KINETIC THEORY & THE BOLTZMANN FACTOR

Q1/ Mean free path of a molecule $\boxed{l = \dfrac{1}{\pi\sqrt{2}\, d^2 n}}$ # molecules / unit volume

(i) d is molecular diameter $= 0.3\times10^{-9}$ m.

If an ideal gas: $pV = \underbrace{\dfrac{nV}{N_A}}_{\#\text{moles}} RT$ and $k_B = \dfrac{R}{N_A}$

$\therefore\quad n = p/k_BT$

$\therefore\quad \boxed{l = \dfrac{k_BT}{\pi\sqrt{2}\, d^2 p}}$ So $l = \dfrac{1.381\times10^{-23}\times(20+273)}{\pi\sqrt{2}\,(0.3\times10^{-9})^2\times101325}$

$= \boxed{9.99\times10^{-8}\text{ m}}$

$kn = \dfrac{l}{d} = \boxed{333}$ so a statistical approach is valid.

ie the mean free path is >> than molecular dimensions so random collisions between molecules, with plenty of empty space in between.

(ii) $\boxed{\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}k_BT}$ for an O_2 molecule.

Mean kinetic energy

$\therefore\quad v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\dfrac{3k_BT}{m}}$

$= \sqrt{\dfrac{3\times1.381\times10^{-23}\times(20+273)}{15.999\times1.661\times10^{-27}}}$

$= \boxed{687\text{ m/s}}$ Pretty fast!

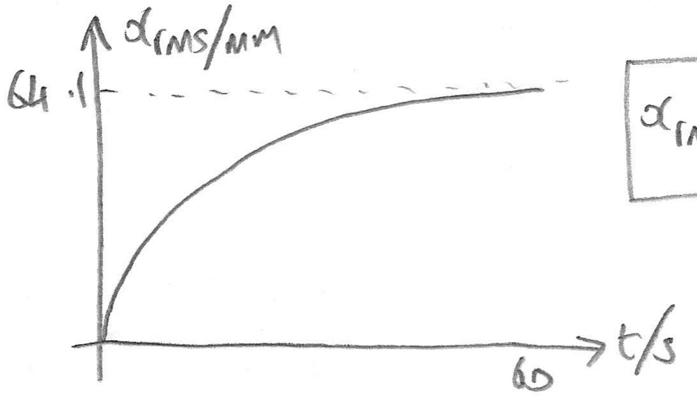
(iii) RMS distance $\sqrt{\langle x^2\rangle} = \sqrt{l\langle v\rangle t}$

$\sqrt{l\langle v\rangle} = \sqrt{9.99\times10^{-8}\times687} = 8.28\times10^{-3}$

so $\boxed{x_{rms} = 8.28\times10^{-3}\sqrt{(t/s)}}$ (m)

In 60s, the O_2 molecule will travel an RMS distance:

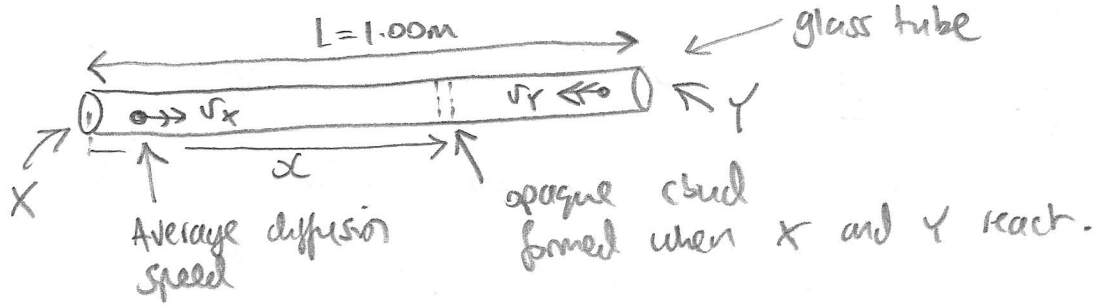
$$x_{rms} = 8.28 \times 10^{-3} \times \sqrt{60} \quad (m)$$
$$= \boxed{64.1\,mm}$$



$$\boxed{x_{rms}/mm = 8.28\sqrt{t/s}}$$

ie about 6.41 cm. so not much really.

(ii)



Constant temperature ∴ all molecules have the same average KE

$$\therefore \tfrac{1}{2} M_X v_X^2 = \tfrac{1}{2} M_Y v_Y^2 \quad \Rightarrow \quad \boxed{\frac{v_X}{v_Y} = \sqrt{\frac{M_Y}{M_X}}}$$

let cloud form after t seconds at x metres from the entry point of gas X.

$$\left.\begin{aligned} x &= v_x t \\ x &= L - v_y t \end{aligned}\right\} \quad \therefore \quad \begin{aligned} v_x t &= L - v_y t \\ (v_x + v_y)t &= L \end{aligned} \quad \Bigg| \quad \therefore \boxed{t = \frac{L}{v_x + v_y}}$$

∴ opaque cloud forms at: $x = \dfrac{v_x L}{v_x + v_y}$

$$x = \frac{v_x/v_y}{v_x/v_y + 1} L \quad \Rightarrow \quad \boxed{x = \frac{\sqrt{M_Y/M_X}}{\sqrt{\frac{M_Y}{M_X}} + 1} L}$$

So if $M_x = 17 g/mol$ and $M_y = 36.5 g/mol$

$\uparrow$ Ammonia (NH_3) — $\uparrow$ Hydrochloric acid vapour (HCl)

$$\therefore \quad x = \frac{\sqrt{35.5/17}}{\sqrt{\frac{35.5}{17}}+1} \times 1.00\,(m) = \boxed{0.59\,m}$$

If $M_y \rightarrow 3M_y$

$$x \rightarrow \frac{\sqrt{3\times 35.5/17}}{\sqrt{\frac{3\times 35.5}{17}}+1} \times 1.00\ m$$

$$\rightarrow \boxed{0.72\,m}$$

(v)

sealed syringe containing gas at volume V and pressure p

Temperature remains at a constant 18°C.

if no leaks $n =$ constant

Ideal gas: $pV = nRT$

so $\boxed{pV = \text{constant}}$ (Boyle's law).

Mean free path: $\boxed{l = \frac{k_B T}{\pi\sqrt{2}\, d^2 p}}$

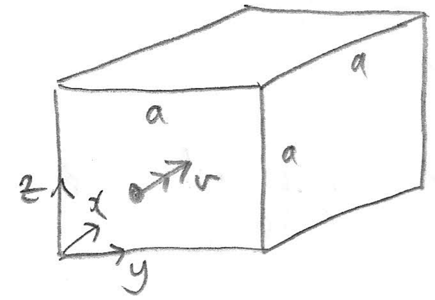
let $l = d$ $\therefore$ $p = \frac{k_B T}{\pi \sqrt{2}\, d^3}$

$$\therefore \quad p = \frac{1.381\times10^{-23}\times(18+273)}{\pi\sqrt{2}\times(0.4\times10^{-9})^3} = 1.413\times10^{7}\ Pa$$

$$= \boxed{139\ atm}$$

If mean free path $\simeq d$ then matter state will be either liquid or solid.

(vi)



(N molecules / Volume a^3)

* Let gas molecule of mass m have velocity $v_{x,y,z}$ in x,y,z directions.
* Assume it bounces off the walls elastically, $\therefore$ momentum change is $2m v_{x,y,z}$ per bounce.
* Each bounce occurs every $\Delta t_{x,y,z} = \dfrac{2a}{v_{x,y,z}}$

So rate of change of momentum is $\dfrac{2m v_{x,y,z}}{2a/v_{x,y,z}} = \dfrac{m v_{x,y,z}^2}{a}$

* Hence force per unit area on any face of the cube is:

$\dfrac{N m \overline{v_{x,y,z}^2}}{a^3}$ where $\overline{v_{x,y,z}^2}$ means the mean average.

Now density $\rho = \dfrac{Nm}{a^3}$ and since $v^2 = v_x^2 + v_y^2 + v_z^2$

and $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \overline{v_{x,y,z}^2}$ if motion is random

$\Rightarrow \overline{v_{x,y,z}^2} = \frac{1}{3}\overline{v^2}$

$\therefore$ Since force per unit area of any cube face = pressure

$\therefore$ $\boxed{p = \frac{1}{3}\rho \overline{v^2}}$

If $\rho = 1.23\ \text{kg/m}^3$, $p = 101{,}325$ Pa

$\Rightarrow v_{rms} = \sqrt{\overline{v^2}} = \sqrt{3p/\rho} = \sqrt{\dfrac{3 \times 101325}{1.23}}$

$= \boxed{497\ \text{m/s}}$

(vii) Time for a chemical reaction to complete is t where:

$$\boxed{\frac{1}{t} = Ae^{-\varepsilon/RT}}$$

$t_1 = 30.0\,s$, $T_1 = 300\,k$ $\therefore$ $e^{\varepsilon/RT_1} = At_1$ (1)

$t_2 = 7.0\,s$, $T_2 = 340\,k$ $e^{\varepsilon/RT_2} = At_2$ (2)

$(1)/(2)$: $\frac{t_1}{t_2} = e^{\frac{\varepsilon}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$

$$\therefore \ln\left(\frac{t_1}{t_2}\right) = \frac{\varepsilon}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\therefore \boxed{\varepsilon = \frac{R\ln\left(t_1/t_2\right)}{\frac{1}{T_1} - \frac{1}{T_2}}}$$

$$\therefore \varepsilon = \frac{8.314\ln\left(\frac{30.0}{7.0}\right)}{\frac{1}{300} - \frac{1}{340}} = \boxed{3.09\times10^4\,J}$$

$(30.9\,kJ)$

$\therefore$ in (1): $A = \frac{e^{\varepsilon/RT_1}}{t_1}$

$$A = \frac{e^{\varepsilon/8.314\times300}}{30.0}$$

$$= \frac{e^{12.37}}{30.0}$$

$$= \boxed{7854\,s^{-1}}$$

So $\frac{1}{t} = 7854e^{-\varepsilon/RT}$

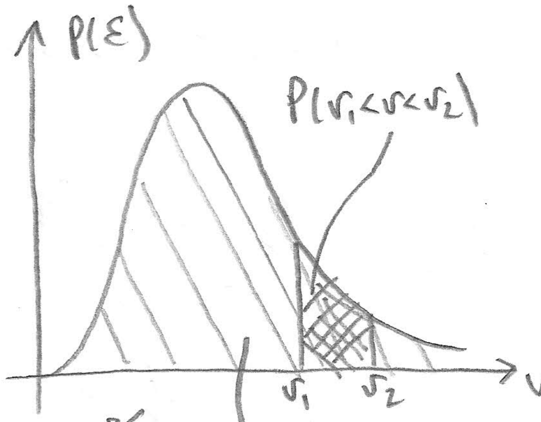
where $\varepsilon = 3.09\times10^4$

(5)

(viii) $\boxed{\text{Maxwell-Boltzmann}}$ distribution of molecular speed

$$p(\varepsilon) = \frac{2}{\sqrt{\pi}}\left(\frac{1}{k_BT}\right)^{3/2}\sqrt{\varepsilon}\, e^{-\varepsilon/k_BT}$$ (KE distribution) $\varepsilon = \frac{1}{2}mv^2$

$$p(v) = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2 e^{-\frac{\frac{1}{2}mv^2}{k_BT}}$$ (speed distribution)



$$\int_0^\infty p(\varepsilon)\,d\varepsilon = \frac{2}{\sqrt{\pi}}\left(\frac{1}{k_BT}\right)^{3/2}\int_0^\infty \sqrt{\varepsilon}\, e^{-\varepsilon/k_BT}\,d\varepsilon$$

$\varepsilon = \frac{1}{2}mv^2$ $\qquad \sqrt{\varepsilon} = \frac{1}{\sqrt{2}}\sqrt{m}\,v$

$d\varepsilon = mv\,dv$

$$\therefore \int_0^\infty p(\varepsilon)\,d\varepsilon = \frac{2}{\sqrt{\pi}}\left(\frac{1}{k_BT}\right)^{3/2}\int_0^\infty v^2 e^{-\frac{1}{2}mv^2/k_BT}\,dv \times \frac{m^{3/2}}{\sqrt{2}}$$

$\int_0^\infty p(v)\,dv = 1$ since a continuous probability distribution.

$$= \frac{\sqrt{2}}{\sqrt{\pi}}\left(\frac{m}{k_BT}\right)^{3/2}\int_0^\infty v^2 e^{-\frac{1}{2}mv^2/k_BT}\,dv$$

$$= \frac{\sqrt{2}(2\pi)^{3/2}}{\sqrt{\pi}}\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^\infty v^2 e^{-\frac{1}{2}mv^2/k_BT}\,dv$$

$$= 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^\infty v^2 e^{-\frac{1}{2}mv^2/k_BT}\,dv$$

$$= \boxed{\int_0^\infty p(v)\,dv}$$

So if $\int_0^\infty p(v)\,dv = 1$ then so is $\int_0^\infty p(\varepsilon)\,d\varepsilon$

$$\int_0^\infty p(v)\,dv = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^\infty v^2 e^{-\frac{1}{2}mv^2/k_BT}\,dv$$

Now $\int_0^\infty x^2 e^{-ax^2}\,dx = \frac{2-1}{2a} I_0 = \frac{1}{2a}\,\frac{1}{2}\sqrt{\frac{\pi}{a}} = \frac{1}{4a}\sqrt{\frac{\pi}{a}}$

$$\therefore \int_0^\infty v^2 e^{-\frac{1}{2}mv^2/k_BT}\,dv = \frac{1}{4}\sqrt{\pi}\left(\frac{\frac{1}{2}m}{k_BT}\right)^{-3/2} = \frac{1}{4\pi}\left(\frac{m}{2\pi k_BT}\right)^{-3/2}$$

$$\therefore \int_0^\infty p(v)\,dv = \cancel{4}\pi \left(\frac{M}{2\pi k_B T}\right)^{3/2} \times \frac{\sqrt{\pi}}{\cancel{4}} \left(\frac{M}{2k_B T}\right)^{-3/2}$$

$$= \pi^{3/2} \; \pi^{-3/2}$$

$$= 1 \; \checkmark$$

$\boxed{\text{So indeed } \int_0^\infty p(v)\,dv = 1 \text{ as required.}}$

$$E\left[\tfrac{1}{2}Mv^2\right] = \tfrac{1}{2}M \int_0^\infty v^2\, p(v)\,dv$$

$$= \tfrac{1}{2}M \times 4\pi \left(\frac{M}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^4 e^{-\frac{1}{2}Mv^2/k_B T}\,dv$$

$$\int_0^\infty v^4 e^{-\frac{1}{2}Mv^2/k_B T}\,dv = \frac{4-1}{2\left(\frac{1}{2}M/k_B T\right)} \int_0^\infty v^2 e^{-\frac{1}{2}Mv^2/k_B T}\,dv$$

Since $\int_0^\infty x^n e^{-ax^2}\,dx = I_n$ and $I_n = \frac{n-1}{2a} I_{n-2}$

Now from above: $\int_0^\infty v^2 e^{-\frac{1}{2}Mv^2/k_B T}\,dv = \frac{1}{4\pi}\left(\frac{M}{2\pi k_B T}\right)^{-3/2}$

$$\therefore E\left[\tfrac{1}{2}Mv^2\right] = \cancel{2\pi M} \left(\frac{M}{2\pi k_B T}\right)^{3/2} \frac{3}{\cancel{M}} k_B T \; \frac{1}{\cancel{4\pi}} \left(\frac{M}{2\pi k_B T}\right)^{-3/2}$$

$$= \boxed{\tfrac{3}{2} k_B T}$$

i.e. the 'equipartition' result.