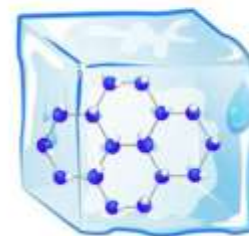


UNIT-IV

GAS, LIQUID & SOLID STATES



Solid



Gas



Liquid



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HOD, Dept. of Chemistry

S.V.M.Arts, Science and Commerce College Ilkal

9448339861 drpskilk@gmail.com

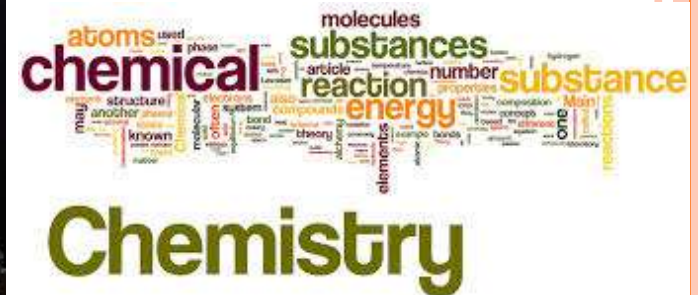
SYLLABUS (OBJECTIVES)

Gaseous state: Review of kinetic theory of gases, van der Waals equation of state, Boyle temperature. Molecular velocity: Maxwell's Boltzmann distribution law of molecular velocities (most probable, average and root mean square velocities). Relation between RMS, average and most probable velocity and average kinetic energies (derivation not required), law of equipartition of energy. Collision frequency, collision diameter, Collision cross-section, collision number and mean free path and coefficient of viscosity, calculation of σ and η , variation of viscosity with temperature and pressure. Critical phenomena: Andrews's isotherms of CO_2 , critical constants and their determination Relation between critical constants and van der Waals equation (Derivation), continuity of states, law of corresponding states. Numerical problems are to be solved wherever applicable. **(7 Lectures)**

- **Solids:** Forms of solid, Unit cell and space lattice, anisotropy of crystals, size and shape of crystals, Laws of Crystallography: Law of constancy of interfacial angles, Law of rational indices, Law of symmetry (Symmetry elements), Crystal systems, Bravais lattice types and identification of lattice planes. Miller indices and its calculation, X-Ray diffraction by crystals: Bragg's law and derivation of Bragg's equation, Single crystal and powder diffraction methods. Defects in crystals, glasses and liquid crystals. Numerical problems.
- **Nernst Distribution Law** - Statement and its derivation. Distribution constant, factors affecting distribution constant, validity of Distribution Law, Modification of distribution law when molecules undergo a) Association b) Dissociation. Application of Distribution Law in Solvent extraction. Derivation for simple and multiple extraction. Principles of distribution law in Parkes Process of desilverisation of lead. Numerical Problems. (7 Lectures)



What is needed for Understanding Chemistry?

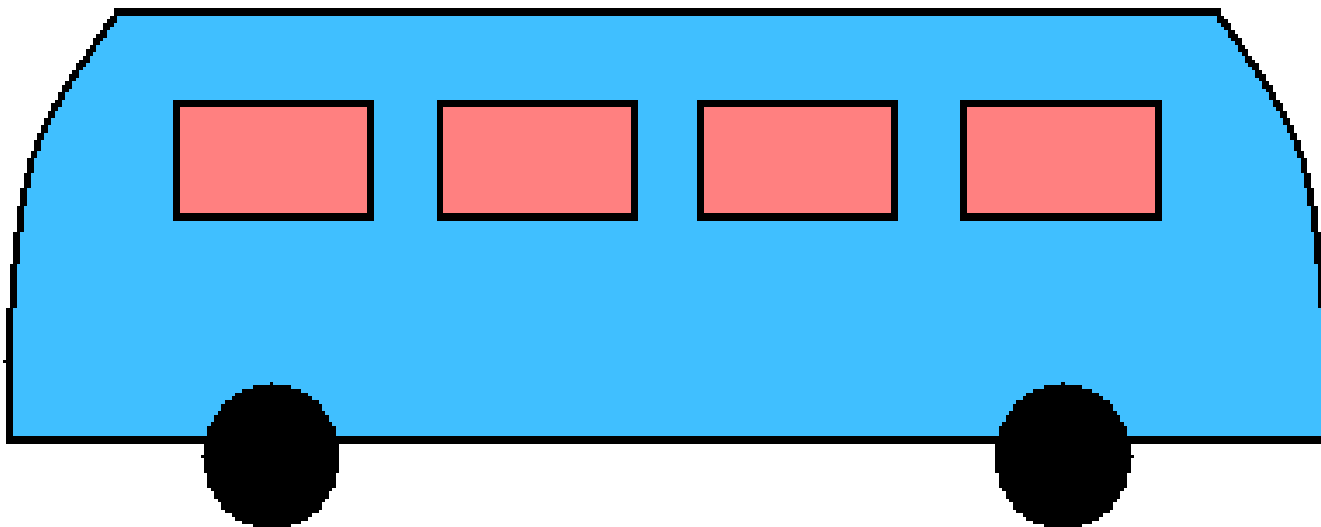




CURIOSITY



CAN YOU IDENTIFY THE DIRECTION IN WHICH
THIS BUS IS MOVING: LEFT OR RIGHT?



ROTE LEARNING

v/s

ACTIVE LEARNING





Chemistry

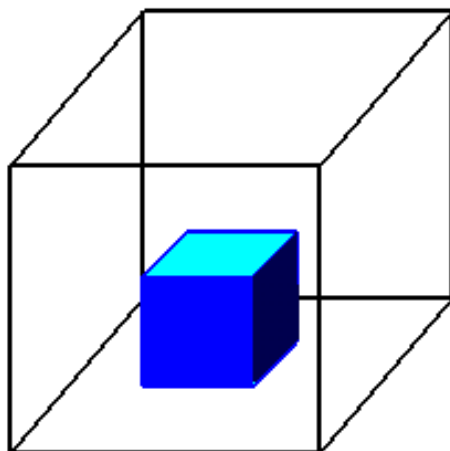
○ Chemistry = Science of Matter

States of Matter

- Solid
- Liquid
- Gas



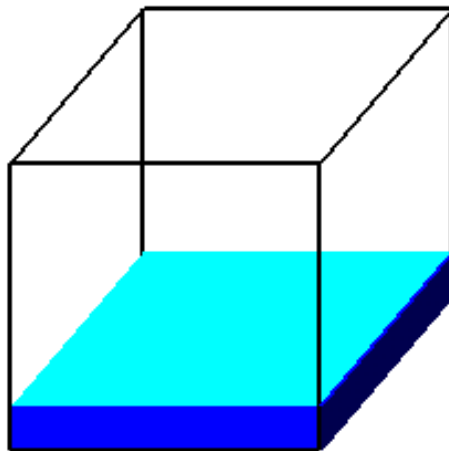
States of Matter



Solid

Holds Shape

Fixed Volume

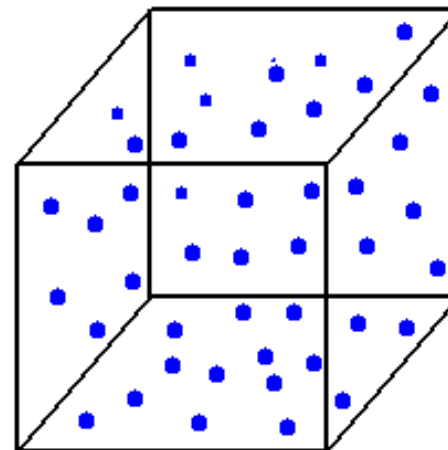


Liquid

Shape of Container

Free Surface

Fixed Volume

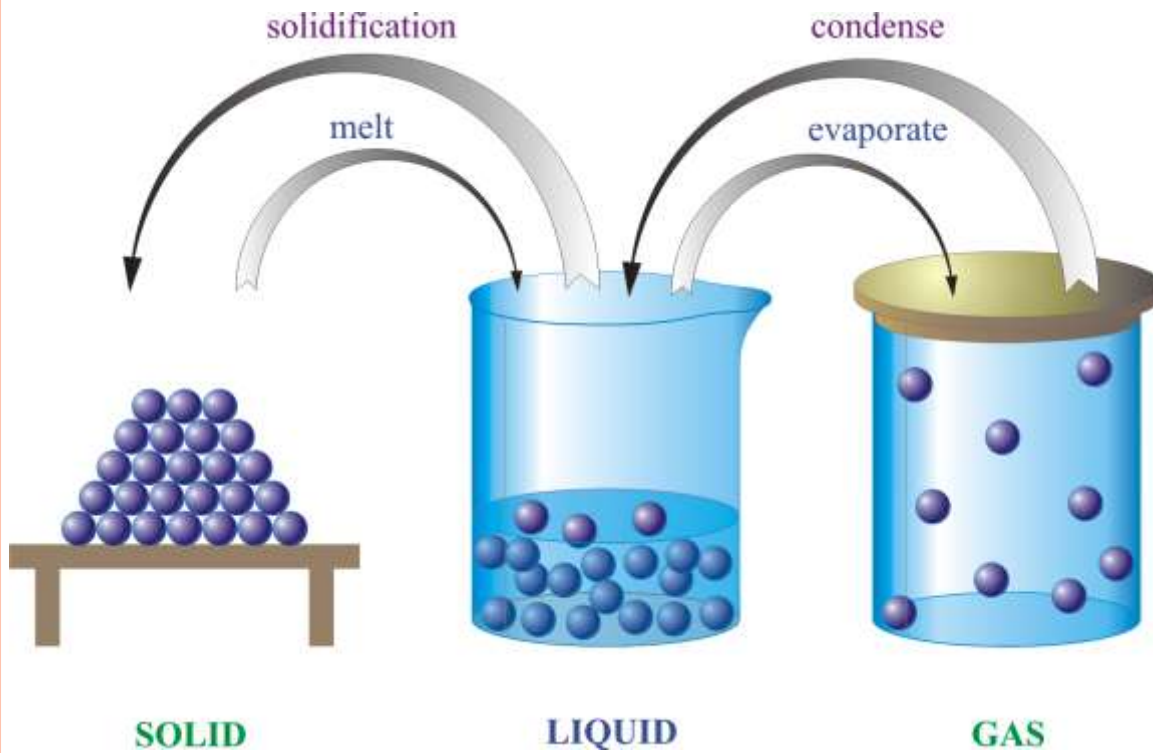


Gas

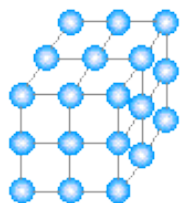
Shape of Container

Volume of Container

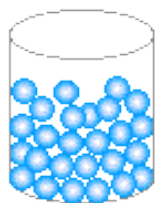




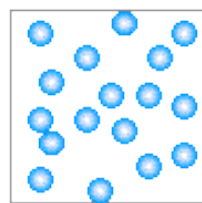
States of Matter



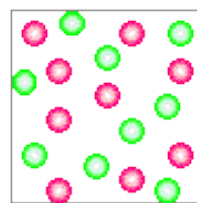
SOLID



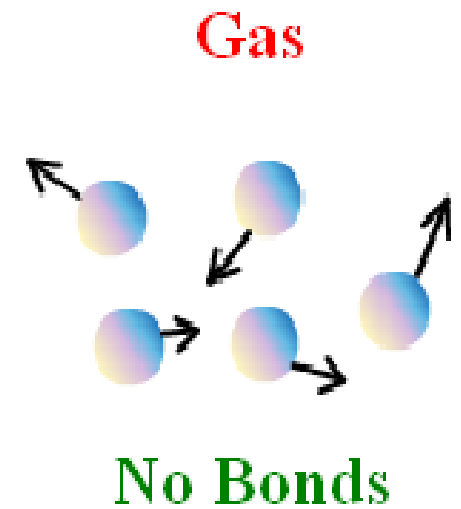
LIQUID



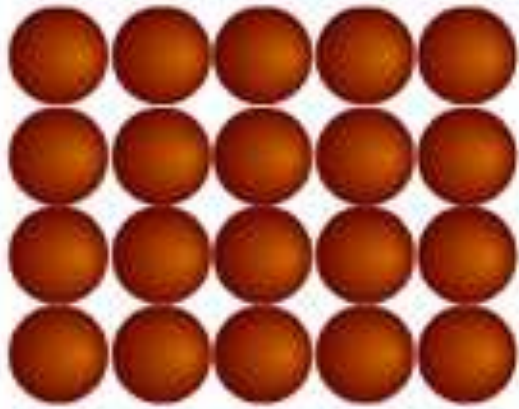
GAS



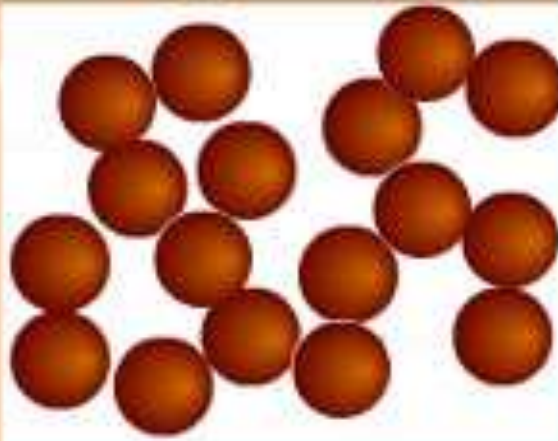
PLASMA



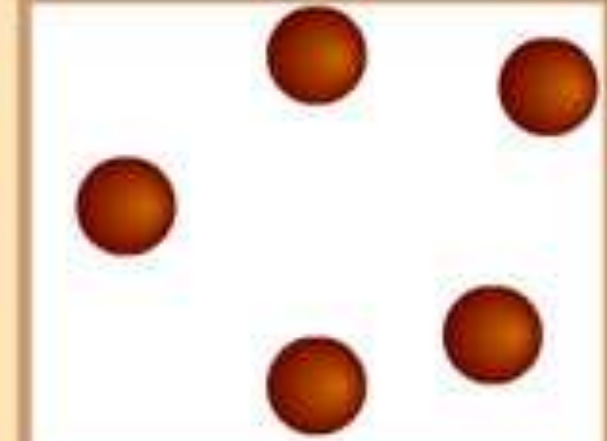
MOLECULAR ARRANGEMENT



Molecules in solids



Molecules in liquids



Molecules in gases

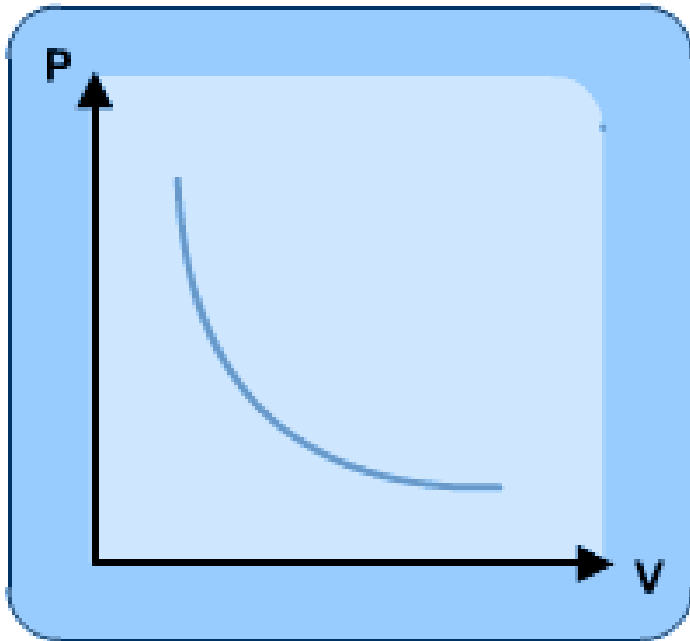


GAS IS COMPRESSIBLE: **SYRINGE EXPT**

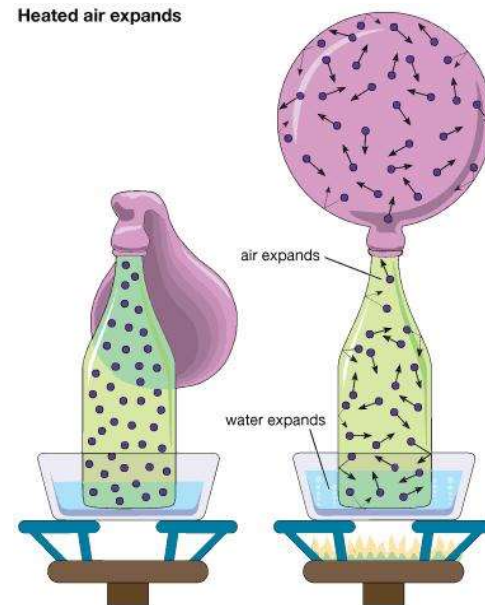


○ Boyle's law

○

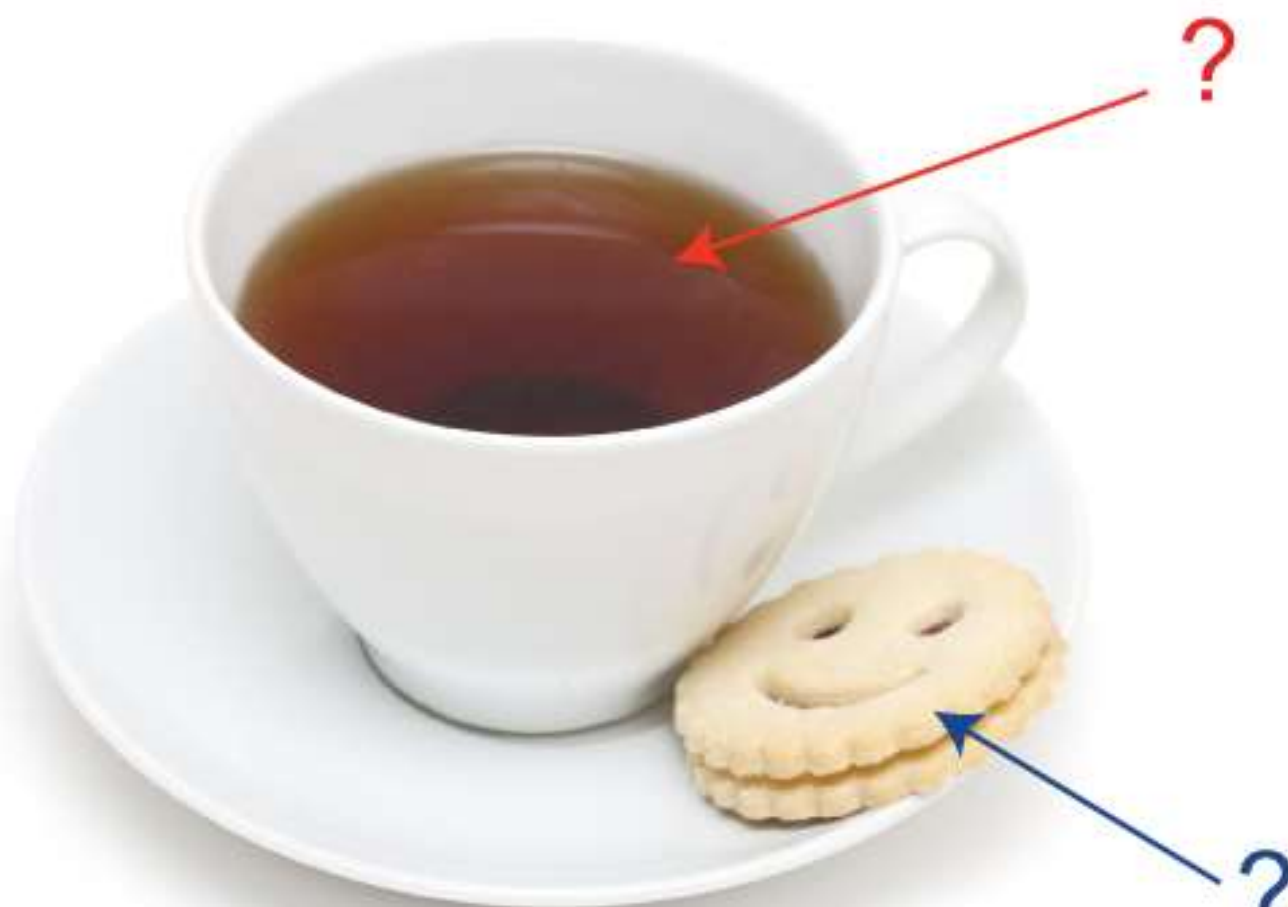


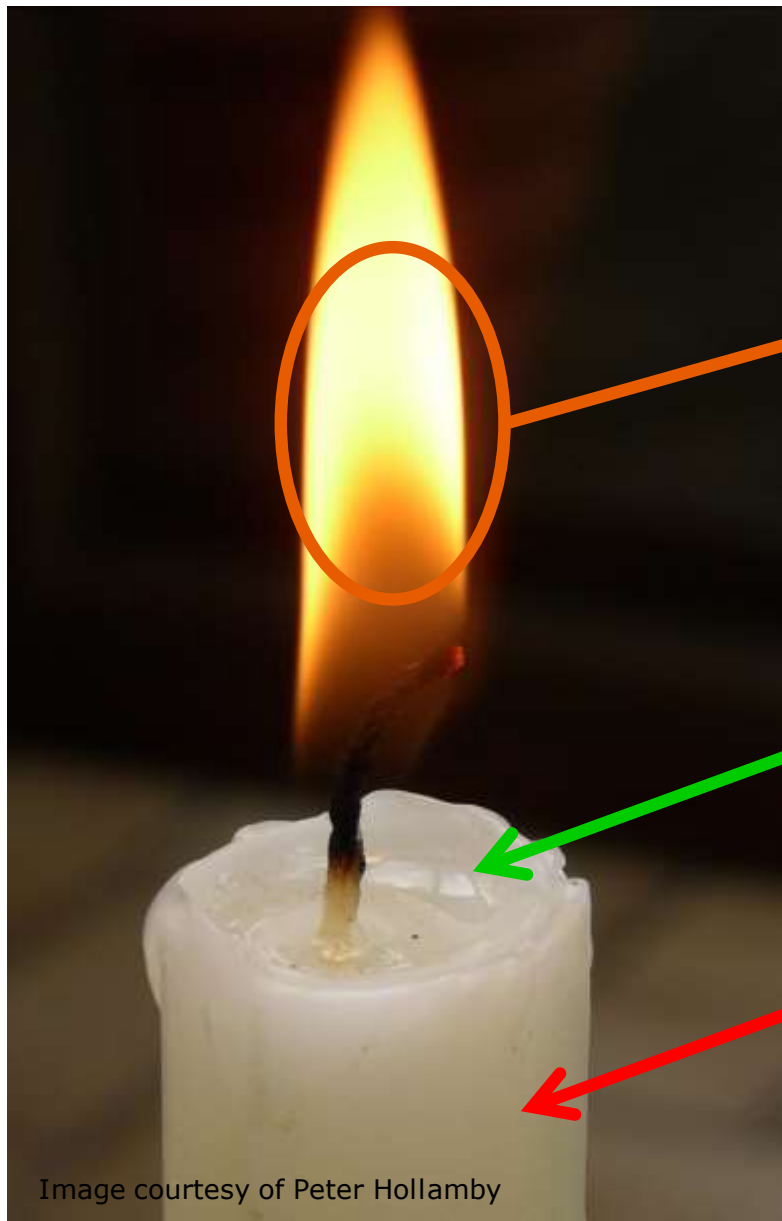
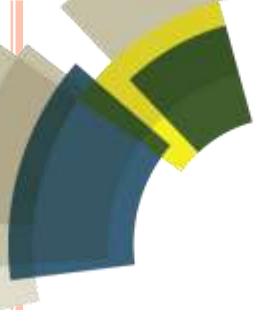
Charles's law





Particle Motion in Solids, Liquids and Gases





What happens when water boils ?



?

?

Image courtesy of Peter Hollamby

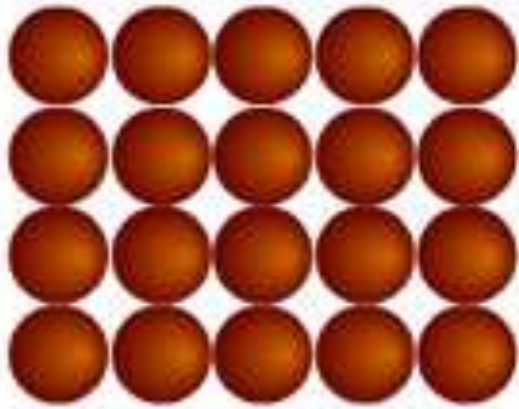


What Happens When Water Boils?

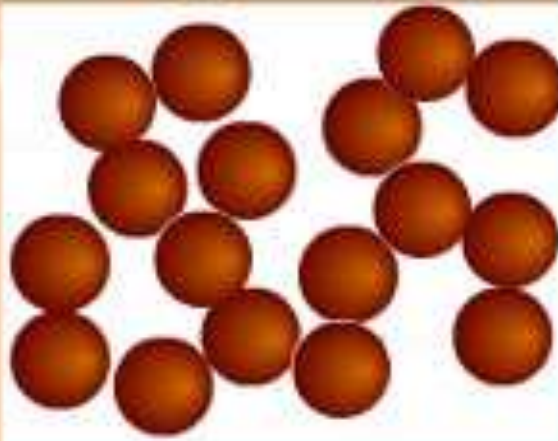
	True	False	Not sure
1.The bubbles contain a mixture of hydrogen and oxygen.		False	
2.The bubbles contain carbon dioxide.		False	
3.The bubbles contain steam (water vapour).	True		
4.The bubbles are empty (vacuum).		False	
5.The bubbles contain air.		False	
6.The bubbles contain oxygen only.		False	



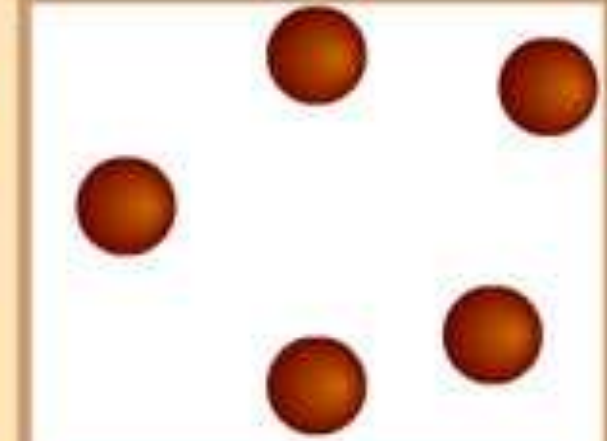
MOLECULAR ARRANGEMENT



Molecules in solids



Molecules in liquids

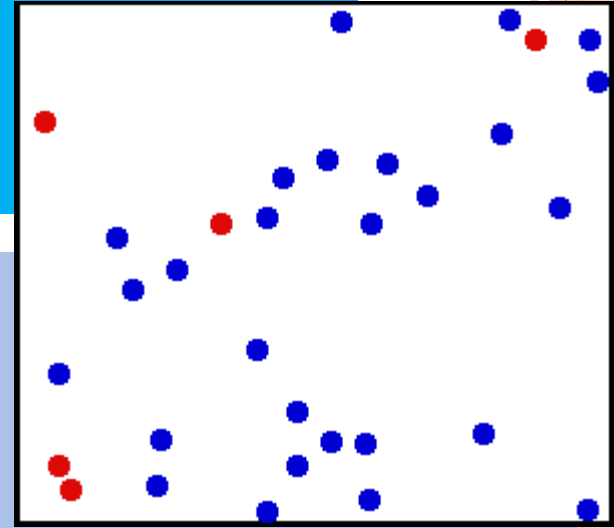


Molecules in gases

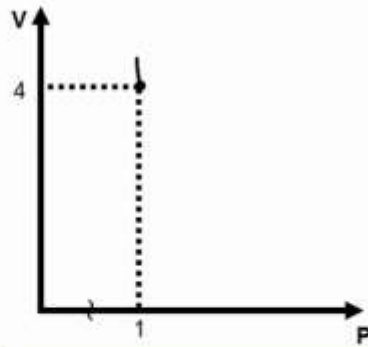
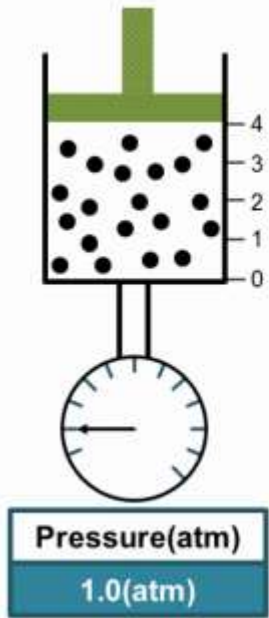


GAS LAWS

- Boyle's Law
- Charles's Law
- Avogadro's law
- Graham's law of diffusion etc.,



1. BOYLE'S LAW



$$PV = C \text{ (C=constant)}$$

T is constant

▲ = Weight

$$P \propto 1/V$$

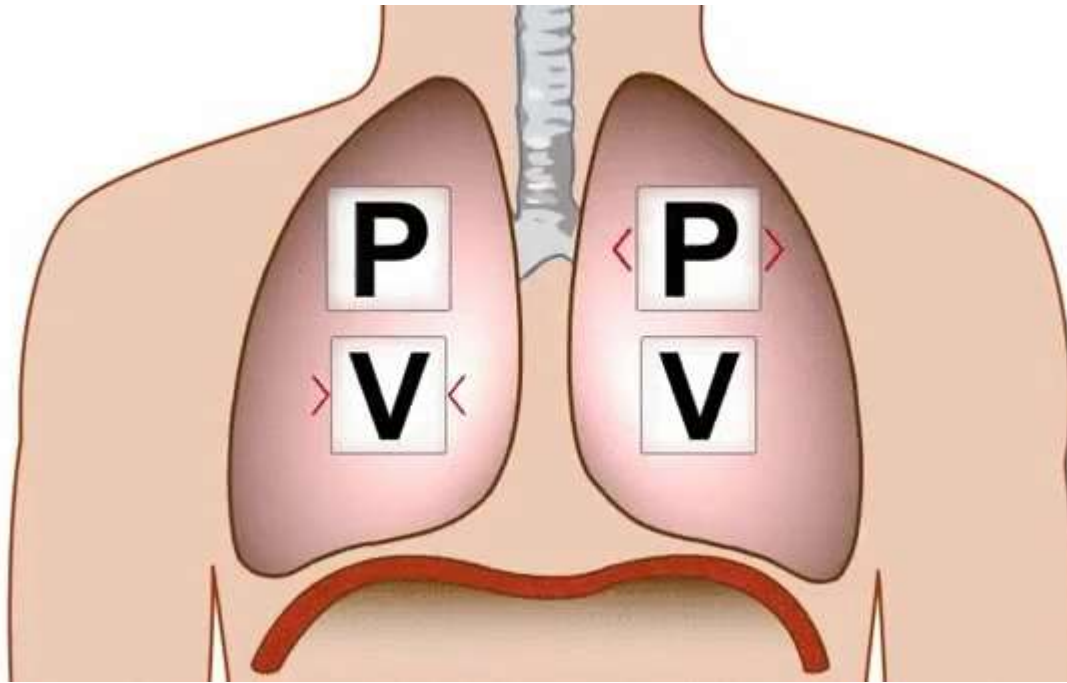
$$PV = \text{Constant}$$

at constant Temp



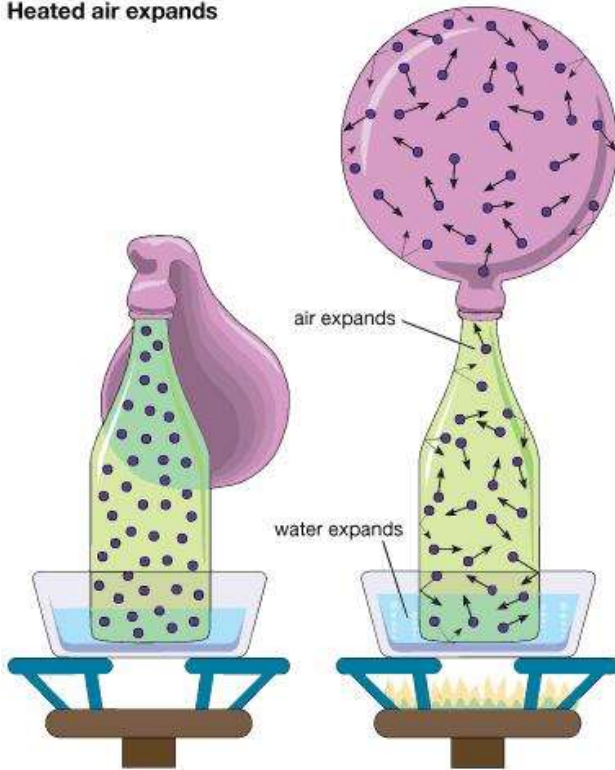
Syringe expt





2 CHARLE'S LAW

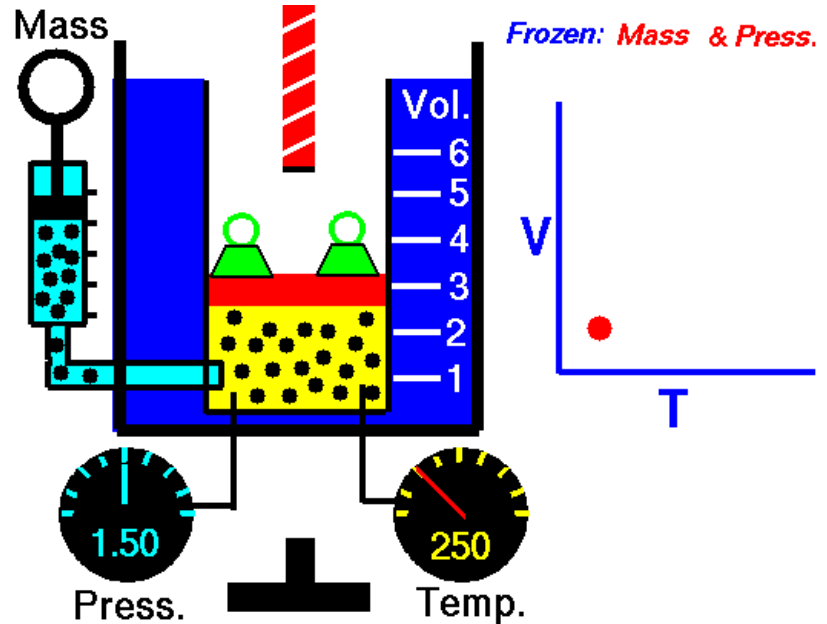
Heated air expands



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$$V \propto T$$
$$V/T = \text{Constant}$$

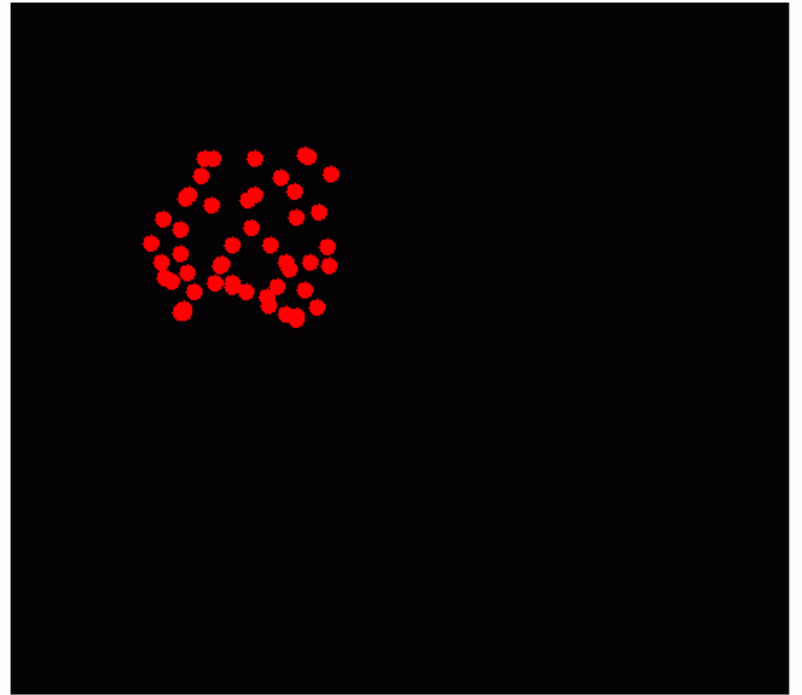
at constant P

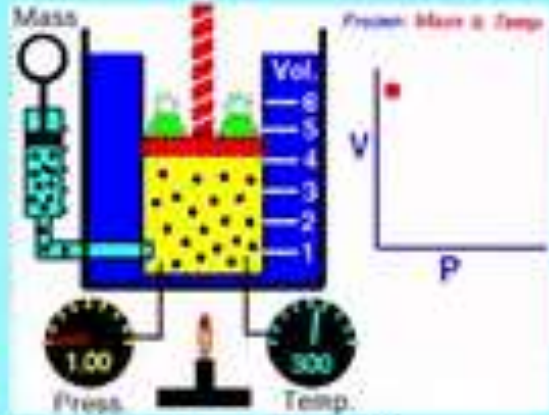


3. GRAHAM'S LAW OF DIFFUSION

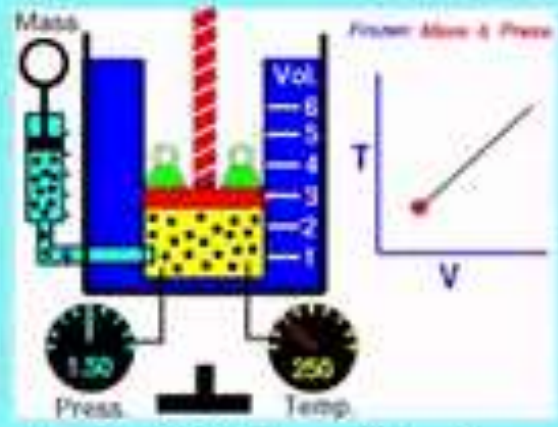
$$\frac{R_1}{R_2} = \sqrt{\frac{M_2}{M_1}}$$

$$r_2 \propto \frac{1}{\sqrt{d_2}}$$

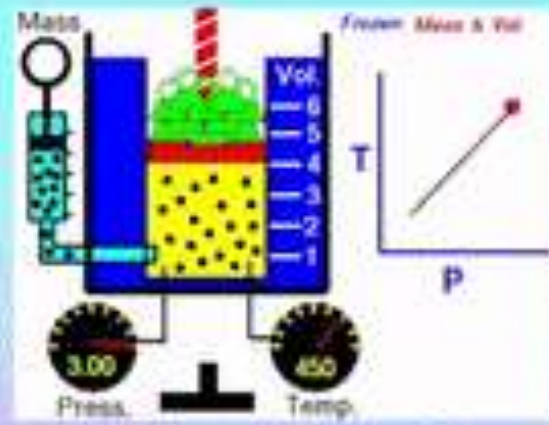




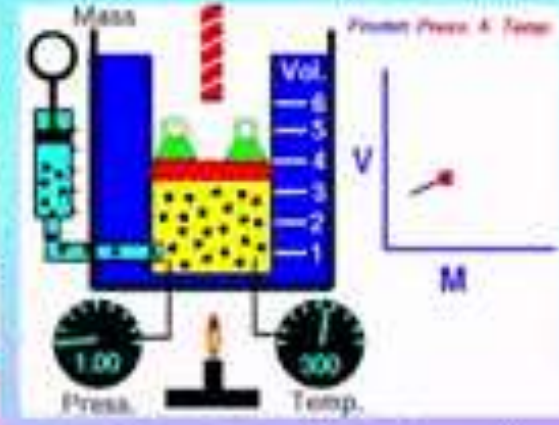
Boyle (1662) $p \cdot V = f(M, T)$



Charles (1787) $V/T = g(M, p)$



Gay-Lussac (1809) $p/T = h(M, V)$



Avogadro (1811) $n/V = k(p, T)$

BEHAVIOUR OF GAS AT MOLECULAR LEVEL

○ Kinetic theory of Gases





Notes



Effect of Pressure on Volume of a Gas-Expt Boyle's Law

$$P \propto \frac{1}{V}$$

P = pressure

V = volume

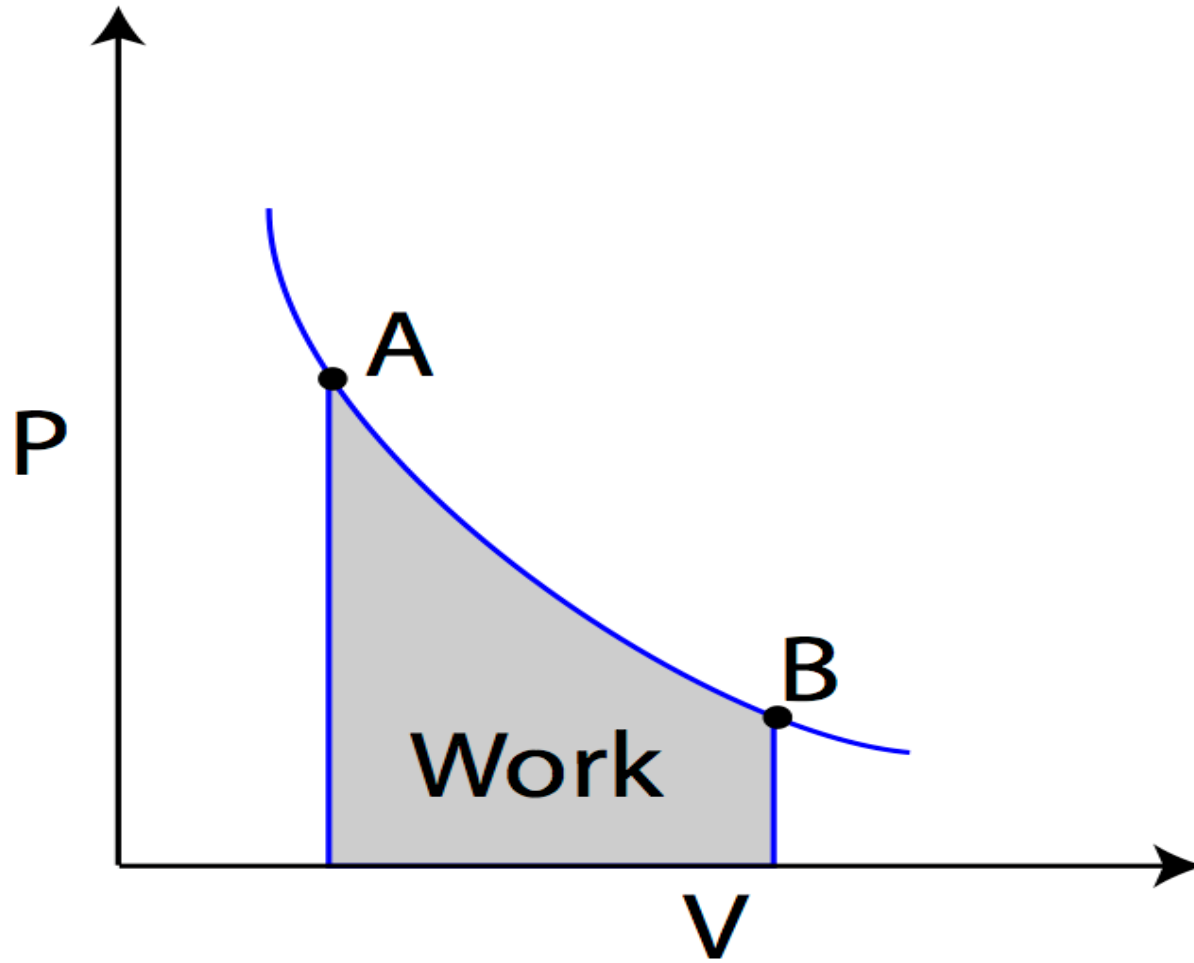
(assumes temperature constant and closed system)



Ideal Gas Isotherms

$$P = nRT/V$$

(hyperbolae)



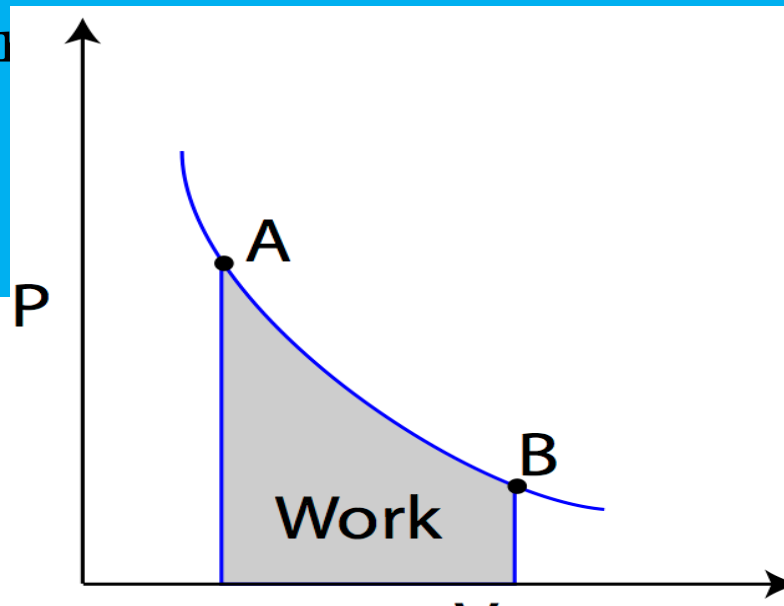
Real Gas Isotherm

For an ideal gas $PV = nRT$,

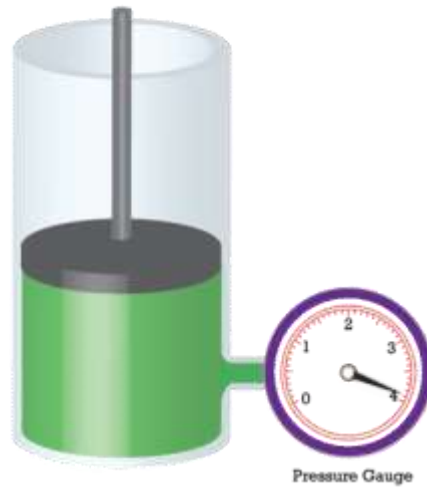
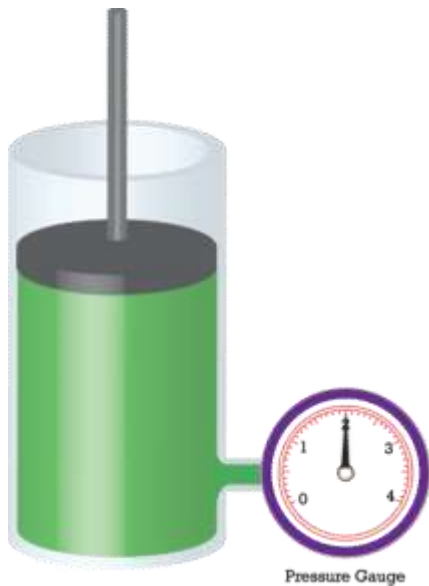
At constant temperature, $PV = \text{Constant}$

A curve in a P-V diagram generated by the equation $PV = \text{Const.}$ at constant temperature is called an **isotherm**.

(Isotherm at constant T)



Andrew's Experiment on Carbon dioxide



Water—How It Changes State

melting

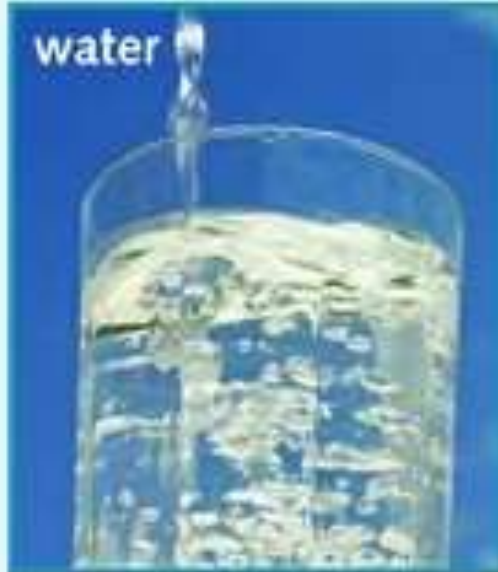
evaporating

HEATING

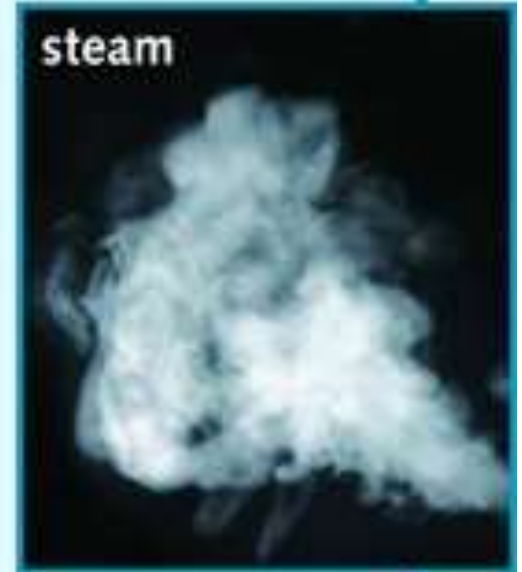
ice



water



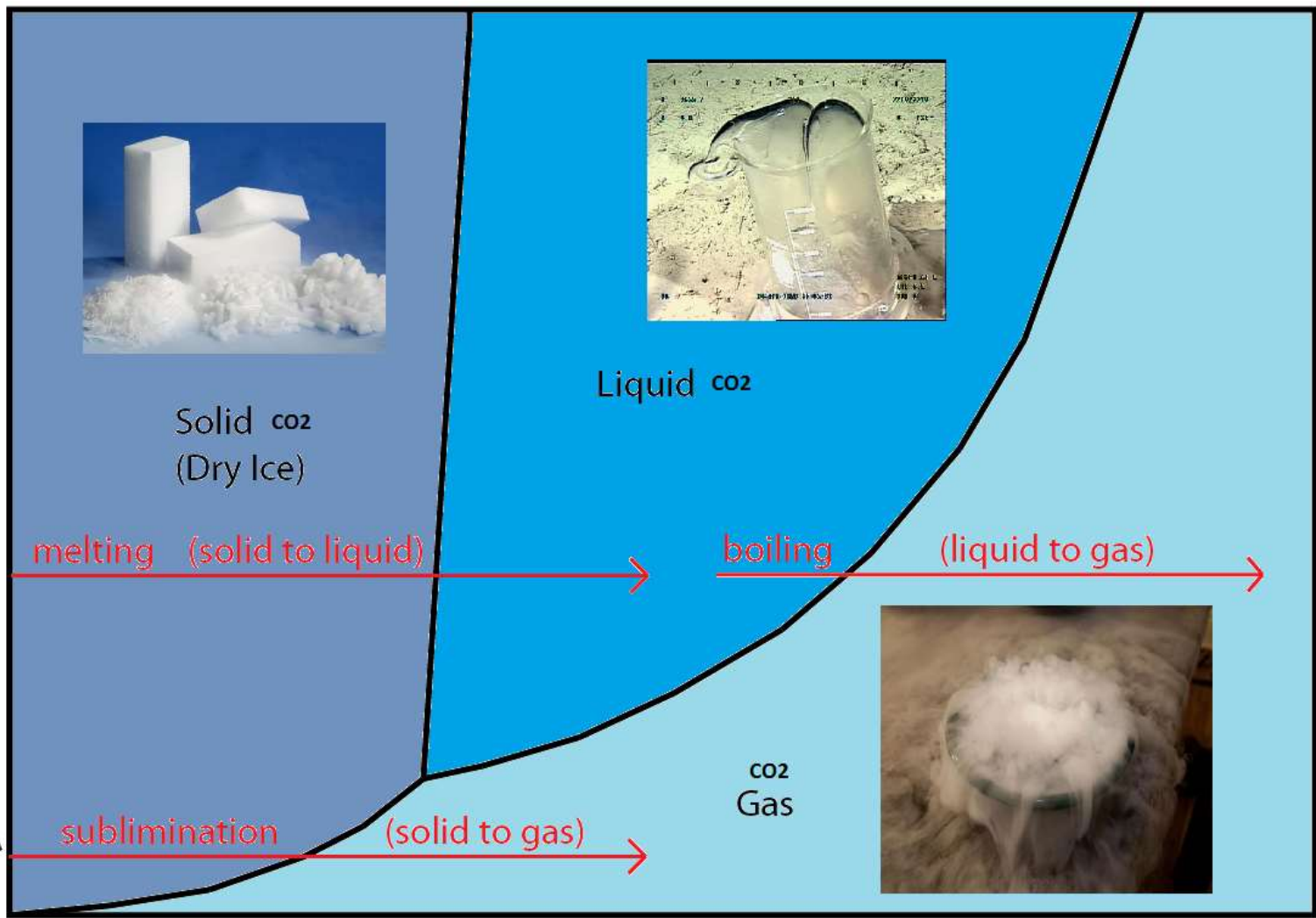
steam



COOLING

freezing

condensing



Solid CO₂
(Dry Ice)



Liquid CO₂



CO₂
Gas

Pressure ↑

surface of the Earth →

Temperature →

melting (solid to liquid)

boiling

(liquid to gas)

sublimation

(solid to gas)

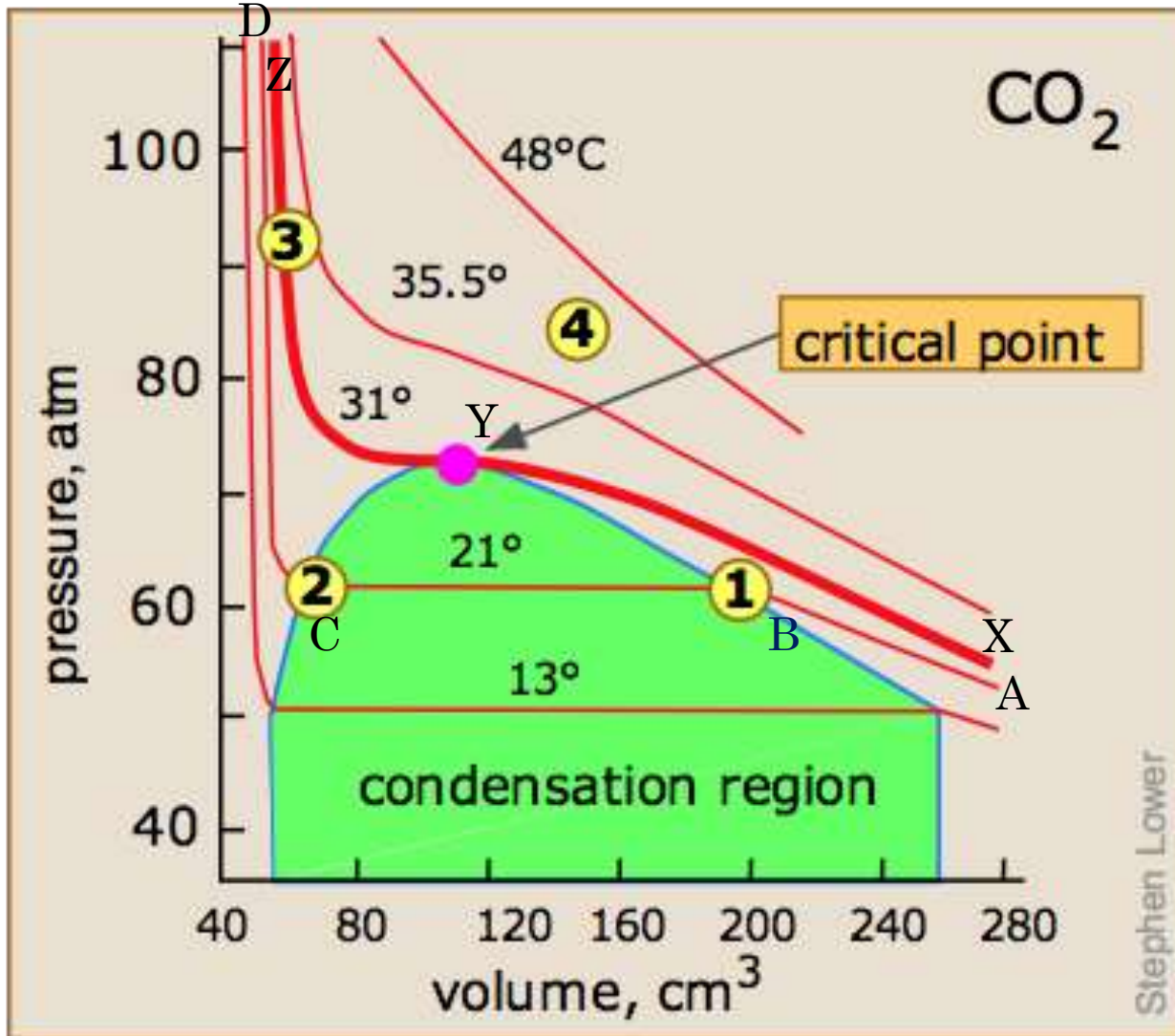
Liquefaction of CO₂-
& its Critical temperature



1. Andrew's Isotherms of Carbon dioxide



From most sincerely
Thomas Andrew



T_c=31.1°C
P_c = 72.9 atm

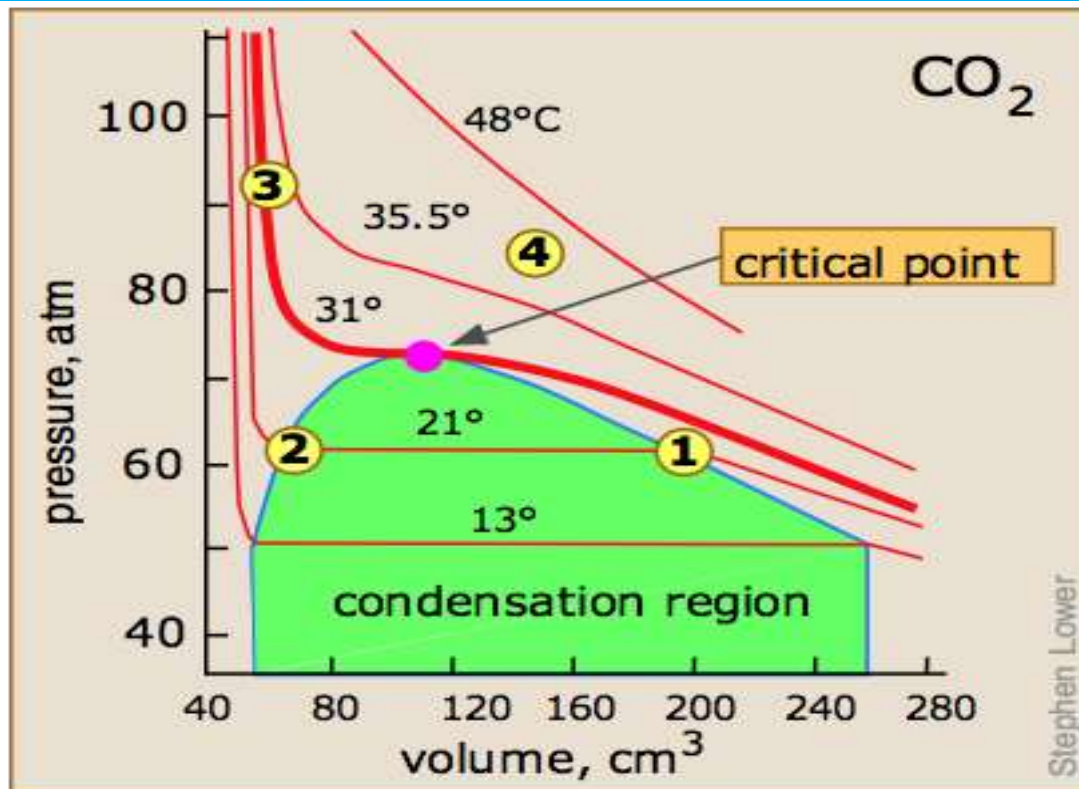


Discussion

Andrew's Isotherms of Carbon

dioxide

1. Isotherms above $31.1\text{ }^{\circ}\text{C}$
2. Isotherms below $31.1\text{ }^{\circ}\text{C}$
3. Isotherm at $31.1\text{ }^{\circ}\text{C}$

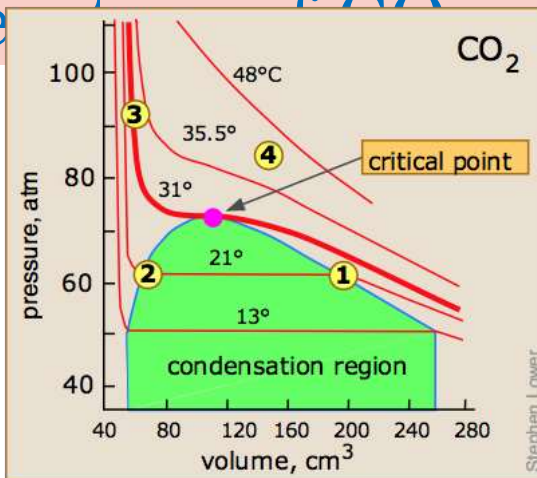


Critical Constants

1. The Critical Temperature (T_c)

“The temperature below which the continuous increase of pressure on a gas ultimately brings about liquefaction and above which no liquefaction can take place no matter what so ever pressure be applied”.

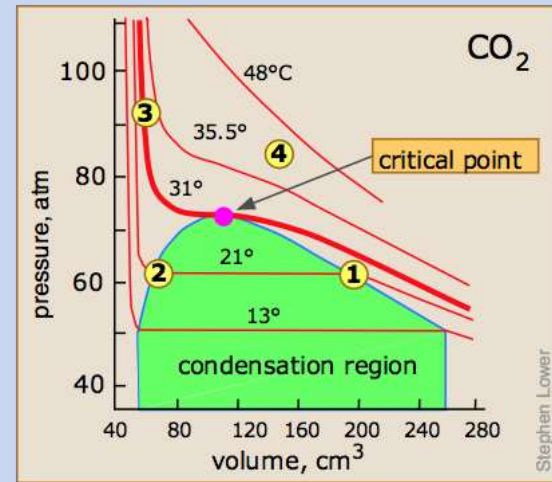
Ex: Critical temperature of CO_2 is 31.1°C (304.1K)



2. Critical Pressure (P_c)

The pressure required to liquefy the gas at critical temperature is called critical pressure

Ex: P_c of $\text{CO}_2 = 72.9 \text{ atm}$



3. Critical Volume (V_c)

The volume occupied by 1 mole of gas under these conditions is called the critical volume.

Ex: V_c of $\text{CO}_2 = 94 \text{ mL/mole}$

Table: The critical constants of some common gases

Gas	Critical temperature (K)	Critical pressure (atm)	Critical volume (ml/mole)
Helium	5.3	2.26	57.8
Hydrogen	33.2	12.8	65.0
Nitrogen	126.0	33.5	90.1
Oxygen	154.3	50.1	74.4
Carbon dioxide	304.0	72.9	94.0
Ammonia	405.5	111.5	72.1
Chlorine	407.1	76.1	123.8

Selective Attention Test



2. Relationship between Critical Constants and Van der Waal's Constants

Van der Waals equation may be written as:

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

$$\text{OR} \quad PV + \frac{a}{V} - pb - \frac{ab}{V^2} = RT$$

$$\text{OR} \quad PV^3 + aV - PbV^2 - ab - RTV^2 = 0$$

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

Operations; 1.Simplify 2. Multiply by V^2 (Take LCM) 3.Divide by P

At Critical Temperature and Critical Pressure $V=V_c$

$$\text{Or } V-V_c=0$$

$$\text{Or } (V-V_c)^3 =0$$

$$\text{Or } V^3-3V^2V_c + 3VV_c^2 -V_c^3 =0 \dots\dots\dots(\text{iii})$$

This is called an equation of critical state.

Substituting $T=T_c$ (critical temperature)

and $P=P_c$ (critical pressure)

in equation (ii), we get,

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

.....(iv)

Comparing eqns. (iii) and (iv) we get

$$3V_c = \frac{RT_c}{P_c} + b \quad \text{.....(v)}$$

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

$$V_c^3 = \frac{ab}{P_c} \quad \text{.....(vii)}$$

- Dividing equation(vii) by equation (vi)
- Substituting the value of V_c in equation (vi)
- Substituting the values of V_c , P_c in equation(v)

On solving the above equations, we get

$$V_c = 3b \dots \dots \dots \text{(viii)}$$

$$P_c = \frac{a}{27b^2} \dots \dots \dots \text{(ix)}$$

$$T_c = \frac{8a}{27bR} \dots \dots \dots \text{(x)}$$



Review-

Derive Expression for Critical Constants
in terms of Van der Waal's constants



T A B L E**van der Waals Constants of Several Gases**

Name	Formula	a (atm L ² mol ⁻²)	b (L mol ⁻¹)
Ammonia	NH ₃	4.170	0.03707
Argon	Ar	1.345	0.03219
Carbon dioxide	CO ₂	3.592	0.04267
Hydrogen	H ₂	0.2444	0.02661
Hydrogen chloride	HCl	3.667	0.04081
Methane	CH ₄	2.253	0.04278
Nitrogen	N ₂	1.390	0.03913
Nitrogen dioxide	NO ₂	5.284	0.04424
Oxygen	O ₂	1.360	0.03183
Sulfur dioxide	SO ₂	6.714	0.05636
Water	H ₂ O	5.464	0.03049



3.DETERMINATION OF CRITICAL CONSTANTS

Video



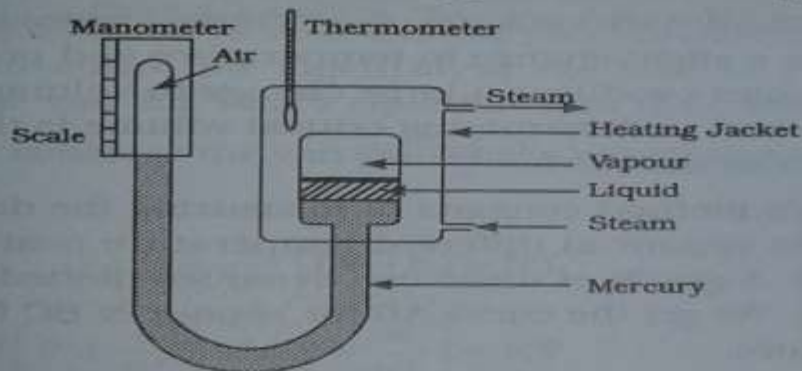
10.17 DETERMINATION OF CRITICAL CONSTANTS

1. Direct method of Andrews: A series of isothermal curves drawn at various temperature and the critical temperature, critical pressure and critical volume are determined.
2. By using the following method.

10.18 DETERMINATION OF CRITICAL TEMPERATURE (T_c) AND CRITICAL PRESSURE (P_c)

By using cagniard de la Tours apparatus

The method is based on the principle that, by noting the temperature when the surface of separation between liquid and vapour in a closed space disappears on gradual heating, also the temperature when the surface reappears on cooling.



In other words, the method is based on the principle that at the critical temperature the surface of separation (i.e., the meniscus) between the liquid and vapour phases disappears.

The apparatus consists of U-type strong glass tube with a big bulb on one end. This bulb is enclosed in a steam jacket. The tube is filled with mercury leads some gap of air. A scale is fixed to measure the pressure, i.e., it acts as manometer.

The liquid under examination is taken in bulb. It is heated by passing steam. The liquid vapourises at the temperature T_1 , i.e., the meniscus disappears. This temperature T_1 and the

10.26

pressure P_1 are recorded. Then the passing of steam in to the heating jacket is stopped. The bulb is then allowed to cool. The vapour condenses to form liquid. At the temperature T_2 the meniscus reappears. This temperature T_2 and pressure P_2 are recorded. The mean temperature of disappearance and appearance gives the critical temperature.

$$\therefore T_c = \frac{T_1 + T_2}{2}$$

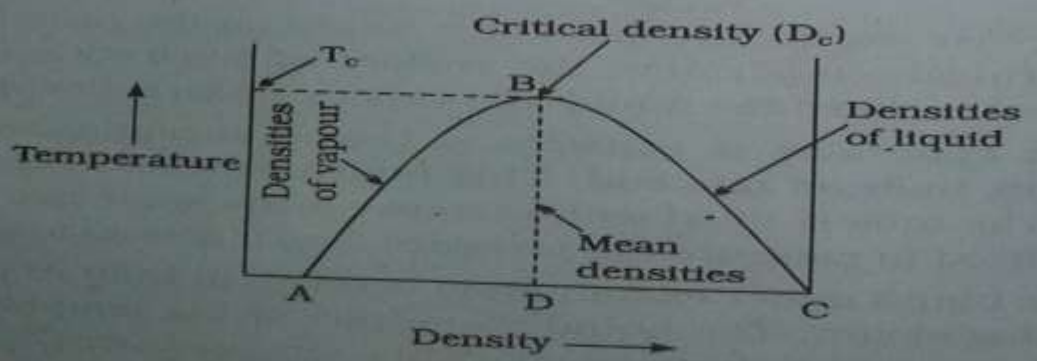
The mean of the pressures read i.e., P_1 & P_2 from the manometer, corresponding to two temperatures gives the critical pressure.

$$\therefore P_c = \frac{P_1 + P_2}{2}$$

10.19 DETERMINATION OF CRITICAL VOLUME (V_c)

It is difficult to measure the critical volume accurately, because even a slight change in temperature and pressure near the critical point produces a large change in volume. The most accurate method of determining critical volume is the Amagat's method of mean densities.

Amagat's method consists of measuring the densities of a liquid and its vapour at different temperature near the critical temperature. A graph of these two densities plotted against the temperature. We get the curve AB for vapour & BC for liquid as shown in figure.



The two curves AB & BC are merge at a point i.e., at critical point, because here the density of the liquid and vapour becomes identical.

The mean values of the densities are then plotted against the various temperatures, we get a straight line BD, pass through the critical point. It intersects the curve ABC at B, the corresponding density at the point B is the critical density. Critical density of a gas is the mass of its one cubic centimeter in the critical state.

If molecular mass of the liquid M is known, then critical volume (V_c) is calculated using the equation.

$$\therefore D_c = \frac{M}{V_c} \text{ or } V_c = \frac{M}{D_c}$$

4. REDUCED EQUATION OF STATE AND LAW OF CORRESPONDING STATES

Van der Waals' equation of state contains a, b and R , the first two of which are the characteristic constants of a gas and the third one is universal gas constant. The presence of a and b makes the nature of the isothermals different for different gases hence, the equation of state is not universal. The attempt of building up an equation of state which is of universal use succeeded in developing reduced equation of state. .

Let us define three reduced quantities:

$$\text{Reduced Pressure} = P/P_c = \pi \text{ (Pi)}$$

$$\text{Reduced Volume} = V/V_c = \phi \text{ (Phi)}$$

$$\text{Reduced Temperature} = T/T_c = \theta \text{ (Theta)}$$

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

Now replace the P , V and T by πP_c , ϕV_c and θT_c respectively in van der Waal's equation,

$$\left(\pi P_c + \frac{a}{(\phi V_c)^2} \right) (\phi V_c - b) = R \theta T_c$$

We know,

$$V_c = 3b, \quad P_c = \frac{a}{27b^2} \quad \text{and} \quad T_c = \frac{8a}{27Rb}$$

Substituting the values V_c , P_c and T_c in the above equation, we have,

$$\left(\pi \frac{a}{27b^2} + \frac{a}{(\phi 3b)^2} \right) (\phi 3b - b) = R \theta \frac{8a}{27Rb}$$

$$\left(\frac{a}{27b^2} \pi + \frac{a}{\phi^2 9b^2} \right) (\phi 3b - b) = \frac{8a\theta}{27b}$$

$$\frac{a}{9b^2} \left(\frac{\pi}{3} + \frac{1}{\phi^2} \right) (\phi 3 - 1) b = \frac{8a\theta}{27b}$$

$$\frac{a}{9b} \left(\frac{\pi}{3} + \frac{1}{\phi^2} \right) (\phi 3 - 1) = \frac{8a\theta}{27b}$$

$$\left(\frac{\pi}{3} + \frac{1}{\phi^2} \right) (\phi 3 - 1) = \frac{8a\theta}{27b} \times \frac{9b}{a}$$

$$\left(\frac{\pi}{3} + \frac{1}{\phi^2} \right) (\phi 3 - 1) = \frac{8\theta}{3}$$

$$3 \left(\frac{\pi}{3} + \frac{1}{\phi^2} \right) (\phi 3 - 1) = 8\theta$$

$$\left(\pi + \frac{3}{\phi^2} \right) (\phi 3 - 1) = 8\theta$$

This equation is called van der Waal's reduced equation of state. This equation involves neither R nor the van der Waal's constants a & b .

LAW OF CORRESPONDING STATES

DEFINITION:

WHEN TWO SUBSTANCES HAVE THE SAME REDUCED TEMPERATURE AND REDUCED PRESSURE , THEY WILL HAVE THE SAME REDUCED VOLUME.

5. Liquefaction of Gases



APPLICATIONS OF LIQUID H₂ & O₂

Cryogenic Technology



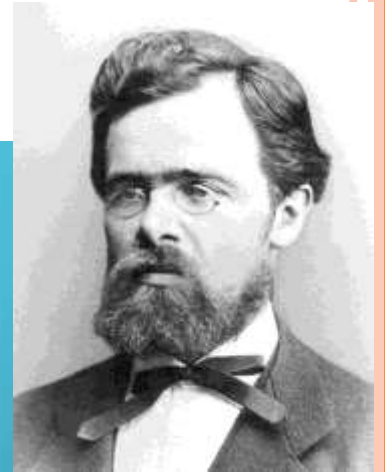
Making Liquid Air by Cooling (Using liquid Nitrogen)

Boiling Point of $N_2 = 77.4 \text{ K}$

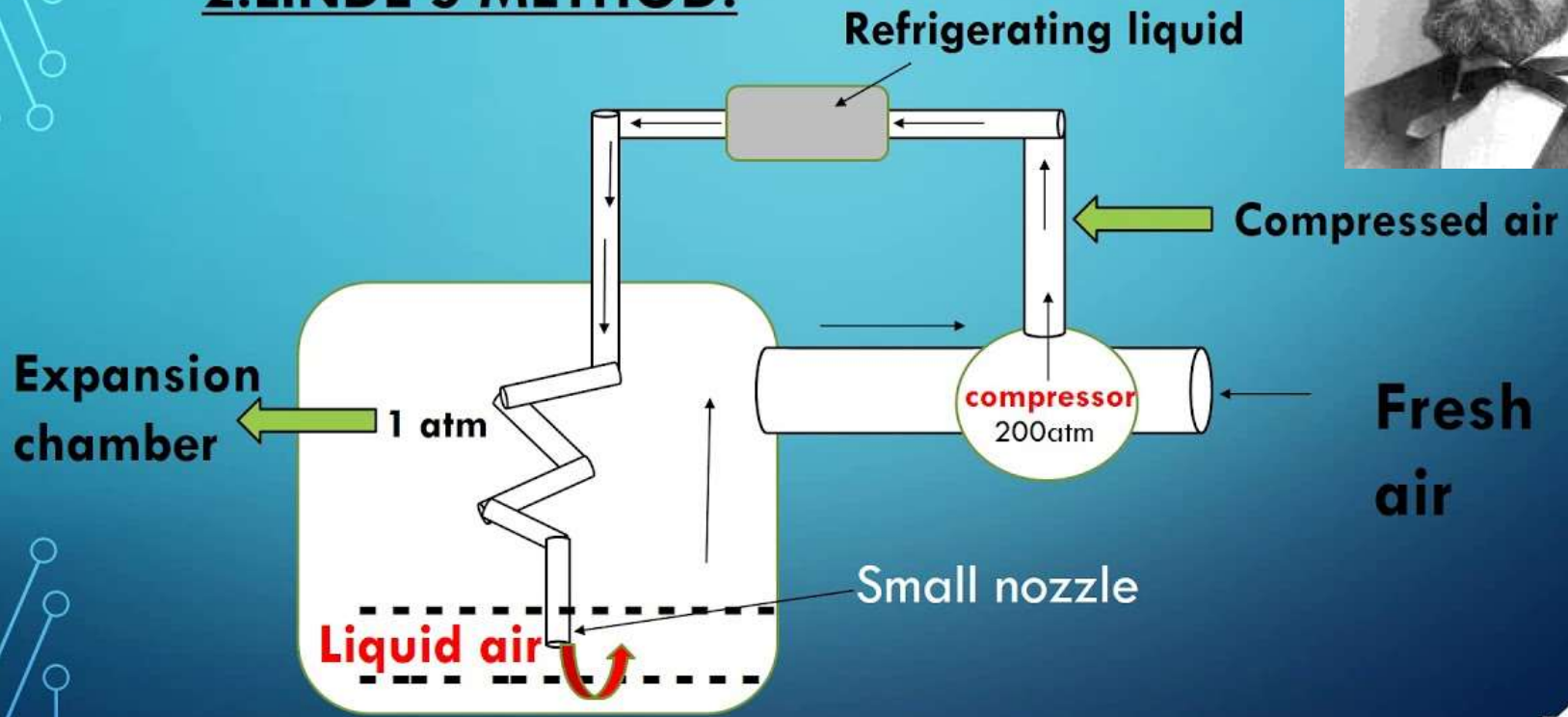
Boiling Point of $O_2 = 90.2 \text{ K}$



Carl Paul Gottfried Linde (11 June 1842 – 16 November 1934) was a German scientist, engineer, and businessman. He discovered [a refrigeration cycle](#) and invented the first industrial-scale [air separation](#) and [gas liquefaction](#) processes

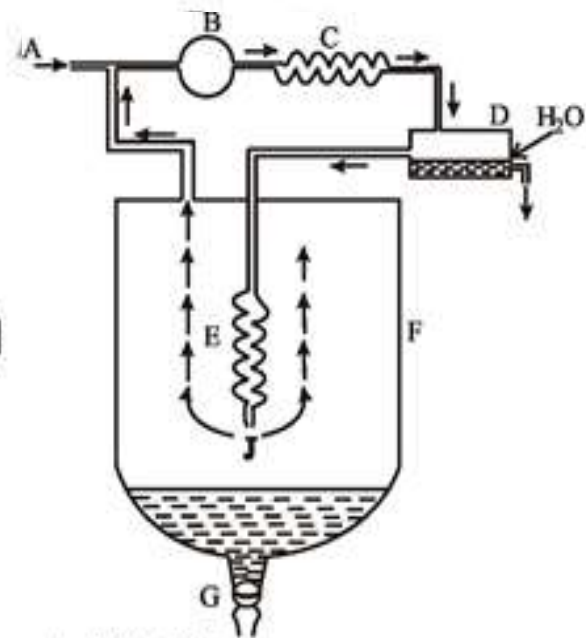


2. LINDE'S METHOD:



LINDE'S METHOD - 1895

- a. Air is compressed to 200 atm.
- b. Most of the water in air is condensed and removed.
- c. The heat generated as a result of compression is removed by passing the gas through coils C.
- d. The dry gas is then passed through a copper spiral coil E.
- e. It is then expanded to almost 1 atm through a controlled valve J.
- f. When the air comes out of the valve, expansion takes place from 200 atm to 1 atm. In this way fall of temperature occurs. This cold air goes up and cools the incoming compressed air.
- g. The cycle is repeated several times.
- h. The temperature of the expanding gas finally drops and the remaining air is liquefied.
- i. The liquid air is collected in chamber F and can be drawn off.



A - Inlet of Air
B - Compressor
C - Condensing Coils
D - Receiver for Water
E - Copper Spiral with a Jet
F - Outer Chamber
G - Outlet for Liquefied Air

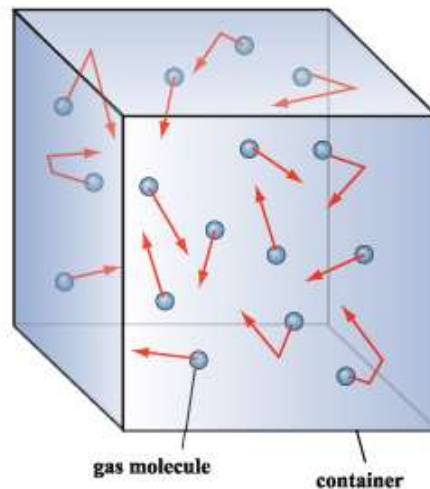
AIR SEPARATION PLANT



6. MAXWELL MOLECULAR SPEED DISTRIBUTION

What do you mean by Kinetic energy of molecules?

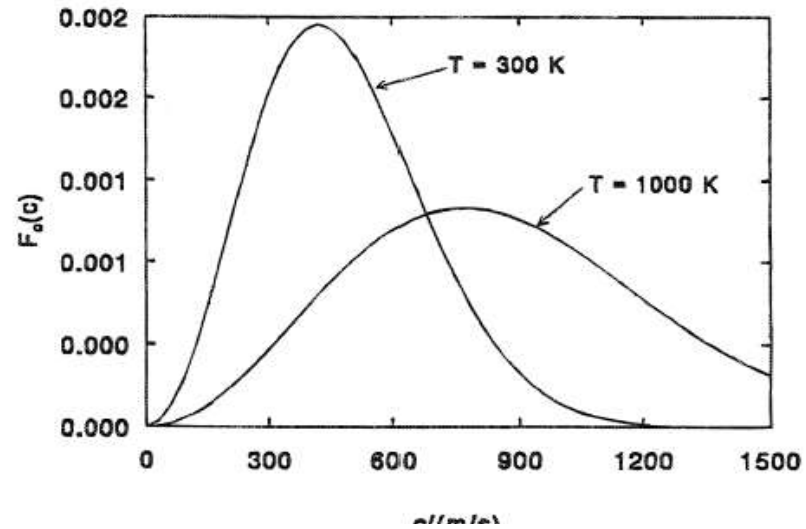
Boltzmann's Theory(upto 3.10)



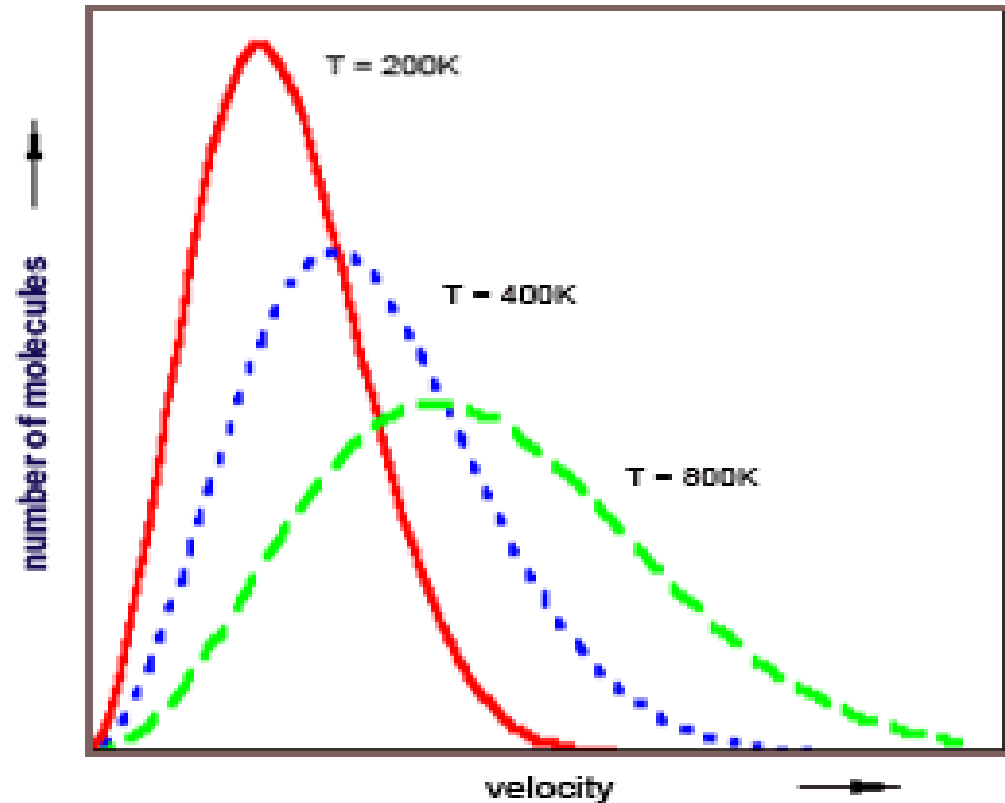
Maxwell Molecular Speed Distribution



Maxwell Molecular Speed Distribution Curves

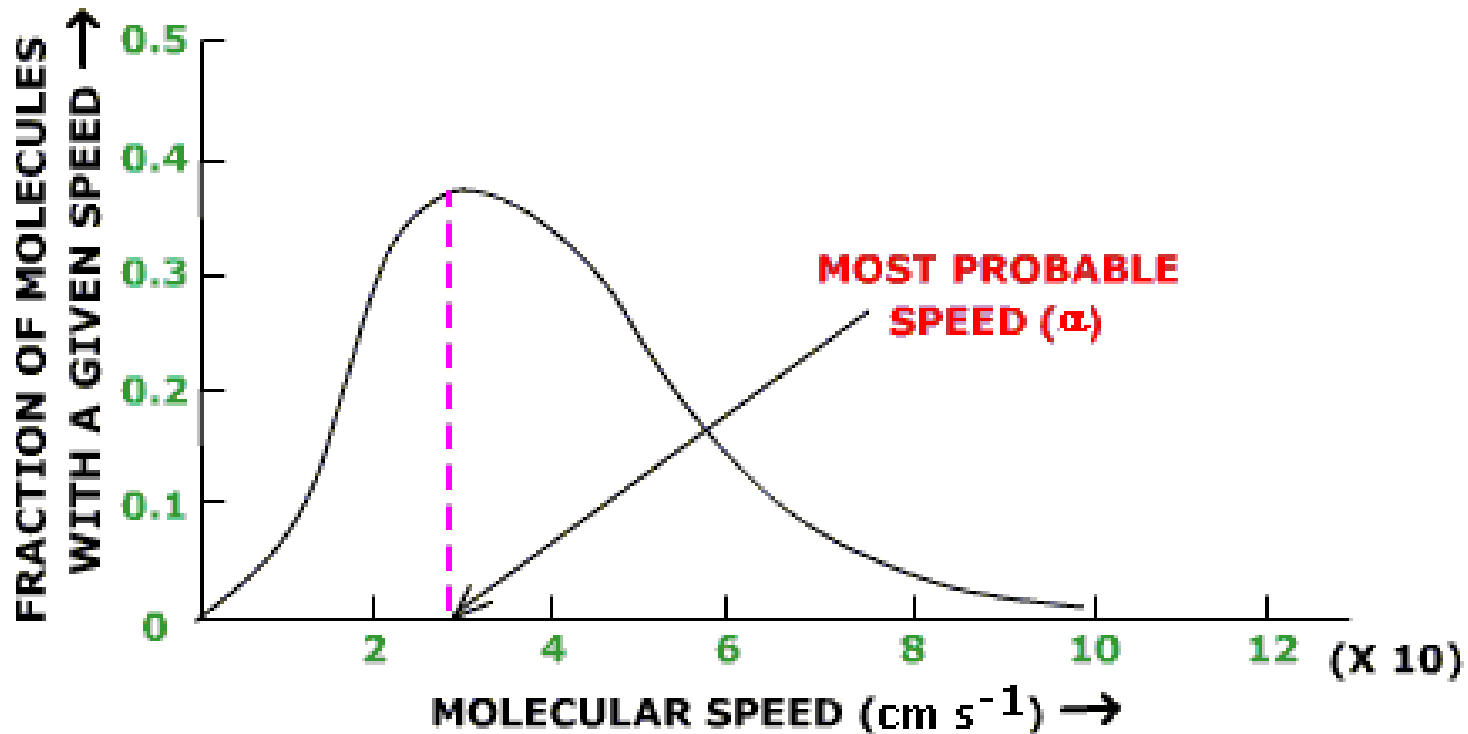


Maxwell-Boltzmann distribution of velocities



MOST PROBABLE VELOCITY

Most Probable velocity corresponds to the maximum of the Maxwell's function



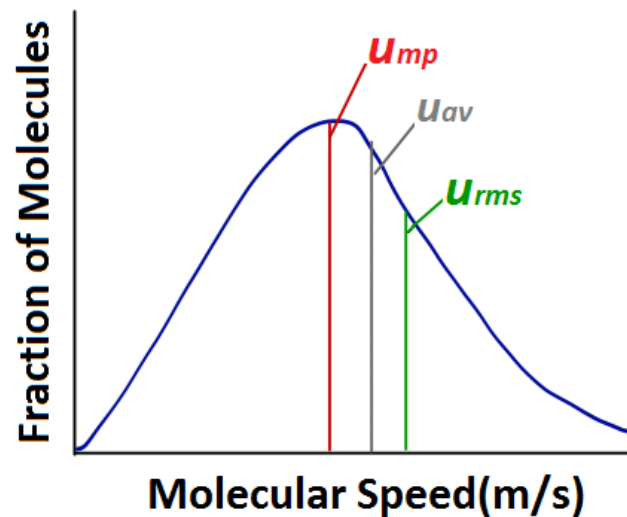
The relationship among velocities are :

$$C_{mp} : C_{av} : C_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

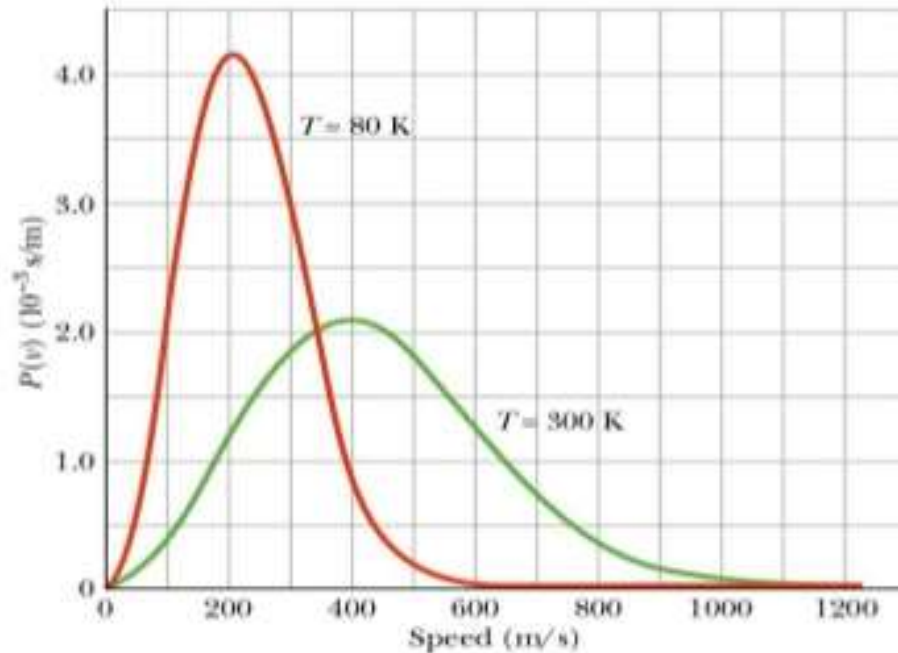
$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= 1.414 : 1.596 : 1.732$$

$$C_{mp} : C_{av} : C_{rms} = 1 : 1.128 : 1.224.$$



Maxwell-Boltzmann distribution



higher T
↓
higher speeds are
more probable

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/(2kT)}$$

Maxwell-Boltzmann
distribution

Maxwell's Distribution

The number of molecules moving with velocity between v and $v+dv$ is:

$$f(v) = N \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{mv^2}{2kT} \right]$$

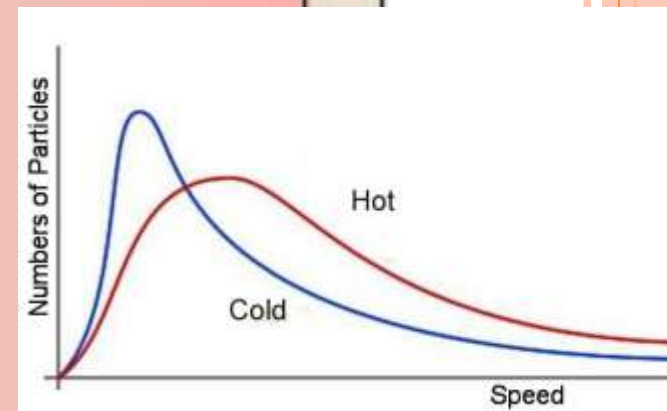
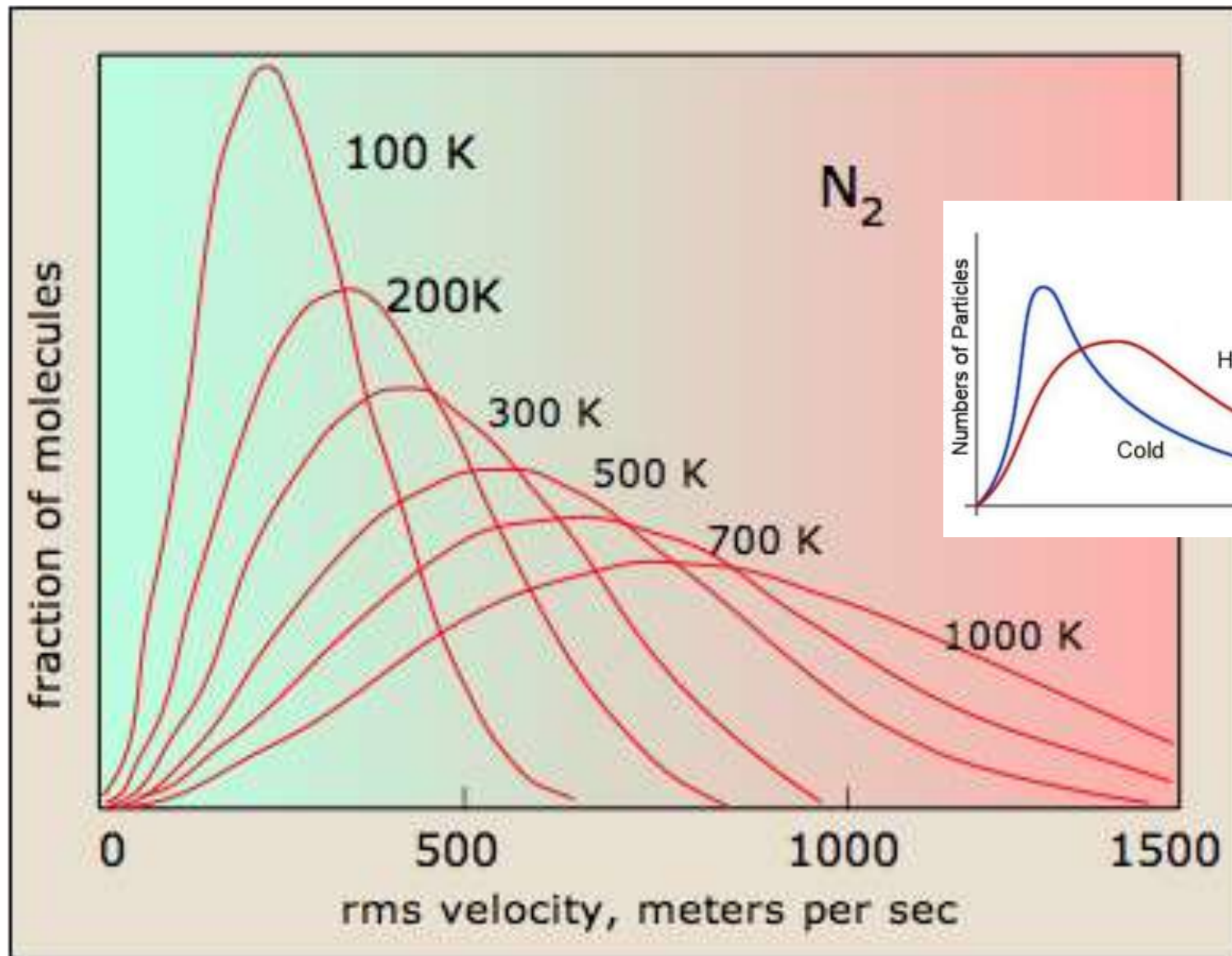
where,

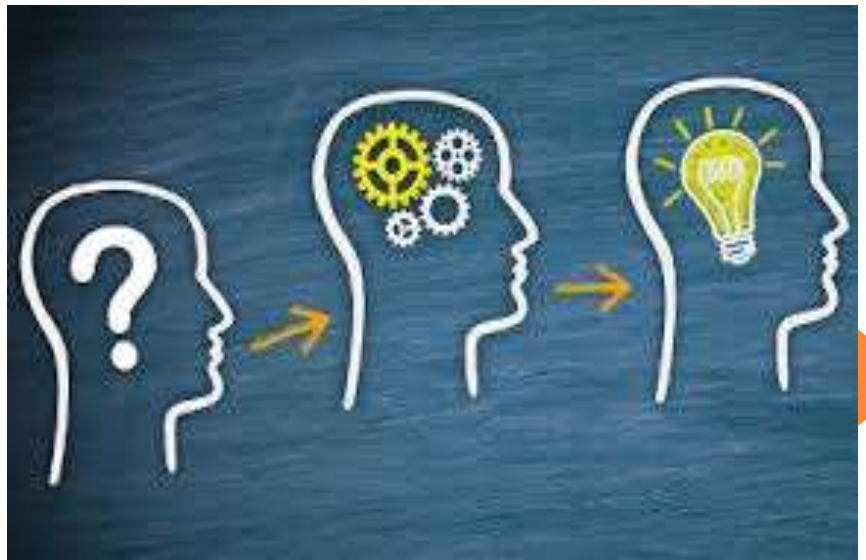
m is the mass of a molecule. N is the total number of molecules.

k is the Boltzmann constant. T is the absolute temperature



EFFECT OF TEMPERATURE ON DISTRIBUTION OF MOLECULAR VELOCITIES (EX: NITROGEN GAS)





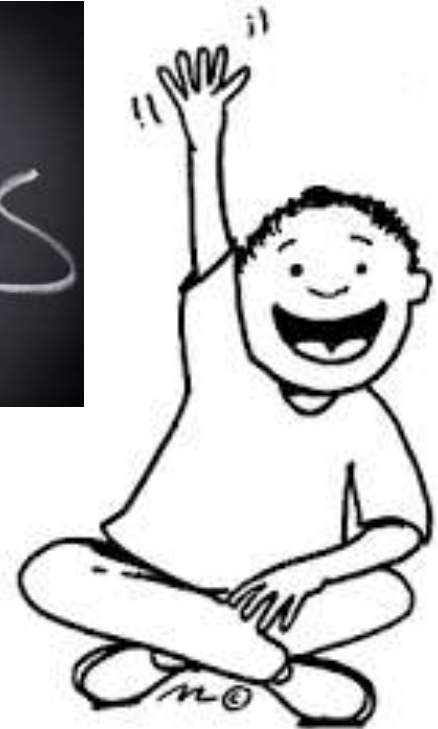
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