

# Solutions to the problem set on the theory of bimolecular reactions

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

$$m_K = \frac{39.098 \text{ g/mol}}{6.022\,142 \times 10^{23} \text{ mol}^{-1}} = 6.4924 \times 10^{-23} \text{ g} \equiv 6.4924 \times 10^{-26} \text{ kg.}$$

Similarly, the mass of a bromine molecule is

$$m_{Br_2} = 2.6537 \times 10^{-25} \text{ kg.}$$

The reduced mass of the reactants is

$$\mu = (m_K^{-1} + m_{Br_2}^{-1})^{-1} = 5.2162 \times 10^{-26} \text{ kg.}$$

The relative speed at 600 K is

$$\bar{v}_r = \sqrt{\frac{8(1.380\,658 \times 10^{-23} \text{ J/K})(600 \text{ K})}{\pi(5.2162 \times 10^{-26} \text{ kg})}} = 636 \text{ m/s.}$$

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  $9.12 \text{ \AA}$ . This is a very large radius. For comparison, the radius of a potassium atom is  $2.20 \text{ \AA}$ . The bond length in the bromine molecule is  $2.29 \text{ \AA}$ . 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.)  $T = 800 \text{ K}$ ,<sup>1</sup> 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,

$$\begin{aligned} \frac{n}{V} &= \frac{P}{RT} = \frac{100000 \text{ Pa}}{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(800 \text{ K})} \\ &= 15.034 \text{ mol/m}^3 \equiv 0.015034 \text{ mol/L.} \\ \therefore k_\infty &= (1.25 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1})(0.015034 \text{ mol L}^{-1} \text{ bar}^{-1}) \\ &= 1.88 \times 10^9 \text{ bar}^{-1} \text{ s}^{-1}. \end{aligned}$$

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

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

get:

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

This relatively large, negative value of  $\Delta\bar{S}^\ddagger$  confirms our guess that the transition state involves a complex of H and CH<sub>4</sub>.

- (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,<sup>2</sup> 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.

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

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<sup>2</sup>The equation used here actually applies whether the reaction is endothermic or exothermic.