Foundations of Chemical Kinetics Lecture 9: Transition-state theory: The thermodynamic formalism

Marc R. Roussel
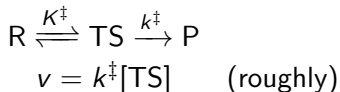
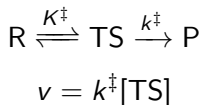October 3, 2021

Breaking down a reaction

- We can break down an elementary reaction into two steps: Reaching the transition state, and going through the transition state into the product valley.

$$R \rightleftharpoons TS \to P$$

- For a high barrier, there will be a Boltzmann distribution of reactant energies which is only slightly disturbed by the leak across the top of the barrier.
- This implies that we can treat the step $R \rightleftharpoons TS$ as being in equilibrium.

$$R \xrightleftharpoons{K^{\ddagger}} TS \xrightarrow{k^{\ddagger}} P$$
$$v = k^{\ddagger}[TS] \qquad \text{(roughly)}$$

Strategy

$$R \xrightleftharpoons{K^{\ddagger}} TS \xrightarrow{k^{\ddagger}} P$$

$$v = k^{\ddagger}[TS]$$

- This is an elementary reaction ($R \rightarrow P$), so its rate ought to be $v = k[R]$.
- We will use the equilibrium condition to eliminate [TS]. This will bring thermodynamic quantities related to the equilibrium constant into the theory.
- We will use a quantum-statistical argument to get a value for the specific rate of crossing of the barrier $k^{\ddagger}$.

Review of some elementary thermodynamics
Free energy

- The Gibbs free energy (G) is defined by

$$G = H - TS$$

  H: enthalpy (ΔH = heat at const. p)
  S: entropy (measure of energy dispersal)

- The Gibbs free energy change is the maximum non-pV work available from a system.

Review of some elementary thermodynamics
Free energy (continued)

- For a reaction $b\text{B} + c\text{C} \rightarrow d\text{D} + e\text{E}$, the Gibbs free energy change is

$$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q$$

where $\Delta_r G_m^\circ$ is the free energy change under standard conditions:

$$\Delta_r G_m^\circ = d\Delta_f G^\circ(\text{D}) + e\Delta_f G^\circ(\text{E}) - [b\Delta_f G^\circ(\text{B}) + c\Delta_f G^\circ(\text{C})]$$

- The reaction quotient Q is defined as

$$Q = \frac{a_\text{D}^d \, a_\text{E}^e}{a_\text{B}^b \, a_\text{C}^c}$$

where a_i is the activity of species i.

Review of some elementary thermodynamics
Activity

- The activity also depends on the definition of the standard conditions:

    In the gas phase $a_i = \gamma_i p_i / p^\circ$ where p° is the standard pressure (usually 1 bar).

    For a solute $a_i = \gamma_i c_i / c^\circ$ where c° is the standard concentration.

    There are several different conventions used for standard concentrations, the most common being 1 mol/kg and 1 mol/L.

    γ_i is the activity coefficient (sometimes known as a fugacity coefficient in the gas phase) of species i, a measure of the deviation from ideal behavior.

    $\gamma_i = 1$ for an ideal substance.

Review of some elementary thermodynamics
Equilibrium

- At equilibrium, $\Delta_r G_m = 0$, i.e.

$$\Delta_r G_m^\circ = -RT \ln K$$

  where K is the numerical constant such that $Q = K$ at equilibrium.
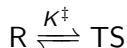
- This equation can be rewritten

$$K = \exp\left(-\frac{\Delta_r G_m^\circ}{RT}\right).$$

  Note that K is related to $\Delta_r G_m^\circ$, the standard free energy change.

The $K^{\ddagger}$ equilibrium

Case 1: First-order elementary reaction

- We are treating the "equilibrium"

$$R \underset{\longleftarrow}{\overset{K^{\ddagger}}{\rightleftharpoons}} TS$$

- For this equilibrium,

$$K^{\ddagger} = \frac{a_{TS}}{a_R} \implies a_{TS} = K^{\ddagger} a_R$$

- If we assume ideal behavior or similar activity coefficients for R and TS, we get

$$[TS] = K^{\ddagger}[R]$$
$$\therefore v = k^{\ddagger} K^{\ddagger}[R]$$
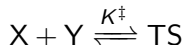$$\therefore k = k^{\ddagger} K^{\ddagger}$$

Side note about concentrations, pressures and notation

- The equations look a bit neater if we write [X] than p_X.
- If we write [X], it looks more "normal" to see a standard concentration c°.
- All of the equations below are valid in either solution or gas phase by just replacing [X] by p_X and c° by p°.

The $K^{\ddagger}$ equilibrium

Case 2: Second-order elementary reaction

- The equilibrium is

$$X + Y \overset{K^{\ddagger}}{\rightleftharpoons} TS$$

- Now,

$$K^{\ddagger} = \frac{a_{TS}}{a_X \, a_Y} \implies a_{TS} = K^{\ddagger} a_X \, a_Y$$

- Since $a_i = \gamma_i c_i / c^{\circ}$, this becomes

$$[TS] = \frac{K^{\ddagger}}{c^{\circ}} \frac{\gamma_X \gamma_Y}{\gamma_{TS}} [X][Y]$$

- Assuming ideal behavior, we get

$$[TS] = \frac{K^{\ddagger}}{c^{\circ}} [X][Y]$$

which gives

$$k = \frac{k^{\ddagger} K^{\ddagger}}{c^{\circ}}$$

The $K^\ddagger$ equilibrium
First- vs second-order rate constants

- Since the difference between the first- and second-order cases is just a factor of c°, we treat the second-order case from here on.

Mathematical interlude: Taylor series

- For any "nice" function,

$$f(x) \approx f(a) + f'(a)(x-a) + \frac{f''(a)}{2}(x-a)^2 + \ldots + \frac{f^{(n)}(a)}{n!}(x-a)^n$$

- For small x, take $a = 0$:

$$f(x) \approx f(0) + f'(0)x + \frac{1}{2}f''(0)x^2 + \ldots$$

- In practice we often stop at the first non-trivial term (i.e. the first term after $f(0)$ that isn't identically zero).

Reminder: units of frequency

- In our treatment of vibration, we have so far used the angular frequency ω, whose units can be thought of as rad s^{-1}.
- We can also express frequencies in Hz, i.e. cycles per second, typically denoted ν.
- Since $\omega = 2\pi\nu$ and $\hbar = h/2\pi$, $\hbar\omega = h\nu$.

Statistical thermodynamic considerations

- From statistical thermodynamics, and neglecting non-ideal effects, we have

$$K^{\ddagger} = \frac{q_{TS}}{q_X \, q_Y} \left(\frac{N}{V} \right) \exp \left(-\frac{\Delta \epsilon^{\ddagger}}{k_B T} \right) = \frac{c^{\circ} [TS]}{[X][Y]},$$

where q_{TS} is the volumic partition function of the transition state and $\epsilon^{\ddagger}$ is the difference in energy between the reactants and transition state, measured from the bottom of the reactant well to the top of the barrier.

$$\therefore [TS] = \frac{[X][Y]}{c^{\circ}} \frac{q_{TS}}{q_X \, q_Y} \left(\frac{N}{V} \right) \exp \left(-\frac{\Delta \epsilon^{\ddagger}}{k_B T} \right)$$

- Writing $X + Y \rightleftharpoons TS \rightarrow P$ involves an implicit assumption, namely that all transition states decay to product.
- A complex that has reached the top of the activation barrier has no intrinsic bias toward reactants or products. Thus, half of those complexes will, all other things being equal, proceed

Statistical thermodynamic considerations
(continued)

- Define the concentration of transition states leading to product formation as

$$[TS_{\rightarrow P}] = \frac{1}{2}[TS] = \frac{1}{2}\frac{[X][Y]}{c^\circ}\frac{q_{TS}}{q_X\,q_Y}\left(\frac{N}{V}\right)\exp\left(-\frac{\Delta\epsilon^\ddagger}{k_B T}\right)$$

- The reaction rate is therefore correctly cast as

$$v = k^\ddagger[TS_{\rightarrow P}] = \frac{1}{2}k^\ddagger\frac{[X][Y]}{c^\circ}\frac{q_{TS}}{q_X\,q_Y}\left(\frac{N}{V}\right)\exp\left(-\frac{\Delta\epsilon^\ddagger}{k_B T}\right)$$

which gives

$$k = \frac{1}{2}\frac{k^\ddagger}{c^\circ}\frac{q_{TS}}{q_X\,q_Y}\left(\frac{N}{V}\right)\exp\left(-\frac{\Delta\epsilon^\ddagger}{k_B T}\right)$$

Statistical thermodynamic considerations
(continued)

- We assume that the transition-state partition function factors, i.e. that motion along the reactive normal mode is independent of other molecular motions:

$$\mathfrak{q}_{TS} = \mathfrak{q}^{\ddagger} q_r$$

where q_r is the part of the partition function associated with the reactive normal mode (i.e. the motion through the saddle) while $\mathfrak{q}^{\ddagger}$ is the rest of the (volumic) partition function.

Statistical thermodynamic considerations
(continued)

- Assume we can treat the reactive mode as a vibration, with partition function

$$q_r = [1 - \exp(-h\nu_r/k_B T)]^{-1}$$

- Since the reactive mode is "loose", assume $h\nu_r/k_B T$ is small.
- Taylor expansion for small x:

$$1 - e^{-x} \approx x$$
$$\therefore \left(1 - e^{-x}\right)^{-1} \approx x^{-1}$$
$$\therefore q_r \approx \frac{k_B T}{h\nu_r}$$

Statistical thermodynamic considerations
(continued)

- The rate constant becomes

$$k = \frac{1}{2}\frac{k^{\ddagger}}{c^{\circ}}\frac{k_B T}{h\nu_r}\frac{q^{\ddagger}}{q_X\, q_Y}\left(\frac{N}{V}\right)\exp\left(-\frac{\Delta\epsilon^{\ddagger}}{k_B T}\right)$$

- ν_r represents the frequency for a full "vibrational" cycle of the reactive mode (back and forth).
- $k^{\ddagger}$ is the frequency for crossing the saddle in one direction only.

$$\therefore k^{\ddagger} = 2\nu_r$$

$$\therefore k = \frac{k_B T}{c^{\circ}h}\frac{q^{\ddagger}}{q_X\, q_Y}\left(\frac{N}{V}\right)\exp\left(-\frac{\Delta\epsilon^{\ddagger}}{k_B T}\right)$$

Statistical formula for the rate constant

Interpretation

$$k = \frac{k_B T}{c^\circ h} \frac{\mathsf{q}^\ddagger}{\mathsf{q}_X \, \mathsf{q}_Y} \left(\frac{N}{V} \right) \exp \left(-\frac{\Delta \epsilon^\ddagger}{k_B T} \right)$$

- $\mathsf{q}^\ddagger$ is the partition function for the transition state omitting the reactive mode.
- $\frac{\mathsf{q}^\ddagger}{\mathsf{q}_X \, \mathsf{q}_Y} \left(\frac{N}{V} \right) \exp \left(-\frac{\Delta \epsilon^\ddagger}{k_B T} \right)$ is of the form of an equilibrium constant with one mode (the reactive mode) removed.

Statistical formula for the rate constant
Application

$$k = \frac{k_B T}{c^\circ h} \frac{\mathfrak{q}^\ddagger}{\mathfrak{q}_X \, \mathfrak{q}_Y} \left(\frac{N}{V} \right) \exp \left(-\frac{\Delta \epsilon^\ddagger}{k_B T} \right)$$

In principle, we can use this equation to compute rate constants.
We need

- The geometry of the transition state
- The height of the barrier and zero-point energies of the reactants and transition state
- The vibrational spectrum of the transition state

Thermodynamic interpretation

$$k = \frac{k_B T}{c^\circ h} \frac{q^\ddagger}{q_X \, q_Y} \left(\frac{N}{V} \right) \exp\left(-\frac{\Delta \epsilon^\ddagger}{k_B T} \right)$$

- Define

$$K^\ddagger = \frac{q^\ddagger}{q_X \, q_Y} \left(\frac{N}{V} \right) \exp\left(-\frac{\Delta \epsilon^\ddagger}{k_B T} \right)$$

- Note that this isn't quite a normal equilibrium constant because we have removed one mode from the transition state partition function.

- We can still write

$$K^\ddagger = \exp\left(-\frac{\Delta^\ddagger G_m^\circ}{RT} \right)$$

Thermodynamic interpretation

(continued)

$$k = \frac{k_B T}{c^\circ h} \exp\left(-\frac{\Delta^\ddagger G_m^\circ}{RT}\right)$$

$$\therefore k = \frac{k_B T}{c^\circ h} \exp\left(\frac{\Delta^\ddagger S_m^\circ}{R}\right) \exp\left(-\frac{\Delta^\ddagger H_m^\circ}{RT}\right)$$

Relationship to Arrhenius parameters

From $\ln k = \ln A - E_a/RT$, we have

$$\frac{d \ln k}{dT} = E_a/RT^2$$

or

$$E_a = RT^2 \frac{d \ln k}{dT}.$$

Relationship to Arrhenius parameters
(continued)

- For the transition-state theory expression,

$$\ln k = \ln \left(\frac{k_B T}{c^\circ h} \right) + \frac{\Delta^\ddagger S_m^\circ}{R} - \frac{\Delta^\ddagger H_m^\circ}{RT}$$

$$\left. \frac{\partial \ln k}{\partial T} \right|_p = \frac{1}{T} + \frac{1}{R} \left. \frac{\partial \Delta^\ddagger S_m^\circ}{\partial T} \right|_p - \frac{1}{RT} \left. \frac{\partial \Delta^\ddagger H_m^\circ}{\partial T} \right|_p + \frac{\Delta^\ddagger H_m^\circ}{RT^2}$$

Relationship to Arrhenius parameters
(continued)

- There is some cancellation of terms, and a few further
  assumptions based on typical values of thermodynamic
  quantities. We eventually get

$$\left.\frac{\partial \ln k}{\partial T}\right|_p = \frac{1}{T} + \frac{\Delta^{\ddagger} H_m^{\circ}}{RT^2} - \frac{\Delta^{\ddagger} n_{\text{gas}}}{T}$$

where $\Delta^{\ddagger} n_{\text{gas}}$ is the dimensionless change in the number of
equivalents of gas on going from the reactants to the
transition state (zero for a unimolecular reaction, -1 for a
bimolecular reaction).

Relationship to Arrhenius parameters

(continued)

- Thus,

$$E_a = RT^2 \frac{d \ln k}{dT}$$

$$\therefore E_a = \Delta^{\ddagger} H_m^{\circ} + RT \left(1 - \Delta^{\ddagger} n_{\text{gas}} \right)$$

- If we solve for $\Delta^{\ddagger} H_m^{\circ}$ in terms of E_a, put the result back into our TST rate constant expression and rearrange, we get

$$k = \frac{k_B T}{c^{\circ} h} \exp \left(\frac{\Delta^{\ddagger} S_m^{\circ}}{R} \right) \exp(1 - \Delta^{\ddagger} n_{\text{gas}}) \exp \left(-\frac{E_a}{RT} \right)$$

- By comparison to the Arrhenius equation, we get

$$A = \frac{k_B T}{c^{\circ} h} \exp \left(\frac{\Delta^{\ddagger} S_m^{\circ}}{R} \right) \exp(1 - \Delta^{\ddagger} n_{\text{gas}})$$

Eyring plot

■ Go back to the thermodynamic TST equation:

$$k = \frac{k_B T}{c^\circ h} \exp\left(\frac{\Delta^\ddagger S_m^\circ}{R}\right) \exp\left(-\frac{\Delta^\ddagger H_m^\circ}{RT}\right)$$

$$\therefore \ln\left(\frac{kc^\circ h}{k_B T}\right) = \frac{\Delta^\ddagger S_m^\circ}{R} - \frac{\Delta^\ddagger H_m^\circ}{RT}$$

■ Plotting $\ln(kc^\circ h/k_B T)$ vs T^{-1} should give a straight line of slope $-\Delta^\ddagger H_m^\circ/R$ and intercept $\Delta^\ddagger S_m^\circ/R$.