

Dynamics and Kinetics. Exercises 11-12: Solutions

Problem 1

We want to use the TST to estimate the rate constant for the reaction $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$.

We know from the class that

$$k_{\text{TST}} = N_{\text{Av}} \frac{k_{\text{B}}T}{h} \frac{q_{\text{V}}^{\ddagger}}{q_{\text{V,H}}q_{\text{V,HBr}}} e^{-\epsilon^0/k_{\text{B}}T} = N_{\text{Av}} \frac{k_{\text{B}}T}{h} \frac{\tilde{q}_{\text{V}}^{\ddagger}}{\tilde{q}_{\text{V,H}}\tilde{q}_{\text{V,HBr}}} e^{-\epsilon_{\text{QM}}^0/k_{\text{B}}T}.$$

See Fig. 1.

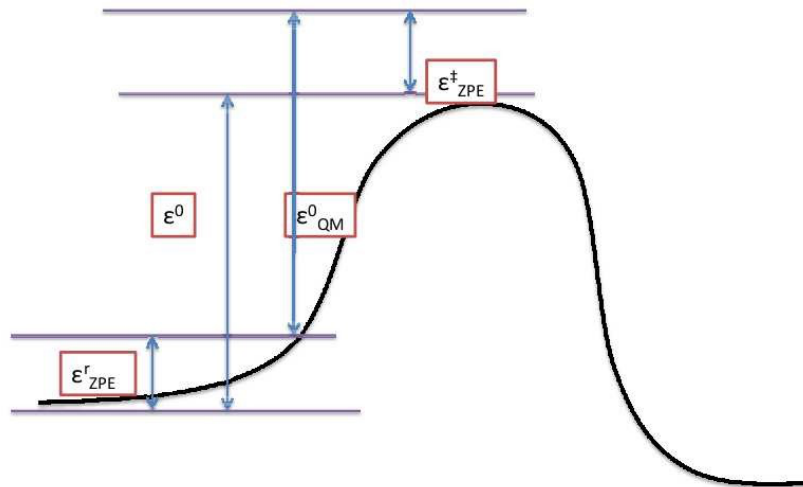


Figure 1: Transition state

(1) First of all we consider the **reactants**: $\text{H} + \text{HBr}$.

Masses:

$$m_{\text{H}} = 1.674 \times 10^{-27} \text{kg},$$

$$m_{\text{HBr}} = \frac{M_{\text{H}} + M_{\text{Br}}}{N_{\text{Av}}} = \frac{(1.008 + 79.92) \times 10^{-3}}{6.022 \times 10^{23}} \text{kg} = 1.338 \times 10^{-25} \text{kg}.$$

Moment of inertia of HBr:

$$I = \mu d^2 = \frac{m_{\text{H}} \cdot m_{\text{Br}}}{m_{\text{H}} + m_{\text{Br}}} d_{\text{HBr}}^2 = 1.674 \times 10^{-27} \text{kg} \times \frac{79.92}{1.008 + 79.92} \times (1.414 \times 10^{-10})^2 \text{m}^2 = 3.306 \times 10^{-47} \text{kg m}^{-2}.$$

(2) Now, let us consider the **collinear transition state** $\text{H} \cdots \text{H} \cdots \text{Br}$:

Mass:

$$m_{\ddagger} = 2m_{\text{H}} + m_{\text{Br}} = 1.37 \times 10^{-25} \text{kg}.$$

Center of mass (see Fig. 2):

$$m_{\text{H}}x + m_{\text{H}}(x - 150) = m_{\text{Br}}(150 + 142 - x) \Rightarrow x = \frac{m_{\text{Br}} \times 292 + m_{\text{H}} \times 150}{2m_{\text{H}} + m_{\text{Br}}} = 283.3 \text{ pm.}$$

Therefore the moment of inertia is

$$I^{\ddagger} = (m_{\text{H}} \times 283.3^2 + m_{\text{H}} \times 133.3^2 + m_{\text{Br}} \times 8.7^2) \text{ pm}^2 = 1.74 \times 10^{-46} \text{ kg m}^2.$$

(3) It is now possible to compute the **partition functions**:

For the **H atom** we have

$$\tilde{q}_{V,H} = q_{V,H} = q_{V,H,tr} = \left(\frac{2\pi m_{\text{H}} k_{\text{B}} T}{h^2} \right)^{3/2} = 9.90 \cdot 10^{29} \text{ m}^{-3}$$

For **molecule HBr** we have

$$\tilde{q}_{V,\text{HBr}} = q_{V,\text{HBr},tr} q_{\text{HBr},rot} q_{\text{HBr},vib},$$

where $q_{V,\text{HBr},tr}$ and $q_{\text{HBr},rot}$ do not have a ZPE (it is exactly zero), while we get $\tilde{q}_{\text{HBr},vib}$ by measuring energies from the ZPE levels:

$$q_{V,\text{HBr},tr} = \left(\frac{2\pi m_{\text{HBr}} k_{\text{B}} T}{h^2} \right)^{3/2} = 7.10 \cdot 10^{32} \text{ m}^{-3}$$

$$q_{\text{HBr},rot} = \frac{8\pi^2 I_{\text{HBr}} k_{\text{B}} T}{h^2} = 24.6$$

$$q_{\text{HBr},vib} = \frac{1}{1 - e^{-x}} \approx 1 \quad \text{since } x = \frac{h\tilde{\nu}c}{k_{\text{B}}T} = 12.7$$

Hence

$$\tilde{q}_{V,\text{HBr}} = 7.10 \times 10^{32} \text{ m}^{-3} \times 24.6 \times 1 = 1.75 \times 10^{34} \text{ m}^{-3}.$$

For the **transition state** $\text{H} \cdots \text{H} \cdots \text{Br}$ we have

$$\tilde{q}_{V}^{\ddagger} = q_{V,tr}^{\ddagger} q_{rot}^{\ddagger} \tilde{q}_{vib}^{\ddagger},$$

where $q_{v,tr}^{\ddagger}$ and $q_{rot,t}^{\ddagger}$ do not have a ZPE (it is exactly zero), while we get $\tilde{q}_{vib}^{\ddagger}$ by measuring energies from the ZPE levels. It is now easy to compute the quantities that we need:

$$q_{V,tr}^{\ddagger} = \left(\frac{2\pi m_{\neq} k_{\text{B}} T}{h^2} \right)^{3/2} = 7.32 \cdot 10^{32} \text{ m}^{-3}$$

$$q_{rot}^{\ddagger} = \frac{8\pi^2 I^{\ddagger} k_{\text{B}} T}{h^2} = 129.7$$

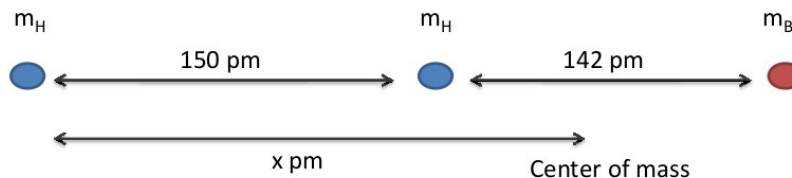


Figure 2: Center of mass

Since $x_{SS} = \frac{hc\tilde{\nu}_{SS}}{k_B T} = 11.2$ and $x_{bend} = \frac{hc\tilde{\nu}_{bend}}{k_B T} = 2.19$, we get

$$\tilde{q}_{vib}^\ddagger = \frac{1}{(1 - e^{-x_{SS}})(1 - e^{-x_{bend}})^2} = 1.27$$

Altogether, the TS partition function is

$$\tilde{q}_V^\ddagger = 7.32 \times 10^{32} \text{m}^{-3} \times 129 \times 7 \times 1.27 = 1.21 \times 10^{35} \text{m}^{-3}$$

(4) Collecting all the intermediate results for partition functions, the TST rate constant is finally

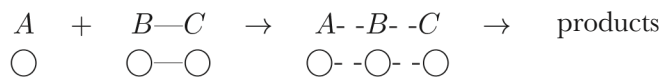
$$\begin{aligned} k_{\text{TST}} &= N_{\text{Av}} \frac{k_B T}{h} \frac{\tilde{q}_V^\ddagger}{\tilde{q}_{V,H} \tilde{q}_{V,\text{HBr}}} e^{-\epsilon_{\text{QM}}^0 / k_B T} \\ &= 6.02 \times 10^{23} \frac{1.38 \times 10^{-23} \times 300}{6.53 \times 10^{-34}} \frac{1.21 \times 10^{35}}{9.9 \times 10^{29} \times 1.75 \times 10^{34}} e^{-5000 / (8.314 \times 300)} \text{m}^3 \text{s}^{-1} \text{mol}^{-1} \\ &= 3.54 \times 10^6 \text{m}^3 \text{mol}^{-1} \text{s}^{-1} = 3.54 \times 10^9 \text{M}^{-1} \text{s}^{-1}. \end{aligned}$$

Problem 2

$$q_{v,\text{tr}}^\ddagger = 10^{32} \text{m}^{-3}$$

$$q_{\text{rot}}^\ddagger = 10$$

$$\tilde{q}_{vib}^\ddagger = 1$$



Reactants:

$$q_{V,A} = q_{V,\text{tr}} \quad [\text{atom: only translations}]$$

$$q_{V,B} = q_{V,\text{tr}} q_{\text{rot}}^2 q_{\text{vib}} \quad [\text{diatom: 3 translations, 2 rotations, 1 vibration.}]$$

Transition state:

$$q_V^\ddagger = q_{V,\text{tr}}^\ddagger q_{\text{rot}}^2 q_{\text{vib}}^{3N-6=3}$$

Explanation: It is a linear molecule so we have 3 translations, 2 rotations, $3N - 5$ vibrations, but 1 vibration becomes reaction coordinate! $\Rightarrow 3N - 6$ vibrations remain in the transition state.

Rate constant

$$\begin{aligned} k_{\text{TST}} &= N_{\text{Av}} \frac{k_B T}{h} \frac{q_V^\ddagger}{q_{V,A} q_{V,B}} e^{-\varepsilon^0/k_B T} \\ &= N_{\text{Av}} \frac{k_B T}{h} \frac{q_{V,\text{tr}} q_{\text{rot}}^2 q_{\text{vib}}^3}{q_{V,\text{tr}} q_{V,\text{tr}} q_{\text{rot}}^2 q_{\text{vib}}} e^{-\varepsilon^0/k_B T} \\ &= N_{\text{Av}} \frac{k_B T}{h} \frac{q_{\text{vib}}^2}{q_{V,\text{tr}}} e^{-\varepsilon^0/k_B T} \end{aligned}$$

We are given $\tilde{q}_{\text{vib}} = 1$, not q_{vib} .

Since $q_{\text{vib}} = e^{-\frac{1}{2}h\nu/k_B T} \tilde{q}_{\text{vib}}$, we have

$$k_{\text{TST}} = N_{\text{Av}} \frac{k_B T}{h} \frac{\tilde{q}_{\text{vib}}^2}{q_{V,\text{tr}}} e^{-\varepsilon_{\text{QM}}^0/k_B T}$$

where

$$\varepsilon_{\text{QM}}^0 = \varepsilon^0 + 2 \times \frac{1}{2} h\nu = \varepsilon^0 + \varepsilon_{\text{ZPE}}^0$$

Pre-exponential factor is

$$\begin{aligned} f &= N_{\text{Av}} \frac{k_B T}{h} \frac{\tilde{q}_{\text{vib}}^2}{q_{V,\text{tr}}} = \frac{RT}{h} \frac{1^2}{10^{32} \text{m}^{-3}} = \frac{8.314 \times 300 \times 10^{-32}}{6.63 \times 10^{-34}} \text{m}^3 \text{mol}^{-1} \text{s}^{-1} \\ &= 3.76 \times 10^7 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \end{aligned}$$

Problem 3

Given the reaction $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$, the equilibrium constant is:

$$K_{\text{eq}} = \frac{q_{V,\text{HD}}^2}{q_{V,\text{H}_2} q_{V,\text{D}_2}}$$

Note that in this case $K_{\text{eq}} = K_V = K_\rho = K_c = K_\beta$ since $\Delta\nu = \nu_{\text{H}_2} + \nu_{\text{D}_2} + \nu_{\text{HD}} = -1 - 1 + 2 = 0$.

The partition functions per unit volume for H_2 , D_2 and HD are:

$$\begin{aligned}
 & \text{Symetry factor} \\
 q_{V,\text{H}_2} &= q_{V,\text{tr}} \times q_{\text{rot}} \times q_{\text{vib}} = \frac{(2\pi k_B T)^{3/2}}{h^3} \cdot m_{\text{H}_2}^{3/2} \times \overbrace{\frac{1}{2} \frac{8\pi^2 k_B T}{h^2}}^{\text{Symetry factor}} \cdot I_{\text{H}_2} \times \frac{e^{-\frac{x_{\text{H}_2}}{2}}}{1 - e^{-x_{\text{H}_2}}} \\
 q_{V,\text{D}_2} &= q_{V,\text{tr}} \times q_{\text{rot}} \times q_{\text{vib}} = \frac{(2\pi k_B T)^{3/2}}{h^3} \cdot m_{\text{D}_2}^{3/2} \times \frac{1}{2} \frac{8\pi^2 k_B T}{h^2} \cdot I_{\text{D}_2} \times \frac{e^{-\frac{x_{\text{D}_2}}{2}}}{1 - e^{-x_{\text{D}_2}}} \\
 q_{V,\text{HD}} &= q_{V,\text{tr}} \times q_{\text{rot}} \times q_{\text{vib}} = \frac{(2\pi k_B T)^{3/2}}{h^3} \cdot m_{\text{HD}}^{3/2} \times \frac{8\pi^2 k_B T}{h^2} \cdot \underbrace{I_{\text{HD}}}_{= r^2 \mu_{\text{HD}}} \times \frac{e^{-\frac{x_{\text{HD}}}{2}}}{1 - e^{-x_{\text{HD}}}}, \\
 & \hspace{15em} = r^2 \mu_{\text{HD}}
 \end{aligned}$$

where $I = \mu r^2$ and $x := \frac{h\nu}{k_B T}$. Substituting the translational and rotational partition functions in the expression for K_{eq} , we find

$$K_{\text{eq}} = \left(\frac{m_{\text{HD}}^2}{m_{\text{H}_2} m_{\text{D}_2}} \right)^{3/2} \times 4 \frac{\mu_{\text{HD}}}{\mu_{\text{H}_2} \mu_{\text{D}_2}} \times \frac{q_{\text{vib,HD}}^2}{q_{\text{vib,H}_2} q_{\text{vib,D}_2}}.$$

Note that many terms in the translational and rotational partition functions cancel out. In particular, in the Born-Oppenheimer approximation, the bond length r is the same for the 3 molecules. Let us compute the required ingredients:

- $m_{\text{H}_2} = 2m_{\text{H}}$, $m_{\text{D}_2} = 2m_{\text{D}}$, $m_{\text{HD}} = m_{\text{H}} + m_{\text{D}}$
- $\mu_{\text{H}_2} = \frac{m_{\text{H}} m_{\text{H}}}{m_{\text{H}} + m_{\text{H}}} = \frac{m_{\text{H}}}{2}$, $\mu_{\text{D}_2} = \frac{m_{\text{D}} m_{\text{D}}}{m_{\text{D}} + m_{\text{D}}} = \frac{m_{\text{D}}}{2}$, $\mu_{\text{HD}} = \frac{m_{\text{H}} m_{\text{D}}}{m_{\text{H}} + m_{\text{D}}}$
- $x_{\text{H}_2} = 20.99$, $x_{\text{D}_2} = 14.85$, $x_{\text{HD}} = 18.18$
- $q_{\text{vib,H}_2} = 2.77 \times 10^{-5}$, $q_{\text{vib,D}_2} = 5.97 \times 10^{-4}$, $q_{\text{vib,HD}} = 1.13 \times 10^{-4}$,

Substituting the ingredients and using the fact that $m_{\text{D}} \cong 2m_{\text{H}}$, we find:

$$\begin{aligned}
 K_{\text{eq}} &= \frac{(m_{\text{H}} + m_{\text{D}})^3}{(4m_{\text{H}}m_{\text{D}})^{3/2}} 4 \frac{(m_{\text{H}}m_{\text{D}})^2}{(m_{\text{H}} + m_{\text{D}})^2 m_{\text{H}} m_{\text{D}}} \frac{q_{\text{vib,HD}}^2}{q_{\text{vib,H}_2} q_{\text{vib,D}_2}} \\
 &= 4 \frac{(m_{\text{H}} + m_{\text{D}})}{2(m_{\text{H}}m_{\text{D}})^{1/2}} \frac{q_{\text{vib,HD}}^2}{q_{\text{vib,H}_2} q_{\text{vib,D}_2}} = \underbrace{4}_{\text{symmetry}} \times \underbrace{\frac{3}{2 \cdot 2^{1/2}}}_{\text{mass effects}} \times \underbrace{\frac{(1.13 \times 10^{-4})^2}{2.77 \times 10^{-5} \cdot 5.97 \times 10^{-4}}}_{\text{mostly ZPE}} = 3.266 \\
 & \hspace{15em} \text{(trans. and rot.)}
 \end{aligned}$$

Problem 4

Reaction 1: $E_{a1} = E_a$, $\Delta S_1^{\ddagger 0}$;

Reaction 2: $E_{a2} = E_a = E_a$, $\Delta S_2^{\ddagger 0} = \Delta S_1^{\ddagger 0} + 50 \text{JK}^{-1} \text{mol}^{-1}$

Using the general thermodynamic formulation of TST for a reaction of any order, we have

$$k_{\text{TST}} = \frac{k_B T}{h} (c^\circ)^{\Delta n^\ddagger} e^{-\Delta G^\ddagger / RT} = \frac{k_B T}{h} (c^\circ)^{\Delta n^\ddagger} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

where $c^\circ = 1 \text{ mol} \cdot \text{dm}^{-3}$ is the standard-state molar concentration.

Relating TST to the Arrhenius law by setting

$$k_{\text{TST}} = A e^{-E_a / RT} \quad (1)$$

we found that the activation energy is related to the standard enthalpy of activation by

$$E_a = \Delta H^\ddagger + (1 - \Delta n^\ddagger) RT$$

with the pre-exponential factor

$$A = \frac{k_B T}{h} (c^\circ)^{\Delta n^\ddagger} e^{-(\Delta n^\ddagger - 1) \Delta S^\ddagger / R} \quad (2)$$

Considering that the reactions are of the same order, i.e., Δn^\ddagger is the same in both cases, the ratio of the rate constants is:

$$\frac{k_{\text{TST},2}}{k_{\text{TST},1}} \stackrel{(1)}{=} \frac{A_2 e^{-E_a / RT}}{A_1 e^{-E_a / RT}} \stackrel{E_{a1} = E_{a2}}{=} \frac{A_2}{A_1} \stackrel{(2)}{=} e^{(\Delta S_2^\ddagger - \Delta S_1^\ddagger) / R} = e^{50/8.314} = 409.$$

Problem 5

We know $k_{\text{TST}} = 2.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $E_a = 150 \text{ kJ/mol}$, and that the order of reaction $n=2$

- ΔG^\ddagger : From TST:

$$k_{\text{TST}} = \frac{k_B T}{h} (c^\circ)^{1-n} e^{-\Delta G^\ddagger / RT}$$

where $c^\circ = 1 \text{ mol} \cdot \text{dm}^{-3}$ is the standard-state molar concentration (note that it is necessary to keep consistency in the units).

$$\Delta G^\ddagger = -RT \ln \left(\frac{k_{\text{TST}} h c^\circ}{k_B T} \right) = 190.4 \text{ kJ/mol}$$

- ΔH^\ddagger : From the expression for the activation energy:

$$E_a = \Delta H^\ddagger + (1 - \Delta n^\ddagger) RT; \quad \Delta n^\ddagger = n^\ddagger - n_{\text{react}} = 1 - 2 = -1$$

(since there are two molecules of reactants and 1 molecule of TST)

$$\Delta H^\ddagger = E_a - 2RT = 138.8 \text{ kJ/mol}$$

- ΔS^\ddagger : We know that

$$G = H - TS \quad \Rightarrow \quad \Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T} = -76.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

- *A*: From $k_{\text{TST}} = Ae^{-E_a/RT}$ we easily find that

$$A = k_{\text{TST}}e^{E_a/RT} = 1.03 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$$