

Phase transitions



Gaseous State

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GASEOUS STATE

The states of gases: Every substance has certain **physical properties**. The **physical state of substance** can be represented by its **physical properties**. These **properties are related with each other** and can be represented by a mathematical equation. The equation is called as **equation of state**. For ideal gas equation of state can be given as,

$$P = \frac{nRT}{V}$$

Where, $P = f(n, V, T)$

'P' is pressure which is defined as force divided by the area to which the force is applied.

'T' is temperature is the property that indicates the flow of energy through a thermally conducting rigid wall.

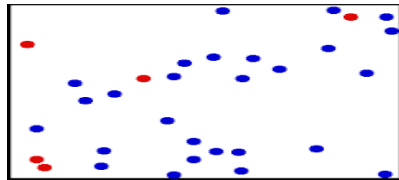
'V' is volume and **'n'** is number of moles.

POSTULATES OF KINETIC THEORY OF GASES

Kinetic theory of gases considers the atoms or molecules of a gas as a **constantly moving point masses**, with huge inter-particle distance and may undergo perfectly **elastic collisions**. Implications of these assumptions are –

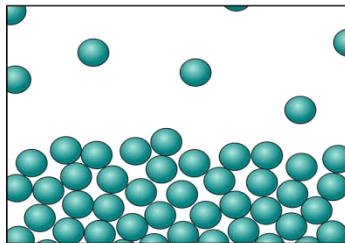
i) Particles:

Gas is a **collection of a large number of atoms or molecules**. **Properties** of the individual **are same** as that of the gas as the whole.



ii) Point Masses:

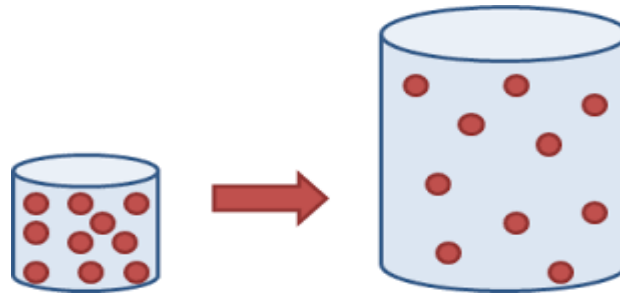
Atoms or molecules making up the **gas are very small particles like a point(dot) on a paper** with a small mass.



iii) Negligible Volume Particles:

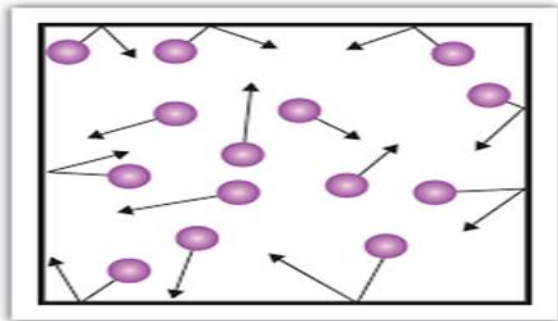
Particles are generally far apart such that their **inter-particle distance is much larger than the particle size** and there is **large free unoccupied space in the container**.

Compared to the volume of the container, the volume of the particle is negligible (zero volume).



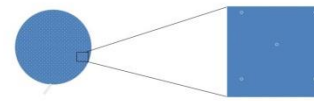
iv) Nil Force of Interaction:

Particles are independent. They **do not have any (attractive or repulsive) interactions** among them.



Kinetic Molecular Theory of Gases

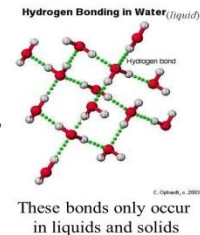
3. Gas molecules **exert neither** attractive nor repulsive **forces** on one another.



“Negligible intermolecular forces”
Inter = “between”

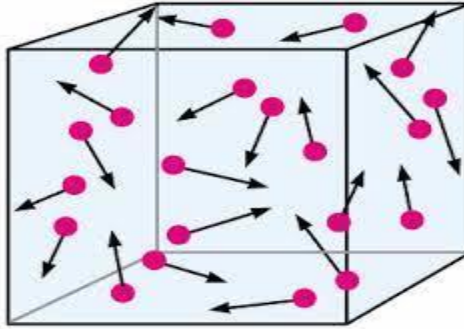
Molecules too far apart to effect each other

- Explains why gases mix completely regardless of identity



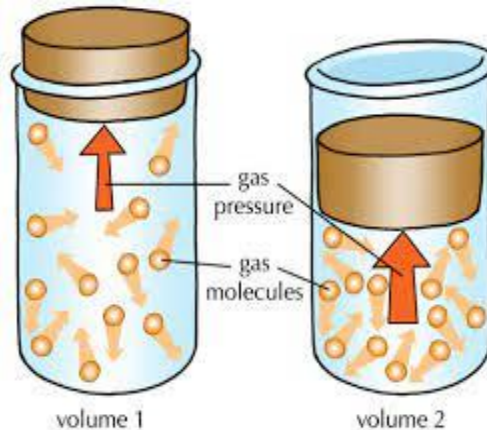
v) Particles in Motion:

The particles are always in **constant motion**. Because of lack of interactions and the **free space** available, the particles randomly move in all directions but in a straight line.



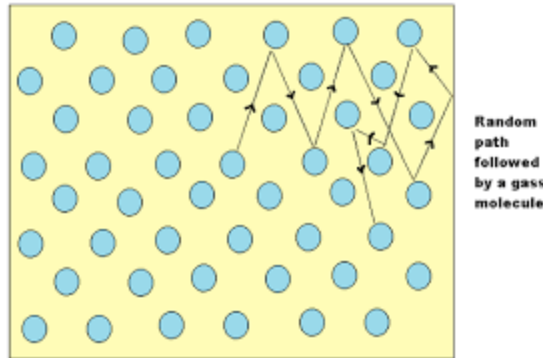
vi) Volume of Gas:

Because of motion, gas particles, **occupy the total volume of the container** whether it is small or big and hence the **volume of the container to be treated as the volume of the gases**.



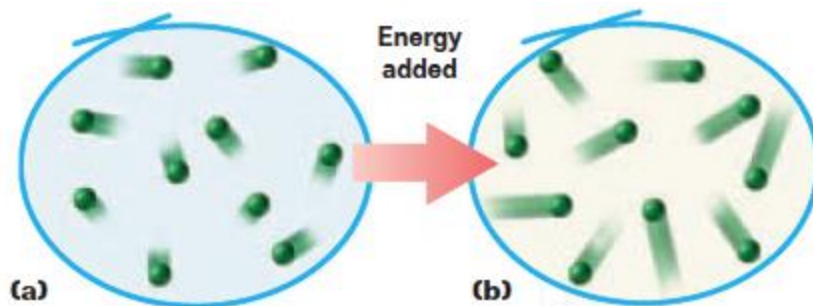
vii) Mean Free Path

This is the **average distance a particle travels to meet** another particle.



viii) Kinetic Energy of the Particle

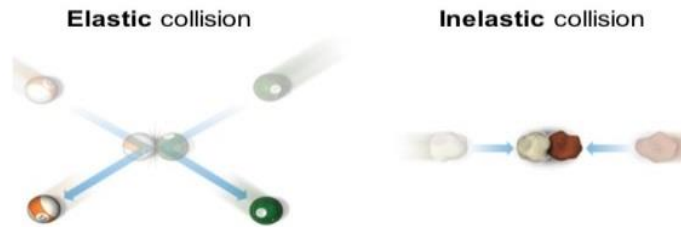
Since the particles are **always in motion**, they **have average kinetic energy** ($K.E \propto T$) proportional to the temperature of the gas.



ix) Constancy of Energy / Momentum

Moving particles **may collide** with other particle or container. But the collisions are **perfectly elastic**. Collisions do **not change** the **energy or momentum** of the particle.

Elastic Collisions



xi) Pressure of Gas:

Collision of the particles on the walls of the container exerts a force on the walls of the container. Force per unit area is the pressure. The pressure of the gas is thus proportional to the number of particles colliding (frequency of collisions) in unit time per unit area on the wall of the container.

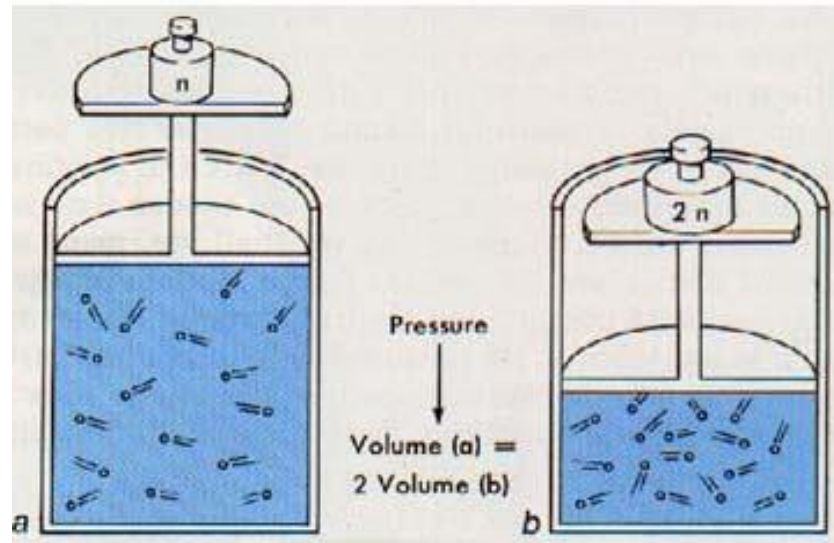
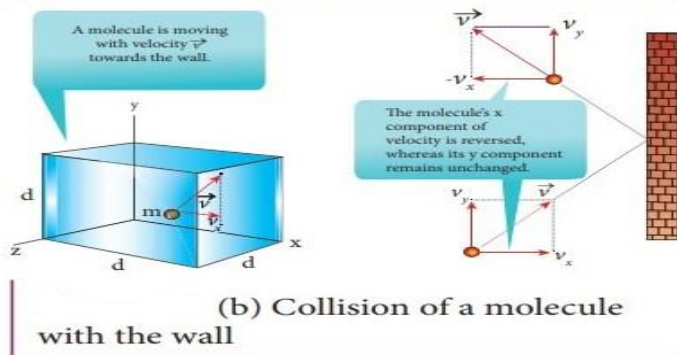
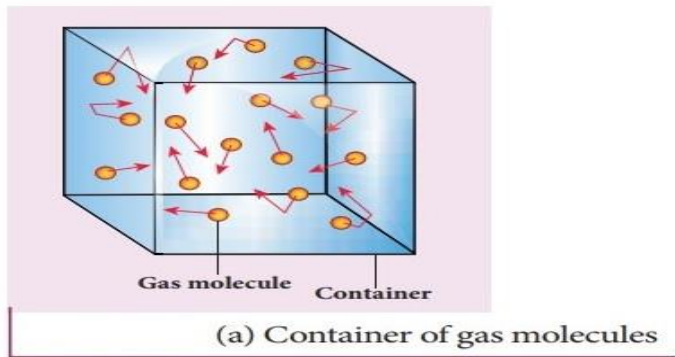
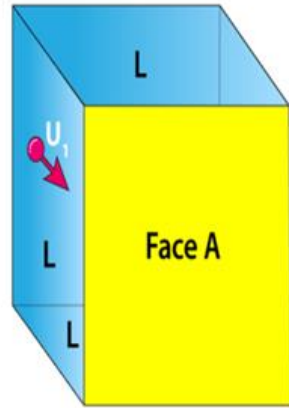


FIGURE 15-2. If the volume of a gas is halved, the number of collisions with the walls of the container doubles. Thus, the pressure in container (b) is twice that of container (a).

Kinetic gas equation:-



- Consider a cubical container of length ' l '
- filled with gas molecules each having mass ' m '
- Let ' N ' be the total number of gas molecules in the container.
- Due to the influence of temperature, the gas molecules move in random directions with a **velocity ' v .'**
- The **pressure of the gas** molecules is the force exerted by the gas molecule per unit area of the wall of the container and is given by the equation,

$$P = \frac{F}{A}$$

- Let us consider a gas molecule moving in the X-direction towards face 'A'.
- The molecule hits the wall with a velocity V_x and rebounds back with the same velocity V_x ,

The momentum (p) of the molecule before it strikes surface,

$p = m \cdot V_x$ The momentum after impact/collision = $p = m \cdot (-V_x)$

and thus experience a change of momentum due to one impact which is equal to

$$\Delta p = -mV_x - (-mV_x)$$

Therefore $\Delta p = -2mV_x$ By the law of conservation of momentum the momentum

transferred by the molecule A_1 to the wall will be,

$$\Delta p = +2mV_x \text{ -----(1)}$$

For a total of 'N' number of gas molecules in the container, all such change in momentum is given by,

$$\Delta p = -2NmV_x \text{ ----- (2)}$$

After the collision, the molecule travels a distance of '2l' before colliding again with wall '1'.

Thus, the time taken is given by,

$$\text{Time} = \frac{\text{Distance travelled}}{\text{Velocity}}$$

$$\text{Therefore, Time} = \frac{2l}{V_x} \text{ ----- (3)}$$

These continuous collisions carry a force, given by

$$F = \frac{\text{Change in momentum } (\Delta p)}{\text{change in time } (\Delta t)} \text{ ----- (4)}$$

Therefore, substituting the values from equation (3) and (4), we get

$$F = \frac{-2NmV_x}{2l/V_x} \text{ ----- (5)}$$

Force exerted by 'n' number of molecules 'F' = $\frac{-NmV^2_x}{l}$ -----(6)

'F' wall = $\frac{NmV^2_x}{l}$ -----(7)

But pressure is the force per unit area.

Pressure 'P' = $\frac{\text{Force on wall (F)}}{\text{Area (A)}}$ so,

Pressure 'P' = $\frac{NmV^2_x/l}{l^2}$ -----(8)

Pressure 'P' = $\frac{NmV^2_x}{l^3}$ -----(9)

Since V_x , V_y and V_z are independent speed in three directions and if we consider the gas molecules in bulk, then $V^2_x = V^2_y = V^2_z$

Hence, $V^2 = 3V^2_x$

Substituting the above condition in eq (9), we get,

$PV = \frac{1}{3} mNV^2$

$PV = \frac{NmV^2}{3}$

This equation is known as the **kinetic theory equation**.

Deduction of gas laws:

Boyle's law: Under a constant temperature when the pressure on a gas increases its volume decreases. In other words according to Boyle's law volume is inversely proportional to pressure when the temperature and the number of molecules are constant.

$$V \propto 1/P \quad \text{at constant temp.}$$

The K.E. of 'n' molecules are equal to $1/2 n m u^2$

we know that kinetic gas postulates K.E. is directly proportional to the temp.

Therefore,

$$1/2 n m u^2 \propto T$$

$$1/2 n m u^2 = K T \text{----- (1)} \quad \text{Where 'K' is proportionality constant.}$$

Rewriting kinetic gas equation we get, $P V = 2/3 (1/2) n m u^2$

Therefore, $P V = 2/3 K T \text{----- (2)}$ Therefore $P V = \text{constant}$,

which is representation of Boyle's law.

Charles's law: According to Charles law Volume is directly proportional to the temperature of gas $V \propto T$

Alternatively, at constant volume, pressure is directly proportional to temperature.

$P \propto T$ (at constant V)

Rearranging equation (2) we get, $PV = \frac{2}{3} KT$

Therefore $V = \frac{2}{3} K/P.T$

at constant pressure, $V = K'T \text{-----(3)}$ Where $K' = \frac{2}{3} K/P$

Therefore, $V \propto T$ which is the representation of Charles law.

C) Avogadro's hypothesis: - According to Avogadro's "equal volumes of gases at the same temperature and pressure contain the same number of molecules".

Let us consider two different gases. The kinetic gas equation can be written as,

$$P_1 V_1 = \frac{1}{3} m_1 n_1 u_1^2 \text{.....(4)}$$

$$\text{and } P_2 V_2 = \frac{1}{3} m_2 n_2 u_2^2 \text{-----(5) at constant temp. } P_1 V_1 = P_2 V_2$$

Therefore, $\frac{1}{3} m_1 n_1 u_1^2 = \frac{1}{3} m_2 n_2 u_2^2$ -----(6)

If these two gases are at same temp., the kinetic energies of the molecules will be the same, that is,

$$\frac{1}{3} m_1 u_1^2 = \frac{1}{3} m_2 u_2^2$$
 -----(7)

Substituting in equation (6) we get; $n_1 = n_2$

Hence Avogadro's law has been deduced.

Grahams Law of diffusion:- According to Graham's "at constant temperature and pressure the rates of diffusion of various gases are inversely proportional to the square roots of their densities or molecular weights"

R (Rate of diffusion) $\propto \frac{1}{\sqrt{d}}$ or $\frac{\sqrt{u_1}}{\sqrt{u_2}} = \frac{\sqrt{\rho_2}}{\sqrt{\rho_1}} = \frac{\sqrt{m_2}}{\sqrt{m_1}}$

Consider equation (6).....

$$\frac{1}{3} m_1 n_1 u_1^2 = \frac{1}{3} m_2 n_2 u_2^2$$

$$u_1^2 / u_2^2 = n_2 m_2 / n_1 m_1 \quad \text{if } n_1 = n_2 = N$$

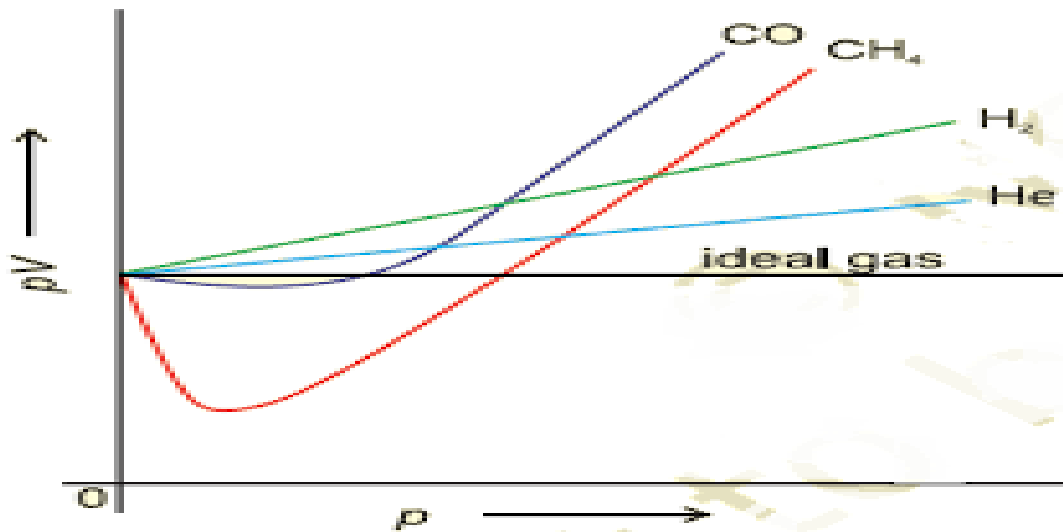
then, $u_1^2 / u_2^2 = N m_2 / N m_1 = M_2 / M_1$

but $M_1 / V = d_1$ and $M_2 / V = d_2$ therefore , $u_1^2 / u_2^2 = d_1 / d_2$ -----(8)

Deviation from ideal behavior: - Ideal gas obeys the gas laws for all values of pressure and temp., in reality, all gases obey the gas laws only over a range of pressure and temp. and not for all values of pressure and temp., hence real gases can be described in terms of the deviations from the gas laws.

Deviations from Boyle's law: -

- If we plot PV against 'P', for an ideal gas should be **straight line** parallel to the X axis .
- This indicates that for an ideal gas **PV should remain constant at constant temp.**
- For **real gas**, such a **straight line** will **not obtain**.
- Gases like **hydrogen, nitrogen** shows **positive deviations**, for these gases product **PV increases** with increase in pressure.
- Some gases like **methane and carbon dioxide** show product **PV** is found to be **decreases**. **Small deviations** from the Boyles law are observed only to **low pressures**.



Deviations from Charles law: -

For a given amount of gas at constant pressure the volume of a gas increases or decreases by $1/273$ times its volume at 0°C , for every degree rise or fall in temperature. $1/273$ or 0.003661 is the temp. Coefficient of the gas.

This remains same for all gases for all range of pressure and temp.

Reasons for the deviations from ideal behavior :-

- Volume of gas molecules that is the **actual volume** occupied by the gas molecules is **negligible** in **comparison** with the volume available to them that is the **volume of the container**.
- Therefore the **actual volume of gas** = Volume of container – Volume of the gas molecules.
- Molecules of the gas **don't exert any force of attraction** over one another. In reality molecules of **real gases** exerts **force of attractions** with each other, as **distance** between two molecules **increases force of attraction increases**. Hence **deviations** from the **ideal behavior** are expected at **high pressure**.
- K.E. of molecules increases, some of K.E. is used to overcome the intermolecular force, hence the gas behaves ideally, but as **temp. is lowered**, the **average K.E. of gas molecule will decrease**. It may **not be sufficient** to **overcome the force of attraction**. Hence, a deviation from ideality may be observed.

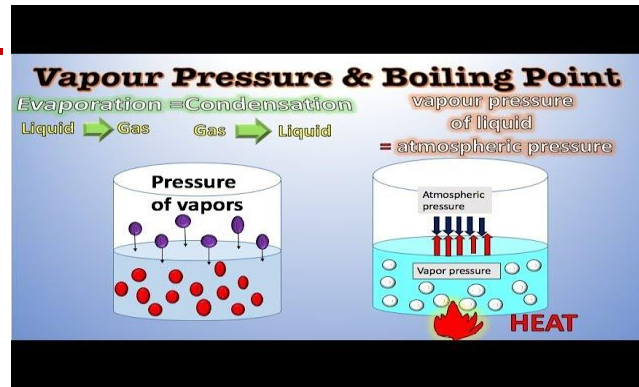
Vanderwaals equation of state: - $\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$

- It shows **relation between all the variables** at the **given state** is called equation of state.
- For gases state 'P', 'V' 'T' and 'n' are variables that defines the states. **PV= n RT** is also an **equation of state**, but this is **not obeyed by real gases** for all the values of pressure, volume and temperature.
- Hence some parameters has to be taken into account to explain the behavior of real gas.
- There are two faulty assumptions of kinetic theory of gases these are,
 - A) the **volume** of gas molecules **is negligible** in comparison with **volume occupied by them**.
 - B) **No intermolecular force of attraction** is present in the gaseous state. Van-der Waals provided an equation of state that will be obeyed by all real gases, at all values of pressure and temperature.

Critical phenomenon: PV isotherms of real gases:-

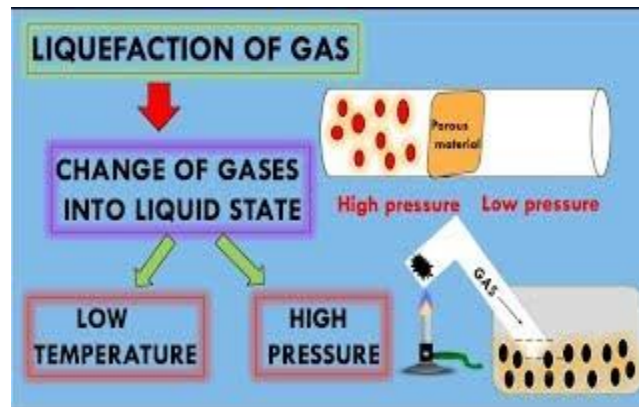
Critical phenomenon:-

Boiling Point:



When a liquid is heated in an open vessel, the vapor pressure of liquid increases. At its boiling point, vapor pressure becomes equal to atmospheric pressure.

Liquifiction:



Liquification:

- 1) on decreasing the temperature of the gas.
- 2) Secondly by increasing the pressure of the gas.

Essential condition for the liquifiction of the gas is described

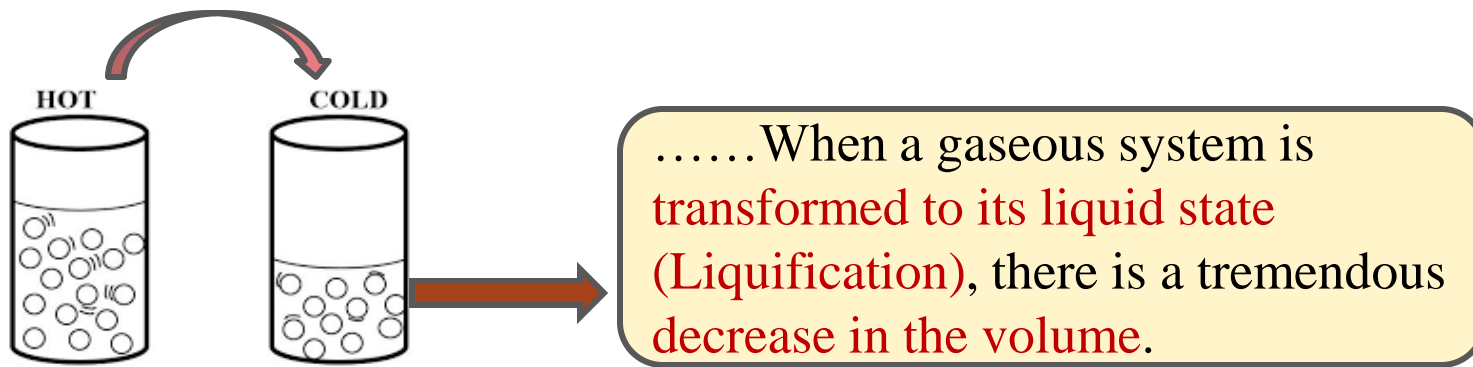
By the study

Critical temperature

Critical pressure

Critical volume

Interrelationships of above three....



- The **ideal gas** law assumes that a gas is composed of **randomly moving, non-interacting point particles**.(refer Postulates of kinetic theory of gases)
- **Real gases** shows **complex behavior** that deviate from the ideal model.
- However as shown by **graph** (**isotherms** refers to the **different curve** so the graphs, which represent a **gas state at different pressure and volume** conditions but at **constant temperature**.)
- **Iso-** means same and **thermo** means temperature-hence isotherm.

PV isotherms of real gases:- Critical phenomenon can be studied from PV curve curve expected to be hyperbola. The isotherms obtained at 40 atm. and above 40 atm. temperatures are hyperbolas.

- At low temp. isotherms **show inflection** (change).e.g. At **temp.31.04 deg.** isotherm shows a point of inflection (point '**P**' in fig.1 or point **E** in fig.2).The isotherm **at temp.13 deg. and 21.5 deg.** Shows **horizontal portion** which represents **no change of pressure for a large change in volume.**
- As temp.is **increased**, the **flat portion** of the **isotherm** is found to **decrease** in **length** until it converges into a **single point** at point **31.10 deg.**
- But when liquid is heated in a sealed tube, initially liquid and vapor will be in equilibrium.

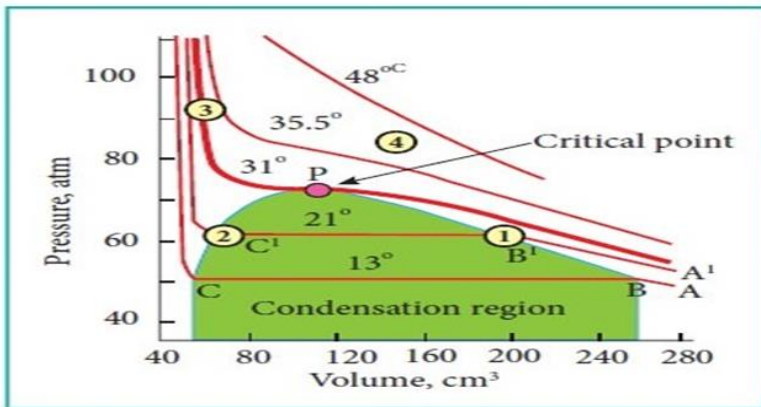
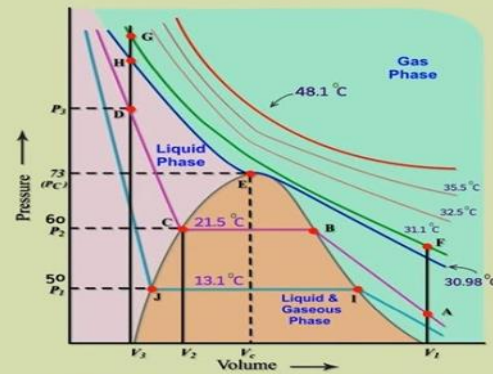
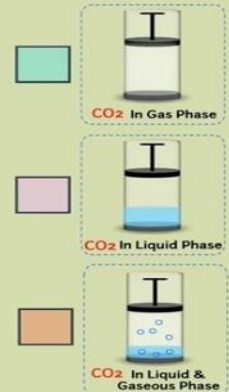


Figure. Isotherms of Carbon dioxide at different temperatures

Conclusions from Graphical Study



Isotherms of Carbon Dioxide at Various Temperatures



- On raising temp. more and more amount of the liquid will vaporize, hence, pressure inside tube increases.
- At every stage there is a line of demarcation (boundary) between the liquid and vapor phase.
- **Critical Temp. or Critical point:** At a particular temp. the liquid meniscus will disappear i.e. the line of separation between the two phases disappears and physical properties of the liquid and the gas become identical. This temp. is called critical temp. and the liquid is said to be at the critical point. ('P' or 'E')
- On heating the tube further, no trace of the liquid can be found.
- The total mass remains in the gaseous state even on increasing the pressure externally. Hence, it can be concluded that no liquid can exit at a temp. greater than its critical temp.

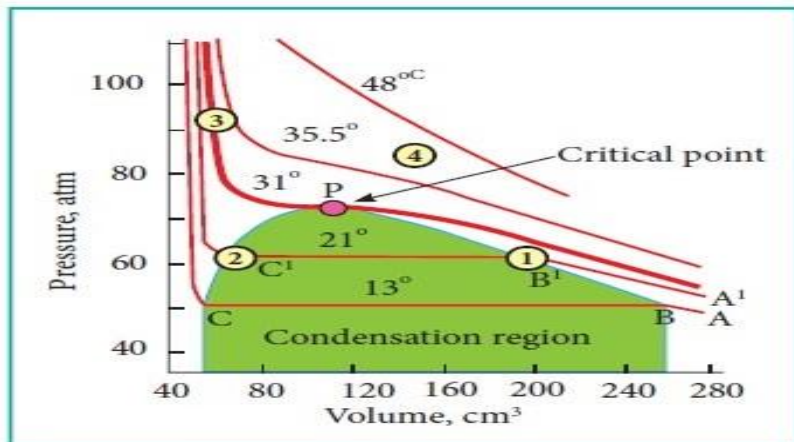
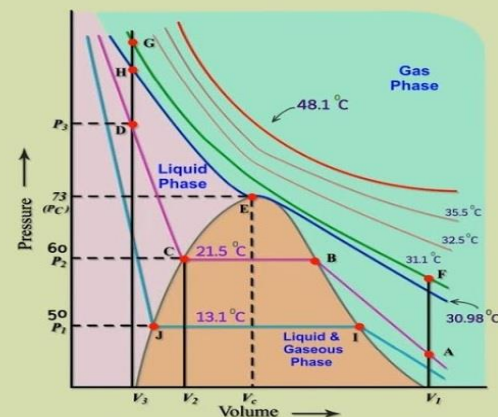
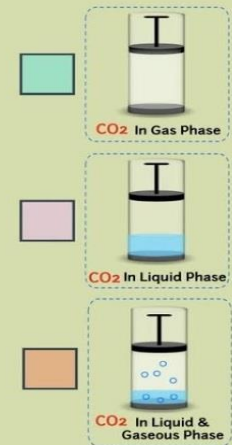


Figure. Isotherms of Carbon dioxide at different temperatures

Conclusions from Graphical Study



Isotherms of Carbon Dioxide at Various Temperatures



Thank you for your attention..

