

Transition state theory

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1 Equilibrium constants revisited

Previously, we saw how equilibrium constants for gas-phase reactions could be calculated from statistical mechanics. The equation obtained was

$$K = \frac{\prod_{i \in \text{products}} \left(\frac{q_i^\circ}{N_i} \right)^{\nu_i}}{\prod_{i \in \text{reactants}} \left(\frac{q_i^\circ}{N_i} \right)^{\nu_i}} e^{-\Delta\epsilon_0/(kT)}, \quad (1)$$

where q_i° is the partition function of species i evaluated in the standard state, N_i is the number of molecules of i ,¹ ν_i is the stoichiometric coefficient of i , and $\Delta\epsilon_0$ is the difference in energy between the reactant and product ground states. For gas-phase reactions, the thermodynamic standard state corresponds to having all reactants and products at a pressure of 1 bar. Of course, we could use a different standard state when this is convenient. For instance, if we wanted to express our equilibrium constants relative to a molarity standard state, we could simply pick $N_i = N_A$ and $V = 0.001 \text{ m}^3$ (1 L). Equation 1 is therefore very general, and can give us equilibrium constants for any desired situation in the gas phase, provided we're a little careful about the data we put into it.

2 Transition-state theory

It's a little easier to derive the equations of transition-state theory if we assume a particular reaction type than to treat the general case. Following your textbook, we will study a reaction of the type $\text{AB} + \text{C} \rightarrow \text{A} + \text{BC}$. The starting point for transition-state theory is to decompose this reaction into two parts: a quasi-equilibrium between the reactants and transition state, and breakdown of the transition state into products:



¹The actual number of molecules ends up canceling out in the calculations we did in class, so we set $N_i = N_A$, but this is not the most general formulation.

where K^\ddagger is the equilibrium constant for the first step, and k^\ddagger is the rate constant for the second step. If we assume that the first step is in quasi-equilibrium, we get

$$K^\ddagger = \frac{[\text{TS}]c^\circ}{[\text{AB}][\text{C}]},$$

where the factor of c° (the standard concentration) comes from assuming that we are using a molarity standard state and writing the activities of the reactants and products as $a_{\text{AB}} = [\text{AB}]/c^\circ$, etc.² From this equation, we can write

$$[\text{TS}] = K^\ddagger[\text{AB}][\text{C}]/c^\circ.$$

The rate of reaction is

$$\frac{d[\text{BC}]}{dt} = k[\text{AB}][\text{C}] = k^\ddagger[\text{TS}] = k^\ddagger K^\ddagger[\text{AB}][\text{C}]/c^\circ.$$

The first equality comes from applying the law of mass action to the original elementary reaction. The second equality comes from the assumed transition-state “mechanism”. Comparing the mass-action form to the transition-state theory expression, we get

$$k = k^\ddagger K^\ddagger/c^\circ. \tag{2}$$

The main problem in transition-state theory is then to provide equations for k^\ddagger and K^\ddagger .

In some sense, K^\ddagger is easy: It is given by equation 1. Specifically,

$$K^\ddagger = \frac{q_{\text{TS}} N_A}{q_{\text{AB}} q_{\text{C}}} e^{-\Delta\epsilon_0^\ddagger/(kT)},$$

where we have set $N_i = N_A$, and we assume that the partition functions will be evaluation for a volume of 1L in order to give us the equilibrium constant in a molarity standard state. Here, $\Delta\epsilon_0^\ddagger$ represents the difference in ground-state energies between the reactants and transition state, illustrated in figure 1. If we have the appropriate spectroscopic data, we can calculate the partition functions of AB and C. The partition function of the transition state is trickier. To see why, suppose that A, B and C are atoms. It doesn’t really matter, but it makes it a little easier to do the math than if we try to do it for the general case. Then, AB has one vibrational mode and two rotational modes. What about the transition state? To some extent, this depends on its geometry. For the sake of argument, let’s say that the transition state has a linear A—B—C geometry. Again, this isn’t critical to the argument, but makes it easier to see what is going on. If the transition state were a normal molecule, it would have two rotational modes, and $3(3) - 5 = 4$ vibrational modes, like CO_2 : two bending modes, a symmetric stretch, and an asymmetric stretch. However, this complex isn’t a stable molecule. It sits at a saddle point on the potential energy surface. The “asymmetric stretch” corresponds to either shortening the AB bond and lengthening

²We are of course also assuming that all reactants and products behave ideally. Transition-state theory can be reformulated for the case where this is not true, and is in fact the central theory for understanding the effects of non-ideal behavior on reaction rates.

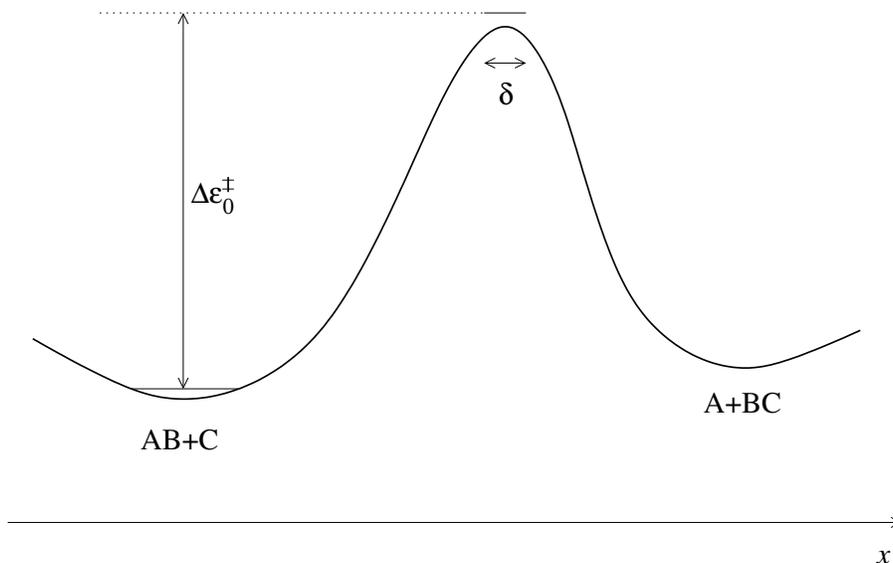


Figure 1: Definitions of some key quantities used in the derivation of the transition-state theory equations. The energy profile of the reaction is shown as a function of the reaction coordinate x . The horizontal lines in the reactant well and above the energy barrier represent the lowest vibrational states, respectively of the reactants and transition state.

the BC bond, which returns the system to the reactant valley, or to lengthening the AB bond and shortening the BC bond, which forms the products. The “asymmetric stretch” is therefore not a vibrational mode at all, but a *relative translational* mode. In fact, this is the mode of motion responsible for the reaction, so it is typically called the **reactive mode**.

In practical terms, this means that we can factor the partition function of the transition state into two terms, one for the reactive mode, q_r , and another term for all the other modes of motion of the transition state, \bar{q}_{TTS} :

$$q_{\text{TTS}} = q_r \bar{q}_{\text{TTS}}.$$

\bar{q}_{TTS} , give or take the “missing” mode, is a normal molecular partition function, calculated using the usual methods. There is a practical difficulty in that, until recently, there wasn’t really any way to collect the spectroscopic data necessary to evaluate this partition function. Transition-state spectroscopy is a rapidly developing field, so this isn’t quite as true as it used to be, but it’s still the case that these measurements are difficult, and so are only available for a handful of reactions. Computational chemistry typically fills the gap here.

What about q_r ? It’s the partition function for motion along the reaction coordinate and, as argued above, it’s a translational mode. The partition function for translation in one dimension is

$$q_T = (L/h) \sqrt{2\pi m k T}.$$

In this case though, we’re not talking about motion of a single molecule of mass m , but about the relative motions of A, B and C. (Recall that we’re still dealing with K^\ddagger , the equilibrium constant for the formation of the transition state from the reactants.) A theorem of mechanics

says that normal mode motions obey essentially the same equations of motion as for a single particle, but with the mass replaced by an effective mass m_{eff} . We have seen example of this before in simple two-body problems, where the reduced mass μ appeared. This is really a three-body motion (with simultaneous lengthening of the A—B bond and shortening of the B—C bond). We will see later that we don't need to know m_{eff} since it drops out of the final expression for the rate constant.

What about L ? The translational partition function was derived from the particle-in-a-box model. The transition state however is not contained in a box. However, to either side of the transition state, the system is either in a reactant or in a product state. We therefore imagine that the transition state occupies a region of width δ around the saddle point in the potential energy surface (figure 1). Outside of this region, it's not a transition state anymore. Note that this is a completely artificial device. The transition state, strictly speaking, is a single point on the potential energy surface. It might at first seem unsatisfying that the rate constant will depend on an arbitrary length δ . However, we will see later that δ also drops out of the final expression. In any event, putting m_{eff} and δ in the appropriate places in the partition function, we get

$$q_r = (\delta/h)\sqrt{2\pi m_{\text{eff}}kT}.$$

We can now substitute q_r into q_{TS} and q_{TS} into K^\ddagger :

$$K^\ddagger = \frac{\delta \bar{q}_{\text{TS}} N_A}{h q_{\text{AB}} q_{\text{C}}} e^{-\Delta\epsilon_0^\ddagger/(kT)} \sqrt{2\pi m_{\text{eff}}kT}. \quad (3)$$

We now need to work on k^\ddagger . This is the first-order rate constant for progress of the transition state to products. Recall that we are treating the reactive mode as translation through the transition-state region. Specifically, the transition state occupies the interval of width δ at the top of the energy barrier. The time required to cross this interval is, on average, $t = \delta/\bar{v}$, where \bar{v} is the average velocity at which this region is crossed from left to right. A first-order rate constant is the frequency of a particular process, i.e. the inverse of the time, so

$$k^\ddagger = \kappa \bar{v}/\delta.$$

We have included in this equation a **transmission coefficient** κ , which accounts for the possibility that some reactive events will abort and reform the reactants.

The motion along the reactive mode is a one-dimensional translational motion. For \bar{v} , we will therefore use the average left-to-right (i.e. positive) velocity in one dimension, which we can calculate from the Maxwell-Boltzmann velocity distribution in one dimension, $f(v)$:

$$\bar{v} = \int_0^\infty v f(v) dv = \sqrt{\frac{kT}{2\pi m_{\text{eff}}}}.$$

Note that we use the effective mass of this mode, for the reasons explained above. Our final expression for k^\ddagger is therefore

$$k^\ddagger = \frac{\kappa}{\delta} \sqrt{\frac{kT}{2\pi m_{\text{eff}}}}. \quad (4)$$

If we now combine equations 2, 3 and 4, we get

$$k = \frac{\kappa kT}{hc^\circ} \frac{\bar{q}_{\text{TS}} N_A}{q_{\text{AB}} q_{\text{C}}} e^{-\Delta\epsilon_0^\ddagger/(kT)}. \quad (5)$$

This is the final expression for the transition-state theory rate constant. Note that N_A here is Avogadro's *number*, not Avogadro's constant, i.e. N_A is a pure dimensionless number. If you work through the units, you should find that k has the expected dimensions of $\text{L mol}^{-1}\text{s}^{-1}$.

Transition-state theory is often used as a basis for *ab initio* calculations of rate constants. From equation 5, you can see how this might be done. First, we need to identify the transition state of the reaction. This can be more or less difficult, depending on the nature of the reaction. In the simplest cases, we simply “walk up” from the reactants to the lowest-energy maximum separating them from the products. In other cases, we may need to explore the potential energy surface first, then refine the solution once we have identified the approximate location of the lowest-energy saddle point. We then need the partition functions of the reactants and transition state, which means that we need their vibrational, rotational and electronic energies, all of which are readily obtained (if difficult to compute accurately, particularly in the case of the vibrational frequencies) by *ab initio* quantum chemistry techniques. We also need the energy of the transition state relative to the ground state of the reactants, which is easily calculated since *ab initio* programs use of the separated atoms as a common reference state. All of these calculations are essentially static in nature, i.e. they consist of a whole bunch of geometry optimizations of single points on the potential energy surface.³ On the other hand, estimating the transmission coefficient κ requires molecular dynamics. To estimate this coefficient, we have to collide the reactants together with adequate energy and in the right orientation. We can then simply count the number of collisions that actually make the products as a fraction of the total number of reactive events attempted. This is much harder, since it requires a great deal of knowledge of the potential energy surface, especially around the transition state. Moreover, dynamics is much more computationally demanding than static calculations.

³Geometry optimization of course entails some exploration of the local vicinity of a point.