CHAPTER 12 KINETIC THEORY

EXERCISES

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Question 1. Estimate the fraction of molecular volume to the actual volume occupied by oxygen gas at STP.' Take the diameter of an oxygen molecule to be 3 A.

Answer: Diameter of an oxygen molecule, $d = 3 A = 3 \times 10^{-10} m$. Consider one mole of oxygen gas at STP, which contain total NA = 6.023 x 10²³ molecules.

Actual molecular volume of 6.023 × 10²³ oxygen molecules

$$V_{\text{actual}} = \frac{4}{3}\pi r^3 \cdot N_A$$

= $\frac{4}{3} \times 3.14 \times (1.5)^3 \times 10^{-3} \times 6.02 \times 10^{23} \text{ m}^3$
= $8.51 \times 10^{-6} \text{ m}^3$
= 8.51×10^{-3} litre [:: $1 \text{ m}^3 = 10^3$ litre]

... Molecular volume of one mole of oxygen

 $V_{actual} = 8.51 \times 10^{-3}$ litre

At STP, the volume of one mole of oxygen

$$V_{\text{molar}} = 22.4 \text{ litre}$$

 $\frac{V_{\text{actual}}}{V_{\text{molar}}} = \frac{8.51 \times 10^{-3}}{22.4} = 3.8 \times 10^{-4} \simeq 4 \times 10^{-4}.$

Question 2. Molar volume is the volume occupied by 1 mol of any (ideal) gas at standard temperature and pressure (STP : 1 atmospheric pressure, 0 °C). Show that it is 22.4 litres.

Answer:

For one mole of an ideal gas, we have

$$PV = RT \Rightarrow V = \frac{RT}{P}$$

Putting R = 8.31 J mol⁻¹ K⁻¹, T = 273K and P = 1 atmosphere = 1.013×10^5 Nm⁻²

$$V = \frac{8.31 \times 273}{1.013 \times 10^5} = 0.0224 \text{ m}^3$$
$$= 0.0224 \times 10^6 \text{ cm}^3 = 22400 \text{ ml} \qquad [1 \text{ cm}^3 = 1 \text{ml}]$$

Question 3. Following figure shows plot of PV/T versus P for 1.00 x 10⁻³ kg of oxygen gas at two different temperatures.

(a) What does the dotted plot signify?

(b) Which is true : $T_1 > T_2$ or $T_1 < T_2$?

(c) What is the value of PV/T where the curves meet on the y-axis?

(d) If we obtained similar plots for 1.00 x 10⁻³ kg of hydrogen, would we get the same value of PV/T at the point where the curves meet on the y-axis? If not, what mass of hydrogen yields the same value of PV/T (for the low-pressure high-temperature region of the plot) ? (Molecular mass of H₂ = 2.02 u, of O₂ = 32.0 u, R = 8.31 J mol⁻¹ K⁻¹.)



Answer: (a) The dotted plot corresponds to 'ideal' gas behaviour as it is parallel to P-axis and it tells that value of PV/T remains same even when P is changed.

(b) The upper position of PV/T shows that its value is lesser for T_1 thus $T_1 > T_2$. This is because the curve at T_1 is more close to dotted plot than the curve at T_2 Since the behaviour of a real gas approaches the perfect gas behaviour, as the temperature is increased.

(c) Where the two curves meet, the value of PV/T on y-axis is equal to μ R. Since ideal gas equation for μ moles is PV = μ RT

- where, $\mu = \frac{1.00 \times 10^{-3} kg}{32 \times 10^{-3} kg} = \frac{1}{32}$ \therefore Value of $\frac{PV}{T} = \mu R = \frac{1}{32} \times 8.31 \text{ JK}^{-1} = 0.26 \text{ JK}^{-1}$
- (*d*) If we obtained similar plots for 1.00×10^{-3} kg of hydrogen, we will not get the same value of $\frac{PV}{T}$ at the point, where the curves meet on the *y*-axis. This is because molecular mass of hydrogen is different from that of oxygen.

For the same value of $\frac{PV}{T}$, mass of hydrogen required is obtained from

$$\frac{PV}{T} = nR = \frac{m}{2.02} \times 8.31 = 0.26$$
$$m = \frac{2.02 \times 0.26}{8.31} \text{ gram} = 6.32 \times 10^{-2} \text{ gram}.$$

Question 4. An oxygen cylinder of volume 30 Hire has an initial gauge pressure of 15 atmosphere and a temperature of 27 °C. After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atmosphere and its temperature drops to 17 °C. Estimate the mass of oxygen taken out of the cylinder. (R = 8.31 J mol⁻¹ K⁻¹, molecular mass of O₂ = 32 u.)

Answer:

| Initial volume, | $V_1 = 30$ litre = 30×10^3 cm ³ | |
|----------------------|---|--|
| | = $30 \times 10^3 \times 10^{-6} \text{ m}^3 = 30 \times 10^{-3} \text{ m}^3$ | |
| Initial pressure, | $P_1 = 15 \text{ atm}$ | |
| | $= 15 \times 1.013 \times 10^5 N m^{-2}$ | |
| Initial temperature, | $T_1 = (27 + 273) \text{ K} = 300 \text{ K}$ | |
| Initial number of mo | oles, | |

$$\mu_{1} = \frac{P_{1}V_{1}}{RT_{1}} = \frac{15 \times 1.013 \times 10^{5} \times 30 \times 10^{-3}}{8.31 \times 300} = 18.3$$

Final pressure, $P_{2} = 11$ atm
 $= 11 \times 1.013 \times 10^{5} N \text{ m}^{-2}$
Final volume, $V_{2} = 30$ litre $= 30 \times 10^{-3} \text{ cm}^{3}$
Final temperature, $T_{2} = 17 + 273 = 290 \text{ K}$
Final number of moles,

$$\mu_2 = \frac{P_2 V_2}{RT_2} = \frac{11 \times 1.013 \times 10^5 \times 30 \times 10^{-3}}{8.31 \times 290} = 13.9$$

Number of moles taken out of cylinder

$$= 18.3 - 13.9 = 4.4$$

Mass of gas taken out of cylinder

$$= 4.4 \times 32$$
 g $= 140.8$ g $= 0.141$ kg.

Question 5. An air bubble of volume 1.0 cm³ rises from the bottom of a lake 40 m deep at a temperature of 12°C. To what volume does it grow when it reaches the surface, which is at a temperature of 35 °C.

Answer:

Volume of the bubble inside, $V_1 = 1.0 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3$ Pressure on the bubble, P_1 = Pressure of water + Atmospheric pressure $= pgh + 1.01 \times 10^5 = 1000 \times 9.8 \times 40 + 1.01 \times 10^5$ $= 3.92 \times 10^5 + 1.01 \times 10^5 = 4.93 \times 10^5 Pa$ $T_1 = 12 \text{ °C} = 273 + 12 = 285 \text{ K}$ Temperature, Also, pressure outside the lake, $P_{2'} = 1.01 \times 10^5$ N m⁻² $T_2 = 35 \text{ °C} = 273 + 35 = 308 \text{ K}$, volume $V_2 = ?$ Temperature, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ Now $V_2 = \frac{P_1 V_1}{T_1} \cdot \frac{T_2}{P_2} = \frac{4.93 \times 10^5 \times 1 \times 10^{-6} \times 308}{285 \times 1.01 \times 10^5} = 5.3 \times 10^{-6} \text{ m}^{-3}$ *.*..

Question 6. Estimate the total number of air molecules (inclusive of oxygen, nitrogen, water vapour and other constituents) in a room of capacity 25.0 m³ at a temperature of 27 °C and 1 atm pressure.

Answer:

Here, volume of room, $V = 25.0 \text{ m}^3$, temperature, T = 27 °C = 300 K and $P = 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$ Pressure, According to gas equation,

$$PV = \mu RT = \mu N_A \cdot k_B T$$

Hence, total number of air molecules in the volume of given gas,

$$N = \mu \cdot N_A = \frac{PV}{k_B T}$$
$$N = \frac{1.01 \times 10^5 \times 25.0}{(1.38 \times 10^{-23}) \times 300} = 6.1 \times 10^{26}.$$

...

Question 7. Estimate the average thermal energy of a helium atom at (i) room temperature (27 °C), (ii) the temperature on the surface of the Sun (6000 K), (iii) the temperature of 10 million kelvin (the typical core temperature in the case of a star).

Answer:

(i) Here, T = 27 °C = 27 + 273 = 300 KAverage thermal energy $= \frac{3}{2} kT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 = 6.2 \times 10^{-21} \text{ J.}$ (ii) At T = 6000 K, Average thermal energy $= \frac{3}{2} kT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 6000 = 1.24 \times 10^{-19} \text{ J.}$ (iii) At T = 10 million $K = 10^7 \text{ K}$ Average thermal energy $= \frac{3}{2} kT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 10^7 = 2.1 \times 10^{-16} \text{ J.}$

Question 8. Three vessels of equal capacity have gases at the same temperature and pressure. The first vessel contains neon (monoatomic), the second contains chlorine (diatomic), and the third contains uranium hexafluoride (polyatomic). Do the vessels contain equal number of respective molecules? Is the root mean square speed of molecules the same in the three cases? If not, in which case is v_{rms} the largest?

Answer: Equal volumes of all the gases under similar conditions of pressure and temperature contains equal number of molecules (according to Avogadro's hypothesis). Therefore, the number of molecules in each case is same.

The rms velocity of molecules is given by

$$v_{\rm rms} = \sqrt{\frac{3kT}{m}}$$

 $v_{\rm rms} \propto \frac{1}{\sqrt{m}}$

Clearly

Since neon has minimum atomic mass m, its rms velocity is maximum.

Question 9. At what temperature is the root mean square speed of an atom in an argon gas cylinder equal to the rms speed of a helium gas atom at -20 °C? (atomic mass of Ar = 39.9 u, of He = 4.0 u).

Answer: Let C and C' be the rms velocity of argon and a helium gas atoms at temperature T K and T K respectively.

Here, M = 39.9; M' = 4.0; T =?; T = -20 + 273 = 253 K

 $C = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{39.9}}$ and $C' = \sqrt{\frac{3RT'}{M'}} = \sqrt{\frac{3R \times 253}{4}}$ Now, Since $\sqrt{\frac{3RT}{39.9}} = \sqrt{\frac{3R \times 253}{4}}$ Therefore, $T = \frac{39.9 \times 253}{4} = 2523.7 \text{ K}.$

Question 10. Estimate the mean free path and collision frequency of a nitrogen molecule in a cylinder containing nitrogen at 2.0 atm and temperature 17 °C. Take the radius of a nitrogen molecule to be roughly 1.0 A. Compare the collision time with the time the molecule moves freely between two successive collisions (Molecular mass of $N_2 = 28.0$ u).

Answer:

| Here, P | - | $2.0 \text{ atm} = 2 \times 1.013 \times 10^5 \text{ Pa} = 2.026 \times 10^5 \text{ Pa}$ | | | |
|---|---|---|--|--|--|
| Т | = | 17 °C = 17 + 273 = 290 | | | |
| Radius, R | = | $1.0 \text{ Å} = 1 \times 10^{-10} \text{ m}$, Molecular mass = 28 u | | | |
| :. m | = | $28 \times 1.66 \times 10^{-27} = 4.65 \times 10^{-26} \text{ kg}$ | | | |
| Also, R | = | 8.31 J mol ⁻¹ K ⁻¹ , $k = 1.38 \times 10^{-23}$ JK ⁻¹ | | | |
| Now for one mole of a gas, | | | | | |
| PV | = | $RT \implies V = \frac{RT}{P} = \frac{8.31 \times 290}{2.026 \times 10^5}$ | | | |
| \Rightarrow V | = | $1.189 \times 10^{-2} \text{ m}^3$ | | | |
| :. Number of molecules per unit volume, $n = \frac{N}{V}$ | | | | | |
| n | = | $\frac{6.023 \times 10^{23}}{1.189 \times 10^{-2}} = 5.06 \times 10^{25} \text{ m}^{-3}$ | | | |
| Now, mean free path, | | | | | |
| λ | = | $\frac{1}{\sqrt{2}\pi nd^2} = \frac{1}{\sqrt{2}\pi n(2r)^2}$ | | | |
| | | 1 | | | |
| | = | $1.414 \times 3.14 \times 5.06 \times 10^{25} \times (2 \times 1 \times 10^{-10})^2$ | | | |
| | = | 1.1 × 10 ⁻⁷ m. | | | |
| Also, v_{rm} | = | $\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 290}{28 \times 10^{-3}}} = 5.08 \times 10^2 \text{ ms}^{-1}$ | | | |
| Collision frequency | , | | | | |
| v | - | $\frac{v_{rms}}{\lambda} = \frac{5.08 \times 10^2}{1.1 \times 10^{-7}} = 4.62 \times 10^9 \mathrm{s}^{-1}$ | | | |

Time between successive collisions = $\frac{1}{v} = \frac{1}{4.62 \times 10^9} = 2.17 \times 10^{-10} \text{ s}$

Also the collision time = $\frac{d}{v_{rms}} = \frac{2 \times 1 \times 10^{-10}}{5.08 \times 10^2} s = 3.92 \times 10^{-13} s.$

or