

Solutions to the problem set on the theory of bimolecular reactions

1. The (average) mass of a potassium atom is

$$m_{\text{K}} = \frac{39.098 \text{ g/mol}}{6.022142 \times 10^{23} \text{ mol}^{-1}} = 6.4924 \times 10^{-23} \text{ g} \equiv 6.4924 \times 10^{-26} \text{ kg}.$$

Similarly, the mass of a bromine molecule is

$$m_{\text{Br}_2} = 2.6537 \times 10^{-25} \text{ kg}.$$

The reduced mass of the reactants is

$$\mu = (m_{\text{K}}^{-1} + m_{\text{Br}_2}^{-1})^{-1} = 5.2162 \times 10^{-26} \text{ kg}.$$

The relative speed at 600 K is

$$\bar{v}_r = \sqrt{\frac{8(1.380658 \times 10^{-23} \text{ J/K})(600 \text{ K})}{\pi(5.2162 \times 10^{-26} \text{ kg})}} = 636 \text{ m/s}.$$

To use the equation relating the cross-section to the preexponential factor, we must convert the preexponential factor to SI units:

$$k_{\infty} = \frac{10^{12} \text{ L mol}^{-1} \text{ s}^{-1}}{1000 \text{ L/m}^3} = 10^9 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The cross-section is therefore

$$\sigma = \frac{k_{\infty}}{\bar{v}_r N_A} = 2.61 \times 10^{-18} \text{ m}^2.$$

This corresponds to a disk of radius $r_{AB} = \sqrt{\sigma/\pi} = 9.12 \times 10^{-10} \text{ m}$ or 9.12 \AA . This is a very large radius. For comparison, the radius of a potassium atom is 2.20 \AA . The bond length in the bromine molecule is 2.29 \AA . If we add these together, we get an r_{AB} which is less than *half* of the value computed from the cross-section. The cross-section calculated here is therefore not due to a simple collisional process. In fact, the large difference in electronegativity of K and Br leads to a transfer of charge from the atom to the molecule at large distances. The cation (K^+) and anion (Br_2^-) are then attracted to each other by electrostatic forces, which enhances the rate of reaction. This process is called “harpooning”. (The potassium atom is imagined to use its electron as a harpoon which it uses to reel in the bromine molecule.) The r_{AB} calculated from the cross-section corresponds to the mean distance at which this harpooning process occurs.

2. (a) The reduced mass is calculated as follows:

$$\begin{aligned}
 M_{\text{CH}_4} &= 16.043 \text{ g/mol.} \\
 \therefore \bar{\mu} &= \left(\frac{1}{1.0079 \text{ g/mol}} + \frac{1}{16.043 \text{ g/mol}} \right)^{-1} = 0.94832 \text{ g/mol.} \\
 \therefore \mu &= \frac{0.94832 \times 10^{-3} \text{ kg/mol}}{6.0221420 \times 10^{23} \text{ mol}^{-1}} = 1.5747 \times 10^{-27} \text{ kg.}
 \end{aligned}$$

Any temperature within the experimental range is reasonable. If we take (e.g.) $T = 800 \text{ K}$,¹ which is about the middle of the range, we get

$$\begin{aligned}
 \bar{v}_r &= \sqrt{\frac{8k_B T}{\pi \mu}} \\
 &= \sqrt{\frac{8(1.3806503 \times 10^{-23} \text{ J/K})(800 \text{ K})}{\pi(1.5747 \times 10^{-27} \text{ kg})}} \\
 &= 4226 \text{ m/s.}
 \end{aligned}$$

The radius of the cross-section should be roughly the sums of the radii of the H atom and methane molecule, so

$$\begin{aligned}
 r &= 3.7 \times 10^{-11} + 1.9 \times 10^{-10} \text{ m} = 2.3 \times 10^{-10} \text{ m.} \\
 \therefore \sigma &= \pi r^2 = \pi(2.3 \times 10^{-10} \text{ m})^2 = 1.6 \times 10^{-19} \text{ m}^2. \\
 \therefore k_{\infty, \text{ct}} &= \sigma \bar{v}_r N_A \\
 &= (1.6 \times 10^{-19} \text{ m}^2)(4226 \text{ m/s})(6.0221420 \times 10^{23} \text{ mol}^{-1}) \\
 &= 4.1 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \equiv 4.1 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}. \\
 \therefore \eta &= \frac{1.25 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}}{4.1 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}} = 0.30.
 \end{aligned}$$

(b) This is a gas-phase reaction, so we need the preexponential factor in units of $\text{bar}^{-1} \text{ s}^{-1}$. At 800 K,

$$\begin{aligned}
 \frac{n}{V} &= \frac{P}{RT} = \frac{100\,000 \text{ Pa}}{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(800 \text{ K})} \\
 &= 15.034 \text{ mol/m}^3 \equiv 0.015034 \text{ mol/L.} \\
 \therefore k_{\infty} &= (1.25 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1})(0.015034 \text{ mol L}^{-1} \text{ bar}^{-1}) \\
 &= 1.88 \times 10^9 \text{ bar}^{-1} \text{ s}^{-1}.
 \end{aligned}$$

We also need to figure out what to use for $\Delta \bar{n}^\ddagger$. My first guess would be that the transition state would be something like $\text{H} \cdot \cdot \cdot \text{H} \cdot \cdot \cdot \text{CH}_3$, i.e. a single chemical species. Then we would have $\Delta \bar{n}^\ddagger = -1$. Let's calculate $\Delta \bar{S}^\ddagger$ and see what we

¹Obviously, your answers will differ a bit from mine if you picked a different temperature.

get:

$$\begin{aligned}
 \Delta \bar{S}^\ddagger &= R \left[\ln \left(\frac{hk_\infty}{k_B T} \right) - 1 + \Delta \bar{n}^\ddagger \right] \\
 &= (8.314\,472 \text{ J K}^{-1} \text{ mol}^{-1}) \\
 &\quad \times \left[\ln \left(\frac{(6.626\,068\,8 \times 10^{-34} \text{ J/Hz})(1.88 \times 10^9 \text{ bar}^{-1} \text{ s}^{-1})}{(1.380\,650\,3 \times 10^{-23} \text{ J/K})(800 \text{ K})} \right) - 1 + (-1) \right] \\
 &= -92.2 \text{ J K}^{-1} \text{ mol}^{-1}.
 \end{aligned}$$

This relatively large, negative value of $\Delta \bar{S}^\ddagger$ confirms our guess that the transition state involves a complex of H and CH₄.

(c) From the data, we can work out $\Delta \bar{E}^\circ$ for the reaction:

$$\begin{aligned}
 \Delta \bar{E}^\circ &= \Delta \bar{E}_{f(\text{H}_2)}^\circ + \Delta \bar{E}_{f(\text{CH}_3)}^\circ - (\Delta \bar{E}_{f(\text{H})}^\circ + \Delta \bar{E}_{f(\text{CH}_4)}^\circ) \\
 &= 0 + 146.9268 - [216.759 + (-72.3941)] \text{ kJ/mol} \\
 &= 2.562 \text{ kJ/mol}.
 \end{aligned}$$

If you sketch an energy profile for an endothermic reaction,² you'll find that the activation energy for the reverse reaction is given by

$$\bar{E}_a^- = \bar{E}_a^+ - \Delta \bar{E}^\circ = 49.8 - 2.562 \text{ kJ/mol} = 47.2 \text{ kJ/mol}.$$

3.

$$\begin{aligned}
 R_{AB} &= \frac{k_B T}{6\pi\eta} \left(\frac{1}{D_A} + \frac{1}{D_B} \right) \\
 &= \frac{(1.380\,650\,3 \times 10^{-23} \text{ J/K})(298.15 \text{ K})}{6\pi(8.91 \times 10^{-4} \text{ Pa s})} \left(\frac{1}{10^{-11} \text{ m}^2/\text{s}} + \frac{1}{10^{-12} \text{ m}^2/\text{s}} \right) \\
 &= 2.70 \times 10^{-7} \text{ m}. \\
 k_d &= 4\pi(6.022\,142\,0 \times 10^{23} \text{ mol}^{-1})(10^{-11} + 10^{-12} \text{ m}^2/\text{s})(2.70 \times 10^{-7} \text{ m}) \\
 &= 2.24 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \equiv 2.24 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}.
 \end{aligned}$$

²The equation used here actually applies whether the reaction is endothermic or exothermic.