Chapter 6: Adiabatic reaction dynamics and Transition State Theory

General reaction: \( A + B + C \ldots \rightleftharpoons X + Y + Z \ldots \)

Rate at which equilibrium is established:

\[
\text{Eg.} \quad -\frac{d[A]}{dt} = \text{rate}(t) = k_p(t) \frac{[A]^w[B]^y[C]^z}{[X]^x[Y]^y[Z]^z} \\
\]

\( [w] \): concentration of species \( w \) (as molarity or partial pressure)

\( k_p(t) \): phenomenological rate constant (might depend on time)

In general, equation might only be valid for limited amounts of time/concentration regimes. General description can be very complicated as many "elementary" steps might be involved in the reaction.

To make progress, we need to reduce a reaction to elementary steps of unimolecular or bimolecular reactions. Then we can apply principles of statistical mechanics.

We will consider reactions on a single potential energy surface (adiabatic, Born-Oppenheimer approximation).

Simplest case: Unimolecular reaction \( A \rightleftharpoons B \)

Rate equation:

\[
\frac{d[A]}{dt} = k_i[A(t)] - k_{-i}[B(t)] \\
\]

Steady State:

\[
\frac{d[A]}{dt} = 0 \\
[A(t)] = [A_{eq}] \\
k_i[A_{eq}] = k_{-i}[B_{eq}] \\
\frac{[B_{eq}]}{[A_{eq}]} = K_{eq} = \frac{k_i}{k_{-i}} \\
\]

We have seen before how to calculate equilibrium constants in stat mech.

Experimental determination \( k_i \). Use excess \( A \), neglect \( k_{-i}[B] \)
\[-\frac{d[A]}{[A]} = k_1 dt\]
\[\ln \frac{[A(t) \text{]}}{[A_0 \text{]}] = -k_1 t\]
\[[A(t) = [A_0] e^{-k_1 t}\]

Exponential decay of \([A]\) under conditions of excess can be fitted to get \(k_1\).

Of course one could also start with excess of \([B]\), and measure \(k_{-1}\). This would allow a check of relations.

\[\frac{k_1}{k_{-1}} = \frac{[B_{eq}]}{[A_{eq}]} = K_{eq}\]

Other types of reactions:

\[A \xrightleftharpoons[k_{-1}]{k_1} B + C\]
\[-\frac{d[A]}{dt} = k_1 [A] - k_{-1} [B][C]\]
\[\frac{[B_{eq}][C_{eq}]}{[A_{eq}]} = K_{eq} = \frac{k_1}{k_{-1}}\]

If \([B][C]\) is negligible \([A(t)] = [A_0] e^{-k_1 t}\]

**Bimolecular reactions**

\[A + B \xrightleftharpoons[k_{-1}]{k_1} C\]
\[-\frac{d[A]}{dt} = k_1 [A][B] - k_{-1} [C]\]

Steady State:
\[\frac{[C_{eq}]}{[A_{eq}][B_{eq}]} = K_{eq} = \frac{k_1}{k_{-1}}\]

In presence of excess \(B\), such that \([B]\) is constant \([A(t)] = [A_0] e^{-k_1 t}, k^* = k_1 [B_0]\)

Bimolecular reaction is the limit. Elementary reaction steps never involves more than 2 colliding molecules. Negligible probability to have 3 molecules colliding simultaneously. If three molecules are needed, then one has to first create a complex of two molecules and collide this with a third molecule needed for reaction.
In our discussion of kinetics (later on) you will learn how to think about building complicated reactions from elementary reaction steps.

Here we focus on elementary reactions and focus on how we can calculate rate constants from first principles using information from quantum chemistry and statistical mechanics calculations.

**Transition State theory**

To develop equations for the rate of reactions we will assume thermal equilibrium for all species $A, \#, B$, where $\#$ refers to the (fleeting) transition state or “activated complex”.

Overall reaction:

$$A \rightleftharpoons B$$

$$K_{eq} = \left[ \frac{[B]}{[A]} \right] = \frac{k_1}{k_{-1}}$$

model: $A \rightleftharpoons \# \rightarrow B$

$$\left[ \frac{[\#]}{[A]} \right] = \frac{k_a}{k_d} = K_{\#}$$

$k_a$: activation, $k_d$: deactivation, $k_{ran}$: rate to go from $\#$ to $B$

Crucial idea: consider forward reaction only ($k_a$ rate to products).

$$k_1[A] = k_{ran}[\#]$$

$$k_1 = k_{ran} \left[ \frac{[\#]}{[A]} \right] = k_{ran} \frac{N_\#}{N_A}$$

(Note: In chemical kinetics one usually uses concentrations to derive things. In statmech we are used to expressing things in partial pressures. I am doing the derivation here, based on partial pressure as a measure of concentration.)

$k_{ran}$: rate of moving to product for molecules at transition state.

$$\left[ \frac{[\#]}{[A]} \right] = K_{\#} = \left( \frac{q_{\#} / N_\#}{q_A / N_A} \right) \rightarrow \frac{q_{\#}}{q_A}$$. 


Use same formula as for chemical equilibrium! Same equilibrium principles. The factor N is included in the translational partition function as usual. It is a bit of a nuisance to write it correctly.

Calculating \( q_A \): calculate molecular structure, vibrational frequencies, energy at minimum.

\[
q_A = q_c^4 q_w^4 q_s^4 q_v^4
\]

For transition state, we can proceed in analogous way

\( q_B \): calculate structure of transition state; calculate vibrational frequencies, transition state electronic energy.

Something special about \# (non-linear TS)

We have \( 3N - 7 \) harmonic, real vibrational frequencies, and one imaginary frequency, which needs to be treated in a special way. The normal mode of the imaginary frequency is along the reaction coordinate.

\[
q_B = q_{\text{trans}}^\# \cdot \left( q_c^\#, q_w^\#, q_s^\#, q_v^\# \right) = q_{\text{trans}}^\# \cdot \tilde{q}_B
\]

\( q_{\text{trans}}^\# \): component of partition function along reaction coordinate

\( \tilde{q}_B \): partition function of transition state, for all motions except ‘vibration’ along reaction coordinate

It then follows that the forward reaction rate is given by

\[
k_1 = k_{\text{trans}} \frac{q_{\text{trans}}^\#}{q_A} = k_{\text{trans}} q_{\text{trans}}^\# \left( \frac{\tilde{q}_B}{q_A} \right)
\]

We will see that

\[
k_{\text{trans}} q_{\text{trans}}^\# = \frac{k_B T}{h} \sim 10^{13} \text{s}^{-1}
\]

\[
k_1 = \frac{k_B T}{h} \left( \frac{\tilde{q}_B}{q_A} \right)
\]

Or: \( k_1 = \frac{k_B T}{h} \left( \frac{\tilde{q}_B}{q_A q_B} \right) \) if bimolecular \((A + B \leftrightarrow \# \rightarrow C)\)

The determining factor in \( \frac{\tilde{q}_B}{q_A} \) is \( K_e K_{zp} \) as it is for chemical equilibria. The theory is very similar.

\[
\frac{\tilde{q}_B}{q_A} = e^{-\left( \Delta H^0 + \Delta F^0 \right) k_B T / h} \frac{q_{\text{trans}}^\# \cdot q_c^\# q_w^\# q_s^\# q_v^\#}{q_c^4 q_w^4 q_s^4 q_v^4}
\]
We get an exponential temperature dependence from $\Delta E_e + \Delta E_{zp}$, power of $T$ dependence from the remaining fraction, often just a constant if same # of molecules for reactants and transition state. Other contribution $\frac{k_BT}{\hbar}$

$\Delta E_{zp}$: the difference in zeropoint energy between reactant and transition state

$$\Delta E_{zp} = \frac{1}{2} \sum_{i=1}^{3N-7} (\hbar \omega)_{TS} - \frac{1}{2} \sum_{i=1}^{3N-6} (\hbar \omega)_{R}$$

Please note the number of normal modes in each sum. If the molecular structure is linear, the number of normal modes increases by 1, as usual.

Derivation of universal factor $\frac{k_BT}{\hbar}$

Potential is flat in transition state region $\left[ x_o - \frac{\delta}{2}, x_o + \frac{\delta}{2} \right]$

→ Assume particle in the box types of partition functions

$$q_{\text{res}}^* = \sqrt{\frac{2\pi mk_BT}{\hbar^2} \cdot \delta}$$

Notes:
1) if reaction coordinate involves a single atom, we can assign mass $m$. In general, reaction coordinate is some collective motion (normal mode of transition structure). We do not know $m$!
2) We do not know $\delta$ either!!
Second assumption: all molecules in the transition state region that have a positive velocity will react. The rate depends on how fast they traverse the transition state region: \( \frac{V}{\delta} \)

We can calculate how fast molecules traverse the TST region:

\[
k_{\text{rot}} = \frac{1}{\delta} \int_0^\infty V_x P(V_x) dV_x
\]

\( P(V_x) \): probability to have \( V_x \)

Once again, use equilibrium arguments. \( V_x \) follows Maxwell-Boltzmann distribution

\[
P(V_x) = \frac{1}{\sqrt{2\pi k_BT}} e^{-\frac{mV_x^2}{2k_BT}}
\]

Here we use a Boltzmann distribution for ‘kinetic energy’

Integrate (Gaussian integrals) \( \rightarrow k_{\text{rot}} = \frac{1}{\delta} \sqrt{\frac{k_BT}{2\pi m}} \)

Assumption: Even at the transition state geometry, the velocity distribution \( V_x \) is given by Maxwell-Boltzmann (where potential energy is very high). This seems a bit counter intuitive. I do not have a good rationale for this.

A great virtue of the above derivation is:

\[
q_{\text{rot}} \cdot k_{\text{rot}} = \left( \frac{2\pi mk_BT}{\hbar^2} \cdot \delta \right) \left( \frac{1}{\delta} \sqrt{\frac{k_BT}{2\pi m}} \right) = \frac{k_BT}{\hbar}
\]

Unknown \( m, \delta \) cancel. How convenient!

It will be clear that this factor is an estimate. Transition state theory is not as robust as other aspects of statistical mechanics. There are variations on the theme in the scientific literature.

**Kinetic Isotope effect**

Isotope effects are strongest (or even observable only) if protons are replaced by Deuterium

1) Primary isotope effect: \( H \) or \( D \) is involved in reaction path, or the main atom that is moving
   a. Isotope substitution does not affect electronic structure calculations \( \rightarrow \) same PES, same stationary points

   However mass enters mass-weighted Hessian, and this affects the frequencies

   \[
   \omega \sim \sqrt{\frac{g}{m}}
   \]

   (For diatomics. Analogous for polyatomics)

   \( \rightarrow \) pure proton frequency is \( \sqrt{2} \) times as large as \( D \) frequency. A good example would be to compare the vibrational frequencies in HCl and DCl.
If proton movements defines reaction coordinate, then in the reactant this vibrational frequency contributes to

\[ E_{zp} = \sum_{i=1}^{3N-6} \frac{1}{2} \hbar \omega_i \, . \]

But it is **missing** from transition state

\[ E_{zp} = \sum_{i=1}^{3N-7} \frac{1}{2} \hbar \omega_{i,i} \, . \]

\[ \frac{k_{\text{light}}}{k_{\text{heavy}}} \approx e^{-\frac{1}{2}(\omega_{\text{heavy}}^2 - \omega_{\text{light}}^2)k_B T} > 1 \quad \omega_{\text{heavy}} \approx \frac{1}{\sqrt{2}} \omega_{\text{light}} \quad \text{(for D vs. H)} \]

\[ \frac{1}{2} \hbar \omega_{\text{heavy}} \] faces less of a barrier than heavy particle

Also note that \( m \) did cancel out in the derivation of \( \frac{k_B T}{h} \). The cause of the effect is **not** that light particles move faster. The effect is due to zeropoint motion (purely quantum!)

\[ k_{\text{rel}} \cdot q_{\text{rel}} \] is the same for any particle (or collective coordinate).

b) In secondary isotope effect, the isotope of interest is not involved in the reaction coordinate
   \[ \rightarrow \] zeropoint effects more or less cancel, minor residual effect on \( k_{\text{light}} / k_{\text{heavy}} \). One can expect the effect of isotopic substitution to be much smaller then. So the effect of isotopic substitution can tell you something about the nature of the transition state.

A good example of a primary kinetic isotope effect would be the HCN to CNH reaction rate vs. DCN to CND. This is clearly a primary isotope effect and easy to calculate using Gaussian calculations plus matlab processing. It will also illustrate the concept of calculations on transition states and reaction rates without bogging us down in computational complexities. We will explore in the computer lab!