Statistical reaction rate theories

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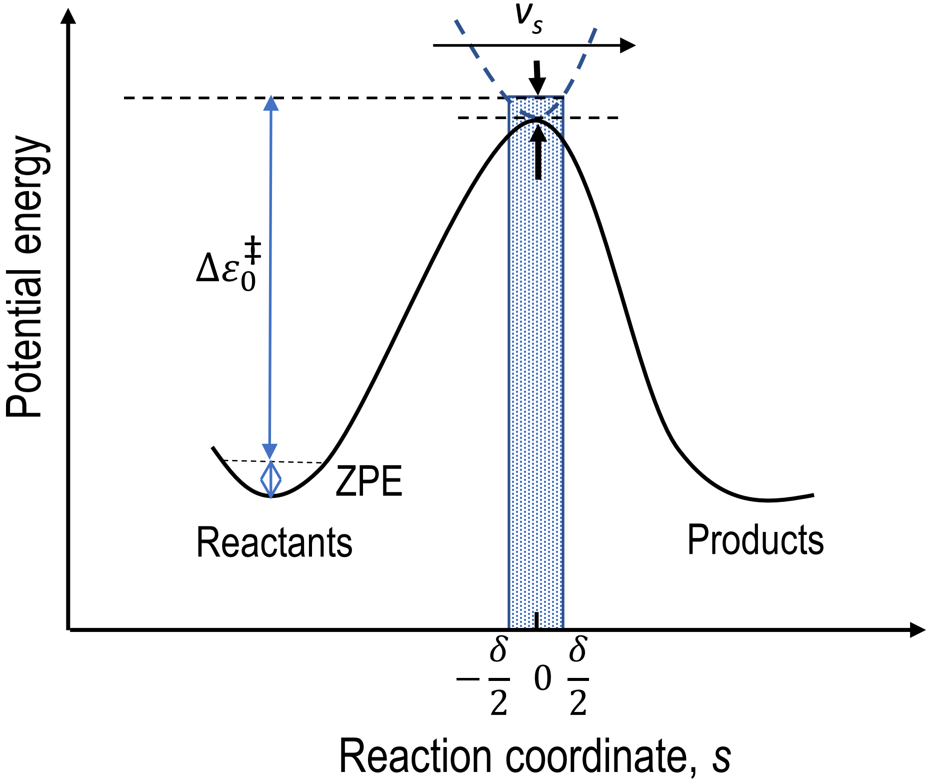
Transition State Theory[1,2]

Basic postulates

1. Molecular systems that cross the critical dividing surface in the direction of products do not return (no-recrossing approximation).
2. During the reaction, the molecular states of reactants follow a Maxwell-Boltzmann distribution (at a given *T*).
3. The complexes crossing the dividing surface towards products have a Maxwell-Boltzmann distribution of energies (at *T*).
4. In the TS, motion along the reaction coordinate may be separated from the rest of modes and treated as a classical translation.



In conventional TST, the dividing surface passes through the TS and is orthogonal to the reaction coordinate.

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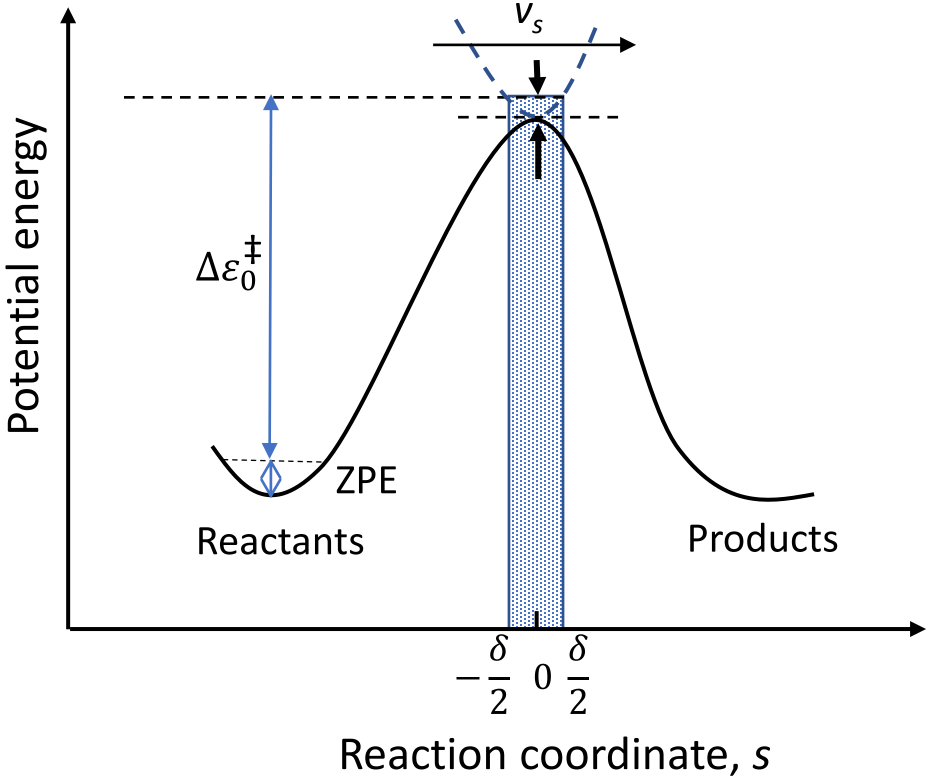
1. H. Eyring, J. Chem. Phys. *3*, 107 (1935).
2. M. G. Evans and M. Polanyi, *Trans. Faraday Soc. 31*, 875 (1935).

Transition State Theory

Derivation (statistical formulation)[1]

Let's consider an elementary reaction B + C → P. We will denote an activated complex by $X_f^{\ddagger}$. We may write the elementary reaction as

$$B + C \rightarrow \{X_f^{\ddagger}\} \rightarrow \text{Products} \qquad (7)$$



TST postulates a Maxwell-Boltzmann distribution of states for B, C as well as for $X_f^{\ddagger}$. Therefore, according to statistical mechanics (for ideal gases), we may write

$$\frac{N_f^{\ddagger}}{N_C N_B} = \frac{q_{\ddagger}}{q_C q_B} \exp\left(-\frac{\Delta\varepsilon_0^{\ddagger}}{k_B T}\right) \qquad (8)$$

where *N* denotes number of molecules, *q*, molecular partition functions and k_B is the Boltzmann constant.

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1. This presentation follows I. N. Levine, Physical Chemistry, 6th ed. McGraw-Hill (2009).

Transition State Theory

Dividing by Avogadro's constant and volume

$$K^{\ddagger} \equiv \frac{\left[\mathrm{X}_f^{\ddagger}\right]}{[\mathrm{B}][\mathrm{C}]} = \frac{q_{\ddagger}/N_A V}{(q_{\mathrm{B}}/N_A V)(q_{\mathrm{C}}/N_A V)} \exp\left(-\frac{\Delta\varepsilon_0^{\ddagger}}{k_{\mathrm{B}}T}\right) \tag{9}$$

According to postulate 4, we treat the motion along the reaction coordinate as a classical translation in one dimension. Therefore, we may write:

$$q_{\ddagger} = q_s q_{\ddagger}' \tag{10}$$

$$q_s = \frac{(2\pi\mu_s k_{\mathrm{B}}T)^{\frac{1}{2}}\delta}{2h} \qquad \text{(only states moving forward)} \tag{11}$$

where *h* is Planck's constant and μ_s is the reduce mass for motion across the dividing surface.

The rate of reaction is given by the rate at which the activated complexes cross the dividing surface. Let τ be the average time needed to cross the dividing surface ($\tau = \delta/\langle v_s \rangle$). The reaction rate will be

$$r = \frac{\left[\mathrm{X}_f^{\ddagger}\right]}{\tau} = \frac{\left[\mathrm{X}_f^{\ddagger}\right]}{\delta}\langle v_s \rangle = \frac{\langle v_s \rangle}{\delta} \frac{q_s q_{\ddagger}'/N_A V}{(q_{\mathrm{B}}/N_A V)(q_{\mathrm{C}}/N_A V)} \exp\left(-\frac{\Delta\varepsilon_0^{\ddagger}}{k_{\mathrm{B}}T}\right) [\mathrm{B}]\,[\mathrm{C}] \tag{12}$$

Transition State Theory

Statistical Formulation

The average velocity for crossing the dividing surface ($\langle v_s \rangle$) is (kinetic theory of gases):

$$\langle v_s \rangle = \frac{\int_0^\infty v_s e^{\left(-\frac{\mu_s v_s^2}{2k_\mathrm{B}T}\right)} dv_s}{\int_0^\infty e^{\left(-\frac{\mu_s v_s^2}{2k_\mathrm{B}T}\right)} dv_s} = \left(\frac{2k_\mathrm{B}T}{\pi \mu_s}\right)^{1/2} \qquad (13)$$

Substituting expression (11) and (13) into (12), we get

$$r = \frac{k_\mathrm{B}T}{h} \frac{q'_\ddagger / N_A V}{(q_\mathrm{B}/N_A V)(q_\mathrm{C}/N_A V)} \exp\left(-\frac{\Delta\varepsilon_0^\ddagger}{k_\mathrm{B}T}\right) [\mathrm{B}][\mathrm{C}] \qquad (14)$$

And since $r = k[\mathrm{B}][\mathrm{C}]$, we finally obtain for the rate constant k

$$\boxed{k = \frac{k_\mathrm{B}T}{h} \frac{q'_\ddagger / N_A V}{(q_\mathrm{B}/N_A V)(q_\mathrm{C}/N_A V)} \exp\left(-\frac{\Delta\varepsilon_0^\ddagger}{k_\mathrm{B}T}\right)} \qquad (15)$$

Units: unimolecular: s^{-1}

bimolecular: $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ (if the molecular partition functions are not divided by N_A, the units are $\mathrm{cm}^3 \cdot \mathrm{molecule}^{-1} \cdot \mathrm{s}^{-1}$).

Transition State Theory

Thermodynamic formulation

Thermodynamic formulation

Equation (15) may be written as

$$k = \frac{k_\mathrm{B}T}{h} K_c^{\ddagger} \qquad \text{with} \quad K_c^{\ddagger} = \frac{q'_{\ddagger}/N_A V}{(q_\mathrm{B}/N_A V)(q_\mathrm{C}/N_A V)} \exp\left(-\frac{\Delta\varepsilon_0^{\ddagger}}{k_\mathrm{B}T}\right) \tag{16}$$

The thermodynamic relationship between the standard Gibbs energy of reaction and the equilibrium constant is given by:

$$\Delta G_c^{\circ} = -RT\ln K_c^{\circ} = -RT\ln\left[K_c/(c^{\circ})^{\Delta n/\text{mol}}\right] \qquad \text{(ideal system)} \tag{17}$$

where Δn is the change in the number of moles and c° is the standard molar concentration (1 M). By analogy, the standard Gibbs energy of activation is defined by

$$\Delta G_c^{\ddagger} \equiv -RT\ln\left[K_c^{\ddagger}(c^{\circ})^{m-1}\right] \tag{18}$$

where *m* is the molecularity of the reaction. Hence, from eq. (16), we have

$$\boxed{k = \frac{k_\mathrm{B}T}{h}(c^{\circ})^{1-m} e^{-\Delta G_c^{\ddagger}/RT}} \qquad \text{(concentration scale)} \tag{19}$$

Transition State Theory

Caveat: the above expression implies Gibbs energies of activation in the concentration scale. If the Gibbs energy of activation is calculated in the pressure scale, then we should use:

$$k = \frac{k_\mathrm{B}T}{h}\left(\frac{p^\circ}{RT}\right)^{1-m} e^{-\Delta G_p^\ddagger/RT} \qquad \text{(pressure-scale)} \qquad (20)$$

where p° is the standard pressure.

Arrhenius parameters and thermodynamic quantities of activation: relationship

$\Delta G_c^\ddagger$ above may be written in terms of the standard enthalpy and entropy of activation:

$$\Delta G_c^\ddagger = \Delta H_c^\ddagger - T\Delta S_c^\ddagger \qquad (21)$$

and so

$$k = \frac{k_\mathrm{B}T}{h}(c^\circ)^{1-m} e^{\Delta S_c^\ddagger/R} e^{-\Delta H_c^\ddagger/RT} \qquad (22)$$

Now, considering the definition of the activation energy and eq. (16), we have

$$E_a \equiv RT^2\frac{\mathrm{d}\ln k}{dT} = RT + RT^2\frac{\mathrm{d}\ln K_c^\ddagger}{dT} \qquad (23)$$

Transition State Theory

Thermodynamic formulation

And by analogy with the van't Hoff equation $\frac{d\ln K_p^\circ}{dT} = \frac{\Delta H^\circ}{RT^2}$ and the relationship

$K_p^\circ = K_c^\circ (RTc^\circ/p^\circ)^{\Delta n/\mathrm{mol}}$ (both for ideal gases),[1] we have

$$\boxed{E_a = \Delta H^\ddagger + mRT = \Delta U^\ddagger + RT} \qquad (24)$$

where *m* is the molecularity of the reaction.

Comparing eqs. (22) and (24) with the Arrhenius equation $k = Ae^{-\frac{E_a}{RT}}$, we get

$$A = ke^{E_a/RT} = \frac{k_\mathrm{B}T}{h}(c^\circ)^{1-m}e^m e^{\Delta S_c^\ddagger/R} \qquad (25)$$

Therefore, TST provides a theoretical framework for the calculation of Arrhenius parameters (A and E_a).

Remark: A common mistake is to think that E_a is equal to the energy barrier to reaction ($\Delta\varepsilon_0^\ddagger$). They are not the same quantity!

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[1] For details, see I. N. Levine, Physical Chemistry, 6th ed. McGraw-Hill (2009).

Partition Functions (ideal gases)

Assuming that the internal degrees of freedom are separable, the molecular partition function is given by (ignoring the contribution of internal nuclear states):

$$q(T,V) \; = \; q_{\text{tr}}(T,V)q_{\text{rot}}(T)q_{\text{vib}}(T)q_{\text{el}}(T) \tag{26}$$

Translational partition function

$$q_{\text{tr}} = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V \tag{27}$$

where m is the mass of the molecule and V the volume.

Caveat: in the Gaussian program, q_{tr} is computed by

$$q_{\text{tr}} = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} \frac{k_{\text{B}} T}{p^{\circ}}$$

In Gaussian, $p^0 \; = 1$ atm.

Rotational partition function

Linear molecule $$q_{\mathrm{rot}} = \frac{1}{\sigma}\frac{2Ik_{\mathrm{B}}T}{\hbar^2} \quad (28)$$

Nonlinear molecule $$q_{\mathrm{rot}} = \frac{\pi^{1/2}}{\sigma}\left(\frac{2k_{\mathrm{B}}T}{\hbar^2}\right)^{3/2}(I_A I_B I_C)^{1/2} \quad (29)$$

Vibrational partition function

$$q_{\mathrm{vib}} = \prod_{i=1}^{3N-6} q_{\mathrm{vib},i} = \prod_{i=1}^{3N-6} \frac{1}{1-e^{-h\nu_i/k_{\mathrm{B}}T}} \quad (30)$$

This expression is obtained by using the harmonic oscillator and taken the energy zero at the lowest energy level.

Electronic partition function

$$q_{\mathrm{el}} = g_0 + g_1 e^{-\varepsilon_1/k_{\mathrm{B}}T} + \cdots \quad (31)$$

where the energy zero is at the ground electronic energy level. g_0 is the degeneracy of the ground energy level.

Symmetry and Statistical Factors[1,2]

Symmetry plays a crucial role in the calculation of rate constants by TST. For convenience, we may group all the rotational symmetry numbers into a single symmetry number for the reaction (B + C → Products):

$$\sigma = \frac{\sigma_{\mathrm{rot},B}\sigma_{\mathrm{rot},C}}{\sigma_{\mathrm{rot}}^{\ddagger}} \frac{n_{oi}^{\ddagger}}{n_{oi}^{R}} \qquad (32)$$

where n_{oi}^{R} and $n_{oi}^{\ddagger}$ are the numbers of optical isomers (i.e., enantiomers) of reactants and TS, respectively.

Point group	σ_{rot}
C_1	1
C_s	1
C_2	2
C_{2v}	2
C_{3v}	3
$C_{\infty v}$	1
D_{2h}	4
D_{3h}	6
D_{5h}	10
$D_{\infty h}$	2
D_{3d}	6
T_d	12
O_h	24

1. E. Pollack and P. J. Pechukas, *J. Am. Chem. Soc.* 100, 2984 (1978)
2. A. Fernández-Ramos, B. A. Ellingson, R. Meana-Pañeda, J. C. Marques, D. G. Truhlar, *Theor. Chem. Acc.* 118, 813 (2007)

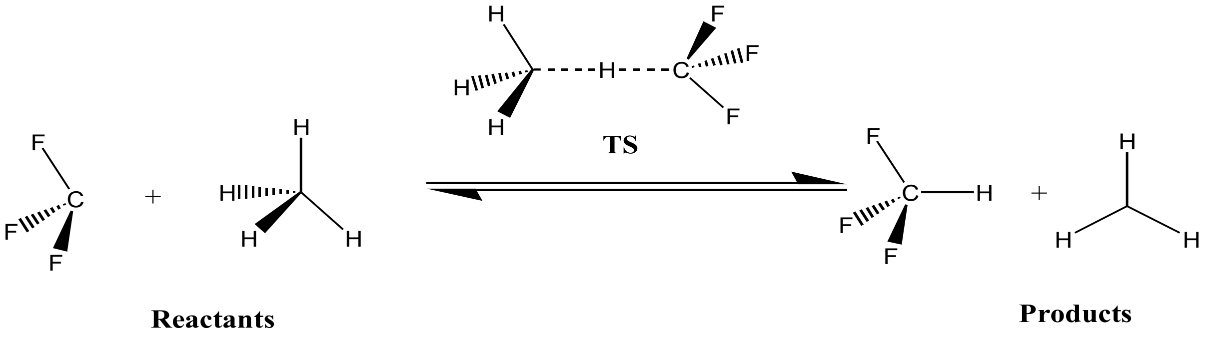
Transition State Theory

Symmetry and Statistical Factors

Example 1: Reaction without optical isomers.

Point group	σ_{rot}
C_1	1
C_s	1
C_2	2
C_{2v}	2
C_{3v}	3
$C_{\infty v}$	1
D_{2h}	4
D_{3h}	6
D_{5h}	10
$D_{\infty h}$	2
D_{3d}	6
T_d	12
O_h	24

$$CF_3 + CH_4 \rightarrow CF_3H + CH_3$$



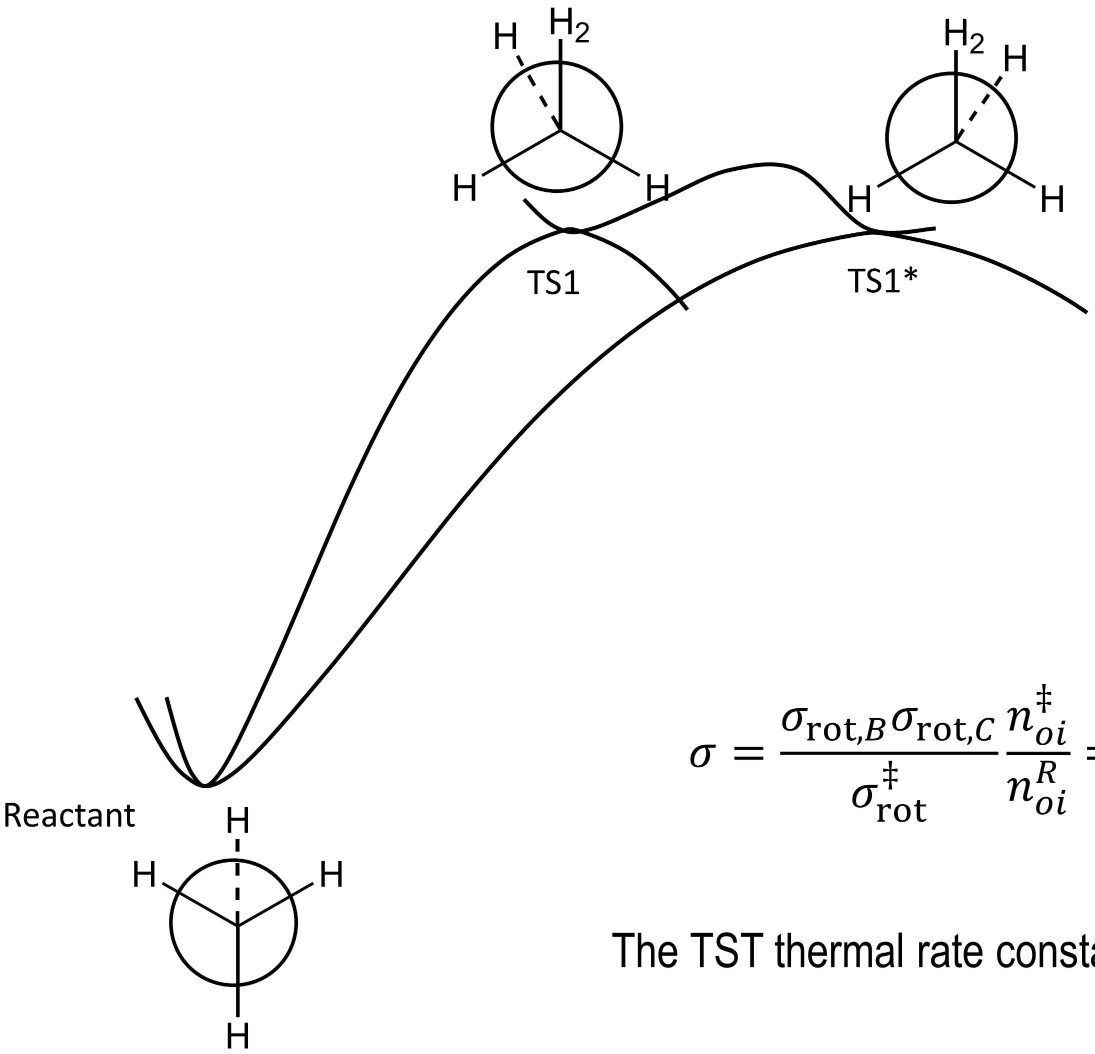
$$\sigma = \frac{\sigma_{rot,CF_3}\sigma_{rot,CH_4}}{\sigma_{rot}^{\neq}} = \frac{3\times 12}{3} = 12$$

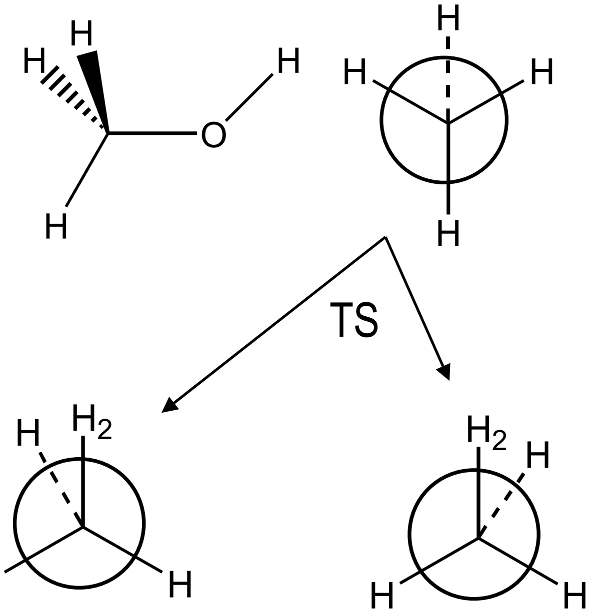
Transition State Theory

Symmetry and Statistical Factors

Example 2: Reaction with optical isomers.

$$H + CH_3OH \rightarrow H_2 + CH_2OH$$





$$\sigma = \frac{\sigma_{\mathrm{rot},B}\,\sigma_{\mathrm{rot},C}}{\sigma^{\ddagger}_{\mathrm{rot}}}\,\frac{n^{\ddagger}_{oi}}{n^{R}_{oi}} = \frac{1 \times 1}{1} \times \frac{2}{1} = 2$$

The TST thermal rate constant should be multiplied by 2.

Transition State Theory

Symmetry and Statistical Factors

Example 3: Symmetric Reactions.

R1: $H + H_2 \rightarrow H \cdots\cdots H \cdots\cdots H \rightarrow H_2 + H$

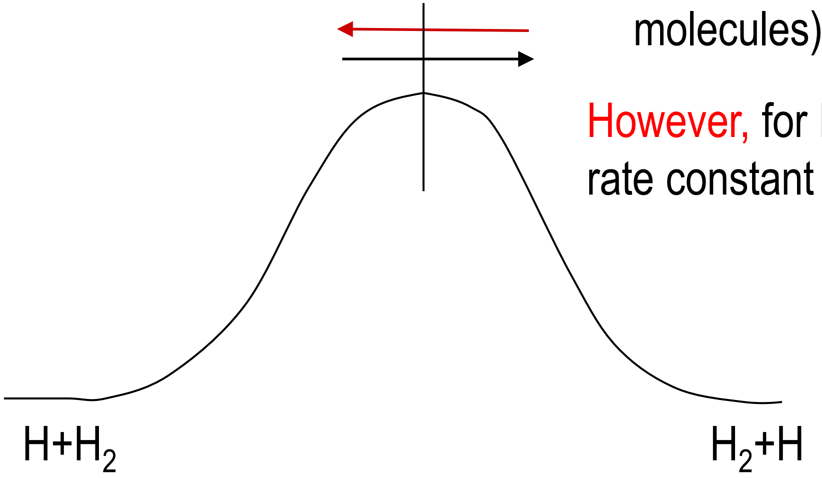
$$\sigma_{R1} = \frac{\sigma^R}{\sigma^{TS}} = \frac{\sigma_H \times \sigma_{\mathrm{H}_2}}{\sigma^{TS}} = \frac{1 \times 2}{2} = 1$$

R2: $H + D_2 \rightarrow H \cdots\cdots D \cdots\cdots D \rightarrow HD + H$

$$\sigma_{R2} = \frac{\sigma^R}{\sigma^{TS}} = \frac{\sigma_H \times \sigma_{\mathrm{D}_2}}{\sigma^{TS}} = \frac{1 \times 2}{1} = 2$$

$\boxed{\sigma_{R1} \neq \sigma_{R2}?}$

¿What is happening?



TST rate constant: is the forward flux (from reactants to products of molecules) crossing the dividing surface.

However, for R1 reactants and products are the same, so the total rate constant should be multiplied by 2.

$$\boxed{\sigma_{R1} = 2\frac{\sigma^R}{\sigma^{TS}} = 2\frac{\sigma_H \times \sigma_{\mathrm{H}_2}}{\sigma^{TS}} = 2\frac{1 \times 2}{2} = 2}$$

The same rule applies to unimolecular reactions, e.g. proton transfer reaction in malonaldehyde

Transition State Theory

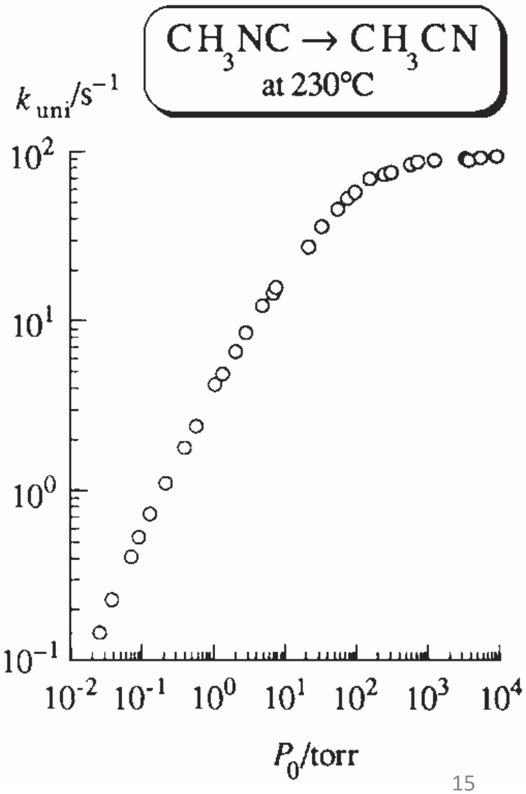
Discussion of the Main Assumptions

The quasi-equilibrium assumption

According to postulates 2 and 3 (the latter is sometimes considered as a consequence of postulate 2), the states of reactants and activated complexes are in thermal equilibrium during the reaction.

In general, this assumption is valid for most bimolecular reactions (gas-phase and solution) because the inelastic collisions efficiently repopulate the reactant rovibrational states, maintaining the Boltzmann distribution.

For gas-phase unimolecular reactions at low pressures, the quasi-equilibrium assumption breaks down and the rate constants become pressure dependent. **TST gives the high-pressure limit**.



Graph from I. N. Levine, Physical Chemistry, 6th ed. McGraw-Hill (2009).

Transition State Theory

Discussion of the Main Assumptions

Quantum effects

We have mixed classical mechanics with quantum mechanics (use of harmonic oscillator energy levels for the vibrational partition function). This “quasi-classical” approach may be very inaccurate for reactions involving very light species (H or D atoms), where tunnelling may be significant (particularly at low and moderate temperatures). We need to incorporate quantum effects into the reaction coordinate.

Anharmonic effects

We used the harmonic oscillator as a model for molecular vibrations. Depending on the nature of reactants and TS, and on the temperature, the inclusion of anharmonic corrections may be important.

Separability of the reaction coordinate

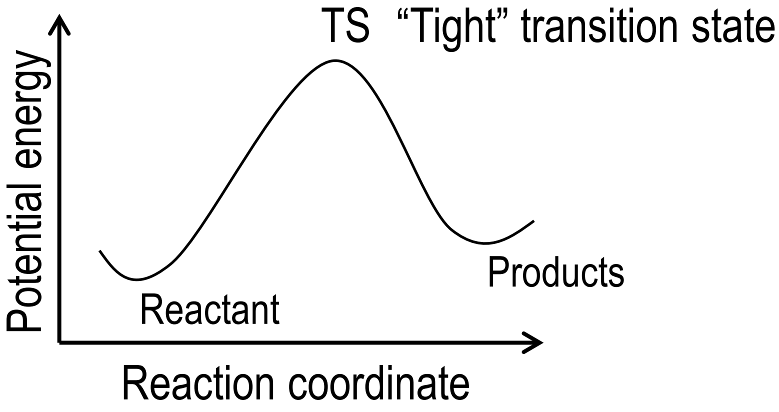
When the reaction coordinate is significantly coupled to other degrees of freedom, this assumption may lead to inaccuracies in the calculation of rate constants.

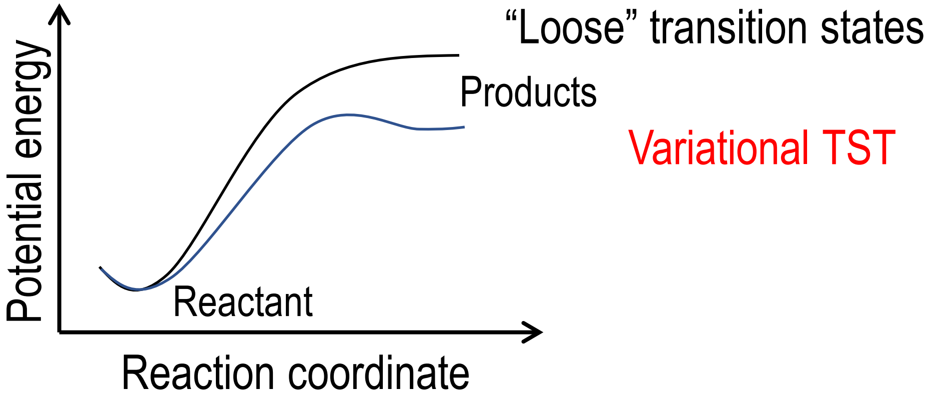
Transition State Theory

Discussion of the Main Assumptions

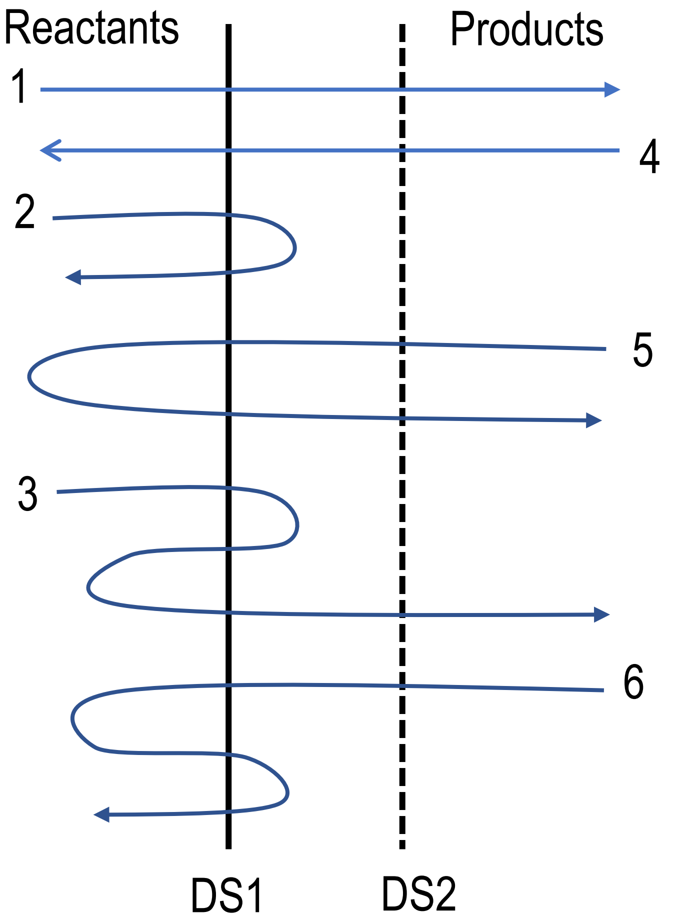
The no-recrossing approximation

Depending on the shape of the PES, the no-recrossing approximation may fail dramatically.





Variational TST



Adapted from Steinfeld, Francisco, Hase. *Chemical Kinetics and Dynamics*, 2nd ed. Prentice-Hall, Inc. (1999)

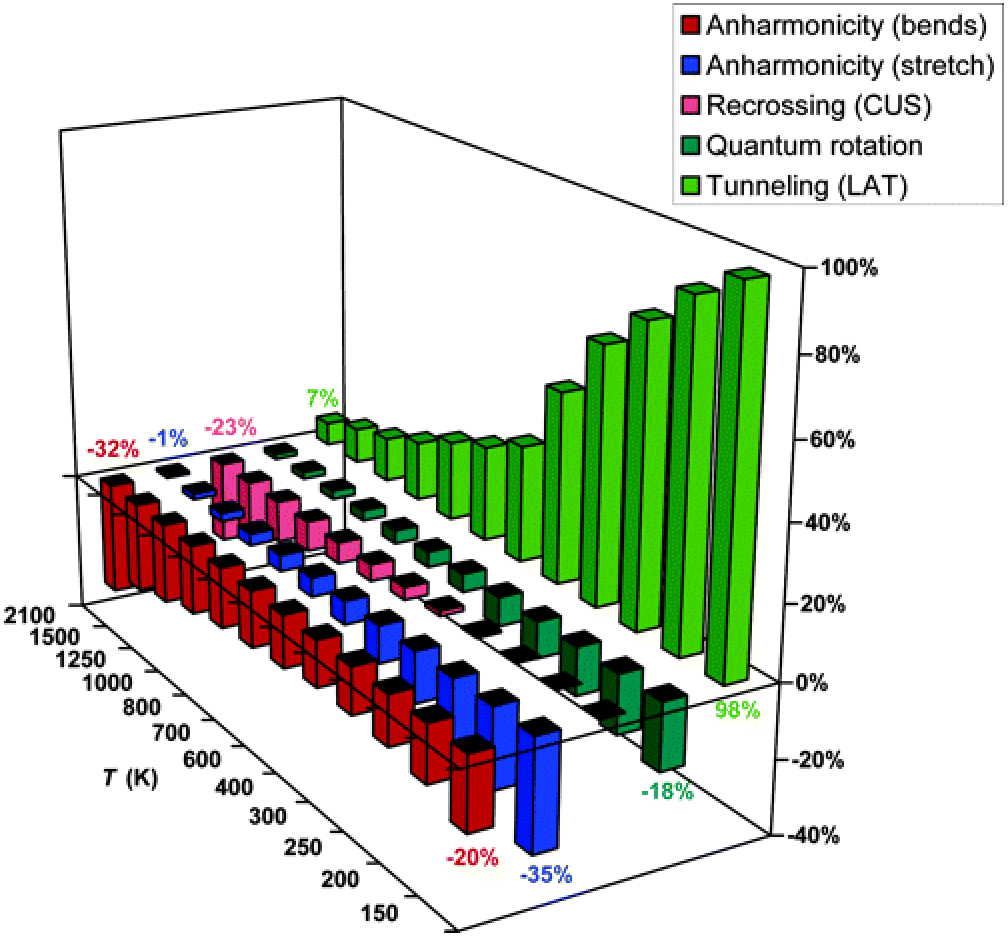
Classical TST gives an upper bound to the correct classical rate constant!

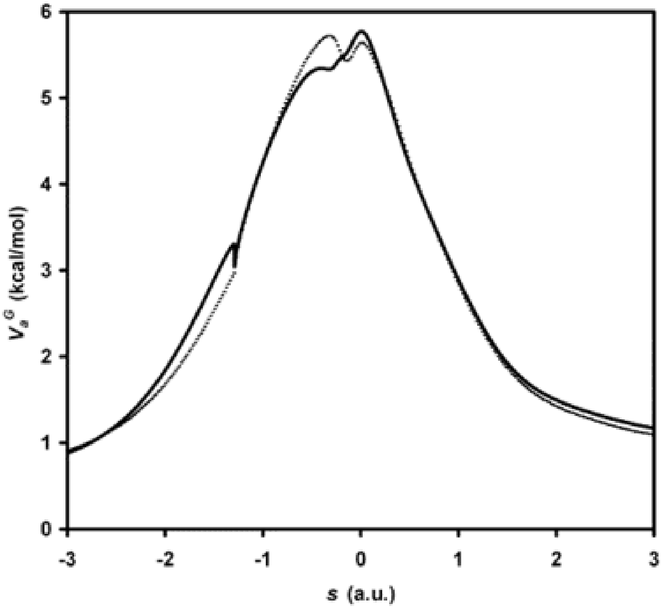
Transition State Theory

Discussion of the Main Assumptions

Example: The H_2 + Cl hydrogen abstraction reaction[1]

Percentage change in the rate constants upon including anharmonicity, recrossing, quantum rotational partition functions and tunneling.





V_a^G (V_{MEP}+ZPE) Solid line: anharmonic ZPEs. Dashed line: harmonic ZPEs.

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[1] J. A. Sansón, M.L. Sánchez and J. C. Corchado, *J. Phys Chem. A 110*, 589 (2006).

Improvements and Extensions

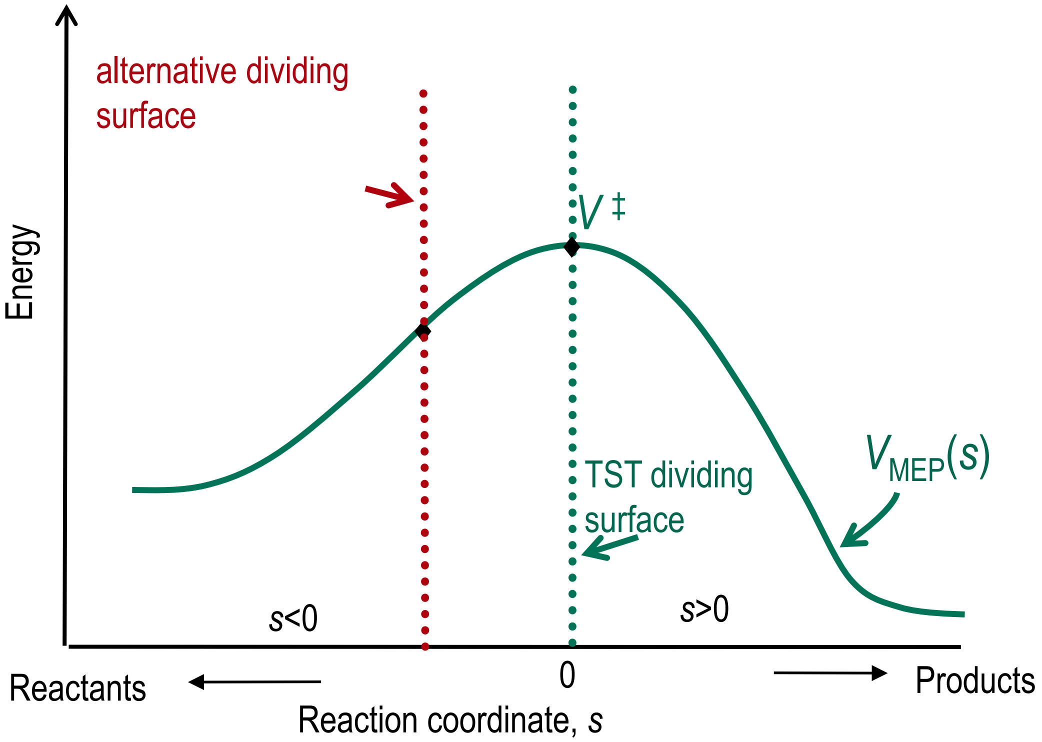
The reaction path

In the search for a dividing surface that minimizes recrossings, we need to define a reaction path. From a classical viewpoint, the best approach is the steepest descent path that connects the TS with reactants and products. This is the Minimum Energy Path (MEP).

The MEP in mass-weighted Cartesian coordinates ($q_i = x_i\sqrt{m_i}$) is called the Intrinsic Reaction Coordinate (IRC).

The reaction coordinate, or progression along the path (*s*), defines the position along the MEP: *s* = 0 at TS, *s* < 0 for the reactant side and *s* > 0 for the product side.

Dividing surfaces are orthogonal to the reaction path and, therefore, to the gradient.



Improvements and Extensions

In variational transitions state theory (VTST), the position of the dividing surface is optimized to minimize recrossings.[1]

A generalized expression for the rate constant is given by (GT = generalized TS):

$$k^{\mathrm{GT}}(T,s) = \sigma \frac{k_{\mathrm{B}}T}{h} \frac{q^{\mathrm{GT}}(T,s)}{q_{\mathrm{R}}(T)} \exp\left[-\frac{V_{\mathrm{MEP}}(s)}{k_{\mathrm{B}}T}\right] \tag{33}$$

Caveats: in VTST, it is customary to use:

- translational partition functions per volume (i.e., q_{tr} is divided by V).
- “number” density instead of molar concentrations (see “units” after eq. 15).
- energy zero at the bottom of the potential well for q_{vib}. $V_{\mathrm{MEP}}(s)$ does not include ZPE corrections.

In canonical variational theory (CVT), we minimize $k^{\mathrm{GT}}(T,s)$ with respect to s

$$k^{\mathrm{CVT}}(T) = \min_{s} k^{\mathrm{GT}}(T,s) = k^{\mathrm{GT}}\left[T, s^{\mathrm{CVT}}(T)\right] \tag{34}$$

where $s^{\mathrm{CVT}}(T)$ is the location of the dividing surface that minimizes eq. (33).

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1. E. Wigner, *J. Chem. Phys.* 5, 720, (1937); J. Horiuti, *Bull. Chem. Soc. Japan 13,* 210 (1938); J. C. Keck, *J. Chem. Phys. 32,* 1035 (1960); D. G. Truhlar and B. C. Garrett, *Annu. Rev. Phys. Chem. 35*, 159 (1984).

Improvements and Extensions

Alternative expressions for eqs. (33) and (34) are

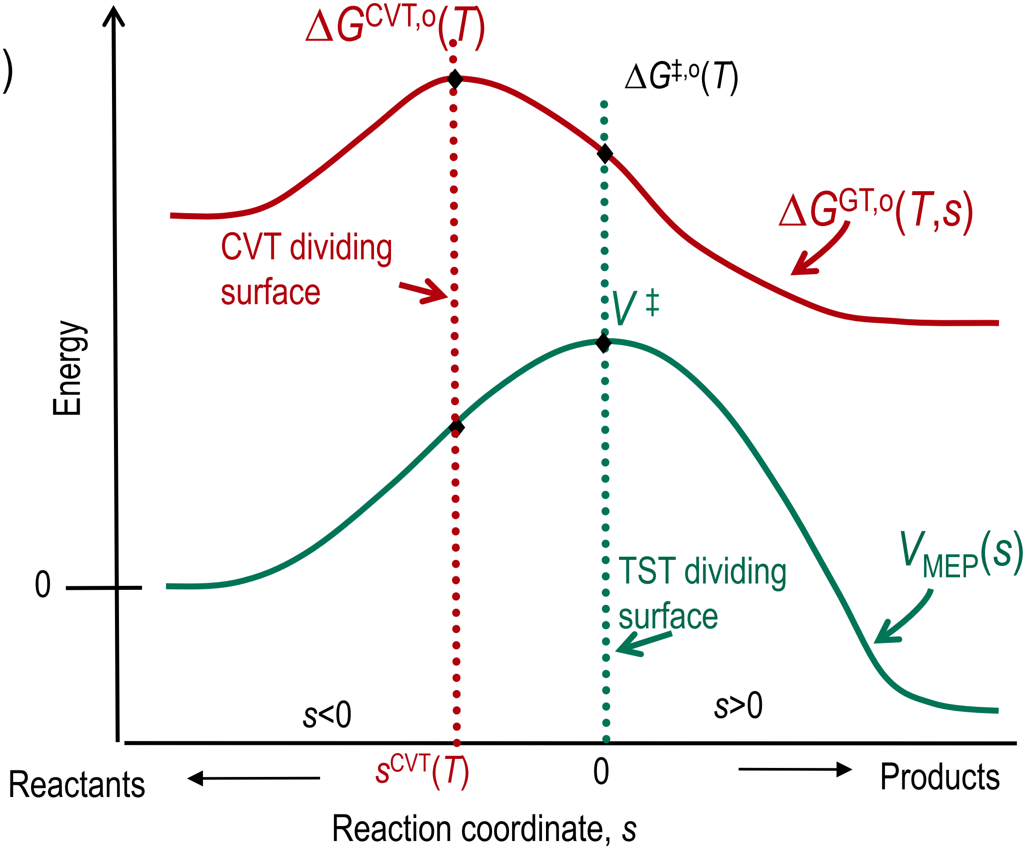
$$k^{\mathrm{GT}}(T,s) = \frac{k_{\mathrm{B}}T}{h(c^{\circ})^{m-1}} \exp\left[-\frac{\Delta G^{\mathrm{GT},\circ}(T,s)}{RT}\right] \qquad (35)$$

$$k^{\mathrm{CVT}}(T) = \frac{k_{\mathrm{B}}T}{h(c^{\circ})^{m-1}} \exp\left[-\frac{\Delta G^{\mathrm{CVT},\circ}(T)}{RT}\right] \qquad (36)$$

where $\Delta G^{\mathrm{CVT},\circ}(T) = \Delta G^{\mathrm{GT},\circ}(T, s^{\mathrm{CVT}})$ and *m* is the molecularity.

The calculation of $\Delta G^{\mathrm{GT},\circ}(T,s)$ is based on projected frequencies along the MEP.[1]

Canonical VTST (CVT) is the most common version of VTST.



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1. Y.-Y. Chuang and D. G. Truhlar, J. Phys. Chem. A, 102, 242 (1998).

Tunneling Corrections

Quantum tunneling may be significant when light atoms are involved in the reaction (e.g., proton-transfer reactions). Classically, the barrier crossing probability is zero for $E < \Delta\varepsilon_0^{\ddagger}$.

Assuming separability between the reaction coordinate and the remaining modes, a quantum probability *P*(*E*) may be calculated by solving a one-dimensional Schrödinger equation:

$$\frac{\partial^2\psi}{\partial s^2} + \frac{2m}{\hbar^2}[E - V(s)]\psi = 0 \qquad (37)$$

The tunnelling correction to the rate constant, usually called the tunnelling transmission coefficient, $\kappa(T)$, is obtained as

$$\kappa(T) = \frac{\int_0^\infty \exp(-E/k_\mathrm{B}T)P_\mathrm{Q}dE}{\int_0^\infty \exp(-E/k_\mathrm{B}T)P_\mathrm{C}dE} \qquad (38)$$

where P_Q and P_C are the quantum and classical probabilities, respectively.

Improvements and Extensions

Particularly, if we consider for *V*(*s*) a parabolic potential, we have the (crude) Wigner correction for tunnelling:

$$\kappa_{\mathrm{W}}(T) = 1 + \frac{1}{24}\left|\frac{h\nu_s}{k_{\mathrm{B}}T}\right|^2 \tag{39}$$

Within the one-dimensional Schrödinger equation approach, a more accurate representation of *V*(*s*) entails using the ground-state, vibrationally adiabatic potential:

$$V_a^G = V_{\mathrm{MEP}}(s) + \sum_{i=1}^{3N-7}\frac{1}{2}h\nu_i(s) \tag{40}$$

where the $\nu_i(s)$ are the projected frequencies along the MEP.

The one-dimensional approach is, in general, a very poor approximation, and more accurate treatments must include the couplings with the internal degrees of freedom. The calculation of multidimensional tunnelling transmission coefficients are carried out by using semiclassical methods.[1]

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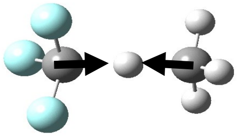
[1] A. Fernández-Ramos, B. A. Ellingson, B. C. Garrett and Donald G. Truhlar, in *Reviews in Computational Chemistry*, Vol. 23, ed., John Wiley & Sons, Inc., Hoboken, NJ (2007).

Improvements and Extensions

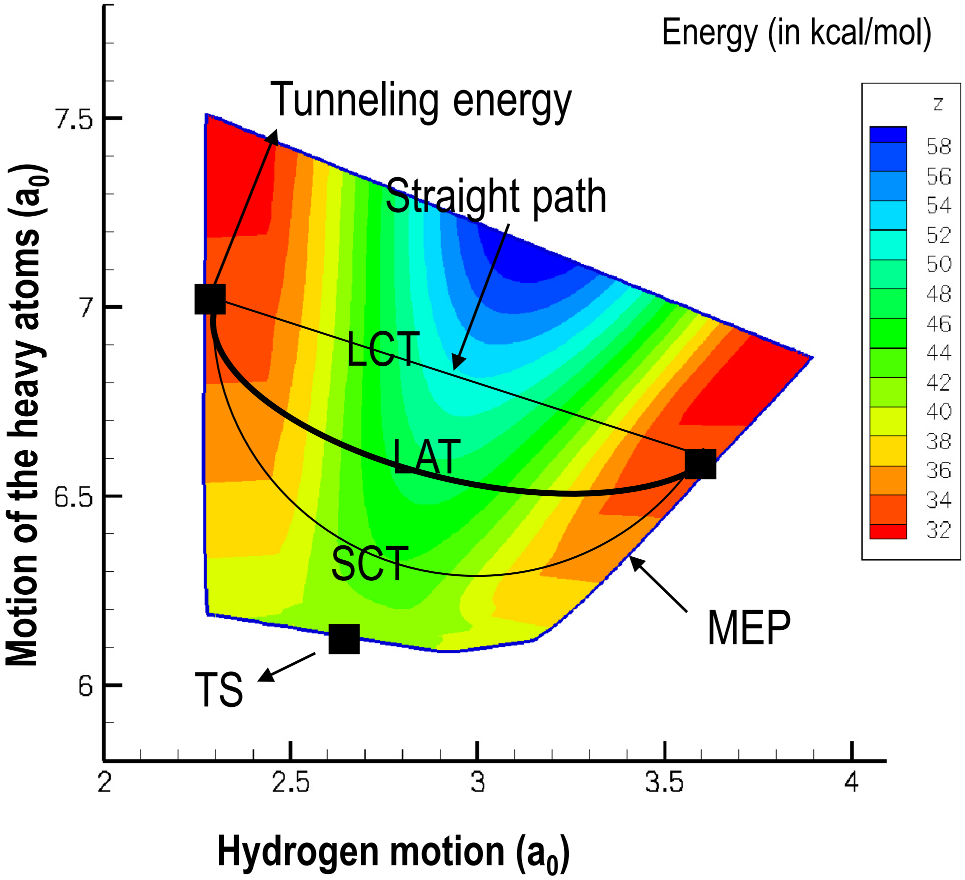
Multidimensional transmission coefficients ($\kappa^{CVT/X}$)

SCT: small-curvature transmission coefficients: accurate if the tunneling effect is not very important.

LCT: large-curvature transmission coefficients: accurate if tunneling is large.

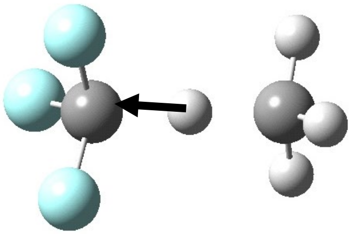


LAT: least-action transmission coefficients. Quite reliable but very expensive from the computational point of view.



Microcanonically-optimized probability

$$P^{\mu OMT}(E) = \max\begin{cases} P^{SCT}(E) \\ P^{LCT}(E) \end{cases}$$



Improvements and Extensions

Summary of Improvements

$$k^{\mathrm{CVT}}(T) = \frac{k_{\mathrm{B}}T}{h(c^{\circ})^{m-1}} \exp\left[-\frac{\Delta G^{\mathrm{CVT},\circ}(T)}{RT}\right] = \gamma^{\mathrm{CVT}}(T) k_{\mathrm{TST}}(T)$$

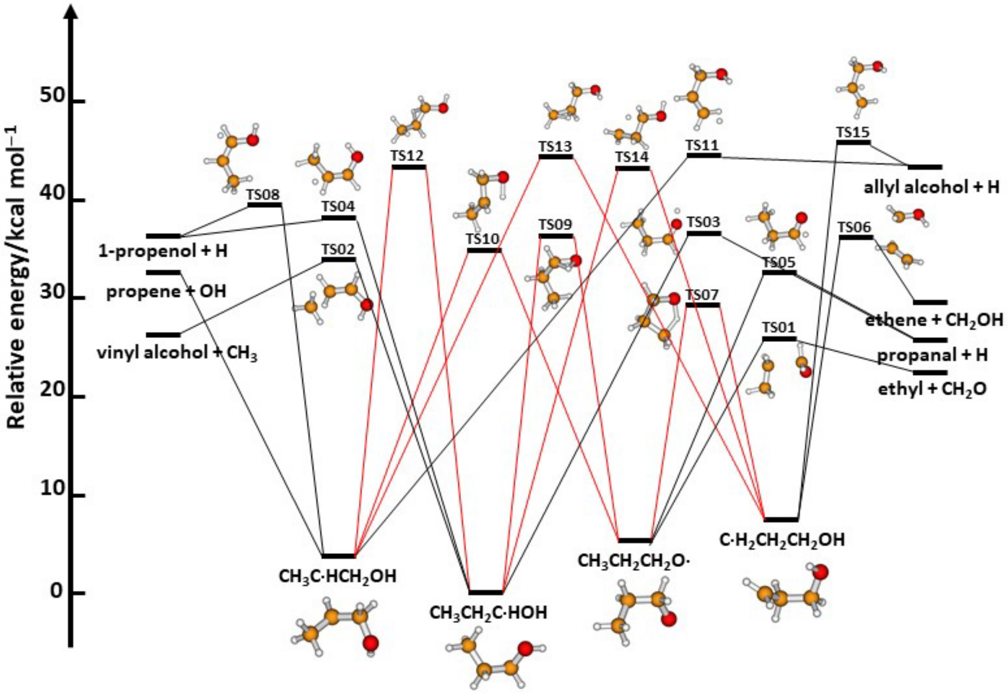
$$\gamma^{\mathrm{CVT}}(T) = \Gamma^{\mathrm{CVT}}(T)\kappa^{\mathrm{CVT/X}}(T)$$

The recrossing is minimized by variationally seeking dividing surfaces perpendicular to the MEP. The theory for calculating thermal rate constant in this way is called canonical variational transition state theory (CVT).

Quantum effects on the reaction coordinate are considered by including the couplings between the reaction coordinate and all the transverse modes. This leads to the canonical transition state theory with multidimensional tunneling CVT/X (X = ZCT, SCT, LCT, etc).

Reactions with Several Conformers

Example: Thermal decomposition of the propanol radical.[1]



Simplified schematic diagram of the main reaction pathways

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1. D. Ferro-Costas et al., *J. Phys. Chem. A 122*, 4790 (2018).

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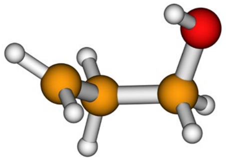
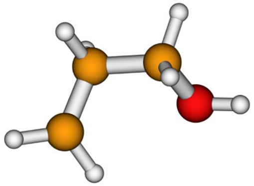
$CH_2CH_2CH_2OH \rightarrow CH_2CH_2 + CH_2OH$

Reactant conformers


PrOH_C$_{\gamma}$.01 (2)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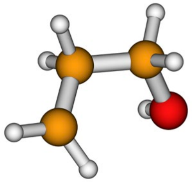
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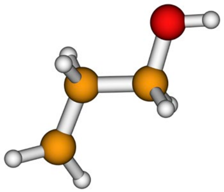
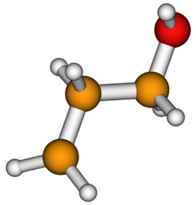
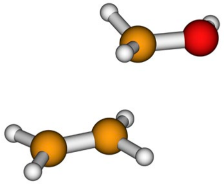
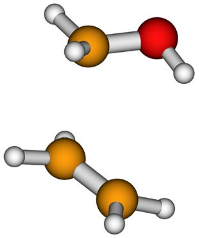
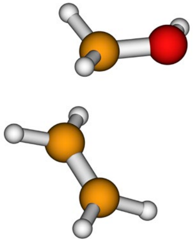

PrOH_C$_{\gamma}$.04 (2)

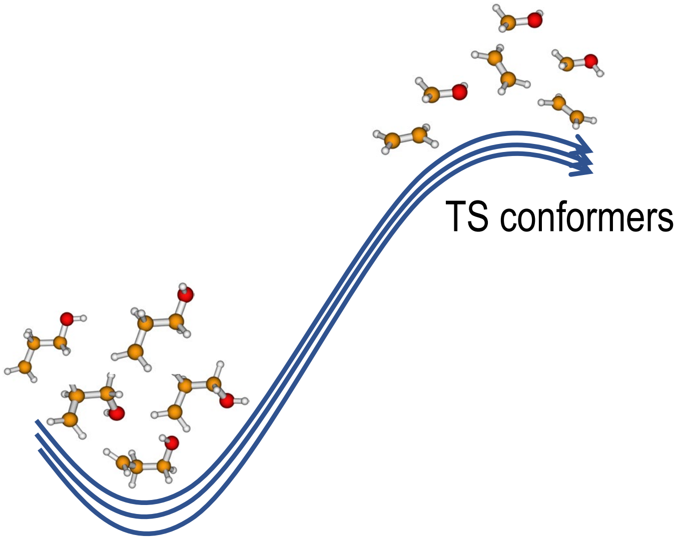

PrOH_C$_{\gamma}$.05 (2)

Transition-state conformers


TS06.01 (2)


TS06.02 (2)


TS06.03 (2)



We define a conformational reaction channel (CRC) as the group of all paths, including specular images, that connect the rotamers of a given reactant with the associated TS rotameric species.

Multistructural Transition-State Theory (MS-TST)[1,2]

Within the rigid-rotor, harmonic-oscillator approximation (RRHO), the partition function of a set of n_C reactant conformers is given by:

$$q^{\text{MS-HO}} = \sum_{i=1}^{n_\text{C}} m_i q_i^{\text{RRHO}} \qquad (41)$$

where $m_i = 2$ if conformer *i* has an enantiomer, and $m_i = 1$ otherwise.

q_i^{RRHO} is a joint RRHO partition function for conformer i

$$q_i^{\text{RRHO}} = q_{\text{rot},i} q_{\text{vib},i}^{\text{HO}} e^{-U_i/kT} \qquad (42)$$

Energy zero: bottom of the potential energy well. The reactant conformers are sorted by increasing electronic energy, with U_i being the energy of the i-th conformation, relative to that of the lowest energy conformer.

The partition function of the set of $n^{\ddagger}$ TS conformers is defined in the same way.

1. J. L. Bao and D. G. Truhlar, *Chem. Soc. Rev. 46*, 7548 (2017).
2. D. Ferro-Costas et al., *J. Phys. Chem. A 122*, 4790 (2018).

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The MS-TST rate constant is calculated as follows:

$$k^{\mathrm{MS-TST}} = B\,\frac{q^{\mathrm{MS-HO},\ddagger}}{q^{\mathrm{MS-HO}}} \qquad \text{with} \qquad B = \frac{k_{\mathrm{B}}T}{h}\,\frac{q_{\mathrm{el}}^{\ddagger}}{\Phi_{\mathrm{rel}}q_{\mathrm{el}}}\,e^{-U^{\ddagger}/kT} \tag{43}$$

where $U^{\ddagger}$ is the difference between the electronic energy of the lowest TS conformer and that of the lowest energy reactant conformer. Φ_{rel} is the partition function for the relative translational motion of reactants (unity for unimolecular reactions). It is an alternative way to express the quotient between the translational partition function of reactants and that of the transition state.

Alternatively, this MS-TST rate constant may also be written as a sum over all the individual rate constants that form the CRC:

$$k^{\mathrm{MS-TST}} = \sum_{i=1}^{n^{\ddagger}} m_i^{\ddagger} k_i^{\mathrm{TST}} \tag{44}$$

where

$$k_i^{\mathrm{TST}} = B\,\frac{q_i^{\mathrm{RRHO},\ddagger}}{q^{\mathrm{MS-HO}}} \tag{45}$$

Multistructural (MS) and Multipath (MP) extensions in VTST

The above may be extended to VTST, by including tunnelling and variational effects:

$$k^{\mathrm{MP-CVT/X}} = \sum_{i=1}^{n^{\ddagger}} m_i^{\ddagger} k_i^{\mathrm{CVT/X}} = \sum_{i=1}^{n^{\ddagger}} m_i^{\ddagger} \gamma_i^{\mathrm{CVT/X}} k_i^{\mathrm{TST}} \qquad (46)$$

with

$$\gamma_i^{\mathrm{CVT/X}} = \Gamma_i^{\mathrm{CVT}} \, \kappa_i^{\mathrm{CVT/X}} \qquad (47)$$

If we assume that the variational and tunneling effects obtained from the MEP starting from the lowest-energy TS conformer are representative of these effects in the whole CRC, then we have the MS-CVT/X thermal rate constant.[1]

1. For more details, see Ferro-Costas et al., *J. Phys. Chem. A 122*, 4790 (2018).

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Example: Results for the thermal decomposition of the propanol radical.[1]

Definition of the relevant CRCs and relative energies of the lowest energy conformers of the reactants and TSs.

Name	Reactant	n_C	*E* (kcal mol^{-1})	TS	$n^{\ddagger}$	*E* (kcal mol^{-1})	Product	Reaction type
CRC01	PrOH_O	2	5.9	TS01	2	25.9	$CH_2O+CH_2CH_3$	C_α–C_β dissociation
CRC02	PrOH_C$_\alpha$	6	0.0	TS02	2	34.1	$HOCHCH_2+CH_3$	C_β–C_γ dissociation
CRC03	PrOH_C$_\alpha$	6	0.0	TS03	3	36.6	$H + OCHCH_2CH_3$	H–O dissociation
***c*-CRC04**	PrOH_C$_\alpha$	6	0.0	*c*-TS04	2	38.2	H + cis-$HOCHCHCH_3$	H–C_β dissociation
***t*-CRC04**	PrOH_C$_\alpha$	6	0.0	*t*-TS04	2	38.4	H + trans-$HOCHCHCH_3$	H–C_β dissociation
CRC05	PrOH_O	2	5.9	TS05	3	32.5	$H + OCHCH_2CH_3$	H–C_α dissociation
CRC06	PrOH_C$_\gamma$	5	6.7	TS06	3	36.6	$CH_2OH + CH_2CH_2$	C_α–C_β dissociation
CRC07	PrOH_O	2	5.9	TS07	1	29.2	PrOH_C$_\gamma$	H-migration
***c*-CRC08**	PrOH_C$_\beta$	4	3.9	*c*-TS08	2	39.6	H + cis-$HOCHCHCH_3$	H–C_α dissociation
***t*-CRC08**	PrOH_C$_\beta$	4	3.9	*t*-TS08	2	39.9	H + trans-$HOCHCHCH_3$	H–C_α dissociation
CRC09	PrOH_O	2	5.9	TS09	3	36.4	PrOH_C$_\alpha$	H-migration
CRC10	PrOH_O	2	5.9	TS10	1	35.3	PrOH_C$_\beta$	H-migration
CRC11	PrOH_C$_\beta$	4	3.9	TS11	9	44.6	$H + HOCH_2CHCH_2$	H–C_γ dissociation
CRC12	PrOH_C$_\alpha$	6	0.0	TS12	4	43.4	PrOH_C$_\beta$	H-migration
CRC13	PrOH_C$_\beta$	4	3.9	TS13	9	44.1	PrOH_C$_\gamma$	H-migration
CRC14	PrOH_C$_\alpha$	6	0.0	TS14	2	43.3	PrOH_C$_\gamma$	H-migration
CRC15	PrOH_C$_\gamma$	5	6.7	TS15	9	45.9	$H + HOCH_2CHCH_2$	H–C_β dissociation
CRC16	PrOH_C$_\beta$	4	3.9	None	-	-	$OH + CH_2CHCH_3$	C_α–O dissociation

1. D. Ferro-Costas et al., *J. Phys. Chem. A 122*, 4790 (2018).

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Rate constants calculated at 1500 K

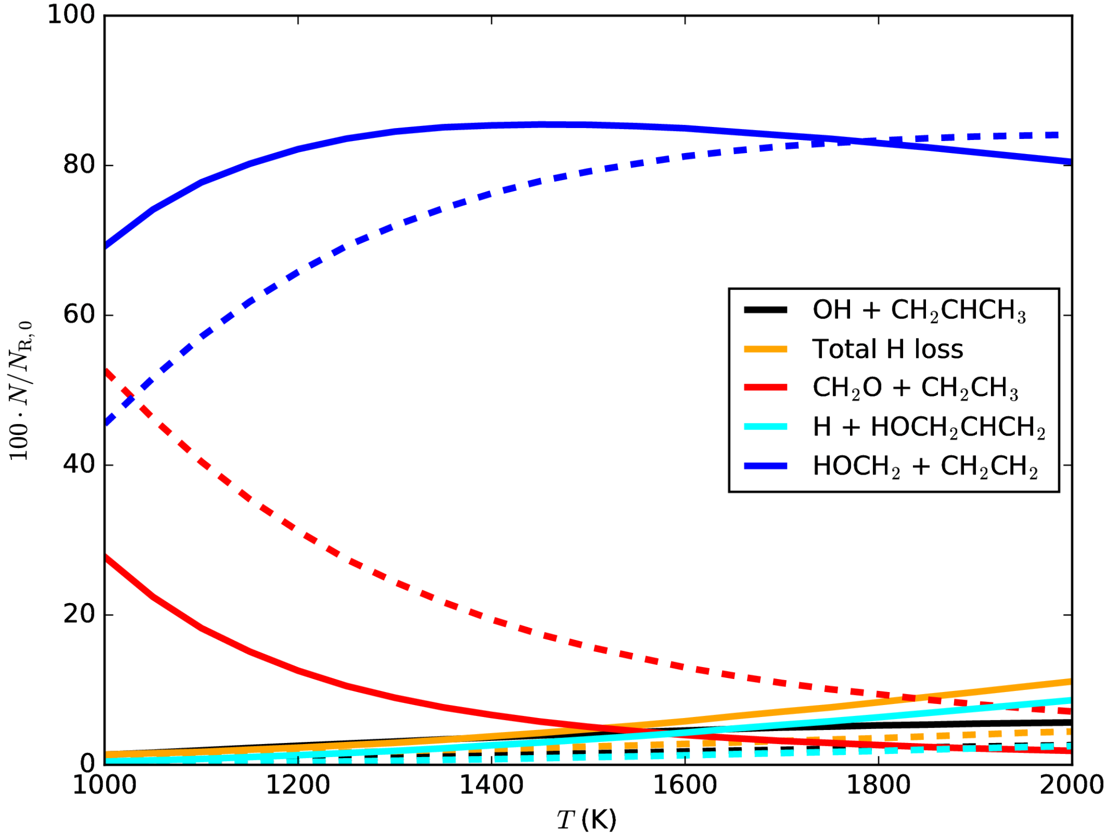
Channel	1W (eq 3)	MP (eq 1)	1W/MP	$n_c/n^{\ddagger}$
CRC01 (f)	9.34×10^{10}	8.43×10^{10}	1.11	2/2
CRC02 (f)	1.89×10^{9}	6.10×10^{8}	3.10	6/2
CRC03 (f)	3.60×10^{8}	1.93×10^{8}	1.87	6/3
c-CRC04 (f)	6.72×10^{7}	2.36×10^{7}	2.85	6/2
t-CRC04 (f)	8.01×10^{7}	2.45×10^{7}	3.27	6/2
CRC05 (f)	6.15×10^{9}	9.69×10^{9}	0.63	2/3
CRC06 (f)	2.17×10^{9}	1.11×10^{9}	1.95	5/3
CRC07 (f)	1.18×10^{9}	6.36×10^{8}	1.86	2/1
CRC07 (b)	4.69×10^{8}	7.43×10^{7}	6.32	5/1
c-CRC08 (f)	1.54×10^{8}	5.10×10^{7}	3.01	4/2
t-CRC08 (f)	8.26×10^{7}	3.27×10^{7}	2.52	4/2
CRC09 (f)	9.15×10^{8}	1.56×10^{9}	0.59	2/3
CRC09 (b)	5.83×10^{7}	2.93×10^{7}	1.99	6/3
CRC10 (f)	5.34×10^{8}	2.88×10^{8}	1.86	2/1
CRC10 (b)	4.52×10^{7}	8.35×10^{6}	5.41	4/1
CRC11 (f)	1.55×10^{7}	3.11×10^{7}	0.50	4/9
CRC12 (f)	1.17×10^{7}	7.14×10^{6}	1.64	6/4
CRC12 (b)	1.55×10^{7}	1.10×10^{7}	1.40	4/4
CRC13 (f)	9.18×10^{6}	1.65×10^{7}	0.56	4/9
CRC13 (b)	4.31×10^{7}	6.65×10^{7}	0.65	5/9
CRC14 (f)	5.43×10^{6}	1.46×10^{6}	3.72	6/2
CRC14 (b)	3.39×10^{7}	9.08×10^{6}	3.73	5/2
CRC15 (f)	2.74×10^{7}	4.17×10^{7}	0.66	5/9
CRC16 (f)^{c}	3.52×10^{9}	6.50×10^{8}	5.41	-

1W: one-well approach
MP: Multipath

Improvements and Extensions

Reactions with Several Conformers

Product branching ratios obtained starting from $C{\cdot}H_2CH_2CH_2OH$ and using MP (Solid lines) and 1W (dashed lines) rate constants.



Further Reading

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3. J. I. Steinfeld, J. S. Francisco and W. L. Hase, Chemical Kinetics and Dynamics, Prentice-Hall, Inc. (1999).
4. D. G. Truhlar, A. D. Isaacson and B. C. Garrett, "Generalized Transition State Theory". In *Theory of Chemical Reaction Dynamics*, Vol. 3, M. Baer, ed., CRC Press, Boca Raton, FL, pp. 65 (1985).
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6. J. L. Bao and D. G. Truhlar, "Variational Transition State Theory: Theoretical Framework and Recent Developments". *Chem. Soc. Rev.*, 46, 7548 (2017).