GAS LAWS

There are these gas laws and these are;

Boyles' law

Charles' law

Pressure law.

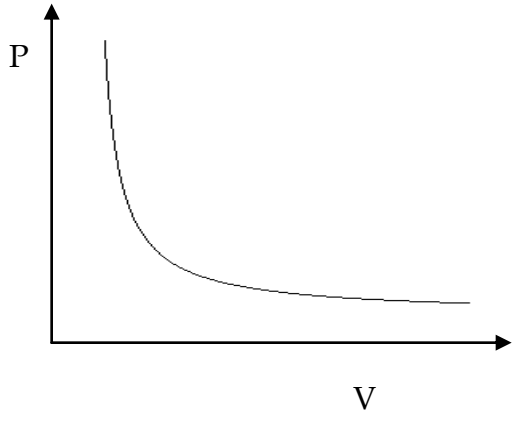
Boyle's law

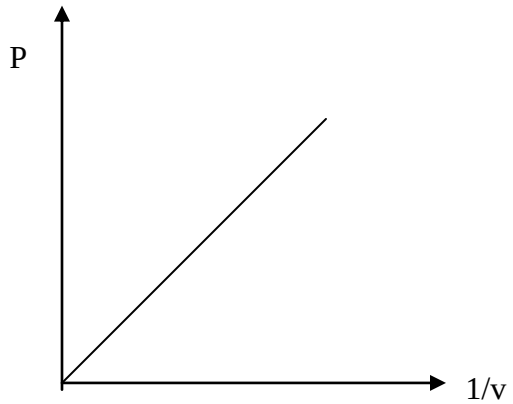
This law explains the relationship between pressure and volume of a fixed mass of a gas.

It states that the volume of a fixed mass of a gas is inversely proportional to its pressure provided its absolute temperature is kept constant.

PV = R where R is a constant of proportionality.

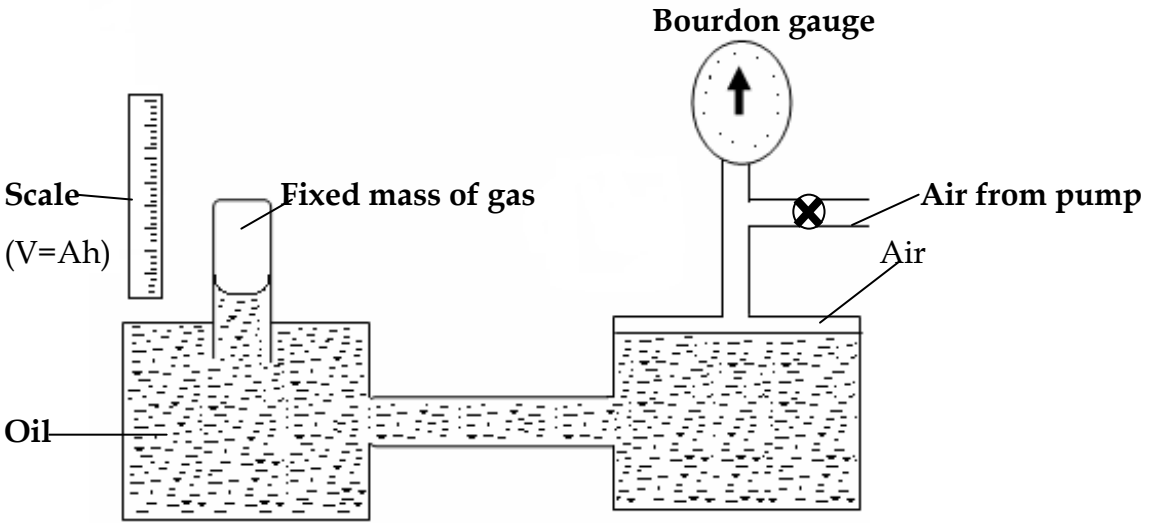
For changes of pressure and volume. Keeping temperature constant $P_1 V_1 = P_2 V_2$





Experimental verification of Boyle's law:

DIAGRAM



The apparatus is set up as shown in the diagram above

The gas under investigation is then air trapped above the oil in the glass tube.

The volume, V of the gas is determined by cross sectional by cross sectional area of the tube multiplied by the height of the gas above the oil i.e. V = Ah.

The gas is compressed by using a foot pump to increase the pressure above the oil in the reservoir and this can be read directly from the bourdon gauge.

The pressure is increased in stages allowing a number of values of P and V be recorded in a suitable table.

A graph of P versus $\frac{1}{V}$ is plotted. It is a straight line graph passing through the origin obtained, then Boyle's law has been verified.

Kinetic theory explanation of Boyle's law:

When the volume of a gas is decreases, the number of molecules of a gas does not change but the number of molecules hitting a unit area per second
will increase. This will eventually increase the pressure that is consistent with Boyle's law.

CHARLES' LAW

This law gives the relationship volume and temperature of a fixed mass of a gas under constant pressure.

It states that the volume of fixed mass of a gas is directly proportional to its absolute temperature provided the pressure remains constant.

V x T

V = RT where R is a constant of proportionality

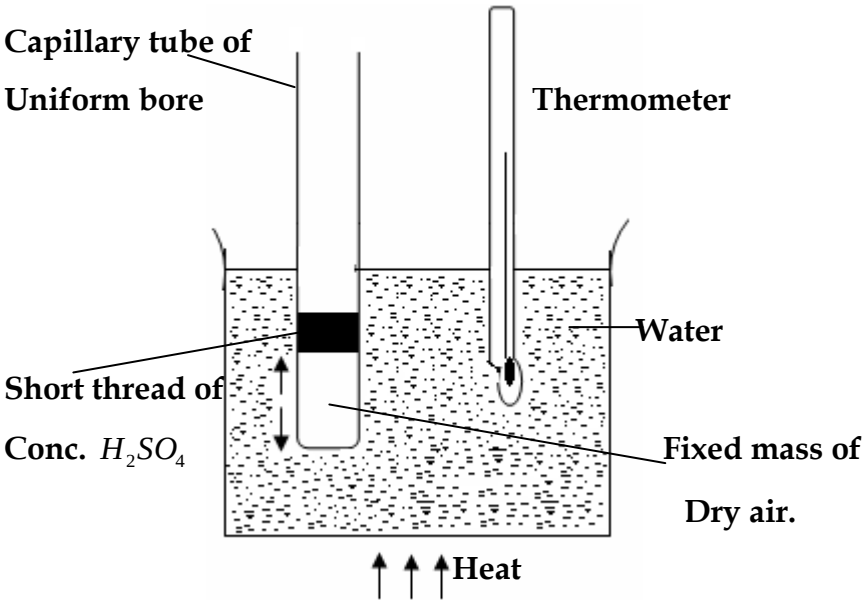
$\frac{V}{T}$ = R

For changes of volume and temperature at constant temperature

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Experimental verification of Charles's law

DIAGRAM



A column of air is trapped inside a capillary tube by a short thread of concentrated sulphuric acid.

The reason for using the acid is that it absorbs all the water that might be in the air and so keep the mass in the air fixed of constant.

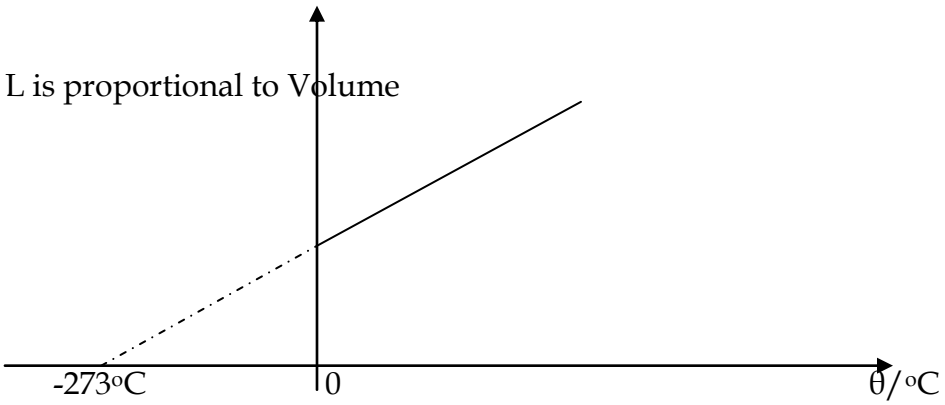
The tube has a uniform bore and therefore the volume of the trapped air is proportional to the length of the column.

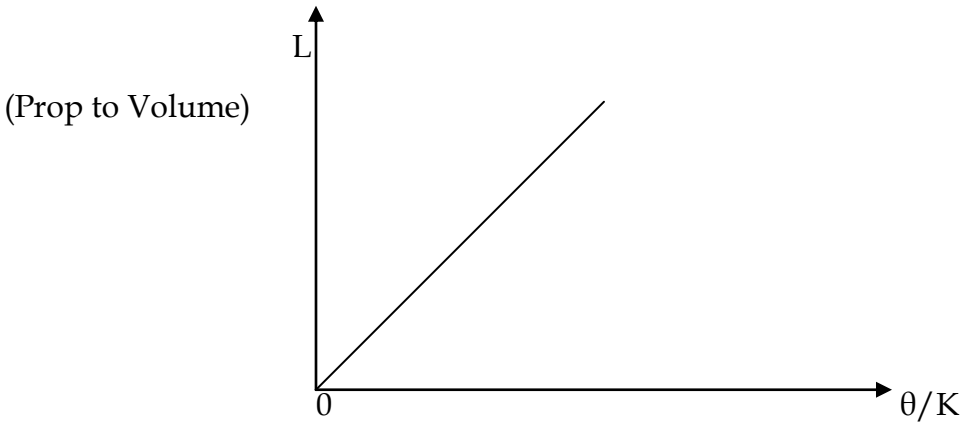
The water is heated and the length, of the air column is measured for a number of different temperatures.

The water should be heated slowly and stirred before each reading to allow the air to reach the temperature of the water.

The pressure of the air throughout the experiment is constant and is equal to the atmospheric pressure plus the pressure exerted by the acid thread.

A graph of L against temperature θ is plotted. The graph will be a straight line showing that for the particular pressure and range of temperatures investigated, the volume of fixed mass of dry air at constant pressure increases uniformly with temperature.





Kinetic theory explanation of Charles law

If the pressure of a fixed mass of a gas has to remain constant as the temperature increases, the rate of change of momentum of molecules on impact to the walls must remain constant.

Since the velocity of the molecules increase with temperature, a change in momentum will be greater and then to keep the rate of change the same, it will be necessary to keep / makes fewer impact per second. Thus the column must increase so that the molecules have to travel further between collisions with the walls. As you have seen, the condition applies if the volume carries as the thermodynamic temperature.

PRESSURE LAW

This law gives the relationship between pressure and temperature under constant conditions of volume.

It states that the pressure of a fixed mass of a gas is directly proportional to its absolute temperature provided the volume is kept constant.

$P \propto T$

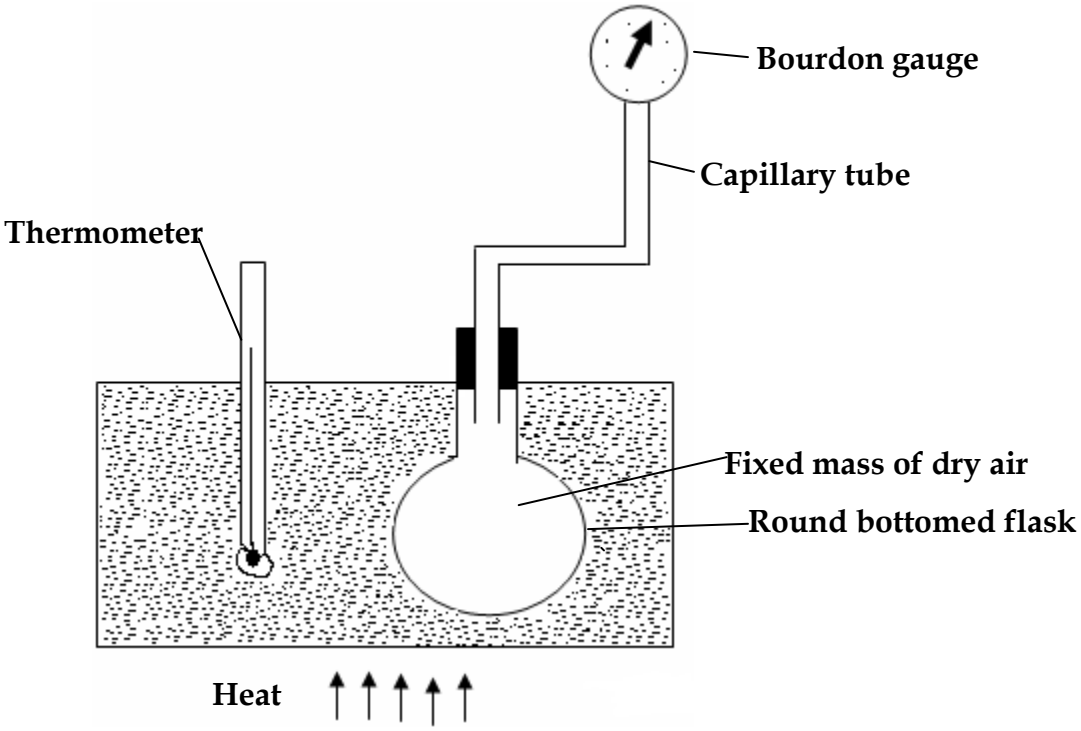
$P = RT$

$\frac{P}{T}$ = R, where R is a constant of proportionality.

For changes of pressure and temperature at constant volume.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Experiment verification of the pressure law:

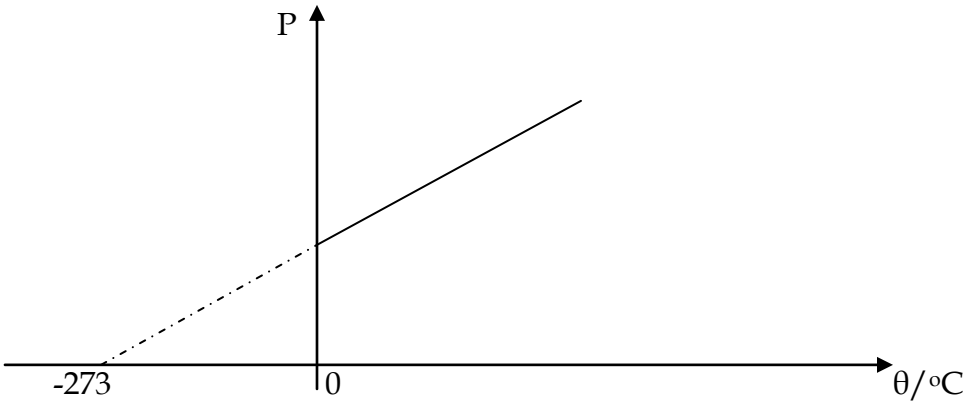


The apparatus enables the pressure variations with temperature of a fixed mass of dry air at constant volume to be investigated.

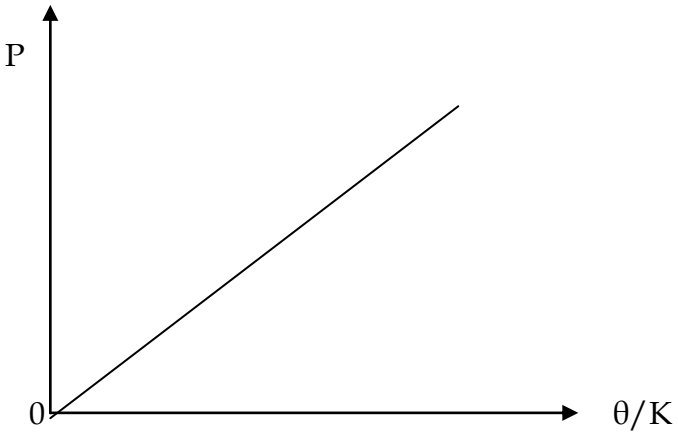
The water is heated and pressure, P of the air in the flask is recorded for a number of different temperatures θ.

The water should be heated slowly and stirred before each reading to allow the air in the flask to reach the temperature of the water.

A graph of P against Celsius temperature θ is plotted



The graph will be a straight line showing that pressure of a fixed mass of dry at constant volume increases uniformly with temperature. Note that it cuts the temperature axis at -273˚C. Yet for Kelvin (K) it cuts it at zero i.e. through origin.



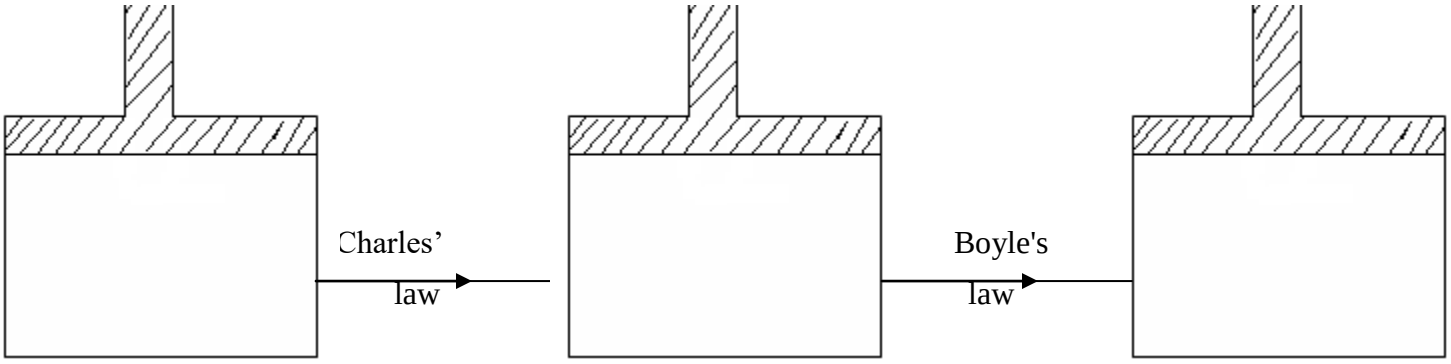
Kinetic theory explanation of pressure law

According to the Kinetic theory, when the temperature of a gas is increased, the molecules gain kinetic energy and their velocity increases.

Because of the increased velocity, the number of collision per second made by the molecule on the walls of the container will hence increase. Hence this will lead to an increase in pressure in the gas.

Equation of state (ideal gas equation):

DIAGRAM



We may find a general relationship between pressure, volume and temperature of a given mass.

This relationship is called the equation of state.

EQUATION OF STATE:

At $i/$ we have the gas occupying the volume V_1 at a pressure P_1 and an absolute temperature T_1.

We wish to calculate its volume V_2 at an absolute temperature T_2 and pressure P_2 as at $iii/$

We proceed via $ii/$ raising the temperature T_2 while keeping the pressure constant at P_1.

If V′ is the volume of the gas at ii/ then by Charles' law.

$\frac{V_1}{T_1} = \frac{V^1}{V_2}$ ……. Charles's law.

Proceeding to $iii/$ by increasing the pressure to P_2 while keeping the temperature constant at T_2 from Boyle's law.

Proceedings to $iii/$ by increasing pressure to P2 while keeping the temperature constant at T2 from Boyle's law.

$P_1V^1 = P_2V_2$…… (2) Boyle's law.

Eliminating V^1 between $i/$ and $ii/$ we have;

From (1)

$V^1 = \frac{V_1T_2}{T_1}$ …… (a)

$V^1 = \frac{P_2V_2}{P_1}$ …… (b)

a = b

$\frac{V_1T_2}{T_1} = \frac{P_2V_2}{P_1}$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{PV}{T} = \text{Constant} = R$$

$\boxed{PV = RT}$ for I mole of a gas.

Where R is the universal gas constant and $R = 8.314 SK^{-1} Mol^{-1}$

For n moles of a gas -----* can be written as;

$\boxed{PV = nRT}$

KINETIC THEORY OF MATTER

This is a theory that tries to explain the behavior of matter in terms of the behavior of its molecules.

For example;

Pressure of a gas; why does evaporation cause cooling? The occurrence of saturated vapour pressure.

Therefore under kinetic theory of gases; the pressure a gas can be explained in terms of these theories by considering the motion of their molecules.

The theory puts it that;

The pressure of a gas is due to the molecules bombarding the walls of the container in which it is contained.

DERIVATION OF THE DEPENDENCE OF THE PRESSURE, P OF A GAS ON THE VELOCITY OF THE MOLECULES:

Assumptions:

This is an explanation of the experiment observed properties of gases by considering the motion of the molecules of the gas. It should further be noted

that pressure of a gas is due to the bombardment of walls of the container by the gas molecules.

Assumptions:

1- The molecules of a particular gas are identical i.e. have the same mass.

2- Collisions between the molecules and with the container are perfectly elastic.

3- There are sufficiently large numbers of molecules for statistics to be meaningfully applied.

4- The molecules exert no forces on each other except during impacts (intermolecular forces both attractive and repulsive are negligible.) and the effect of gravity is ignored so that;

   (a) Between collisions the molecules move in straight lines at constant speed.

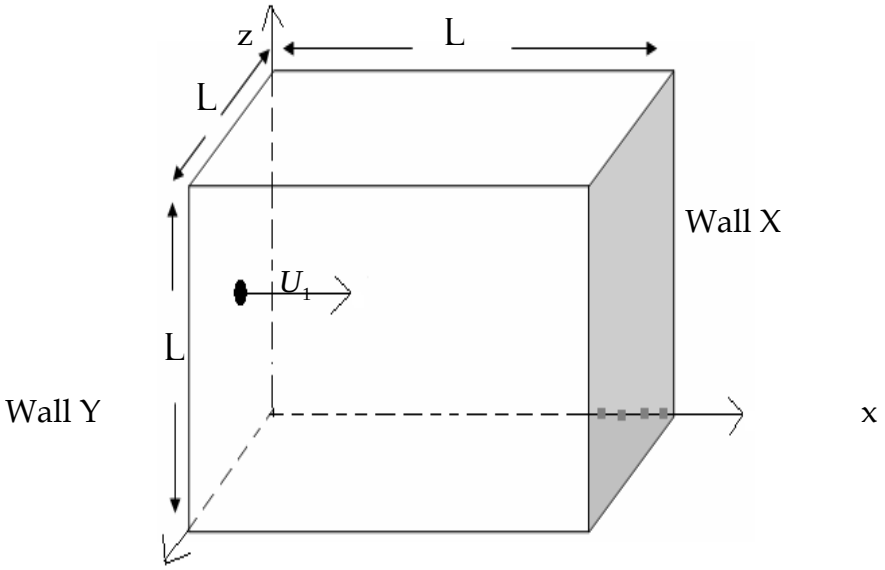
   (b) The motion is random

5- The laws of Newtonian mechanics apply.

6- The duration of the collision (the time molecules spent in contact with walls) is negligible as compared with the time between collisions (time the molecules takes to move to the opposite wall and back.)

7- The size of the molecules is negligible compared to the separation.

DIAGRAM



y

Consider a gas enclosed in a cubical container of side L.

Let each molecule of the gas have mass, M

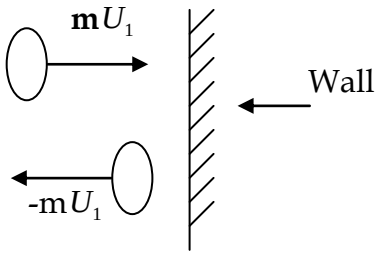
Consider initially a single molecule that is moving towards wall X and suppose that its x – component of velocity is U_1

This molecule will have an x component of momentum, M_1U_1 towards wall x.

The molecule will eventually reverse the direction of its momentum by colliding with the wall X.

Since the collision will be elastic, it will rebound with the same speed so that its momentum will be $^{-}M_1U_1$.

DIAGRAM



The change in the X – component of momentum is thus

$2mu_1$ i.e. $|mu_1 - {}^{-}mu_1|$

$= 2mu_1$

The molecule has to travel a distance 2L (from wall x to y and back to x) before it next collides with wall x.

The time taken by such a trip is $\frac{2L}{U_1}$ and therefore this molecule's rate of change of momentum due to collision with wall x will be $\frac{2MU_1}{2L/U_1} = \frac{M_1U_1^2}{L}$.

By Newton's second law, the rate of change of momentum is equal to the force and hence $\frac{MU_1^2}{L_1}$ is the force exerted on the molecule by the wall.

By Newton's third law, the molecule exerts an equal but oppositely directed force on the wall thus force on X IS; Force, F = $\frac{MU_1^2}{L}$

Force per unit area on x , F= $\frac{MU^2}{L^3}$ = $\frac{MU^2}{L}/L^2$ (Since area of X is L^2)

Therefore pressure on wall x due to a single molecule having X-component of velocity, U_1 = $\frac{MU_1^2}{L^3}$

If there are N molecules in the container and their components of the velocity are N_1 U_1 U_2 U_3……..U_N

Then the total pressure on the wall X will be given by

P = $\frac{M}{L^3}$ ($U_1^2 + U_2^2 + U_3^2 +$……U_N^2).

Therefore P = $\frac{MN\overline{U^2}}{L^3}$ …….. (1)

Where $\overline{U^2}$ = $\dfrac{U_1^2 + U_2^2 + U_3^2 + \ldots\ldots\ldots\ldots\ldots\ldots U_N^2}{N}$

=> $N\overline{U^2} = \overline{U_1^2} + \overline{U_2^2} + \overline{U_3^2} +$----------+ $\overline{U_N^2}$

Where $\overline{U^2}$ is the mean square velocity in the X-direction.

Since MN is the total mass of the gas in the container, then $\dfrac{MN}{L^3}$ is the density of the gas and therefore from (1)

(1) Becomes P = $\rho\,\overline{U^2}$ …… (*)

If C is the resultant velocity of a molecule whose X, Y and Z components of velocity are U, V, W respectively, then due to random movement of the molecules we shall have

$C^2 = U^2 + V^2 + W^2$

$\overline{C^2} = \overline{U^2} + \overline{V^2} + \overline{W^2}$..... ....

Where $\overline{C^2}$ is the mean square velocity of the molecules.

$\overline{U^2}$ is the mean square velocity of the molecules in the X-direction.

$\overline{V^2}$ is the mean square velocity of the molecules in the Y-direction

$\overline{W^2}$ is the mean square velocity of the molecules in the Z-direction.

Since they are large numbers of molecules and they are moving randomly without any preference for the particular direction.

$\overline{U^2} = \overline{V^2} = \overline{W^2}$ …… (3)

Imposing (3) into (2)

$\Rightarrow \overline{C^2} = \overline{U^2} + \overline{U^2} + \overline{U^2}$

$\Rightarrow \overline{C^2} = 3\overline{U^2}$

$\Rightarrow \overline{U^2} = \frac{1}{3}\overline{C^2}$

Substituting (4) in to (*) we have;

$P = \frac{1}{3}\rho\overline{C^2}$. Hence derived the equation for the dependence of pressure P on the velocity of the molecules. (VERY IMPORTANT EXPRESSION! You Should always remember it even when asleep)

IDEAL GAS:

An ideal gas is one that obeys the 'gas laws' and in practice no such gas exists. Gas laws obeyed by an ideal gas include the following.

Boyle's law

Pressure law

Graham's law of diffusion

Dalton's law of partial pressures.

Charles' law

An ideal gas obeys the equation of state PV = nRT and also it should be noted that the assumptions employed in the derivation of $P = \frac{1}{3}\rho\overline{C^2}$ only apply to an ideal gas.

Statement of fact:

'The internal energy of an ideal gas is entirely kinetic and depends entirely on its temperature'. This can be shown in the following derivation.

Relationship between molecular kinetic energy and temperature:

On the basis of the kinetic theory of gases pressure P = $\frac{1}{3}\rho\overline{C^2}$

Therefore for any volume, V of the gas.

PV = $\frac{1}{3}\rho V\ \overline{C^2}$

PV = $\frac{1}{3}M\overline{C^2}$ (i.e. $\rho = \frac{M}{V}$)

When there are N number of molecules, then the total mass of the gas is NM

⇨ PV = $\frac{1}{3}MN\overline{C^2}$

⇨ PV = $\frac{2}{3}$N ($\frac{1}{2}$M$\overline{C^2}$) (I just introduced a $\frac{2}{2}$=1, which has no effect don't get scared!! Why because I want to get an element of kinetic energy i.e. $\frac{1}{2}$)

Remember that for an ideal gas, PV = nRT ……(2)

⇨ $$\frac{2N}{3}\left(\frac{1M\overline{C^2}}{2}\right) = nRT$$

⇨ $$\frac{1M\overline{C^2}}{2} = \frac{3}{2}\left(\frac{n}{N}\right)RT.$$

n = number of moles of the gas

Since N is the number of molecules.

Then $\frac{N}{n}$ is the number of molecules per mole.

Then $\frac{N}{n}$ = N_A which is Avogadro's number

3 becomes

$$\frac{1}{2}M\overline{C^2} = \frac{3}{2}\frac{R}{N_A}T$$

Let $\frac{R}{N_A} = K$

Where K is called Boltzmann constant.

Therefore;

$$\Rightarrow \frac{1}{2}M\overline{C^2} = \frac{3}{2}KT$$

$$\therefore \frac{1}{2}M\overline{C^2} \ \alpha \ T$$

The left hand side term is the average translational Kinetic energy and thus;

Average translational Kinetic energy = $\frac{3}{2}KT$

Therefore molecular kinetic energy (average translational kinetic energy) is directly proportional to the absolute temperature.

Examples

1- A mole of an ideal gas at 300K is subjected to a pressure of 10^5Pa and its volume is $0.025M^3$.

Calculate.

(c) The molar gas constant

(d) The Boltzman constant

(e) The average translation Kinetic energy of a molecule of the gas. (Assume $N_A = 6.02 \times 10^{23}$ mole $^{-1}$).

Solution.

n = 1

T = 300R

P = 10^5Pa

V = 0.025M^3

R?

(a) PV = nRT

$$R = \frac{PV}{nT}$$

= 1 X 50^5 X 0.025

R = 8.33JK^{-1} Mol^{-1}

b.) Boltzmann constant,

$$K_B = \frac{R}{N_A}$$

$$K_B = \frac{833}{6.02X10^{-23}}$$

$$K_B = 1.38X10^{-23}\,JK^{-1}$$

(b) Average translational = $\frac{3}{2}K_BT$

Kinetic energy of one molecule

= $\frac{3}{2}\times 1.38\times 10^{-23}\times 300$

= $6.21\times 10^{-21}J$

2. Calculate the root mean square speed (r.m.s speed) of the molecules of oxygen at 76cmHg pressure and 0^oC, at which temperature and pressure, the density of oxygen is $1.43Kgm^{-3}$.

Solution

P_{Oxygen} = 76CMHg

T = 0^o C = 273K

$\rho = 1.43kgm^{-3}$

$P = \frac{1}{3}\rho\overline{C^2}$

$\overline{C^2} = \frac{3P}{\rho}$

$$\sqrt{\overline{C^2}} = \sqrt{\frac{3P}{\rho}}$$

$$= \frac{3x13600x\frac{76}{100}x9.81}{1.43}$$

$= 4.61 \times 10^2 ms^{-1}$

3 (a) Define the root mean square speed of a gas.

(b) The masses of hydrogen and oxygen atoms are 1.66×10^{-27}kg and 2.66×10^{-26}kg respectively

What is the ratio of the root mean square speed of hydrogen to that of oxygen molecules at the same temperature? (Assume both gases are one molar)

Solution:

(a) Root mean square speed of a gas if the square root of the mean square speed of a molecule of a gas.

(b)

$$M_h = 1.66X10^{-27}kg$$

$$M_O = 2.66X10^{-27}kg$$

$$n = 1$$

$$\overline{C_h}^2 = \frac{3nRT}{M_h}$$

20

$$\overline{C_0}^2 = \frac{3nRT}{M_O}$$

$$P = \frac{1}{3}\wp\overline{C^2}$$

$$P = \frac{1}{3}\frac{M}{V}\overline{C^2}$$

$$PV = \frac{1}{3}M\overline{C^2}$$

$$PV = nRT$$

$$\frac{1}{3}M\overline{C^2} = nRT$$

$$\overline{C^2} = \frac{3nRT}{M}$$

$$\sqrt{\overline{C^2}} = \sqrt{\frac{3nRT}{M}}$$

$$\sqrt{\frac{C_h^{\,2}}{\overline{C_O^{\,2}}}} = \sqrt{\frac{M_O}{M_h}}$$

$$\frac{\sqrt{Ch^2}}{C_o^{\,2}} = \sqrt{\frac{M_O}{M_h}}$$

$$\frac{\sqrt{Ch^{\overline{2}}}}{Co^2} = \sqrt{\frac{2.66X10^{-26}}{1.66X10^{-27}}}$$

$$= 4$$

$$\sqrt{\frac{C^{\overline{2}}}{C_O^{\overline{2}}}} = 4:2$$

$$\sqrt{\frac{C_h^{\overline{-2}}}{C_O^{-2}}} = \frac{4}{1}$$

DEDUCTIONS FROM THE KINETIC THEORY OF AN IDEAL GAS:

Using the kinetic expression for pressure, P = $\frac{1}{3}\rho\overline{C^2}$ and the relationship between average translation energy of temperature.

A number of deductions can be made; these include;

Avogadro's law, pressure law, Charles' law, Boyles' law, Graham's law of diffusion and Dalton's law of partial pressure.

1. Avogadro's law"

Avogadro's law states that equal volumes of all gases under the same conditions of temperature and pressure have equal number of molecules.

Consider 2 gases; Gas 1 and Gas II

Gas 1	Gas II
P_1, V_1, T_1	P_2, V_2, T_2
$N_1, M_1, \overline{C^2}$	$N_2, M_2, \overline{C^2}$

For gas 1

$$P_1V_1 = \frac{1}{3}N_1M_1\overline{C^2} = \frac{2}{3}N_1\left(\frac{1}{2}M_1\overline{C_1^2}\right) \quad \ldots\ldots\ldots\ldots \quad (1)$$

For gas II

$$P_2V_2 = \frac{1}{3}N_2M_2\overline{C_2^2} = \frac{2}{3}N_2\left(\frac{1}{2}M_2\overline{C_2^2}\right) \quad \ldots\ldots\ldots\ldots \quad (2)$$

According to Avogadro's law;

$P_1 = P_2$, $V_1 = V_2$,

⇨ $P_1V_1 = P_2V_2$

Therefore (1) = (2)

⇨ $\frac{2}{3} N_1 (\frac{1}{2} M_1 \overline{C_1^2}) = \frac{2}{3} N_2 (\frac{1}{2} M_2 \overline{C_2^2})$

According to Avogadro's law;

$T_1 = T_2$

Recall; $\frac{1}{2} M \overline{C^2} \alpha T$

$\therefore \quad \frac{1}{2} M_1 \overline{C_1^2} = \frac{1}{2} M_2 \overline{C_2^2}$

Therefore $N_1 = N_2$, i.e. both gases have an equal number of molecules.

Hence Avogadro's law deduced.

2. Boyle's law:

Boyle's law states that a fixed mass of a gas kept at constant temperature, the volume is inversely proportion to pressure.

$P \propto \frac{1}{V}$ PV = Constant = R

$P = \frac{1}{3} \rho \overline{C^2}$

PV = $\frac{1}{3}M\overline{C^2} = \frac{1}{3}Nm\overline{C^2}$

PV = $\frac{1}{3}Nm\overline{C^2} = \frac{2}{3}N\left(\frac{1}{2}M\overline{C^2}\right)$

Boyle's law holds if we have a fixed mass of a gas, hence N is fixed and N is a constant.

Again since T for Boyle's law is constant then;

$\frac{1}{2}M\overline{C^2}$ is also a constant.

Therefore;

PV = Constant which verifies Boyle's law.

3. Charles' Law:

Charles law states that the volume of a fixed mass of gas kept at constant pressure is directly proportional to absolute temperature, T.

V $\propto$ T = $\frac{V}{T}$ = constant

PV = $\frac{1}{3}M\overline{C^2} = \frac{1}{3}Nm\overline{C^2}$

PV = $\frac{2}{3}N\left(\frac{1}{2}M\overline{C^2}\right)$

$$V = \frac{2}{3}\frac{N}{P}\left(\frac{1}{2}M\overline{C^2}\right)$$

Since P is a constant for Charles' law, mass of gas is fixed i.e. N is constant then $\frac{2N}{3P}$ is also a constant.

However, under Charles' law, temperature is varying (not fixed).

$$T \propto \frac{1}{2}M\overline{C^2}$$

Hence $\frac{1}{2}M\overline{C^2}$ is not a constant and is a representative of temperature.

T. $\therefore$ V $\propto$ T or V = (constant) T

This deduces Charles' law.

4. Pressure law:

Pressure law states that the pressure of a fixed mass of a gas is directly proportional to its absolute temperature provided volume is kept constant.

P $\propto$ T $\quad \frac{P}{T}$ = constant

$$P = \frac{1}{3}\rho\overline{C^2}$$

$P = \frac{1}{3}\frac{M}{V}\overline{C^2}$ Since pressure law states that P $\propto$ T, then N is a constant for a fixed mass, V is a constant for a fixed volume and hence $\frac{2N}{3V}$ is a constant.

PV = $\frac{1}{3}M\overline{C^2}$ Since under pressure law, T is varying but $\left(\frac{1}{2}M\overline{C^2} \propto T\right)$, then $\frac{1}{2}M\overline{C^2}$ is also varying.

$$PV = \frac{2}{3}N\left(\frac{1}{2}M\overline{C^2}\right)$$

Hence not a constant

$P = \frac{2N}{3V}\left(\frac{1}{2}M\overline{C^2}\right)$ P = (Constant) T

P $\propto T$ (Pressure law)

5. Graham's law of diffusion:

The rate of diffusion of a gas is inversely proportional to the square root of its density.

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{Densityofgas}}$$

The sender the gas, the lower its rate of diffusion and the reverse is true.

Its reasonable to state that the rate of diffusion of a gas is proportional to the root mean square speed.

Consider 2 gas at the same pressure separated by a porous plug from

$$P = \frac{1}{3}\rho\overline{C^2}$$

$$\overline{C^2} = \frac{3P}{\rho}$$

$$\sqrt{\overline{C^2}} = \sqrt{\frac{3P}{\rho}}$$

If Gas 1 has density S_1 and Gas 2 has density S_2 but the two gases are at the same pressure, P then comparing the root mean square speeds for the two gases we have.

$$\frac{\sqrt{\overline{C_1^2}}}{\sqrt{\overline{C_2^2}}} = \frac{\sqrt{\frac{3P}{\rho_1}}}{\sqrt{\frac{3P}{\rho_2}}}$$

$$= \sqrt{\frac{\left(\frac{3P}{\rho_1}\right)}{\left(\frac{3P}{\rho_2}\right)}}$$

$$= \sqrt{\frac{3P}{\rho_1} \times \frac{\rho_2}{3P}}$$

$$= \sqrt{\frac{\rho_2}{\rho_1}}$$

$$\frac{\sqrt{\overline{C_1}^2}}{\sqrt{\overline{C_1}^2}} = \frac{\sqrt{\rho_2}}{\sqrt{\rho_1}}$$

The rate of diffusion of Gas 1

The rate of diffusion of Gas 2 = $\frac{\sqrt{\rho_2}}{\sqrt{\rho_1}}$

In conclusion, rate of diffusion $\propto \frac{1}{\sqrt{\rho}}$

6. Dalton's law of partial pressure

It states that the total pressure of a mixture of gases that do not interact chemically is equal to the sum of partial pressures i.e. to the sum of the pressures that each would exert if it alone occupied the volume containing the mixture at the same temperature.

Suppose that a volume V contains n_1 moles of a gas whose partial pressure is P_1 and n_2 moles of a gas whose partial pressure is P_2, if the temperature of the gas, T.

For gas 1:

$P_1V_1 = n_1RT$……..

For gas 2:

$P_2V_2 = n_2RT$…….. (2)

Diving (1) by (2) but $V_1 = V_2 = V$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

However, from Dalton's law of partial pressures.

$P = P_1 + P_2$……. (*) (*)

Where P refers to the pressure of a mixture of gases 1 and 2 occupying a volume, V at a temperature, T

Where P_1 and P_2 are partial pressures.

Partial Pressure;

Partial pressure of a gas is the pressure the gas would have if it occupied the whole container alone.

From (*)

we have; $P_2 = \frac{P_1 n_2}{n_1}$ ……. (a)

30 (a) (*) (*)

Putting into

We have; $P = P_1\left(1+\frac{n_2}{n_1}\right)$

$P = P_1\left(\frac{n_1+n_2}{n_1}\right)$

$$P_1 = P\left(\frac{n_1}{n_1+n_2}\right) \quad \text{.....(b)}$$

From (*) $P_1 = \frac{n_1 p_2}{n_2}$ ..... (b)

Subs (b) into (*) (*)

$$P = \frac{n_1 P_2}{n_2} + P_2$$

$P = P_2 \left(\frac{n_1}{n_2} + 1 \right)$

$$P = P_2 \left(\frac{n_1}{n_2} + 1 \right)$$

$$\boxed{P_2 = P \left(\frac{n_2}{n_1 + n_2} \right)}$$

$$P = P_2 \left(\frac{n_1 + n_2}{n_2} \right)$$

Do you realize that (P_1 + P_2 = P) ?

IDEAL AND REAL GASES:

Ideal gas;

An ideal gas obeys the gas laws e.g. Boyle's law. It is represented by the general equation of state.

(pressure of the gas in the bulk) X (free volume of movement of the gas molecules for one mole of gas) = RT…….

From the kinetic theory assumptions;

- ➔ When the attractive forces between molecules are ignored, the pressure in the bulk of the gas is equal to the pressure P at the walls.
- ➔ When the repulsive forces are ignored and the volume of the molecules themselves is also ignored, the free volume of movement is equal to the volume V of the container.

Hence (1) becomes;

$PV = RT$ for one mole of a gas.

REAL GASES;

Oxygen, Nitrogen, Helium, Argon and all other gases are referred to as real gases.

Real gases have both attractive and repulsive forces. Real gases obey the ideal gas equation PV = RT only when they are at very low pressures and temperatures well above their critical temperatures.

Terms

1- **Critical temperature; T_c**

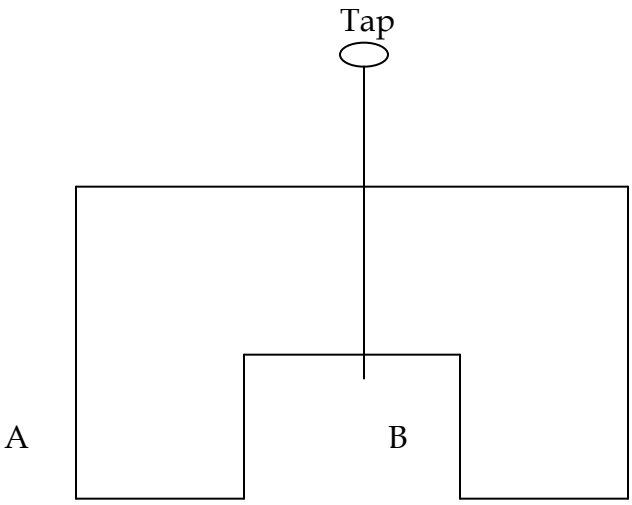
This is the temperature beyond which a gas cannot be liquefied by mere compression however great the pressure.

e.g. for carbondioxide $T_C = 31.1^oC$

2- **Critical pressure, P_C;**

This is the minimum pressure that will cause liquefaction of a gas at its critical temperature.

For CO_2, $P_C = 73 \times 10^5 P_a$



The cylinder A and B of volume V and 3V respectively are separated and filled with gas. They are connected together and the tap closed. The pressures of the gas in A and B are P an 4P respective.

When the [tap is open, the common pressure becomes $60P_a$. assuming no thermal conditions. Find the value of P.

Solution

$P_A = P$ $P_3 = 4P$

$V_A = V$ $V_B = 3V$

$P_m = 60MMhG/60P_a$

For gas in A before tap is opened

$P_A V_A = n_A R_A T_A$…….. (1)

For gas in B before tap is opened;

$P_B V_B = n_B R_B T_B$…….. (2)

For the gas in the two cylinders after the tap is opened.

$P_m V_m = n_m R_m T_m$ ..... (3)

Note that $n_m = n_A + n_B$ ..... (*)

From (1) $n_A = \frac{P_A V_A}{RT_A}$

From (2) $n_B = \frac{P_B V_B}{RT_B}$

From (3) $n_M = \frac{P_m V_m}{RT_m}$

Imposing (1) (2) (3) into (*)

$n_m = n_A + n_B$

$$\frac{P_m V_m}{RT_m} = \frac{P_A V_A}{RT_A} + \frac{P_B V_B}{RT_B}$$

For isothermal conditions;

$T_A = T_B = T_m$

$P_m V_m = P_A V_A + P_B V_B$

$60 (3V + V) = PV + 4P (3V)$

$240 = PV + 12PV$

$240V = 13PV$

$\frac{240}{13} = P$ $\quad P = 18.46Pa$

3- Specific critical volume V_C;

This is the volume occupied by one kilogram of a gas at its critical temperature and pressure.

4- A gas;

Is the substance, which is in the gaseous state and is above its critical temperature.

5- Vapour;

A vapour is a substance that is in the gaseous phase and is below its critical temperature.

Thus, vapour can be liquefied simply by increasing the pressure while a gas cannot.

The main deviations from ideal behavior to arise from the finite size of the molecules and the forces between them.

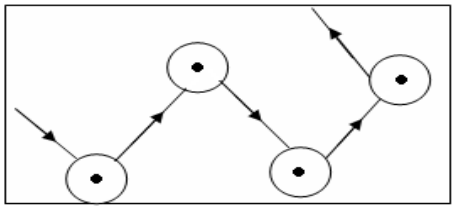
In order to obtain a better equation for real gases, two of the simplifying assumptions made in the simple kinetic theory of gases (during the derivation of $P = \frac{1}{3}\wp \bar{C}^2$ for an ideal gas) have to be modified.

(i) Intermolecular forces can't be ignored.

(ii) The volume of the molecules themselves can't be ignored.

Effects of repulsive forces

DIAGRAM



V = Volume of container

Molecule random motion of Co-volume.

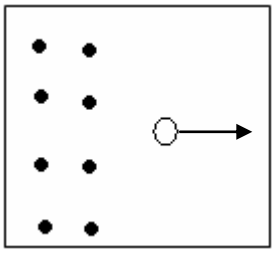
The volume of the molecules may not be negligible in relation with the volume V occupied by the gas. The molecular have a particular volume because repulsive forces occur when they approach each other closely and hence cannot be compressed indefinitely.

Surrounding each molecule, there is a definite volume called the co-volume, which cannot be occupied by any other molecule.
The free volume of movement of molecules is not the volume V1 of the container but (V - b) where b is a factor which depend the co-volume of the molecule hence b accounts for the finite volume of movement of molecules = (V - b)…….. ii

N.B – The value of b differs from gas to gas.

EFFECT OF ATTRACTIVE FORCES

DIAGRAM



In real gas, the attractive forces between the molecules are not negligible. Any molecule approaching the walls of the container would experience an attractive force from the bulk molecule. Thus, this would reduce the momentum of the bombarding molecules thereby reducing the pressure exerted on the walls.

The pressure P_1 exerted at the walls is less than the pressure in the bulk. Hence pressure in the bulk = pressure of walls + pressure defect DP.

$P_{bulk} = P_{wall} + DP$

The pressure defect DP is proportional to the number of molecules striking the surface per unit area per second. That is, to the density. It is also proportional to the number of molecules attracting the molecules from the bulk and reducing the momentum imparted to the wall on impact.

This is also proportional to:

$$DP \propto \int . \int$$

$$DP \propto \int^2 \qquad \text{But} \quad \int = m/v$$

$$DP = \frac{Km^2}{V^2}$$

For a fixed mass of a gas, M is constant

$$DP = \frac{a}{v^2}$$ Where a = km^2.

Thus pressure defect $\frac{a}{v^2}$ accounts for the intermolecular forces of attraction

hence pressure in the bulk = $\left(P + \frac{a}{v^2} \right)$ ……(iii)

Combining (i), (ii), (iii)

$\left(P + \frac{a}{v^2} \right)(v.b)$ = RT……..*

For one mole of a gas, we have (*) called the vanderwaals equation of state for a real gas. This equation varied over wide ranges of temperature but eventually has shortfalls at certain temperatures.

NB:-

Real gases obey vanderwaals equation only at temperatures above their critical temperature.

COMPARISON OF REAL AND IDEAL GASES:

Predicted theoretical sketch graphs of pressure P against volume for various values of temperature T indicated by the ideal gas equation and vanderwaals equation are shown below.

i) Fig (1) ideal gas PV = nRT

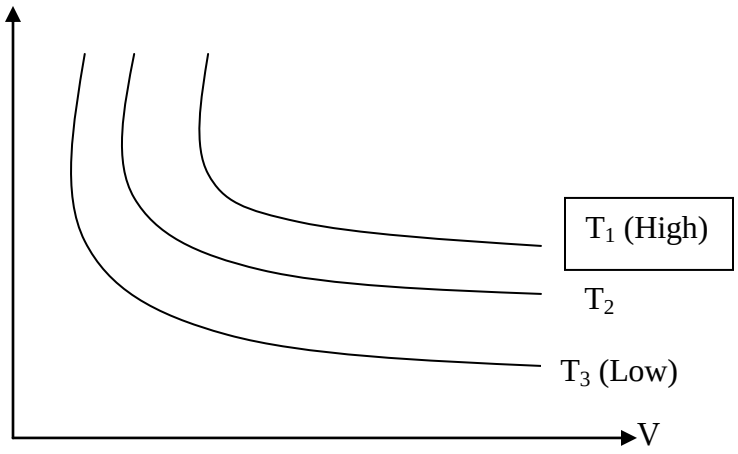
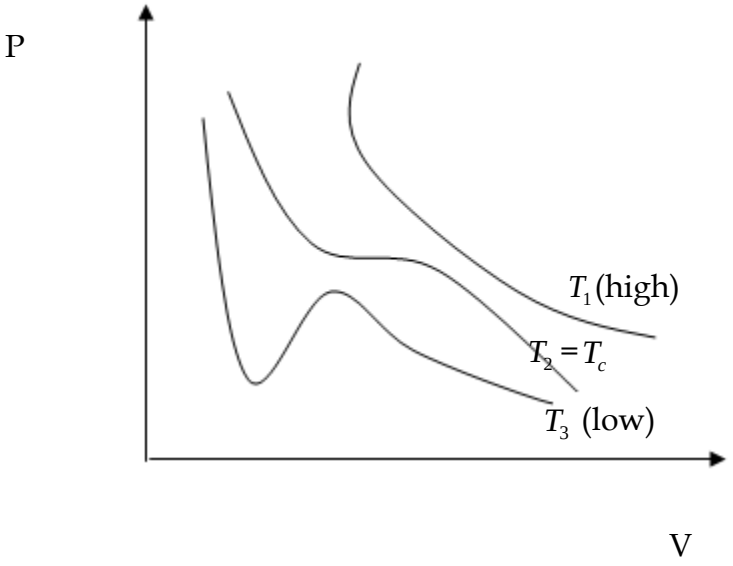


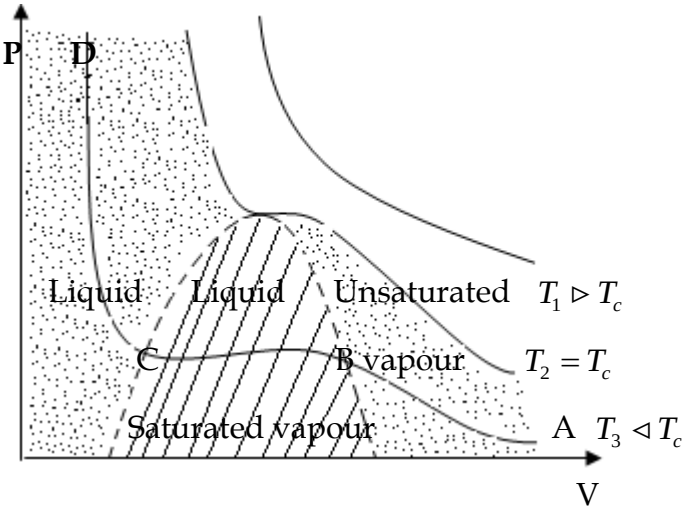
Fig (2) Vanderwaal's equation $\left(1+\frac{a}{V^2}\right)(v-b)=RT$

Diagram



PV Sketches for a real substance obtained experimentally like by Andrew for CO2 are shown below in fig 3

DIAGRAM



Interpretation of the theoretical predictions and the experimental findings

(i) At high temperature T, the experimental isothermals for (3) are similar to those in (1) and (2) thus real gases behave like ideal gases at high temperatures.

(ii) As the temperature is reduced, the isothermals in (2) change in shape. The isothermal at T_2 has a part of inflexion at T_c , which corresponds to the critical part of a real gas. This is similar to that in (3). T2 is called the critical temperature T_c Vanderwaals equation roughly applies to real gases above their critical temperature.

(iii) Below the critical temperature, the isothermals in (2) differ from those in (3) e.g. if we consider region AB in (2), it can be deduced or inferred that the pressure increases with volume which is not in line with the true experimental findings in (3). It should be noted that Vanderwaals equation doesn't hold for real substances below their critical temperature.

Figure 3

Figure (3) is Andrew's isothermal or P – V curves for a fixed mass of CO_2, which is a real gas.

Consider the gas to be in the state of pressure, volume and temperature that is represented by point A on the isothermal T_3.

In this state, the real gas is an unsaturated vapour and if its compressed, the P – V curve is very nearly hyperbolic until the pressure reaches that represented by B.

At B, the gas begins to liquidity. Between B and C the volume decreases but there is no increase in pressure. The decrease in volume is due to the fact that in moving from B to C more and more liquid is formed that at C the gas is entirely liquid.

From C to B and beyond, large increases in volume as might be expected since liquid are virtually.

Differences between real and ideal gases

1- The volume of the molecules of an ideal gas is negligible while that of a real gas is significant and appreciable.
2- Ideal goes have negligible intermolecular forces (attractive and repulsive) while in real gases, intermolecular forces are appreciable and significant.
3- The volume of ideal gas molecules in contact between collisions while real gases do not have a constant volume due to intermolecular forces.
4- Ideal gases obey Boyle's law and equation of state PV = nRT at all temperatures while real gases obey the equator o state PV = nRT at very high temperatures well above their critical temperature.

VAPOURS

A substance in gaseous phases and is below its critical temperature.

Evaporation:

Process through while a liquid becomes a vapour or gas.

It can take place at all temperature but occurs at the greatest rate when the liquid is at its boiling.

Factors that determine the rate of evaporation

(i) Increase the area of liquid surface.
(ii) Increase the temperature of liquid. (This increases the average kinetic energy of all the molecules without increasing the strength of the intermolecular forces of attraction)
(iii) Causing a draught by removing the vapour molecules before they change to return to the liquid.
(iv) Reducing the our pressure above the liquid. (Since this decreases the possibility of a vapour molecule rebounding off air molecule.)

N.B

When a liquid evaporates, it loses some of its molecules that have the greatest kinetic energy and cools.

Saturated and unsaturated vapors

Saturated vapour;

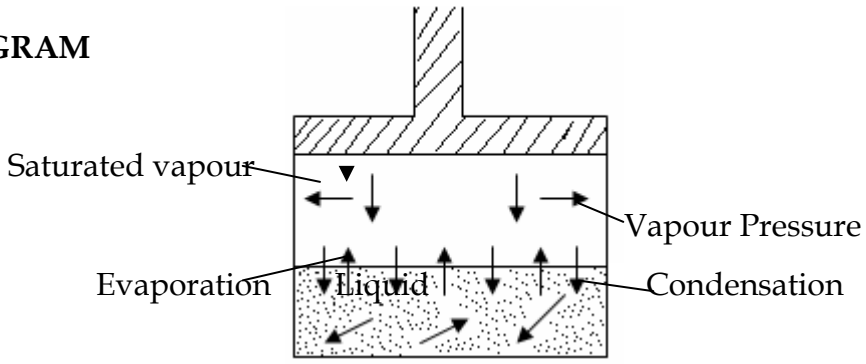
A vapour that is in dynamic equilibrium with its own liquid where the rate of evaporation is equal to the rate of condensation.

Saturated vapour pressure

It's a pressure exerted by the saturated vapour.

Kinetic theory explanation of the occurrence of saturated vapour pressure

DIAGRAM



Suppose that the container is partly filled with a hot liquid and then sealed, some molecules escape from the liquid by process of evaporation and exist as vapour in the region above. The vapour molecules move about randomly and some of them return to the liquid. The rate of condensation (rate at which molecules return to liquid) is determined by number of molecules in the vapour phase.

Initially, this is low and the rate of evaporation exceeds rate of condensation. There is therefore a net gain of molecules by the vapour are eventually a dynamic equilibrium is established in which the rate at which molecules enters the vapour is equal to rate at which they return to the liquid.

The region above the liquid is said to be saturated for it now contains the maximum possible number of molecules that the conditions will allow.

The vapour molecules collide with the walls of vessel / container giving rise to a vapour pressure. This pressure being exerted by the saturated vapour is called saturated vapour pressure (S.V.P) and its value depends only on temperature.

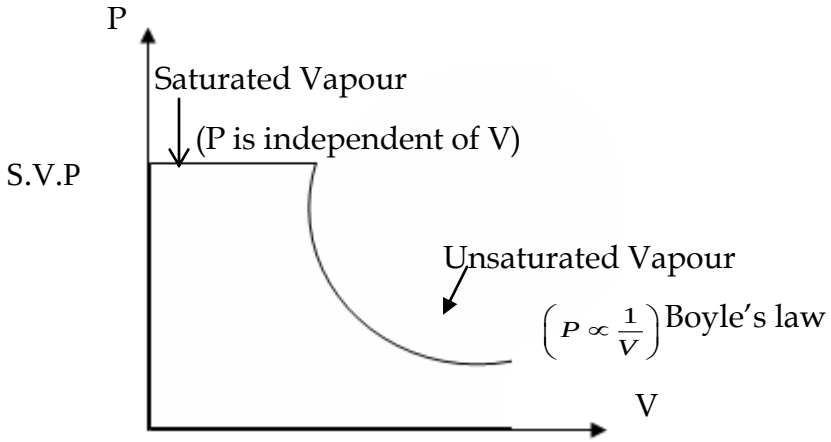
If the volume of the space above the liquid is increase, there is a momentary decrease in density of the vapour, in particular immediately above the liquid surface.

This decreases the rte of condensation and restores the pressure of its previous value i.e. S.V.P is independent to volume.

If the increase in volume is continued, more and more liquid evaporates and eventually there is none left. Any further increase in volume cruses the vapour to become unsaturated in other words there is no more liquid present.

Unsaturated vapour is one which is not in contact with its was liquid. Once this happens the pressure varies with volume in a manner that is approximately consistent with Boyle's law.

The plot of pressure against volume at a fixed temperature is shown below:



For a system that is in thermal equilibrium, if the temperature of such a system is increased there are two district consequences;

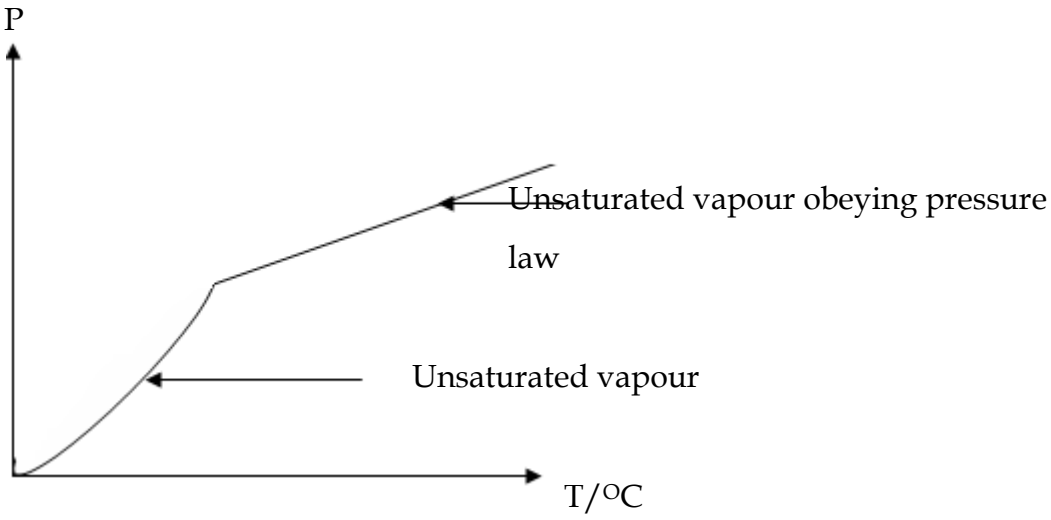
i. Kinetic energy of vapour molecules increases.

ii. Rate of evaporation increases and therefore there is an increase in number of molecules in the vapour phase.

If volume of a system is constant, each of these effects produces an increase in pressure. The effect of (i) alone would be able to give a pressure increase of the form predicted by the pressure law approximately.
(ii) means that increase in pressure with increasing temperature is much more rapid than this.

A plot of P versus T for a vapour in sealed container:

DIAGRAM



If the temperature is increased at constant pressure, the volume increases, but because of (ii), it increases much more rapid than required by Charles' law.

Note:

1. The gas laws refer to fixed masses of gases, changing the state of saturated vapour involves condensation or evaporation and therefore changes its mass. It follows that saturation vapors do not obey the gas laws in particular S. V. P depends only in temperature.

2. Unsaturated vapors like real gases obey the gas laws approximately.

In carrying out calculat5ions at this level unsaturated vapors can be taken to obey the gas laws.

MIXTURES OF GASES AND VAPOURS:

When solving calculations or vapors, the first and most important step is to identify whether the problem involves a mixture of gas and saturated vapour or a mixture of a gas and saturated vapour.

i. Mixture of a gas and an unsaturated vapour:

Both the gas and the unsaturated vapour, obey the equation of state.

Therefore we should feel free to apply the equation of the state to the mixture.

ii. **Mixture of a gas and a saturated vapour**:

The gas obeys the equation of state, hence its important to not the above while the saturated vapour does not obey equation of state hence use Dalton's law of partial pressures to separate pressure of the gas, Pg, from the S.V.P, Ps, and apply equation of state to the gas alone.

N.B:

Dalton's law of partial pressure states that the pressure of a mixture of gases is the sum of the partial pressures to the mixture of the gases. Therefore, applying Dalton's law of partial pressure to the mixture of the gases and saturated vapour pressure gives power of mixture = pressure of the gas + S.V.P.

$$P = Pg + Ps$$

BOILING:

Boiling point of a liquid is that temperature at which its S.V.P is equal to its external pressure.

The external pressure is equal to;

i. Pressure of atmosphere above the liquid plus

ii. The hydrostatic pressure due to the liquid it self plus

iii. The pressure due to the surface tension effect

Boiling differs from evaporation in that;

i. Boiling occurs throughout the volume of the liquid whereas evaporation occurs only at the surfaces of the liquid.

ii. For any given external pressure as liquid boils at a single temperature only whereas evaporation takes place at all temperatures.

Experimental determination of variation of saturation vapours pressure:
(S.V.P) of water at various temperatures (Dynamic method).

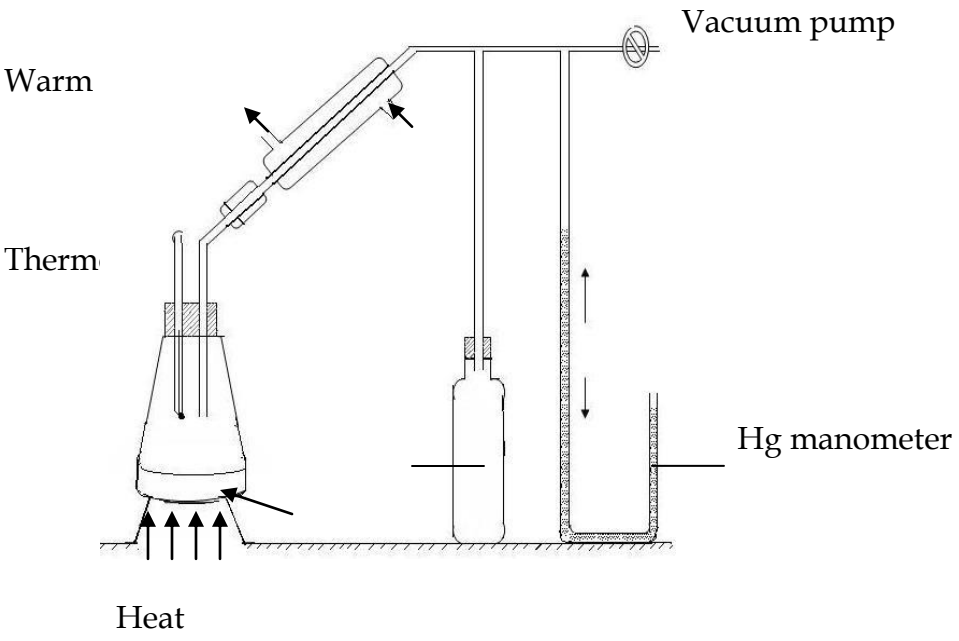
A liquid boils when its S.V.P equals the external pressure.
The dynamic method involves finding the boiling point of the liquid at different external pressure. These external pressures will be equal to the saturation vapour pressures.

The vacuums pump or compressor enables the pressure to be set at any desired value below and above atmospheric pressure.
The liquid in the flask is heated until it boils and the temperature of the vapour measured.

The saturation vapour pressure (S.V.P) P = H – hgg.

Note: the reservoir helps to minimize the price fluctuations.

DIAGRAM



H – Atmospheric pressure.

g – Density of H_2O

Example:

A closed vessel contains air saturated with water vapour at 77^o c

The total pressure in the vessel is 1000 mmHg. Calculate the new pressure in the vessel if the temperature is reduced to 27^o c.

(S.V.P of water at 77^o c is 314mmHg; S.V.P of water at 27^o c is 27mmHg

Solution:

$P_{mixture}$ at 77^o c = 1000mmHg.

$P_{mixture} = P_{air} + 314$

P_{air} at 77^o c = 1000 – 314

= 686mmHg.

Note that the vessel is closed, hence, the volume, V, is constant. We can apply the equation of state for an ideal gas onto the air but not the saturated vapour.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{686 \times V}{273+77} = \frac{P_2 \times V}{273+27}$$

$$\frac{686V}{350} = \frac{P_2 \times V}{300}$$

$$\frac{686}{350} = \frac{P_2}{300}$$

$$P_2 = \frac{686}{350} \times 300$$

$$P_2 = 588mmHg.$$

Where P2 = 588mmg and is the pair at 27oC.

P mixture at 27OC = Pair at 27OC + S.V.P at 27Oc

= 588 = 27

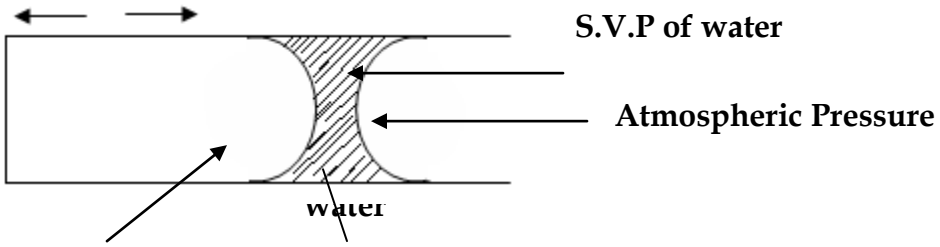
= <u>615mmHg</u>

2. A horizontal tube of uniform bore closed at one end has some air trapped by a small quantity of water. If the length of the enclosed air column is 20cm at

14oc, what will it be if the temperature is raised to 40oc and atmospheric pressure remains constant at 760mmHg?

(S.V.P of water at 14^{o}c and 40oc is 10.5mmHg respectively)

DIAGRAM



At equilibrium;

Atmospheric pressure $P_{mixture}$ = Pair + S.V.P of H_2O

At 14^{o}c,

$P_{mixture}$ = P_{air} + S.V.P of water.

Atmosphere pressure = P_{air} + S.V.P of water.

760 = P_{air} + 10.5

P_{air} at 14^{o}c = 760 – 10.5

= 749.5mmHg.

At 40^{o}c.

Atmosphere pressure = P_{air} + S.V.P of water.

760 = P_{air} + 49.5

P_{air} = 760 + 49.5

P_{air} = 710.5mmHg.

Since the tube has a uniform cross sectional area, A, and we are interested in the air column, we can apply the equation of state.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_1} \quad \text{.....} \ (*)$$

P_1 = 749.5mmHg P_2 = 710.5mmHg

V_1 = Al_1 = 20A V_2 = Al_2

T_1 = (14 + 273) k T_2 = 40 + 273

T_1 = 287k = 313k

From (*)

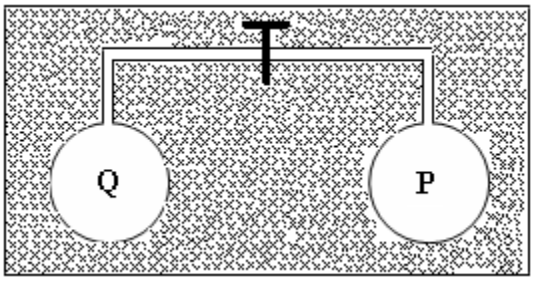
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{749.5 \times 20A}{287} = \frac{710.5 \times Al_2}{313}$$

$$l_2 = \frac{749.5 \times 20 \times 313}{710.5 \times 287}$$

L_2 = 23.01cm as the length of the air column

3. DIAGRAM



Two cylinders P and Q each of volume 1.5littres are joined in the middle by a close tap T and placed in a constant temperature bath at 60^{o}c as shown above. P contains a vacuum while Q contains air and saturated water vapour. The total pressure in Q is 200mmHg

When T is opened equilibrium is reached with water vapour remaining saturated. If the final pressure in the cylinders is 150mmHg, calculate the saturation vapour pressure of water at 60^{o}c.

Solution:

Let P_o represent the S.V.P of water at 60^{o}c.

It is important to note that S.V.P is independent of volume and hence will have the same value before and after opening the tap.

Before tap, T is opened.

Cylinder P	Cylinder Q	
P_{air} = 0 (Vacuum)	P = 200mmHg	Pair = 200 – P_o

T = 333K

V = 1.5litres

After opening Tap, T

V = 1.5litrers

T = 333K

Pair = 150 - P_o

T = 333k

V = 1.5litres

T = 333k

P_{air} = 150 - P_o

It is important to note that the total number of moles of air before and after opening the tap, T is constant.

Before opening type, T

Using Pv = nRT

$$n = \frac{Pv}{RT}$$

Number of moles of air in P; = 0

Number of moles of air in Q = $\frac{(200 - P_0)}{333R} 1.5$

$$= \frac{PV}{RT} = \frac{(200 - P_0)1.5}{333R}$$

Total number of moles of air before opening tap = $\frac{(200 - P_0)}{333R} 1.5$

After opening the tap, T

Number of moles of air in P = $\frac{(150-P_0)}{333R}1.5$

Number of moles of air in Q = $\frac{(150-P_0)}{333R}1.5$

Total number of moles of air after opening the tap = $\frac{(150-P_0)}{333R}1.5 + \frac{(150-P_0)}{333R}1.5$

$= \frac{3(150-P_0)1.5}{33R}$

Since the total number of moles of air is constant before and after opening the tap. (*) = (*) (*)

$(200 - P_a)\ 1.5 = 3\ (150 - P_a)$

$333R \qquad 333R$

$1.3\ (200 - P_a) = 3\ (150 - P_a)$

$300 - 1.5P_a = 450 - 3P_a$

$3Pa - 1.5Pa = 450 - 300$

$1.5Pa = 150$

P_a = 150

= 1.5

$\underline{P_0 = 100mmHg.}$

Therefore, the S.V.P of water at 60^oC is 100mmHg