

## Chapter 12

## Chemical Kinetics



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## 12.1 Kinetics

- ▶ The study of rates of reactions and reaction mechanisms (e.g., how fast a reaction will go and what steps it goes through)
- ▶ What is rate?
- ▶ Definition of reaction rate: the change in concentration of a reactant or product over change in time  $\rightarrow \Delta[A] / \Delta t$



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## 12.1 Factors that Affect Rate

- ▶ Concentrations
- ▶ Temperature
- ▶ Pressure
- ▶ Catalysts
- ▶ Surface area



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- ▶ How can rate be represented on a graph?
- ▶ What happens to  $\text{NO}_2$  over time?  $\text{NO}$ ?  $\text{O}_2$ ?
- ▶ How can their rates be expressed relative to each other?

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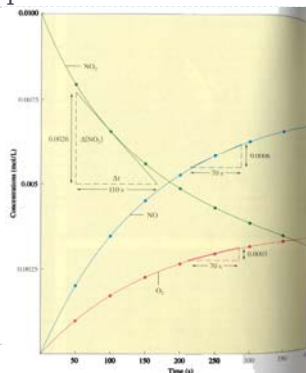
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### 12.1 Graph of Reaction




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### 12.1 Relative Rates

- ▶ Rate of  $\text{NO}_2$  consumption =
- Rate of  $\text{NO}$  production =
- $2 \times$  Rate of  $\text{O}_2$  production

$$-\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t} = 2 \frac{\Delta[\text{O}_2]}{\Delta t}$$

- ▶ Then

$$-\frac{\Delta[\text{NO}_2]}{2\Delta t} = \frac{\Delta[\text{NO}]}{2\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

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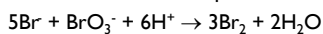
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### 12.1 Relative Rates

- ▶ If  $\text{NO}_2$  is disappearing at a rate of  $4.2 \times 10^{-5} \text{ M/s}$ , what is the rate of appearance of  $\text{O}_2$ ?

$$-\left(\frac{1}{2}\right) \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

- ▶ Write the rates of the species in the following reaction:



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### Group Quiz #1

- ▶ According to the following **unbalanced** reaction, if the rate of appearance of oxygen gas is  $4.00 \times 10^{-2} \text{ M/s}$ , what is the rate of disappearance of  $\text{KClO}_3 (\text{g})$ ?



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### 12.2 Rate Laws & Reaction Order

- ▶ What happens to a chemical reaction over time?
- ▶ Over time, the change in concentration will depend on the forward and reverse reactions.
- ▶ To simplify things, choose conditions before products become significant
  - ▶ This allows us to examine rates using **only** reactants

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## 12.2 Rate Laws

- ▶ Reaction:
  - ▶  $aA + bB \rightarrow \text{Products}$
- ▶ Rate Law:

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

- ▶ **k is Rate Constant**
- ▶ **m & n are the order of reactants (NOT the coefficient); m & n must be determined experimentally!**
- ▶ **Reaction Order = sum of reactant orders**

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## 12.2 Rate Laws

- ▶ **Rate law** of the decomposition reaction of  $\text{NO}_2$ 
  - ▶  $\text{Rate} = k[\text{NO}_2]^m$
  - ▶ **k = rate constant**
  - ▶ **m is order of reactant (NOT the coefficient); m must be determined experimentally**
- ▶ Why do we want to determine the rate of a reaction?

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## 12.2 Types of Rate Laws

- ▶ **Differential Rate Law (or Rate Law)**
  - ▶ rate depends on concentration

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^m$$

- ▶ **Integrated Rate Law**
  - ▶ rate depends on time

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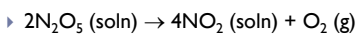
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### 12.3 Determining the Rate Law



$[\text{N}_2\text{O}_5]$	Rate (M/s)
0.90 M	$5.4 \times 10^{-4}$
0.45 M	$2.7 \times 10^{-4}$

- ▶ What happens to rate as concentration is halved?  
 ▶ What order is  $\text{N}_2\text{O}_5$ ?

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### 12.3 Initial Rates

- ▶ Initial rates are measured just after a reaction begins

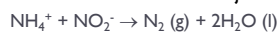


TABLE 14.3 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

Experiment Number	Initial $\text{NH}_4^+$ Concentration (M)	Initial $\text{NO}_2^-$ Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	$5.4 \times 10^{-7}$
2	0.0200	0.200	$10.8 \times 10^{-7}$
3	0.0400	0.200	$21.5 \times 10^{-7}$
4	0.0600	0.200	$32.3 \times 10^{-7}$
5	0.200	0.0202	$10.8 \times 10^{-7}$
6	0.200	0.0404	$21.6 \times 10^{-7}$
7	0.200	0.0606	$32.4 \times 10^{-7}$
8	0.200	0.0808	$43.3 \times 10^{-7}$

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### 12.3 Initial Rates

- ▶ The reaction is first order in  $\text{NO}_2^-$ .  
 ▶ The reaction is first order in  $\text{NH}_4^+$ .  
 ▶ What is the overall order of the reaction?  
 ▶ Sum of exponents  
 ▶ Note: exponents can also be negative, fraction  
 ▶ How can you find the value of the rate constant?  
 ▶ What units will  $k$  have?

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### Group Quiz #2

- ▶ The following experimental data was collected for this reaction.  $2 \text{NO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$ . What is the rate law? Show your work and circle your final answer.

Trial	[NO] (M)	[H <sub>2</sub> ] (M)	Rate (M/s)
1	0.60	0.15	0.076
2	0.60	0.30	0.15
3	0.60	0.60	0.30
4	1.20	0.60	1.21

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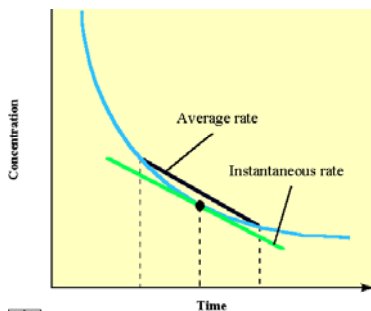
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### 12.3 Instantaneous vs. Average Rates




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### 12.3 Initial Rates

- ▶ What is the overall order of the reaction of the following?
- ▶ Rate =  $k[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$
  - ▶ Rate =  $k[\text{I}^-][\text{OCl}^-]/[\text{OH}^-]$

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### 12.4 Integrated Rate Law

- ▶ Only look at 0<sup>th</sup>, 1<sup>st</sup>, and 2<sup>nd</sup> order reactions
- ▶ What do these orders mean (how does a change in concentration affect the rate)?

▶ Ex:  $\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^n$

- ▶ Integrate w.r.t. time to get 1<sup>st</sup> order IRL (calculus ☺)

$$\ln \frac{[\text{NO}_2]_t}{[\text{NO}_2]_0} = -kt$$

$$\ln[\text{NO}_2]_0 - \ln[\text{NO}_2]_t = kt$$

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### 12.4 Integrated Rate Law

- ▶ Can modify to get linear form: (refer to Appendix A, p.A5-6 for log functions)

- ▶ Reaction A → products

- ▶  $\ln [A]_t = -kt + \ln [A]_0$

- ▶  $y = \ln [A]$

- ▶  $m = -k$

- ▶  $x = t$

- ▶  $b = \ln [A]_0$

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### 12.4 Integrated Rate Law

Table A.1 in Appendix A

Eqn ( $y=mx+b$ )	y vs. x	m	b
$[A] = -kt + [A]_0$	$[A]$ vs. $t$	$-k$	$[A]_0$
$\ln [A] = -kt + \ln [A]_0$	$\ln[A]$ vs. $t$	$-k$	$\ln[A]_0$
$1/[A] = kt + 1/[A]_0$	$1/[A]$ vs. $t$	$k$	$1/[A]_0$

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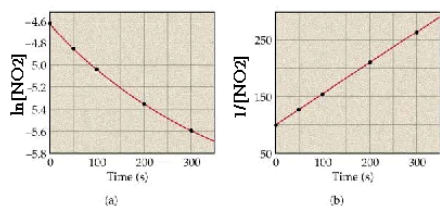
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## 12.4 IRL

► What order is this reaction?




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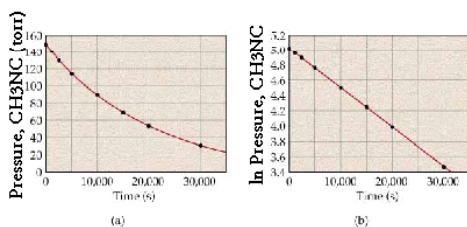
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## 12.4 IRL

► What order is this reaction?




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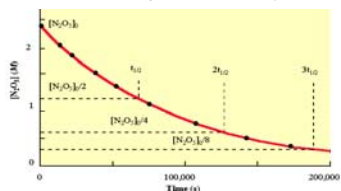
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## 12.5 IRL &amp; Half-lives

► By definition,  $[A] = [A]_0/2$ , when  $\tau = \tau_{1/2}$



- 0<sup>th</sup> order:  $\tau_{1/2} = [A]_0/2k$
- 1<sup>st</sup> order:  $\tau_{1/2} = 0.693/k$
- 2<sup>nd</sup> order:  $\tau_{1/2} = 1/k[A]_0$
- Table 12.6 gives summary of equations

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### 12.5 IRL & Half-lives

- ▶ Example: Determine the half life of a substance that has a rate constant of  $1.7 \times 10^{-3} \text{ s}^{-1}$  (1<sup>st</sup> order)

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### Rate Laws Summary

- ▶ Be able to find the orders of reactants given table of rate and concentration data
- ▶ Know what it means to say a reactant is a certain order
- ▶ Given a rate law, know how changing concentration changes rate
- ▶ Know the graphs of the orders of reactions
- ▶ Be able to interpret the order of reaction from a graph

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### 12.8 Reaction Mechanisms

- ▶ Mechanisms outline the steps in a reaction that will convert the reactant(s) into product(s)
- ▶ May be one or many steps involved
- ▶ Chemical equation **may or may not** describe the mechanism

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### 12.8 Reaction Mechanisms

- ▶  $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$
- ▶  $\text{Rate} = k[\text{NO}_2]^2$
- ▶ Does the rate match the equation?
- ▶ Divide reaction into elementary steps:
  - ▶  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$       Slow
  - ▶  $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$       Fast

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### 12.9 Rate Laws for Elementary Steps

- ▶ Elementary steps are defined by their **molecularity** - the number of molecules that have to collide to give the defined products.
  - ▶ **Unimolecular** - 1 reactant      = Rate =  $k[\text{A}]$
  - ▶ **Bimolecular** - 2 reactants      = Rate =  $k[\text{A}]^2$   
or Rate =  $k[\text{A}][\text{B}]$
  - ▶ **Termolecular** - 3 reactants      = Rate =  $k[\text{A}]^3$   
or Rate =  $k[\text{A}]^2[\text{B}]$   
or Rate =  $k[\text{A}][\text{B}][\text{C}]$
- ▶ See Table 12.5, p. 466

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### 12.8 Reaction Mechanisms

- ▶  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$       Slow
- ▶  $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$       Fast
- ▶  $\text{NO}_3$  is an intermediate (produced in 1st step, consumed in last)
- ▶  $\text{NO}_2$  is a catalyst (consumed in 1st step, produced in last)
- ▶ Elementary steps sum to give overall equation (Hess's Law)

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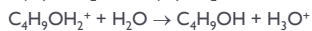
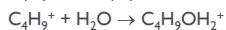
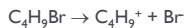
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### 12.8 Reaction Mechanisms

- ▶ Identify the intermediate(s) and catalyst(s) in the following steps:



- ▶ What is the overall equation?
- ▶ Write the rate law for each step.

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### 12.10 Rate Law for Overall Reactions

- ▶ Analogy: Running Errands
- ▶ Overall reaction can only occur as fast as the slowest step (**R**ate **D**etermining **S**tep - rds)
- ▶ If rds is the first step, rate law is easy
- ▶ If rds is second or later, more mathematically involved (we won't do this ☺)

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### 12.10 Rate Law for Overall Reactions

- ▶ Mechanisms must agree with the rate law:
- ▶ Example
  - ▶  $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$
  - ▶ Rate =  $k[\text{NO}_2][\text{F}_2]$  → determined experimentally
  - ▶ Suggested mechanism:
    - ▶  $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$       slow
    - ▶  $\text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F}$               fast
- ▶ Is this an acceptable mechanism?
- ▶ What's the intermediate? Catalyst?

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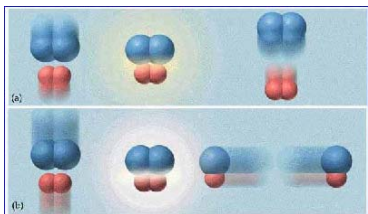
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## 12.11 Model for Kinetics

- ▶ What makes molecules react and form new species?
- ▶ What would result in no reaction?




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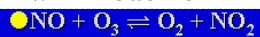


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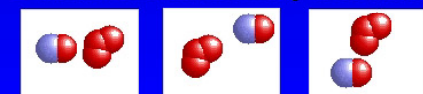


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## 12.11 Model for Kinetics



- Which collisions are likely to be effective?



- ▶ Draw pictures of some effective and ineffective collisions.

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## 12.11 Model for Kinetics

- ▶ Only a small fraction of collisions will produce a reaction. Why?
- ▶ The *threshold energy*, or activation energy, must be overcome for a reaction to occur.
- ▶ It takes energy to break and make bonds;

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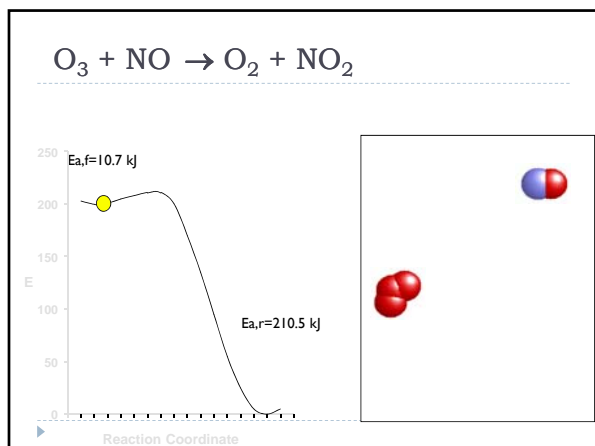
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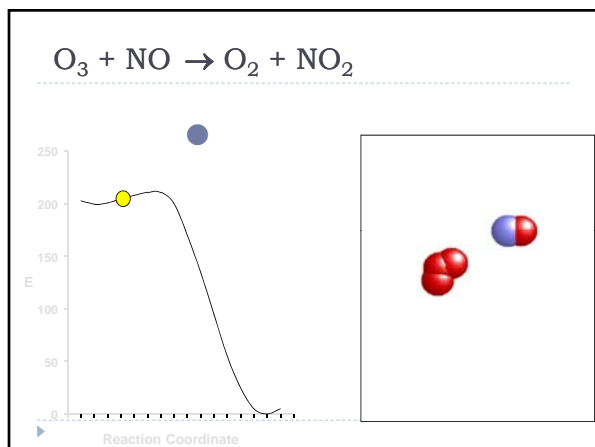
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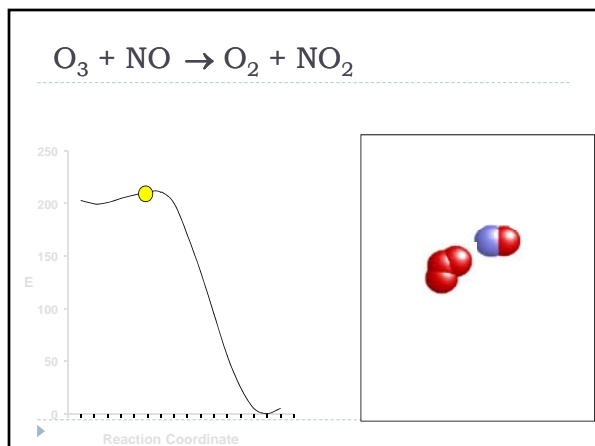
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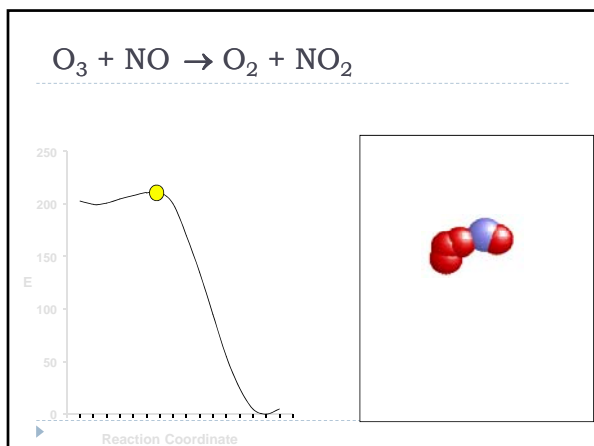
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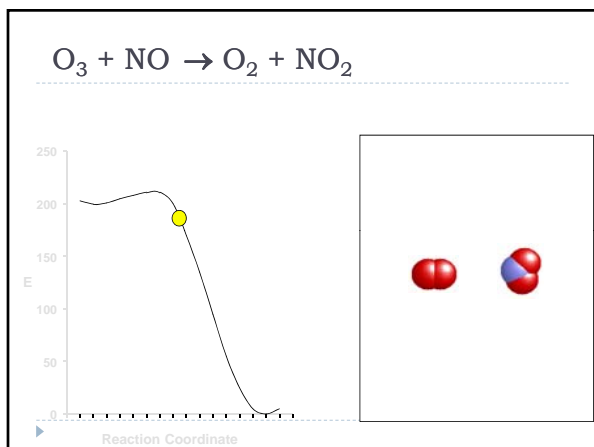
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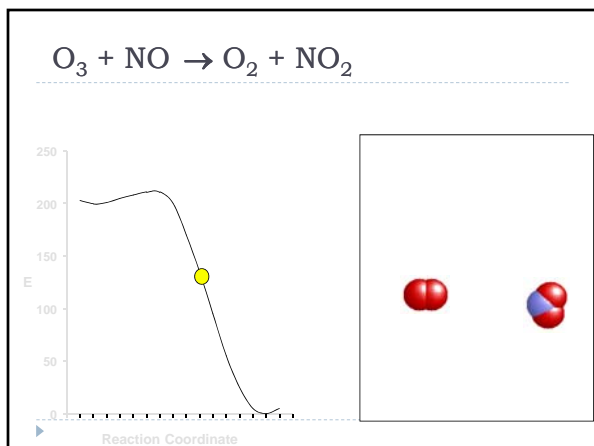
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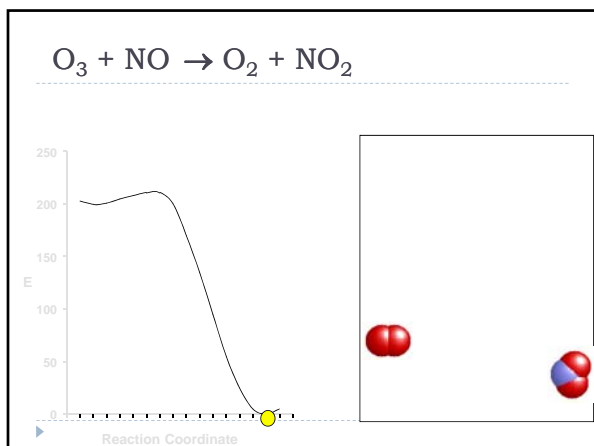
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### 12.11 Reaction Mechanisms

- At maximum energy, energy barrier, the atoms form a transition state

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### 12.11 Reaction Mechanisms

- Why does the rate depend on  $E_a$  and not on  $\Delta E$ ?

Exothermic reaction	Endothermic reaction
<p>Reaction coordinate A. Exothermic reaction: <math>O_3 + NO \rightarrow O_2 + NO_2</math></p>	<p>Reaction coordinate B. Endothermic reaction: <math>O_2 + Cl_2 \rightarrow O_2Cl_2</math></p>

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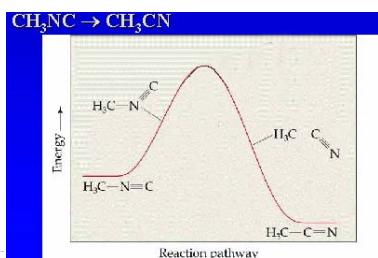
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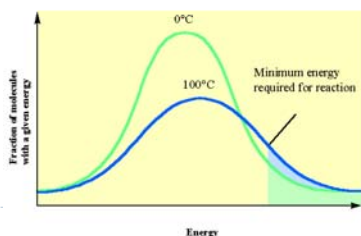
### 12.11 Reaction Mechanisms

- ▶ Identify  $E_{a,f}$ ,  $E_{a,r}$ ,  $\Delta E$ , transition state, and exo- or endothermicity for the reaction below.



### 12.11 Model for Kinetics

- ▶ Only the collisions with energy  $> E_a$  will react to give products
- ▶ What can increase the number of collisions?



### 12.11/12.12 Arrhenius

- ▶ The fraction of collisions increases exponentially with temperature.
- ▶ Arrhenius:  $k = Ae^{-E_a/RT}$ 
  - ▶  $k$  = # of collisions at  $E_a$  (rate constant predicted by collision theory)
  - ▶  $A$  = frequency factor
  - ▶  $E_a$  = activation energy
  - ▶  $R$  = gas constant (8.3145 J/mol K)
  - ▶  $T$  = temperature in K
- ▶ Linear form:  $\ln k = -E_a/RT + \ln A$

## 12.12 Arrhenius

- ▶ Can find  $E_a$  from 2 reactions: subtract 2nd equation from the first to give

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

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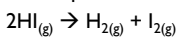
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## 12.12 Arrhenius

- ▶ Example:



Temperature (°C)	$k(\text{M}^{-1}\text{s}^{-1})$
283	$3.52 \times 10^{-7}$
356	$3.02 \times 10^{-5}$
393	$2.19 \times 10^{-4}$
427	$1.16 \times 10^{-3}$
508	$3.95 \times 10^{-2}$

- Find  $E_a$  using all five data points
- Calculate  $E_a$  from rate constants at 283°C and 508°C
- Given rate constant at 283°C and  $E_a$  from b), what is the rate constant at 293°C

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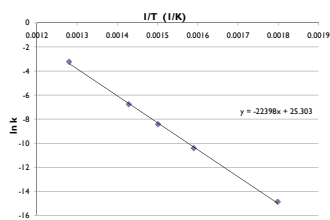
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## 12.12 Arrhenius

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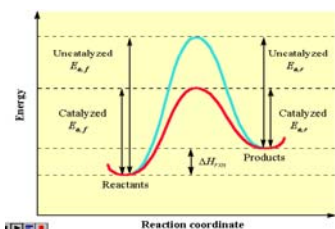
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### 12.13 Catalysis

- ▶ Catalysts speed up a reaction without being consumed
- ▶ Gives reactions a new (lower) activation energy and larger percent of successful collisions



### 12.14 Catalysis

- ▶ Homogeneous catalysis - catalyst is in the same phase as the reacting molecules
- ▶ Heterogeneous catalysis - catalyst is in a different phase (usually a solid)

### 12.14 Catalysis

- ▶ Homogeneous catalysts - nitric oxide toward ozone
  - $N_2 + O_2 \rightarrow 2NO$  (in lower atmosphere)
  - $2NO + O_2 \rightarrow 2NO_2$
  - $NO_2 \rightarrow NO + O$  ( $NO_2$  absorbs light)
  - $O_2 + O \rightarrow O_3$  (ozone is toxic, reacts with other pollutants to form irritating substances)

The End

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