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

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

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

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

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

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

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

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

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

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

Expression for frequency factor, according to collision theory

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

$$V_r = \left(\frac{8 k_b T}{\pi \mu}\right)^{1/2} \quad \& \quad \mu = \frac{M_A M_B}{M_A + M_B}$$

Now, $\mu = \frac{1 \times 32}{1 + 32} = 0.97 g/mol = \underline{0.97 \times 10^{-3} \text{ kg mol}^{-1}}$

$$V_r = \left(\frac{8 \times 1.38 \times 10^{-23} J \cancel{K^{-1}} \times 273 \cancel{K} \times 6.022 \times 10^{23}}{3.14 \times 0.97 \times 10^{-3} Kg}\right)^{1/2} \qquad 1J = 1 kg\, m^2 s^{-2}$$

$V_r = \underline{2441 \text{ m/sec}}$

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

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

$$= 2.19 \times 10^{8} \text{ m}^3 s^{-1} \text{molecule mol}^{-1} \quad \text{or} \quad 3.6 \times 10^{14} (A^\circ)^3 \text{ molecule } s^{-1}$$

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

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

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

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

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

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

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

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

$E_a = 200\ kJ = 200 \times 10^3\ J$

$T = 450K$

$\mu = 3.93\ amu = 3.93 \times 1.66 \times 10^{-27}\ kg$

$$k = 0.3 \times 10^{-18}\ m^2 \left[\frac{8 \times 1.38 \times 10^{-23}\ J K^{-1} \times 450K}{3.14 \times 3.93 \times 1.66 \times 10^{-27}}\right]^{1/2} \times 6.022 \times 10^{23}\ mol^{-1}$$

$$\times \exp\left[\frac{-200 \times 10^3\ \cancel{J} \cancel{mol^{-1}}}{8.314\ \cancel{J} \cancel{K^{-1}} \cancel{mol^{-1}} \times 450 \cancel{K}}\right]$$

$$k = 0.3 \times 10^{-18}\ m^2 \times 1557\ ms^{-1} \times 6.022 \times 10^{23}\ mol^{-1} \times 6.08 \times 10^{-24}$$

$$= 17102 \times 10^{-19}\ m^3 s^{-1} mol^{-1}$$

$$= 1.7102 \times 10^{-15}\ m^3 s^{-1} mol^{-1}$$

5. a) Calculation of Temperature at which Vrms for SO_2 & O_2 becomes equal.

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

For O_2 at 27°C or 300 K 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

$$\frac{\cancel{3R}(300)}{\cancel{32}} = \frac{\cancel{3R}(T+273)}{\cancel{64}\,2}$$

$$T+273 = 600$$

$$\boxed{T = 327°C}$$

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

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

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

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

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

✓ ; vol m not given ; density not given

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

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

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

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