Chapter 12: Kinetic Theory

Exercises — Exercises

Q1 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 Å.

SOLUTION

Given:

Diameter of O2 molecule d = 3 Å = 3×10^{-10} m => radius r = 1.5×10^{-10} m

At STP, 1 mole of ideal gas occupies V_molar = 22.4 L = 22.4×10^{-3} m^3

NA = 6.022×10^{23} molecules/mol

Volume of one O2 molecule (treated as a sphere):

$V_{molecule} = (4/3)\ \pi\ r^3 = (4/3) \times \pi \times (1.5 \times 10^{-10})^3$

$V_{molecule} = 1.41 \times 10^{-29}$ m^3

Total molecular volume per mole:

$V_{mol_total} = NA \times V_{molecule} = 6.022 \times 10^{23} \times 1.41 \times 10^{-29}$

$V_{mol_total} = 8.50 \times 10^{-6}$ m^3

Fraction of molecular volume to actual volume:

$f = V_{mol_total} / V_{molar} = (8.50 \times 10^{-6}) / (22.4 \times 10^{-3})$

$f \approx 3.8 \times 10^{-4}$

Answer: Fraction ≈ 3.8×10^{-4} (molecular volume is about 0.038% of the total volume, confirming that molecules in a gas are far apart)

Q2 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.

SOLUTION

Given:

μ = 1 mol, T = 0 °C = 273.15 K, P = 1 atm = 1.013×10^5 Pa

R = 8.314 J mol^{-1} K^{-1}

From the ideal gas equation PV = μRT:

V = μRT / P

$V = (1\ mol \times 8.314\ J\ mol^{-1}\ K^{-1} \times 273.15\ K) / (1.013 \times 10^5\ Pa)$

$V = 2271.1 / 1.013 \times 10^5$

$V = 2.241 \times 10^{-2}\ m^3$

Converting to litres (1 m^3 = 1000 L):

$V = 22.4\ L$

Answer: Molar volume = 22.4 L at STP, as shown from PV = μRT with μ = 1 mol, T = 273.15 K, P = 1.013×10^5 Pa

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Q3 Figure 12.8 shows plot of PV/T versus P for 1.00×10^{-3} kg of oxygen gas at two different temperatures.
(a) What does the dotted plot signify?
(b) Which is true: T1 > T2 or T1 < T2?
(c) What is the value of PV/T where the curves meet on the y-axis?
(d) If we obtained similar plots for 1.00×10^{-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 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}.)

SOLUTION

(a) The dotted plot is a horizontal straight line.
For an ideal gas, PV = μRT => PV/T = μR = constant, independent of P.
The dotted plot represents the behaviour of an ideal gas — PV/T is constant at all pressures.

(b) Comparing T1 and T2:
At higher pressures, the T1 curve lies above the dotted line (PV/T > μR) while T2 lies below.
A gas at higher temperature has molecules with greater kinetic energy, so the repulsive
hard-core interactions (which increase PV/T above ideal) dominate over attractive forces.
At lower temperature, attractive interactions pull molecules together, reducing PV/T below ideal.
Therefore T1 > T2.

(c) At very low pressure (P → 0), both real gases behave ideally: PV/T → μR.
μ = mass / molar mass = $(1.00 \times 10^{-3}\ kg) / (32.0 \times 10^{-3}\ kg/mol)$
$\mu = 1/32\ mol = 3.125 \times 10^{-2}\ mol$

$PV/T = \mu R = 3.125 \times 10^{-2} \times 8.31 = 0.26\ J\ K^{-1}$

(d) No, 1.00×10^{-3} kg of H_2 would NOT give the same PV/T value, because the number of moles differs.

$\mu(H_2) = (1.00 \times 10^{-3}) / (2.02 \times 10^{-3}) = 0.495$ mol (much larger than $\mu(O_2) = 0.03125$ mol)

=> PV/T for H_2 would be much larger.

For H_2 to give $PV/T = 0.26\ J\ K^{-1}$, we need $\mu(H_2) = \mu(O_2) = 0.03125$ mol:

$mass(H_2) = \mu \times M(H_2) = 0.03125 \times 2.02 \times 10^{-3}$ kg

$mass(H_2) = 6.31 \times 10^{-5}$ kg = 0.0631 g

Answer: (a) Dotted plot = ideal gas (PV/T = constant). (b) $T_1 > T_2$. (c) $PV/T = \mu R \approx 0.26\ J\ K^{-1}$. (d) No; mass of H_2 needed = 0.0631 g

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Q4 An oxygen cylinder of volume 30 litre has an initial gauge pressure of 15 atm and a temperature of 27 °C. After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atm 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 $O_2 = 32$ u).

SOLUTION

Given:

Volume of cylinder $V = 30\ L = 30 \times 10^{-3}\ m^3$ (fixed)

Initial gauge pressure $P_1 = 15$ atm => absolute pressure = 15 + 1 = 16 atm = $16 \times 1.013 \times 10^5$ Pa

Initial temperature $T_1 = 27\ °C = 300\ K$

Final gauge pressure $P_2 = 11$ atm => absolute pressure = 11 + 1 = 12 atm = $12 \times 1.013 \times 10^5$ Pa

Final temperature $T_2 = 17\ °C = 290\ K$

$R = 8.31\ J\ mol^{-1}\ K^{-1}$, $M(O_2) = 32 \times 10^{-3}$ kg/mol

Initial number of moles using $PV = \mu RT$:

$\mu_1 = P_1 V / (R T_1) = (16 \times 1.013 \times 10^5 \times 30 \times 10^{-3}) / (8.31 \times 300)$

$\mu_1 = (1.621 \times 10^6 \times 30 \times 10^{-3}) / (2493)$

$\mu_1 = 48.624 / 2493 \approx 19.50$ mol

Final number of moles:

$\mu_2 = P_2 V / (R T_2) = (12 \times 1.013 \times 10^5 \times 30 \times 10^{-3}) / (8.31 \times 290)$

$\mu_2 = (1.216 \times 10^6 \times 30 \times 10^{-3}) / (2409.9)$

$\mu_2 = 36.47 / 2409.9 \approx 15.13$ mol

Moles of O_2 withdrawn:

$\Delta\mu = \mu_1 - \mu_2 = 19.50 - 15.13 = 4.37$ mol

Mass of O_2 withdrawn:

$\Delta m = \Delta\mu \times M(O_2) = 4.37 \times 32 \times 10^{-3}$ kg

$\Delta m \approx 0.140$ kg = 140 g

Answer: Mass of oxygen withdrawn ≈ 140 g (≈ 0.140 kg)

Q5 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?

SOLUTION

Given:

Volume at bottom $V_1 = 1.0$ cm³ $= 1.0 \times 10^{-6}$ m³

Depth $h = 40$ m, temperature at bottom $T_1 = 12$ °C = 285 K

Temperature at surface $T_2 = 35$ °C = 308 K

Atmospheric pressure $P_{atm} = 1.013 \times 10^5$ Pa

Density of water $\rho = 1000$ kg m^{-3}, $g = 9.8$ m s^{-2}

Pressure at the bottom of the lake:

$P_1 = P_{atm} + \rho gh = 1.013 \times 10^5 + 1000 \times 9.8 \times 40$

$P_1 = 1.013 \times 10^5 + 3.92 \times 10^5 = 4.933 \times 10^5$ Pa

Pressure at the surface:

$P_2 = P_{atm} = 1.013 \times 10^5$ Pa

The amount of air in the bubble is fixed. Applying the combined gas law:

$P_1 V_1 / T_1 = P_2 V_2 / T_2$

$V_2 = (P_1 V_1 T_2) / (P_2 T_1)$

$V_2 = (4.933 \times 10^5 \times 1.0 \times 10^{-6} \times 308) / (1.013 \times 10^5 \times 285)$

$V_2 = (0.1519) / (28870)$

$V_2 = 5.26 \times 10^{-6}$ m³ = 5.3 cm³

Answer: Volume of bubble at surface ≈ 5.3 cm³

Q6 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.

SOLUTION

Given:

Volume V = 25.0 m³

Temperature T = 27 °C = 300 K

Pressure P = 1 atm = 1.013×10^5 Pa

kB = 1.38×10^{-23} J K^{-1}

From the ideal gas equation: PV = NkBT

N = PV / (kB T)

N = $(1.013 \times 10^5 \times 25.0) / (1.38 \times 10^{-23} \times 300)$

N = $(2.5325 \times 10^6) / (4.14 \times 10^{-21})$

N ≈ 6.12×10^{26} molecules

Answer: Total number of air molecules in the room ≈ 6.1×10^{26}

Q7 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).

SOLUTION

Helium is monatomic. By the law of equipartition of energy, each molecule has 3 translational degrees of freedom, so average thermal energy = (3/2) kB T.

kB = 1.38×10^{-23} J K^{-1}

(i) Room temperature T1 = 27 °C = 300 K:

E1 = (3/2) kB T1 = $(3/2) \times 1.38 \times 10^{-23} \times 300$

E1 = 6.21×10^{-21} J

(ii) Surface of the Sun, T2 = 6000 K:

E2 = (3/2) kB T2 = $(3/2) \times 1.38 \times 10^{-23} \times 6000$

E2 = 1.24×10^{-19} J

(iii) Core of a star, T3 = 10^7 K:

E3 = (3/2) kB T3 = $(3/2) \times 1.38 \times 10^{-23} \times 10^7$

E3 = 2.07×10^{-16} J

Answer: (i) 6.21×10^{-21} J at 300 K; (ii) 1.24×10^{-19} J at 6000 K; (iii) 2.07×10^{-16} J at 10^7 K

Q8 Three vessels of equal capacity have gases at the same temperature and pressure. The first vessel contains neon (monatomic), 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 vrms the largest?

SOLUTION

Equal number of molecules?

By Avogadro's law, equal volumes of all gases at the same temperature and pressure contain

the same number of molecules (for ideal gases). Since all three vessels have equal capacity

at the same T and P, they contain equal numbers of molecules (N is the same in all three).

Is vrms the same?

vrms = sqrt(3kB T / m) = sqrt(3RT / M)

where m is the mass of one molecule and M is the molar mass.

Since T is the same but M differs, vrms is NOT the same for the three gases.

Molar masses:

Neon (Ne): M = 20.18 g/mol

Chlorine (Cl2): M = 70.9 g/mol

Uranium hexafluoride (UF6): M = 238 + 6 × 19 = 352 g/mol

Since vrms ∝ 1/√M (at fixed T), the lighter molecule has the largest vrms.

vrms(Ne) > vrms(Cl2) > vrms(UF6)

Neon, having the smallest molar mass, has the largest vrms.

Answer: Yes, all three vessels contain equal number of molecules (Avogadro's law). No, vrms is not the same; neon (smallest molar mass) has the largest vrms.

Q9 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).

SOLUTION

Given:

Temperature of helium: $T_{He} = -20\ °C = 253\ K$

$M_{Ar} = 39.9$ g/mol, $M_{He} = 4.0$ g/mol

The rms speed is: $v_{rms} = \sqrt{3RT/M}$

Setting $v_{rms}(Ar) = v_{rms}(He)$:

$\sqrt{3R\,T_{Ar} / M_{Ar}} = \sqrt{3R\,T_{He} / M_{He}}$

Squaring both sides:

$T_{Ar} / M_{Ar} = T_{He} / M_{He}$

$T_{Ar} = T_{He} \times (M_{Ar} / M_{He})$

$T_{Ar} = 253 \times (39.9 / 4.0)$

$T_{Ar} = 253 \times 9.975$

$T_{Ar} = 2523.7\ K \approx 2524\ K$

Answer: $T_{Ar} \approx 2524$ K (about 2251 °C)

Q10 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 Å. Compare the collision time with the time the molecule moves freely between two successive collisions. (Molecular mass of N2 = 28.0 u).

SOLUTION

Given:

Pressure $P = 2.0\ atm = 2.0 \times 1.013 \times 10^5 = 2.026 \times 10^5$ Pa

Temperature $T = 17\ °C = 290\ K$

Radius of N2 molecule $r = 1.0$ Å => diameter $d = 2.0$ Å $= 2.0 \times 10^{-10}$ m

$M(N2) = 28.0 \times 10^{-3}$ kg/mol

$k_B = 1.38 \times 10^{-23}\ J\ K^{-1}$, $R = 8.314\ J\ mol^{-1}\ K^{-1}$, $N_A = 6.022 \times 10^{23}$

Step 1: Number density $n = P/(k_B T)$

$n = (2.026 \times 10^5) / (1.38 \times 10^{-23} \times 290)$

$n = 5.06 \times 10^{25}\ m^{-3}$

Step 2: Mean free path $l = 1 / (\sqrt{2} \times \pi \times d^2 \times n)$

$l = 1 / (1.414 \times 3.1416 \times (2.0 \times 10^{-10})^2 \times 5.06 \times 10^{25})$

$l = 1 / (1.414 \times 3.1416 \times 4.0 \times 10^{-20} \times 5.06 \times 10^{25})$

$l = 1 / (8.993 \times 10^6)$

$l \approx 1.11 \times 10^{-7}$ m ≈ 111 nm

Step 3: Average speed of N2 molecules

$\langle v \rangle = \text{sqrt}(8RT / (\pi M)) = \text{sqrt}(8 \times 8.314 \times 290 / (\pi \times 28.0 \times 10^{-3}))$

$\langle v \rangle = \text{sqrt}(19310.08 / 0.08796) = \text{sqrt}(219535) \approx 468$ m s^{-1}

Step 4: Collision frequency $f = \langle v \rangle / l$

$f = 468 / (1.11 \times 10^{-7})$

$f \approx 4.21 \times 10^9$ s^{-1}

(i.e., each N2 molecule undergoes about 4.2×10^9 collisions per second)

Step 5: Compare collision time with free-flight time

Mean free time (time between collisions): $\tau = l / \langle v \rangle = 1.11 \times 10^{-7} / 468$

$\tau \approx 2.37 \times 10^{-10}$ s

Collision time (duration of one collision) $\approx d / \langle v \rangle = 2.0 \times 10^{-10} / 468$

$t_{coll} \approx 4.27 \times 10^{-13}$ s

Ratio: $\tau / t_{coll} = 2.37 \times 10^{-10} / 4.27 \times 10^{-13} \approx 556$

The molecule moves freely for about 556 times longer than the duration of each collision.

This confirms that the assumption of negligible collision time (compared to free flight time)

used in kinetic theory is well justified.

Answer: Mean free path $l \approx 1.11 \times 10^{-7}$ m; collision frequency $\approx 4.21 \times 10^9$ s^{-1}; the mean free time (2.37×10^{-10} s) is about 556 times larger than the collision duration (4.27×10^{-13} s).