Transition State Theory

\[
A \xrightarrow{k_1} P \\
\downarrow \quad [TS]^+ \xrightarrow{k_1} P \\
A \xleftrightarrow{k_1} [TS]^+ \xrightarrow{k_1} P
\]

Previously,

\[
\frac{n_{TS}}{n_A} = e^{-\frac{(E_{TS} - E_A)}{k_B T}} = e^{-\varepsilon / k_B T}
\]

But this is a microscopic equation. For thermodynamic analysis, need functions of whole systems.
Analogous expression in the bulk would be:

$$\frac{N_{TS}}{N_A} = e^{-(E_{TS} - E_A)/RT} = e^{-\Delta E^\ddagger / RT}$$

But this equation only describes zero-point energy difference. Not correct.
Analogous expression in the bulk \textit{would} be:

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But this equation only describes zero-point energy difference. \textit{Only correct at zero K.}

Instead, need to express in terms of distribution of molecules in vibrational modes (that depends on $T$).
Transition State Theory

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Challenge: How to deal with that funny reaction-coordinate vibrational mode? Can’t describe energetics until we do.
Transition State Theory: Zero-Point Energies and Partition Functions

Define “partition function” $Q$ as distribution of energy states for each degree of freedom

$Q$ defines how these states are filled at temperature $T$.

$$ Q = q_{vib} q_{rot} q_{trans} = (q_{vib1} q_{vib2} \cdots) \cdots $$

$$ Q_A = \frac{N_A}{N_{A,0K}} \quad Q_{TS} \boxed{q_{vibRC}} = \frac{N_{TS}}{N_{TS,0K}} $$

*Reaction coordinate mode can’t be represented by partition function. So we include extra factor $q_{vibRC}$.*
Transition State Theory:
Zero-Point Energies and Partition Functions

\[
K^\ddagger = \frac{k_1}{k^\ddagger} = \frac{N_{TS}}{N_A} = \frac{q_{vibRC} Q_{TS} N_{TS,0K}}{Q_A N_{A,0K}}
\]

\[
= q_{vibRC} \frac{Q_{TS}}{Q_A} e^{-\frac{\Delta E_{0K}^\ddagger}{RT}}
\]

\[
= q_{vibRC} e^{-\frac{\Delta G^\ddagger}{RT}}
\]

(with \(\Delta G^\ddagger\) representing free energy of activation for any temperature)
Transition State Theory: Zero-Point Energies and Partition Functions

We assume $k^\ddagger = \nu^\ddagger$. 

\[
\frac{k_1}{k^\ddagger} = q_{\text{vibRC}} e^{-\Delta G^\ddagger / RT} 
\]

\[
k_1 = k^\ddagger \left( \frac{k_B T}{h \nu^\ddagger} \right) e^{-\Delta G^\ddagger / RT} 
\]

standard vibrational partition function

\[
k_1 = \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT} 
\]
Transition State Theory: The Eyring Equation

$$k_{rxn} = \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$, so

$$k_{rxn} = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

Eyring equation.
Relates rate constant to $T$ in a physical way.

$\Delta H^\ddagger$: Enthalpy required to reach transition state (like $E_a$)
$\Delta S^\ddagger$: Entropy lost/gained getting to transition state
Transition State Theory: Eyring Plots

\[
k_{\text{rxn}} = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}
\]

can also be written:

\[
\ln\left(\frac{k_{\text{rxn}}}{T}\right) = \left(\ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R}\right) - \frac{\Delta H^\ddagger}{R} \left(\frac{1}{T}\right)
\]

(Has form \(y = mx + b\).)

slope = \(-\Delta H^\ddagger / R\)
intercept = \(\ln(k_B/h) + \Delta S^\ddagger / R\)

Different from Arrhenius plot—vertical axis \(\ln(k/T)\).
Transition State Theory: Eyring and Arrhenius

\[ k_{\text{rxn}} = \frac{k_B T}{h} e^{\frac{\Delta S^\dagger}{R}} e^{-\frac{\Delta H^\dagger}{RT}} \]

Has Arrhenius form!
But, \( E_a \) and \( \Delta H \) vary (slightly) differently w/ \( T \).

Fix this by re-writing as

\[ k_{\text{rxn}} = \frac{ek_B T}{h} e^{\frac{\Delta S^\dagger}{R}} e^{-\left(\frac{\Delta H^\dagger + RT}{RT}\right)} \]

\[ A = \frac{ek_B T}{h} e^{\frac{\Delta S^\dagger}{R}}, \quad E_a = \Delta H^\dagger + RT \]

Makes intuitive sense.
Better to graph than transform.
Transition State Theory: Activation Parameters

What does $\Delta H^\ddagger$ tell us about a reaction?

$\Delta H^\ddagger$ dominates $\Delta G^\ddagger$.

<table>
<thead>
<tr>
<th>$\Delta H^\ddagger$ (kcal/mol)</th>
<th>$t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(for $\Delta S^\ddagger = 0$)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>30 ns</td>
</tr>
<tr>
<td>10</td>
<td>2.6 $\mu$s</td>
</tr>
<tr>
<td>15</td>
<td>12 ms</td>
</tr>
<tr>
<td>20</td>
<td>57 s</td>
</tr>
<tr>
<td>25</td>
<td>3.2 days</td>
</tr>
<tr>
<td>30</td>
<td>41 years</td>
</tr>
</tbody>
</table>

*chemists work here.*
Transition State Theory: Activation Parameters

What does $\Delta S^\ddagger$ tell us about a reaction?
Illustrates structure of transition state.

Obvious examples:

$$\text{Cl} \cdot + \text{H--H} \rightarrow \left[ \text{Cl--H--H} \right]^\ddagger \rightarrow \text{Cl--H} + \cdot \text{H}$$

$\Delta S^\ddagger = -12 \text{ cal/mol} \cdot \text{K (e.u., entropy units)}$

$$\begin{array}{c}
\text{phenyl ester} \\
\rightarrow \\
\left[ \begin{array}{c}
\text{phenyl ester} \\
\end{array} \right]^\ddagger \\
\rightarrow 2 \text{phenyl ester}
\end{array}$$

$\Delta S^\ddagger = +10 \text{ cal/mol} \cdot \text{K}$