

Day 11: Transition State Theory

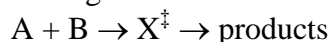
In the last set of lecture notes, we arrived at the conclusion that we know how to, in principle, calculate rate parameters from first principles by deriving a potential surface from the solution of the Schrödinger equation for the electrons at different positions of the nuclei and then solving the Schrödinger equation for motion of the nuclei on that potential surface. However, except for the simplest of molecules and reactions, it is not practical to do so. So, here we discuss statistical theories of reaction rates (transition state theory) that require much less information about the potential surface, but involve several significant approximations.

Transition state theory allows us to replace the detailed trajectory or scattering calculations with a simpler, less detailed model. Instead of calculating individual trajectories from reactants in a particular state to products in a particular state, we use the tools of statistical mechanics to calculate the total rate at which molecules cross through some surface that divides reactants from products. Transition state theory was first introduced in the mid-1930's by Eyring and by Evans and Polanyi. There are a number of approximations and assumptions about the system that are made in transition state theory. The basic ones are:

- (1) The Born-Oppenheimer approximation (or its classical equivalent) is valid, so that the motion of the electrons can be separated from the motions of the nuclei.
- (2) The reactant molecules are distributed in their energetic states in accordance with the Maxwell-Boltzmann distribution. This means that the translational, vibrational, and rotational degrees of freedom of the molecules are in thermal equilibrium. The number of molecules in a state with energy ε_i is proportional to $\exp(-\varepsilon_i/(kT))$.
- (3) Molecular systems that have crossed the transition state (the dividing surface) in the direction of products do not turn around to form reactants.
- (4) In the transition state, motion along the reaction coordinate may be separated from the other motions and treated classically as a translation.
- (5) Even in the absence of equilibrium between reactant and product molecules, the transition states that are becoming products are distributed among their states according to the Maxwell-Boltzmann distribution. It can be shown that this assumption is not really necessary, as it is implied by the second and third assumptions.

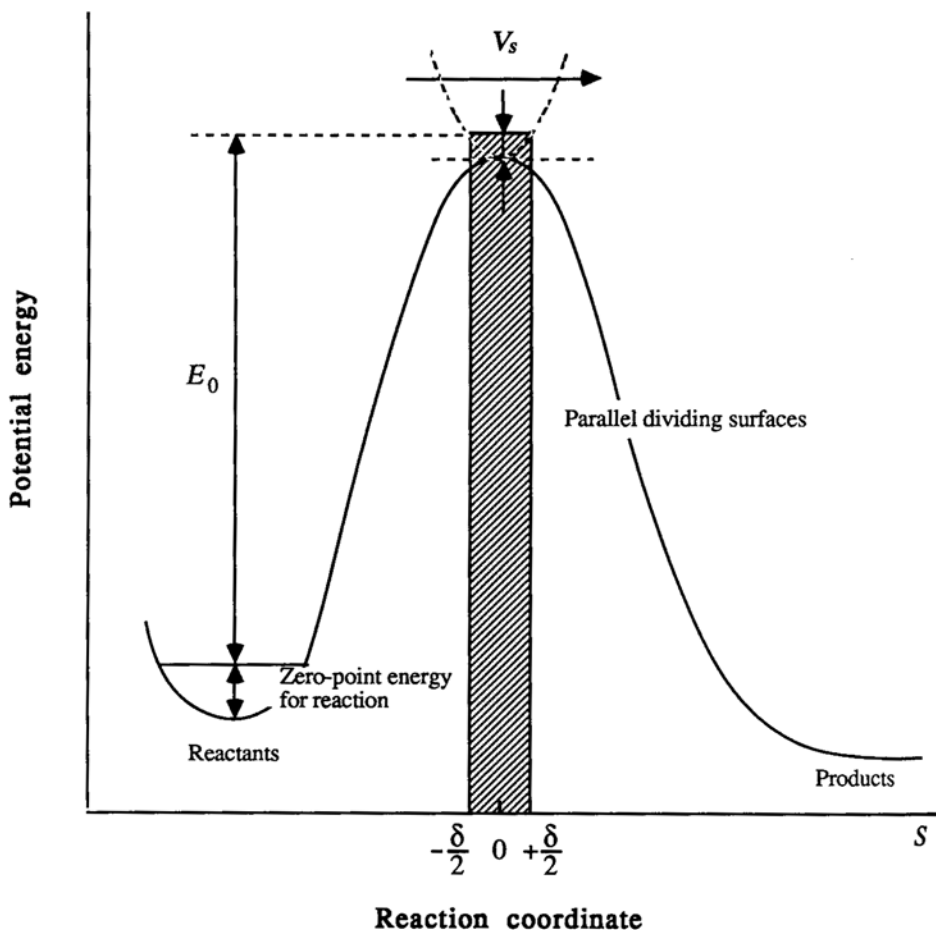
We now present the standard or 'quasi-equilibrium' derivation of transition-state theory. There is also a more rigorous, dynamical derivation (which we will not present here) that gives the same result with fewer assumptions.

Consider the generic reaction



Where A and B are the reactants, and X^\ddagger is the transition state (the structure located at the saddle point on the potential energy surface). Now, suppose we can construct a small region at the top of the potential energy barrier (perpendicular to the reaction path) such that all systems entering

that region from the reactant side pass through to form products and all systems entering that region from the product side form reactants. This region will be bounded by two surfaces (hypersurfaces) called *dividing surfaces* that are separated by some infinitesimally small distance δ . Systems within this region are, by definition, transition states. Systems on one side are reactants, and systems on the other side are products. If we only consider motion along the reaction coordinate (the direction of the minimum energy path) then this looks like the figure shown below. In this figure, systems on the left are reactants and systems on the right are products.



If there were equilibrium between the reactants and products, then the number of transition states moving from left to right would be the same as the number moving from right to left so that the rate of the forward reaction is equal to the rate of the reverse reaction. If we denote the number of forward-moving ones as N_f^\ddagger and the backward-moving ones as N_b^\ddagger , then

$$N_f^\ddagger = N_b^\ddagger = \frac{1}{2} N^\ddagger$$

where N^\ddagger is the total number of transition states (the total number of molecules between $-\delta/2$ and $+\delta/2$). Since the whole system is in equilibrium, the concentration of transition states is related to the reactant concentrations by

$$N^\ddagger = K^\ddagger[A][B]$$

Where K^\ddagger is the equilibrium constant that relates the reactants to the transition state (see below). The number of transition states that are moving from reactant to product are:

$$N_f^\ddagger = \frac{1}{2} N^\ddagger = \frac{1}{2} K^\ddagger[A][B]$$

Since, by one of our assumptions, systems that cross in one direction never turn back to cross in the other direction, the number of forward moving transition states will not change if we remove all of the products (everything to the right of the transition state). So, even if reactants and products are not in equilibrium, the number of transition states will still be

$$N_f^\ddagger = \frac{1}{2} K^\ddagger[A][B]$$

This is called the ‘*quasi-equilibrium hypothesis*’ of transition state theory.

To calculate the reaction rate, we need the rate at which transition states pass over the barrier to products rather than the number that exist at a given time. If the transition states that are crossing in the forward direction have an average velocity \bar{v}_s , then the average time that it will take them to cross through the transition state (between the dividing surfaces) is given by

$$\delta t = \frac{\delta}{v_s}$$

where, as before, δ is the distance between the dividing surfaces. The total rate at which molecules pass through the transition state from reactant to product is then given by the number of transition states divided by the average time that it takes them to go through the transition state region. This is also the reaction rate

$$r = -\frac{dN}{dt} = \frac{N_f^\ddagger}{\delta t} = \frac{N_f^\ddagger \bar{v}_s}{\delta} = \frac{\bar{v}_s}{\delta} \frac{1}{2} K^\ddagger[A][B]$$

To make this expression for the reaction rate useful, we must get rid of the somewhat artificial constructs \bar{v}_s and δ . If there is an equilibrium distribution of velocities (which there is, by assumption) then the average velocity of the transition state moving in the forward direction is

$$\bar{v}_s = \left(\frac{2kT}{\pi\mu_s} \right)^{1/2}$$

where μ_s is yet another somewhat artificial construct – the reduced mass for motion through the transition state region. This expression can be derived in the same way that the average speed of molecules in an ideal gas is derived, except that motion is confined to one direction. Substituting this into the expression for the reaction rate gives

$$r = \left(\frac{2kT}{\pi\mu_s} \right)^{1/2} \frac{1}{2\delta} K^\ddagger[A][B]$$

The equilibrium constant relating the reactant concentration to the transition state concentration can be obtained from equilibrium statistical mechanics as

$$K^\ddagger = \frac{(Q_{tot}^\ddagger / V)}{(Q_A / V)(Q_B / V)} \exp\left(\frac{-E_o}{kT}\right)$$

where Q_{tot}^\ddagger is the partition function of the transition state (for all degrees of freedom, including motion along the reaction coordinate), Q_A and Q_B are the partition functions of the reactants, and E_o is the energy difference between the reactant and transition state (including zero-point energy). V is the molecular volume (volume per molecule). The units of the equilibrium constant (and later the rate constant) come from V . We will discuss the complete forms of the partition functions shortly. In the standard derivation of transition state theory, we treat the motion along the reaction coordinate as a translational motion. We assume that it is separable from the other motions of the molecule (represented by the other $3N-1$ degrees of freedom). This allows us to write

$$Q_{tot}^\ddagger = Q_s Q^\ddagger$$

where Q_s is the partition function for motion along the reaction coordinate, while Q^\ddagger is the partition function for the remaining $3N-1$ degrees of freedom of the transition state. The partition function for motion of a freely-moving particle of effective mass μ_s in a 1-dimensional system of length δ is

$$Q_s = \frac{\delta}{h} \sqrt{2\pi\mu_s kT}$$

where h is Planck's constant and the other variables are as defined before. This gives, for the equilibrium constant

$$K^\ddagger = \frac{\delta \sqrt{2\pi\mu_s kT}}{h} \frac{(Q^\ddagger / V)}{(Q_A / V)(Q_B / V)} \exp\left(\frac{-E_o}{kT}\right)$$

Finally, substituting this back into the expression for the reaction rate gives

$$r = \left(\frac{2kT}{\pi\mu_s}\right)^{1/2} \frac{1}{2\delta} \frac{\delta \sqrt{2\pi\mu_s kT}}{h} \frac{(Q^\ddagger / V)}{(Q_A / V)(Q_B / V)} \exp\left(\frac{-E_o}{kT}\right) [A][B]$$

Now, the artificial constructs δ and μ_s cancel out. The final expression for the reaction rate is then

$$r = \frac{kT}{h} \frac{(Q^\ddagger / V)}{(Q_A / V)(Q_B / V)} \exp\left(\frac{-E_o}{kT}\right) [A][B]$$

Thus, the forward reaction rate constant is given by

$$k_f = \frac{kT}{h} \frac{(Q^\ddagger / V)}{(Q_A / V)(Q_B / V)} \exp\left(\frac{-E_o}{kT}\right)$$

The factor kT/h is called the *universal frequency factor*. It has units of s^{-1} , and is of the order of magnitude of slow molecular vibrations (around $10^{13} s^{-1}$).

So, in order to apply transition state theory to calculate rate constants we must be able to calculate the partition functions of the reactant(s) and transition state, and we must know the energetic barrier to reaction E_o . Calculation of the partition functions, which will be discussed below, requires that we know the vibrational frequencies and moments of inertia of the reactant(s) and transition state. This is information that was once very difficult to obtain, but with the advent of fast computers and modern computational chemistry techniques, these quantities can be calculated relatively easily, at least for small molecules made up of atoms in the first 3 rows of the periodic table.

The transition state theory expression given above can also be formulated in terms of thermodynamic quantities. The rate constant can be written as

$$k_f = \frac{kT}{h} \frac{(Q^\ddagger / V)}{(Q_A / V)(Q_B / V)} \exp\left(\frac{-E_o}{kT}\right) = \frac{kT}{h} K_c^\ddagger$$

where K_c^\ddagger is the equilibrium constant for equilibrium between the transition state (neglecting the degree of freedom along the reaction coordinate) and the reactants. It can be written in thermodynamic terms as

$$K_c^\ddagger = \exp\left(\frac{-\Delta G_o^\ddagger}{RT}\right) = \exp\left(\frac{\Delta S_o^\ddagger}{R}\right) \exp\left(\frac{-\Delta H_o^\ddagger}{RT}\right)$$

then the rate constant can be expressed as

$$k_f = \frac{kT}{h} \exp\left(\frac{\Delta S_o^\ddagger}{R}\right) \exp\left(\frac{-\Delta H_o^\ddagger}{RT}\right)$$

in these expressions, ΔG_o^\ddagger , ΔS_o^\ddagger , and ΔH_o^\ddagger are referred to as the *Gibbs energy of activation*, the *entropy of activation*, and the *enthalpy of activation*, respectively. These are simply the difference between the transition state properties and the reactant properties (free energy, entropy, and enthalpy), neglecting any contribution to those properties by the motion along the reaction coordinate. Since the definition of K_c^\ddagger is somewhat arbitrary, one can also simply think of the above as a definition for ΔG_o^\ddagger , ΔS_o^\ddagger , and ΔH_o^\ddagger . This formulation could also be arrived at by using the statistical mechanical relationships between the thermodynamic quantities and the partition functions, i.e. $S = k \ln(Q) + kT \frac{\partial \ln(Q)}{\partial T}$, etc.

In order to make use of transition state theory, we need to be able to calculate the partition functions that appear in the expression for the rate constant. Rather than go any further in turning this into a course on statistical mechanics I will just give the formulas here. Derivations are in many textbooks, including 'Statistical Mechanics' by Donald A. McQuarrie. If the rotational, vibrational, translational, and electronic degrees of freedom are separable (they do not interact) then we can write the total partition function as the product of separate partition functions for each type of degree of freedom. So, we write the total partition function (for a reactant, product, transition state, or whatever) as

$$Q = Q_{rot} Q_{vib} Q_{elec} Q_{trans}$$

The translational partition function is given by

$$Q_{trans} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

where m is the molecular weight, k is Boltzmann's constant, T is temperature, h is Planck's constant, and V is the volume *per particle*.

The vibrational partition function is given by

$$Q_{vib} = \prod_i \frac{1}{1 - \exp\left(\frac{-h\nu_i}{kT}\right)}$$

where the product is over all of the vibrational modes (3N-6 for a nonlinear molecule, 3N-5 for a linear molecule) and ν_i is the frequency of the i^{th} vibrational mode.

The rotational partition function for a linear molecule (which has 2 rotational degrees of freedom and 1 moment of inertia which we will call I) is

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2}$$

For a non-linear molecule with three moments of inertia about its three principal axes given by I_A , I_B , and I_C , the partition function is

$$Q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 I_A kT}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_B kT}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_C kT}{h^2} \right)^{1/2}$$

where σ is the rotational symmetry number of the molecule. The rotational symmetry number is the number of different ways you can rotate the molecule and still have the same type of atoms in the same locations. For example, it is 2 for H₂, N₂, CO₂, or H₂O. It is 3 for NH₃. It is 6 for C₂H₆, and 12 for CH₄.

The electronic partition function is given by

$$Q_{elec} = \sum_i g_i \exp\left(\frac{-E_i}{kT}\right)$$

where E_i is the energy of the i^{th} electronic state and g_i is the degeneracy of that state. The sum is over all electronic states, but those with energies more than a few times kT will not contribute. These states are not accessible at the given temperature because they are too high in energy. If the only accessible state is the electronic ground state and it is non-degenerate, then $Q_{elec} = 1$. For free radicals that have a doubly degenerate ground state, $Q_{elec} = 2$. If there are low-lying electronically excited states of a molecule, they will make a contribution to this partition function, but this is not usually the case.

Using the above expressions, we could now apply transition state theory to calculate a rate constant. Let's consider a simple example:

The reaction $F + H_2 \rightarrow HF + H$ proceeds through a linear transition state, and the properties of the reactants and the transition state are:

Parameter	F—H—H (TS)	F	H ₂
Frequencies			
$\bar{\nu}_1 \text{ cm}^{-1}$	4007.6		4395.2
$\bar{\nu}_2 \text{ cm}^{-1}$	397.9		
$\bar{\nu}_3 \text{ cm}^{-1}$	397.9		
$\bar{\nu}_4 \text{ cm}^{-1}$	310.8i		
E_o (kJ/mole)	6.57		
m (amu)	21.014	18.998	2.016
I (amu Å ²)	7.433		0.277
g_{elec}	4	4	1

The partition function of the F atom is the easiest (except for identifying the degeneracy of the electronic ground state):

$$Q_{elec} = 4$$

$$Q_{trans} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = 1.56 \times 10^{28} VT^{3/2}$$

where V is the volume (in m³) per molecule and T is the temperature in K. So, the total partition function for the F atom is

$$Q_F = 6.22 \times 10^{28} VT^{3/2}$$

The electronic partition function for H₂ is $Q_{elec} = 1$.

The translational partition function for H₂ is

$$Q_{trans} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = 5.38 \times 10^{26} VT^{3/2}$$

The vibrational partition function for H₂ is

$$Q_{vib} = \frac{1}{1 - \exp\left(\frac{-h\nu}{kT}\right)} = \frac{1}{1 - \exp\left(\frac{-hc\bar{\nu}}{kT}\right)} = \frac{1}{1 - \exp\left(\frac{-6331}{T}\right)}$$

The rotational partition function for H₂ is

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = 0.00571T$$

So, the total partition function for H₂ is

$$Q_{H_2} = 3.072 \times 10^{24} VT^{3/2} \left(\frac{1}{1 - \exp\left(\frac{-6331}{T}\right)} \right)$$

Finally, we can formulate the partition function for the transition state

$$Q_{elec} = 4$$

$$Q_{trans} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = 1.81 \times 10^{28} VT^{3/2}$$

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = 0.306T$$

$$Q_{vib} = \prod_i \frac{1}{1 - \exp\left(\frac{-h\nu_i}{kT}\right)} = \prod_i \frac{1}{1 - \exp\left(\frac{-hc\bar{\nu}_i}{kT}\right)}$$

$$Q_{vib} = \left(\frac{1}{1 - \exp(-5760/T)} \right) \left(\frac{1}{1 - \exp(-570/T)} \right)^2$$

so

$$Q^\ddagger = 2.22 \times 10^{28} VT^{5/2} \left(\frac{1}{1 - \exp(-5760/T)} \right) \left(\frac{1}{1 - \exp(-570/T)} \right)^2$$

Finally, we can use these partition functions in the expression for the rate constant:

$$k_f = \frac{kT}{h} \frac{2.22 \times 10^{28} T^{5/2} \left(\frac{1}{1 - \exp(-5760/T)} \right) \left(\frac{1}{1 - \exp(-570/T)} \right)^2 \exp\left(\frac{-E_o}{kT}\right)}{3.072 \times 10^{24} T^{5/2} \left(\frac{1}{1 - \exp\left(\frac{-6331}{T}\right)} \right) 6.22 \times 10^{28} T^{3/2}}$$

$$k_f = \frac{2.42 \times 10^{-15} \left(1 - \exp\left(\frac{-6331}{T}\right) \right)}{\sqrt{T} \left(1 - \exp(-5760/T) \right) \left(1 - \exp(-570/T) \right)^2} \exp\left(\frac{-790}{T}\right) \left(\frac{\text{m}^3}{\text{molecule s}} \right)$$

To put this in more familiar units, we can multiply by Avagadro's number and also convert the volume units to cm^3 .

$$k_f = \frac{1.46 \times 10^{15} \left(1 - \exp\left(\frac{-6331}{T}\right) \right)}{\sqrt{T} \left(1 - \exp(-5760/T) \right) \left(1 - \exp(-570/T) \right)^2} \exp\left(\frac{-790}{T}\right) \left(\frac{\text{cm}^3}{\text{mole s}} \right)$$

This is almost the Arrhenius form, but there is some temperature dependence of the pre-exponential constant. At $T=300$ K, the pre-exponential is

$$A = \frac{(1.46 \times 10^{15})(1)}{\sqrt{300}(1)(0.850)^2} = 1.17 \times 10^{14} \left(\frac{\text{cm}^3}{\text{mole s}} \right)$$

So, near room temperature, we have

$$k_f = 1.17 \times 10^{14} \exp\left(\frac{-790}{T}\right) \left(\frac{\text{cm}^3}{\text{mole s}} \right)$$

The experimental rate constant is

$$k_f = 2 \times 10^{14} \exp\left(\frac{-800}{T}\right) \left(\frac{\text{cm}^3}{\text{mole s}}\right)$$

so the transition state theory prediction is quite good in this case (of course the goodness of prediction is mostly dependent on the transition state parameters used).

Before leaving the topic of transition state theory let's reconsider some of its limitations

- (1) It is based on classical mechanics. It cannot include purely quantum mechanical effects, particularly tunneling. In transition state theory, a molecule with energy less than the barrier height can never react. However, quantum mechanics tells us that there is a finite probability that the system will *tunnel* through the potential barrier to react. This is particularly important for reactions involving light atoms like hydrogen. It is sometimes corrected for by a transmission coefficient that gives some probability for tunneling.
- (2) Systems with more than the minimum energy needed to react need not pass through the transition state at the saddle point. Particularly at high temperatures, where the molecules have high energy, the system may go to parts of the surface that are relatively far from the minimum energy path.
- (3) The assumption that species never re-cross the transition state may not be valid.
- (4) The assumption that the reactants maintain a Boltzmann distribution of energies (in all degrees of freedom) may not be valid.

Nevertheless, transition state theory has been successful in understanding and predicting rate parameters for many gas phase elementary reactions. With the modern computers and *ab initio* quantum mechanical calculation of potential surfaces, it is becoming increasingly possible to calculate usefully accurate rate constants by these methods.

After completing your study of these lecture notes and the associated homework, you should be able to:

- (1) Understand the derivation of transition state theory presented here
- (2) State and justify the key assumptions upon which transition state theory is based
- (3) Apply transition state theory to calculate a rate constant for a reaction given the reactant and transition state geometries and harmonic vibrational frequencies
- (4) Interpret the transition state theory expression for the rate constant in terms of thermodynamic quantities (the enthalpy and entropy of activation)
- (5) Recall and explain the key limitations of transition state theory and identify cases where it is not likely to perform well.