

Final

Dec. 14th, Tuesday, 2 PM to 3:40 PM

Dong Zhong Yuan 2-105

Dong Zhong Yuan 2-205

Dong Zhong Yuan 2-201

Dong Zhong Yuan 2-301

All contents

Same rules as previous tests

Recap

- Integrated rate law (predict concentration, time)
- Elementary reactions, molecularity, RDS
- Deriving rate law from proposed reaction mechanism

Models of Reactions: Effects of Temperature

Rates almost always increase with temperature.



Figure 7D.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman photo by Ken Karp

magnesium in cold water

magnesium in hot water

An indicator shows pH of the solution

Models of Reactions: Effects of Temperature

In the late nineteenth century, the Swedish chemist Svante Arrhenius found that the logarithm plot of rate constant ($\ln k$) against the inverse of the absolute temperature ($1/T$) is a straight line.

$$\ln k = \text{intercept} + \text{slope} \times \frac{1}{T}$$

The intercept is denoted $\ln A$, the slope is denoted $-E_a/R$ (more on this later), where R is the gas constant. With this notation, the empirical **Arrhenius equation** is,

Models of Reactions: Effects of Temperature

Arrhenius equation $\ln k = \ln A - \frac{E_a}{RT}$ or $k = Ae^{-E_a/RT}$

The two constants, A and E_a , are known as the Arrhenius parameters for the reaction and are found from experiment.

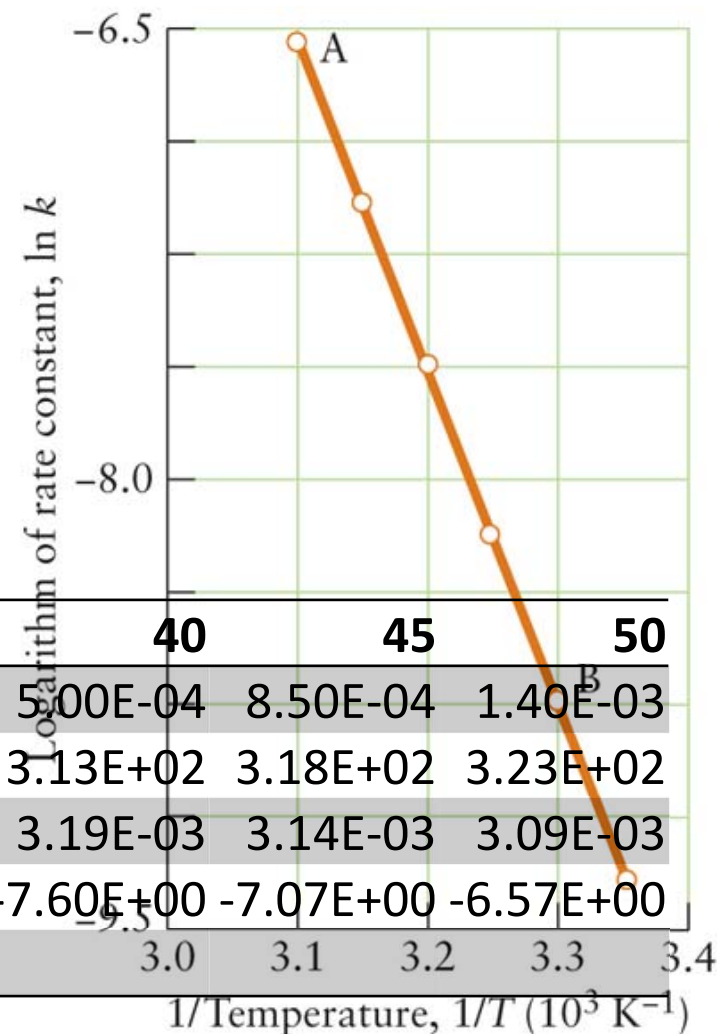
A is called the **pre-exponential factor**.

E_a is the **activation energy**.

Both A and E_a are nearly independent of temperature but have values that depend on the reaction being studied.

Example 7D.1 The rate constant for the second-order reaction between bromoethane and hydroxide ions in water, $\text{C}_2\text{H}_5\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{aq}) + \text{Br}^-(\text{aq})$, was measured at several temperatures, with the results shown here.

The first step is to make a table, a computerized spreadsheet works best, to find (1) the temperature in Kelvin; (2) $1/T$; (3) $\ln k$; and (4) the slope either by graph or spreadsheet.



Temp °C	25	30	35	40	45	50
$k \times 10^{-3} (\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$	8.80E-05	1.60E-04	2.80E-04	5.00E-04	8.50E-04	1.40E-03
T (K)	2.98E+02	3.03E+02	3.08E+02	3.13E+02	3.18E+02	3.23E+02
$1/T \times 10^{-3} (\text{K}^{-1})$	3.35E-03	3.30E-03	3.25E-03	3.19E-03	3.14E-03	3.09E-03
ln k	-9.34E+00	-8.74E+00	-8.18E+00	-7.60E+00	-7.07E+00	-6.57E+00
slope	-10698.8					

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The first step is to make a table, a computerized spreadsheet works best, to find (1) the temperature in Kelvin; (2) $1/T$; (3) $\ln k$; and (4) the slope either by graph or spreadsheet.

The slope is $-E_a/R$, or $E_a = -R \times m$,

Here the slope is $-1.07 \times 10^4 \text{ K}$.

$$E_a = -R \times m, \quad -(8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) (-1.07 \times 10^4 \text{ K}) = 8.9 \times 10^4 \text{ J}\cdot\text{mol}^{-1} \\ = 89 \text{ kJ}\cdot\text{mol}^{-1}$$

Arrhenius Behavior

E_a and temperatures are closely tied to each other.

A low E_a , for example $10 \text{ kJ}\cdot\text{mol}^{-1}$, will have a low slope and is not so entirely dependent on temperature.

A high E_a , say above $60 \text{ kJ}\cdot\text{mol}^{-1}$, produces a steep slope and temperature-dependent reactions.

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

y-intercept = slope + b

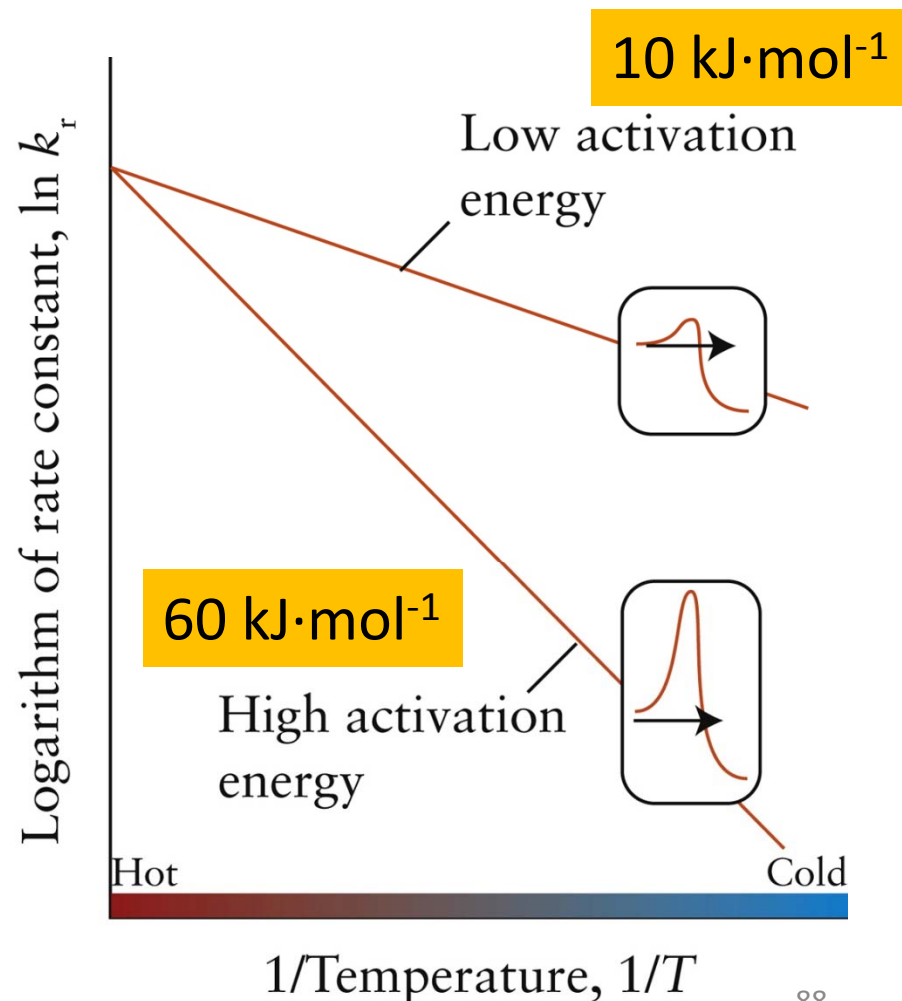


Figure 7D.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Two-Point Arrhenius Equation

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

At two different temperatures and two different k 's

$$\ln k_2 - \ln k_1 = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

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

This can also be written with a positive E_a except note the change in T_2 and T_1 .

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

Example 7D.2 The hydrolysis of sucrose is a part of the digestive process. To investigate how strongly the rate depends on our body temperature, calculate the rate constant for the hydrolysis of sucrose at 35.0 °C, given that $k = 1.0 \text{ mL}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ at 37.0 °C (normal body temperature) and that the activation energy of the reaction is $108 \text{ kJ}\cdot\text{mol}^{-1}$.

We're asked to solve for k_2 , so we use

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

$$108 \text{ kJ}\cdot\text{mol}^{-1} = 108,000 \text{ J}\cdot\text{mol}^{-1}$$

$$35.0^\circ\text{C} + 273.15 = 308.2\text{K}$$

$$37.0^\circ\text{C} + 273.15 = 310.5\text{K}$$

$$k_1 = 1.0 \text{ mL}\cdot\text{mol}^{-1}\cdot\text{s}^{-1} \text{ at } 37.0^\circ\text{C}, T_1 = 310.5\text{K}$$

Example 7D.2 The hydrolysis of sucrose is a part of the digestive process. To investigate how strongly the rate depends on our body temperature, calculate the rate constant for the hydrolysis of sucrose at 35.0 °C, given that $k = 1.0 \text{ mL}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ at 37.0 °C (normal body temperature) and that the activation energy of the reaction is $108 \text{ kJ}\cdot\text{mol}^{-1}$.

$$\text{The right side, } -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \quad -\frac{108,000 \text{ J}\cdot\text{mol}^{-1}}{8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}} \left(\frac{1}{308.2\text{K}} - \frac{1}{310.5\text{K}} \right) = -0.27$$

$$\text{From } x = e^{\ln x}, \quad \frac{k_2}{k_1} = e^{-0.27}$$

$$\frac{k_2}{1.0 \text{ mL}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}} = e^{-0.27}, \quad k_2 = 0.76 \text{ mL}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$$

The high E_a means it is temperature sensitive.

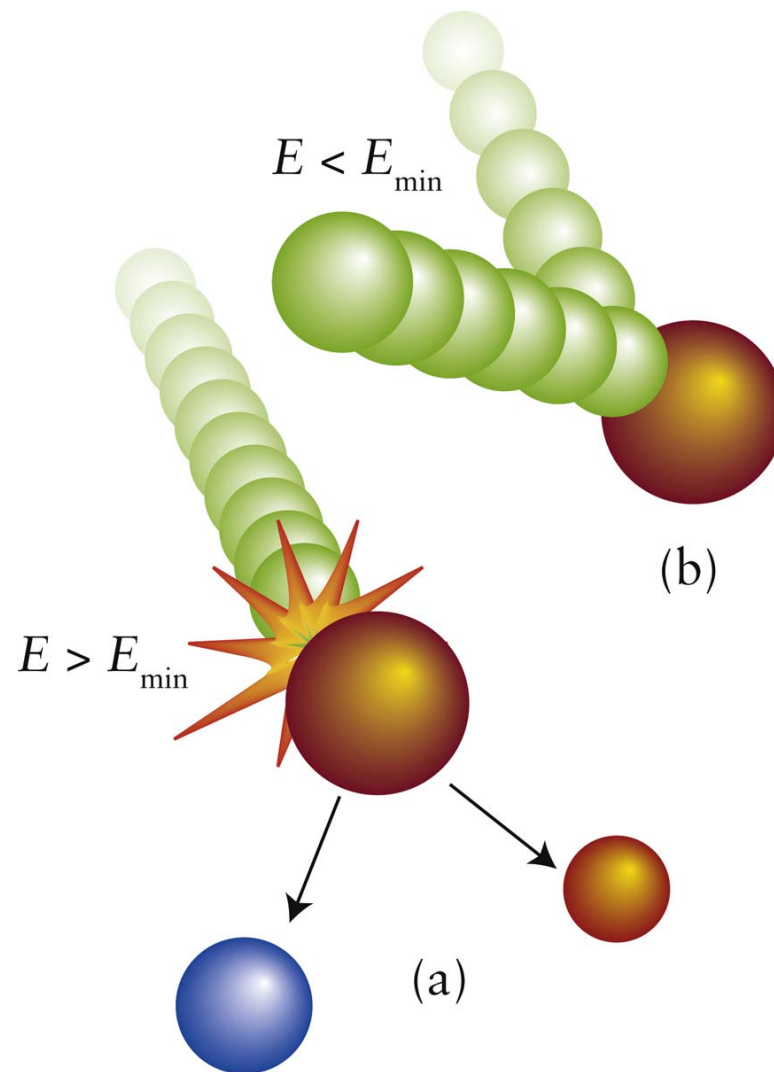
Collision Theory

The Arrhenius equation can help us build a model of chemical reactions at the molecular level.

Specifically, our model must account for the **temperature dependence** of rate constants, as well as the **energy of activation**.

Collision Theory

Hard spheres like billiard balls collide.



If they collide too slowly, nothing will happen.

Figure 7D.4
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They need a minimum energy (speed) called E_{\min} to react.

Collision Frequency (Cross-section, speed, number of atoms)

The collision frequency between A and B molecules in a gas at a temperature T is shown in the below equation:

$$\text{Collision frequency} = \sigma \bar{v}_{\text{rel}} N_A^2 [A][B] \quad (\text{rudimentary form})$$

σ (sigma) is the collision cross section and often determines collision frequency.

Bigger molecules have a larger collision cross section, because they are easier targets than smaller molecules, and thus have higher collisional frequencies.

\bar{v}_{rel} is the mean relative speed, the mean speed of a gas.



Collision Frequency

Collision frequency = $\sigma \bar{v}_{\text{rel}} N_A^2 [A][B]$ (rudimentary form)

$$\bar{v}_{\text{rel}} = \left(\frac{8RT}{\pi \mu} \right)^{\frac{1}{2}} \quad \text{where} \quad \mu = \frac{M_A M_B}{M_A + M_B}$$

Note: for a 10 °C increase in temperature the rate of the reaction doubles.

N_A is Avogadro's constant.

Collision Frequency: Boltzmann Correction

Boltzmann distribution takes into account E_{\min} and fits in to the blue curve.

Rate of reaction = collision frequency \times fraction with sufficient energy,

$$\text{Rate} = \sigma \bar{v}_{\text{rel}} N_A^2 [A][B] \times e^{-E_{\min}/RT}$$

Since, rate = $k[A][B]$

$$k = \frac{\text{rate}}{[A][B]} = \sigma \bar{v}_{\text{rel}} N_A^2 \times e^{-E_{\min}/RT}$$

E_{\min} , like E_a , is the minimum kinetic energy required for a successful collision.

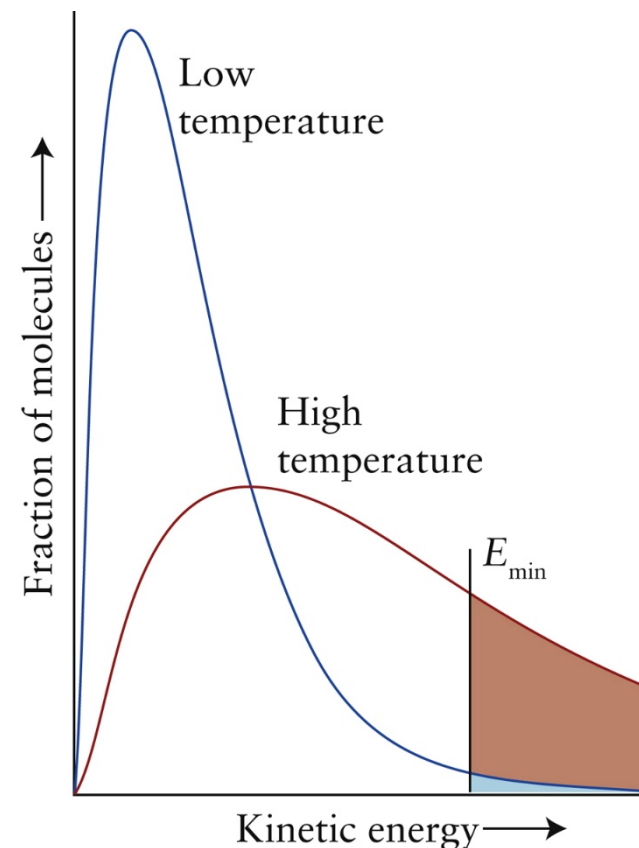


Figure 7D.5
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Collision Frequency: Boltzmann Correction

$$\text{Boltzmann: } k = \frac{\text{rate}}{[A][B]} = \sigma \bar{v}_{\text{rel}} N_A^2 \times e^{-E_{\text{min}}/RT}$$

This has the resemblance of Arrhenius's equation

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

Where A is the pre-exponential factor $\sigma \bar{v}_{\text{rel}} N_A^2$.

E_a , Activation Energy Relationship to k and K



$\uparrow \rightarrow$ (shift to the right)

E_a is the minimum kinetic energy to activate a successful collision.

For **endothermic reactions**, since E_a **forward is large**, it is sensitive to increases in temperature. Raising the temperature will increase K , the equilibrium constant, and is exactly what Le Chatelier's principle predicts.

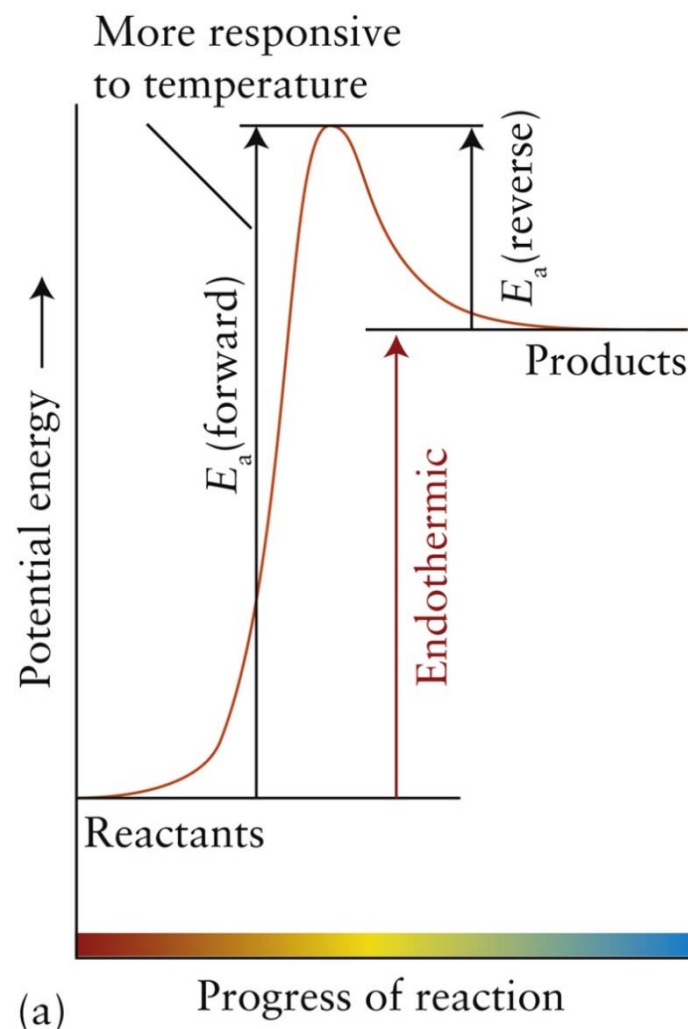
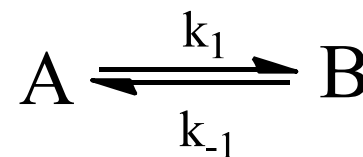


Figure 7D.6a

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E_a large forward, so it is Temp dependent

E_a , Activation Energy Relationship to k and K

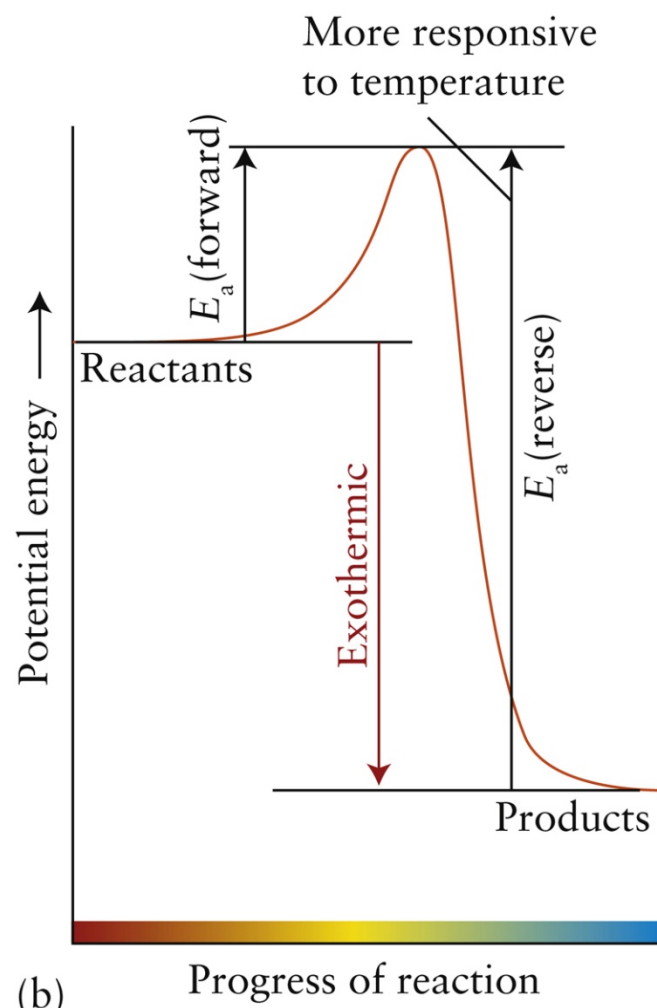
$$K = \frac{k_1}{k_{-1}}$$



(shift to the left) ←

$$k_1 > k_{-1}$$

E_a is small going forward, so it is not temperature dependent.



(b) Figure 7D.6b

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Steric Requirement

Improving the model depends on how easily the molecules line up for a collision.

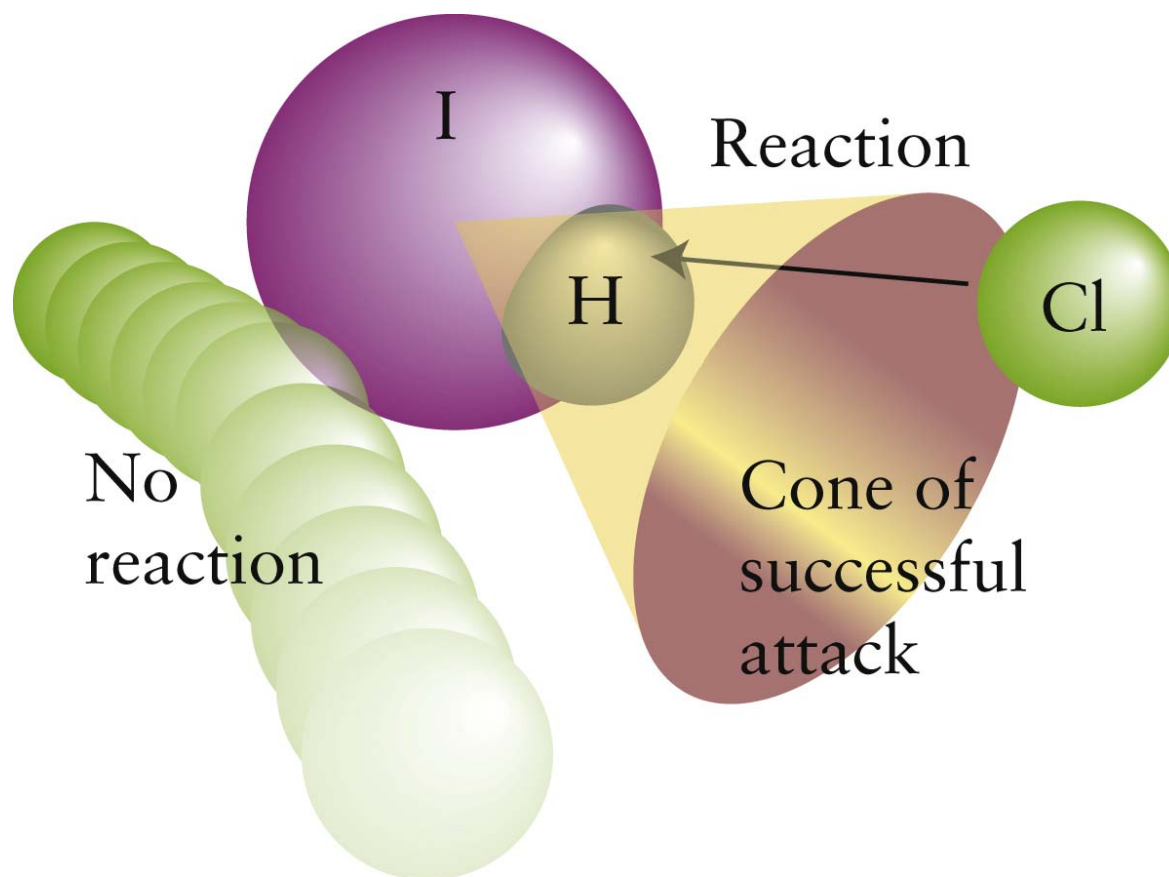


Figure 7D.7

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Steric Requirement

$$k = P \times \sigma \bar{v}_{\text{rel}} N_A^2 \times e^{-E_{\text{min}}/RT}$$

P is the steric requirement. P is always less than 1 because it reduces the collision probability.

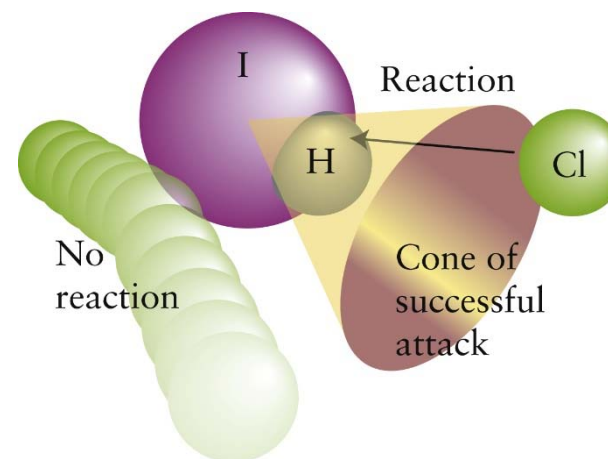


Figure 7D.7
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Transition State Theory

Transition state theory applies to molecules with more complex steric requirements.

This is also called activated complex theory.

Normally, during a collision process, lots of jostling and back and forth movement takes place. Bonds are stretching to their limit. There is a point of no return when the reactants go to products.

Transition State Theory

In a reaction profile, the different stages leading up to the activated complex are shown.

As the molecules meet, repulsive forces increase the energy, so the molecule must have enough E_{\min} to overcome this opposing force.

As the molecules climb to the top of the E_a , the reaction can go either way.

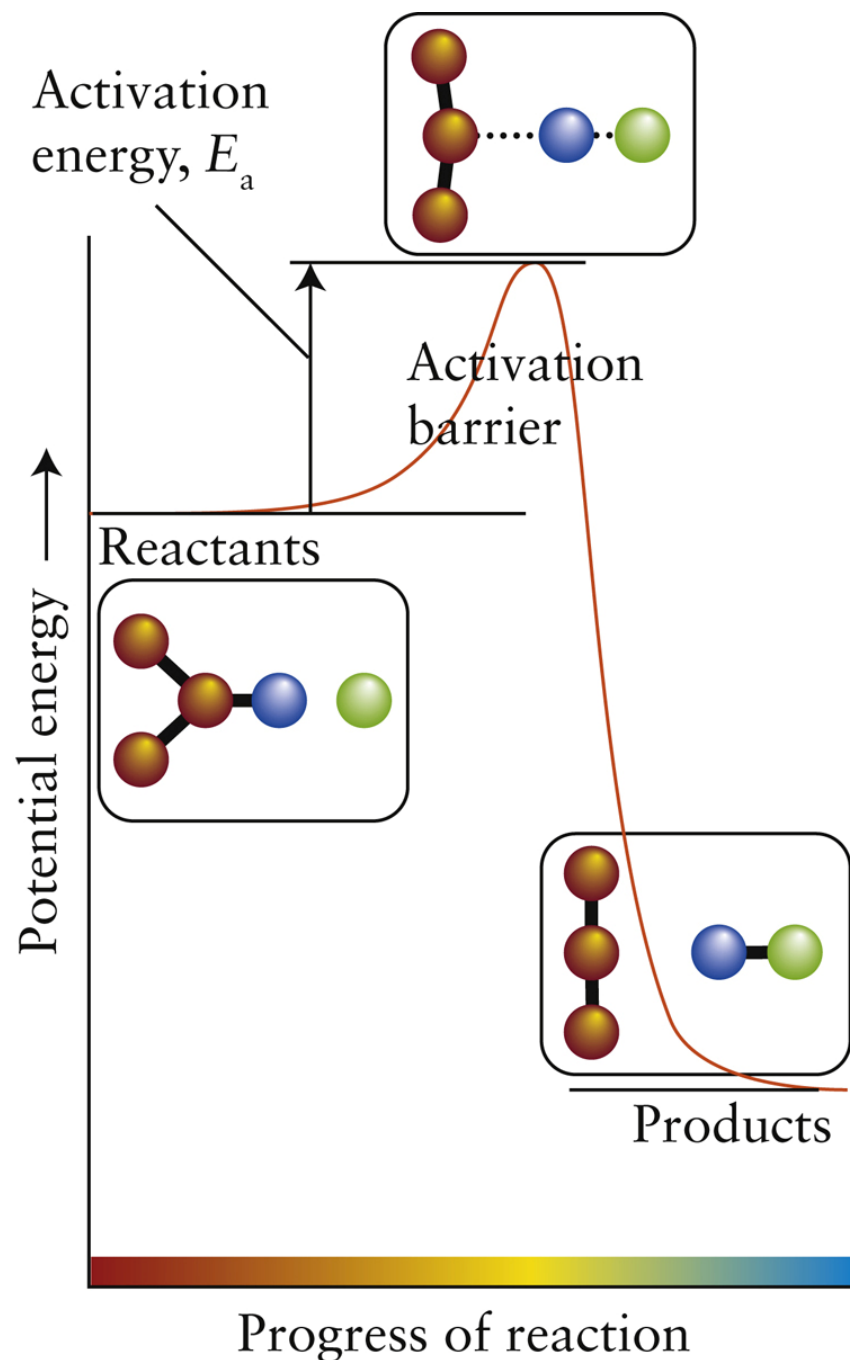


Figure 7D.9

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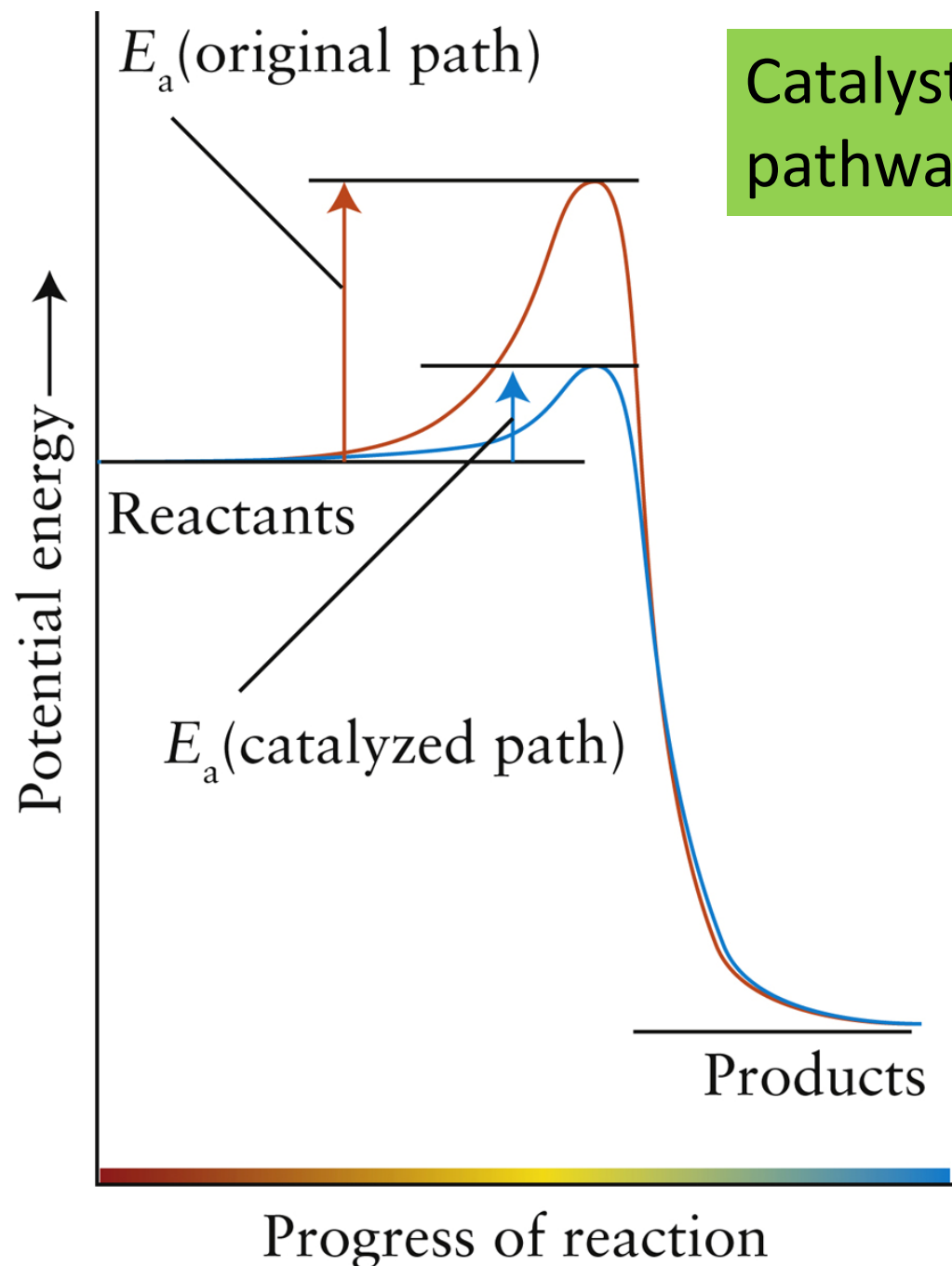
Impact on Materials and Biology: Accelerating Reactions

We have seen how rates increase by increasing both the concentration of reactants and temperature. There are other ways.

Catalysis

A catalyst increases the rate, without being consumed.

The name comes from the Greek words meaning “breaking down by coming together.” In many cases, only a small amount of catalyst is necessary because it acts over and over again (and is not consumed).



Catalysts provide a new reaction pathway.

A catalyst **lowers the activation energy**, thereby allowing more reactant molecules to cross the barrier and form products.

How they do this will be seen in a few slides.

Figure 7E.2

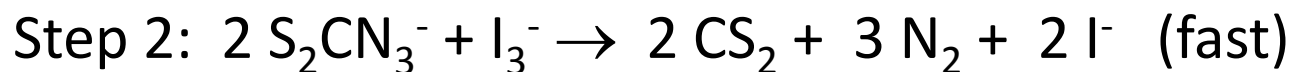
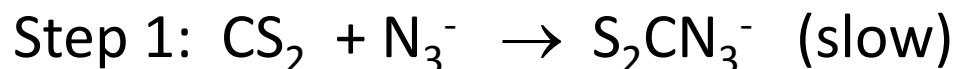
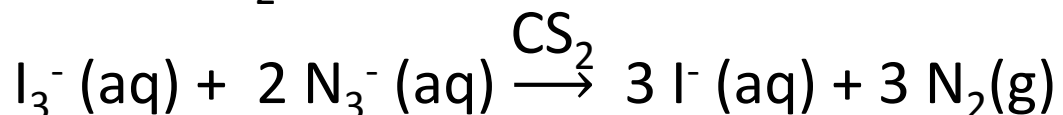
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Catalyst in Rate Laws

Catalysts do not appear in the balanced equation for a reaction, but their concentrations do appear in the rate law.

The reaction between the triiodide ion and the azide ion is very slow unless CS₂ catalyst is added.



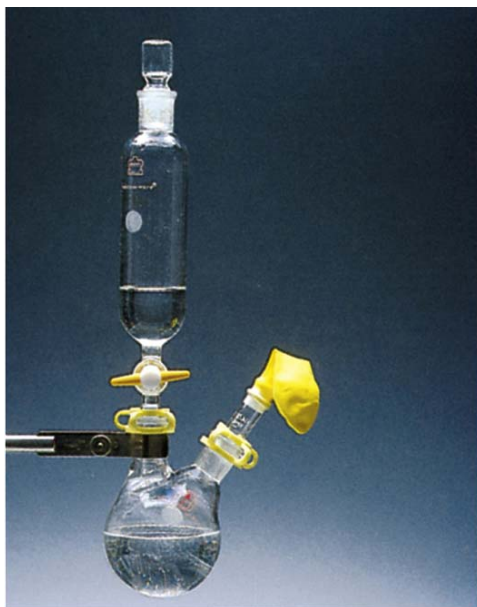
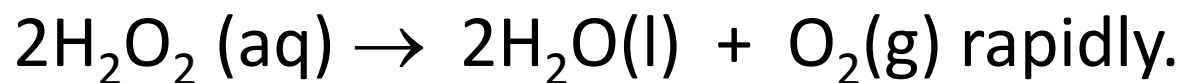
The rate law derived is the Rate of consumption of $\text{I}_3^- = k[\text{CS}_2][\text{N}_3^-]$.

Notice that the rate law is **first order** in the catalyst, **carbon disulfide**, but **zeroth order** in **triiodide ion**, which appears only in the fast step following the slow step.

Homogeneous Catalyst

Homogeneous catalysts are in the same phase as the reactants.

Peroxide can be stored safely for months but adding a catalyst, Br_2 , causes rapid decomposition:



(a)



(b)

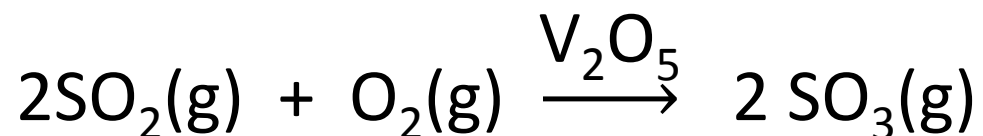
Figure 7E.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman photos by Ken Karp

Heterogeneous Catalyst

Heterogeneous catalysts are in a **different phase** than the reactants.

Common heterogeneous catalysts are finely-divided or porous solids that have a large surface area.

A common one is the iron catalyst used in the Haber process for ammonia . Another catalyst is finely-divided vanadium pentoxide, V_2O_5 , which is used in the “contact process” for the production of sulfuric acid.



How does a catalyst lower the E_a ?

Catalysts grab and hold onto reactants.

Once held, catalysts position reactants so they react with minimal steric hindrance.

Railroad rails provide a train the path of least resistance, so rails are like a catalysts, positioning the train so it can travel with the least amount of potential energy.

How does a catalyst lower the E_a ?

Shown is a reaction between ethene, $\text{CH}_2=\text{CH}_2$, and hydrogen on a Pt metal catalytic surface.

The ethene and hydrogen **stick** to the metal surface (**adsorb**).

The **metals dissociate the hydrogen**.

The ethene molecule meets two hydrogen atoms to form bonds making CH_3CH_3 ; ethane is formed and escapes from the surface.

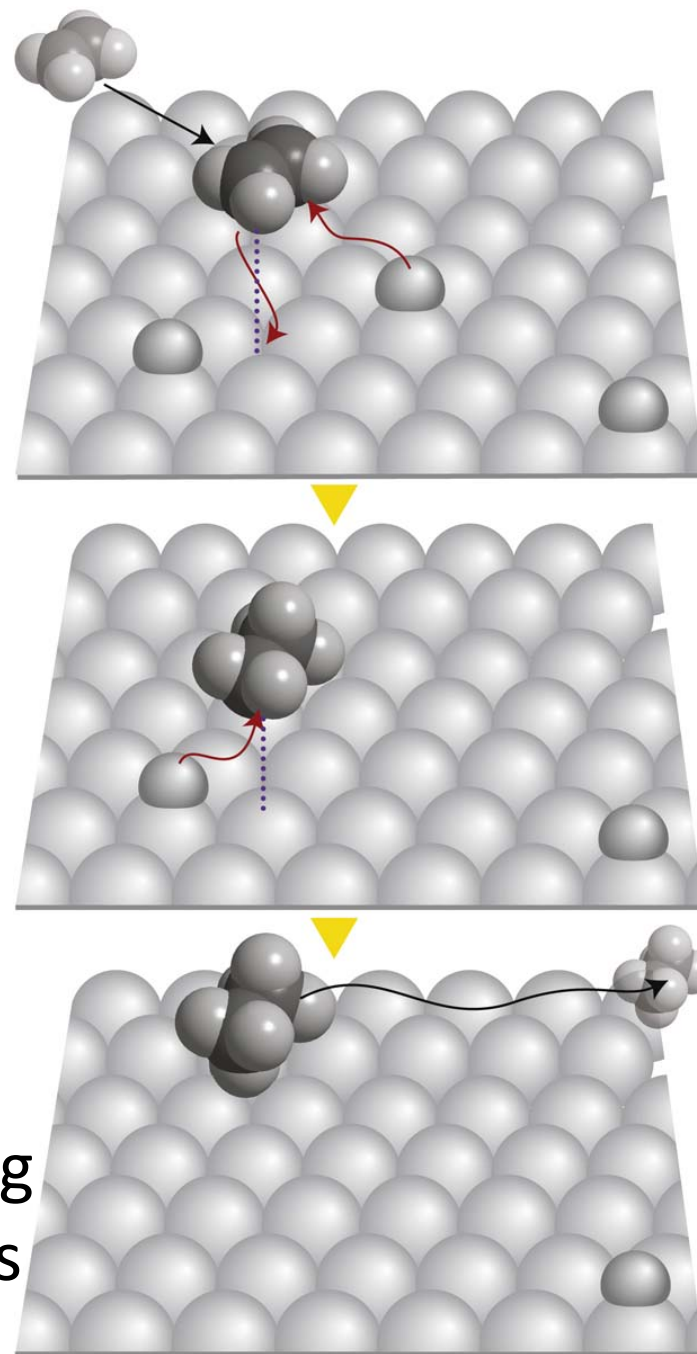


Figure 7E.3

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Poisoned Catalysts

Catalysts can be poisoned, or inactivated.

A common cause of poisoning is the adsorption of a molecule to catalyst that seals the surface.

Heavy metals, especially *lead*, are very potent poisons for heterogeneous catalysts, which is why *lead-free gasoline* must be used in engines fitted with catalytic converters.

Ozone

Every year the Sun bombards our planet with enough energy to destroy all life.

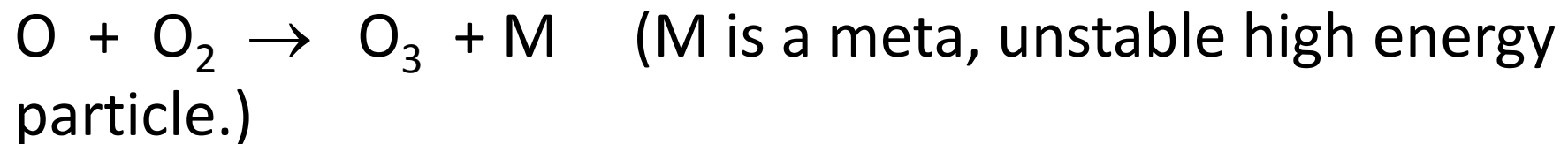
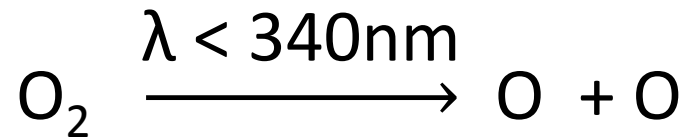
Ozone in the stratosphere protects us from that onslaught.

Chemicals used as coolants and propellants, such as chlorofluorocarbons (CFCs), and the nitrogen oxides in jet exhausts, have been found to create holes in Earth's protective ozone layer.

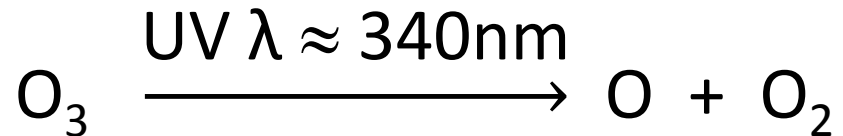
Because CFCs act as catalysts, they can cause large changes in the vast reaches of the stratosphere.

Ozone

Ozone forms in two steps.



The protection comes from ozone absorbing UV light.

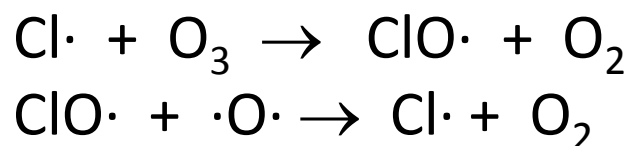


Susan Solomon and James Anderson showed that CFCs containing chlorine atoms catalyzed destruction of stratospheric ozone.

Ozone

CFCs are not water soluble, so they do not precipitate with rain, but are light and airborne enough to reach the stratosphere.

At one time CFCs emanated from everyday objects, such as cans of hair spray, refrigerators, and air conditioners.



Most nations signed the Montreal Protocol of 1987 which required the more dangerous CFCs to be phased out by 1996.

Current data show that the levels of compounds that deplete ozone are gradually beginning to decrease.

Living Catalysts: Enzymes

Living cells contain thousands of different kinds of catalysts.

Many **catalysts are proteins called enzymes**, with a slot-like active site, where reaction takes place.

However, unlike an ordinary lock, a protein molecule distorts slightly as the substrate molecule approaches, and its ability to undergo the correct distortion also determines whether the “key” will fit.

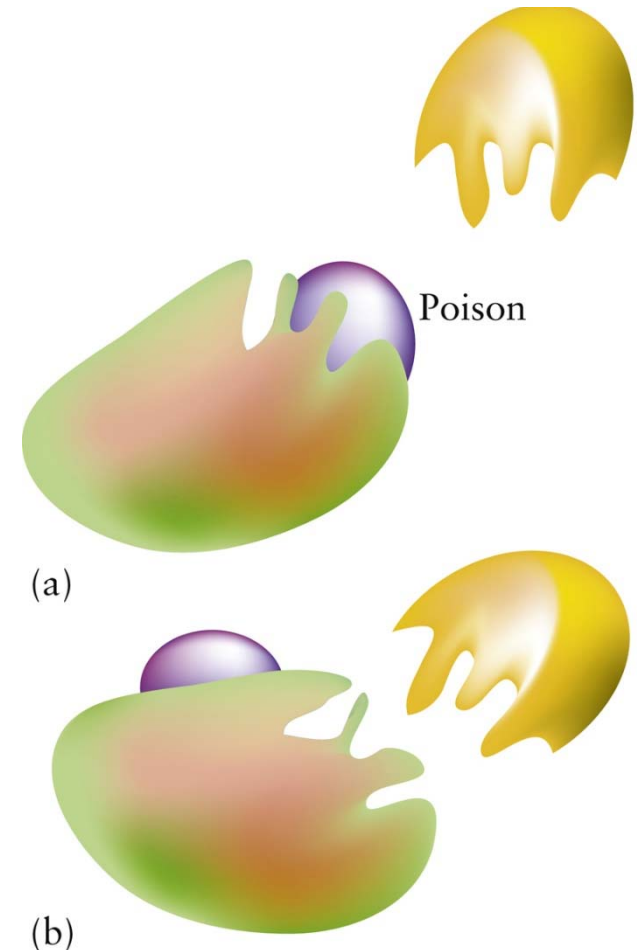


Figure 7E.9
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