

Calculations of Rate Constants

A very important topic in chemistry is the study of the rate of chemical reactions, i.e. the rate of transitions from one arrangement of the atoms to another. The study of the relationship between the rate constant of a reaction and the basic properties of the chemicals involved is an important part of physical chemistry. Which chemical reactions occur rapidly and which ones are slow? To answer this question one needs to be able to calculate the rate constant for the chemical reactions of interest. Also, as theoretical methods become more powerful and computers become faster, the prediction of the numerical value of rate constants of chemical reactions from basic, fundamental equations becomes possible for more complex systems.

The most important theoretical approach in analysing the rate of chemical reactions is the so-called 'transition state theory' (TST). It also goes under the name of 'absolute rate theory' (ART) and, derived from a slightly different point of view, as 'activated complex theory' (ACT). This is one of the most important topics in physical chemistry. Despite its importance, the presentation of TST is often misleading. In 1974 Prof. Bruce Mahan published an article in the *Journal of Chemical Education* where he states: *In view of [its] success, it is unfortunate that the theory does not enjoy a better understanding and confidence among non-specialists. Some of this difficulty can be traced to the rather unconvincing derivations of the ART expression for the rate constant which are found in many physical chemistry texts and monographs on chemical kinetics.* Unfortunately, not much progress has been made, it seems, in the presentation of TST in textbooks in the 30 years since the publication of Mahan's article.

Before presenting the theory itself, it is necessary to motivate the statistical treatment of the problem and discuss the way in which statistical mechanics is used to describe classical systems, i.e. systems that follow Newton's equation of motion. As for quantum mechanical systems (which undergraduate chemistry students are, ironically, typically more familiar with), the Boltzmann distribution of energy plays a central role. Then, TST will be derived in a simple way and the various assumptions TST rests on will be illustrated. The corrections to TST and the variational optimization of the TST calculation will then be discussed. Finally, the harmonic approximation to TST will be presented. It gives a precise theoretical foundation for the commonly observed Arrhenius dependence of the rate constant on temperature and illustrates how the activation energy and the prefactor relate to the shape of the potential energy surface, and thereby the chemical interaction between the atoms.

Separation of time scales

Given that the classical approximation will be used to describe the motion of the atoms, it would seem that the task of estimating reaction rate constants would simply involve the calculation of classical trajectories by solving Newton's equations of motion numerically once a potential surface has been specified. Such a calculation can be carried out using finite difference methods (the so-called Verlet algorithm). But, there is a time scale problem here which makes this approach intractable.

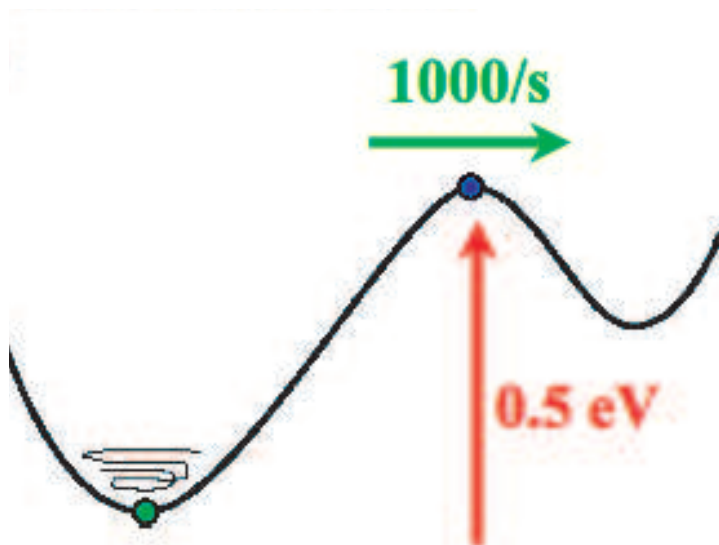


Figure 1: A schematic energy landscape for a chemical reaction, with an energy minimum corresponding to reactants to the left and a minimum corresponding to products to the right. If the energy barrier is 0.5 eV and the entropic effects are typical for a solid state reaction (a prefactor of 10^{13}sec^{-1}) the average time between reactive events is a millisecond, which is fast on a laboratory time scale, but on the time scale of the atomic vibrations the reactive events are very rare, about one in every 10^{10} vibrational periods.

Instead, a statistical approach can be used. The problem then reduces to a calculation of the probability that the system makes it into the most restrictive and least like region along the way from the reactants to the products. This region is usually referred to as the transition state and the methodology is referred to as the transition state

theory (TST) approximation. Before formulating TST, it is good to review classical statistical mechanics.

Classical statistical mechanics

The state of a classical system is characterized by the coordinates and velocities of all the atoms, (\vec{x}, \vec{v}) . The total energy is a function of these variables

$$E_{tot}(\vec{x}, \vec{v}) = E_{kin} + E_{pot} = \sum_i \frac{1}{2} m_i v_i^2 + V(\vec{x})$$

The sum runs over the Cartesian coordinates of all the atoms in the system. The probability distribution for a system of classical particles is given by the Boltzmann distribution, similar to quantum mechanical systems. The probability that the system is in a state corresponding to the atomic coordinates being in the range from \vec{x} to $\vec{x} + d\vec{x}$ and atomic velocities being in the range \vec{v} to $\vec{v} + d\vec{v}$ is

$$P(\vec{x}, \vec{v}) d\vec{x}d\vec{v} = A e^{-E(\vec{x}, \vec{v})/k_B T} d\vec{x}d\vec{v}$$

where A is some normalization constant. Note that this distribution function factorizes into a distribution function for coordinates and a distribution function for velocities because the kinetic energy only depends on the velocities and the potential energy only depends on the coordinates

$$P(\vec{x}, \vec{v}) d\vec{x}d\vec{v} = A_v e^{-\sum_i \frac{1}{2} m_i v_i^2 / k_B T} A_c e^{-V(\vec{x})/k_B T} = p_v(\vec{v}) p_c(\vec{x})$$

Here A_v and A_c are normalization constants. The distribution function for the velocity components is just the Maxwell distribution. It is the same everywhere in configuration space since it is independent of \vec{x} .

The dividing surface and the transition state

Before starting to describe the reaction $R \rightarrow P$ it is necessary to decide which part of configuration space belongs to the reactants, R, and which part belongs to products, P. A dividing surface needs to be drawn to separate the two parts. If we have N atoms in three dimensional space, then there are $D = 3N$ degrees of freedom (the coordinates) in the configurational space. One can think of a configuration of the system as a point in $3N$ -dimensional space. The dividing surface represents a subspace with one fewer degrees of freedom, $D - 1 = 3N - 1$. If $N = 100$, there are 299 degrees of freedom in the dividing surface. The dividing surface must be placed in such a way that any classical trajectory going from R to P (or vice versa) must go through the dividing surface.

Most of the time the system is close to one of the potential minima representing R and P. For configuration in between the minima, the potential energy is large and

the probability of finding the system there is small. It is natural to place the dividing surface through the region where the probability of finding the system is small.

Given that the system is initially located in the reactant region, the probability distribution can be normalized. The total probability of finding the system in the part of configuration space that corresponds to R must be unity

$$1 = \int_R p_c(\vec{x}) d\vec{x} = A_c \int_R e^{-V(\vec{x})/k_B T} d\vec{x}$$

The integral is carried out over the whole region corresponding to R. This gives

$$A_c = \frac{1}{\int_R e^{-V(\vec{x})/k_B T} d\vec{x}}.$$

The probability of finding the system in some subregion of R, denoted by S, is then

$$P_S = \frac{\int_S e^{-V(\vec{x})/k_B T} d\vec{x}}{\int_R e^{-V(\vec{x})/k_B T} d\vec{x}}.$$

The transition state (TS) is defined as a subspace that consists of a narrow region around the dividing surface. The width of the TS, σ , is infinitesimal. The dividing surface and thereby the TS should be chosen so as to represent a bottle neck for the transition of the system from R to P. It is the part of the reaction path where the probability of finding the system is particularly small. A transition, such as a typical chemical reaction, is a rare event, it takes a large fluctuation of the energy (coming from the heat bath) in just the right coordinates for the system to be able to reach the transition state and proceed over to P. The in between such reactive events is many orders of magnitude longer than the time of vibrational motion. The key approximation in TST is that if the system makes it to the transition state and is heading towards P, then we can assume that the system will end up in P for an extended time. In most cases, there is a natural separation of time scale. The time it takes the system to leave the TS is very short compared with the time between thermally activated transitions from R to P or from P to R.

The TST approximation to the rate constant

If the transition state represents a tight bottle neck for going from R to P, then one can approximate the rate constant in a simple way

$$k^{TST} = (\text{probability of making it to the TS}) \cdot (\text{rate of crossing TS from R to P})$$

$$= \frac{\sigma \int_{\ddagger} e^{-V(\vec{x})/k_B T} d\vec{x}}{\int_R e^{-V(\vec{x})/k_B T} d\vec{x}} \frac{\langle v_{\perp} \rangle}{\sigma}$$

where $\langle v_{\perp} \rangle$ is the average velocity in crossing the TS, in a direction normal to the dividing surface. The key assumption here is that if the system leaves the TS in the direction towards the product region, P, then the system will continue to stay in the product region and spend an extended time there until another energetic fluctuation takes it back to R. This is the central approximation in TST. This is a good approximation if the dynamics are simple and the classical trajectories do not go back and forth over the dividing surface before landing in either R or P. The other two other approximations in TST are the assumption that classical dynamics on the Born-Oppenheimer surface is a valid description of the dynamics, and that the reactant has reached equilibrium conditions, i.e. the energy in each degree of freedom is described by the Boltzmann distribution. For a typical transition rate, there is a very large number of vibrations in between reactive events (on the order of 10^{10}), so the last approximation is usually an excellent one.

Since the width of the TS is infinitesimal, the potential energy can be taken to be constant in the direction normal to the dividing surface. The average velocity in crossing the TS $\langle v_{\perp} \rangle$ can be calculated from the Maxwell distribution

$$\langle v_{\perp} \rangle = \frac{\int_0^{\infty} v e^{-\sum_i \frac{1}{2}\mu v_i^2/k_B T} dv}{\int_{-\infty}^{\infty} e^{-\sum_i \frac{1}{2}\mu v_i^2/k_B T} dv} = \sqrt{\frac{k_B T}{2\pi\mu}}$$

Here μ is an effective mass for the motion across the TS, a linear combination of the masses of the atoms that get displaced in the transition. The TST approximation to the rate constant can then be written as

$$k^{TST} = \sqrt{\frac{k_B T}{2\pi\mu}} \frac{Z^{\ddagger}}{Z^R}$$

where Z denotes the integral of the Boltzmann factor over the specified region of configuration space.

Simple example: Effusion

It is important to emphasize that the bottle neck that makes it difficult for the system to go from R to P can arise from a limitation on the number of ways that the system can proceed in the transition and does not necessarily have to involve a potential energy barrier. A good example of this is effusion of a gas through a small hole on a container. The fact that the hole is small (smaller than the mean free path of the gas molecules) makes this region a bottle neck for the motion of the gas molecules from inside the box (region R) to the outside (region P). There is no potential energy barrier. This kind of bottle neck can be regarded as an entropic barrier.

The rate of effusion is proportional to the number of gas molecules in the box, and the constant of proportionality is the rate constant $r = kN$. We can estimate k from

TST in a simple way. The reactant region is the inside of the box, of volume V and the dividing surface is the hole, of area A . Note that the dividing surface has one fewer dimensions than the reactant region. The potential energy can be chosen to be zero both in R and in the TST (everywhere except at the walls) and the configuration integrals are therefore $Z_R = V$ and $Z_{\ddagger} = A$. The TST expression for the rate constant is

$$k^{TST} = \sqrt{\frac{k_B T}{2\pi m}} \frac{A}{V}$$

Since the gas molecules move one at a time through the hole, μ is simply the mass of a gas molecule, m , in this case. By using the ideal gas law, $PV = Nk_B T$ this can be rewritten as

$$k^{TST} = \frac{PA}{\sqrt{2\pi m k_B T} N}$$

and the rate of effusion is predicted to be

$$r = \frac{PA}{\sqrt{2\pi m k_B T}}$$

This is precisely the same result as was obtained from the kinetic theory of gases. The TST approximation, therefore, gives exact results in this case even though there is no potential energy barrier.

More generally, a bottle neck in a chemical reaction can arise from both an energy barrier and an entropy barrier. The definition of a *free energy* barrier combines the entropic and energetic aspects in a consistent way.

Dynamical corrections and the variational principle

If a classical trajectory crosses the TS and then for some reason gets reflected and ends up again in the reactant region, R, before settling down in the product region, then the TST approximation will have overcounted the number of reactive trajectories and the TST rate constant estimate will be too high. Also, if a trajectory crosses the dividing surface three times, the TST approximation will count that as two reactive trajectories even though it really is only one. Again the TST approximation will lead to an overestimate of the rate constant. It can be shown that these and other corrections to the "no recrossing" approximation in TST all lead to an overestimate, so we have

$$k^{TST} \geq k^{exact}$$

This gives a variational principle for placing the dividing surface, i.e. one can vary its position so as to obtain a minimal value of k^{TST} . That is the best estimate that can be obtained from TST. It can be shown that this minimization of k^{TST} corresponds to finding the dividing surface that has the maximum free energy.

If a good dividing surface is found, then the TST estimate of the rate constant is typically within a factor of two or so of the exact rate constant. This is typically accurate enough, there are other errors that tend to be more important, such as the construction of the potential energy surface. However, if a more accurate estimate of the rate constant is needed, then it is quite easy to start classical trajectories from the TS and count how often recrossings occur. This only requires short trajectories because the system falls quite rapidly from the TS towards either R or P. This way a correction factor, κ , can be computed such that

$$k^{exact} = \kappa k^{TST}.$$

In the end, TST is then just an intermediate construct that enables the computation of k^{exact} without having to do the impossibly long classical dynamics calculations of a trajectory that oscillates back and forth in the reactant region before getting a rare, high energy kick from the heat bath that is large enough to make it through the bottle neck region.

The harmonic approximation

For systems where the atoms are vibrating about fixed average positions, such as atoms in solids, or molecules reacting on the surface of a solid, the region of the potential surface that is of greatest importance can be represented by a harmonic approximation. For a diatomic molecule, the interaction potential, which is only a function of the distance between the atoms, can be expanded in a Taylor expansion that gets truncated at the second power to give $v(r) \approx v(r_0) + \frac{1}{2}kx^2$ where $x = r - r_0$ and r_0 is the distance at which the potential energy is minimal. The generalization of this to systems with more than one vibrational degree of freedom involves the calculation of mixed second derivatives, such as $\partial^2 V / \partial x_1 \partial x_2$. However, if one uses instead the coordinates corresponding to normal modes of vibration, q_i , such mixed second derivatives vanish (the normal modes are independent and do not mix within the harmonic approximation). The construction of the normal modes of vibration can be carried out for any point on the potential energy surface, in particular at the minimum in the potential surface corresponding to R. Since the force is zero at the minimum, the first derivative of the potential vanishes and the expansion of the potential is

$$V^R(\vec{q}) \approx V_{min} + \sum_i^D \frac{1}{2} k_i^R q_{R,i}^2$$

in the region close to the minimum. While this will not be a good approximation for regions far from the minimum, the approximation is good enough if the potential energy is high enough in those regions so that the probability of finding the system there is small.

If the dividing surface is chosen to lie along the potential energy ridge that separates the reactant state from the product state, then the most important point on the dividing surface, the point with largest statistical weight, is a saddle point. It is a minimum with respect to all the degrees of freedom within the dividing surface, but a maximum with respect to the motion normal to the dividing surface. If more than one saddle point exists on the potential energy ridge, then the lowest energy one is most important. For each low lying saddle point, one can carry out a second order Taylor expansion of the potential energy within the dividing surface

$$V^\ddagger(\vec{q}) \approx V_{SP} + \sum_i^{D-1} \frac{1}{2} k_i^\ddagger q_{\ddagger,i}^2$$

The first term on the right, V_{SP} , is the energy at the saddle point. The normal mode corresponding to motion normal to the dividing surface is not included. The width, σ , of the TS is so small normal to the dividing surface that the potential is taken to be constant in that direction. With these approximations to the potential energy surface, the configuration integrals can be carried out analytically and one obtains the harmonic TST expression for the rate constant, k^{HTST}

$$k^{HTST} = \sqrt{\frac{k_B T}{2\pi\mu}} \frac{Z^\ddagger}{Z^R} = \sqrt{\frac{k_B T}{2\pi\mu}} \frac{e^{-V_{SP}/k_B T} \int_{-\infty}^{\infty} e^{-\sum_i^{D-1} \frac{1}{2} k_i^\ddagger q_{\ddagger,i}^2 / k_B T} dq_{\ddagger,i}}{e^{-V_{min}/k_B T} \int_{-\infty}^{\infty} e^{-\sum_i^D \frac{1}{2} k_i^R q_{R,i}^2 / k_B T} dq_{R,i}}$$

For each one of the normal modes, the integral over the Gaussian gives

$$\int_{-\infty}^{\infty} e^{-\frac{1}{2} k_i q_i^2 / k_B T} dq_i = \sqrt{\frac{2\pi k_B T}{k_i}}$$

So,

$$k^{HTST} = \sqrt{\frac{k_B T}{2\pi\mu}} \frac{\prod_i^{D-1} \sqrt{\frac{2\pi k_B T}{k_{\ddagger,i}}}}{\prod_i^D \sqrt{\frac{2\pi k_B T}{k_{R,i}}}} e^{-(V_{SP}-V_{min})/k_B T}$$

The factors of $k_B T$ cancel out and all factors of 2π except for one

$$k^{HTST} = \frac{1}{2\pi} \frac{\prod_i^D \sqrt{k_{R,i}/\mu}}{\prod_i^{D-1} \sqrt{k_{\ddagger,i}/\mu}} e^{-(V_{SP}-V_{min})/k_B T}$$

Here, the square root of the effective mass for the normal modes has been multiplied both in the numerator and the denominator. Recall that the vibrational frequency is $\nu = \omega/2\pi = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ so

$$k^{HTST} = \frac{\prod_i^D \nu_{R,i}}{\prod_i^{D-1} \nu_{\ddagger,i}} e^{-(V_{SP}-V_{min})/k_B T}$$

The HTST approximation agrees with the empirically observed Arrhenius expression for the temperature dependence of the rate constant. It is not possible to interpret the activation energy. It is simply the potential energy difference between the saddle point and the minimum corresponding to the reactant region. The prefactor has to do with the vibrational entropy. If the vibrational frequencies are low at the saddle point compared with the minimum, corresponding to a wide mountain pass, then the prefactor is large. If the potential energy rises quickly away from the SP within the dividing surface, quicker than in the vicinity of the minimum, then the prefactor is small.

The discussion here has been entirely in terms of classical mechanics. At low temperature the classical treatment of vibration is often not good enough. First of all, one needs to take into account the zero point energy of the vibrational ground state. In the most extreme case, one needs to take into account that the system might tunnel from R to P. The full extension of TST to quantum systems is still an area of active research. The simplest inclusion of zero point energy can be made if the system is most likely in the lowest energy level both initially and at the transition state. Then, one can replace $V_{min} - V_{SP}$ with

$$E_a = \left(V_{SP} + \sum_i^{D-1} \frac{h\nu_{\ddagger,i}}{2} \right) - \left(V_{min} + \sum_i^D \frac{h\nu_{R,i}}{2} \right).$$

Since there is one fewer vibrational modes at the SP than at the minimum, the addition of the zero point energy tends to reduce the energy barrier. One consequence of this is that transitions involving the displacement of a deuterium atom tend to have higher barrier than transitions where a hydrogen atom is displaced. The zero point energy of D is smaller because of the larger mass (more classical). This is often referred to as the kinetic isotope effect. However, this is not necessarily so, if the vibrational frequencies are higher at the SP than at the minimum, then the total zero point energy at the SP can be higher than at the minimum, even though there is one fewer modes there. This can lead to the so-called *reverse* isotope effect.

A better quantum mechanical correction to the HTST expression for the rate constant is to replace the classical harmonic partition function for each vibrational normal mode with the corresponding quantum mechanical harmonic partition function.

A full quantum mechanical rate constant that takes into account the possibility of tunneling can be formulated using, for example, the Feynman path integral formulation of quantum mechanics. A central question that remains to be answered, however, is how to best define the quantum mechanical transition state. A full, quantum mechanical extension of TST remains a topic of active research today.