Dynamics and Kinetics. Exercises 8: Solutions

Problem 1

Change of momentum for a single particle:

$$\Delta p_1 = |-mv - (+mv)| = 2mv$$

Force exerted on the wall by N particles:

$$F_N = \frac{\Delta p_N}{\Delta t} = \frac{N\Delta p_1}{\Delta t} = \frac{2Nmv}{\Delta t} = \frac{2 \times 10^{23} \times 28 \times 1.67 \times 10^{-27}\text{kg} \times 450\text{m}}{1\text{s}} = 4.2\ \text{N}$$

Pressure :

$$p = \frac{F_N}{A} = \frac{4.2\text{N}}{10 \times 10^{-4}\text{m}^2} = 4,200\ \text{Pa}$$

Problem 2

(a) Note that you do not need to remember complicated formulas!
This problem consists of computing collision densities, given by intuitive formulas: from lecture:

$$Z_{AB} = c_A c_B \sigma_{AB} \langle v_{AB} \rangle \qquad \text{and} \qquad Z_{AA} = \frac{1}{2} {c_A}^2 \sigma_{AA} \langle v_{AA} \rangle.$$

The rest is just computing all the ingredients:

Number density: $c := \frac{N}{V} = \frac{p}{k_B T}$

$$c_{\text{H}_2} = c_{\text{I}_2} = c = \frac{0.5 \times 101,325\text{Pa}}{1.38 \times 10^{-23}\text{JK}^{-1} \times 400\text{K}} = 9.18 \times 10^{24}\text{m}^{-3}$$

Mean relative velocity:

$$\langle v_{AB} \rangle = \left(\frac{8RT}{\pi M_{\text{red}}} \right)^{1/2}$$

Reduced masses:

$\text{H}_2/\text{H}_2 : M_{\text{red}} = \frac{M_{\text{H}_2}}{2} = \frac{2 \times 1.008\text{g} \times 10\text{mol}^{-1}}{2} = 1.008 \times 10^{-3}\text{kg} \cdot \text{mol}^{-1}$
$\text{I}_2/\text{I}_2 : M_{\text{red}} = \frac{M_{\text{I}_2}}{2} = 0.1269\ \text{kg} \cdot \text{mol}^{-1}$
$\text{H}_2/\text{I}_2 : M_{\text{red}} = \frac{M_{\text{H}_2} M_{\text{I}_2}}{M_{\text{H}_2} + M_{\text{I}_2}} = \frac{2 \times 1.008\text{g} \times 126.9\text{mol}^{-1}}{127.9} = 2.0002 \times 10^{-3}\text{kg} \cdot \text{mol}^{-1}$

Mean relative velocities:

$\langle v_{\text{H}_2/\text{H}_2} \rangle = 2900\ \text{m} \cdot \text{s}^{-1}$
$\langle v_{\text{I}_2/\text{I}_2} \rangle = 258\ \text{m} \cdot \text{s}^{-1}$
$\langle v_{\text{H}_2/\text{I}_2} \rangle = 2060\ \text{m} \cdot \text{s}^{-1}$ 10 18m2 2900 m s 1 =

Collision densities :

$$Z_{\mathrm{H_2/H_2}} = \frac{1}{2}c_{\mathrm{H_2}}{}^2\sigma_{\mathrm{H_2/H_2}}\langle v_{\mathrm{H_2/H_2}}\rangle = \frac{1}{2}\times(9.18\times10^{24})^2\mathrm{m}^{-6}\times 0.27\times10^{-18}\mathrm{m}^2\times 2900\ \mathrm{m\cdot s^{-1}} = 3.30\times10^{34}\mathrm{m^{-3}s^{-1}}$$

$$Z_{\mathrm{I_2/I_2}} = 1.30\times10^{34}\mathrm{m^{-3}s^{-1}}$$

$$Z_{\mathrm{H_2/I_2}} = c_{\mathrm{H_2}}c_{\mathrm{I_2}}\sigma_{\mathrm{H_2/I_2}}\langle v_{\mathrm{H_2/I_2}}\rangle$$

Still do not know $\sigma_{H2/I2}$, so estimate it:

$$\sigma_{\mathrm{H_2/I_2}} = \pi d^2 = \pi(\frac{d_{\mathrm{H_2}}+d_{\mathrm{I_2}}}{2})^2 = (\frac{\sqrt{\sigma}_{\mathrm{H_2}}+\sqrt{\sigma}_{\mathrm{H_2}}}{2})^2 = 0.65\ \mathrm{nm}^2$$

$$Z_{\mathrm{H_2/I_2}} = 1.13\times10^{35}\mathrm{m^{-3}s^{-1}}$$

(b) Rate of reaction:

$$v = k[\mathrm{H_2}][\mathrm{I_2}] = 8.3\times10^{-3}\mathrm{M^{-1}s^{-1}}\left(\frac{9.18\times10^{21}\mathrm{l^{-1}}}{6.022\times10^{23}\mathrm{mol^{-1}}}\right)^2 = 1.9\times10^{-6}\mathrm{M\cdot s^{-1}}$$

Collision density:

$$Z_{\mathrm{H_2/I_2}} = 1.13\times10^{35}\mathrm{m^{-3}s^{-1}} = \frac{1.13\times10^{35}\times10^{-3}}{6.022\times10^{23}\mathrm{mol^{-1}}}\mathrm{l^{-1}s^{-1}} = 1.9\times10^{8}\mathrm{M\cdot s^{-1}}$$

$$v \ll Z_{\mathrm{H_2/I_2}}$$
$$v \simeq 10^{-14}\times Z_{\mathrm{H_2/I_2}}$$

Therefore, fraction of reactive collisions is only about 10^{-14}:

Problem 3

For the frequency at which a given molecule strikes a wall, only the velocity component orthogonal to this wall, say u_x, matters. Molecules with velocity component u_x strike the wall per unit time and unit area with a rate of

$$z_{\mathrm{coll}}(u_x) = u_x\rho$$

The distribution of the velocity component u_x is simply a one-dimensional distribution

$$f(u_x)du_x \propto e^{-\frac{mu_x^2}{2k_BT}}$$

which we can normalize to give

$$f(u_x)du_x = \sqrt{\frac{m}{2\pi k_BT}}e^{-\frac{mu_x^2}{2k_BT}}$$

We obtain for the collision flux by averaging the rate over the velocity distribution

$$\int_0^\infty f(u_x)u_x\rho du_x = \rho\sqrt{\frac{m}{2\pi k_B T}}\int_0^\infty u_x e^{-\frac{mu_x^2}{2k_B T}}du_x = \rho\sqrt{\frac{m}{2\pi k_B T}}\frac{k_B T}{m} = \rho\sqrt{\frac{k_B T}{2\pi m}}$$

which is exactly the same result as we obtained in class.