

## Chemistry 132 NT

**Nothing great was ever  
achieved without  
enthusiasm.**

Ralph Waldo Emerson

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## Rates of Reaction

### Module 4

- Reaction Mechanisms
- Elementary Reactions
- The Rate Law and the Mechanism
  - Catalysts



The burning of steel wool

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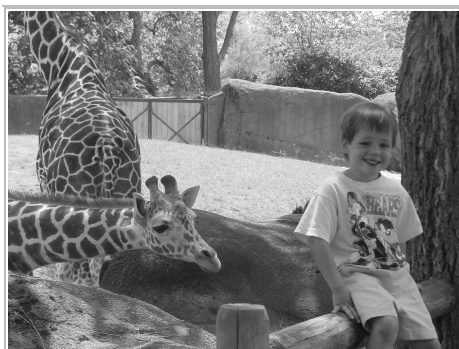
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## Review

- ✦ **Collision Theory** and the rate constant.
- ✦ The **Arrhenius equation**.

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## 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**.

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## Elementary Reactions

- ✦ Each **elementary** step is a singular molecular event resulting in the formation of products.
  - ◆ The set of **elementary reactions** that result in an **overall reaction** is called the reaction mechanism.
  - ◆ A **reaction intermediate** is a species produced during a reaction but is re-consumed in a later step. Consequently, it will not appear in the overall reaction.

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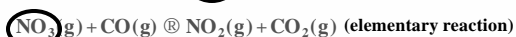
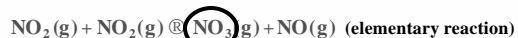
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## Elementary Reactions

- ✱ Consider the reaction of nitrogen dioxide with carbon monoxide.



- ✱ This reaction is believed to take place in two steps.



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## 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.



**Overall reaction**

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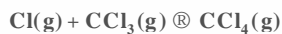
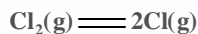
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## A Problem To Consider

- ✱ Carbon tetrachloride is obtained by the chlorination of chloroform,  $\text{CHCl}_3$ . The mechanism for the gas phase reaction is:



- ✱ Obtain the net, or overall, chemical equation from this mechanism.

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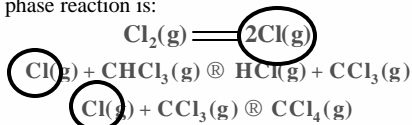
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### A Problem To Consider

- Carbon tetrachloride is obtained by the chlorination of chloroform,  $\text{CHCl}_3$ . The mechanism for the gas phase reaction is:



- The first step produces two Cl atoms (a reaction intermediate). One Cl atom is used in the second step and another is used in the third step.

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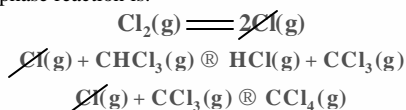
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### A Problem To Consider

- Carbon tetrachloride is obtained by the chlorination of chloroform,  $\text{CHCl}_3$ . The mechanism for the gas phase reaction is:



- Thus, all Cl atoms cancel

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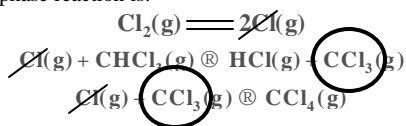
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### A Problem To Consider

- Carbon tetrachloride is obtained by the chlorination of chloroform,  $\text{CHCl}_3$ . The mechanism for the gas phase reaction is:



- Similarly, the intermediate  $\text{CCl}_3$ , produced in the second step, is used up in the third step.

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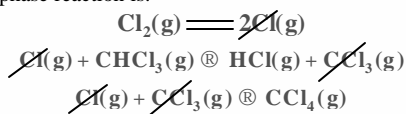
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### A Problem To Consider

- Carbon tetrachloride is obtained by the chlorination of chloroform,  $\text{CHCl}_3$ . The mechanism for the gas phase reaction is:



- You can cancel both  $\text{CCl}_3$  species.

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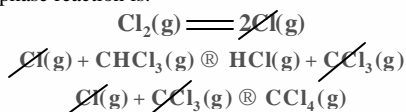
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### A Problem To Consider

- Carbon tetrachloride is obtained by the chlorination of chloroform,  $\text{CHCl}_3$ . The mechanism for the gas phase reaction is:



**The overall equation.**

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### 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.

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## 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.

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## Rate Equations for Elementary Reactions

- ✦ Since a chemical reaction may occur in several steps, there is no easy relationship between its **overall reaction** and its rate law.
- ✦ However, for **elementary reactions** (an individual single-step) the **rate is proportional to the concentrations of all reactant molecules involved**.

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## Rate Equations for Elementary Reactions

- ✦ For example, consider the generic (elementary) equation below.

**A** → **products**

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

$$\text{Rate} = k[A]$$

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### Rate Equations for Elementary Reactions

- ✦ However, for the elementary reaction



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

$$\text{Rate} = k[A][B]$$

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### Rate Equations for Elementary Reactions

- ✦ For a termolecular elementary reaction



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

$$\text{Rate} = k[A][B][C]$$

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### 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 elementary reaction



would have the rate law:

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

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### A Problem To Consider

- ◆ Ozone is converted to  $O_2$  by NO in a single step (that is, it is an elementary reaction).



Write the rate law for this elementary reaction.

- ◆ The rate law equation can be written directly from the elementary reaction (but only for an elementary reaction).

$$\text{Rate} = k[O_3][NO]$$

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### 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**.

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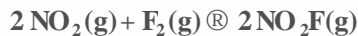
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### Rate Laws and Mechanisms

- ◆ Consider the reaction below.



- ◆ Experiments performed with this reaction show that the rate law is:

$$\text{Rate} = k[NO_2][F_2]$$

- ◆ The reaction is first-order with respect to each reactant even though the coefficient for  $NO_2$  in the overall reaction is two.

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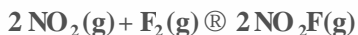
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## Rate Laws and Mechanisms

- ✦ Consider the reaction below.



- ✦ Experiments performed with this reaction show that the rate law is:

$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$

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

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## 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**.

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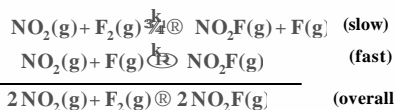
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## Rate Determining Step

- ✦ 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.



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## 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 =  $k_1[\text{NO}_2][\text{F}_2]$** .



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## Rate Determining Step

- ✦ So, 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.

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## 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 only be expressed in terms of substances that appear in the overall reaction.**

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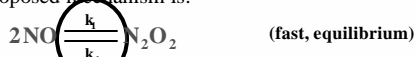
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## Rate Determining Step

- Consider the reduction of nitric oxide with  $\text{H}_2$ .



- A proposed mechanism is:



- It has been experimentally determined that the rate law is: **Rate = k [NO]<sup>2</sup>[H<sub>2</sub>]**

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## Rate Determining Step

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



(Rate law for the rate determining step)

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

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## Rate Determining Step

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



(Rate law for the rate determining step)

- It is necessary to re-express this proposed rate law eliminating  $[\text{N}_2\text{O}_2]$ .

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## Rate Determining Step

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

$$\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$$

(Rate law for the rate determining step)

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

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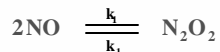
## Rate Determining Step

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

$$\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$$

(Rate law for the rate determining step)

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



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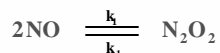
## Rate Determining Step

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

$$\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$$

(Rate law for the rate determining step)

$$\text{Rate forward} = k_1[\text{NO}]^2$$



$$\text{Rate reverse} = k_{-1}[\text{N}_2\text{O}_2]$$

equal

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## Rate Determining Step

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

$$\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$$

(Rate law for the rate determining step)

- ✦ At equilibrium, the forward rate and the reverse rate are equal.

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

Rate forward = Rate reverse

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## Rate Determining Step

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

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

(Rate law for the rate determining step)

- ✦ Therefore,

$$[\text{N}_2\text{O}_2] = (k_1/k_{-1})[\text{NO}]^2$$

- ✦ If we substitute this into our proposed rate law we obtain:

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## Rate Determining Step

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

$$\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$$

(Rate law for the rate determining step)

$$\text{Rate} = k_2 \left( \frac{k_1}{k_{-1}} [\text{NO}]^2 \right) [\text{H}_2]$$

- ✦ If we replace the constants ( $k_2, k_1/k_{-1}$ ) with  $k$ , we obtain the observed rate law: **Rate =  $k[\text{NO}]^2[\text{H}_2]$**

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## 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.

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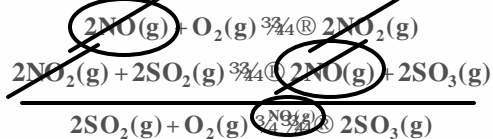
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## Catalysts

✱ **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.



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## Catalysts

✱ Note that the catalyst is an **active participant** in the reaction.

- ◆ The catalyzed reaction mechanism provides an **alternative reaction pathway** having an increased rate.
- ◆ It increases the rate by either increasing the frequency factor, **A** (from the Arrhenius equation) or by lowering the activation energy, **E<sub>a</sub>**.

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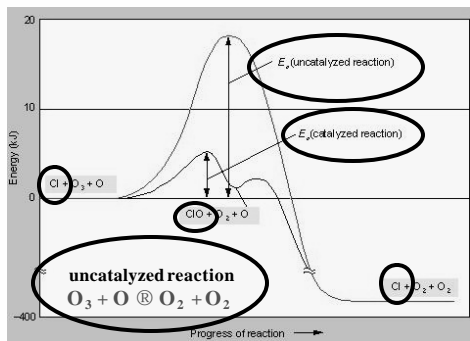
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Comparison of activation energies in the uncatalyzed and catalyzed decomposition of ozone.



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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 adsorption** of the reactants onto the surface of the catalyst.
- ◆ **Adsorption** is the attraction of molecules to a surface.

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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.

- ◆ **Surface catalysts** are used in the catalytic converters of automobiles to aid in the combustion of exhaust gases.

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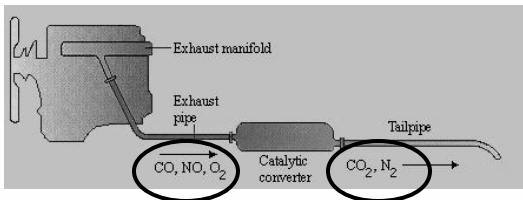
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### Automobile catalytic converter.



Exhaust gases from the engine pass to the exhaust manifold, then to the catalytic converter, where pollutants NO and CO are converted to CO<sub>2</sub> and N<sub>2</sub>.

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## Enzyme Catalysis

### Enzymes have enormous catalytic activity.

- ◆ The substance whose reaction the enzyme catalyzes is called the **substrate**.
- ◆ There is a reduction in activation energy resulting from the formation of an **enzyme-substrate complex**.

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## Key Equations

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad \log \frac{[A]_t}{[A]_0} = \frac{-kt}{2.303}$$

$$t_{1/2} = \frac{0.693}{k} \quad \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

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## Operational Skills

- ✦ Writing the overall chemical equation from a mechanism
- ✦ Determining the molecularity of an elementary reaction
- ✦ Writing the rate equation for an elementary reaction
- ✦ Determining the rate law from a mechanism

Time for a few review questions.

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