

On the basis of kinetic theory of gases, the rate of diffusion through a fine hole will be proportional to the average or root mean square velocity c_{rms} . From Eqn. (10.4) we recall that

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

or
$$\sqrt{\bar{c}^2} = c_{rms} = \sqrt{\frac{3P}{\rho}}$$

That is, the root mean square velocities of the molecules of two gases of densities ρ_1 and ρ_2 respectively at a pressure P are given by

$$(c_{rms})_1 = \sqrt{\frac{3P}{\rho_1}} \quad \text{and} \quad (c_{rms})_2 = \sqrt{\frac{3P}{\rho_2}}$$

Thus,

$$\frac{\text{Rate of diffusion of one gas}}{\text{Rate of diffusion of other gas}} = \frac{(c_{rms})_1}{(c_{rms})_2} = \sqrt{\frac{\rho_2}{\rho_1}} \quad (10.14)$$

Thus, rate of diffusion of gases is inversely proportional to the square root of their densities at the same pressure, which is Graham's law of diffusion.

Example 10.2 : Calculate the root mean square speed of hydrogen molecules at 300 K. Take $m(\text{H}_2)$ as $3.347 \times 10^{-27} \text{ kg}$ and $k = 1.38 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1}$

Solution : We know that

$$c_{rms} = \sqrt{\frac{3P}{m}} = \sqrt{\frac{3 \times (1.38 \times 10^{-23} \text{ J K}^{-1}) (300 \text{ K})}{3.347 \times 10^{-27} \text{ kg}}}$$

$$= 1927 \text{ m s}^{-1}$$

Example 10.3 : At what temperature will the root mean square velocity of hydrogen be double of its value at S.T.P., pressure being constant (STP = Standard temperature and pressure).

Solution : From Eqn. (10.8), we recall that

$$c_{rms} \propto \sqrt{T}$$

Let the rms velocity at S.T.P. be c_0 .

If T K is the required temperature, the velocity $c = 2 c_0$ as given in the problem

$$\therefore \frac{c}{c_0} = \frac{2c_0}{c_0} = \sqrt{\frac{T}{T_0}}$$



Notes



Notes

The above definition of specific heat capacity holds good for solids and liquids but not for gases, because it can vary with external conditions. In order to study the heat capacity of a gas, we keep the pressure or the volume of a gas constant. Consequently, we define two specific heat capacities :

- (i) Specific heat at constant volume, denoted as c_v .
- (ii) Specific heat at constant pressure, denoted as c_p .
- (a) **The specific heat capacity of a gas at constant volume (c_v)** is defined as the amount of heat required to raise the temperature of unit mass of a gas through 1K, when its volume is kept constant :

$$c_v = \left(\frac{\Delta Q}{\Delta T} \right)_v \tag{10.19}$$

- (b) **The specific heat capacity of a gas at constant pressure (c_p)** is defined as the amount of heat required to raise the temperature of unit mass of a gas through 1K when its pressure is kept constant.

$$c_p = \left(\frac{\Delta Q}{\Delta T} \right)_p \tag{10.20}$$

When 1 mole of a gas is considered, we define **molar heat capacity**.

We know that when pressure is kept constant, the volume of the gas increases. Hence in the second case note that the heat required to raise the temperature of unit mass through one degree at constant pressure is used up in two parts :

- (i) heat required to do external work to produce a change in volume of the gas, and
- (ii) heat required to raise the temperature of the gas through one degree (c_v).

This means the specific heat capacity of a gas at constant pressure is greater than its specific heat capacity at constant volume by an amount which is thermal equivalent of the work done in expanding the gas against external pressure. That is

$$c_p = W + c_v \tag{10.21}$$

10.7 RELATION BETWEEN C_p AND C_v

Let us consider one mole of an ideal gas enclosed in a cylinder fitted with a frictionless movable piston (Fig. 10.5). Since the gas has been assumed to be ideal (perfect), there is no intermolecular force between its molecules. When such a gas expands, some work is done in overcoming internal pressure.

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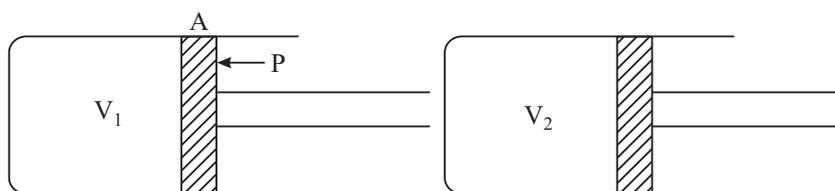


Fig. 10.5 : Gas heated at constant pressure

Let P be the external pressure and A be the cross sectional area of the piston. The force acting on the piston $= P \times A$. Now suppose that the gas is heated at constant pressure by 1K and as a result, the piston moves outward through a distance x , as shown in Fig. 10.5. Let V_1 be the initial volume of the gas and V_2 be the volume after heating. Therefore, the work W done by the gas in pushing the piston through a distance x , against external pressure P is given by

$$\begin{aligned} W &= P \times A \times x \\ &= P \times (\text{Increase in volume}) \\ &= P (V_2 - V_1) \end{aligned}$$

We know from Eqn. (10.22) that $c_p - c_v = \text{Work done (W) against the external pressure in raising the temperature of 1 mol of a gas through 1 K, i.e.}$

$$c_p - c_v = P (V_2 - V_1) \quad (10.22)$$

Now applying perfect gas equation to these two stages of the gas i.e. before and after heating, we have

$$PV_1 = RT \quad (10.23)$$

$$PV_2 = R (T + 1) \quad (10.24)$$

Subtracting Eqn. (10.23) from Eqn.(10.24), we get

$$P (V_2 - V_1) = R \quad (10.25)$$

Hence from Eqns. (10.19) and (10.22) we get

$$c_p - c_v = R \quad (10.26)$$

where R is in $\text{J mol}^{-1} \text{K}^{-1}$

Converting joules into calories, we can write

$$c_p - c_v = \frac{R}{J} \quad (10.27)$$

where $J = 4.18 \text{ cal}$ is the mechanical equivalent of heat.



Notes

8. A container of volume of 50 cm^3 contains hydrogen at a pressure of 1.0 Pa and at a temperature of 27°C . Calculate (a) the number of molecules of the gas in the container, and (b) their root-mean square speed.
($R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$, $N = 6 \times 10^{23} \text{ mol}^{-1}$. Mass of 1 mole of hydrogen molecule = $20 \times 10^{-3} \text{ kg mol}^{-1}$).
9. A closed container contains hydrogen which exerts pressure of 20.0 mm Hg at a temperature of 50 K .
- (a) At what temperature will it exert pressure of 180 mm Hg ?
- (b) If the root-mean square velocity of the hydrogen molecules at 10.0 K is 800 m s^{-1} , what will be their root-mean square velocity at this new temperature?
10. State the assumptions of kinetic theory of gases.
11. Find an expression for the pressure of a gas.
12. Deduce Boyle's law and Charle's law from kinetic the theory of gases.
13. What is the interpretation of temperature on the basis of kinetic theory of gases?.
14. What is Avagardo's law? How can it be deduced from kinetic theory of gases
15. Calculate the root-mean square of the molecules of hydrogen at 0°C and at 100°C (Density of hydrogen at 0°C and 1760 mm of mercury pressure = 0.09 kg m^{-3}).
16. Calculate the pressure in mm of mercury exerted by hydrogen gas if the number of molecules per m^3 is 0.8×10^{24} and the root-mean square speed of the molecules is $1.90 \times 10^3 \text{ m s}^{-1}$. Avogadro's number 6.02×10^{23} and molecular weight of hydrogen = 2.02).
17. Define specific heat of a gas at constant pressure. Derive the relationship between c_p and c_v .
18. Define specific heat of gases at constant volume. Prove that for a triatomic gas $c_v = 3R$
19. Calculate c_p and c_v for argon. Given $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$.



Notes



ANSWERS TO INTEXT QUESTIONS

10.1

1. (i) Because in a gas the cohesive force between the molecules are extremely small as compared to the molecules in a liquid.
- (ii) Because the molecules in a solid are closely packed. The bonds between the molecules are stronger giving a ordered structure.