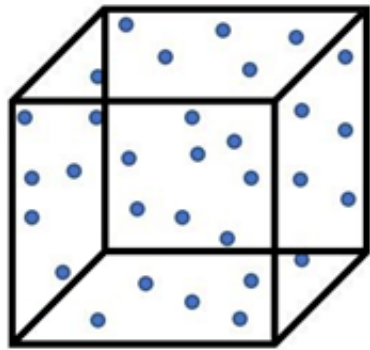
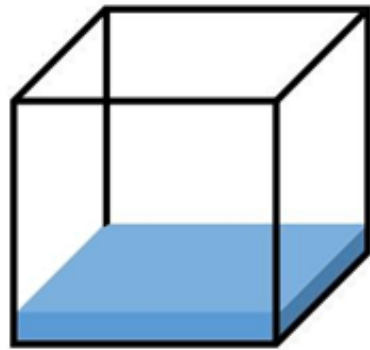


CRITICAL PHENOMENA

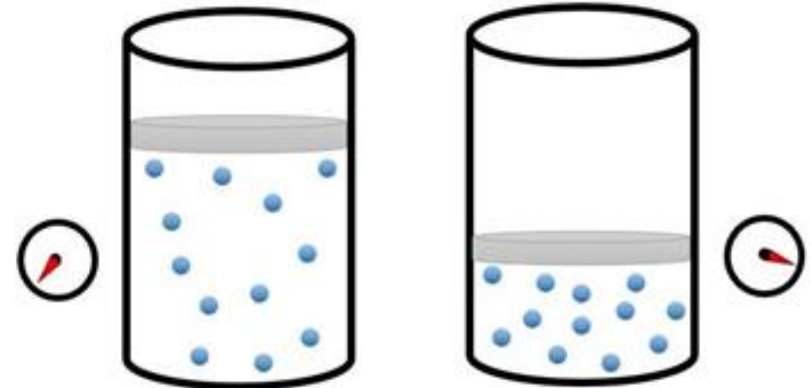
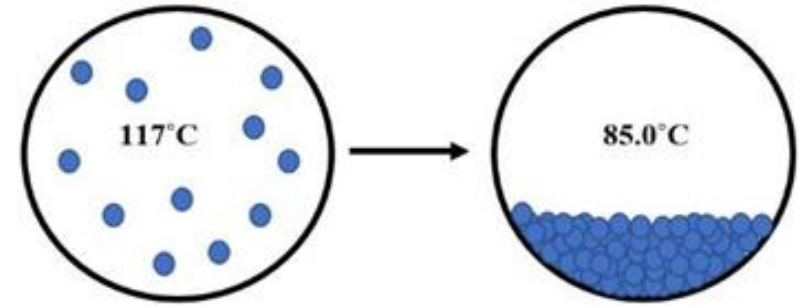
- The essential condition for the liquefaction of the gas is described by the study of critical temperature, critical pressure and critical volume and their inter relationships.
- The decrease in volume can be effectively brought about by **lowering of temperature**, or by **increasing pressure** (or) by both.



Gas



Liquid



(a) Low Pressure

(b) High Pressure

Critical temperature (T_c)

It is defined as the characteristic temperature of a gas above which no liquefaction occurs although the pressure may be increased many fold. For instance T_c of CO_2 is $31.1\text{ }^\circ\text{C}$.

Critical pressure (P_c)

It is defined as the minimum pressure required to liquefy 1 mole of a gas present at its critical temperature. For instance P_c of CO_2 is 73 atm.

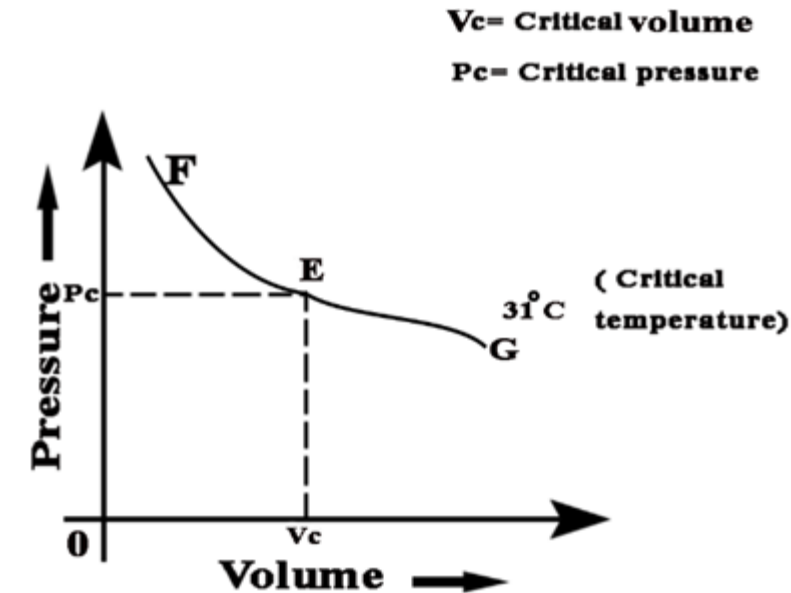
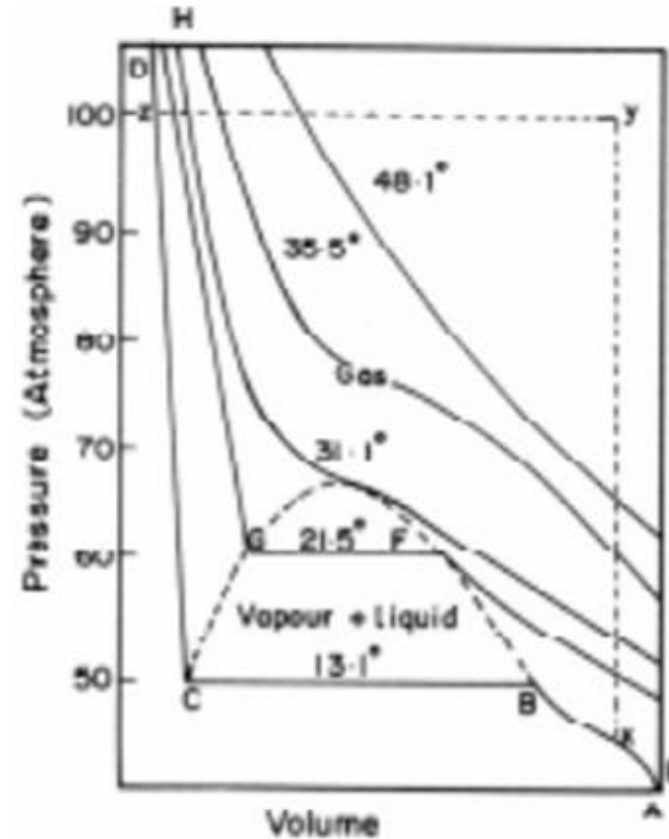
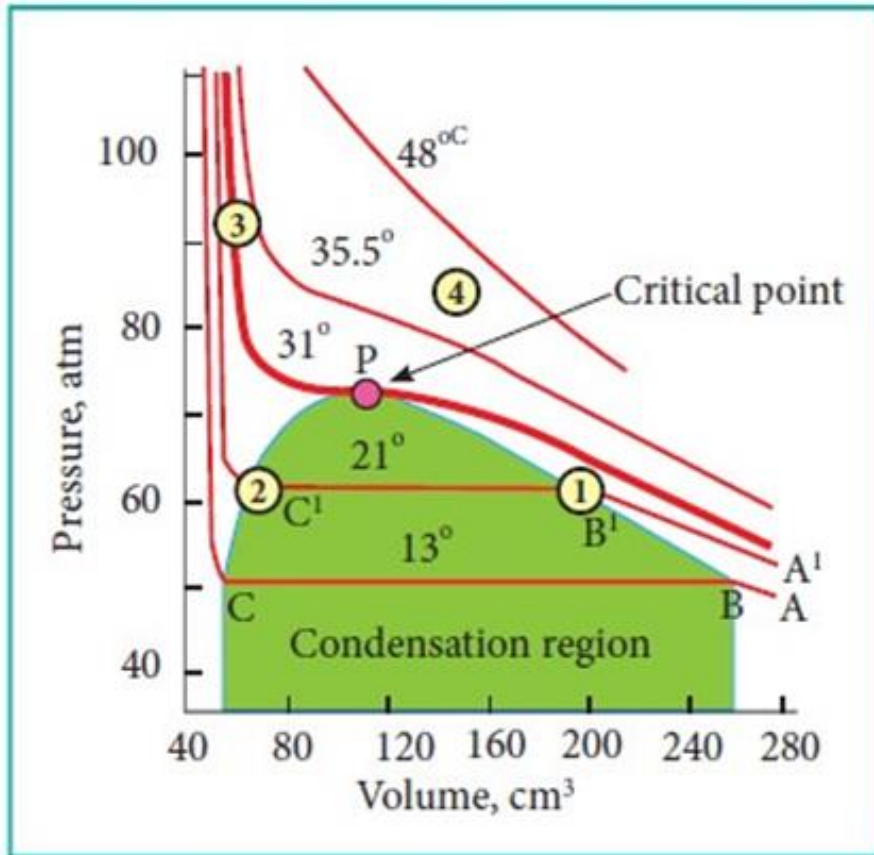
Critical volume (V_c)

The volume occupied by 1 mole of a gas at its critical pressure and at critical temperature is the critical volume (V_c) of the gas. For instance V_c of CO_2 is 95 cm^3 .

- A gas is said to be at its **critical state** when its pressure, volume and temperature are P_c , V_c and T_c .
- At the critical state, *the physical properties of the liquid and gaseous forms of the substance become identical and no distinction can be observed between the two.*
- The smooth merging between a gas and its liquid state at the critical state and the related phenomena are called **critical phenomenon**.

Andrews' Experiments : The Isotherms of a Real Gas

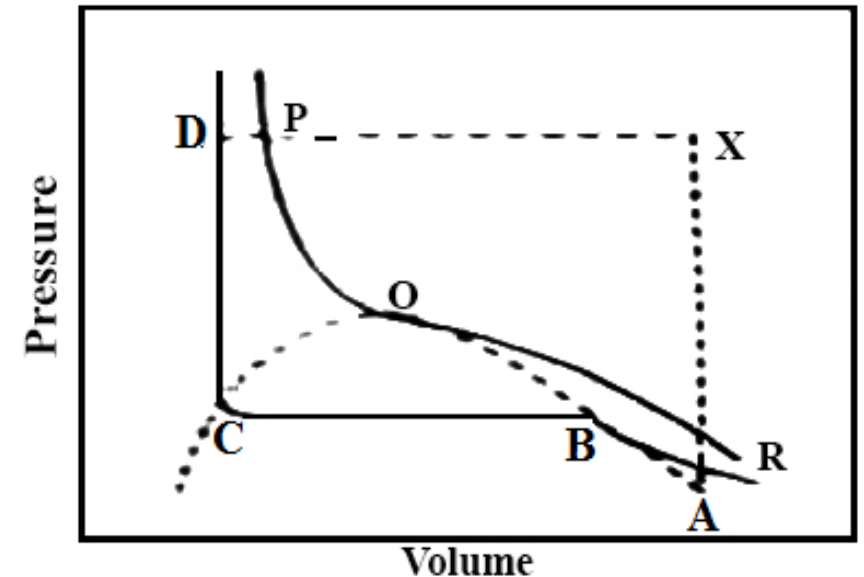
- The importance of critical temperature of a gas was first discovered by Thomas Andrews in his experiments on pressure - volume isotherms of carbon dioxide gas at a series of temperature.
- The isotherm of carbon dioxide determined by him at different temperatures are shown below.



CONTINUITY OF STATES:

A gas can be liquefied by sufficient compression at or below its critical temperature. *According to the principle of continuity of state, the liquid state does not represent a sharp and discontinuous transition from gaseous state, but is rather a continuation of the gaseous phase into the region of very strong intermolecular attractions and small volumes.*

- *During this transition from gas to liquid, there has been never been more than one phase present at any time.*
- *The change from gas to liquid must have occurred at P on the critical isotherm because the transition between the phases occurs continuously at the critical temperature.*
- *This signifies the continuity between gaseous and liquid states.*



RELATIONSHIP BETWEEN VAN DER WAAL'S CONSTANTS & CRITICAL CONSTANTS

The Van der Waal's equation for 1 mole of gas:

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

$$PV - Pb + \left(\frac{a}{V}\right) - \left(\frac{ab}{V^2}\right) - RT = 0$$

Multiplying the above equation with $\left(\frac{V^2}{P}\right)$, we get

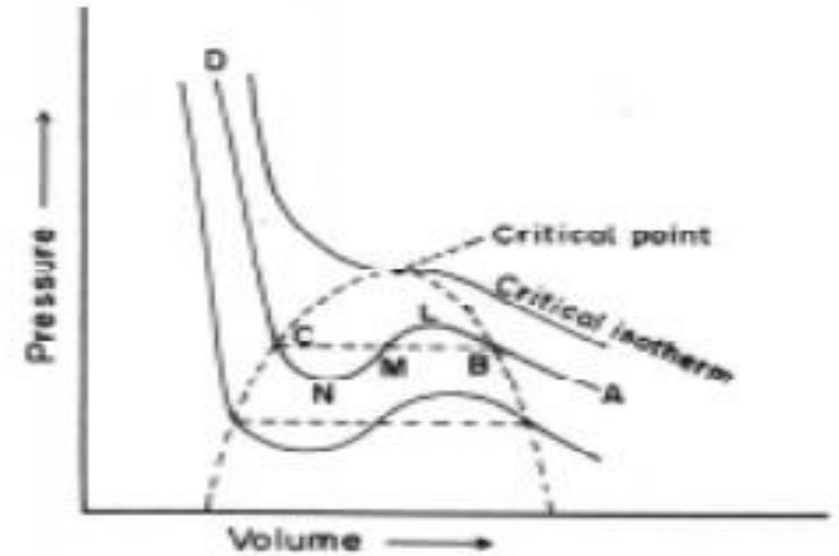
$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \left(\frac{a}{P}\right)V - \left(\frac{ab}{P}\right) = 0 \quad \text{----- (1)}$$

For a given value of P & T, there will be 3 values of V.

The theoretical isotherms plotted using the above equation are similar to experimental isotherms by Thomas Andrews.

However below critical isotherm, wave like portions appear in place of horizontal portions.

- In the wave-like portion, for a particular value of P, we can have three values of V.
- The values of 'V' becomes closer as the temperature increases.
- *At the critical point on the critical isotherm, three roots of V are not only positive and real but are also identical.*
- Above critical isotherm, only one value of V is real and the other two values are imaginary



Thomson's isotherms of CO₂

$$V = V_c$$

$$V - V_c = 0$$

$$(V - V_c)^3 = 0$$

$$V^3 - 3V_c \cdot V^2 + 3V_c^2 \cdot V - V_c^3 = 0$$

------(2)

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

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

Comparing the coefficients of equal powers of V in the above equations, we get:

$$3V_c = \left(b + \frac{RT_c}{P_c} \right) \quad \text{-----(4)}$$

$$3V_c^2 = \frac{a}{P_c} \quad \text{-----(5)}$$

$$V_c^3 = \frac{ab}{P_c} \quad \text{-----(6)}$$

Dividing equation 6 by 5, we get

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} \cdot \frac{P_c}{a}$$

Or, $V_c = 3b$

Putting the above value of V_c in equation (5), we get

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

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

Putting the value of V_c and T_c in equation (4), we get

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

$$9b - b = \frac{RT_c \times 27b^2}{a}$$

$$8b = \frac{RT_c \times 27b^2}{a}$$

Or, $T_c = \frac{8a}{27Rb}$

Critical Compressibility Factor:

The critical compressibility factor is given by:

$$Z_c = \frac{P_c V_c}{RT_c}$$

Putting the values of critical constants and universal gas constant, we get

$$Z_c = 0.375$$

By calculating the critical compressibility factor for any gas and by seeing whether it is equal to 0.375 or not, it can be tested whether the above gas behaves as van der Waal's gas or not.

Relation between T_B and T_c :

We have, $T_B = \frac{a}{Rb}$ and $T_c = \frac{8a}{27Rb}$

The critical temperature equation can be modified as: $T_c = \frac{8}{27} \cdot T_B$

Or, $T_B = 3.375 \cdot T_c$

LIQUEFACTION OF GASES

The Joule Thomson effect is of great practical importance in the liquefaction of gases.

Two processes - Linde's process and Cloude's process

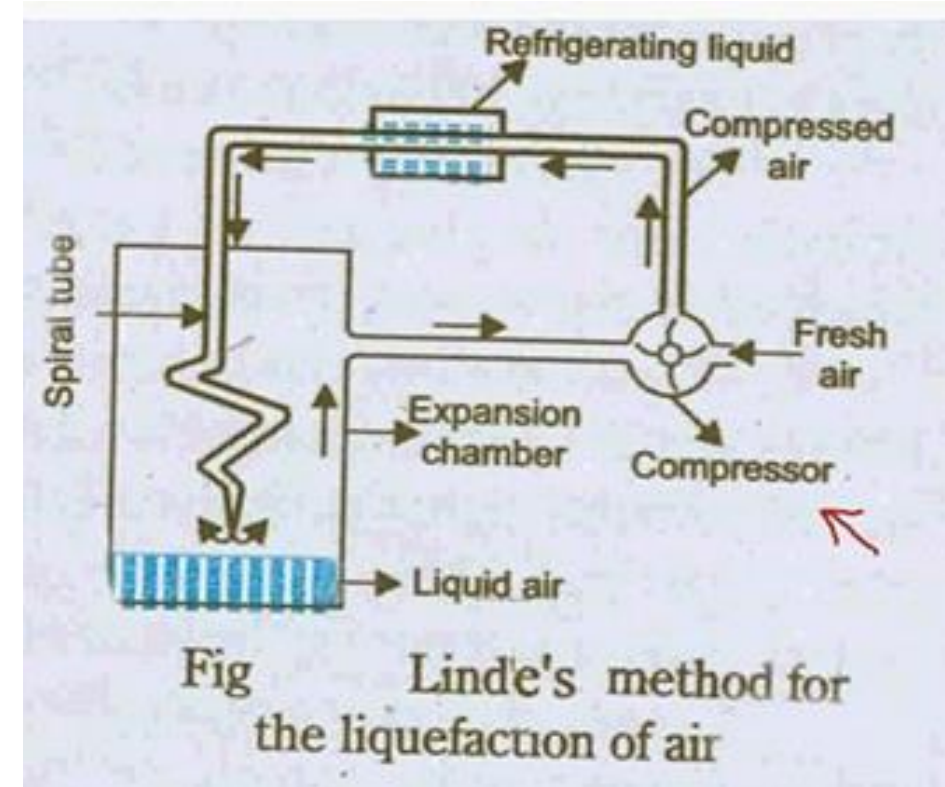
Joule-Thomson effect

- *When a gas under high pressure is allowed to expand under adiabatic conditions through a porous plug into a region of low pressure, there occurs a change in its temperature. This phenomenon is termed Joule-Thomson effect.*
- The difference in temperature observed is proportional to the pressure difference maintained.
- A gas gets cooled by Joule Thomson adiabatic expansion only if its temperature below a certain characteristic temperature. This temperature is called its **inversion temperature** (T_i).

$$T_i = \frac{2a}{Rb}$$

LINDE'S PROCESS:

- Linde's process is based on **Joule-Thomson effect**.
- The pure gas is compressed to about 200 atmospheres and passed through a water-cooled pipe to remove the heat of compression.
- It is then passed through a spiral pipe having a jet at the end. Through the jet, the gas expands out into a region of low pressure.
- In this process, it gets cooled by Joule-Thomson effect. This cooled gas passes up over the spiral, thereby externally cooling the incoming compressed gas, and is returned to the compression pump.
- Repetition of this cycle liquefy the gas.



Claude's process:

In Claude's process for the liquefaction of a gas, the required low temperature is produced by allowing the gas

- (i) to perform mechanical work in an adiabatic expansion engine and
- (ii) to expand adiabatically through a narrow jet into a region of low pressure, below its inversion temperature (Joule Thomson effect).

In both cases, cooling occurs because some work is done by the gas in overcoming the intermolecular attraction at the cost of the kinetic energy of its molecules.

