## Overview of Chapter 15

### Kinetics

- Rates of Reactions
- Effects on reaction rates:
  - Temperature effects
  - Concentration effects
  - Effects of catalysts
- Integrated Rate Laws
- Reaction Mechanisms

## Questions to consider:

- How do enzymes work?
- What is a rate limiting step?
- What is activation energy?

## Today's Topics

- Arrhenius equation
- Rate equations
- Reaction mechanisms

## MECHANISMS

### A Microscopic View of Reactions

Mechanism: how reactants are converted to products at the molecular level.

RATE LAW ----> MECHANISM

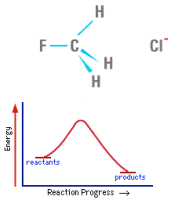
experiment ----> theory

## Activation Energy

Molecules need a minimum amount of energy to react.

Visualized as an energy barrier - activation energy, $E_a$.

Figure 15.12 An analogy to chemical activation energy. For the volleyball to go over the net, the player must give it sufficient energy.




Reaction coordinate diagram

## More About Activation Energy

Arrhenius equation —

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

Rate constant → k

Frequency factor → A

Activation energy → $E_a$

Temp (K) → T

8.31 J/(mol K) or 8.31 x $10^{-3}$ kJ/(mol K) → R

Frequency factor is related to frequency of collisions with correct geometry.

## More About Activation Energy

**Arrhenius equation**

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

**Take natural log of both sides:**

$$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

**Plot ln k vs. 1/T (called an Arrhenius plot):**

- **straight line with slope = $-E_a/R$**
- **intercept = ln A**

## Arrhenius equation at 2 temperatures

$$\ln k = \left(\frac{-E_a}{R}\right)\frac{1}{T} + \ln A$$

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

$$-\quad \ln k_1 = \left(\frac{-E_a}{R}\right)\frac{1}{T_1} + \ln A$$

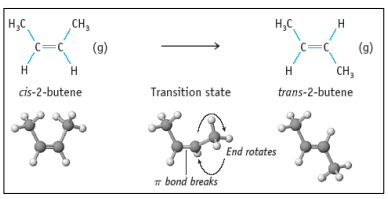
$$\ln k_2 - \ln k_1 = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow \ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

**or**

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

(This is similar to the Clausius-Clapeyron equation from chapter 13)

## MECHANISMS & Activation Energy

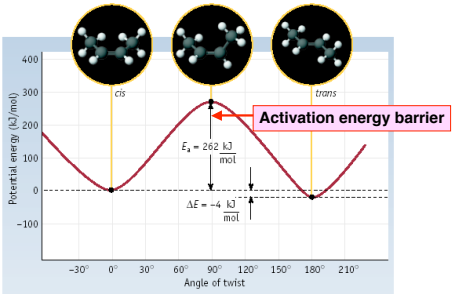



**Conversion of *cis*-butene to *trans*-butene requires twisting around the C=C bond.**

**Rate = k [cis-2-butene]**

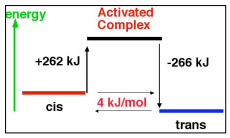
## MECHANISMS

**Cis** **Transition state** **Trans**




## Mechanisms

- **Reaction passes thru a TRANSITION STATE where there is an activated complex that has sufficient energy to become a product.**



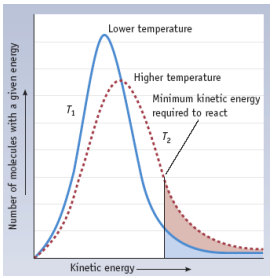

**ACTIVATION ENERGY, $E_a$**

**= energy req'd to form activated complex.**

**Here $E_a$ = 262 kJ/mol**

## Activation Energy and Temperature

**Reactions are faster at higher T because a larger fraction of reactant molecules have enough energy to convert to product molecules.**




**In general, differences in activation energy cause reactions to vary from fast to slow.**