

# Transition state theory

## 1. The equilibrium constant

Equilibrium constants can be calculated for any chemical system from the partition functions for the species involved. In terms of the partition function  $q$ , the chemical potential of a species (essentially the molar Gibbs free energy) is given by

$$\mu = RT \ln \frac{N}{q}$$

Consider the reaction  $aA + bB \rightleftharpoons pP + qQ$ . At equilibrium the free energy of the reactants is equal to the free energy of the products.

$$G_{\text{react}} = G_{\text{prod}}$$

$$a \mu_A + b \mu_B = p \mu_P + q \mu_Q$$

$$RT \ln(N_A/q_A)^a + RT \ln(N_B/q_B)^b = RT \ln(N_P/q_P)^p + RT \ln(N_Q/q_Q)^q$$

Rearranging gives

$$\frac{N_P^p N_Q^q}{N_A^a N_B^b} = \frac{q_P^p q_Q^q}{q_A^a q_B^b} = K_n$$

We recognise this as the equilibrium constant formulated in terms of concentrations. We are often interested in  $K_p$ , the equilibrium constant in terms of partial pressures. For the case in which all species involved are gases, we can convert from  $K_n$  to  $K_p$  using the ideal gas equation,  $p = nRT/V$ .

$$K_p = \frac{p_P^p p_Q^q}{p_A^a p_B^b} = \frac{N_P^p N_Q^q}{N_A^a N_B^b} \left(\frac{k_B T}{V}\right)^{(p+q-a-b)} = \frac{q_P^p q_Q^q}{q_A^a q_B^b} \left(\frac{k_B T}{V}\right)^{\Delta n}$$

where  $\Delta n = p + q - a - b$  is the change in the number of moles during reaction. If we use vibrational partition functions defined with energies measured from the zero-point energy for each reactant and product species, then we also need to include the extra factor  $e^{D_0/k_B T}$  (see Statistical Mechanics tutorial) in order to ensure that all of the molecular partition functions are referenced to the same zero of energy. The equilibrium constant then becomes

$$K_p = \frac{q_P^p q_Q^q}{q_A^a q_B^b} \left(\frac{k_B T}{V}\right)^{\Delta n} \exp\left(\frac{p\Delta D_0^P + q\Delta D_0^Q - a\Delta D_0^A - b\Delta D_0^B}{k_B T}\right) = \frac{q_P^p q_Q^q}{q_A^a q_B^b} \left(\frac{k_B T}{V}\right)^{\Delta n} \exp\left(\frac{\Delta D_0}{k_B T}\right)$$

The quantity  $\Delta D_0 = (pD_0^P + qD_0^Q - aD_0^A - bD_0^B)$  is the difference between reactant and product zero-point energies. Usually, we can set  $\Delta D_0 = -\Delta H_0$ , with  $\Delta H_0$  the enthalpy of reaction.

## 2. The rate constant

We can also use statistical mechanics to obtain rate constants from partition functions. For a reaction  $A + B \rightleftharpoons AB^\ddagger \rightarrow P$ , we assume that the reactions involved in forming the activated complex  $AB^\ddagger$  are much faster than the formation of products from the complex. Kinetically, the reaction can then be treated as a pre-equilibrium (see first year Kinetics notes), with

$$K^\ddagger = \frac{[AB^\ddagger]}{[A][B]}$$

$$\text{rate} = k^\ddagger [\text{AB}^\ddagger] = k^\ddagger K^\ddagger [\text{A}][\text{B}] = k_{\text{obs}}[\text{A}][\text{B}]$$

where  $k_{\text{obs}} = k^\ddagger K^\ddagger$  is the observed rate constant, and  $k^\ddagger$  is the rate constant for decomposition of the activated complex into products. The equilibrium constant  $K^\ddagger$  can be rewritten in terms of the appropriate partition functions, giving

$$k_{\text{obs}} = k^\ddagger \frac{q_{\text{AB}^\ddagger}}{q_{\text{A}}q_{\text{B}}} e^{-\Delta H^\ddagger/RT}$$

where the partition functions are evaluated with respect to the zero-point levels of the reactants and transition state. We can derive a complete expression for  $k_{\text{obs}}$  by treating the motion of the activated complex over the top of the energy barrier (i.e. the reaction coordinate) as either a very loose vibration or as a translation.

### Derivation 1: Reaction coordinate as a vibration

Reactants A and B have  $3N-6$  vibrational degrees of freedom if non-linear,  $3N-5$  if linear. The same is true of the activated complex, which has  $3(N_{\text{A}}+N_{\text{B}})-6$  vibrational modes if it is non-linear. One of these modes is of a different character from the rest, corresponding to a very loose vibration that allows the complex to dissociate into products. For this degree of freedom we can use a vibrational partition function  $q^*$  in which the vibrational frequency  $\nu$  tends to zero. i.e.

$$q^* = \lim_{\nu \rightarrow 0} \frac{1}{1 - e^{-h\nu/k_{\text{B}}T}} = \frac{1}{1 - (1 - h\nu/k_{\text{B}}T)} = \frac{k_{\text{B}}T}{h\nu}$$

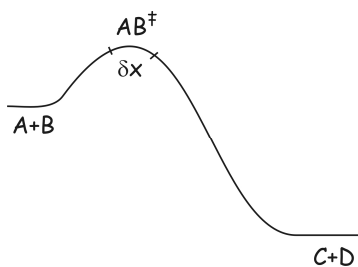
The rate constant is now given by

$$k_{\text{obs}} = k^\ddagger \frac{k_{\text{B}}T}{h\nu} \frac{q_{\text{AB}^\ddagger}}{q_{\text{A}}q_{\text{B}}} e^{-\Delta H^\ddagger/RT}$$

where  $q_{\text{AB}^\ddagger}$  is now less one degree of freedom corresponding to the reaction coordinate. The frequency  $\nu$  is the vibrational frequency of the activated complex in the degree of freedom corresponding to its decomposition. It is therefore the frequency of decomposition i.e. the rate constant  $k^\ddagger$ . This means that  $k^\ddagger q^* = k_{\text{B}}T/h$ , and the rate constant is given by

$$k_{\text{obs}} = \frac{k_{\text{B}}T}{h} \frac{q_{\text{AB}^\ddagger}}{q_{\text{A}}q_{\text{B}}} e^{-\Delta H^\ddagger/RT}$$

### Derivation 2: Reaction coordinate as a translation



Instead of using a vibrational partition function to describe the motion of the activated complex over the reaction barrier, we can also use a translational partition function. We consider all complexes lying within a distance  $\delta x$  of the barrier (see diagram) to be activated complexes. The translational partition function for a particle of mass  $m$  in a box of length  $\delta x$  is given by

$$q^* = \frac{(2\pi m^\ddagger k_{\text{B}}T)^{1/2} \delta x}{h}$$

giving a rate constant

$$k_{\text{obs}} = k^{\ddagger} \frac{(2\pi m^{\ddagger} k_B T)^{1/2}}{h} \delta x \frac{q_{\text{AB}}^{\ddagger}}{q_A q_B} e^{-\Delta H^{\ddagger}/RT}$$

where  $q_{\text{AB}}^{\ddagger}$  is less one degree of freedom as before. The average velocity of the particles moving from left to right over the barrier is given by kinetic theory as

$$v^{\ddagger} = \left( \frac{k_B T}{2\pi m^{\ddagger}} \right)^{1/2}$$

The frequency with which the complexes pass over the barrier is the rate constant  $k^{\ddagger}$ , given by

$$k^{\ddagger} = \frac{v^{\ddagger}}{\delta x} = \frac{1}{\delta x} \left( \frac{k_B T}{2\pi m^{\ddagger}} \right)^{1/2}$$

When we substitute this equation into our expression for  $k_{\text{obs}}$ , we obtain the same expression as in derivation 1.

$$\begin{aligned} k_{\text{obs}} &= \frac{1}{\delta x} \left( \frac{k_B T}{2\pi m^{\ddagger}} \right)^{1/2} \frac{(2\pi m^{\ddagger} k_B T)^{1/2}}{h} \delta x \frac{q_{\text{AB}}^{\ddagger}}{q_A q_B} e^{-\Delta H^{\ddagger}/RT} \\ &= \frac{k_B T}{h} \frac{q_{\text{AB}}^{\ddagger}}{q_A q_B} e^{-\Delta H^{\ddagger}/RT} \end{aligned}$$

This equation is sometimes known as the Eyring equation. The main difficulty in applying transition state theory lies in determining  $q_{\text{AB}}^{\ddagger}$ . However, modern methods and educated guesswork on the nature of the activated complex  $\text{AB}^{\ddagger}$  usually allow rate constants for bimolecular reactions to be estimated to within a factor of two using this theory.

### 3. Kinetic isotope effects

There are two origins of the kinetic isotope effect. The first, quantum mechanical tunnelling through the reaction potential energy barrier, is usually only important at very low temperatures and for reactions involving very light atoms. For the simplest model case of a square barrier of width  $a$ , the probability of tunnelling through the barrier is approximately

$$P = \exp \left[ -2 \left( \frac{2m(V_0 - E)}{\hbar^2} \right)^{1/2} a \right]$$

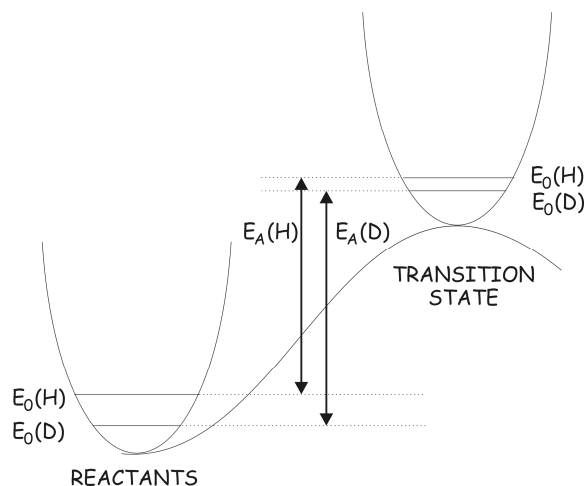
The tunnelling probability therefore depends on the particle mass  $m$ , the particle energy  $E$  and the height  $V_0$  and width  $a$  of the barrier, but is independent of temperature. At normal temperatures, tunnelling usually makes only a small contribution to the overall reaction rate. However, since the rate of normal reaction falls off with temperature as fewer reactants have enough energy to surmount the activation barrier, at low temperatures the constant tunnelling contribution can make up a significant fraction of the overall reaction. The mass dependence of the tunnelling probability means that tunnelling rates are significantly different for different isotopes, which can lead to large kinetic isotope effects in some cases.

More usually, kinetic isotope effects are caused by differences in the activation energy for reactions involving different isotopes due to either the reactants, the transition state, or both, having different zero-

point vibrational energies. Vibrational frequencies, and therefore vibrational zero-point energies, depend on the force constant  $k$  and reduced mass  $\mu$  of the vibrating system.

$$\omega_e = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2}$$

The vibrational zero point energy  $\frac{1}{2}\hbar\omega_e$  is inversely proportional to  $\mu^{1/2}$ . The effect on the activation barrier for a reaction involving an H/D atom is shown below.



Since the transition state is (usually) more loosely bound than the reactants, the vibrational levels are more closely spaced. The net effect is that the activation energy is higher, and therefore reaction slower, for the heavier isotopomer (a 'normal' isotope effect). The maximum isotope effect is obtained when the bond involving the isotope is completely broken in the transition state, in which case the difference in activation energies is simply the difference in zero point energies of the reactants. In some reactions it is the zero point energy difference between the transition states which governs the kinetic isotope effect. In this case the activation energy is greater for the lighter isotope and an inverse isotope effect is observed, in which the heavier isotopomer undergoes faster reaction.

To obtain a mathematical expression for the kinetic isotope effect we can use either the Arrhenius equation or the Eyring equation from transition state theory. Using the Arrhenius equation, the rates for the two isotopomers are

$$k_H = A_H \exp[-E_A(H)/k_B T]$$

$$k_D = A_D \exp[-E_A(D)/k_B T]$$

Assuming the pre-exponential factors are the same for both isotopes (this is usually a reasonable approximation, though if using transition state theory we can treat the problem properly and calculate the ratio using the partition functions for the two isotopic cases), the kinetic isotope effect,  $k_H/k_D$ , is therefore

$$\frac{k_H}{k_D} = \exp\left(-\frac{E_a(H) - E_a(D)}{k_B T}\right)$$

or in the limiting case of the maximum kinetic isotope effect,

$$\frac{k_H}{k_D} = \exp\left(-\frac{E_0(H) - E_0(D)}{k_B T}\right)$$

where  $E_0(H)$  and  $E_0(D)$  are the zero-point energies of the H- and D-containing reactants.