Lecture 14 – Chapter 15, Section 6
Temperature Dependence of Reaction Rates

• Reaction Energy Profiles
• Transition State – Activation Energy
• Arrhenius Equation
• Activation E vs. $\Delta G_{\text{rxn}}$

At any $T$, some fraction of molecules has $E > E_a$

For larger $E_a$, a smaller fraction of molecules has $E > E_a$

At higher $T$, more molecules have $E > E_a$
Chemistry – Bonds

• We’ve talked a lot about mechanisms
• Elementary reactions tell us what happens at each step

• But what about right at the moment of making and/or breaking a bond?
Computer Simulation Example

- This is a little more complicated than book examples
- Double bond and triple bond break and two single bonds form simultaneously
- Don’t worry about details – just look at structural changes
Distortions Raise Energy

- The molecules start out at nice, relaxed minimum energies
- Structural distortions to accommodate making and/or breaking bonds must raise energy

- This means the energy of our system must increase in order to react
- As reaction proceeds we get that energy back

- This temporary change in energy is completely separate from the overall energy changes in the reaction – $\Delta H$
Simpler Example

\[ \text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2 \]
Activation Energy Diagram

(IMPORTANT)

$E_a \equiv$ Activation Energy
Which beaker will have fastest rate?

<table>
<thead>
<tr>
<th>25%</th>
<th>1.  Hot</th>
</tr>
</thead>
<tbody>
<tr>
<td>25%</td>
<td>2. Room temp</td>
</tr>
<tr>
<td>25%</td>
<td>3. Cold</td>
</tr>
<tr>
<td>25%</td>
<td>4. They will all be the same</td>
</tr>
</tbody>
</table>
What is different?

• Think about rate law

\[
\text{Rate} = k \ [\text{Red}][\text{Bleach}]
\]

• What is changing in the different beakers?

• Concentrations are the same
• Rate “constant” must be what is different
What is the name of this shape? (from chapt 5)

20% 1. Normal Distribution
20% 2. Maxwell-Boltzmann Distribution
20% 3. Newtonian Distribution
20% 4. The Einstein Effect
20% 5. The Joule-Thomson Coefficient
Why does hot = fast?

For larger $E_a$, a smaller fraction of molecules has $E > E_a$.

At any $T$, some fraction of molecules has $E > E_a$.

At higher $T$, more molecules have $E > E_a$. 

$T_2 > T_1$ 

$E_a > E_{a1}$

Molecular energy

Number of molecules
Arrhenius Equation
(also important)

- Combination of activation energy with Maxwell-Boltzmann distribution…
- Leads to the Arrhenius Equation
  - Proposed in 1889 by Svante Arrhenius (1859-1927)

\[ k = Ae^{-\frac{E_a}{RT}} \]

- \( A \) tells us the rate constant if the activation energy were zero
  - includes collision and orientation effects
  - Called the Arrhenius prefactor
Linear Form of Arrhenius

- Typically used to compute $E_a$ from rate data

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

\[
\begin{align*}
\ln k &= y \\
\frac{1}{T} &= x \\
\frac{E_a}{R} &= -\text{slope} \\
\ln A &= \text{intercept}
\end{align*}
\]
Two-point Arrhenius Eq.

\[ k = A e^{\frac{E_a}{RT}} \]

\[ \frac{k_1}{k_2} = \frac{A_1 e^{-\frac{E_a}{RT_1}}}{A_2 e^{-\frac{E_a}{RT_2}}} \]

but \( A_1 \approx A_2 \)

\[ \frac{k_1}{k_2} = e^{\left(\frac{E_a}{RT_1} - \frac{E_a}{RT_2}\right)} \]

\[ \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \]
Kinetics vs. Thermodynamics

• Many examples of reactions with very negative $\Delta G$ that do not appear to be spontaneous
  – Gasoline burning
  – Hydrogen burning
  – Diamond converting to graphite
• Gasoline sits pleasantly in your fuel tank because activation energy is large

• For example: $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$
  $\Delta H = -484 \text{ kJ/mol}$  $\Delta G = -457 \text{ kJ/mol}$
  But $E_a \approx 50 \text{ kJ/mol}$ (thermal energy at 300K $\approx 2.5 \text{ kJ/mol}$)

• Just because reaction is spontaneous doesn’t mean it will occur quickly
  – It could be so slow as to effectively not happen (kinetically controlled)
Today

• Start CAPA #9
• Physics seminar (3:00 VDW 102)
  – Counts for extra credit
• Keep rolling on exam review

Wednesday

• Finish CAPA #9
• Work lots and lots of problems
• Last lecture on kinetics