

Problem: The diameter of nitrogen molecule is 3.15×10^{-10} m. What are the mean free and the average rate of collision for nitrogen at room temp. 300K and at atmospheric pressure.

The number of molecules per unit volume under given conditions is given by

$$PV = NkT$$

$$\frac{N}{V} = \frac{P}{kT}$$

$$n = \frac{P}{kT} = \frac{1.01 \times 10^5 \text{ Nm}^{-2}}{1.38 \times 10^{-23} \times 300}$$

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$$= 2.44 \times 10^{23} \text{ molecules}$$

diameter of nitrogen molecule $d = 3.15 \times 10^{-10}$ m
 λ mean free path is given by

$$\lambda = \frac{1}{\sqrt{2} n \pi d^2} = \frac{1}{\sqrt{2} \times 2.44 \times 10^{23} \times 3.14 \times (3.15 \times 10^{-10})^2}$$

$$\lambda = 9.3 \times 10^{-8} \text{ m}$$

which is about 300 times the diameter of nitrogen molecules

To find the average rate of collision we first find the average speed given by

$$v_{r.m.s} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 300}{0.0028 \text{ kg}}}$$

important:

$$M = 28 \text{ g} = 0.028 \text{ kg}$$

molecular mass

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$$\text{Average rate of collision} = \frac{v}{\lambda}$$

$$= 5.6 \times 10^9 \text{ per second.}$$

Problem: Calculate (i) Average k.E of translation of 1 molecule of hydrogen
(ii) Average k.E of translation for mole of hydrogen
(iii) Root mean square velocity of hydrogen molecule at 27°C

$$\langle k.E \rangle = \frac{3}{2} kT$$
$$v = \sqrt{\frac{3kT}{m}}$$

(i) Use for 1 molecule

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT \quad \text{--- (1)}$$
$$= \frac{3}{2} \times 3.81 \times 10^{-23} \times 300$$
$$= 6.21 \times 10^{-21} \text{ Joules}$$

(ii) For 1 mole of gas

$$N_A \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k N_A T$$
$$= \frac{3}{2} RT$$
$$= \frac{3}{2} \times 1.83 \times 300$$

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

mass of hydrogen molecule = $2 \times 1.67 \times 10^{-27}$
 $3.34 \times 10^{-27} \text{ kg}$

$$v_{rms} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 300}{3.34 \times 10^{-27}}}$$

$$= \sqrt{\frac{1242 \times 10^{-22}}{3.34 \times 10^{-27}}} = \sqrt{371.85 \times 10^5} = 6097.95$$

$$= 1.94 \times 10^5 \text{ m s}^{-1}$$

MAXWELL'S VELOCITY DISTRIBUTION:

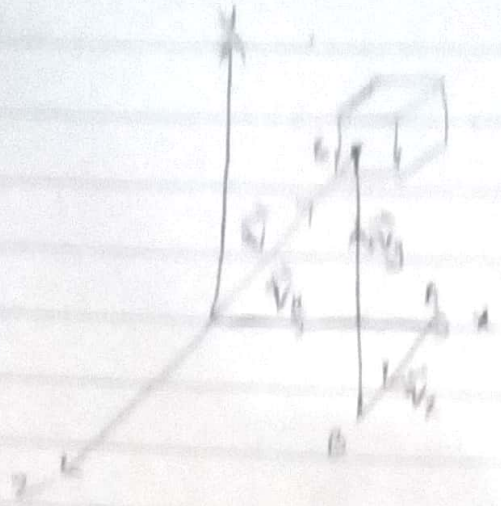
The average square velocity of molecule is defined by the relation

$$\bar{v}^2 = \frac{\sum_{i=1}^N v^2}{N}$$

$$\text{or } \bar{v}^2 = \frac{1}{N} \int v^2 dN(v)$$

where $dN(v)$ denote the number of molecules having velocity in the range v and $v+dv$.

An expression for $dN(v)$ in terms of v is known as Maxwell's law of distribution of velocities



Consider a velocity space in which the components v_x, v_y, v_z of a velocity vector \vec{v} are plotted along rectangular axes with $v^2 = v_x^2 + v_y^2 + v_z^2$

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

Each velocity vector in the velocity space is completely defined by the coordinates of its end point. Thus the number of points in any volume element

dV_x, dV_y and dV_z in the velocity space gives the number of molecules if the number of molecules having velocity components b/w v_x and $v_x + dv_x, v_y$ and $v_y + dv_y, v_z$ and $v_z + dv_z$

\Rightarrow There are N molecules as endpoints only a fraction $\frac{dN(v_x)}{N}$ will have a component of velocity in the range v_x and $v_x + dv_x$

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→ The assumption of chaos ^(Ergodic) says that this fraction is a function of v_x only and is proportional to dv_x . That

$$\frac{dN(v_x)}{N} = f(v_x) dv_x$$

$$dN(v_x) = N f(v_x) dv_x \quad \text{--- (1)}$$

Similarly we have for y and z directions

$$dN(v_y) = N f(v_y) dv_y \quad \text{--- (2)}$$

$$dN(v_z) = N f(v_z) dv_z \quad \text{--- (3)}$$

Since a molecule having x component of velocity v_x and have y component of velocity v_y , the fraction of molecules having both x & y components of velocity can be said to be equal to the fraction of the total number of having y component of velocity in the range v_y and $v_y + dv_y$ that is

$$\frac{dN^2(v_x, v_y)}{dN(v_y)} = \frac{dN(v_x)}{N}$$

using eq (1) & (2) we get

$$dN^2(v_x, v_y) = \frac{dN(v_x)}{N} dN(v_y)$$

using eq (1) & (2)

$$dN^2(v_x, v_y) = \frac{N f(v_x) dv_x \cdot N f(v_y) dv_y}{N}$$

$$\text{Using eq (1) \& (2)} \quad dN^2 = N f(v_x) f(v_y) dv_x dv_y$$

→ Reasoning as before the number of molecules simultaneously having velocities in the range v_x and $v_x + dv_x$, v_y and $v_y + dv_y$, v_z and $v_z + dv_z$ is given by

$$dN^3(v_x, v_y, v_z) = N f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z \quad \text{--- (4)}$$

where $dN^3(v_x, v_y, v_z)$ is a differential of 3rd order eq (4) the number of endpoints in the volume elements $(dv_x dv_y dv_z)$ and (density of points in points is unit volume). in

The velocity space is given by

$$\rho = \frac{dN^3(v_x, v_y, v_z)}{dv_x dv_y dv_z} = N f(v_x) f(v_y) f(v_z) \quad \text{--- (5)}$$

Since velocity is isotropic, ^{same structure} density should be constant at all points on the sphere

$v_x^2 + v_y^2 + v_z^2 = v^2$ of radius v is the velocity space.

Hence $N f(v_x) f(v_y) f(v_z) = \text{constant}$ --- (6)

when $v_x^2 + v_y^2 + v_z^2 = \text{constant}$ --- (7)

The eq (7) is called the eq of constraint as it reduces independent variables from ~~3~~ three to two.

important: partial differentiation of the eq (6) & (7)