

Reaction Mechanism (continued)

The reaction

$$2 C_3 H_4 O_3 + 5O_2 \longrightarrow 6CO_2 + 4H_2O_2$$

• has many steps in the reaction mechanism.

Objectives

- Be able to describe the collision and transition-state theories
- Be able to use the Arrhenius theory to determine the activation energy for a reaction and to predict rate constants
- Be able to relate the molecularity of the reaction and the reaction rate and describle the concept of the "ratedetermining" step
- Be able to describe the role of a catalyst and homogeneous, heterogeneous and enzyme catalysis

Reaction Mechanisms

- Even though a balanced chemical equation may give the ultimate result of a reaction, what actually happens in the reaction **may take place in several steps.**
 - This "pathway" the reaction takes is referred to as the reaction mechanism.
 - The individual steps in the larger overall reaction are referred to as elementary reactions.

Reaction Mechanisms

- The series of steps by which a chemical reaction occurs.
- A chemical equation does not tell us how reactants become products - it is a summary of the overall process.

Often Used Terms

•Intermediate: formed in one step and used up in a subsequent step and so is never seen as a product.

•Molecularity: the number of species that must collide to produce the reaction indicated by that step.

•Elementary Step: A reaction whose rate law can be written from its molecularity.

•uni, bi and termolecular

Elementary Reactions

• Consider the reaction of nitrogen dioxide with carbon monoxide.

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

- This reaction is believed to take place in two steps.
- $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$ (elementary reaction)

 $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (elementary reaction)

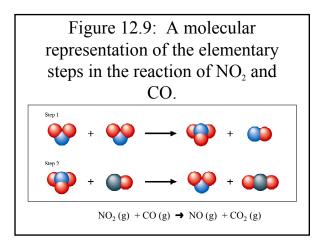
Elementary Reactions

- Each step is a singular molecular event resulting in the formation of products.
 - The overall chemical equation is obtained by adding the two steps together and canceling any species common to both sides.

 $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$

 $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

 $NO_2(g) + NO_2(g) + NO_3(g) + CO(g) \rightarrow NO_3(g) + NO(g) + NO_2(g) + CO_2(g)$



Molecularity

- We can classify reactions according to their **molecularity**, that is, the number of molecules that must collide for the elementary reaction to occur.
 - A **unimolecular** reaction involves only one reactant molecule.
 - A **bimolecular** reaction involves the collision of two reactant molecules.
 - A termolecular reaction requires the collision of three reactant molecules.

Elementary Reactions

- Each step is a singular molecular event resulting in the formation of products.
 - Note that NO₃ does not appear in the overall equation, but is formed as a temporary reaction intermediate.

Molecularity

- We can classify reactions according to their **molecularity**, that is, the number of molecules that must collide for the elementary reaction to occur.
 - Higher molecularities are rare because of the small statistical probability that four or more molecules would all collide at the same instant.

Rate Equations for Elementary Reactions

- Since a chemical reaction may occur in several steps, there is no easily stated relationship between its overall reaction and its rate law.
- For elementary reactions, the rate is proportional to the concentrations of all reactant molecules involved.

Rate Equations for Elementary Reactions

• For a termolecular reaction

$A + B + C \rightarrow products$

the rate is dependent on the populations of all three participants.

Rate = k[A][B][C]

Rate Equations for Elementary Reactions

• For example, consider the generic equation below. $A \rightarrow products$

The rate is dependent only on the concentration of A; that is,

Rate = k[A]

Elementary Step	Molecularity	Rate Law
$A \rightarrow products$	Uni molecular	Rate $-k[A]$
$\begin{array}{l} A + A \rightarrow \text{ products} \\ (2\Lambda \rightarrow \text{ products}) \end{array}$	<i>Bi</i> molecular	Rate = $k[A]^2$
$A + B \rightarrow products$	Bimolecular 64	Rate = $k[A][B]$
$\begin{array}{l} A + A + B \rightarrow \text{ products} \\ (2A + B \rightarrow \text{ products}) \end{array}$	Termolecular	$Rate = k[A]^2[B]$
$A + B + C \rightarrow products$	Termolecular	Rate = $k[A][B][C]$

Rate Equations for Elementary Reactions

• However, for the reaction

$A + B \rightarrow products$

the rate is dependent on the concentrations of both A and B.

Rate = k[A][B]

Rate Equations for Elementary Reactions

• Note that if two molecules of a given reactant are required, it appears twice in the rate law. For example, the reaction

$2A + B \rightarrow products$

would have the rate law:

Rate = k[A][A][B] or Rate = $k[A]^{2}[B]$

Rate Equations for Elementary Reactions

- So, in essence, for an elementary reaction, the coefficient of each reactant becomes the power to which it is raised in the rate law for that reaction.
 - Note that many chemical reactions occur in multiple steps and it is, therefore, **impossible** to predict the rate law **based solely on the overall reaction**.

Rate Laws and Mechanisms

• Consider the reaction below.

$2 \operatorname{NO}_2(g) + F_2(g) \rightarrow 2 \operatorname{NO}_2 F(g)$

• Experiments performed with this reaction show that the rate law is

Rate = $k[NO_2][F_2]$

• This implies that the reaction above is not an elementary reaction but rather the result of multiple steps.

Rate-Determining Step

•In a multistep reaction, it is the slowest step. It therefore determines the rate of reaction.

Rate-Determining Step

- In multiple-step reactions, one of the elementary reactions in the sequence is often slower than the rest.
 - The overall reaction cannot proceed any faster than this slowest **rate-determining step**.

Rate Laws and Mechanisms

• Consider the reaction below.

$2 \operatorname{NO}_2(g) + F_2(g) \rightarrow 2 \operatorname{NO}_2 F(g)$

• Experiments performed with this reaction show that the rate law is

Rate = $k[NO_2][F_2]$

• The reaction is first order with respect to each reactant, even though the coefficient for NO₂ in the overall reaction is.

Rate-Determining Step

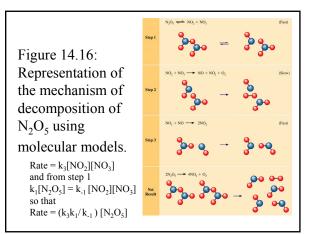
- In multiple-step reactions, one of the elementary reactions in the sequence is often slower than the rest.
 - Our previous example occurs in two elementary steps where the first step is much slower.

 $\frac{\text{NO}_2(g) + F_2(g) \xrightarrow{k_1} \text{NO}_2F(g) + F(g)}{\text{NO}_2(g) + F(g) \xrightarrow{k_2} \text{NO}_2F(g)}$ (fast) $\frac{2 \text{NO}_2(g) + F_2(g) \rightarrow 2 \text{NO}_2F(g)}{\text{MO}_2(g) + F_2(g) \rightarrow 2 \text{NO}_2F(g)}$

Rate-Determining Step

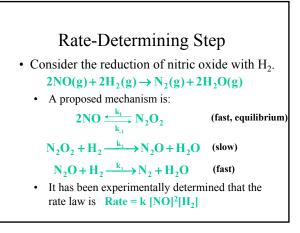
- In multiple-step reactions, one of the elementary reactions in the sequence is often slower than the rest.
 - Since the overall rate of this reaction is determined by the slow step, it seems logical that the observed rate law is Rate = k₁[NO₂][F₂].

 $NO_2(g) + F_2(g) \xrightarrow{k_1} NO_2F(g) + F(g)$ (slow)



Rate-Determining Step

- In a mechanism where the first elementary step is the rate-determining step, the overall rate law is simply expressed as the elementary rate law for that slow step.
 - A more complicated scenario occurs when the rate-determining step contains a reaction intermediate, as you'll see in the next section.



Rate-Determining Step

- · Mechanisms with an Initial Fast Step
 - There are cases where the rate-determining step of a mechanism contains a **reaction intermediate** that does not appear in the overall reaction.
 - The experimental rate law, however, can be expressed only in terms of substances that appear in the overall reaction.

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.

$Rate = k_2[N_2O_2][H_2]$

(Rate law for the rate-determining step)

• As mentioned earlier, the overall rate law can be expressed only in terms of substances represented in the overall reaction and cannot contain reaction intermediates.

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.

$Rate = k_2[N_2O_2][H_2]$

(Rate law for the rate determining step)

 It is necessary to re-express this proposed rate law after eliminating [N₂O₂].

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.

$Rate = k_2[N_2O_2][H_2]$

(Rate law for the rate-determining step)

• Therefore,

$[N_2O_2] = (k_1/k_{-1})[NO]^2$

• If we substitute this into our proposed rate law we obtain:

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.

$Rate = k_2[N_2O_2][H_2]$

(Rate law for the rate determining step)

• We can do this by looking at the first step, which is fast and establishes equilibrium.

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.

$\mathbf{Rate} = \mathbf{k}_2 [\mathbf{N}_2 \mathbf{O}_2] [\mathbf{H}_2]$

(Rate law for the rate determining step)

Rate =
$$\frac{k_2 k_1}{k_{-1}} [NO]^2 [H_2]$$

If we replace the constants (k₂k₁/k₋₁) with k, we obtain the observed rate law: Rate = k[NO]²[H₂].

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.

$Rate = k_2 [N_2 O_2] [H_2]$

(Rate law for the rate-determining step)

• At equilibrium, the forward rate and the reverse rate are equal.

 $k_1[NO]^2 = k_{-1}[N_2O_2]$

Collision Theory

- **Collision theory** assumes that for a reaction to occur, reactant molecules must collide with sufficient energy and the proper orientation.
- The minimum energy of collision required for two molecules to react is called the activation energy, E_a .

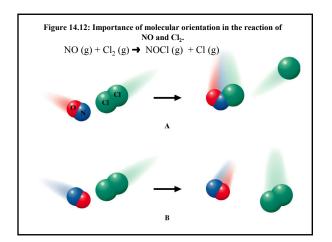


Figure 12.13: Several possible orientations for a collision between two BrNO molecules. Orientations (a) and (b) can lead to a reaction, but orientation (c) cannot. $\boxed{2 \text{ NOBr } (g) \rightarrow 2 \text{ NO } (g) + \text{Br}_2 (g)}$

Collision Model

•Key Idea: Molecules must collide to react.

•However, only a small fraction of collisions produces a reaction. Why?

•Arrhenius: An activation energy must be overcome.

Collision Theory and the Arrhenius Equation

- Collisions must have enough energy to produce the reaction (must equal or exceed the activation energy).
- Orientation of reactants must allow formation of new bonds.

Collision Theory

- Rate constants vary with temperature. Consequently, the actual rate of a reaction is very temperature dependent.
- Why the rate depends on temperature can by explained by collision theory.

Figure 12.11: (a) The change in potential energy as a function of reaction progress for the reaction 2BrNO $2NO + Br_2$. The activation energy Ea represents the energy needed to disrupt the BrNO molecules so that they can form products. The quantity DE represents the net change in energy in going from reactant to products. (b) A molecular representation of the reaction.

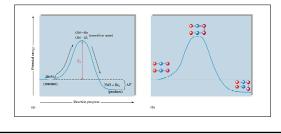
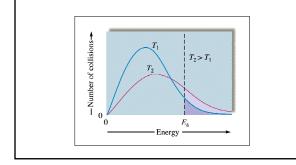
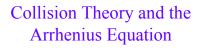


Figure 12.12: Plot showing the number of collisions with a particular energy at T_1 and T_2 , where $T_2 > T_1$.





- Z is only slightly temperature dependent.
 - This alone does not account for the observed increases in rates with only small increases in temperature.
 - From kinetic theory, it can be shown that a 10 °C rise in temperature will produce only a 2% rise in collision frequency.

Collision Theory and the Arrhenius Equation

- Collision theory maintains that the rate constant for a reaction is the product of three factors.
 - 1. Z, the collision frequency
 - **2. f**, the fraction of collisions with sufficient energy to react
 - **3. p**, the fraction of collisions with the proper orientation to react

 $\mathbf{k} = \mathbf{Z}\mathbf{p}\mathbf{f}$

Collision Theory and the Arrhenius Equation

- On the other hand, **f**, the fraction of molecules with sufficient activation energy, turns out to be very temperature dependent.
 - It can be shown that f is related to E_a by the following expression.



Here e = 2.718..., and R is the ideal gas constant, 8.31 J/(mol·K).

Collision Theory and the Arrhenius Equation

- Z is only slightly temperature dependent.
 - This is illustrated using the kinetic theory of gases, which shows the relationship between the velocity of gas molecules and their absolute temperature.

velocity =
$$\sqrt{\frac{3RT_{abs}}{M_m}}$$
 or velocity $\propto \sqrt{T_{abs}}$

Collision Theory and the Arrhenius Equation

- On the other hand, **f**, the fraction of molecules with sufficient activation energy turns out to be very temperature dependent.
 - From this relationship, as temperature increases, f increases.

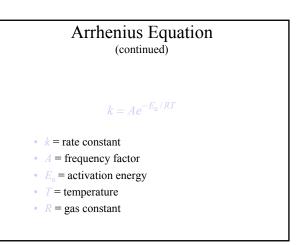
$$\mathbf{f} = \mathbf{e}^{\frac{-\mathbf{E}_a}{\mathbf{R}T}}$$

• Also, a decrease in the activation energy, E_a, increases the value of f.

Collision Theory and the Arrhenius Equation

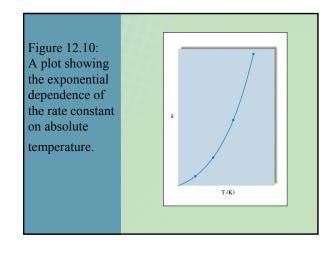
- On the other hand, **f**, the fraction of molecules with sufficient activation energy turns out to be very temperature dependent.
 - This is the primary factor relating temperature increases to observed rate increases.

 $\mathbf{f} = \mathbf{e}^{\frac{-\mathbf{E}_a}{\mathbf{R}T}}$



Collision Theory and the Arrhenius Equation

- The reaction rate also depends on **p**, the fraction of collisions with the proper orientation.
 - This factor is independent of temperature changes.
 - So, with changes in temperature, Z and p remain fairly constant.
 - We can use that fact to derive a mathematical relationship between the rate constant, **k**, and the **absolute temperature**.



The Arrhenius Equation

• If we were to combine the relatively constant terms, Z and p, into one constant, let's call it A. We obtain the Arrhenius equation:



• The Arrhenius equation expresses the dependence of the rate constant on absolute temperature and activation energy.

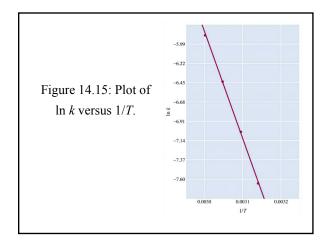


Table 14.3 Rate Constant for the Decomposition of N ₂ O ₅ at Various Temperatures		
Temperature (°C)	k (/s)	
45.0	4.8×10^{-4}	
50.0	$8.8 imes 10^{-4}$	
55.0	1.6×10^{-3}	
60.0	$2.8 imes 10^{-3}$	

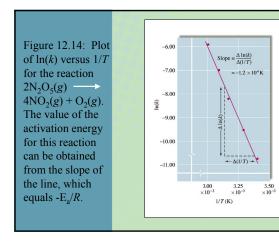
The Arrhenius Equation

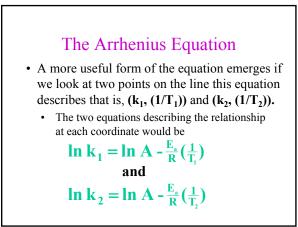
- It is useful to recast the Arrhenius equation in logarithmic form.
 - We can relate this equation to the (somewhat rearranged) general formula for a straight line.

$$\ln \mathbf{k} = \ln \mathbf{A} - \frac{\mathbf{E}_a}{\mathbf{R}} \left(\frac{1}{\mathbf{T}}\right)$$

y = b + m x

 A plot of ln k versus (1/T) should yield a straight line with a slope of (-E_a/R) and an intercept of ln A. (see Figure 14.15)





The Arrhenius Equation

- It is useful to recast the Arrhenius equation in logarithmic form.
 - Taking the natural logarithm of both sides of the equation, we get:

$$\ln \mathbf{k} = \ln \mathbf{A} - \frac{\mathbf{E}_a}{\mathbf{R}\mathbf{T}}$$

The Arrhenius Equation

- A more useful form of the equation emerges if we look at two points on the line this equation describes that is, $(k_1, (1/T_1))$ and $(k_2, (1/T_2))$.
 - We can eliminate ln A by subtracting the two equations to obtain

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

The Arrhenius Equation

- A more useful form of the equation emerges if we look at two points on the line this equation describes that is, $(\mathbf{k}_1, (1/T_1))$ and $(\mathbf{k}_2, (1/T_2))$.
 - With this form of the equation, given the activation energy and the rate constant k₁ at a given temperature T₁, we can find the rate constant k₂ at any other temperature, T₂.

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

A Problem to Consider

• The rate constant for the formation of hydrogen iodide from its elements

$H_2(g) + I_2(g) \rightarrow 2HI(g)$

is 2.7 x 10⁻⁴ L/(mol·s) at 600 K and 3.5 x 10⁻³ L/(mol·s) at 650 K. Find the activation energy, $E_a.$

• Solving for E_a:

$$E_{a} = \frac{1.11 \times 8.31 \text{ J/mol}}{1.28 \times 10^{-4}} = 1.66 \times 10^{5} \text{ J}$$

A Problem to Consider • The rate constant for the formation of hydrogen iodide from its elements $H_2(g)+I_2(g) \rightarrow 2HI(g)$

is 2.7 x 10⁻⁴ L/(mol·s) at 600 K and 3.5 x 10⁻³ L/(mol·s) at 650 K. Find the activation energy, $\rm E_a.$

• Substitute the given data into the Arrhenius equation.

 $\ln \frac{3.5 \times 10^{-3}}{2.7 \times 10^{-4}} = \frac{E_{a}}{8.31 \text{ J/(mol \cdot K)}} \left(\frac{1}{600 \text{ K}} - \frac{1}{650 \text{ K}}\right)$

Transition-State Theory

- **Transition-state theory** explains the reaction resulting from the collision of two molecules in terms of an **activated complex**.
 - An activated complex (transition state) is an unstable grouping of atoms that can break up to form products.
 - A simple analogy would be the collision of three billiard balls on a billiard table.

A Problem to Consider

• The rate constant for the formation of hydrogen iodide from its elements

$H_2(g) + I_2(g) \rightarrow 2HI(g)$

is 2.7 x 10^{-4} L/(mol·s) at 600 K and 3.5 x 10^{-3} L/(mol·s) at 650 K. Find the activation energy, $E_a.$

• Simplifying, we get:

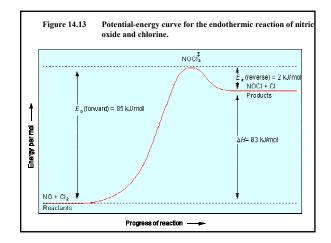
$$\ln (1.30 \times 10^{1}) = 1.11 = \frac{E_{a}}{8.31 \text{ J/(mol)}} \times (1.28 \times 10^{-4})$$

Transition-State Theory

- **Transition-state theory** explains the reaction resulting from the collision of two molecules in terms of an **activated complex**.
 - Suppose two balls are coated with a slightly stick adhesive.
 - We'll take a third ball covered with an extremely sticky adhesive and collide it with our joined pair.

Transition-State Theory

- **Transition-state theory** explains the reaction resulting from the collision of two molecules in terms of an **activated complex**.
 - The "incoming" billiard ball would likely stick to one of the joined spheres and provide sufficient energy to dislodge the other, resulting in a new "pairing."
 - At the instant of impact, when all three spheres are joined, we have an unstable transition-state complex.



Transition-State Theory

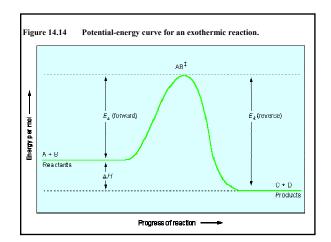
- **Transition-state theory** explains the reaction resulting from the collision of two molecules in terms of an **activated complex**.
 - If we repeated this scenario several times, some collisions would be successful and others (because of either insufficient energy or improper orientation) would not be successful.
 - We could compare the energy we provided to the billiard balls to the activation energy, E_a.

Potential-Energy Diagrams for Reactions

- The **potential-energy diagram** for an exothermic reaction shows that the products are more stable than the reactants.
 - Figure 14.14 illustrates the potential-energy diagram for an exothermic reaction.
 - We see again that the forward activation energy is required to form the transition-state complex.
 - In both of these graphs, the reverse reaction must still supply enough activation energy to form the activated complex.

Potential-Energy Diagrams for Reactions

- To illustrate graphically the formation of a transition state, we can plot the **potential energy** of a reaction versus **time**.
 - Figure 14.13 illustrates the endothermic reaction of nitric oxide and chlorine gas.
 - Note that the forward activation energy is the energy necessary to form the activated complex.
 - The △H of the reaction is the net change in energy between reactants and products.



Catalysis

•Catalyst: A substance that speeds up a reaction without being consumed

•Enzyme: A large molecule (usually a protein) that catalyzes biological reactions.

•Homogeneous catalyst: Present in the same phase as the reacting molecules.

•Heterogeneous catalyst: Present in a different phase than the reacting molecules.

Figure 12.16: Effect of a catalyst on the number of reaction-producing collisions.

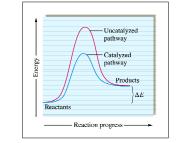
Catalysts

- A catalyst is a substance that provides a good "environment" for a reaction to occur, thereby increasing the reaction rate without being consumed by the reaction.
 - Its presence increases the rate of reaction by either increasing the frequency factor, A (from the Arrhenius equation) or lowering the activation energy, E_a .

Catalysts

- A catalyst is a substance that provides a good "environment" for a reaction to occur, thereby increasing the reaction rate without being consumed by the reaction.
 - To avoid being consumed, the catalyst must participate in at least one step of the reaction and then be regenerated in a later step.

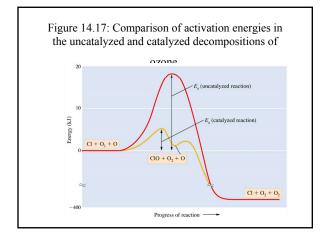
Figure 12.15: Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction.

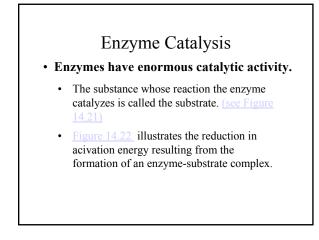


Catalysts

- Homogeneous catalysis is the use of a catalyst in the same phase as the reacting species.
 - The oxidation of sulfur dioxide using nitric oxide as a catalyst is an example where all species are in the gas phase.

 $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

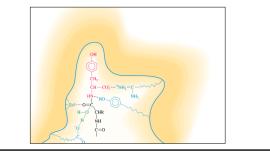




Catalysts

- Heterogeneous catalysis is the use of a catalyst that exists in a different phase from the reacting species, usually a solid catalyst in contact with a liquid or gaseous solution of reactants.
 - Such surface catalysis is thought to occur by chemical adsorbtion of the reactants onto the surface of the catalyst.
 - Adsorbtion is the attraction of molecules to a surface. (see Figure 14.18)

Figure 12.21: Protein-substrate interaction. The substrate is shown in black and red, with the red representing the terminal amino acid. Blue indicates side chains from the enzyme that help bind the substrate.



Heterogeneous Catalysis

Steps:

- 1. Adsorption and activation of the reactants.
- 2. Migration of the adsorbed reactants on the surface.
- 3. Reaction of the adsorbed substances.
- 4. Escape, or desorption, of the products.

Figure 14.22: Potential-energy curves for the reaction of substrate, S, to products, P.

