

is misleading. The gas is full of activity and the equilibrium is a dynamic one. In dynamic equilibrium, molecules collide and change their speeds during the collision. Only the average properties are constant.

Atomic theory is not the end of our quest, but the beginning. We now know that atoms are not indivisible or elementary. They consist of a nucleus and electrons. The nucleus itself is made up of protons and neutrons. The protons and neutrons are again made up of quarks. Even quarks may not be the end of the story. There may be string like elementary entities. Nature always has surprises for us, but the search for truth is often enjoyable and the discoveries beautiful. In this chapter, we shall limit ourselves to understanding the behaviour of gases (and a little bit of solids), as a collection of moving molecules in incessant motion.

13.3 BEHAVIOUR OF GASES

Properties of gases are easier to understand than those of solids and liquids. This is mainly because in a gas, molecules are far from each other and their mutual interactions are negligible except when two molecules collide. Gases at low pressures and high temperatures much above that at which they liquefy (or solidify) approximately satisfy a simple relation between their pressure, temperature and volume given by (see Ch. 11)

$$PV = KT \quad (13.1)$$

for a given sample of the gas. Here T is the temperature in kelvin or (absolute) scale. K is a constant for the given sample but varies with the volume of the gas. If we now bring in the idea of atoms or molecules then K is proportional to the number of molecules, (say) N in the sample. We can write $K = Nk$. Observation tells us that this k is same for all gases. It is called Boltzmann constant and is denoted by k_B .

$$\text{As } \frac{P_1 V_1}{N_1 T_1} = \frac{P_2 V_2}{N_2 T_2} = \text{constant} = k_B \quad (13.2)$$

if P , V and T are same, then N is also same for all gases. This is Avogadro's hypothesis, that the number of molecules per unit volume is same for all gases at a fixed temperature and pressure. The number in 22.4 litres of any gas is 6.02×10^{23} . This is known as Avogadro number and is denoted by N_A . The mass of 22.4 litres of any gas is equal to its molecular weight in grams at S.T.P (standard temperature 273 K and pressure 1 atm). This amount of substance is called a mole (see Chapter 2 for a more precise definition). Avogadro had guessed the equality of numbers in equal volumes of gas at a fixed temperature and pressure from chemical reactions. Kinetic theory justifies this hypothesis.

The perfect gas equation can be written as

$$PV = \mu RT \quad (13.3)$$

where μ is the number of moles and $R = N_A k_B$ is a universal constant. The temperature T is absolute temperature. Choosing kelvin scale for



John Dalton (1766- 1844)

He was an English chemist. When different types of atoms combine, they obey certain simple laws. Dalton's atomic theory explains these laws in a simple way. He also gave a theory of colour blindness.

Amedeo Avogadro (1776 - 1856)

He made a brilliant guess that equal volumes of gases have equal number of molecules at the same temperature and pressure. This helped in understanding the combination of different gases in a very simple way. It is now called Avogadro's hypothesis (or law). He also suggested that the smallest constituent of gases like hydrogen, oxygen and nitrogen are not atoms but diatomic molecules.



absolute temperature, $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$. Here

$$\frac{M}{M_0} = \frac{N}{N_A} \quad (13.4)$$

where M is the mass of the gas containing N molecules, M_0 is the molar mass and N_A the Avogadro's number. Using Eqs. (13.4) and (13.3) can also be written as

$$PV = k_B NT \quad \text{or} \quad P = k_B nT$$

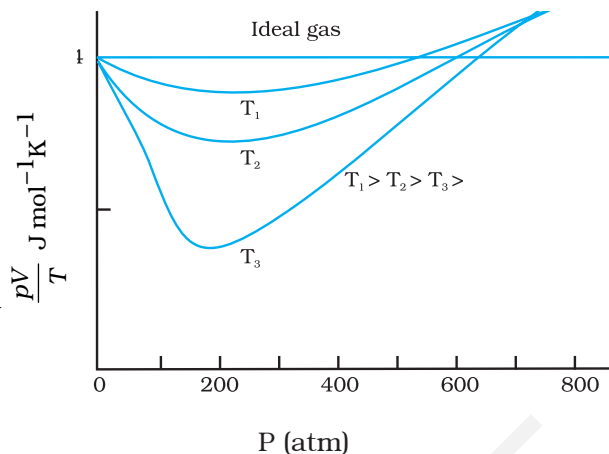


Fig.13.1 Real gases approach ideal gas behaviour at low pressures and high temperatures.

where n is the number density, i.e. number of molecules per unit volume. k_B is the Boltzmann constant introduced above. Its value in SI units is $1.38 \times 10^{-23} \text{ J K}^{-1}$.

Another useful form of Eq. (13.3) is

$$P = \frac{\rho RT}{M_0} \quad (13.5)$$

where ρ is the mass density of the gas.

A gas that satisfies Eq. (13.3) exactly at all pressures and temperatures is defined to be an **ideal gas**. An ideal gas is a simple theoretical model of a gas. No real gas is truly ideal. Fig. 13.1 shows departures from ideal gas behaviour for a real gas at three different temperatures. Notice that all curves approach the ideal gas behaviour for low pressures and high temperatures.

At low pressures or high temperatures the molecules are far apart and molecular interactions are negligible. Without interactions the gas behaves like an ideal one.

If we fix μ and T in Eq. (13.3), we get

$$PV = \text{constant} \quad (13.6)$$

i.e., keeping temperature constant, pressure of a given mass of gas varies inversely with volume. This is the famous **Boyle's law**. Fig. 13.2 shows comparison between experimental P - V curves and the theoretical curves predicted by Boyle's law. Once again you see that the agreement is good at high temperatures and low pressures. Next, if you fix P , Eq. (13.1) shows that $V \propto T$ i.e., for a fixed pressure, the volume of a gas is proportional to its absolute temperature T (**Charles' law**). See Fig. 13.3.

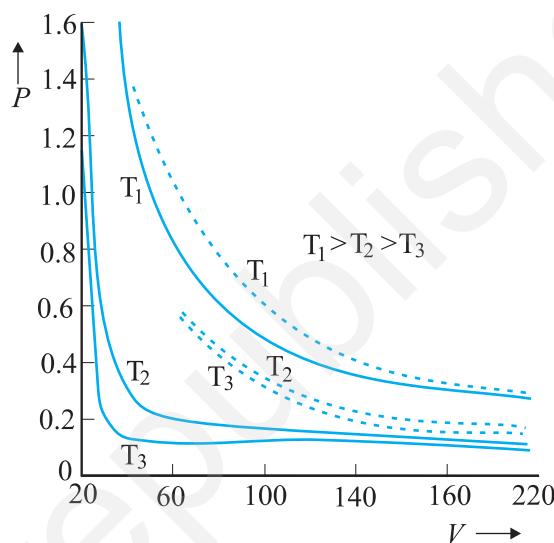


Fig.13.2 Experimental P - V curves (solid lines) for steam at three temperatures compared with Boyle's law (dotted lines). P is in units of 22 atm and V in units of 0.09 litres.

Finally, consider a mixture of non-interacting ideal gases: μ_1 moles of gas 1, μ_2 moles of gas 2, etc. in a vessel of volume V at temperature T and pressure P . It is then found that the equation of state of the mixture is :

$$PV = (\mu_1 + \mu_2 + \dots) RT \quad (13.7)$$

$$\text{i.e. } P = \mu_1 \frac{RT}{V} + \mu_2 \frac{RT}{V} + \dots \quad (13.8)$$

$$= P_1 + P_2 + \dots \quad (13.9)$$

Clearly $P_1 = \mu_1 RT/V$ is the pressure gas 1 would exert at the same conditions of volume and temperature if no other gases were present. This is called the partial pressure of the gas. Thus, the total pressure of a mixture of ideal gases is the sum of partial pressures. This is Dalton's law of partial pressures.

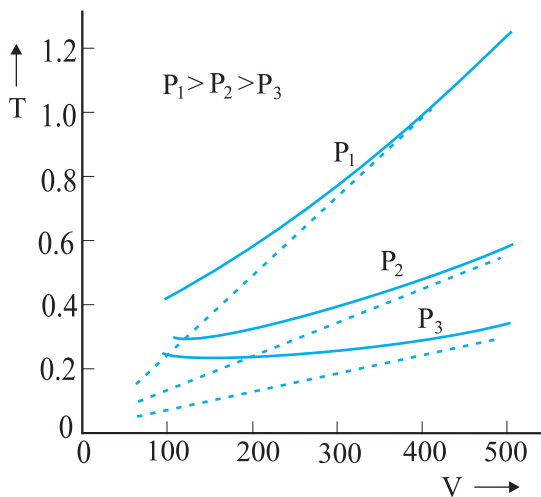


Fig. 13.3 Experimental T - V curves (solid lines) for CO_2 at three pressures compared with Charles' law (dotted lines). T is in units of 300 K and V in units of 0.13 litres.

We next consider some examples which give us information about the volume occupied by the molecules and the volume of a single molecule.

► **Example 13.1** The density of water is 1000 kg m^{-3} . The density of water vapour at 100°C and 1 atm pressure is 0.6 kg m^{-3} . The volume of a molecule multiplied by the total number gives what is called, molecular volume. Estimate the ratio (or fraction) of the molecular volume to the total volume occupied by the water vapour under the above conditions of temperature and pressure.

Answer For a given mass of water molecules, the density is less if volume is large. So the volume of the vapour is $1000/0.6 = 1/6 \times 10^4$ times larger. If densities of bulk water and water molecules are same, then the fraction of molecular volume to the total volume in liquid state is 1. As volume in vapour state has increased, the fractional volume is less by the same amount, i.e. 6×10^{-4} .

► **Example 13.2** Estimate the volume of a water molecule using the data in Example 13.1.

Answer In the liquid (or solid) phase, the molecules of water are quite closely packed. The

density of water molecule may therefore, be regarded as roughly equal to the density of bulk water = 1000 kg m^{-3} . To estimate the volume of a water molecule, we need to know the mass of a single water molecule. We know that 1 mole of water has a mass approximately equal to

$$(2 + 16)\text{g} = 18 \text{ g} = 0.018 \text{ kg}.$$

Since 1 mole contains about 6×10^{23} molecules (Avogadro's number), the mass of a molecule of water is $(0.018)/(6 \times 10^{23}) \text{ kg} = 3 \times 10^{-26} \text{ kg}$. Therefore, a rough estimate of the volume of a water molecule is as follows :

$$\begin{aligned} \text{Volume of a water molecule} &= (3 \times 10^{-26} \text{ kg}) / (1000 \text{ kg m}^{-3}) \\ &= 3 \times 10^{-29} \text{ m}^3 \\ &= (4/3) \pi (\text{Radius})^3 \end{aligned}$$

$$\text{Hence, Radius} \approx 2 \times 10^{-10} \text{ m} = 2 \text{ \AA}$$

► **Example 13.3** What is the average distance between atoms (interatomic distance) in water? Use the data given in Examples 13.1 and 13.2.

Answer : A given mass of water in vapour state has 1.67×10^3 times the volume of the same mass of water in liquid state (Ex. 13.1). This is also the increase in the amount of volume available for each molecule of water. When volume increases by 10^3 times, the radius increases by $V^{1/3}$ or 10 times, i.e., $10 \times 2 \text{ \AA} = 20 \text{ \AA}$. So the average distance is $2 \times 20 = 40 \text{ \AA}$.

► **Example 13.4** A vessel contains two non-reactive gases : neon (monatomic) and oxygen (diatomic). The ratio of their partial pressures is 3:2. Estimate the ratio of (i) number of molecules and (ii) mass density of neon and oxygen in the vessel. Atomic mass of Ne = 20.2 u, molecular mass of O_2 = 32.0 u.

Answer Partial pressure of a gas in a mixture is the pressure it would have for the same volume and temperature if it alone occupied the vessel. (The total pressure of a mixture of non-reactive gases is the sum of partial pressures due to its constituent gases.) Each gas (assumed ideal) obeys the gas law. Since V and T are common to the two gases, we have $P_1 V = \mu_1 RT$ and $P_2 V = \mu_2 RT$, i.e. $(P_1/P_2) = (\mu_1/\mu_2)$. Here 1 and 2 refer to neon and oxygen respectively. Since $(P_1/P_2) = (3/2)$ (given), $(\mu_1/\mu_2) = 3/2$.

- (i) By definition $\mu_1 = (N_1/N_A)$ and $\mu_2 = (N_2/N_A)$ where N_1 and N_2 are the number of molecules of 1 and 2, and N_A is the Avogadro's number. Therefore, $(N_1/N_2) = (\mu_1 / \mu_2) = 3/2$.
- (ii) We can also write $\mu_1 = (m_1/M_1)$ and $\mu_2 = (m_2/M_2)$ where m_1 and m_2 are the masses of 1 and 2; and M_1 and M_2 are their molecular masses. (Both m_1 and M_1 ; as well as m_2 and M_2 should be expressed in the same units). If ρ_1 and ρ_2 are the mass densities of 1 and 2 respectively, we have

$$\frac{1}{2} \frac{m_1/V}{m_2/V} = \frac{m_1}{m_2} \frac{1}{2} = \frac{M_1}{M_2}$$

$$\frac{3}{2} \frac{20.2}{32.0} = 0.947$$

13.4 KINETIC THEORY OF AN IDEAL GAS

Kinetic theory of gases is based on the molecular picture of matter. A given amount of gas is a collection of a large number of molecules (typically of the order of Avogadro's number) that are in incessant random motion. At ordinary pressure and temperature, the average distance between molecules is a factor of 10 or more than the typical size of a molecule (2 Å). Thus the interaction between the molecules is negligible and we can assume that they move freely in straight lines according to Newton's first law. However, occasionally, they come close to each other, experience intermolecular forces and their velocities change. These interactions are called collisions. The molecules collide incessantly against each other or with the walls and change their velocities. The collisions are considered to be elastic. We can derive an expression for the pressure of a gas based on the kinetic theory.

We begin with the idea that molecules of a gas are in incessant random motion, colliding against one another and with the walls of the container. All collisions between molecules among themselves or between molecules and the walls are elastic. This implies that total kinetic energy is conserved. The total momentum is conserved as usual.

13.4.1 Pressure of an Ideal Gas

Consider a gas enclosed in a cube of side l . Take the axes to be parallel to the sides of the cube, as shown in Fig. 13.4. A molecule with velocity

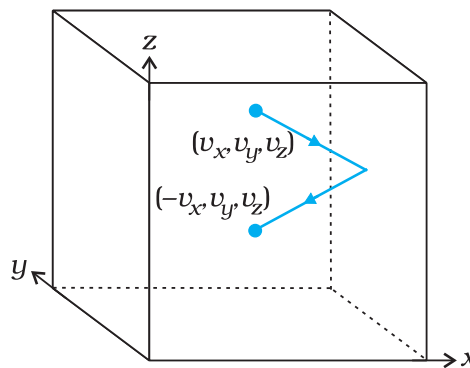


Fig. 13.4 Elastic collision of a gas molecule with the wall of the container.

(v_x, v_y, v_z) hits the planar wall parallel to yz -plane of area $A (= l^2)$. Since the collision is elastic, the molecule rebounds with the same velocity; its y and z components of velocity do not change in the collision but the x -component reverses sign. That is, the velocity after collision is $(-v_x, v_y, v_z)$. The change in momentum of the molecule is : $-mv_x - (mv_x) = -2mv_x$. By the principle of conservation of momentum, the momentum imparted to the wall in the collision = $2mv_x$.

To calculate the force (and pressure) on the wall, we need to calculate momentum imparted to the wall per unit time. In a small time interval Δt , a molecule with x -component of velocity v_x will hit the wall if it is within the distance $v_x \Delta t$ from the wall. That is, all molecules within the volume $A v_x \Delta t$ only can hit the wall in time Δt . But, on the average, half of these are moving towards the wall and the other half away from the wall. Thus the number of molecules with velocity (v_x, v_y, v_z) hitting the wall in time Δt is $\frac{1}{2} A v_x \Delta t n$ where n is the number of molecules per unit volume. The total momentum transferred to the wall by these molecules in time Δt is :

$$Q = (2mv_x) (\frac{1}{2} n A v_x \Delta t) \tag{13.10}$$

The force on the wall is the rate of momentum transfer $Q/\Delta t$ and pressure is force per unit area :

$$P = Q / (A \Delta t) = n m v_x^2 \tag{3.11}$$

Actually, all molecules in a gas do not have the same velocity; there is a distribution in velocities. The above equation therefore, stands for pressure due to the group of molecules with speed v_x in the x -direction and n stands for the number density of that group of molecules. The