Assignment-11 Solutions

Ans 1 since we have to calculate number of molecules with speed close to $300 ms^{-1}$ and $100 ms^{-1}$, not exact $300 ms^{-1}$ & $100 ms^{-1}$. which means we are looking at a small range, therefore we can approximate the number of molecules follows

$$\frac{dN_{300}}{dN_{100}} = \frac{f(300 m/s)\cancel{dv}}{f(100 m/s)\cancel{dv}} = \frac{f(300 m/s)}{f(100 m/s)}$$

All we have to do is to take the ratio of f values.

Given $T = 273°C = 300K$

$M = 28 g/mol = 0.028 \, kg/mol = 4.65 \times 10^{-26} \, kg$

also, $k_B = 1.38 \times 10^{-23} \, J/K$

$$f(300 ms^{-1}) = \frac{\cancel{4\pi}\left(\frac{\cancel{m}}{\cancel{2\pi k_B T}}\right)^{3/2} e\left[-m(300 m/s)^2/2k_BT\right] \times (300 m/s)^2}{\cancel{4\pi}\left(\frac{\cancel{m}}{\cancel{2\pi k_B T}}\right)^{3/2} e\left[-m(100 m/s)^2/2k_BT\right] \times (100 m/s)^2}$$

$$= 3^2 \exp\left[-\frac{m(300 m/s)^2}{2k_BT} + \frac{m(100 m/s^2)}{2k_BT}\right]$$

$$= 9 \exp\left[\frac{-4.65 \times 10^{-26} kg}{2 \times 1.38 \times 10^{-23} J \cancel{K}^{-1} \times 300 \cancel{K}}\left[(300 m/s)^2 - (100 m/s)^2\right]\right]$$

$1 J = 1 Kg \, m^2 \, s^{-2}$

$$= 9 \exp\left[-0.4488\right] = 9 \times 0.63839 = \underline{\underline{5.74}}$$

2. We have to calculate frequency factor 'A' or pre exponential factor for the following reaction

$$H + O_2 \longrightarrow OH + O \qquad \left[\sigma_H = \frac{\sigma_{H_2}}{2} = \frac{\text{Diameter of } H_2}{4}\right]$$

$$\sigma_H = \frac{2.74 A^\circ}{4} = 0.68\times10^{-10} m$$

$$\sigma_{O_2} = \frac{3.1 A^\circ}{2} = 1.5\times10^{-10} m$$

Expression for frequency factor, according to Collision theory

$A = \pi\sigma_{AB}^2 v_r N_{avo}$ where v_r = relative velocity

$$v_r = \left(\frac{8k_bT}{\pi\mu}\right)^{1/2} \quad \& \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

Now, $\mu = \frac{1\times32}{1+32} = 0.97 g/mol = \underline{0.97\times10^{-3} kg\,mol^{-1}}$

$$v_r = \left(\frac{8\times1.38\times10^{-23} J\cancel{K}^{-1}\times 273\cancel{K}\times 6.022\times10^{23}}{3.14\times0.97\times10^{-3} kg}\right)^{1/2}$$ 1J = 1kg $m^2 s^{-2}$

$v_r = \underline{2441 m/sec}$

$$\sigma_{AB} = \sigma_A + \sigma_B = (0.68+1.5)\times10^{-10} m = 2.18\times10^{-10} m$$

$A = 3.14\,(2.18\times10^{-10})^2 m^2 \times 2441\, m\, sec^{-1} \times 6.022\times10^{23}$ molecule/mol

$= 2.19\times10^{8}\, m^3 s^{-1}$ molecule mol^{-1} or $3.6\times10^{14}(A^\circ)^3$ molecule s^{-1}

for 1 mol

3. $X(g) + Y(g) \longrightarrow Z(g)$ —(1)

$M(g) + N(g) \longrightarrow P(g)$ —(2)

Let us assume, for first reaction the pre-exponential factor is A_1

for 2nd " " " A_2

Now, $A = \pi \sigma_{AB}^2 V_{\mu} N_A$

$$\frac{A_1}{A_2} = \frac{\cancel{\pi} \sigma_{xy}^2 V_{xy} \cancel{N_A}}{\cancel{\pi} \sigma_{NM}^2 V_{NM} \cancel{N_A}} = \frac{\sigma_{xy}^2 V_{xy}}{\sigma_{MN}^2 V_{MN}}$$

where, V_{xy} & V_{MN} are relative velocities;

$$V_{xy} = \sqrt{\frac{8K_bT}{\pi \mu_{xy}}} \quad \& \quad V_{MN} = \sqrt{\frac{8K_bT}{\pi \mu_{MN}}}$$

$$\frac{V_{xy}}{V_{MN}} = \sqrt{\frac{\mu_{MN}}{\mu_{xy}}} \quad -(1)$$

Calculating (1) $\rightarrow$ $\mu_{MN} = \frac{10 \times 10}{10+10} = 5$

$$\mu_{xy} = \frac{5 \times 20}{5+20} = 4$$

$$\frac{V_{xy}}{V_{MN}} = \sqrt{\frac{5}{4}} = 1.118$$

$$\sigma_{xy} = \frac{0.3}{2} + \frac{0.5}{2} = 0.4$$

$$\sigma_{MN} = \frac{0.4}{2} + \frac{0.4}{2} = 0.4$$

$$\frac{A_1}{A_2} = \frac{(0.\cancel{4})^2}{(\cancel{0.4})^2} \times 1.118 = 1.118$$

4. According to collision theory, rate constant is given by the expression

$$k = \sigma\left(\frac{8K_bT}{\pi\mu}\right)^{1/2} N_A \exp\left(\frac{-E_a}{RT}\right)$$

$\sigma = 0.3\,nm^2 = 0.3(10^{-9}m)^2 = 0.3\times10^{-18}\,m^2$

$E_a = 200\,kJ = 200\times10^3\,J$

$T = 450K$

$\mu = 3.93\,amu = 3.93\times1.66\times10^{-27}\,kg$

$$k = 0.3\times10^{-18}\,m^2\left[\frac{8\times1.38\times10^{-23}\,JK^{-1}\times450K}{3.14\times3.93\times1.66\times10^{-27}}\right]^{1/2}\times 6.022\times10^{23}\,mol^{-1}$$

$$\times\exp\left[\frac{-200\times10^3\,\cancel{J}\,\cancel{mol^{-1}}}{8.314\,\cancel{J}\,\cancel{K^{-1}}\,\cancel{mol^{-1}}\times450\cancel{K}}\right]$$

$k = 0.3\times10^{-18}\,m^2\times1557\,ms^{-1}\times6.022\times10^{23}\,mol^{-1}\times\ 6.08\times10^{-24}$

$= 17102\times10^{-19}\,m^3s^{-1}\,mol^{-1}$

$= 1.7102\times10^{-15}\,m^3\,s^{-1}\,mol^{-1}$

5. a) Calculation of Temperature at which V_{rms} for SO_2 & O_2 becomes equal.

$$V_{rms} = \sqrt{\frac{3RT}{M}}$$

For O_2 at 27°C or 300K we have,

$$V_{rms,O_2} = \left(\frac{3R(300)}{32}\right)^{1/2} \quad -(1)$$

For SO_2 at T°C or (T+273) K, we have

$$V_{rms,SO_2} = \left(\frac{3R(T+273)}{64}\right)^{1/2} \quad -(2)$$

Equating (1) & (2)

$$\left[\frac{3R(300)}{32}\right]^{1/2} = \left[\frac{3R(T+273)}{64}\right]^{1/2}$$

Squaring Both Sides

$$\frac{\cancel{3}\cancel{R}(300)}{\cancel{32}} = \frac{\cancel{3}\cancel{R}(T+273)}{\cancel{64}_2}$$

$$T+273 = 600$$

$$\boxed{T = 327°C}$$

b) Calculation of most probable speed for O_2.

$$V_{mp} = \sqrt{\frac{2RT}{m}} = \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2P}{\rho}} \quad \left(\rho = \frac{M}{V}\right)$$

Given $\rho = 0.0081 \, g \, ml^{-1}$

$= 0.0081 \, g \, cm^{-3}$

$P = 1 \, atm = 101325 \, N \, m^{-2}$

$= 101325 \, Kg \, m \, s^{-2} \, m^{-2}$

$= 101325 \, Kg \, m^{-1} \, s^{-2}$

In CGS $1 atm = 101325 \times 10^{3} g \times 10^{-2} cm^{-1} s^{-2}$

$$\therefore V_{mp} = \sqrt{\frac{2 \times 101325 \times 10^{1} \, g \, cm^{-1} s^{-2}}{0.0081 \, g \, cm^{-3}}}$$

$= 1.58 \times 10^{4} \, cms^{-1}$

c) Root mean square speed of ethane at 27°C (300K) at 720 mm of Hg.

$$V_{rms} = \sqrt{\frac{3RT}{m}} = \sqrt{\frac{3PV}{m}} = \sqrt{\frac{3P}{\rho}} \quad \left[\because \rho = \frac{m}{V}\right]$$

✓

$\downarrow$ vol m not given

$\downarrow$ density not given

$m_{ethane} = 30 \, g \, mol^{-1}$
(C_2H_6)

$$V_{RMS} = \sqrt{\frac{3 \times 8.314 \, J \, \cancel{K^{-1}} \, \cancel{mol^{-1}} \times 300 \cancel{K}}{30 g \, \cancel{mol}^{-1}}} = \sqrt{\frac{3 \times 8.314 \times 10^{+3} g \, m^2 s^{-2} \cancel{K^{-1}} \times 300 \cancel{K} \, \cancel{mol^{-1}}}{30 g \, \cancel{mol^{-1}}}}$$

= [illegible] $= 499.4 \, m s^{-1}$

$= 4.99 \times 10^{4} \, cm \, sec^{-1}$