CHM202

Energetics and dynamics of chemical reactions

Solutions Assignment –X

Q.1 Calculate the collision frequency (z) and the collision density (Z) in carbon monoxide. Given: r = 180 pm at 25 °C and 100 kPa. What is the percentage increase when the temperature is raised by 10 K at constant volume?

Sol.:

The collision frequency is

$$z = \frac{2^{1/2}\sigma \langle \bar{c} \rangle p}{kT} \quad \text{where } \sigma = \pi d^2 = 4\pi r^2 \text{ and } \langle \bar{c} \rangle = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

so $z = \dfrac{2^{1/2}p}{kT}(4\pi r^2)\left(\dfrac{8RT}{\pi M}\right)^{1/2} = \dfrac{16pN_A r^2 \pi^{1/2}}{(RTM)^{1/2}}$

$$= \frac{16 \times (100 \times 10^3 \text{ Pa}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (180 \times 10^{-12} \text{ m})^2 \times (\pi)^{1/2}}{[(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (298 \text{ K}) \times (28.01 \times 10^{-3} \text{ kg mol}^{-1})]^{1/2}}$$

$$= \boxed{6.64 \times 10^9 \text{ s}^{-1}}$$

The collision density is

$$Z_{AA} = \frac{1}{2}zN/V = \frac{zp}{2kT} = \frac{(6.64 \times 10^9 \text{ s}^{-1}) \times (100 \times 10^3 \text{ Pa})}{2(1.381 \times 10^{-23}\text{J K}^{-1}) \times (298 \text{ K})} = \boxed{8.07 \times 10^{34} \text{ m}^{-3}\text{s}^{-1}}$$

Raising the temperature at constant volume means raising the pressure in proportion to the temperature

$$Z_{AA} \propto \sqrt{T}$$

so the percent increase in z and Z_{AA} due to a 10 K increase in temperature is $\boxed{1.6 \text{ percent}}$.

Q.2 Use the collision theory of gas-phase reactions to calculate the theoretical value of the second-order rate constant for the reaction $D_2(g) + Br_2(g) \rightarrow 2DBr(g)$ at 450 K. Assuming that it is elementary bimolecular. Take the collision cross-section as 0.30 nm², the reduced mass as 3.930 u, and the activation energy as 200 kJ mol⁻¹.

Sol.:

The reaction rate is given by

$$v = P\sigma\left(\frac{8k_B T}{\pi\mu}\right)^{1/2} N_A \exp(-E_a/RT)[D_2][Br_2]$$

so, in the absence of any estimate of the reaction probability P, the rate constant is

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

$$= [0.30 \times (10^{-9}\,\text{m})^2] \times \left(\frac{8(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (450\,\text{K})}{\pi(3.930\,\text{u}) \times (1.66 \times 10^{-27}\,\text{kg u}^{-1})} \right)^{1/2}$$

$$\times (6.022 \times 10^{23}\,\text{mol}^{-1}) \exp \left(\frac{-200 \times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (450\,\text{K})} \right)$$

$$= 1.71 \times 10^{-15}\,\text{m}^3\,\text{mol}^{-1}\text{s}^{-1} = \boxed{1.7 \times 10^{12}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

Q.3 Calculate the collision frequency per unit area for nitrogen at 25 °C and 1 bar.

Sol.: The number density is given by

$$\rho = \frac{N_A n}{V} = \frac{N_A P}{RT} = \frac{(6.022 \times 10^{23}\,\text{mol}^{-1})(1\,\text{bar})}{(0.08314\,\text{L·bar·mol}^{-1}\text{·K}^{-1})(298\,\text{K})}$$

$$= 2.43 \times 10^{22}\,\text{L}^{-1} = 2.43 \times 10^{25}\,\text{m}^{-3}$$

and

$$\langle u \rangle = \left(\frac{8RT}{\pi M} \right)^{1/2} = \left(\frac{8(8.314\,\text{J·K}^{-1}\text{·mol}^{-1})(298\,\text{K})}{\pi(0.02802\,\text{kg})} \right)^{1/2}$$

$$= 475\,\text{m·s}^{-1}$$

Therefore

$$z_{\text{coll}} = 2.88 \times 10^{27}\,\text{s}^{-1}\text{·m}^{-2} = 2.88 \times 10^{23}\,\text{s}^{-1}\text{·cm}^{-2}$$

Q.4 Calculate the mean free path of a hydrogen molecule at 25 °C and 10^{-5} torr. Given $\sigma = 0.230 \times 10^{-5}\,\text{m}^2$.

Sol.: Since the mean free path is given by

$$l = \frac{1}{\sqrt{2} n \sigma}$$

But

$$n = \frac{N}{V} = \frac{pN}{RT}$$

$$l = \frac{RT}{\sqrt{2} N p \sigma}$$

$$l = \frac{(0.08206\,\text{L·atm·mol}^{-1}\text{·K}^{-1})(298\,\text{K})}{2^{1/2}(6.022 \times 10^{23}\,\text{mol}^{-1})(0.230 \times 10^{-18}\,\text{m}^2)(1 \times 10^{-5}\text{torr})(1\text{atm}/760\,\text{torr})}$$

$$= 9500\,\text{L·m}^{-2} = 9.5\,\text{m}$$

Q.5 Calculate the frequency of nitrogen-nitrogen collisions in one cubic centimetre of air at 20 °C and 1 bar. Assume that 80% of the molecule are nitrogen molecules. Given: $\sigma_{N_2} = 4.5 \times 10^{-19} m^2$.

Sol.:

The partial pressure of nitrogen is 0.80 bar and the number density is

$$\rho = \frac{N_A P_{N_2}}{RT} = \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(0.80 \text{ bar})}{(0.08314 \text{ L·bar·mol}^{-1} \cdot K^{-1})(293 \text{ K})}$$
$$= 2.0 \times 10^{22} \text{ L}^{-1} = 2.0 \times 10^{25} \text{ m}^{-3}$$

The average speed is

$$\langle u \rangle = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left[\frac{8(8.314 \text{ J·K}^{-1})(293 \text{ K})}{\pi(0.02802 \text{ kg})}\right]^{1/2}$$
$$= 470 \text{ m·s}^{-1}$$
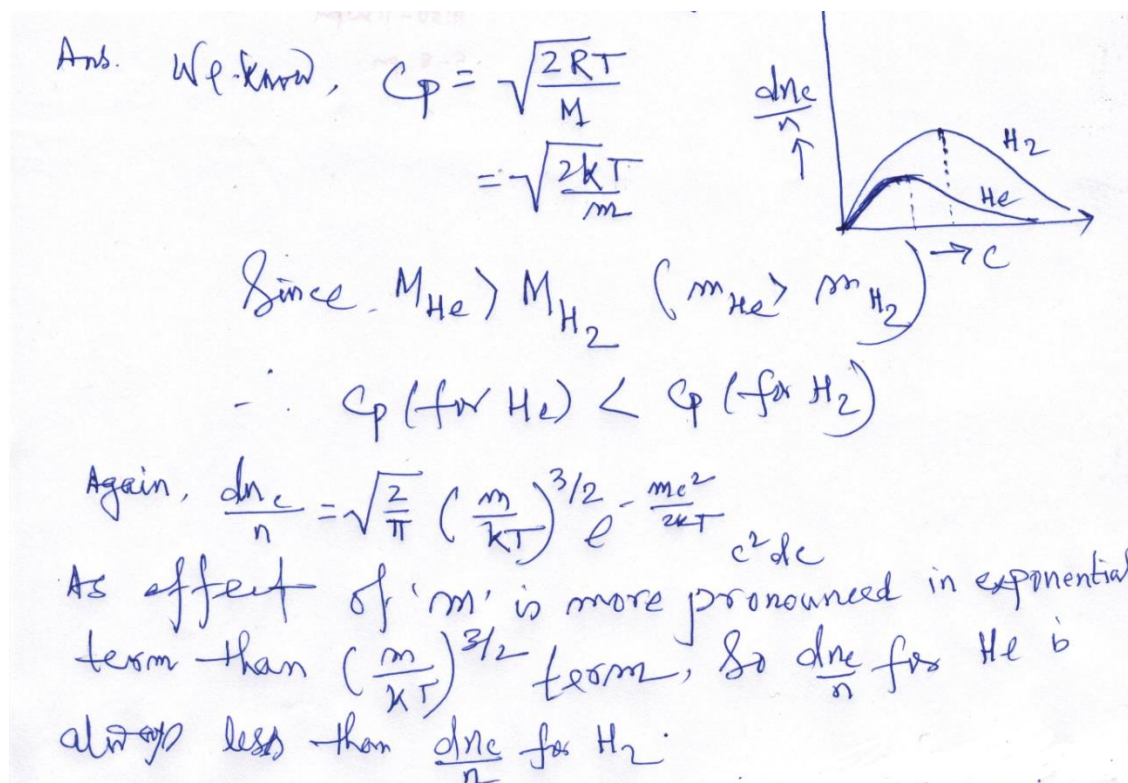
$$Z_{N_2, N_2} = \frac{(4.50 \times 10^{-19} \text{ m}^2)(470 \text{ m·s}^{-1})(2.0 \times 10^{25} \text{ m}^{-3})^2}{2^{1/2}}$$
$$= 6.0 \times 10^{34} \text{ s}^{-1} \cdot m^{-3} = 6.0 \times 10^{28} \text{ s}^{-1} \cdot cm^{-3}$$

Q 6. Draw the Maxwell-Boltzmann distribution of speeds for Hydrogen and Helium gases (in one graph) at the same temperature.

Sol.:

Ans. We know, $C_p = \sqrt{\frac{2RT}{M}}$

$$= \sqrt{\frac{2kT}{m}}$$

Since $M_{He} > M_{H_2}$ $\left(m_{He} > m_{H_2}\right)$

∴ C_p (for He) $< C_p$ (for H_2)

Again, $\frac{dn_c}{n} = \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^{3/2} e^{-\frac{mc^2}{2kT}} c^2 dc$

As effect of 'm' is more pronounced in exponential term than $\left(\frac{m}{kT}\right)^{3/2}$ term, So $\frac{dn}{n}$ for He is always less than $\frac{dn}{n}$ for H_2.

Q 7. (a) Does the Maxwell Boltzmann distribution apply to imperfect gas or condensed phase system? (b) A gas is obeying the Maxwell Boltzmann distribution law, what will happen if pressure is tripled?

Sol.:

(a) Maxwell-Boltzmann distribution will not be applicable for the condensed phase system as well as imperfect gas because the M-B distribution makes the assumption that it is working with an ideal gas. The M-B distribution for all gases depends on the mass of the particle and the temperature. That means, any gas phase reaction which depends strongly on the orientation of the collision would likely be assumed by M-B to happen much more frequently than it really does.

(b) One of the assumptions is made in the derivation of M-B distribution is that the number density of the gas should be the same everywhere. So, the gas must be ideal. Now, if the pressure of an ideal gas is tripled, there is a possibility of the gas behaving like a real. Then it may not obey M-B distribution.