Rate Constants Including Tunneling Effect

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1 General Description

The classical rate constant is given by the Eyring equation [1],

$$k_{classical}(T) = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/k_B T}. \tag{1}$$

In general, this variable is represented in an Arrhenius plot: $\ln k$ vs $1/T$ ('linear' plot),

$$\ln k = \ln\left(\frac{k_B T}{h}\right) - \frac{\Delta G^{\ddagger}}{k_B} \cdot \frac{1}{T}. \tag{2}$$

In order to take into account the tunneling effect, the semi-classical rate constant is defined as

$$k_{SC}(T) = \kappa(T) k_{classical}(T), \tag{3}$$

where $\kappa(T)$ is the transmission coefficient that depends on the transmission probability of the tunneling effect [2]. The analytic expression of this coefficient is different depending on the potential barrier approximation used. However, its general equation is

$$\kappa(T) = \frac{\int_{E_0}^{+\infty} P^T(E) e^{-\beta E} dE}{\int_{E_0}^{+\infty} P^C(E) e^{-\beta E} dE}, \tag{4}$$

where $\beta = 1/k_B T$, $P^T(E)$ is the quantum transmission probability, $P^C(E)$ is the classical transmission probability and $E_0 = \max(E_r, E_p)$ with E_r the reactant's energy and E_p the product's energy [2]. It is very important that all the energies include the Zero Point Energy (ZPE) and they must have the same energy origin (this is particularly key in the Eckart barrier case).

The Variational Transition State Theory (VTST) states that the classical transmission probability is given by

$$P^C(E) = H(E - E^{\ddagger}), \tag{5}$$

where $E^{\ddagger}$ stands for the maximum energy of the potential barrier and $H(x)$ is the Heaviside step function [2]. Thus, the transmission coefficient results in

$$\kappa(T) = \beta e^{\beta E^{\ddagger}} \int_{E_0}^{+\infty} P^T(E) e^{-\beta E} dE. \tag{6}$$

In the next sections, the following 1D potentials are studied:

- Asymmetric squared barrier
- Asymmetric truncated parabolic barrier
- Asymmetric and approximated Eckart barrier
- General potential barrier

In general, the uni-dimensional potential barrier underestimates the transmission coefficient because it does not take into account the curvature of the reaction path.

Finally, a possible way to numerically implement the mentioned barriers is described in section 3 for the purpose of addressing these numerical issues.

2 Theoretical Description of the Potential Barriers

In this section, the potential barriers and their transmission coefficients are described. The characteristic parameters and some approximations are also included.

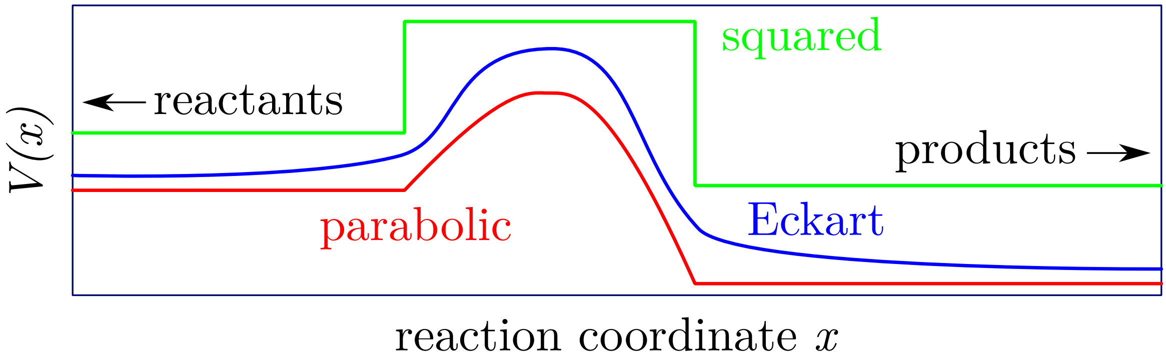

Figure 1: Symbolic representation of the described potentials.

2.1 Asymmetric Squared Barrier

Potential:

$$V(x) = \begin{cases} E_r & x \leq 0 \\ E^\ddagger & 0 < x \leq l \\ E_p & l < x \end{cases} \tag{7}$$

where l is the barrier's width. This parameter can be estimated from the characteristic length of the parabolic or Eckart potential:

$$l_{parabolic} = \sqrt{\frac{V_{max}}{2\pi^2\mu|\nu^\ddagger|^2}} + \sqrt{\frac{V_{max} - \Delta V}{2\pi^2\mu|\nu^\ddagger|^2}} \tag{8}$$

$$l_{Eckart} = \frac{1}{|\nu^\ddagger|}\sqrt{\frac{2}{\mu}}\left(\frac{1}{\sqrt{V_r}} + \frac{1}{\sqrt{V_f}}\right)^{-1} \tag{9}$$

where $\nu^\ddagger$ is the imaginary frequency of the transition state (TS), μ is the reduced mass associated to this mode, $V_{max} = E^\ddagger - E_r$, $\Delta V = E_p - E_r$, $V_f = E^\ddagger - E_r$ and $V_r = E^\ddagger - E_p$ [2–4]. It is worth mentioning here that some formulae in [3] are not correct). The nomenclature V_r and V_f corresponds to *reverse* and *forward*, respectively, and r should not be confused with 'reactants'.

Using the expressions of subsection 2.4, it can be noticed that $s_1 = 0$ and $s_2 = l$, so

$$\theta(E) = \frac{\sqrt{2\mu}}{\hbar}\int_0^l \sqrt{E^\ddagger - E}\, dx = \frac{l}{\hbar}\sqrt{2\mu(E^\ddagger - E)}\,. \tag{10}$$

Then, the transmission probability can be written as

$$P_{squared}(E) = \begin{cases} 0 & E \leq E_0 \\ \left(1 + e^{2\theta(E)}\right)^{-1} & E_0 < E \leq E^\ddagger \\ 1 - \left(1 + e^{2\theta(2E^\ddagger - E)}\right)^{-1} & E^\ddagger < E \leq 2E^\ddagger - E_0 \\ 1 & 2E^\ddagger - E_0 < E \end{cases} \tag{11}$$

In order to determine the transmission coefficient, the following integral has to be computed

$$I \equiv \int_{E_0}^{+\infty} P_{squared}(E) e^{-\beta E} dE \equiv I_1 + I_2 + I_3, \tag{12}$$

where

$$I_3 = \int_{2E^{\ddagger}-E_0}^{+\infty} e^{-\beta E} dE = \frac{1}{\beta} e^{-\beta(2E^{\ddagger}-E_0)} \tag{13}$$

and I_1 and I_2 have to be numerically integrated.

2.2 Asymmetric Parabolic Barrier

Potential:

$$V(x) = \begin{cases} 0 & x \leq -\sqrt{\dfrac{V_{max}}{2\pi^2\mu|\nu^{\ddagger}|^2}} \\ V_{max} - 2\pi^2\mu|\nu^{\ddagger}|^2 x^2 & -\sqrt{\dfrac{V_{max}}{2\pi^2\mu|\nu^{\ddagger}|^2}} < x \leq \sqrt{\dfrac{V_{max}-\Delta V}{2\pi^2\mu|\nu^{\ddagger}|^2}} \\ \Delta V & \sqrt{\dfrac{V_{max}-\Delta V}{2\pi^2\mu|\nu^{\ddagger}|^2}} < x \end{cases} \tag{14}$$

where $\nu^{\ddagger}$ is the imaginary frequency of the TS, μ is the reduced mass associated with this mode, $V_{max} = E^{\ddagger} - E_r$ and $\Delta V = E_p - E_r$ [2]. It is important to notice that this potential has its energy origin on the reactants, $V(x \to -\infty) = 0$.

The transmission coefficient is found to be

$$\kappa(T) = \begin{cases} \dfrac{\pi/K}{\sin(\pi/K)} + \exp\left[(1-K)\dfrac{V_b}{k_B T}\right]/(1-K) & K > 1 \\ V_b/k_B T & K = 1 \\ \left(\exp\left[(1-K)\dfrac{V_b}{k_B T}\right] - 1\right)/(1-K) & K > 1 \end{cases} \tag{15}$$

where $K = 2\pi k_B T/h|\nu^{\ddagger}|$ and $V_b = V_{max} - \max(0, \Delta V)$ [2].

2.3 Asymmetric Eckart Barrier

Potential:

$$V(x) = \frac{Ae^{(x-x_0)/l}}{1+e^{(x-x_0)/l}} + \frac{Be^{(x-x_0)/l}}{\left(1+e^{(x-x_0)/l}\right)^2} \tag{16}$$

where

$$\begin{aligned} A &= V_f - V_r \\ B &= \left(\sqrt{V_r} + \sqrt{V_f}\right)^2 \\ l &= \frac{1}{|\nu^{\ddagger}|}\sqrt{\frac{2}{\mu}}\left(\frac{1}{\sqrt{V_r}} + \frac{1}{\sqrt{V_f}}\right)^{-1} \\ x_0 &= \frac{l}{2}\ln(1 - \Delta V/V_{max}) \quad \text{corresponds to the position of the maximum of the potential} \end{aligned} \tag{17}$$

with $V_{max} = E^{\ddagger} - E_r$, $\Delta V = E_p - E_r$, $V_f = E^{\dagger} - E_r$ and $V_r = E^{\dagger} - E_p$ [2,4]. The nomenclature of V_r and V_f is the *reverse* and *forward* potential, respectively. It is important to notice that the potential has its energy origin on the reactants, $V(x \to -\infty) = 0$.

The transmission probability is given by

$$P_{Eckart}(E) = \frac{\cosh(a+b) - \cosh(a-b)}{\cosh(a+b) + \cosh(d)}, \tag{18}$$

where

$$
\begin{aligned}
a &= \frac{4\pi}{h|\nu^\ddagger|}\left(\frac{1}{\sqrt{V_r}}+\frac{1}{\sqrt{V_f}}\right)^{-1}\sqrt{E} \\
b &= \frac{4\pi}{h|\nu^\ddagger|}\left(\frac{1}{\sqrt{V_r}}+\frac{1}{\sqrt{V_f}}\right)^{-1}\sqrt{E-V_f+V_r} \\
d &= 4\pi\sqrt{\frac{V_f V_r}{(h|\nu^\ddagger|)^2}-\frac{1}{16}}
\end{aligned}
\tag{19}
$$

as described in [2,4].

The expression of the transmission coefficient is

$$
\kappa(T) = \beta e^{\beta E^\ddagger}\int_{E_0}^{+\infty} P_{Eckart}(E-E_r)e^{-\beta E}dE \tag{20}
$$

because the energy origin of $P_{Eckart}(E)$ is different from the integral variables. For example, when in the integral $E = E_r$, then $P(E_r - E_r) = P(0)$ that agrees with the energy origin of the Eckart potential. Moreover, as the minimum value of E in the integral is $E_0 = \max(E_r, E_p)$, there will be no problem in evaluating $\sqrt{E-E_r}$ or $\sqrt{E-E_r-V_f+V_r}$ when $E \in [E_0, +\infty)$ as

- $\sqrt{E-E_r}$, $E - E_r \geq 0$ because $E \in [\max(E_r, E_p), +\infty)$
- $\sqrt{E-E_r-V_f+V_r} = \sqrt{E-E_r-E_p+E_r} = \sqrt{E-E_p}$, $E-E_p \geq 0$ for the same reason.

In addition, certain approximations can be done to simplify the calculations of $\kappa(T)$ [2]. Assuming that the barrier is symmetric ($\Delta V = 0$) and that it is very high or wide, in other words

$$
\gamma = \frac{2\pi V_{max}}{h|\nu^\ddagger|} \gg 1, \tag{21}
$$

then the transmission coefficient can be approximated to

$$
\kappa(T) = \frac{h|\nu^\ddagger|}{2\pi k_B T}\int_{-\gamma}^{+\infty}\frac{\exp\left[-h|\nu^\ddagger|x/2\pi k_B T\right]}{1+\exp\left[2\gamma\left(1-\sqrt{1+x/\gamma}\right)\right]}dx \tag{22}
$$

where $x = \gamma(E - E_{max})/V_{max}$.

Moreover, assuming also high temperatures (i.e. $2\pi k_B T/h|\nu^\ddagger| \gg 1$) leads to the analytical expression

$$
\kappa(T) = \frac{h|\nu^\ddagger|/2k_B T}{\sin(h|\nu^\ddagger|/2k_B T)}. \tag{23}
$$

Finally, this expression can be simplified in order to obtain the Wigner tunneling expression

$$
\kappa(T) = 1 + \frac{1}{24}\left(\frac{h|\nu^\ddagger|}{k_B T}\right)^2. \tag{24}
$$

2.4 General Potential Barrier

Potential: any $V(x)$ that fulfills $V(x \to -\infty) = E_r$ and $V(x \to +\infty) = E_p$.

This general barrier is a zero-curvature tunneling model (ZCT), which uses the semi-classical WKB approximation. The model is considered multidimensional if the potential includes all the vibrational ZPE in the orthogonal directions of the reaction path [2].

The transmission probability is given by

$$P_{ZCT}(E) = \begin{cases} 0 & E \leq E_0 \\ \left(1 + e^{2\theta(E)}\right)^{-1} & E_r < E \leq E^{\ddagger} \\ 1 - \left(1 + e^{2\theta(2E^{\ddagger}-E)}\right)^{-1} & E^{\ddagger} < E \leq 2E^{\ddagger} - E_0 \\ 1 & 2E^{\ddagger} - E_0 < E \end{cases} \tag{25}$$

where

$$\theta = \frac{1}{\hbar}\int_{s_1}^{s_2} \sqrt{2\mu(V(x) - E)}\, dx \tag{26}$$

with s_1 and s_2 being the crossing points between $V(x)$ and E. In other words, they are the points that fulfill $V(s_1) = E = V(s_2)$.

The transmission coefficient is then

$$\kappa(T) = \beta e^{\beta E^{\ddagger}} \int_{E_0}^{+\infty} P_{ZCT}(E) e^{-\beta E} dE. \tag{27}$$

The ZCT underestimates the transmission by tunneling effect because it does not take into account the curvature of the reaction path. In [2], several sophisticated methods are described, such as small-curvature tunneling, large-curvature tunneling, microcanonically optimized tunneling and least-action tunneling.

3 Numerical Implementation of the Barriers

Units

Firstly, units have to be properly chosen in such a way that the values of the variables and constants are close to one, which tends to decrease the numerical issues, specially truncation errors.

A possible option is working with eV for Energies, K for Temperatures and cm^{-1} for Frequency. For example, 100.000 J/mol $\approx$ 1 eV $\approx$ 0.038 Hartree. Morevoer, the constants are

$$h = 1.23984193 \cdot 10^{-4}\ \text{eV} \cdot \text{cm} \quad \text{and} \quad k_B = 1380649/16021766340\ \text{eV} \cdot \text{K}^{-1} \approx 8.6173 \cdot 10^{-5}\ \text{eV} \cdot \text{K}^{-1}$$

and close to 1. [1] Another important unit converion is 1 Hartree = 27.2113845 eV.

Values can be also made close to one by changing the origin of energies to E_0. Then, for example -3000, -3001 and -2999 are transformed to 0, 1 and -1 respectively (avoiding errors of $e^{-\beta E} = e^{3000\beta} \to \infty$). However, it is recommended to work with expressions involving energy differences instead of absolute energies.

Numerical Errors in Exponentials

The vast majority of the expressions that describe the potential barriers contain exponentials, like $e^{\beta E^\ddagger}$. This fact can lead to overflow errors because the maximum numerical float precision is usually around 10^{300}. Working with low temperatures and/or energies far from one causes very high exponentials and thus numerical overflows.

The main problem is that $\kappa \to \infty$ and $k_{classical} \to 0$ which leads to indeterminate forms, such as $0 \cdot \infty$ or ∞/∞. In order to solve this, a possible solution is to factor exponentials from the numerator and denominator and evaluating k_{SC} all together, instead of evaluating first κ and $k_{classical}$ separately and then multiplying them. For example,

$$\frac{e^{3000} + e^{3001}}{e^{3000} + e^{2999}} = \frac{1 + e^{1}}{1 + e^{-1}} \tag{28}$$

and

$$a = e^{3000} + e^{3001} \to \infty, \quad b = \frac{1}{e^{3000} + e^{2999}} \to 0 \quad \Rightarrow \quad a \cdot b = \frac{1 + e^{1}}{1 + e^{-1}} \neq 0 \cdot \infty. \tag{29}$$

Numerical Integration with Infinite Limits

In order to calculate the transmission coefficient, an infinite-limit integration has to be used. A possible trick is to determine the energy from which the $P(E) \to 1$ (E_{MAX}) as it can be assumed to be a non-decreasing function), and then integrate the expression analytically

$$I = \int_{E_0}^{\infty} P(E) e^{-\beta E} dE \approx \int_{E_0}^{E_{MAX}} P(E) e^{-\beta E} dE + \frac{1}{\beta} e^{-\beta E_{MAX}}. \tag{30}$$

The value of E_{MAX} can be found analytically if the expression for the probability is simple, or it can be numerically calculated by iteration.

Expressions and Tricks used for each Barrier

In the next page, the expressions and numerical tricks employed to calculate all the variables in the script are described.

[1] Click on the constants to open the references of the values: h and k_B.

3.1 Asymmetric Squared Barrier

The expression for the width of the barrier is given by

$$l = \frac{1}{\pi|\nu^{\ddagger}|}\sqrt{\frac{2V_{max}}{\mu}}, \tag{31}$$

which is an approximation to $l_{parabolic}$.

The parts of the transmission probability are integrated numerically and analytically

$$\kappa(T) = \beta \int_{E_0}^{E^{\ddagger}} \frac{e^{-\beta(E-E^{\ddagger})}dE}{1+e^{A\sqrt{E^{\ddagger}-E}}} - \beta \int_{E^{\ddagger}}^{2E^{\ddagger}-E_0} \frac{e^{-\beta(E-E^{\ddagger})}dE}{1+e^{A\sqrt{E-E^{\ddagger}}}} + 1 \tag{32}$$

$$k_{SC}(T) = \frac{1}{h}\int_{E_0}^{E^{\ddagger}} \frac{e^{-\beta(E-E^{\ddagger}+\Delta G^{\ddagger})}dE}{1+e^{A\sqrt{E^{\ddagger}-E}}} - \frac{1}{h}\int_{E^{\ddagger}}^{2E^{\ddagger}-E_0} \frac{e^{-\beta(E-E^{\ddagger}+\Delta G^{\ddagger})}dE}{1+e^{A\sqrt{E-E^{\ddagger}}}} + \frac{k_B T}{h}e^{-\beta\Delta G^{\ddagger}} \tag{33}$$

where $A = 2l\sqrt{2\mu}/\hbar = 8\sqrt{V_{max}}/h|\nu^{\ddagger}|$ and both finite integrals are determined numerically.

3.2 Asymmmetric Parabolic Barrier

The expression for the rate constant is given by

$$k_{SC}(T)\cdot\frac{h}{k_B T} = \begin{cases} \frac{\pi/K}{\sin(\pi/K)}e^{-\Delta G^{\ddagger}/k_B T} + \exp\left[-\frac{\Delta G^{\ddagger}-V_b(1-K)}{k_B T}\right]/(1-K) & K>1 \\ V_b e^{-\Delta G^{\ddagger}/k_B T}/k_B T & K=1 \\ \left(\exp\left[-\frac{\Delta G^{\ddagger}-V_b(1-K)}{k_B T}\right] - e^{-\Delta G^{\ddagger}/k_B T}\right)/(1-K) & K>1 \end{cases} \tag{34}$$

The only problem is evaluating close to $K = 1$ as $1/(1-K) \to \infty$. This issue can be solved by manually introducing a certain threshold: $K > 1 + 10^{-\epsilon}$, $K \in [1 + 10^{-\epsilon}, 1 - 10^{-\epsilon}]$ and $K < 1 - 10^{-\epsilon}$.

In addition, for $K > 1$, there could be an overflow problem in the exponential, but the maximum value is $(V_b - \Delta G^{\ddagger})/k_B T$.

3.3 Asymmetric Eckart Barrier

For the asymmetric Eckart barrier, see subsection 3.4.

For the approximated Eckart barrier, the integral can be analytically integrated if the denominator tends to 1 (i.e. for $e^{2\gamma(1-\sqrt{1+x_{MAX}/\gamma})} \leq 10^{-\epsilon}$). In this limit,

$$x_{MAX} = \gamma\left(\left(1+\frac{\epsilon\ln 10}{2\gamma}\right)^2 - 1\right). \tag{35}$$

Then,

$$\kappa(T) = \frac{h|\nu^{\ddagger}|}{2\pi k_B T}\int_{-\gamma}^{x_{MAX}} \frac{\exp\left[-h|\nu^{\ddagger}|x/2\pi k_B T\right]}{1+\exp\left[2\gamma\left(1-\sqrt{1+x/\gamma}\right)\right]}dx + \exp\left[\frac{-h|\nu^{\ddagger}|x_{MAX}}{2\pi k_B T}\right] \tag{36}$$

$$k_{SC}(T) = \frac{|\nu^{\ddagger}|}{2\pi}\int_{-\gamma}^{x_{MAX}} \frac{\exp\left[-(h|\nu^{\ddagger}|x + 2\pi\Delta G^{\ddagger})/2\pi k_B T\right]}{1+\exp\left[2\gamma\left(1-\sqrt{1+x/\gamma}\right)\right]}dx + \exp\left[-\frac{h|\nu^{\ddagger}|x_{MAX}+2\pi\Delta G^{\ddagger}}{2\pi k_B T}\right] \tag{37}$$

where the finite integrals are calculated numerically.

3.4 General Potential Barrier

Similarly to the other barriers, E_{MAX} is determined from which $P(E \geq E_{MAX}) \geq 1 - 10^{-\epsilon}$. As no analytical expression exists for $P(E)$, the value of E_{MAX} is numerically determined by iteration: increasing E until the condition $P(E \geq E_{MAX}) \geq 1 - 10^{-\epsilon}$ is fulfilled.

Then, the integral is divided in two parts which are calculated numerically and analytically respectively:

$$\kappa(T) = \beta \int_{E_0}^{E_{MAX}} P(E) e^{-\beta(E - E^{\ddagger})} dE + e^{-\beta(E_{MAX} - E^{\ddagger})} \tag{38}$$

$$k(T) = \frac{1}{h} \int_{E_0}^{E_{MAX}} P(E) e^{-\beta(E - E^{\ddagger} + \Delta G^{\ddagger})} dE + \frac{k_B T}{h} e^{-\beta(E_{MAX} - E^{\ddagger} + \Delta G^{\ddagger})} \tag{39}$$

References

[1] Henry Eyring. The activated complex in chemical reactions. *The Journal of Chemical Physics*, 3(2):107–115, 1935.

[2] Junwei Lucas Bao and Donald G Truhlar. Variational transition state theory: theoretical framework and recent developments. *Chemical Society Reviews*, 46(24):7548–7596, 2017.

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[4] Phillip S Peters, Denis Duflot, Alexandre Faure, Claudine Kahane, Cecilia Ceccarelli, Laurent Wiesenfeld, and Céline Toubin. Theoretical investigation of the isomerization of trans-hcoh to h2co: an example of a water-catalyzed reaction. *The Journal of Physical Chemistry A*, 115(32):8983–8989, 2011.