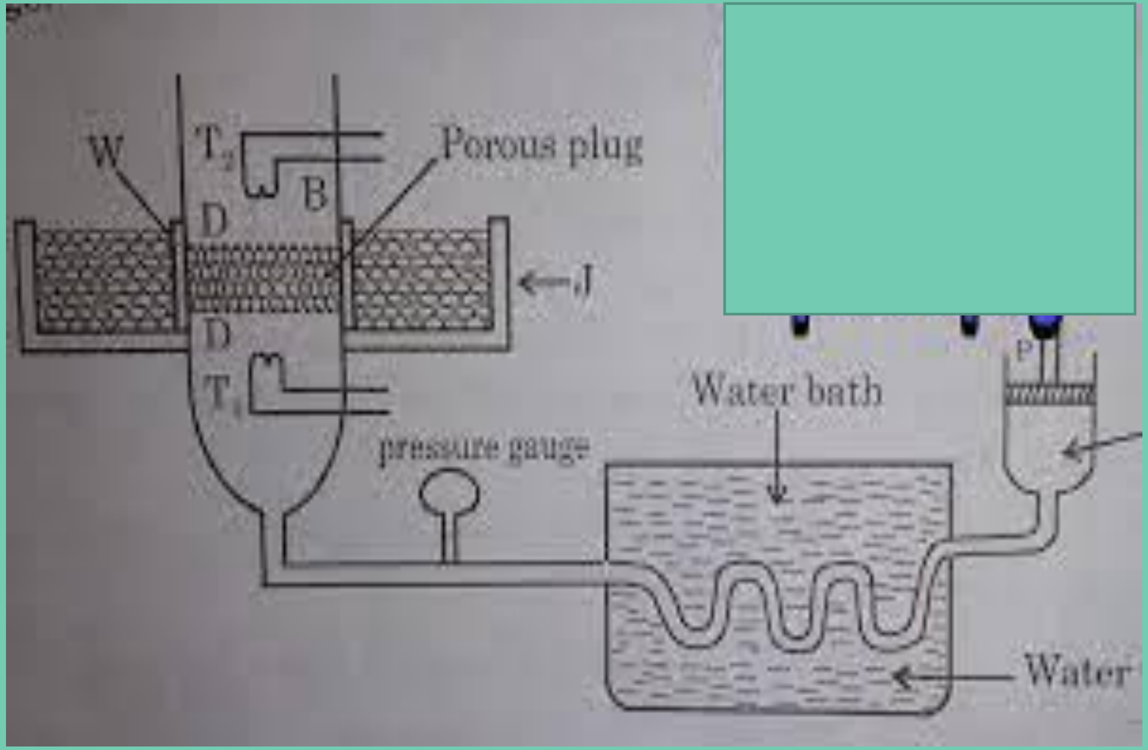
Apparatus:

Prous plug having perforated brass discs D,D

Space is packed with cotton wool or silk fibre

Porous plug is fitted in a cylindrical box wood tube surrounds vessel containing cotton wool to avoid loss or gain of heat from surrounding

T1 and T2 are sensitive thermometrs



POROUS PLUG EXPERIMENT:

Joule –Tomson Effect :

Gas is compressed to high pressure with the help of piston P

Passed through spiral tube immersed in water bath maintained at constant temperature

Heat developed due to compression is taken by circulating water

Working:

Compressed gas passed through porous plug

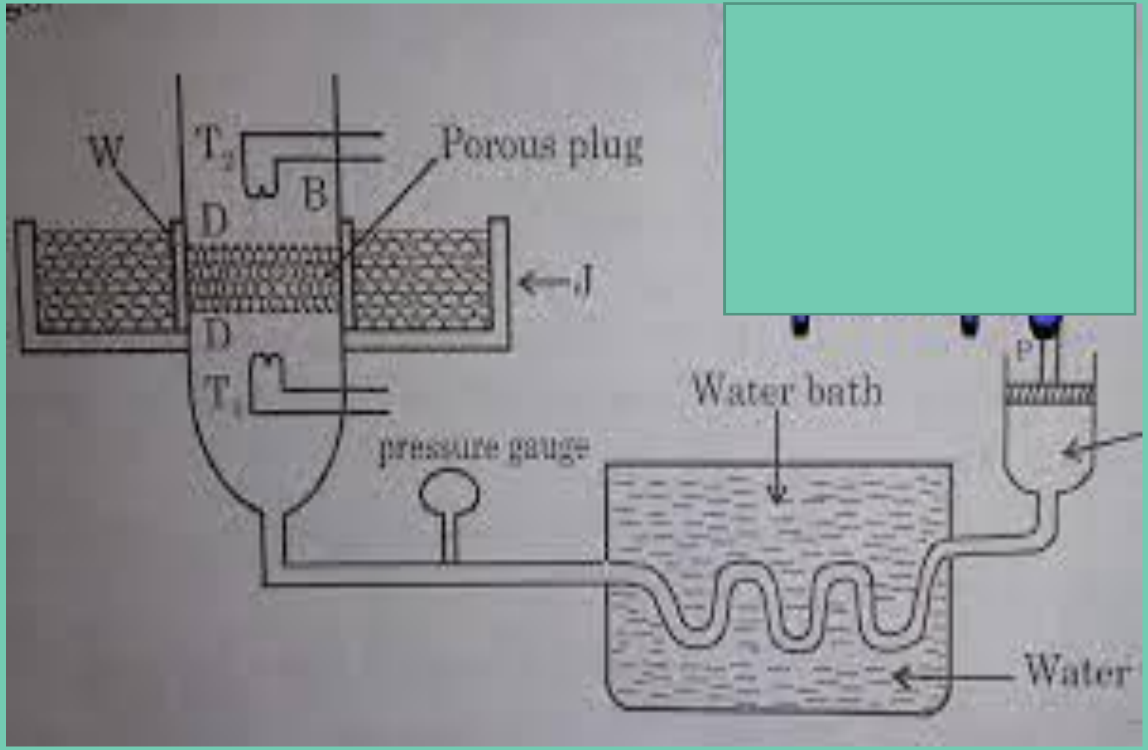
Plug acts as narrow orifices in parallel

Throttling process

Work is done by the gas in overcoming the intermolecular attraction

T2 measures temperature of outgoing

Pressure gauge measures pressure of incomings



POROUS PLUG EXPERIMENT:

Joule –Tomson Effect :

The behaviour of different gases O_2 ,N_2 etc over range of temp.(4^o to 100^oC) and (4.5 to 1 atm) pressure range

Observations:

1 All gas shows change in temperature or J-T effect on passing through porous plug

2 At low enough temperature all gas shows cooling effect

3 At ordinary temp, most gas shows cooling effect except hydrogen

4 Greater the pressure difference, greater fall in temperature and vice a versa

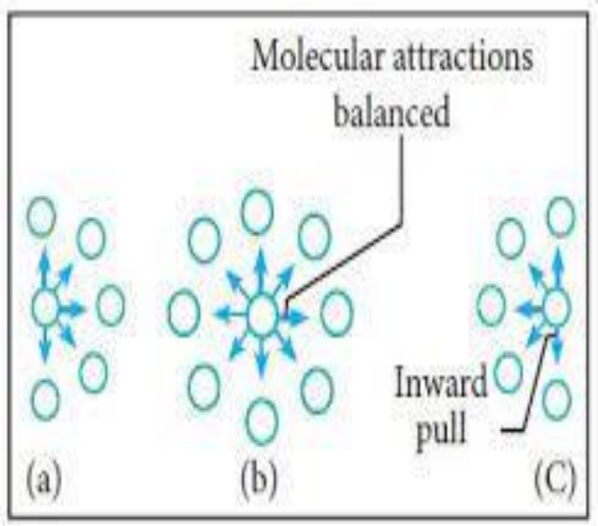
5 Fall in temperature decreases as initial temperature of the gas is raised

6 There is inversion temperature (T_i)for every gas at which J-T effect is zero i.e. fall in temp. passing through porous plug becomes zero and above which it shows heating effect

VAN DER WAALS EQUATION OF STATE:

1897 an der Waal modified perfect gas equation PV=RT by applying correction in

1. Intermolecular forces of attraction
2. Finite size of molecule



Correction for pressure:

Net force acting on molecule inside the vessel is zero

At wall it is pulled back by other

Velocity and momentum is less than in the absence of force of attraction

Reduction in momentum result in decrease in pressure tan actual

Correction depends on

VAN DER WAALS EQUATION OF STATE:

Correction depends on

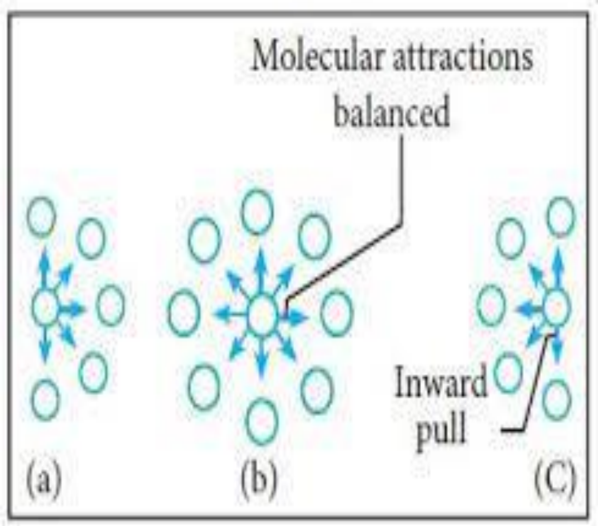
1. No. Of molecules striking per unit area per unit time on walls
2. Resultant inward pull of cohesion on striking molecule

   Each of these proportional to density of gas

∴ Correction for pressure

$$p \propto \rho^2 \propto \frac{1}{V^2}$$

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

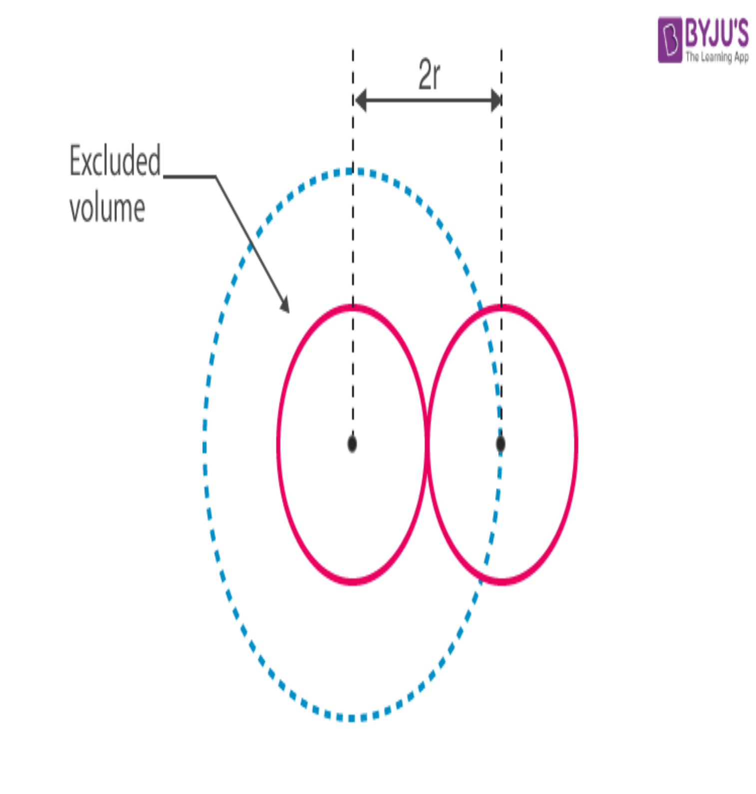


Corrected or Real pressure= $P + p = \left[P + \frac{1}{V^2}\right]$

P is observed pressure

VAN DER WAALS EQUATION OF STATE:

Correction for volume:
Due to finite size of gas molecule actual size available for movement is less than volume of vessel
Molecules have sphere of influence around radius (2r) within no molecule can penetrate



Volume of molecule=$x = \frac{4}{3}\pi r^3$

Volume of sphere of influence of each molecule= $x = \frac{4}{3}\pi (2r)^3$

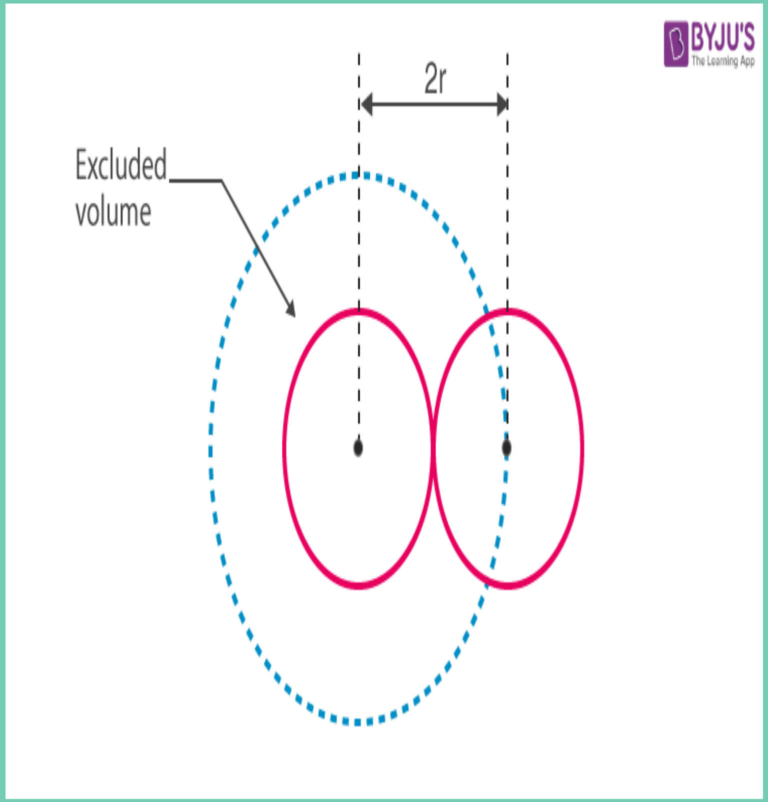
$$s = \frac{4}{3}\pi (2r)^3 = 8x$$

Volume available for first molecule =V

Volume available for second molecule =$V - 8x$

Volume available for nth molecule =$[V - (n-1)s]$

VAN DER WAALS EQUATION OF STATE:



Correction for volume:

Average space available for each molecule

$$\frac{V + (V - s) + (V - 2s) + \cdots + [V - (n-1)s]}{n}$$

$$= \frac{n\,V}{n} - \frac{s}{n}[1 + 2 + 3 + \cdots . +(n-1)]$$

$$= V - \frac{s}{n}.\frac{(n-1)n}{2}$$

$V - \frac{ns}{2} + \frac{s}{2}$ As no. of molecules are larger than s/2

Average space available for each molecule = $V - \frac{ns}{2}$

VAN DER WAALS EQUATION OF STATE:

Correction for volume:

Average space available for each molecule = $V - \frac{ns}{2}$

$$= V - \frac{n(8x)}{2}$$

$$= V - 4nx$$

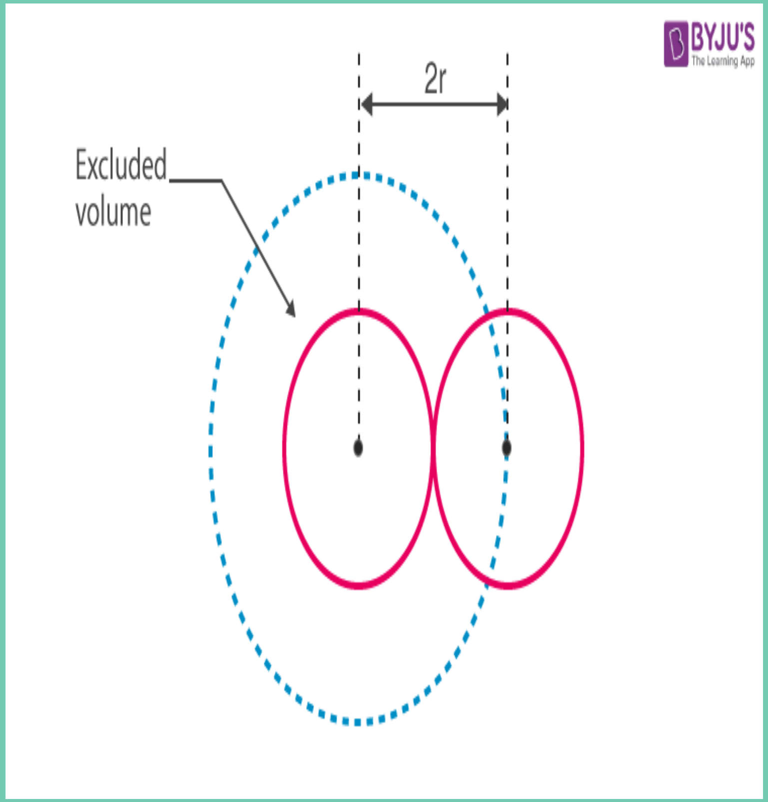
$$= V - b$$

Where b = $4nx$ four times actual volume of molecule

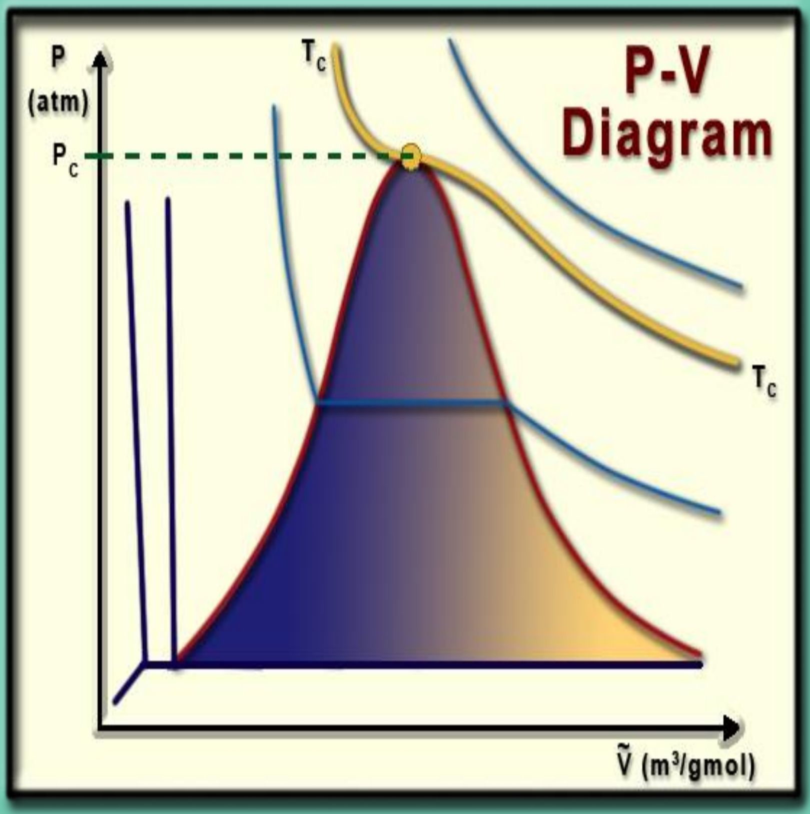
Van der Waals equation for state

$$\left[P + \frac{1}{V^2}\right](V - b) = RT$$

a and b are Van der Waals constants



CRITICAL CONSTANTS:



At critical point the ratio of $\frac{dP}{dV} = 0$ called point of inflection

At point of inflection $\frac{d^2P}{dV^2} = 0$

Van der Waals equation $\left[P + \frac{1}{V^2}\right](V - b) = RT$

$P = \frac{RT}{V-b} - \frac{a}{V^2}$ ---1

$\therefore \frac{dP}{dV} = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3}$ --2

And $\frac{d^2P}{dV^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$ --3

CRITICAL CONSTANTS:

At critical point we have $T=T_C$, $P=P_C$, $V=V_C$, $\frac{dP}{dV}=0$ and $\frac{d^2P}{dV^2}=0$

Substituting

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{{V_c}^2} \qquad (4)$$

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{{V_c}^3} \qquad (5)$$

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{{V_c}^4} \qquad (6)$$

Dividing 5 by 4

$\frac{V_c - b}{2} = \frac{V_C}{3}$ OR $3Vc - 3b = 2Vc$ OR $V_C = 3b$ ---(7)

CRITICAL CONSTANTS:

Substituting Vc in 5

$$\frac{RT_c}{(3b-b)^2} = \frac{2a}{(3b)^3} \qquad = \frac{RT_c}{4b^2} = \frac{2a}{27\,b^3}$$

$$T_c = \frac{8a}{27bR} \quad \text{--------(8)}$$

Substituting V_C and T_c in eq. 4

$$P_c = \frac{8aR}{27\,bR\,(3b-b)} - \frac{a}{(3b)^2} \quad = \frac{8a}{27\times 2b^2} - \frac{a}{9b^2}$$

$$P_c = \frac{a}{27b^2} \qquad \text{---(9)}$$

VAN DER WAALS CONSTANTS:

$$T_c = \frac{8a}{27bR}$$

$$\frac{a}{b} = \frac{27\ RTc}{8} \quad \text{--(10)}$$

but

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

$$\frac{a}{b^2} = 27P_c \quad \text{---(11)}$$

Dividing 10 by 11

$$\frac{a}{b} \times \frac{b^2}{a} = \frac{27\ RTc}{8} \times \frac{1}{27P_c} \qquad = b = \frac{RT_c}{8Pc}$$

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

REDUCED EQUATION OF STATE:

The quantity $\frac{RTc}{P_c VC}$ is called critical coefficients

$\frac{RTc}{P_c VC} = \frac{8}{3}$ and is same for all gases

Let $\alpha = \frac{P}{P_c}, \beta = \frac{V}{V_c}$ and $\gamma = \frac{T}{T_c}$ and $P = \alpha P_c$, $V = \beta V_c$,and $T = \gamma T_c$

Vander Waals equation $\left[P + \frac{1}{V^2}\right](V - b) = RT$

Substituting P ,V and T

We get

$\left[\alpha + \frac{3}{\beta^2}\right](3\beta - 1) = 8\gamma$ is reduced equation of state

Boyle Temperature, Temperature of Inversion and critical temperature and relations between them

Boyle temperature (T_B): Temperature above which a real gas behaves like an ideal gas and obeys Boyles law

Temperature of inversion(T_i): Particular temperature at which J-T effect changes its sign

Critical Temperature (Tc): The highest temperature at which a gas can be liquified by increase of pressure alone

Relations

$$T_B = \frac{a}{Rb} \quad T_i = \frac{2a}{Rb} \quad \text{and} \quad T_c = \frac{8a}{27bR}$$

$$T_i = 2\,T_B$$

$\frac{T_i}{T_c} = \frac{27}{4} = 6.75$ and does not depends upon nature of gas