### Kinetic Theory



1. Calculate the fraction of molecular volume to the actual volume occupied by oxygen gas at STP. Consider taking the diameter of an oxygen molecule to be 3 Å.

#### Ans:

The diameter of an oxygen molecule is given as: d = 3A

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

At STP, the actual volume occupied by 1 mole of oxygen gas is given as:  $22400 \text{ cm}^3$ .

The molecular volume of oxygen gas is given as:  $V = \frac{4}{3}\pi r^3 N_A$ 

Where,  $N_A$  is Avogadro's number:  $6.023 \times 10^{23}$  molecules / mole. Hence:

V = 
$$\frac{4}{3}$$
πr<sup>3</sup>.N<sub>A</sub>  
⇒  $\frac{4}{3}$ ×3.14×(1.5×10<sup>-8</sup>)<sup>3</sup> 6.023×10<sup>23</sup>  
⇒ 8.51cm<sup>3</sup>

Therefore, the molecular volume of one mole of oxygen gas will be 8.51cm<sup>3</sup>.

Now, the ratio of the molecular volume to the actual volume of oxygen can be given as:

$$\frac{V_{molar}}{V_{actual}} = \frac{8.51}{22400} = 3.8 \times 10^{-4}$$

2. The volume which is occupied by 1 mole of any (ideal) gas at standard temperature and pressure (STP: 1 atmospheric pressure,  $0^{\circ}C$ ) is molar volume. Show that it is 22.4 liters.

#### Ans:

The ideal gas equation is:

PV = nRT

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

n is the number of moles, n = 1

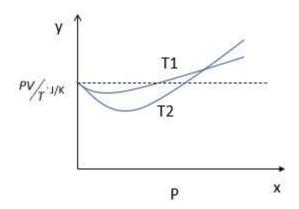
T is standard temperature, T = 273K

P is standard pressure,  $P = 1atm = 1.013 \times 10^5 Nm^{-2}$ 

:. 
$$V = \frac{nRT}{P}$$
  
 $V = \frac{1 \times 8.314 \times 273}{1.013 \times 10^5} = 0.0224 \text{ m}^3 = 22.4 \text{ litres}$ 

So, we can say that the molar volume of a gas is 22.4 liters at STP.

3. The diagram below shows a plot of  $\frac{PV}{T}$  versus P for  $1.00 \times 10^{-3}$  Kg oxygen gas at two different temperatures.



a) What does the dotted plot signify?

#### Ans:

In the graph, the dotted plot signifies the ideal behavior of the gas, i.e., the ratio  $\frac{PV}{T}$  is equal.  $\mu R$  is a constant quality.

 $\mu$  is the number of moles

R is the universal gas constant

It is independent on the pressure of the gas.

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

#### Ans:

In the given graph, the dotted plot represents an ideal gas. At temperature  $T_1$ , the curve of the gas is very closer to the dotted plot than for the curve of the gas at temperature  $T_2$ . The behavior of a real gas approaches ideal gas when its temperature increases. Therefore,  $T_1 > T_2$  is true.

# c) $\frac{PV}{T}$ value, where the curves meet on the y-axis is?

#### Ans:

The ratio  $\frac{PV}{T}$  for the meeting of two curves is  $\mu R$ . So, the ideal gas equation is,

 $PV = \mu RT$ 

Where P is the pressure

T is the temperature

V is the volume

 $\mu$  is the number of moles

R is the universal constant

The molecular mass of oxygen=32.0g

Mass of oxygen =  $1 \times 10^{-3}$ kg = 1g

 $R = 8.314 Jmol^{-1}K^{-1}$ 

$$\therefore \frac{PV}{T} = \frac{1}{32} \times 8.314 = 0.26 J K^{-1}$$

The value of the ratio

So, the value of the ratio  $\frac{PV}{T}$ , where the curves meet on the *y*-axis, is 0.26JK<sup>-1</sup>

d) Will we be getting the same value of  $PV_T$  at the point where the curves meet on the y-axis, if for  $1.00 \times 10^{-3}$ Kg of hydrogen we get similar plots? Mass of hydrogen that produces the same value of  $PV_T$  (for a lowpressure high-temperature region of the plot) if it is not the case? (Molecular mass of  $H_2 = 2.02u$ ,  $O_2 = 32.0u$ , and R = 8.314Jmol<sup>-1</sup>K<sup>-1</sup>)

#### Ans:

If a similar plot for  $1.00 \times 10^{-3}$ Kg of hydrogen, then we won't get the same value of  $\frac{PV}{T}$  at the point where the curves meet the y-axis. Since the molecular mass of hydrogen (2.02 u) is not the same as that of oxygen (32.0 u).

We have:

$$\therefore \frac{\mathrm{PV}}{\mathrm{T}} = 0.26 \mathrm{JK}^{-1}$$

 $R = 8.314 Jmol^{-1}K^{-1}$ 

Molecular mass M of  $H_2 = 2.02u$ 

 $PV = \mu RT$  at constant temperature

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

m is the mass of  $H_2$ 

$$m = \frac{PV}{T} \times \frac{M}{R} = \frac{0.26 \times 2.02}{8.31} = 6.3 \times 10^{-2} g = 6.3 \times 10^{-5} kg$$

Hence,  $6.3 \times 10^{-2}$  g of H<sub>2</sub> will get the same value of  $\frac{PV}{T}$ 

4. A 30 liters oxygen cylinder has an initial gauge pressure of 15 atm and a temperature of  $27^{\circ}$ C. The gauge pressure drops to 11 atm, and its temperature drops to  $17^{\circ}$ C when some oxygen is withdrawn from the cylinder. Estimate the mass of oxygen taken out of the cylinder (R = 8.314Jmol<sup>-1</sup>K<sup>-1</sup>, the molecular mass of O<sub>2</sub> = 32u).

Ans:

The volume of oxygen,  $V_1 = 30$  litres  $= 30 \times 10^{-3}$  m<sup>3</sup>

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

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

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

Consider the initial number of moles of oxygen gas in the cylinder be  $n_1$ 

The gas equation is given as:

P<sub>1</sub>V<sub>1</sub> = n<sub>1</sub>RT<sub>1</sub>  
∴ n<sub>1</sub> = 
$$\frac{P_1V}{RT_1} = \frac{15.195 \times 10^5 \times 30 \times 10^{-3}}{8.314 \times 300} = 18.276$$

But  $n_1 = \frac{m_1}{M}$ 

Where,

 $m_1$  = the initial mass of oxygen

M = The molecular mass of oxygen = 32g

 $\therefore m_1 = n_1 M = 18.276 \times 32 = 584.84g$ 

The pressure and temperature reduce after some oxygen is withdrawn from the cylinder.

Volume,  $V_2 = 30$  itres  $= 30 \times 10^{-3}$  m<sup>3</sup>

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

Temperature,  $T_2 = 17^0 C = 290 K$ 

Let consider  $n_2$ , the number of moles of oxygen left in the cylinder.

The gas equation is given as:

P<sub>2</sub>V<sub>2</sub> = n<sub>2</sub>RT<sub>2</sub>  
∴ n<sub>2</sub> = 
$$\frac{P_2V_2}{RT_2}$$
 =  $\frac{11.143 \times 10^5 \times 30 \times 10^{-3}}{8.314 \times 290}$  = 13.86  
But, n<sub>2</sub> =  $\frac{m_2}{M}$ 

Where,

The remaining mass of oxygen in the cylinder is  $m_2$ 

 $\therefore m_2 = n_2 M = 13.86 \times 32 = 443.52g$ 

So, the mass of oxygen taken out is:

The initial mass of oxygen in the cylinder - Final mass of oxygen in the cylinder

 $\Rightarrow$  m<sub>1</sub> - m<sub>2</sub> = 584.84 - 443.522 = 141.32g = 0.141kg

0.141kg of oxygen is hence taken out of the cylinder.

5. An air bubble which is having a volume 1.0cm<sup>3</sup> rises from the bottom of a lake 40 m deep at a temperature of 12<sup>°</sup>C. When it reaches the surface, which is at a temperature of 35<sup>°</sup>C, to what volume does it grow?

#### Ans:

The volume of the air bubble,  $V_1 = 1.0$  cm<sup>3</sup> =  $1.0 \times 10^{-6}$  m<sup>3</sup>

The bubble rises to height, d = 40m

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

The temperature is  $T_2 = 35^{\circ}C = 308K$ , at the surface of the lake

On the surface of the lake the pressure,

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

The pressure at the depth of 40m,  $P_1 = 1atm + d\rho g$ 

Where,

 $\rho$  is the density of water =  $10^3$  kgm<sup>-3</sup>

g is the acceleration due to  $gravity = 9.8 m s^{-1}$ 

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

We have: 
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

 $V_2$  is the air bubbles volume when it reaches the surface

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{493300 \times 1.0 \times 10^{-6} \times 308}{285 \times 1.013 \times 10^5} = 5.263 \times 10^{-6} \text{ m}^3 = 5.263 \text{ cm}^3$$

The volume of air bubble becomes 5.263 cm<sup>3</sup> when it reaches the surface.

6. Determine the total number of air molecules (that includes oxygen, nitrogen, water vapor, and other constituents) in a room of capacity 25.0m<sup>3</sup> at a temperature of (27<sup>o</sup>C) and 1atm pressure.

#### Ans:

The volume of the room,  $V = 25.0 \text{m}^3$ 

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

Pressure in the room,  $P = 1atm = 1 \times 1.1013 \times 10^5 Pa$ 

The ideal gas equation:

 $PV = K_BNT$ 

Where,

 $K_{B}$  is Boltzmann constant,  $K_{B} = 1.38 \times 10^{-23} \text{ m}^{2} \text{kgs}^{-2} \text{K}^{-1}$ 

Number of air molecules in the room be N.

N = 
$$\frac{PV}{k_BT}$$
 =  $\frac{1.013 \times 10^5 \times 25}{1.38 \times 10^{-23} \times 300}$  = 6.11×10<sup>26</sup> molecules

The total number of air molecules is  $6.11 \times 10^{26}$ 

- 7. Find out the average thermal energy of a helium atom at the following cases:
- i. Room temperature  $(27^{\circ}C)$

#### Ans:

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

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

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

$$\therefore \frac{3}{2} \mathrm{kT} = \frac{3}{2} \times 1.38 \times 10^{-38} \times 300 = 6.21 \times 10^{-21} \mathrm{J}$$

So, the average thermal energy is  $(27^{\circ}C)$  is  $6.21 \times 10^{-21}$  J

#### ii. The temperature on the sun's surface (6000K)

#### Ans:

On the surface of the sun, T = 6000K

Average thermal energy =  $\frac{3}{2}$ kT =  $\frac{3}{2}$ ×1.38×10<sup>-38</sup>×6000 = 1.241×10<sup>-19</sup> J

Hence, the average thermal energy is  $1.241 \times 10^{-19}$  J

### iii. At a temperature of 10 million kelvin ( the typical core temperature in the case of a star).

#### Ans:

At temperature,  $T = 10^7 K$ 

Average thermal energy =  $\frac{3}{2}$ kT =  $\frac{3}{2}$ ×1.38×10<sup>-23</sup>×10<sup>7</sup> = 2.07×10<sup>-16</sup>J

Hence, the average thermal energy is  $2.07 \times 10^{-16}$  J.

- 8. Three vessels all of the same capacity have gases at the same pressure and temperature. It consists of neon which is monatomic, in the first one, the second contains diatomic chlorine, and the third contains uranium hexafluoride (polyatomic).
- a) Do you think all the vessels contain an equal number of respective molecules?

#### Ans:

Yes. The same number of the respective molecules is there in all the vessels.

They have the same volume since the three vessels have the same capacity.

All gases are of same pressure, volume, and temperature.

Avogadro's law states the three vessels consist of an equal number of molecules. This equals Avogadro's number,  $N = 6.023 \times 10^{23}$ .

## b) Is in all three cases, the root mean square speed of molecules the same? If it is not the case, in which case is $v_{rms}$ the largest?

#### Ans:

No. Neon has the largest root-mean-square speed.

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

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

Where k is Boltzmann constant

k and T are constants for the given gases.

 $\boldsymbol{v}_{\text{rms}}$  only depends on the mass of the atoms, i.e.,

$$v_{rms}\alpha\sqrt{\frac{1}{m}}$$

So, in the three cases, the root-means-square speed of the molecules is not the same.

The mass of neon is the smallest among neon, chlorine, and uranium hexafluoride and so possesses the largest root mean square speed.

9. Calculate the temperature at which the root mean square speed of an argon atom in a gas cylinder is equal to the RMS speed of a helium gas atom at  $-20^{\circ}$  C? (atomic mass of Ar = 39.9 u, of He = 4.0 u)

#### Ans:

The temperature of the helium atom,  $T_{He} = -20^{\circ}C = 253K$ 

The atomic mass of argon,  $M_{Ar} = 39.9u$ 

The atomic mass of helium,  $M_{He} = 4.0u$ 

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

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

Argon as an rms speed of,

$$\left(v_{rms}\right)_{Ar} = \sqrt{\frac{3RT_{Ar}}{M_{Ar}}}$$
 .....(i)

Where,

R is the universal gas constant

 $T_{\!A\!r}$  is the temperature of argon gas

Helium has an rms speed of,

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

It is given that:

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

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

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

$$T_{Ar} = \frac{T_{He}}{M_{He}} \times M_{Ar} = \frac{253}{4} \times 39.9 = 2523.675 = 2.52 \times 10^3 \text{ K}$$

Argon atom is at a temperature of  $2.52 \times 10^3 \text{K}$ 

10. Find out the collision frequency and also the mean free path of a nitrogen molecule in a cylinder containing nitrogen at 2.0 atm and temperature

 $17^{\circ}$ C. The nitrogen molecule has a radius of roughly 1.0Å. How collision time is related with the time the molecule moves freely between two successive collisions (Molecular mass of N<sub>2</sub> = 28.0u).

#### Ans:

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

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

Successive collision time  $\approx 500 \times \text{collision}$  time

The pressure inside the cylinder containing nitrogen,  $P = 2.0atm = 2.026 \times 10^5 Pa$ 

Temperature inside the cylinder,  $T = 17^{\circ}C = 290K$ The radius of nitrogen molecule,  $r = 1.0 \stackrel{o}{A} = 1 \times 10^{10} \text{ m}$ Diameter,  $d = 2 \times 1 \times 10^{10} = 2 \times 10^{10} \text{ m}$ Molecular mass of nitrogen,  $M = 28.0g = 28 \times 10^{-3} \text{ kg}$ 

For the nitrogen, root mean square speed is,

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

Where,

R = 8.314 mole<sup>-1</sup> $K^{-1}$ , is universal gas constant

$$\frac{\overline{3 \times 8.314 \times 290}}{28 \times 10^{-3}}$$
The mean free path (1) is, = 508.26ms
$$1 = \frac{kT}{\sqrt{2} \times d^2 \times P}$$

Where,

 $k\!=\!1.38\!\times\!10^{-23}kgm^2s^{-2}K^{-1}$  is the Boltzmann constant

$$\therefore 1 = \frac{1.38 \times 10^{-23} \times 290}{\sqrt{2} \times 3.14 \times (2 \times 10^{-10})^2 \times 2.026 \times 10^5} = 1.11 \times 10^{-7} \,\mathrm{m}$$

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

The collision time is given as:

$$T = \frac{d}{v_{rms}} = \frac{2 \times 10^{-10}}{508.26} = 3.93 \times 10^{-13} s$$

Between successive collisions, the time taken is

$$T' = \frac{1}{v_{rms}} = \frac{1.11 \times 10^{-7} \text{ m}}{508.26 \text{ ms}^{-1}} = 2.18 \times 10^{-10} \text{ s}$$
$$\therefore \frac{T'}{T} = \frac{2.18 \times 10^{-10}}{3.93 \times 10^{-13}} = 500$$

For successive collisions, the time taken is 500 times the time taken for a collision.