Kinetics, so far...

- The balanced chemical equation for a reaction provides a connection between the overall rate of reaction and the rates of disappearance of reactants and appearance of products.
- Experimentally determined rate laws describe the relationship between reactant concentration(s) and rates of reaction.
- Integrated rate law equations express reactant concentrations as a function of time. The form of the equation will depend on the order of the reaction.

Today’s Topics—Chemical Kinetics III

- Collision Theory
- Temperature dependence of reaction rates & the Arrhenius equation
- Activated Complex Theory
- Catalysis

Related Problems from Spring 2008 Exam 1: 2, 9 & Spring 2009 Exam I: 6
Corresponding Connect Problems: Set 1: 15, 16; Set 2: 1

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Learning Objectives (Lecture 3)

You should

1. understand the role played by collisions in chemical reactions.
2. be able to identify the reactants, products, transition state, and intermediates (if any) on the reaction potential and determine if the overall reaction is exothermic or endothermic.
3. understand the role played by temperature in overcoming barriers to reaction and how increasing or decreasing temperature affects the rates of chemical reactions.
4. be able to provide a physical interpretation of the activation energy $E_a$ and the pre-exponential factor $A$ from the Arrhenius equation based on Collision Theory and Activated Complex Theory.
5. know how to apply the Arrhenius equation to quantitatively predict how a rate constant $k$ will change with temperature.
6. be able to use experimental data (rate constants measured as a function of temperature) to find $E_a$ and $A$ either graphically or by simultaneously solving equations for data collected at two temperatures.

7. understand that catalysts enhance the rates of chemical reactions without being consumed by providing pathways with lower activation barriers for conversion of reactants to products.
Chemical Reactions and Collisions (Collision Theory)

*What happens in a chemical reaction?*
Atoms are rearranged as bonds are broken and new bonds are formed.

*Chemical reactions require collisions. Why?*
- Collisions bring reactants together. (Note that in order for a reaction to occur the reactants must be oriented properly with respect to each other.)
- Collisions provide the energy required to overcome barriers to reaction. Recall that energy is required to break bonds.
- Even so called “unimolecular” reactions involving decomposition of a single molecule into atoms and/or smaller molecules require collisions to provide the energy needed to break bonds.

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Potential Energy Profile Along the Reaction Coordinate (Reaction Potential)

(Figure-McMurray & Fay)
Key Terms Associated with the Reaction Potential

Reaction coordinate: pathway between reactants and products used to describe the progress of the reaction

Transition state: local maximum along the reaction potential corresponding to the point at which the reactants have collided to form the activated complex. The transition state is an unstable point along the reaction coordinate from which the activated complex can either separate and return to reactants or proceed to form products.

Activated complex: unstable arrangement of atoms at the highest energy point along the reaction potential. The activated complex can either dissociate back to reactants or complete the transformation to products. The activated complex cannot be isolated.

Intermediates: species produced and then consumed during the reaction corresponding to minima along the reaction potential. While intermediates do not appear in the balanced equation for the overall reaction, they can be isolated during the reaction.

Activation energy, $E_a$: Minimum energy required to form the activated complex = Energy difference between the reactants and the activated complex; barrier to reaction that controls the rate of reaction (kinetics)

Overall reaction energy change, $\Delta E$: energy difference between reactants and products; energy released or consumed in the reaction (thermodynamics)

More Complex Reaction Potentials
Influence of Temperature on Reaction Rates

Based on the temperature-dependent Boltzmann distribution of velocities \(v\) and kinetic energies \(E = \frac{mv^2}{2}\), we know that higher temperatures result in

1. higher collision frequencies (rates)
2. a greater fraction of the atoms or molecules having kinetic energies in excess of the activation energy \(E_a\) (minimum energy required for reaction).

(Figure-McMurray & Fay)

Arrhenius Equation

The temperature dependence of the rate constant \(k\) for a chemical reaction is described by the Arrhenius equation

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

where

- \(E_a\) represents the activation energy
- \(R\) is the gas constant (8.3145 J K\(^{-1}\) mol\(^{-1}\))
- \(T\) is the absolute temperature in K
- \(A\) is the frequency factor (aka pre-exponential term)

The exponential term \(e^{-E_a/RT}\) represents the fraction of molecules with energy in excess of the minimum required to overcome the energetic barrier \(E_a\) to reaction.

The pre-exponential term \(A\) (frequency factor) represents the number of collisions per unit time with the proper orientation.

\[
A = \text{(fraction of collisions with the proper orientation)} \times \text{(collisions per unit time)}
\]

For reactions that are less sensitive to the orientation of the reactants the value of \(A\) will be close to the number of collisions that occur per unit time.
Using the Arrhenius Equation

In order to predict the dependence of the rate constant $k$ on temperature $T$, both the activation energy $E_a$ and frequency factor $A$ must be known.

The activation energy and frequency factor are determined experimentally by making measurements at least two temperatures. Why are two temperatures required? There are two unknowns $E_a$ and $A$ that must be determined in the Arrhenius equation.

Approach 1:

Begin by taking the natural logarithm of both sides of the Arrhenius equation

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A + \ln(e^{-E_a/RT})$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

This equation fits the slope-intercept form ($y = mx + b$) where $\ln k$ corresponds to the dependent variable $y$ and $1/T$, where $T$ is the absolute temperature, corresponds to the independent variable $x$.

Consequently, plotting $\ln k$ vs. $1/T$ will yield a straight line with a slope $= -E_a/R$ and a y-intercept $= \ln A$. (Figure-McMurray & Fay)
Approach 2:
Make measurements at two temperatures and simultaneously solve the two resulting
equations to find $E_a$.

Measurement 1: $\ln k_1 = \ln A - \frac{E_a}{RT_1}$ (1)

Measurement 2: $\ln k_2 = \ln A - \frac{E_a}{RT_2}$ (2)

Subtract Equation 2 from Equation 1

$$\ln \left( \frac{k_1}{k_2} \right) = -\frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

After $E_a$ is determined, its value can be substituted into either Equation 1 or Equation 2, which then can be solved to find $\ln A$ and $A$.

Problem: Application of the Arrhenius Equation

The rate of a reaction increases by a factor of 16 when the temperature is increased from 25 °C to 75 °C. What is the activation energy for this reaction?
Activated Complex Theory

- Review: According to Collision Theory, reactions occur when reactants collide with energies equal to or greater than $E_a$ and the colliding molecules are oriented “properly” with respect to each other.

- Activated Complex Theory is another approach to understanding the temperature dependence of the rates of chemical reactions. In contrast with Collision Theory, where no assumptions were made about the structure of the activated complex, the structure (arrangement of atoms) of the activated complex is specified in Activated Complex Theory.

- Recall that the activated complex is found at an unstable point on the reaction potential, and as such, it can either fall back to products or complete the transformation to products.

- Activated Complex Theory assumes that the activated complex is in equilibrium with the reactants with equilibrium constant $K^*$:

  $$ \text{reactants} \rightleftharpoons \text{complex} $$

  $$ K^* = \frac{[\text{complex}]}{[\text{reactants}]} $$

- The rate of the reaction then depends on number of activated complexes present

  $$ \text{Rate} = [\text{complex}] = K^*[\text{reactants}] $$

  where the constant $K^*$ describing the equilibrium between the reactants and activated complex effectively serves as a rate constant.

- Equilibrium constants are related to a thermodynamic quantity known as the Gibbs free energy, $\Delta G = \Delta H - T\Delta S$, by the expression

  $$ K^* = e^{\Delta G^*/RT} = e^{-\Delta H^*/RT} e^{\Delta S^*/R} $$

- Now let’s compare the expressions obtained for rate constants from Activated Complex Theory and Collision Theory:

  $$ K^* = e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (\text{Activated Complex Theory}) $$

  $$ k = A e^{-E_a/RT} \quad (\text{Collision Theory}) $$

- We can see that $E_a$ corresponds to $\Delta H^*$ (enthalpy of activation). Both represent the energetic barrier to reaction.
• The pre-exponential term $A$ corresponds to $e^{\Delta S^\# / R}$, where $\Delta S^\#$ is the entropy of activation. As the rigidity of the activated complex becomes greater and the orientation constraints on forming the activated complex increase, $\Delta S^\#$ will become increasingly negative, which will make $e^{\Delta S^\# / R}$ smaller and reduce the rate constant and the reaction rate. This is equivalent to saying that fewer of the collisions between the reactants have the required orientation.

Catalysis

A catalyst provides an alternate reaction pathway between reactants and products having a lower activation energy for the rate-determining step, which in turn increases the rate of the reaction. Catalysts alter the mechanism (series of steps that transform reactants to products) of the reaction. (Figure-McMurray & Fay)
Catalysts

Key properties of catalysts:

- Catalysts are not consumed in the overall reaction. The catalyst may be consumed in one step of the mechanism for the catalyzed reaction, but it is regenerated in a subsequent step.

- They do not appear in the overall balanced chemical equation describing the reaction, but they do appear in the mechanism (series of steps that transform reactants to products). The role of a catalyst in the overall reaction is noted by putting the catalyst above or below the reaction arrow.

\[
\text{catalyst}
\quad \text{reactants} \rightarrow \text{products}
\]

- Catalysts change the mechanism of the reaction

- The concentration of the catalyst may appear in the rate law equation for the catalyzed reaction.

- Catalysts may be homogeneous or heterogeneous.

Note that enzymes (biological catalysts) increase the rates of biological reactions by decreasing \( E_a \) and increasing \( A \).

Homogeneous Catalysis

Homogeneous catalysts are found in the same phase as the reactants in the catalyzed reaction.

Example: Decomposition of \( \text{H}_2\text{O}_2 \)

Normally, decomposition of \( \text{H}_2\text{O}_2 \) is a very slow reaction because it has a high activation energy barrier of 76 kJ/mol.

However, addition of the iodide ion \( \text{I}^- \) provides another path to products

\[
\begin{align*}
\text{Step 1: } & \quad \text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^- \quad \text{(slow)} \\
\text{Step 2: } & \quad \text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{I}^- \quad \text{(fast)} \\
\text{Overall: } & \quad 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

The catalyst \( \text{I}^- \) does not appear in the balanced overall reaction. \( \text{IO}^- \) also does not appear in the balanced equation for the overall reaction. \( \text{IO}^- \) is an intermediate in this reaction; it is produced in Step 1 and then consumed in Step 2.
The experimentally determined rate equation for the catalyzed reaction is

\[
\text{Rate} = k [\text{H}_2\text{O}_2][\text{I}^-]
\]

The catalyst appears in the rate law equation because \( \text{I}^- \) participates in the slow (\textit{rate-determining}) step in the reaction mechanism.

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**Heterogeneous Catalysis**

Heterogeneous catalysts are found in a \textit{different phase} from the reactants. Typically, heterogeneous catalysts are solid substances that catalyze reactions involving reactants found in the gas phase, liquid phase, or solution. (\textit{Example}: Catalytic converters in cars reduce NO to \( \text{N}_2 \) using a solid catalyst (Pt, Pd, and/or Rh).

**There are 3 steps in heterogeneous catalysis involving a solid catalyst:**

1. Adsorption or chemisorption of reactants on solid surface
2. Migration of reactants on the surface until they come together to react
3. Desorption of products from the solid surface

Barriers for adsorption/chemisorption and desorption are typically lower than barriers to reaction.
Catalytic Hydrogenation of Ethylene (Figure-McMurray & Fay)

\[ \text{H}_2\text{C} = \text{CH}_2\text{(g)} + \text{H}_2 \xrightarrow{\text{Ni}} \text{H}_3\text{C} = \text{CH}_3\text{(g)} \]

Problem—Catalysts

Which of the following statements about a catalyst is not true?

1. A catalyst can speed up a reaction.
2. A catalyst can cause a reaction to proceed by a different pathway.
3. A catalyst takes part in a reaction but is not used up.
4. A catalyst can be involved in an intermediate step in a reaction mechanism.
5. A catalyst can decrease the activation energy for a reaction.
6. A catalyst can increase the yield of product at equilibrium.