Transition State Theory: Applications

Let us use a simple reaction as an example of applying Transition State Theory (TST). The reaction we will use, mainly because we have information about its transition state from computations related to my research, is

\[ O + HCl \rightarrow [O..H..Cl]^+ \rightarrow OH + Cl. \]

Constants:

In order to calculate the partition functions, we first define the following constants:

- Planck’s constant: \( h = 6.626 \times 10^{-34} \text{ J s} \)
- Boltzmann constant: \( k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} \)
- Avogadro’s Number: \( N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \)
- Gas constant: \( R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \)
- Velocity of light: \( c = 2.998 \times 10^{10} \text{ cm s}^{-1} \)
- Atomic masses:
  - \( m_O = \frac{15.994 \times 10^{-3} \text{ kg mol}^{-1}}{N_A}; \ m_O = 2.6559 \times 10^{-26} \text{ kg} \)
  - \( m_H = \frac{1.008 \times 10^{-3} \text{ kg mol}^{-1}}{N_A}; \ m_H = 1.6739 \times 10^{-27} \text{ kg} \)
  - \( m_{Cl} = \frac{35.453 \times 10^{-3} \text{ kg mol}^{-1}}{N_A}; \ m_{Cl} = 5.8872 \times 10^{-26} \text{ kg} \)
- Temperature: \( T = 600 \text{ K} \)

Translational partition functions:

\[
q^{O}_t = \left( \frac{2\pi m_O k_B T}{h^2} \right)^{3/2} = 1.7675 \times 10^{32} \left( \sqrt{\frac{\text{kg}}{(\text{J s}^2)}} \right)^3 \\
q^{HCl}_t = \left( \frac{2\pi (m_H + m_{Cl}) k_B T}{h^2} \right)^{3/2} = 6.0836 \times 10^{32} \left( \sqrt{\frac{\text{kg}}{(\text{J s}^2)}} \right)^3 \\
q^{(OHCl)}^+_t = \left( \frac{2\pi (m_O + m_H + m_{Cl}) k_B T}{h^2} \right)^{3/2} = 1.0498 \times 10^{33} \left( \sqrt{\frac{\text{kg}}{(\text{J s}^2)}} \right)^3
\]

You must verify that the units on the right hand side cancel to yield units of m\(^{-3}\), because we have calculated the translational partition functions per *unit volume*. Partition functions are just statistically obtained numbers of states and, therefore, should not have units. In this case, the remaining unit, i.e., m\(^{-3}\), simply indicates that so many states are available for unit volume of the species under consideration at the given temperature. Since molecules occupy the states, we will later interpret these units as “states per cubic meter,” or “molecules per cubic meter.”
Rotational Partition Functions:

For the HCl molecule, the equilibrium bond distance is $R_e = 1.27455 \times 10^{-10}$ m.
The moment of inertia is given by $I = \mu R_e^2$, where $\mu$ is the reduced mass. The symmetry number $\sigma$ for HCl is 1.
Moment of inertia: $I = \left(\frac{m_H m_{Cl}}{m_H + m_{Cl}}\right) R_e^2$; $I = 2.644 \times 10^{-47}$ (kg) m$^2$
Rotational partition function for a diatomic molecule:

$$q_{HCl} = \frac{2 I k_B T}{(\hbar/(2\pi))^2} = 39.4 (kg) \frac{m^2}{(J) s^2}.$$

(Once again, verify that the units cancel.)

In order to evaluate the rotational partition function for the bent O-H-Cl transition state, we need the moments of inertia $I_A, I_B,$ and $I_C$. These have to be calculated from the known (from quantum chemistry calculations) geometry of the transition state: $(R_{OH}, R_{HCl}, \angle OHCl) = (1.2669 \text{Å}, 1.4785 \text{Å}, 132.9^\circ)$, where the bond lengths are given in Ångstoms ($1 \text{Å} = 10^{-10}$ m). Since the oxygen and chlorine atoms are so much more massive than the hydrogen atom, we may assume that the center of mass of the three particle system is the same as the center of mass of the oxygen and the chlorine, which lies along the line connecting these two atoms, which has a length of $r_{OCl}$.

Using the law of cosines, we get

$$r_{OCl} = \sqrt{1.2669^2 + 1.4785^2 - 2 \times 1.2669 \times 1.4785 \times \cos(132.9^\circ \frac{\pi}{180})} = 2.5182,$$

where the fraction inside the cosine is to convert the angle from degrees to radians. Now, since hydrogen is so much lighter, we may (as an acceptable, but not a very good, approximation) ignore the presence of the hydrogen atom and evaluate the moment of inertia of the three particle system as if it is the diatomic molecule ClO, with a bond distance of $r_{OCl} = 2.5182 \times 10^{-10}$ m. This is what we do below:

Moment of inertia: $I^{(OHC)} = \left(\frac{m_O m_{Cl}}{m_O + m_{Cl}}\right) r_{OCl}^2$; $I_{OHC} = 1.1606 \times 10^{-45}$ (kg) m$^2$

Rotational partition function of the transition state:

$$q^{(OHC)} = \frac{2 I_{OHC} k_B T}{(\hbar/(2\pi))^2} = 1729.5 (kg) \frac{m^2}{(J) s^2}.$$

Vibrational Partition Functions:

The vibrational frequency of the HCl molecule and the two vibrational frequencies of the O-H-Cl transition state are listed below:

$\omega_{HCl} = 2991.0 \text{cm}^{-1}$  $\omega_1 = 1407.9 \text{cm}^{-1}$  $\omega_2 = 266.8 \text{cm}^{-1}$.

For convenience, we also define a new quantity,

$$\beta = \frac{\hbar c}{k_B T} \cdot \beta = 2.3974 \times 10^{-3} \text{ cm}.$$

The vibrational mode partition functions are, therefore,

$q_{HCl}^{\omega_{HCl}} = (1 - \exp(-\beta \omega_{HCl}))^{-1} = 1.0008$
$q_{\omega_1}^{\omega_{HCl}} = (1 - \exp(-\beta \omega_1))^{-1} = 1.0354$
$q_{\omega_2}^{\omega_{HCl}} = (1 - \exp(-\beta \omega_2))^{-1} = 2.1164$
The energy difference $U^z_0$:

The electronic energy difference between the O/HCl system and the O-H-Cl transition state is 45.971 kJ/mol. Taking the zero point energies of the two systems into account, we get:

\[ U_{el}^z = 45.971 \text{ kJ/mol} \]

\[ \Delta U_0^z = U_{el} + \frac{1}{2} \hbar c (\omega_1 + \omega_2 - \omega_{HCl}) N_A = 38098. \frac{J}{mol} \]

The transition state theory rate constant:

Now, the transition state theory rate constant is given by

\[ k = \left( \frac{k_B T}{\hbar} \right) \frac{q_{OHCl}}{q_{O} \times q_{HCl}} \exp[-\Delta U_0^z/(RT)]. \]

Substituting from above, we define

\[ q_O = 1.7675 \times 10^{32} \text{ m}^{-3} \]
\[ q_{HCl} = 6.0836 \times 10^{32} \text{ m}^{-3} \times 39.4 \times 1.0008 = 2.3989 \times 10^{34} \text{ m}^{-3} \]
\[ q_{OHCl} = 1.0498 \times 10^{35} \times 1729.5 \times 2.1164 = 3.9786 \times 10^{36} \text{ m}^{-3} \]

Therefore, the rate constant is:

\[ k = \left( \frac{k_B T}{\hbar} \right) \frac{q_{OHCl}}{q_O \times q_{HCl}} \exp[-38098. \frac{J}{mol}/(RT)] \]

\[ = 5.659 \times 10^{-21} \text{ m}^3 \text{ s}^{-1}. \]

These units have to be interpreted with caution. Recall that the translational partition function is the only one that provides the units to the rate constant. These units should correctly be expressed as “states per cubic meter” or, since it is molecules that are occupying the states, as “molecules per cubic meter.” Therefore, we may report this rate constant as

\[ k = 5.659 \times 10^{-21} \text{ molecules}^{-1} \text{ m}^3 \text{ s}^{-1}, \]

which are the correct units for a second order rate constant.

Note that if we had used the “typical magnitudes” for the partition functions (lower limits), we would have obtained

\[ k = \left( \frac{k_B T}{\hbar} \right) \frac{q_1^3 q_2^3 q_3^5}{q_1^3(q_1^3 q_2^3 q_3)} \exp[-\Delta U_0^z/(RT)] = \left( \frac{k_B T}{\hbar} \right) \frac{10^{11}}{10^{30}} \exp[-38098. \frac{J}{mol}/(RT)] \]

\[ = \frac{1.2505 \times 10^{-16}}{s} \exp(-7.637(\text{kg}) \frac{m^2}{s^2 \text{J}}) = 6.0308 \times 10^{-20} \text{ m}^3 \text{ s}^{-1}. \]

This is only a factor of 10 larger than the result from the more tedious evaluation we just went through. Considering all the approximations that go into the latter calculation, it is actually rather remarkable that the difference between the two is so small. Therefore, we have also verified that using the “typical” magnitudes in these calculations is often fairly satisfactory. On the other hand, a very accurate version of transition state theory, known as variational transition state theory, predicts this rate constant at 600K to be $2.62 \times 10^{-20} \text{ molecules}^{-1} \text{ m}^3 \text{ s}^{-1}$, while experimental data indicate that the value should be $(3.35 \pm 0.4) \times 10^{-20} \text{ molecules}^{-1} \text{ m}^3 \text{ s}^{-1}$. It is rather remarkable that these values are only a factor of 2 or so different from the “typical magnitude” estimate. I believe that this is just a coincidence in this case.