Applying Chemical Kinetics

hapter 6.5

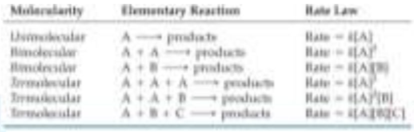
Reaction Mechanisms

- The sequence of events that describes the actual process by which reactants become products is called the **reaction mechanism**.
- The balanced chemical equation for the reaction specifies only the reactants and products, and gives no information on the mechanism.

Reaction Mechanisms

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an **elementary reaction** or **elementary process**.

Reaction Mechanisms



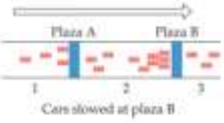
Molecularity	Elementary Reaction	Rate Law
Unimolecular	$A \longrightarrow$ products	Rate $= k[A]$
Bimolecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
Bimolecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
Termolecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
Termolecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
Termolecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

- The **molecularity** of a process tells how many molecules are involved in the process.
  (Molecularity is the number of pieces that must come together)
  (Termolecular steps are almost never heard of because the chances of three molecules coming into contact at the same time are miniscule)
- The rate law for an elementary step is written directly from that step.

Multistep Mechanisms

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, **rate-determining step**.

Cars slowed at plaza A



Cars slowed at plaza B

Slow Initial Step

$$NO_2\ (g) + CO\ (g) \longrightarrow NO\ (g) + CO_2\ (g)$$

- The rate law for this reaction is found experimentally to be

$$\text{Rate} = k\,[NO_2]^2$$

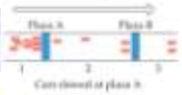
- CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.
- This suggests the reaction occurs in two steps.

Slow Initial Step

- A proposed mechanism for this reaction is

  Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$ (slow)

  Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$ (fast)
- The NO_3 intermediate is consumed in the second step.
- As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.



Fast Initial Step

$$2\,NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

- The rate law for this reaction is found (experimentally) to be

$$rate = k\,[NO]^2\,[Br_2]$$

- Because termolecular (= trimolecular) processes are rare, this rate law suggests a two-step mechanism.

Fast Initial Step

- A proposed mechanism is

$$Step\ 1:\ \ NO + Br_2 \rightleftharpoons NOBr_2\ \ (fast)$$
$$Step\ 2:\ \ NOBr_2 + NO \rightarrow 2NOBr\ \ (slow)$$

Step 1 is an *equilibrium*-
it includes the forward *and* reverse reactions.

Fast Initial Step

$$Step\ 1:\ \ NO + Br_2 \rightleftharpoons NOBr_2\ \ (fast)$$
$$Step\ 2:\ \ NOBr_2 + NO \rightarrow 2NOBr\ \ (slow)$$

- The rate of the overall reaction depends upon the rate of the slow step.
- The rate law for that step would be

$$rate_2 = k_2\,[NOBr_2]\,[NO]$$

- But how can we find $[NOBr_2]$?

Fast Initial Step

$$Step\ 1:\ \ NO + Br_2 \rightleftharpoons NOBr_2\ \ (fast)$$
$$Step\ 2:\ \ NOBr_2 + NO \rightarrow 2NOBr\ \ (slow)$$

- $NOBr_2$ can react two ways:
  - With NO to form NOBr
  - By decomposition to reform NO and Br_2
- The reactants and products of the first step are in equilibrium with each other.
- Therefore,

  $Rate_f = Rate_r$

Fast Initial Step

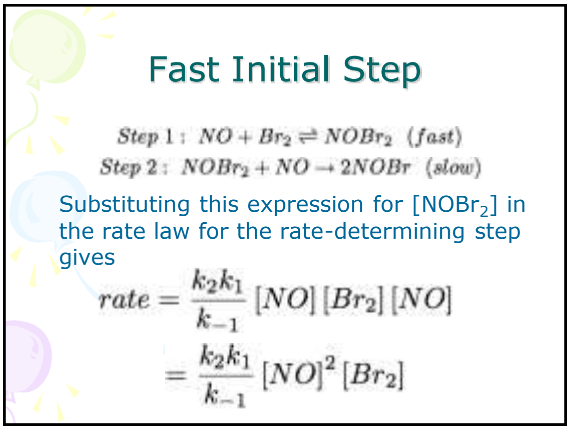
$$Step\ 1:\ \ NO + Br_2 \rightleftharpoons NOBr_2\ \ (fast)$$
$$Step\ 2:\ \ NOBr_2 + NO \rightarrow 2NOBr\ \ (slow)$$

- Because $Rate_f = Rate_r$,

  $k_1\,[NO]\,[Br_2] = k_{-1}\,[NOBr_2]$

Solving for $[NOBr_2]$ gives us

$$\frac{k_1}{k_{-1}}\,[NO]\,[Br_2] = [NOBr_2]$$

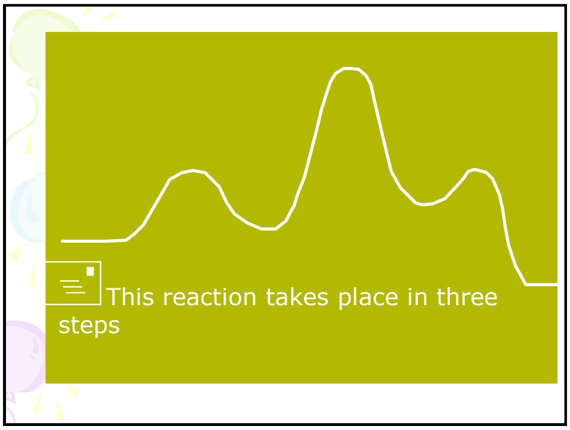


Fast Initial Step

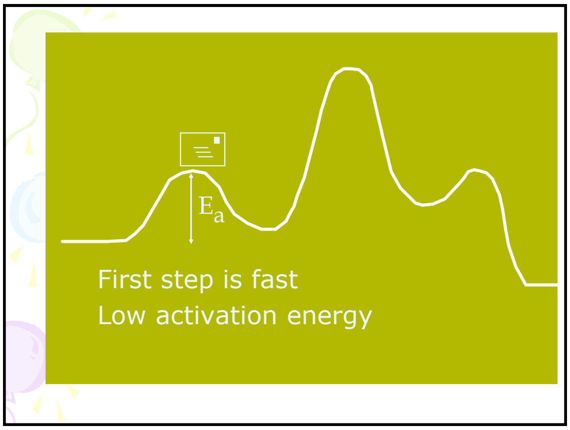
$$\textit{Step 1: } NO + Br_2 \rightleftharpoons NOBr_2 \;\; (fast)$$
$$\textit{Step 2: } NOBr_2 + NO \rightarrow 2NOBr \;\; (slow)$$

Substituting this expression for $[NOBr_2]$ in the rate law for the rate-determining step gives

$$rate = \frac{k_2 k_1}{k_{-1}}[NO][Br_2][NO]$$
$$= \frac{k_2 k_1}{k_{-1}}[NO]^2[Br_2]$$

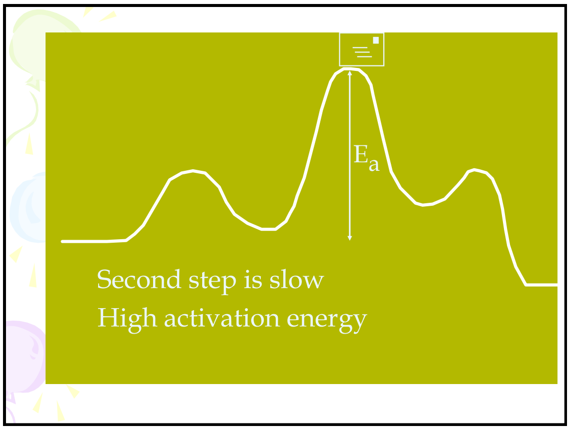


This reaction takes place in three steps



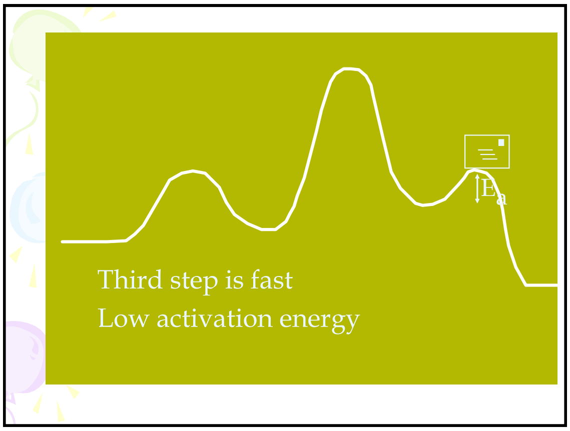
First step is fast

Low activation energy



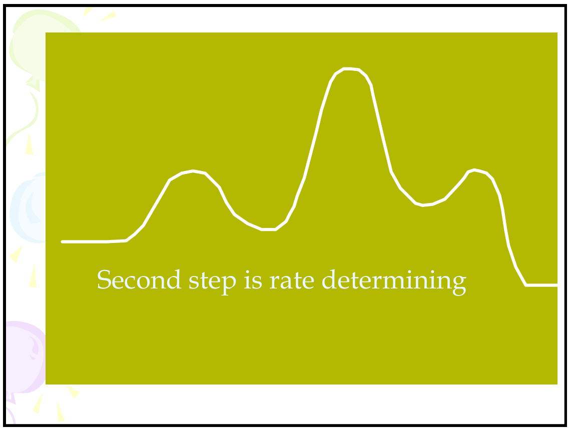
Second step is slow

High activation energy

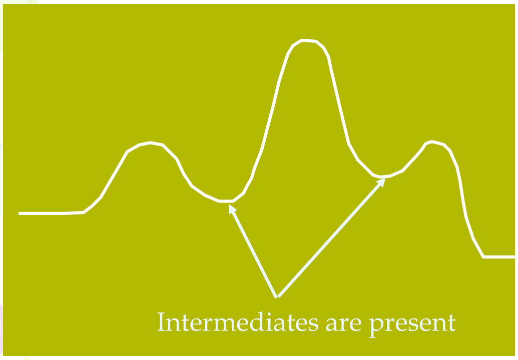


Third step is fast

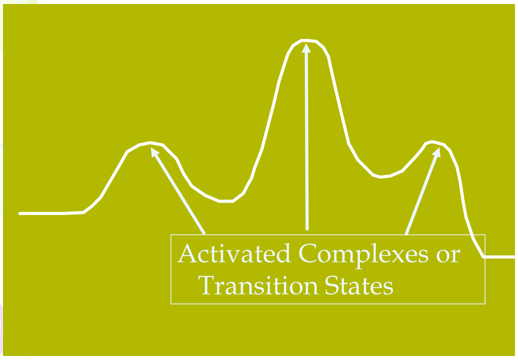
Low activation energy



Second step is rate determining



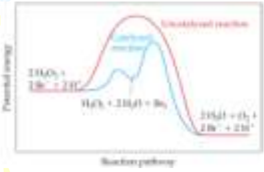
Intermediates are present



Activated Complexes or Transition States

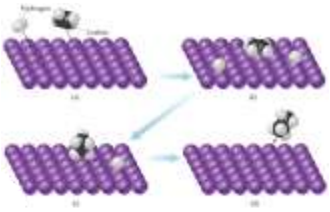
Catalysts

- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.



Catalysts

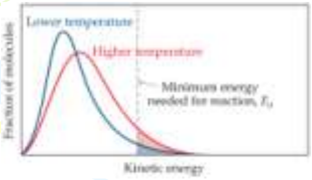
One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.



Enzymes

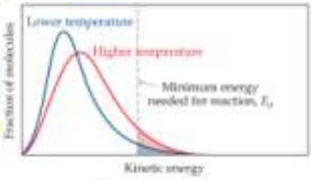
- Enzymes are catalysts in biological systems.
- The substrate fits into the active site of the enzyme much like a key fits into a lock.

Maxwell–Boltzmann Distributions



- Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.
- At any temperature there is a wide distribution of kinetic energies.

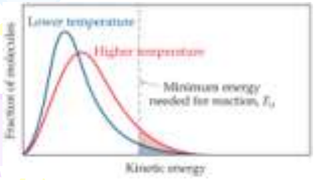
Maxwell–Boltzmann Distributions



- As the temperature increases, the curve flattens and broadens.
- Thus at higher temperatures, a larger population of molecules has higher energy.

Maxwell–Boltzmann Distributions

- If the dotted line represents the activation energy, as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.



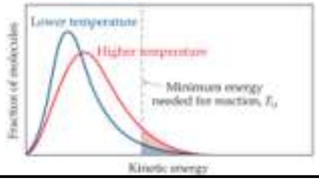
- As a result, the reaction rate increases.

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression:

$$f = e^{-\frac{E_a}{RT}}$$

where *R* is the gas constant and *T* is the temperature in Kelvin .



Arrhenius Equation

- Svante Arrhenius said that the reaction rate should increase with temperature.
- At high temperature more molecules have the energy required to get over the barrier.
- The number of collisions with the necessary energy increases exponentially.

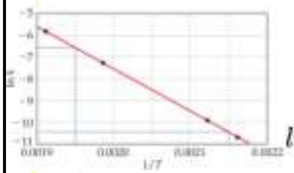
Arrhenius Equation

Arrhenius developed a mathematical relationship between *k* and E_a:

$$k = Ae^{-\frac{E_a}{RT}}$$

Where *A* is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

$$ln(k) = -\frac{E_a}{RT} + lnA$$

$$y = mx + b$$

When *k* is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of ln *k* vs. 1/*T*.

Arrhenius Equation

- There is an activation energy for each elementary step.
- Activation energy determines k.
- $k = Ae^{-(E_a/RT)}$
- k determines rate
- Slowest step (rate determining) must have the highest activation energy.