

# **Introduction to Transition State Theory**

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2025

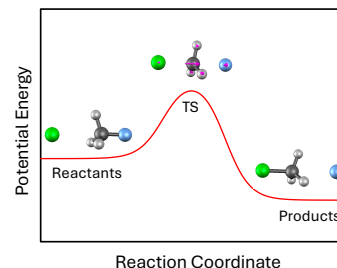
An Open-Source Textbook

# Transition State Theory

# 1

The basic postulates of transition state theory are:

- ▶ Rates of reactions are determined by the rate at which 'activated complexes' pass through a transition state, which is generally a saddle point on a potential energy surface.
- ▶ The activated complexes that exist near the transition state (but just on the reactants side) are in a special kind of equilibrium (quasi- or pre-equilibrium) with the reactant molecules.
- ▶ The activated complexes can convert into products if they have sufficient kinetic energy to do so.

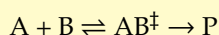


## Derivation of TST expression for rate constant $k$

Consider the elementary reaction  $A + B \rightarrow P$  that obeys the rate law:

$$\frac{d[P]}{dt} = k[A][B] \quad (1.1)$$

Activated complex theory proposes that the reactants are in quasi-equilibrium with an activated complex that is close to the transition state. The transition state is the point on a potential energy surface (generally a saddle point) through which each and all successful reactive encounters will pass, and proceed with 100% probability to form products.



Hence, the rate law for the reaction may also be formulated in terms of activated complex concentration,  $[AB^\ddagger]$ , and the frequency with which each activated complex reaches the transition state and proceeds to form products,  $f$ :

$$\frac{d[P]}{dt} = f[AB^\ddagger] \quad (1.2)$$

Equating (1.1) and (1.2) we find:

$$k = \frac{f[AB^\ddagger]}{[A][B]} = fK_{\text{act}}^\ddagger \quad (1.3)$$

Now, the question becomes - how can we predict the relative concentrations of the reactants and activated complexes from first principles?

The trick is to realise that all of these species are in thermal equilibrium with each other, and we may therefore apply the tools of statistical thermodynamics to compute their relative concentrations.

Broadly speaking, in the same way the thermal population of each quantum state of a molecule is proportional to its Boltzmann factor, the thermal population of a molecule in a mixture is proportional to its partition function. Dividing by volume to obtain concentrations:

$$k = f \frac{(q_{AB^\ddagger}/V)}{(q_A/V)(q_B/V)} \quad (1.4)$$

$$K_{\text{act}}^\ddagger = \frac{[AB^\ddagger]}{[A][B]}$$

Quasi-equilibrium constant quantifying concentrations of reactants and activated complexes in a pre-reactive 'soup'

$$q_i = g_i e^{-(\epsilon_i - \epsilon_0)/k_B T}$$

Boltzmann factor

$$q = \sum_{i=0}^{\infty} g_i e^{-(\epsilon_i - \epsilon_0)/k_B T}$$

Partition function

There are two issues to resolve before we can use equation (1.4):  $q_{AB^\ddagger}$  is missing a contribution from the “reaction coordinate” mode of motion, and we do not know what fraction of active complexes,  $f$ , moving along this reaction coordinate will reach the transition state.

Defining a small region just before the transition state quantified by a displacement of  $\delta x$  along the reaction coordinate, the tools of statistical thermodynamics may again be applied to derive an expression for the barrier crossing frequency from this region,  $f$ , and write down the partition function for the “missing” mode of motion,  $q_{\text{trans}}$ , as explained in the margin. Now:

$$k = f q_{\text{trans}} \frac{(q_{AB^\ddagger}/V)}{(q_A/V)(q_B/V)} \quad (1.5)$$

So finally:

$$k = \frac{k_B T}{h} \frac{(q_{AB^\ddagger}/V)}{(q_A/V)(q_B/V)} \quad (1.6)$$

Now all that remains is to evaluate the molecular partition functions  $q_A$ ,  $q_B$  and  $q_{AB^\ddagger}$  from microscopic quantities such as electronic energies, vibrational frequencies and moments of inertia, which may be obtained through *ab initio* calculations, excluding the reaction coordinate mode of the transition state, which has already been accounted for.

However, it is helpful to first expand out these overall molecular partition functions into translational, vibrational, rotational and electronic terms.

### TST expression for $k$ factorised into nuclear and electronic terms

$$k = \frac{k_B T}{h} \left( \frac{[(q_{AB^\ddagger}^{\text{trans}}/V) q_{AB^\ddagger}^{\text{rot}} q_{AB^\ddagger}^{\text{vib}}]}{[(q_A^{\text{trans}}/V) q_A^{\text{rot}} q_A^{\text{vib}}][(q_B^{\text{trans}}/V) q_B^{\text{rot}} q_B^{\text{vib}}]} \right) \left( \frac{q_{AB^\ddagger}^{\text{elec}}}{q_A^{\text{elec}} q_B^{\text{elec}}} \right) \quad (1.7)$$

The electronic contributions may be further expanded, as they depend only on the electronic energies\* of each component of the reaction mixture:

$$k = \frac{k_B T}{h} \left( \frac{[(q_{AB^\ddagger}^{\text{trans}}/V) q_{AB^\ddagger}^{\text{rot}} q_{AB^\ddagger}^{\text{vib}}]}{[(q_A^{\text{trans}}/V) q_A^{\text{rot}} q_A^{\text{vib}}][(q_B^{\text{trans}}/V) q_B^{\text{rot}} q_B^{\text{vib}}]} \right) e^{-\frac{(E_{AB^\ddagger} - (E_A + E_B))}{k_B T}} \quad (1.8)$$

It is already clear from equation (3.2) that, according to transition state theory, rate constants increase exponentially with temperature primarily due to a higher proportion of reactants forming activated complexes; the frequency of activated complexes reaching the transition state from the activated complex region increases only linearly with temperature while the population of the activated complex region increases exponentially.

$$f = \frac{v_{\text{av}}}{\delta x} \quad v_{\text{av}} = \sqrt{\frac{k_B T}{2\pi m^\ddagger}}$$

Barrier-crossing frequency is directly proportional to the average relative velocity of reactants towards one another,  $v_{\text{av}}$ , and inversely proportional to the extent of the activated complex region.

$$q_{\text{trans}} = \frac{\delta x}{\sqrt{\Lambda}} \quad \Lambda = \frac{h^2}{2\pi m^\ddagger k_B T}$$

Partition function for the 1D translational mode of motion that brings the reactants towards each other within the activated complex region.

$$q = q^{\text{trans}} q^{\text{rot}} q^{\text{vib}} q^{\text{elec}}$$

The overall molecular partition function is a product of contributions from each different mode of motion, due to additivity of the corresponding energy terms.

\*Electronic energies may, optionally, be corrected for zero-point vibrational effects

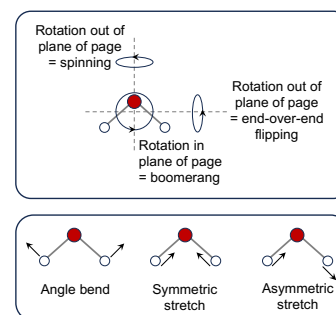
# Molecular Partition Functions

# 2

For a polyatomic molecule with  $n$  atoms, the total number of coordinate degrees of freedom is  $3n$ , as each atom is free to move in three independent directions ( $x$ ,  $y$  and  $z$ ). However, when dealing with molecular motions, it is more useful to think in terms of internal coordinates - bond lengths, angles, torsional angles, and external coordinates - translational motion of the molecule's centre of mass, and rotational motion about the molecule's centre of mass.

All gas phase molecules have three translational degrees of freedom, corresponding to movement along each Cartesian axis ( $x$ ,  $y$ ,  $z$ ). Most molecules also have three rotational degrees of freedom (pitch, roll, yaw) and therefore  $3n - 6$  vibrational modes. Linear molecules possess only two rotational degrees of freedom, as rotation about the bond axis causes no change, and therefore have  $3n - 5$  vibrational modes.

The overall molecular partition function is a product of translational, rotational and vibrational terms, each a product of contributions from each degree of freedom, which in turn correspond to sums of Boltzmann factors over the available quantum energy levels.



**Figure 2.1:** Rotational and vibrational modes of water

## Translational Partition Function

The translational energy levels of a molecule in a cubic box with sizes of length  $L$  are:

$$\epsilon_{n_x, n_y, n_z}^{\text{trans}} = \frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8mL^2} \quad (2.1)$$

where  $n_x$ ,  $n_y$  and  $n_z$  are the quantum numbers in the  $x$ ,  $y$  and  $z$  directions,  $m$  is the mass of the particle and  $h$  is Planck's constant.

Therefore:

$$q^{\text{trans}} = \sum_{n_x=1}^{\infty} e^{-\beta \frac{h^2 n_x^2}{8mL^2}} \sum_{n_y=1}^{\infty} e^{-\beta \frac{h^2 n_y^2}{8mL^2}} \sum_{n_z=1}^{\infty} e^{-\beta \frac{h^2 n_z^2}{8mL^2}} \quad (2.2)$$

It is possible in theory to directly evaluate this triple sum but in practice the number of terms that must be included is extremely large, as the spacing between energy levels is very small compared with the available energy, even at very low temperatures.

Instead, this sum may be very accurately approximated as an integral:

$$q^{\text{trans}} \approx \int_0^{\infty} e^{-\beta \frac{h^2 n_x^2}{8mL^2}} dn_x \int_0^{\infty} e^{-\beta \frac{h^2 n_y^2}{8mL^2}} dn_y \int_0^{\infty} e^{-\beta \frac{h^2 n_z^2}{8mL^2}} dn_z \quad (2.3)$$

whose evaluation yields:

$$q^{\text{trans}} = \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} L^3 \quad (2.4)$$

which may be expressed in the more concise and general form:

$$q^{\text{trans}} = \frac{V}{\Lambda^3} \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad (2.5)$$

$$\beta = \frac{1}{k_B T}$$

$$V = L^3 = \text{volume}$$

### Rotational Partition Function

The rotational Schrödinger equation can be solved exactly for spherical tops, molecules with three equivalent axes of rotation:

$$\epsilon_J = BJ(J+1) \quad g_J = (2J+1)^2 \quad (2.6)$$

The rotational partition function may be evaluated directly:

$$q^{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)^2 e^{-BJ(J+1)/k_B T} \quad (2.7)$$

but is also amenable to evaluation in integral form, provided that a large number of energy levels ( $> 1000$ ) are significantly populated at a given temperature. This criterion is typically satisfied for most gas phase molecules at room temperature.

$$\begin{aligned} q^{\text{rot}} &= \int_{J=0}^{\infty} (2J+1)^2 e^{-BJ(J+1)/k_B T} dJ \\ &= \frac{\sqrt{\pi}}{\sigma} \left( \frac{T}{\Theta} \right)^{3/2} \end{aligned} \quad (2.8)$$

The rotational symmetry number  $\sigma$  corresponds to the number of ways of regenerating the starting orientation during a full period of molecular rotation and is included to compensate for overcounting.

Equation (2.8) may be straightforwardly generalised to asymmetric tops, molecules with non-equivalent axes of rotation:

$$q^{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left( \frac{T}{\Theta_A} \right)^{1/2} \left( \frac{T}{\Theta_B} \right)^{1/2} \left( \frac{T}{\Theta_C} \right)^{1/2} \quad (2.9)$$

For completeness, the partition function for a linear rotor is:

$$q^{\text{rot,linear}} = \frac{1}{\sigma} \frac{T}{\Theta} \quad (2.10)$$

$g_J$  = rotational energy level degeneracy

$$B = \frac{\hbar^2}{2I}$$

The rotational constant,  $B$ , is inversely proportional to the moment of inertia,  $I$ , for rotation about any one of the three equivalent rotational axes, defined via construction and diagonalisation of the inertia tensor with elements:

$$\begin{aligned} I_{xx} &= \sum_{i=1}^{n_{\text{atom}}} m_i (y_i^2 + z_i^2) \\ I_{xy} &= - \sum_{i=1}^{n_{\text{atom}}} m_i (x_i y_i) \end{aligned}$$

$$\Theta = \frac{B}{k_B} = \frac{\hbar^2}{2Ik_B}$$

The characteristic rotational temperature,  $\Theta$ , is equal to the rotational constant divided by Boltzmann's constant.

$$\Theta_{A/B/C} = \frac{\hbar^2}{2I_{A/B/C} k_B}$$

Asymmetric tops have different characteristic rotational temperatures, reflecting different moments of inertia for rotation about each non-equivalent axis.

### Vibrational Modes and Harmonic Frequencies

Before it is possible to evaluate the molecular vibrational partition function, it is first necessary to identify the  $3n - 6$  vibrational modes of the system and determine their characteristic vibrational frequencies. Fortunately, both of these objectives can be achieved through diagonalisation of the mass-weighted "Hessian" matrix,  $\mathbf{H}_{\text{mw}}$ :

$$\mathbf{H}_{\text{mw}} = \begin{bmatrix} \frac{1}{m_1} \frac{d^2 E}{dx_1^2} & \frac{1}{m_1} \frac{d^2 E}{dx_1 dy_1} & \frac{1}{m_1} \frac{d^2 E}{dx_1 dz_1} & \cdots & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dx_1 dx_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dx_1 dy_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dx_1 dz_n} \\ \frac{1}{m_1} \frac{d^2 E}{dy_1 dx_1} & \frac{1}{m_1} \frac{d^2 E}{dy_1^2} & \frac{1}{m_1} \frac{d^2 E}{dy_1 dz_1} & \cdots & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dy_1 dx_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dy_1 dy_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dy_1 dz_n} \\ \frac{1}{m_1} \frac{d^2 E}{dz_1 dx_1} & \frac{1}{m_1} \frac{d^2 E}{dz_1 dy_1} & \frac{1}{m_1} \frac{d^2 E}{dz_1^2} & \cdots & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dz_1 dx_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dz_1 dy_n} & \frac{1}{\sqrt{m_1 m_n}} \frac{d^2 E}{dz_1 dz_n} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \end{bmatrix}$$

The Hessian is a  $3n \times 3n$  matrix which contains second derivatives of the electronic energy with respect to atomic displacements.

Mass weighting is achieved by dividing each element by the square root of the mass of each displaced atom.

The eigenvalues of this matrix correspond to the  $3n - 6$  harmonic vibrational frequencies of the molecule, plus 6 values that are close to zero which correspond to translational and rotational modes. The  $3n - 6$  eigenvectors with non-zero eigenvalues are each of length  $3n$ , and may be broken up into  $n$  sets of  $(x, y, z)$  atomic displacements that define the normal modes of vibration.

### Vibrational Partition Function

For a molecule with  $3n - 6$  independent vibrational modes, the overall vibrational partition function is a product of contributions from each individual mode:

$$q^{\text{vib}} = \prod_{i=1}^{n_{\text{mode}}} q_i^{\text{vib}} \quad (2.11)$$

Each mode is characterised by a harmonic fundamental frequency of  $\nu_i$  with associated non-degenerate quantum energy levels:

$$\epsilon_n = h\nu_i \left( n + \frac{1}{2} \right) \quad (2.12)$$

Therefore,

$$q_i^{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta(\epsilon_n - \epsilon_0)} = \sum_{n=0}^{\infty} e^{-\beta n h \nu_i} \quad (2.13) \quad \beta = \frac{1}{k_B T}$$

Surprisingly, the infinite sum in equation (2.13) may be evaluated in closed form. Letting  $x = e^{-\beta h \nu_i}$

$$\begin{aligned} q_i^{\text{vib}} &= 1 + x + x^2 + x^3 + \dots \\ &= \frac{1}{1 - x} \\ &= \frac{1}{1 - e^{-h\nu_i/k_B T}} \end{aligned} \quad (2.14) \quad 0 < x < 1$$

So, finally we have a complete and compact expression for the overall molecular vibrational partition function within the quantum harmonic oscillator approximation:

$$q^{\text{vib}} = \prod_{i=1}^{n_{\text{mode}}} \frac{1}{1 - e^{-h\nu_i/k_B T}} \quad (2.15)$$

**General TST Expression for Rate Constant**

$$k = \frac{k_B T}{h} \frac{(q_{\text{ts}^\ddagger}/V)}{\prod(q_{\text{react}}/V)} \quad (3.1)$$

**Factorised into Electronic and Nuclear Components**

$$k = \frac{k_B T}{h} \left( \frac{[(q_{\text{ts}^\ddagger}^{\text{trans}}/V) q_{\text{ts}^\ddagger}^{\text{rot}} q_{\text{ts}^\ddagger}^{\text{vib}}]}{\prod[(q_{\text{react}}^{\text{trans}}/V) q_{\text{react}}^{\text{rot}} q_{\text{react}}^{\text{vib}}]} \right) e^{-\frac{(E_{\text{AB}^\ddagger} - \sum E_{\text{react}})}{k_B T}} \quad (3.2)$$

**Translational Partition Function**

$$q^{\text{trans}} = \frac{V}{\Lambda^3} \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad (3.3)$$

**Rotational Partition Function**

$$q^{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left( \frac{T}{\Theta_A} \right)^{1/2} \left( \frac{T}{\Theta_B} \right)^{1/2} \left( \frac{T}{\Theta_C} \right)^{1/2} \quad (3.4)$$

$$\Theta_{\text{A/B/C}} = \frac{\hbar^2}{2I_{\text{A/B/C}} k_B}$$

$$q^{\text{rot,linear}} = \frac{1}{\sigma} \frac{T}{\Theta} \quad (3.5)$$

$$\Theta = \frac{\hbar^2}{2Ik_B}$$

**Vibrational Partition Function**

$$q^{\text{vib}} = \prod_{i=1}^{n_{\text{mode}}} \frac{1}{1 - e^{-h\nu_i/k_B T}} \quad (3.6)$$

# Constants and Conversion Factors

# 4

Name	Symbol	Value
Boltzmann constant	$k_B$	$1.380649 \times 10^{-23} \text{ J K}^{-1}$
Planck constant	$h$	$6.62607015 \times 10^{-34} \text{ J s}$
$\hbar$	$\hbar$	$h/2\pi = 1.05457182 \times 10^{-34} \text{ J s}$
Avogadro's number	$N_A$	$6.02214076 \times 10^{23} \text{ particles/mole}$
speed of light	$c$	$29979245800 \text{ cm s}^{-1}$

Quantity	Reported Units	Required Units	Conversion process
Electronic energy, $E$	Hartree	J	$1 E_h = 4.35974472 \times 10^{-18} \text{ J}$
Zero-point vib'l energy, ZPVE	kcal/mol	J	Multiply by 4.184 $\rightarrow$ kJ/mol Multiply by 1000 $\rightarrow$ J/mol Divide by $N_A = 6.02214076 \times 10^{23}$
Mass, $m$	$\text{g mol}^{-1}$ (amu)	kg	Divide by 1000 $\rightarrow$ kg/mol Divide by $N_A = 6.02214076 \times 10^{23}$
Moment of inertia, $I$	amu Bohr <sup>2</sup>	kg m <sup>2</sup>	Convert amu to kg as above Convert Bohr to m, $1 \text{ Bohr} = 0.529177249 \times 10^{-10} \text{ m}$
Vibrational frequency, $\nu$	$\text{cm}^{-1}$	$\text{s}^{-1}$	Multiply by speed of light in $\text{cm s}^{-1}$ $c = 29979245800 \text{ cm s}^{-1}$