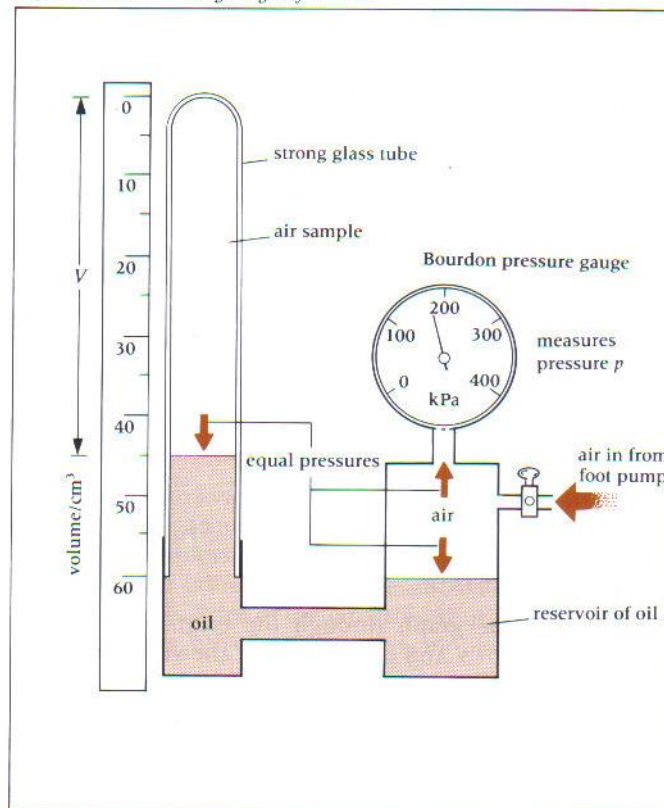


THE KINETIC THEORY OF GASES

Boyle's Law: Investigating the dependence of Volume on Pressure (Temperature kept constant)

The diagram below shows the apparatus which gives a direct reading for both the volume and pressure of a fixed mass of gas.

Figure 10.31 Investigating Boyle's law



Air is trapped in a glass tube by a column of oil. The oil is supplied from a reservoir, where it can be pressurized by using a tyre pump. The pressure above the oil in the reservoir is read by using a Bourdon pressure gauge. The pressure above the oil in the reservoir is transferred to the trapped air in the glass tube. The experiment is performed at room temperature to keep the temperature constant.

Since no air is pumped into the reservoir, the gauge reads atmospheric pressure, (100 KPa). The pressure, P , is increased by pumping air and the volume, V , is recorded from the vertical scale.

The graphs below demonstrate the relationship between pressure, P , and Volume, V .

Fig 7.1 and 7.2 illustrate two ways in which the results may be presented.

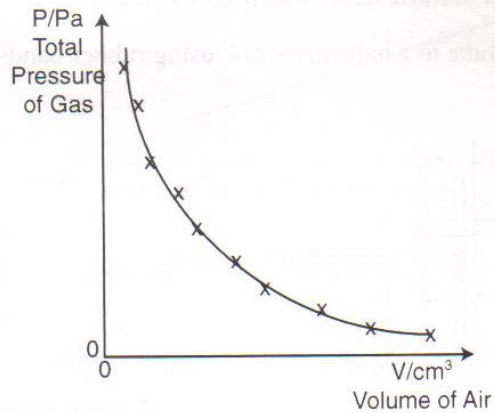


Fig 7.1 P vs V for air

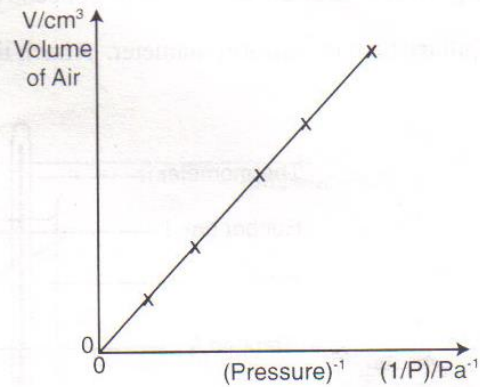


Fig. 7.2 Graph of V vs $(1/P)$.

The linear relationship indicated by Fig. 7.2 suggests that the pressure, P , of a gas and its volume, V , are inversely related

$$\text{i.e. } V \propto \left(\frac{1}{P}\right) \text{ (T kept constant)}$$

or $PV = \text{constant}$ (at constant temperature)

This relationship is stated as Boyle's Law:

The volume of a fixed mass of gas is inversely proportional to its pressure if the temperature is constant.

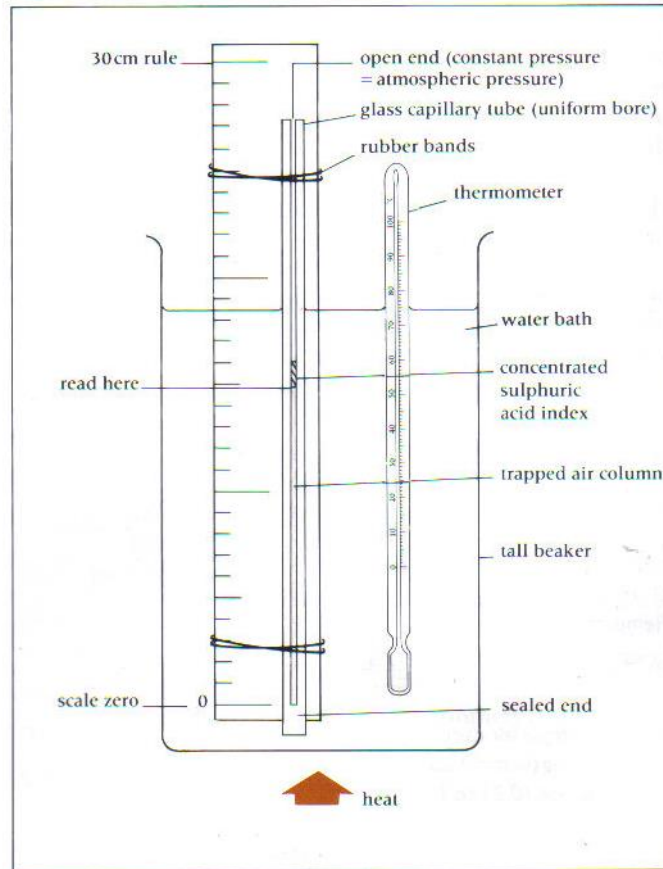
Boyle's Equation:

$$P_1 V_1 = P_2 V_2$$

Charles' Law: Investigating the variation of the Volume of a gas with Temperature (Pressure kept constant)

The diagram below shows the apparatus which gives a direct reading for both the volume and temperature of a fixed mass of gas.

Figure 10.29 Investigating Charles' law



A column of air is trapped by a bead of concentrated sulfuric acid in a capillary tube. The tube was then attached to a half-meter rule by using rubber bands.

This apparatus is placed inside of a beaker containing water and it is kept upright by using a clamp-stand. The water surrounding the capillary tube is heating with a bunsen burner, while stirring with the thermometer. The readings of the thermometer, T , and the volume, V , were taken at 15°C intervals.

The graphs below demonstrate the relationship between Volume, V , and Temperature, T .

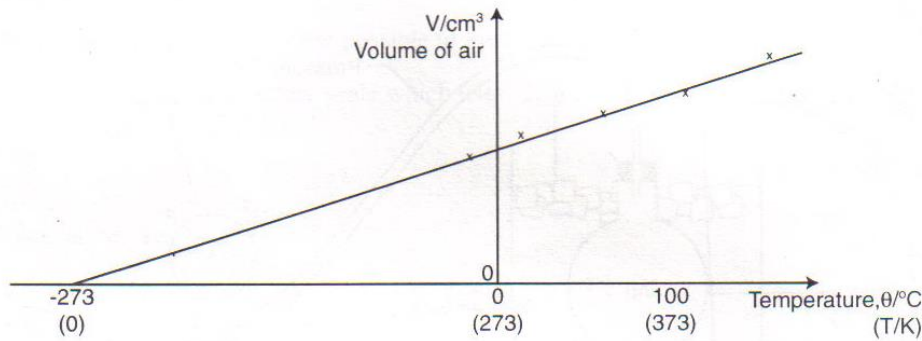


Fig. 7.4 Volume, V/cm^3 against Temperature, $\theta/^\circ\text{C}$

If you extrapolate the graph backwards you should note that the straight line cuts the temperature axis at about -273°C . This suggests that if you were able to decrease the temperature of the gas, without causing it to liquefy, its the volume would decrease to zero at -273°C .

It should be noted also that the graph would pass through the origin if an arbitrary temperature scale which has its zero at -273°C were chosen. Then there would be a simple proportionality between the volume, V and the temperature expressed on that scale. We shall represent temperature on this scale, called the ideal gas temperature scale, by T/K .

so $V \propto (\theta + 273)$; i.e. $V \propto T$

or $\frac{V}{T} = \text{constant}$ (at constant pressure) for a fixed mass of gas.

This relationship is stated as Charles' Law:

The volume of a fixed mass of gas is directly proportional to its absolute temperature (on the Kelvin scale) if the pressure is constant.

Charles' Equation:

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

Pressure Law: Investigating the variation of the Pressure of a gas with Temperature (Volume kept constant)

The diagram below shows the apparatus which gives a direct reading for both the pressure and temperature of a fixed mass of gas.

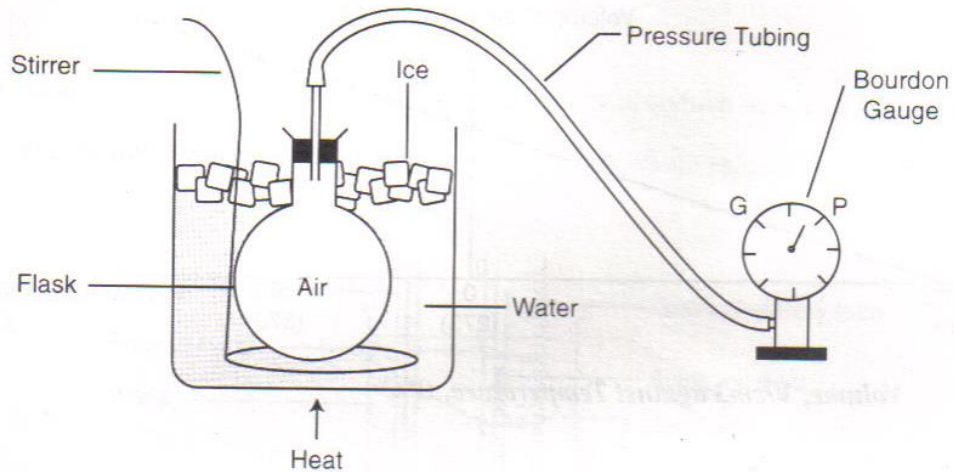
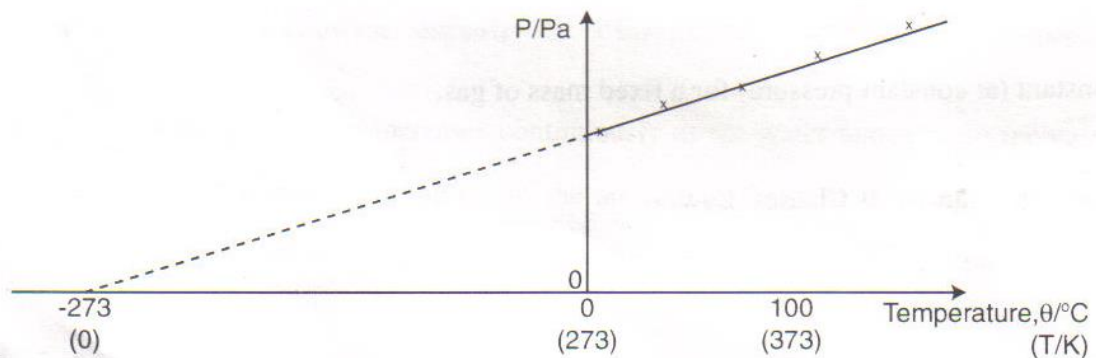


Fig. 7.5 Pressure vs Temperature (Constant Volume)

The apparatus consists of a large flask filled with dry air connected by pressure tubing to a Bourdon pressure gauge. The bulb is placed inside a large container and is completely filled with water. The pressure of the air is recorded over a wide range of temperatures including 0°C and 100°C .

The graphs below demonstrate the relationship between Pressure, P , and Temperature, T



We note here also that when the graph is extrapolated backwards, it cuts the temperature axis at approximately -273°C . This notable coincidence, suggests that, as for the volume, the pressure of the gas would be zero if it were possible to lower its temperature to -273°C . The observation also indicates that the temperature scale which uses -273°C as its zero is of fundamental physical significance.

Thus, as before,

$$P \propto (\theta + 273)$$

$$\text{i.e. } P \propto T \quad (T/\text{K} = (\theta + 273) / ^{\circ}\text{C})$$

$$\text{i.e. } \frac{P}{T} = \text{constant} \quad (\text{for a constant volume of a fixed mass of gas.})$$

This relationship is stated as Pressure Law:

The pressure of a fixed mass of gas is directly proportional to its absolute temperature if its volume is constant.

Pressure Equation:

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

Gas Law: (For a fixed mass of gas)

The three relationships

$PV = \text{constant}$ (constant temperature): Boyle's Law

$\frac{V}{T} = \text{constant}$ (constant pressure): Charles' Law and

$\frac{P}{T} = \text{constant}$ (constant volume): The Pressure Law

can be combined, for a fixed mass of gas, to give the Equation of State for an Ideal Gas,

$$\frac{PV}{T} = \text{constant.}$$

Gas Law Equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Ideal Gas Law

No gas obeys the laws exactly. However, the laws provide a fairly accurate description of how gases behave under different conditions of pressure, temperature and volume.

One useful concept is the Ideal (or perfect) Gas Law. The following equation can be used for gases which exactly obey the gas laws:

$$PV = nRT$$

where

- P is pressure (Nm^{-2} or Pa)
- V is volume (m^3)
- n is the number of moles of gas (mol)
- R is the universal molar gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$)
- T is the temperature (K)

(**N. B.** In order for a gas to obey this equation, it must be subject to the following assumptions. There are no forces between the molecules of the gases and the internal energy of the gas is entirely kinetic and only depends on its temperature.)

Let N , be the number of particles in a substance. Then we can say that the number of moles of the substance, n , is given by the equation:

$$n = \frac{N}{N_A}$$

where N_A is Avogadro's number (6.023×10^{23})

Then the Ideal Gas Law can be rewritten as:

$$PV = \frac{N}{N_A} RT$$

But we also know that Boltzmann Constant (k) which is a gas constant per molecule ($1.38 \times 10^{-23} \text{ JK}^{-1}$); can be calculated by using:

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

Hence we can also state the Ideal Gas Law as:

$$PV = NkT$$

Kinetic Theory Equations

Kinetic Theory is used to explain all the gas laws by observing the movement of the particles. Several assumptions are made to derive these equations:

- The molecules of the gas can be assumed to be point molecules. This means that they have negligible volume.
- There is no intermolecular forces of attraction. The particles are in random motion and the average speed of the random motions produce a constant force. (constant force \rightarrow constant pressure)
- Collisions are (perfectly) elastic, the particles rebound after collision and kinetic energy is conserved.
- Impact time is minimum. The rate of change of momentum during the impact gives an average force provided that the time of impact is much less than the time between impacts.
- All molecules of a particular gas are identical.

- Newton's Three Laws are adhered to.
- There is a sufficiently large number of molecules for statistics to be meaningfully applied.

Pressure of a gas can be given by the following equations:

Equation 1:

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

where ρ is the density of gas
 $\overline{c^2}$ is the mean squared speed of molecules of gas

Equation 2:

$$PV = \frac{1}{3} M_g \overline{c^2}$$

where V is the volume
 M_g is the mass of gas

Equation 3:

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

where N is the number of molecules
 m is the mass of a molecule

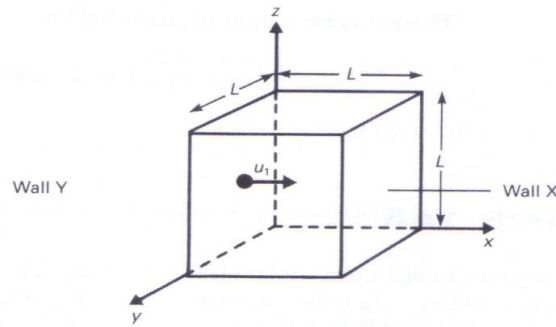
We can also state the mean (average) translational kinetic energy per monatomic molecule of a gas by using

$$KE = \frac{1}{2} m \overline{c^2} = \frac{3}{2} \frac{R}{N_A} T$$

Hence

$$\text{mean (average) translational KE of a molecule} = \frac{3}{2} kT$$

Deriving Kinetic Theories of Gas Equations ($P = \frac{1}{3}\rho\overline{c^2}$)



Let us consider a closed cubical container of length, L . Each molecule of the gas has a mass, m . Consider a single molecule which is moving towards Wall X and its x -component of velocity is, u .

The molecule has a x -component of momentum, m, u_x towards the wall X. When the molecule collides with Wall X, it changes the direction of momentum.

Since the collision is elastic, it will rebound at the same speed and the momentum will be $-m, u_x$. Hence the change of momentum due to collision with the wall is $2mu_x$.

The molecule has to travel a distance $2L$ (from Wall X to Wall X again) before it collides with Wall X again.

We can calculate the time that the molecule takes by using the formula

$$\text{time} = \frac{\text{distance}}{\text{speed}}$$

$$t = \frac{2L}{u_x}$$

We can also calculate the force which is the rate of change of momentum:

$$F = \frac{\text{change of momentum}}{\text{time}}$$

$$F = 2mu_x \div \frac{2L}{u_x}$$

$$\therefore F = \frac{mu_x^2}{L}$$

Hence the pressure at X can be calculated by using the equation

$$\text{Pressure at X} = \frac{\text{Force at X}}{\text{Area at X}}$$

$$\text{Pressure at X} = \frac{mu_1^2}{L} \div L^2$$

$$\text{Pressure at X} = \frac{mu_1^2}{L^3}$$

If there N molecules in the container and their x – components velocity are

$$u_1^2, u_2^2, \dots, u_n^2$$

Then the total pressure on the Wall X is

$$\text{Pressure at X} = \frac{m(u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2)}{L^3}$$

Hence

$$P = \frac{mN\overline{u^2}}{L^3}$$

where $\overline{u^2}$ is the mean squared velocity in component x – direction

m is the mass of molecules

N is the number of molecules

Since mN is the total mass of a gas in the container the total density is $\rho = \frac{mN}{L^3}$

Therefore we can rewrite the equation of pressure at X as

$$P = \rho\overline{u^2}$$

If $\overline{c^2}$ is the resultant velocity of a molecule in x , y and z planes; then the components of velocity can be represented by u , v and w respectively.

We can therefore state that

$$\overline{c^2} = \overline{u^2} + \overline{v^2} + \overline{w^2}$$

Where $\overline{c^2}$ is the mean square velocity of molecules
 $\overline{u^2}$ is the mean square velocity in x – direction
 $\overline{v^2}$ is the mean square velocity in y – direction
 $\overline{w^2}$ is the mean square velocity in z - direction

Since most of the molecules are moving randomly, we can state

$$\overline{u^2} = \overline{v^2} = \overline{w^2}$$

Hence

$$\overline{u^2} = \frac{1}{3}\overline{c^2}$$

Finally we can state that the pressure at X can be determined by using

$$P = \frac{1}{3}\rho\overline{c^2} \quad \text{[as required]}$$

Deriving Kinetic Theories of Gas Equations ($PV = \frac{1}{3} Nm \overline{c^2}$)

Recall that to calculate Pressure at X by a molecule , we use the equation

$$P_x = \frac{mu_1^2}{L^3}$$

since $V = L \times W \times H$

$$P_x = \frac{mu_1^2}{V}$$

The pressure of many molecules moving in one plane, can be calculated by

$$P_1 = \frac{mu_1^2}{V}$$

$$P_2 = \frac{mu_2^2}{V} \dots\dots\dots$$

$$P_n = \frac{mu_N^2}{V}$$

Hence the total pressure is given by $P_T = P_1 + P_2 + P_3 + \dots + P_N$

Therefore

$$P_T = \frac{m(u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2)}{V}$$

We can say that the mean (or average) of N molecules velocity, denoted by $(\overline{u^2})$ can be calculated by

$$\overline{u^2} = \frac{(u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2)}{N}$$

Therefore

$$N \overline{u^2} = (u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2)$$

Hence

$$P_T = \frac{mN \overline{u^2}}{V}$$

Since the motion of the molecules in a gas is totally random, the pressure exerted in each place is the same

$$P_T = \frac{Nm \overline{u_x^2}}{V} = \frac{Nm \overline{u_y^2}}{V} = \frac{Nm \overline{u_z^2}}{V}$$

If we let $\overline{c^2}$ be the resultant velocity of all three components, then

$$\overline{c^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}$$

And we can deduce that

$$\overline{c^2} = 3\overline{u_x^2} = 3\overline{u_y^2} = 3\overline{u_z^2}$$

(because all the molecules travel at the same velocity in each plane)

Hence

$$\frac{1}{3}\overline{c^2} = \overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2}$$

And we can rewrite the equation $P_T = \frac{Nm\overline{u_x^2}}{V}$ as

$$P_T = \frac{Nm\frac{1}{3}\overline{c^2}}{V}$$

Therefore we can conclude that

$$PV = Nm\frac{1}{3}\overline{c^2} \quad \text{[as required]}$$

Average Translational Kinetic Energy of Monatomic Molecules

The mean kinetic energy of a molecule of an ideal gas is given by

$$\text{average KE} = \frac{\text{total kinetic energy}}{\text{total number of molecules}}$$

We know that

$$PV = nRT \quad \text{and} \quad PV = Nm\frac{1}{3}\overline{c^2}$$

We can say that

$$Nm \frac{1}{3} \overline{c^2} = n RT$$

But we know that $n = \frac{N}{N_A}$. So we can rewrite the equation as

$$\frac{1}{3} Nm \overline{c^2} = R \frac{N}{N_A} T$$

Given that $k = \frac{R}{N_A}$ the equation becomes

$$\frac{1}{3} Nm \overline{c^2} = NkT$$

$$\frac{1}{3} m \overline{c^2} = kT$$

$$m \overline{c^2} = 3kT$$

Since $KE = \frac{1}{2} m \overline{c^2}$

$$\frac{1}{2} m \overline{c^2} = \frac{3}{2} kT$$

Hence

$$\text{mean (average) translational KE of a molecule} = \frac{3}{2} kT$$

N.B. From using the equation derived above, we can make the following statements:

- The total kinetic energy in 1 mole of an ideal gas can be calculated by

$$KE_T = \frac{3}{2} RT$$

- The total kinetic energy of n moles of an ideal gas can be calculated by

$$KE_T = \frac{3}{2} nRT$$