

Chapter 13: KINETIC THEORY

Examples

Example 13.1 The density of water is 1000kgm^{-3} . The density of water vapour at 100°C and **1 atm** pressure is 0.6kg 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:

When the volume of water molecules is big, the density is smaller for a given quantity of water molecules.

So, the volume of the vapour is $1000 / 0.6 = 1 / (6 \times 10^{-4})$ times larger.

If the densities of bulk water and water molecules are comparable, the molecular volume fraction to the total volume in the liquid state is

As the volume of the vapour state increases, the fractional volume reduces 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: Water molecules are very densely packed in the liquid (or solid) phase.

As a result, the density of a water molecule is about equivalent to the density of bulk water.
 $= 1000\text{kg m}^{-3}$.

We need to know the mass of a single water molecule to determine the volume of a water molecule. We know that one mole of water has a mass of roughly $(2 + 16)\text{g} = 18\text{g} = 0.018\text{kg}$.

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

As a result, a rough estimation of a water molecule's volume is as follows:

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

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

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:

The volume of a particular quantity of water in the vapour state is 1.67×10^3 that of the same mass of water in the liquid state (Ex.13.1).

This also refers to the increase in the quantity of space available for each water molecule.

The radius rises by $V^{1/3}$ or 10 times when the volume increases by 1000, i.e., $10 \times 2 \text{ \AA} = 20 \text{ \AA}$.

As a result, the average distance is $2 \times 20 = 40 \text{ \AA}$.

Example 13.4 A vessel contains two nonreactive 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 = 20.2u , molecular mass of $O_2 = 32.0u$.

Answer:

The partial pressure of a gas in a mixture is the pressure it would have if it were alone in the vessel at the same volume and temperature. (A mixture of non-reactive gases has a total pressure equal to the sum of partial pressures owing to its component gases.)

The gas law applies to each gas (assumed ideal).

Since V and T are common to the two gases, we have,

$$P_1 V = \mu_1 R T \text{ and}$$

$$P_2 V = \mu_2 R T,$$

$$\text{i.e. } (P_1 / P_2) = (\mu_1 / \mu_2).$$

Here 1 and 2 refer to neon and oxygen respectively. Since

$$(P_1 / P_2) = (3 / 2) (\text{given}), \quad (\mu_1 / \mu_2) = 3 / 2.$$

(i) By definition,

$$\mu_1 = (N_1 / N_A) \text{ and}$$

$$\mu_2 = (N_2 / N_A)$$

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

$$\begin{aligned} \frac{\rho_1}{\rho_2} &= \frac{m_1 / V}{m_2 / V} = \frac{m_1}{m_2} = \frac{\mu_1}{\mu_2} \times \left(\frac{M_1}{M_2} \right) \\ &= \frac{3}{2} \times \frac{20.2}{32.0} = 0.947 \end{aligned}$$

Example 13.5 A flask contains argon and chlorine in the ratio of 2 : 1 by mass. The temperature of the mixture is 27°C . Obtain the ratio of (i) average kinetic energy per molecule, and (ii) root mean square speed? v_{rms} of the molecules of the two gases. Atomic mass of argon = 39.9u ; Molecular mass of chlorine = 70.9u .

Answer:

The crucial thing to remember is that every (ideal) gas's average kinetic energy (per molecule), whether monatomic, diatomic, or polyatomic, is always equal to $(3/2)k_B T$.

It is only affected by temperature and is unaffected by the gas's composition.

(i) Because the temperature of argon and chlorine in the flask is the same, the average kinetic energy (per molecule) of the two gases is 1 : 1.

(ii) Now $\frac{1}{2}mv_{\text{rms}}^2 = \text{average kinetic energy per molecule} = (3/2)k_B T$ where m is the mass of a molecule of the gas. Therefore,

$$\frac{\left(v_{\text{rms}}^2\right)_{\text{Ar}}}{\left(v_{\text{rms}}^2\right)_{\text{Cl}}} = \frac{(m)_{\text{Cl}}}{(m)_{\text{Ar}}} = \frac{(M)_{\text{Cl}}}{(M)_{\text{Ar}}} = \frac{70.9}{39.9} = 1.77$$

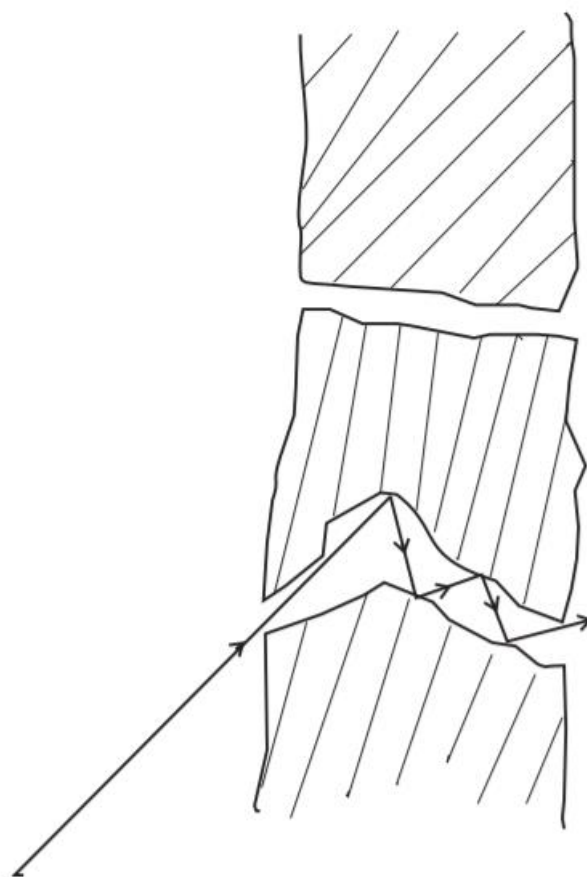
where M denotes the molecular mass of the gas. (For argon, a molecule is just an atom of argon.)

By multiplying both sides by the square root of the square root of the square root of the square root of the,

$$\frac{\left(v_{\text{rms}}\right)_{\text{Ar}}}{\left(v_{\text{rms}}\right)_{\text{Cl}}} = 1.33$$

It's worth noting that the mass composition of the combination has no bearing on the computation. If the temperature is not changed, any other proportion of argon and chlorine by mass will provide the identical responses to (i) and (ii).

Example 13.6 Uranium has two isotopes of masses 235 and 238 units. If both are present in Uranium hexafluoride gas which would have the larger average speed? If atomic mass of fluorine is 19 units. Estimate the percentage difference in speeds at any temperature.



Answer: At a fixed temperature the average energy $= \frac{1}{2} m \langle v^2 \rangle$ is constant. The lower the molecule's mass, the faster it will move. The square root of the mass-to-speed ratio is inversely proportional to the ratio of speeds.

The masses are 349 and 352 units. So,

$$v_{349}/v_{352} = (352/349)^{1/2} = 1.0044$$

Hence difference $\frac{\Delta V}{V} = 0.44\%$

[^{235}U is the isotope needed for nuclear fission.

The mixture is encased by a porous cylinder to segregate it from the more prevalent isotope ^{233}U . The porous cylinder must be thick and narrow enough for the molecule to wander through it alone, clashing with the lengthy pore's walls. Because the quicker molecule leaks out more than the slower one, the lighter molecule (enrichment) is found outside the porous cylinder (*Fig.13.5*).

The procedure is inefficient, and it must be performed numerous times to get adequate enrichment.]

Example 13. (a) When a molecule (or an elastic ball) hits a (massive) wall, it rebounds with the same speed. When a ball hits a massive bat held firmly, the same thing happens. However, when the bat is moving towards the ball, the ball rebounds with a different speed. Does the ball move faster or slower? (Ch.6 will refresh your memory on elastic collisions.)

Answer: Allow the ball's speed to be proportional to the wicket behind the bat.

The relative speed of the ball to bat is $V + u$ towards the bat,
 if the bat is travelling towards the ball at a speed V relative to the wicket.
 When the ball rebounds (after hitting the enormous bat), it moves away from the bat at a speed of
 $V + u$. The rebounding ball's speed relative to the wicket is $V + (V + u) = 2V + u$
 as it moves away from the wicket.
 As a result of the hit with the bat, the ball accelerates.
 If the bat is not enormous, the rebound speed will be less than u .
 A molecule's temperature would rise because of this.

(b) When gas in a cylinder is compressed by pushing in a piston, its temperature rises. Guess at an explanation of this in terms of kinetic theory using (a) above.

Answer:

When a bat strikes the ball after compressing gas in a cylinder using a piston, the ball goes quicker, and the temperature of the gas rises.

(c) What happens when a compressed gas pushes a piston out and expands. What would you observe?

Answer: The speed of the molecules slows down as a compressed gas pushes a piston out.

Their KE is decreasing.

(d) Sachin Tendulkar used a heavy cricket bat while playing. Did it help him in anyway?

Answer: Yes!! It makes extensive use of physics ideas and principles!!

One of the fundamental principles is...

When the ball strikes the bat, a big impulsive force is formed, but owing to the heavier mass of the bat,
 the impulse communicated to the bat offers less backward velocity.
 Another cause might be that..., even at a very low velocity, a huge momentum is created, therefore the
 ball moves with more velocity.

Example 13.8 A cylinder of fixed capacity **44.8 litres** contains helium gas at standard temperature and pressure. What is the amount of heat needed to raise the temperature of the gas in the cylinder by 15.0°C ? ($R = 8.31\text{J mol}^{-1}\text{K}^{-1}$)

Answer: According to the gas law $PV = \mu RT$,

i.e., 1 mol of any (ideal) gas at standard temperature (273 K) and pressure ($1\text{atm} = 1.01 \times 10^5\text{ Pa}$) occupies a volume of **22.4 litres**. Molar volume is the name given to this global volume.

In this case, the cylinder contains **2 mol** of helium.

Furthermore, because helium is monatomic, its molar specific heat at constant volume is expected (and observed).

$C_v = (3/2)R$, and molar specific heat at constant pressure, $C_p = (3/2)R + R = (5/2)R$. As the volume of the cylinder is fixed, the heat required is determined by C_v . So,

Heat required = no. of moles \times molar specific heat \times rise in temperature

$$= 2 \times 1.5R \times 15.0 = 45R$$

$$R = 45 \times 8.31 = 374 \text{ J}$$

Example 13.9 Estimate the mean free path for a water molecule in water vapour at 373 K. Use information from Exercises 13.1 and Eq. (13.41).

Answer: Water vapour has the same d value as air.

The absolute temperature is inversely related to the numerical density.

$$\text{So } n = 2.7 \times 10^{25} \times \frac{273}{373} = 2 \times 10^{25} \text{ m}^{-3}$$

Hence, mean free path $l = 4 \times 10^{-7} \text{ m}$.

Exercises

13.1 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 \AA .

Answer: Diameter of an oxygen molecule, $d = 3 \text{ \AA}$

$$\text{Radius, } r = \frac{d}{2} = \frac{3}{2} \text{ \AA} = 1.5 \text{ \AA} = 1.5 \times 10^{-8} \text{ cm}$$

Actual volume occupied by 1 mole of oxygen gas at STP = 22400 cm^3

$$\text{Molecular volume of oxygen gas, } V = \frac{4}{3} \pi r^3 \cdot N^2$$

Where, N is Avogadro's No. = 6.023×10^{23} molecules / mole

$$\therefore V = \frac{4}{3} \times 3.14 \times (1.5 \times 10^{-8})^3 \times 6.023 \times 10^{23} = 8.51 \text{ cm}^3$$

Ratio of the molecular volume to the actual volume of oxygen,

$$\begin{aligned}
 &= \frac{8.51}{22400} \\
 &= 3.8 \times 10^{-4}
 \end{aligned}$$

13.2 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: The ideal gas equation relating pressure (P), volume (V), and absolute temperature (T) is given as:

$$P V = n R T$$

Where,

R is the universal gas constant

$$= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

n = Number of moles = 1

T = Standard temperature = 273 K

P = Standard pressure = 1 atm = $1.013 \times 10^5 \text{ Nm}^{-2}$

$$\therefore V = \frac{nRT}{P}$$

$$= \frac{1 \times 8.314 \times 273}{1.013 \times 10^5} = 0.0224 \text{ m}^3$$

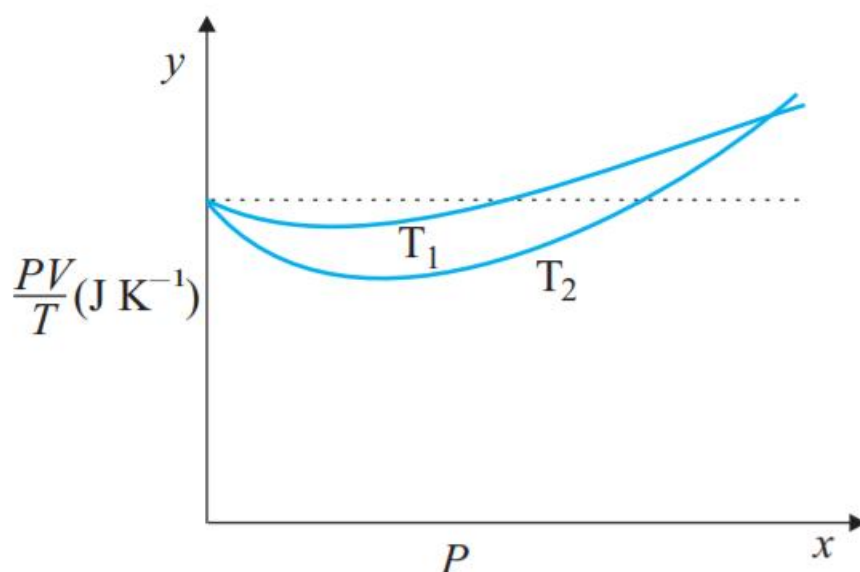
So, the molar volume of a gas at STP is 22.4 litres.

13.3 Figure shows plot of PV/T versus P for $1.00 \times 10^{-3} \text{ kg}$ of oxygen gas at two different temperatures, What does the dotted plot signify?

Which is true: $T_1 > T_2$ or $T_1 < T_2$?

What is the value of PV/T where the curves meet on the y – axis ?

If we obtained similar plots for $1.00 \times 10^{-3} \text{ kg}$ 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 $\text{H}_2 = 2.02\text{u}$, of $\text{O}_2 = 32.0\text{u}$, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$.)



Answer: The ideal behaviour of the gas is represented by the dotted plot in the graph.i.e., the ratio $\frac{PV}{T}$ is equal. μR (μ is the number of moles and R is the universal gas constant) is a constant quality. It isn't affected by the gas's pressure.

The ideal gas is represented by the dotted plot in the graph.
The dotted plot is closer to the curve of the gas at temperature T_1 than the curve of the gas at temperature T_2 .

When the temperature of a real gas rises, it approaches the behaviour of an ideal gas.
As a result, $T_1 > T_2$ for the given plot, is true.

The ratio value PV/T at the intersection of the two curves is μR . This is because the ideal gas equation is given as:

$$PV = \mu RT$$

$$\frac{PV}{T} = \mu R$$

Where,

P is the pressure

T is the temperature

V is the volume

μ is the number of moles

R is the universal constant

Molecular mass of oxygen = 32.0g

Mass of oxygen = 1×10^{-3} kg = 1g

$$R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\frac{PV}{T} = \frac{1}{32} \times 8.314$$

$$\therefore = 0.26 \text{ J K}^{-1}$$

Therefore, the value of the ratio PV/T , where the curves meet on the y -axis, is 0.26 J K^{-1} .

If we obtain similar plots for $1.00 \times 10^{-3} \text{ kg}$ of hydrogen, then we will not get the same value of PV/T at the point where the curves meet the y -axis. This is because the molecular mass of hydrogen (2.02u) is different from that of oxygen (32.0u). We have:

$$\frac{PV}{T} = 0.26 \text{ J K}^{-1}$$

$$R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$$

Molecular mass (M) of $\text{H}_2 = 2.02\text{u}$

$$\frac{PV}{T} = \mu R \text{ at constant temperature}$$

Where, $\mu = \frac{m}{M}$

$$m = \text{Mass of } \text{H}_2$$

$$\therefore m = \frac{PV}{T} \times \frac{M}{R} = \frac{0.26 \times 2.02}{8.31}$$

$$= 6.3 \times 10^{-2} \text{ g} = 6.3 \times 10^{-5} \text{ kg}$$

Hence, $6.3 \times 10^{-5} \text{ kg}$ of H_2 will yield the same value of $P V / T$.

13.4 An oxygen cylinder of volume 30 litres 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 ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, molecular mass of $\text{O}_2 = 32\text{u}$).

Answer: Volume of oxygen, $V_1 = 30 \text{ litres} = 30 \times 10^{-3} \text{ m}^3$

Gauge pressure, $P_1 = 15 \text{ atm} = 15 \times 1.013 \times 10^5 \text{ Pa}$

Temperature, $T_1 = 27^\circ \text{C} = 300 \text{ K}$

Universal gas constant, $R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$

Let's say there are n_1 moles of oxygen gas in the cylinder at the start.

The gas equation is given as:

$$\begin{aligned}
 P_1V_1 &= n_1RT_1 \\
 \therefore n_1 &= \frac{P_1V_1}{RT_1} \\
 &= \frac{15.195 \times 10^5 \times 30 \times 10^{-3}}{(8.314) \times 300} = 18.276
 \end{aligned}$$

But, $n_1 = \frac{m_1}{M}$ Where, m_1 = Initial mass of oxygen

M = Molecular mass of oxygen = 32g

$$m_1 = n_1M = 18.276 \times 32 = 584.84 \text{ g}$$

The pressure and temperature drop when some oxygen is removed from the cylinder.

Volume, $V_2 = 30 \text{ litres} = 30 \times 10^{-3} \text{ m}^3$

Gauge pressure, $P_2 = 11 \text{ atm} = 11 \times 1.013 \times 10^5 \text{ Pa}$

Temperature, $T_2 = 17^\circ \text{ C} = 290 \text{ K}$

Assume n_2 is no. of moles of oxygen remains in the cylinder.

The gas equation is :

$$\begin{aligned}
 P_2V_2 &= n_2RT_2 \\
 \therefore n_2 &= \frac{P_2V_2}{RT_2} \\
 &= \frac{11.143 \times 10^5 \times 30 \times 10^{-3}}{8.314 \times 290} = 13.86
 \end{aligned}$$

But, $n_2 = \frac{m_2}{M}$ Where, m_2 is the mass of oxygen

remaining in the cylinder : $m_2 = n_2M = 13.86 \times 32 = 453.1 \text{ g}$

The amount of oxygen extracted from the cylinder is:

$$\begin{aligned}
 &\text{Mass of oxygen in the cylinder at the start} - \text{Mass of oxygen in the cylinder at the end} \\
 &= m_1 - m_2 \\
 &= 584.84 \text{ g} - 453.1 \text{ g} \\
 &= 131.74 \text{ g} \\
 &= 0.131 \text{ kg}
 \end{aligned}$$

So, 0.131kg of oxygen is taken out of the cylinder.

13.5 An air bubble of volume 1.0 cm^3 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 air bubble, $V_1 = 1.0\text{ cm}^3 = 1.0 \times 10^{-6}\text{ m}^3$

Bubble rises to height, $d = 40\text{ m}$

Temperature at a depth of 40 m , $T_1 = 12^\circ\text{ C} = 285\text{ K}$

Temperature at the surface of the lake, $T_2 = 35^\circ\text{ C} = 308\text{ K}$

The pressure on the lake's surface is as follows:

$$P_2 = 1\text{ atm} = 1 \times 1.013 \times 10^5\text{ Pa}$$

The pressure at the depth of 40 m :

$$P_1 = 1\text{ atm} + d\rho g$$

Where, ρ is the density of water $= 10^3\text{ kg / m}^3$ g is the acceleration due to gravity

$$\therefore P_1 = 1.013 \times 10^5 + 40 \times 10^3 \times 9.8 = 493300\text{ Pa}$$

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

When the air bubble reaches the surface, its volume V_2 is $V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$

$$= \frac{(493300)(1.0 \times 10^{-6}) 308}{285 \times 1.013 \times 10^5}$$

$$= 5.263 \times 10^{-6}\text{ m}^3 \text{ or } 5.263\text{ cm}^3$$

As a result, when the air bubble reaches the surface, its volume is 5.263 cm^3 .

13.6 Estimate the total number of air molecules (inclusive of oxygen, nitrogen, water vapour and other constituents) in a room of capacity 25.0 m^3 at a temperature of 27° C and 1 atm pressure.

Answer: Volume of the room, $V = 25.0\text{ m}^3$

Temperature of the room, $T = 27^\circ\text{ C} = 300\text{ K}$

Pressure in the room, $P = 1\text{ atm} = 1 \times 1.013 \times 10^5\text{ Pa}$

The ideal gas equation relating pressure (P), Volume (V), and absolute temperature (T) can be written as:

$$P V = k_B N T$$

Where,

$$K_B \text{ is Boltzmann constant} = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$$

N is the number of air molecules in the room

$$\therefore N = PVk_B T$$

$$= \frac{1.013 \times 10^5 \times 25}{1.38 \times 10^{-23} \times 300} = 6.11 \times 10^{26} \text{ molecules}$$

As a result, the total number of air molecules in a room is 6.11×10^{26} .

13.7 Estimate the average thermal energy of a helium atom at

(i) room temperature (27°C),

Answer: At room temperature, $T = 27^\circ \text{C} = 300 \text{K}$

$$\text{Average thermal energy} = \frac{3}{2} kT$$

Where k is Boltzmann constant $= 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$

$$\begin{aligned} \therefore \frac{3}{2} kT &= \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 \\ &= 6.21 \times 10^{-21} \text{ J} \end{aligned}$$

As a result, at ambient temperature, the average thermal energy of a helium atom is (27°C) is $6.21 \times 10^{-21} \text{ J}$

(ii) the temperature on the surface of the Sun (6000 K),

Answer: On the surface of the sun, $T = 6000 \text{K}$

$$\text{Average thermal energy} = \frac{3}{2} kT$$

$$\begin{aligned} &= \frac{3}{2} \times 1.38 \times 10^{-23} \times 6000 \\ &= 1.241 \times 10^{-19} \text{ J} \end{aligned}$$

As a result, a helium atom on the sun's surface has an average thermal energy of $1.241 \times 10^{-19} \text{ J}$.

(iii) the temperature of 10 million Kelvin (the typical core temperature in the case of a star).

Answer: At temperature, $T = 10^7$ K

$$\text{Average thermal energy} = \frac{3}{2}kT$$

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 10^7 = 2.07 \times 10^{-16} \text{ J}$$

Hence, the average thermal energy of a helium atom at the core of a star is $2.07 \times 10^{-16} \text{ J}$.

13.8 Three vessels of equal capacity hoopen with 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 v_{rms} the largest?

Answer:

Yes. All of them have the same number of molecules in them. No. Neon has the highest root mean square speed.

The three jars have the same volume since their capacities are equal. As a result, each gas has the same pressure, volume, and temperature.

According to Avogadro's law, each of the three containers will contain an equal amount of the corresponding molecules.

This is the same as Avogadro's number, $N = 6.023 \times 10^{23}$.

The root mean square speed (v_{rms}) of a gas of mass m , and temperature T , is given by the relation:

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

Where, k is Boltzmann constant

For the given gases, k and T are constants.

So, v_{rms} rely on the mass of the atoms,

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

As a result, in each of the three cases, the root mean square speed of the molecules vary. The smallest of the three elements, neon, chlorine, and uranium hexafluoride, is neon. As a result, neon has the quickest root mean square speed of all the gases given.

13.9 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 = 39.9u, of He = 4.0u)

Answer: Temperature of the helium atom, $T_{\text{He}} = -20^{\circ}\text{C} = 253\text{K}$

Atomic mass of argon, $M_{\text{Ar}} = 39.9\text{u}$

Atomic mass of helium, $M_{\text{He}} = 4.0\text{u}$

Let, $(v_{\text{rms}})_{\text{Ar}}$ be the rms speed of argon.

Let $(v_{\text{rms}})_{\text{He}}$ be the rms speed of helium.

The *rms* speed of argon is given by:

$$(v_{\text{rms}})_{\text{Ar}} = \sqrt{\frac{3RT_{\text{Ar}}}{M_{\text{Ar}}}} \dots (i)$$

Where,

R is the universal gas constant

T_{Ar} is temperature of argon gas

The *rms* speed of helium is given by:

$$(v_{\text{rms}})_{\text{He}} = \sqrt{\frac{3RT_{\text{He}}}{M_{\text{He}}}} \dots (ii)$$

It is given that:

$$(v_{\text{rms}})_{\text{Ar}} = (v_{\text{rms}})_{\text{He}}$$

$$(v_{\text{rms}})_{\text{Ar}} = (v_{\text{rms}})_{\text{He}}$$

$$\sqrt{\frac{3RT_{\text{Ar}}}{M_{\text{Ar}}}} = \sqrt{\frac{3RT_{\text{He}}}{M_{\text{He}}}} \Rightarrow \frac{T_{\text{Ar}}}{M_{\text{Ar}}} = \frac{T_{\text{He}}}{M_{\text{He}}}$$

$$T_{\text{Ar}} = \frac{T_{\text{He}}}{M_{\text{He}}} \times M_{\text{Ar}}$$

$$= \frac{253}{4} \times 39.9$$

$$= 2523.675 = 2.52 \times 10^3 \text{ K}$$

So, the temperature of the argon atom is $2.52 \times 10^3 \text{ K}$.

13.10 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\AA . Compare the collision time with the time the molecule moves freely between two successive collisions (Molecular mass of $\text{N}_2 = 28.0\text{u}$).

Answer: Mean free path = $1.11 \times 10^{-7}\text{ m}$

Collision frequency = $4.58 \times 10^9\text{ s}^{-1}$

Successive collision time $\approx 500 \times (\text{Collision time})$

Pressure inside the cylinder containing nitrogen, $P = 2.0\text{ atm} = 2.026 \times 10^5\text{ Pa}$

Temperature inside the cylinder, $T = 17^\circ\text{C} = 290\text{ K}$

Radius of a nitrogen molecule, $r = 1.0\text{\AA} = 1 \times 10^{-10}\text{ m}$

Diameter, $d = 2 \times 1 \times 10^{-10} = 2 \times 10^{-10}\text{ m}$

Molecular mass of nitrogen, $M = 28.0\text{ g} = 28 \times 10^{-3}\text{ kg}$

The root mean square speed of nitrogen is:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Where,

R is the universal gas constant = $8.314\text{ J mole}^{-1}\text{ K}^{-1}$

$$\therefore v_{\text{rms}} = \sqrt{\frac{3 \times 8.314 \times 290}{28 \times 10^{-3}}} = 508.26\text{ m/s}$$

The mean free path (l) is given by the relation:

$$l = \frac{kT}{\sqrt{2} \times d^2 \times P}$$

Where, k is the Boltzmann constant = $1.38 \times 10^{-23}\text{ kg}$

$\text{m}^2\text{ s}^{-2}\text{ K}^{-1}$

$$\therefore l = \frac{1.38 \times 10^{-23} \times 290}{\sqrt{2} \times 3.14 \times (2 \times 10^{-10})^2 \times 2.026 \times 10^5}$$

$$= 1.11 \times 10^{-7}\text{ m}$$

$$\text{Collision frequency} = \frac{v_{\text{rms}}}{l}$$

$$= \frac{508.26}{1.11 \times 10^{-7}} = 4.58 \times 10^9\text{ s}^{-1}$$

Collision time is:

$$\begin{aligned}
 T &= \frac{d}{v_{\text{rms}}} \\
 &= \frac{2 \times 10^{-10}}{508.26} = 3.93 \times 10^{-13} \text{ s}
 \end{aligned}$$

Time taken between successive collisions:

$$\begin{aligned}
 T' &= \frac{l}{v_{\text{rms}}} \\
 &= \frac{1.11 \times 10^{-7} \text{ m}}{508.26 \text{ m/s}} = 2.18 \times 10^{-10} \text{ s} \\
 \therefore \frac{T'}{T} &= \frac{2.18 \times 10^{-10}}{3.93 \times 10^{-13}} = 500
 \end{aligned}$$

As a result, the period between subsequent collisions is *500 times* that of a single collision.

Additional Exercises

13.11 A metre long narrow bore held horizontally (and closed at one end) contains a 76 cm long mercury thread, which traps a 15 cm column of air. What happens if the tube is held vertically with the open end at the bottom?

Answer: Length of the narrow bore, $L = 1 \text{ m} = 100 \text{ cm}$

Length of the mercury thread, $l = 76 \text{ cm}$

Length of the air column between mercury and the closed end, $l_a = 15 \text{ cm}$

The mercury length that occupies the air space is: Because the bore is held vertically in air with the open end at the bottom, the mercury length that occupies the air space is: $100 - (76 + 15) = 9 \text{ cm}$

Hence, the total length of the air column $= 15 + 9 = 24 \text{ cm}$

Let $h \text{ cm}$ of mercury flow out because of atmospheric pressure.

So, Length of the air column in the bore $= 24 + h \text{ cm}$

And length of the mercury column $= 76 - h \text{ cm}$

Initial pressure, $P_1 = 76 \text{ cm}$ of mercury

Initial volume, $V_1 = 15 \text{ cm}^3$

Final pressure, $P_2 = 76 - (76 - h) = h \text{ cm}$ of mercury

Final volume, $V_2 = (24 + h)\text{cm}^3$

Throughout the procedure, the temperature remains constant.

$$\therefore P_1V_1 = P_2V_2$$

$$76 \times 15 = h(24 + h)h^2 + 24h - 1140 = 0$$

$$\therefore h = \frac{-24 \pm \sqrt{(24)^2 + 4 \times 1 \times 1140}}{2 \times 1}$$

$$= 23.8\text{cm or } -47.8\text{cm}$$

Height cannot be negative. Hence, 23.8cm of mercury will flow out from the bore and 52.2cm of mercury will remain in it. The length of the air column will be $24 + 23.8 = 47.8\text{cm}$.

13.12 From a certain apparatus, the diffusion rate of hydrogen has an average value of $28.7\text{cm}^3\text{s}^{-1}$. The diffusion of another gas under the same conditions is measured to have an average rate of $7.2\text{cm}^3\text{s}^{-1}$. Identify the gas.

[Hint: Use Graham's law of diffusion: $R_1 / R_2 = (M_2 / M_1)^{1/2}$, where R_1, R_2 are diffusion rates of gases 1 and 2, and M_1 and M_2 their respective molecular masses. The law is a simple consequence of kinetic theory.]

Answer: Rate of diffusion of hydrogen, $R_1 = 28.7\text{cm}^3\text{s}^{-1}$

Rate of diffusion of another gas, $R_2 = 7.2\text{cm}^3\text{s}^{-1}$

Using Graham's Law of diffusion,

$$\frac{R_1}{R_2} = \sqrt{\frac{M_2}{M_1}}$$

Where,

M_1 is the molecular mass of hydrogen = 2.020g

M_2 is the molecular mass of the unknown gas.

$$\therefore M_2 = M_1 \left(\frac{R_1}{R_2} \right)^2$$

$$= 2.02 \left(\frac{28.7}{7.2} \right)^2 = 32.09\text{g}$$

So, the molecular mass of oxygen is 32g. Hence, the unknown gas is oxygen.

13.13 A gas in equilibrium has uniform density and pressure throughout its volume. This is strictly true only if there are no external influences. A gas column under gravity, for example,

does not have uniform density (and pressure). As you might expect, its density decreases with height. The precise dependence is given by the so-called law of atmospheres

$$n_2 = n_1 \exp\left[-mg(h_2 - h_1)/k_B T\right]$$

Where n_2, n_1 refer to number density at heights h_2 and h_1 respectively. Use this relation to derive the equation for sedimentation equilibrium of a suspension in a liquid column:

$$n_2 = n_1 \exp\left[-mgN_A(\rho - \rho')(h_2 - h_1)/(\rho RT)\right]$$

Where ρ is the density of the suspended particle, and ρ' that of surrounding medium. [N_A is Avogadro's number, and R the universal gas constant.] [Hint: Use Archimedes principle to find the apparent weight of the suspended particle.]

Answer: Using the law of atmospheres:

$$n_2 = n_1 \exp\left[-mg(h_2 - h_1)/k_B T\right] \dots (i)$$

here, n_1 = number density at height h_1

n_2 = number density at height h_2

mg = weight of the particle suspended in the gas column,

Density of the medium = ρ'

Density of the suspended particle = ρ

Mass of one suspended particle = m'

Mass of the medium displaced = m

Volume of a suspended particle = V

Archimedes' principle asserts that for a particle suspended in a liquid column, the effective weight of the suspended particle is: Weight of the medium displaced - Weight of the suspended particle,

$$= mg - m'g = mg - V$$

$$\rho'g = mg - \left(\frac{m}{\rho}\right)\rho'g$$

$$= mg \left(1 - \frac{\rho'}{\rho}\right)$$

Gas constant,

$$R = k_B$$

$$k_B = \frac{R}{N} \dots (iii)$$

Putting equation (ii) in place of

$$= n_1 \exp \left[- mg \left(1 - \frac{\rho'}{\rho} \right)_{(h_2-h_1)} \frac{N}{RT} \right]$$

$$= n_1 \exp \left[- mg (\rho - \rho')_{(h_2-h_1)} \frac{N}{RT\rho} \right]$$

13.14 Given below are densities of some solids and liquids. Give rough estimates of the size of their atoms:

Substance	Atomic Mass (u)	Density (10^3 Kgm^{-3})
Carbon (diamond)	12.01	2.22
Gold	197.00	19.32
Nitrogen (liquid)	14.01	1.00
Lithium	6.94	0.53
Fluorine (liquid)	19.00	1.14

[Hint: Assume the atoms to be 'tightly packed' in a solid or liquid phase and use the known value of Avogadro's number. You should, however, not take the actual numbers you obtain for various atomic sizes too literally. Because of the crudeness of the tight packing approximation, the results only indicate that atomic sizes are in the range of a few Å].

Answer:

Substance	Radius Å
Carbon (diamond)	1.29
Gold	1.59
Nitrogen (liquid)	1.77
Lithium	1.73
Fluorine (liquid)	1.88

Atomic mass of a substance = M

Density of the substance = ρ

Avogadro's number = $N = 6.023 \times 10^{23}$

Volume of each atom = $\frac{4}{3} \pi r^3$

Volume of N number of molecules = $\frac{4}{3} \pi r^3 N \dots (i)$

Volume of one mole of a substance = $\frac{M}{\rho} \dots (ii)$

$$\frac{4}{3}\pi r^3$$

$$N = \frac{M}{\rho}$$

$$\therefore r = \sqrt[3]{\frac{3M}{4\pi\rho N}}$$

For carbon: $M = 12.01 \times 10^{-3} \text{ kg}$, $\rho = 2.22 \times 10^3 \text{ kg m}^{-3}$

$$\therefore r = \left(\frac{3 \times 12.01 \times 10^{-3}}{4\pi \times 2.22 \times 10^3 \times 6.023 \times 10^{23}} \right)^{\frac{1}{3}} = 1.29 \text{ \AA}$$

Hence, the radius of a carbon atom is 1.29 \AA .

For gold: $M = 197.00$

$$\times 10^{-3} \text{ kg} \rho = 19.32 \times 10^3 \text{ kg m}^{-3}$$

$$\therefore r = \left(\frac{3 \times 197 \times 10^{-3}}{4\pi \times 19.32 \times 10^3 \times 6.023 \times 10^{23}} \right)^{\frac{1}{3}} = 1.59 \text{ \AA}$$

$$\times 10^{-3} \text{ kg} \rho = 19.32 \times 10^3 \text{ kg m}^{-3}$$

$$\therefore r = \left(\frac{3 \times 197 \times 10^{-3}}{4\pi \times 19.32 \times 10^3 \times 6.023 \times 10^{23}} \right)^{\frac{1}{3}} = 1.59 \text{ \AA}$$

Hence, the radius of a gold atom is 1.59 \AA .

For liquid nitrogen:

$$M = 14.01 \times 10^{-3} \text{ kg}$$

$$\rho = 1.00 \times 10^3 \text{ kg m}^{-3}$$

$$\therefore r = \left(\frac{3 \times 14.01 \times 10^{-3}}{4\pi \times 1.00 \times 10^3 \times 6.23 \times 10^{23}} \right)^{\frac{1}{3}} = 1.77 \text{ \AA}$$

Hence, the radius of a liquid nitrogen atom is 1.77 \AA .

For lithium:

$$M = 6.94 \times 10^{-3} \text{ kg}$$

$$\rho = 0.53 \times 10^3 \text{ kg m}^{-3}$$

$$\therefore r = \left(\frac{3 \times 6.94 \times 10^{-3}}{4\pi \times 0.53 \times 10^3 \times 6.23 \times 10^{23}} \right)^{\frac{1}{3}} = 1.73 \text{ \AA}$$

Hence, the radius of a lithium atom is 1.73 \AA .

For liquid fluorine:

$$M = 19.00 \times 10^{-3} \text{ kg}$$

$$\rho = 1.14 \times 10^3 \text{ kg m}^{-3}$$

$$\therefore r = \left(\frac{3 \times 19 \times 10^{-3}}{4\pi \times 1.14 \times 10^3 \times 6.023 \times 10^{23}} \right)^{\frac{1}{3}} = 1.88 \text{ \AA}$$

As a result, a liquid fluorine atom's radius is 1.88 Å.