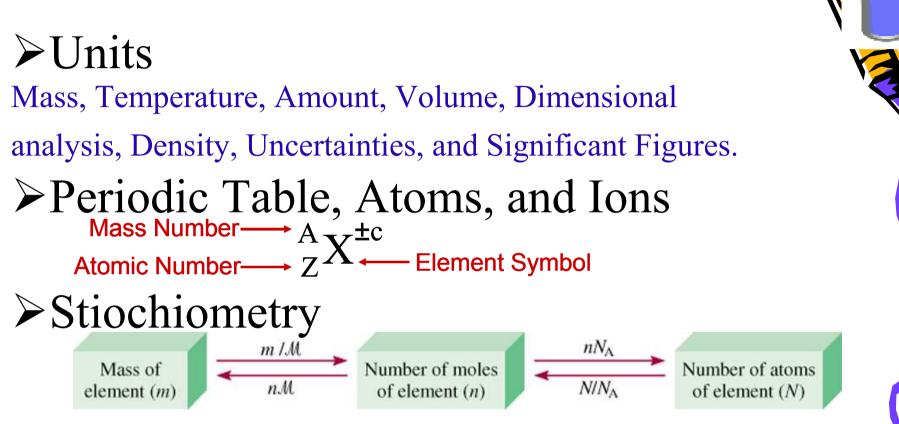


# CHEM 102

# **General Chemistry II**

Dr. M. A. Morsy Chemistry Department, KFUPM

# CHEM 101 Review



#### Concentration units



Mass Percent (%), Mole Fraction (X), Molarity(M), Molality (m), Normality (N)

# CHEM 101 Review

Reaction: Balance and Stoichiometry

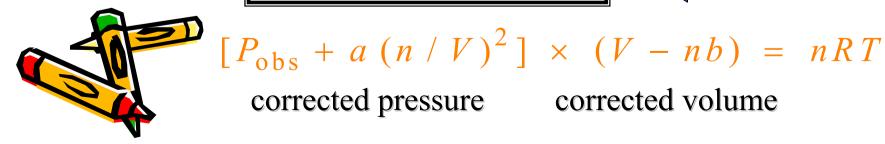
Types: Precipitation, Acid-base, Redox...



➤Thermochemistry First law of thermodynamics:  $\Delta E = q + w$  $q = C\Delta t = ms\Delta t$  and  $w_{exp} = -P\Delta V$ 

Gas Laws

$$P X V = nRT$$



corrected pressure corrected volume

Ideal Gas Law

# CHEM 101 Review

Vapor Pressure Lowering,

Freezing Point Depression,

**Boiling Point**, Elevation

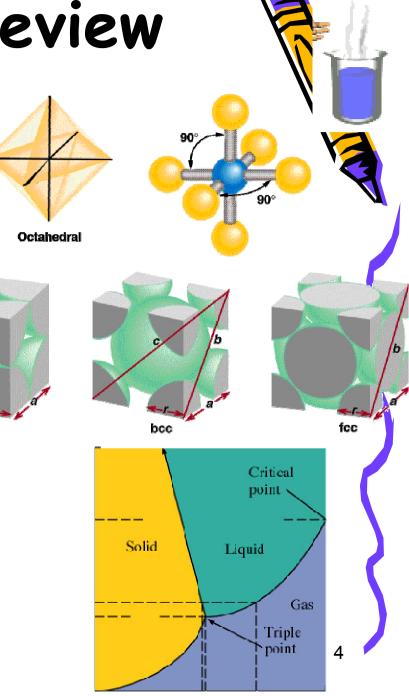
Osmotic Pressure..

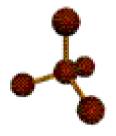
S00

Molecules and Geometry Ionic, Covalent, Lewis Structure, VSEPR, Hybridization, Molecular Orbital Model

Liquid and Solids IMF (Dipole-dipole, Dispersion, Hydrogen Bonding), Solids (Unit cell-SC, BCC, FCC),..

➢ Properties of Solutions





# Chapter 12

# **Chemical Kinetics**



# **Course Outline**



- Chemical Kinetics (Chap.12)
- Chemical Equilibrium (Chap. 13)
- Acid-Base and Aqueous Equilibria (Chap. 14 & 15)
- Spontaneity, Entropy, and Free Energy (Chap. 16)
- Electrochemistry (Chap. 17)
- The nucleus: A chemist View (Chap. 18)
- The Representative Elements: 1A to 8A (Chap. 19 & 20)
- Transition Chemistry: Coordination Chemistry (Chap. 21)
- Organic Chemistry: Biological Molecules (Chap. 22)



# Chapter 12 Preview

#### **Chemical Kinetics**



Reaction Rates Stoichiometry, Conditions, Concentration Rate Laws Types (Order), Initial Rate, First Order, Second Order and Zero Order Rxns Reaction Mechanisms and Model of **Chemical Kinetics** Catalysis Heterogeneous and Homogeneous



### Introduction



- The main goal of Chemical Kinetics is to understand the steps by which a reaction take place.
- The understanding will allow us to find ways to facilitate or inhibit the reactions,

e.g., Haber process for Ammonia production requires high temperature (more cost for commercially feasibility), while presence of iron oxide speeds up the reaction.

**Thermodynamics** – does a reaction take place?

**Kinetics** – how fast does a reaction proceed?



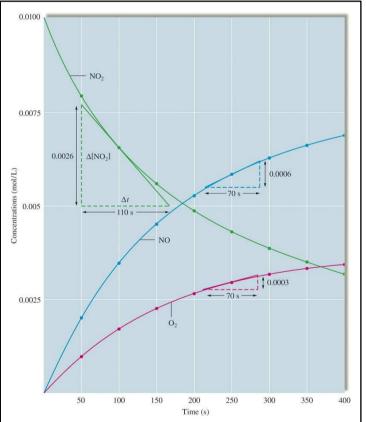
## **12.1 Reaction Rates**

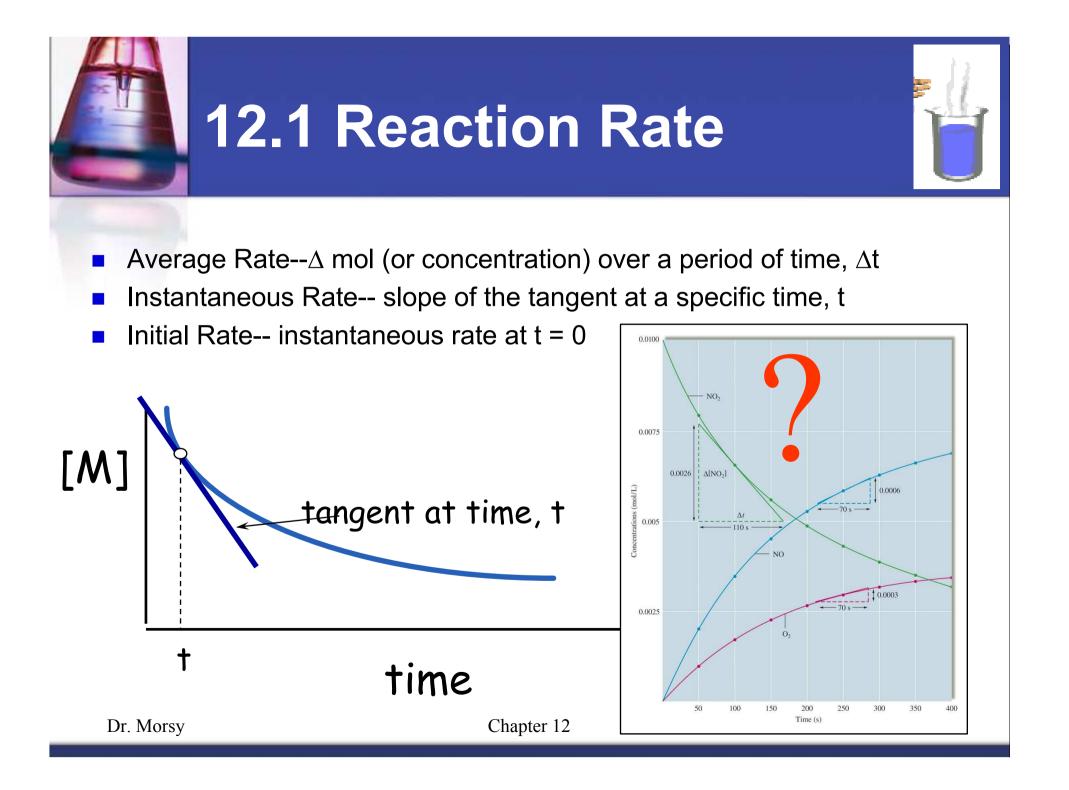
**Reaction rate** is the change in the concentration of a reactant or a product with time (*M*/s).

Figure 12.1 Following reaction at 300 °C and Oxygen are Plotted versus Time

$$2NO_{2}(g) \longrightarrow 2NO(g) + O_{2}(g)$$
  
Average Rate 
$$= \frac{\Delta M}{\Delta t}$$

Rate of the *disappearance* of NO2 is equal in magnitude but opposite in sign to the rate of the *appearance* of NO and half of the *appearance* of  $O_2$ 

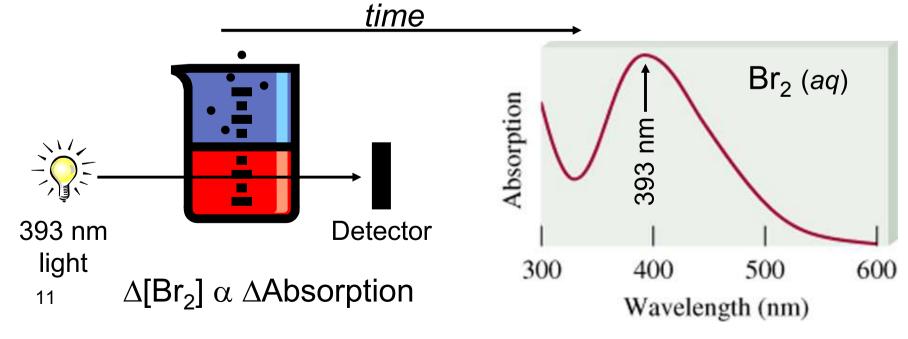


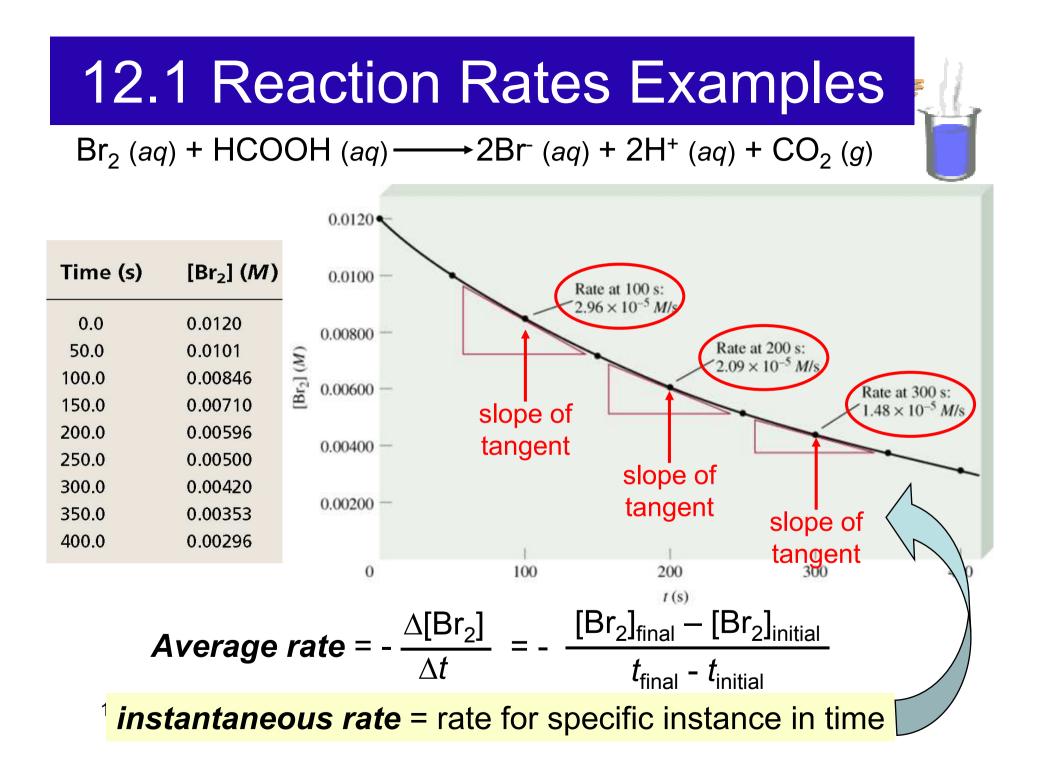


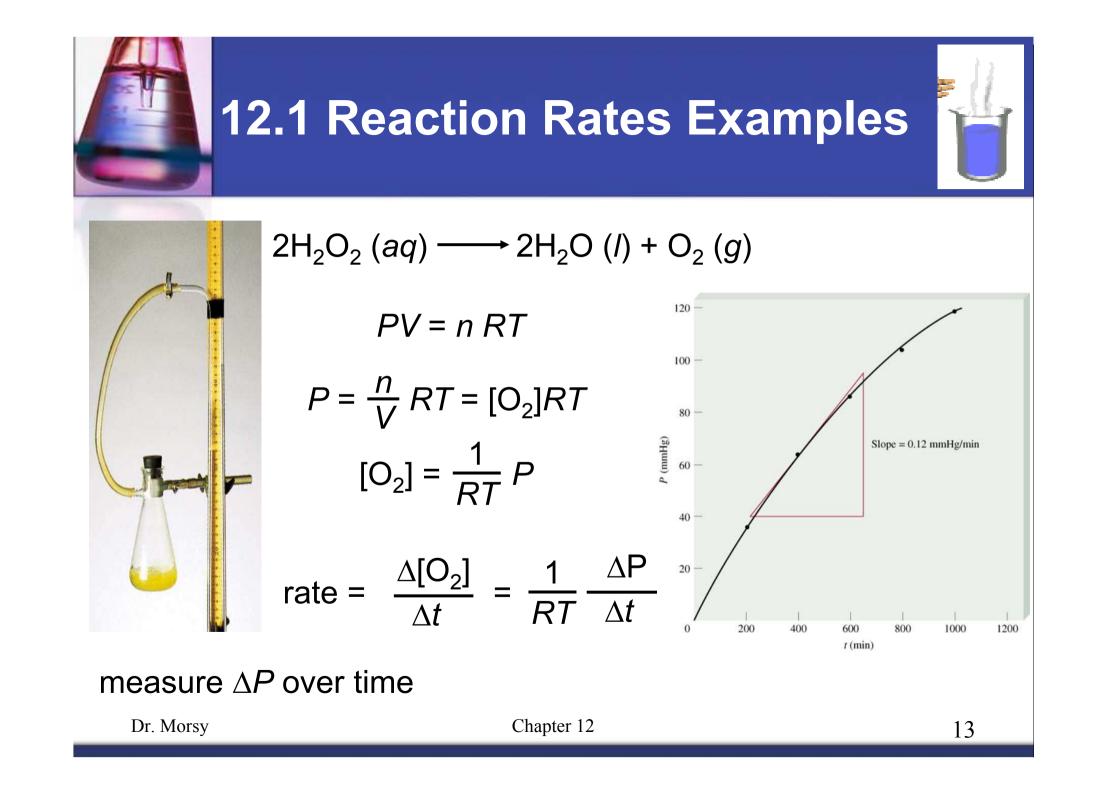
## 12.1 Reaction Rates Examples

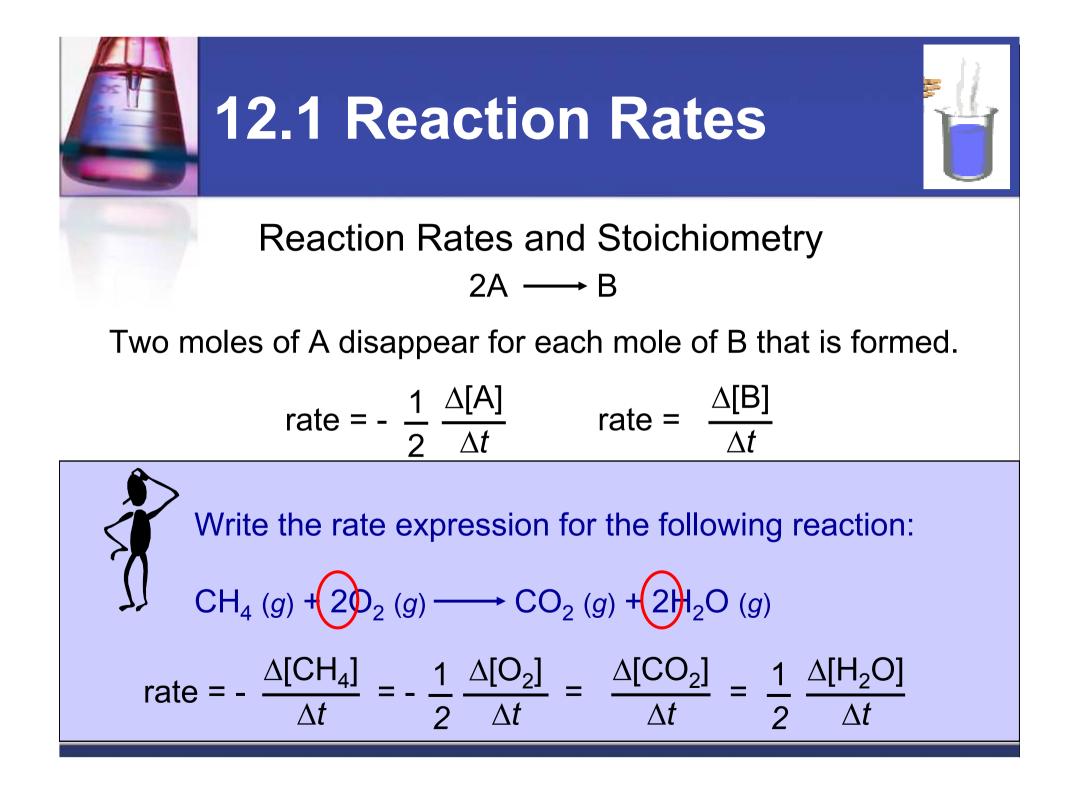
 $Br_2(aq) + HCOOH(aq) \longrightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(q)$ 













The *rate law* expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.



 $aA + bB \longrightarrow cC + dD$ 

Rate = 
$$k [A] \times B$$

reaction is *x***th order** in A reaction is *y***th order** in B

reaction is (x +y)th order overall

*k* is the rate constant for the reaction

#### **Types of Rate Laws**

A. Differential rate law: how rate depend on concentration.

B. Integrated rate law: how the concentration depend on time.



#### **Examples:**



 $= 2N_2O_5 => 4NO_2 + O_2$ rate =  $k[N_2O_5]$  1<sup>st</sup> order  $\blacksquare 2NO + Cl_2 => 2NOCI$ rate =  $k[NO]^2[CI_2]$  3<sup>rd</sup> order  $= 2NH_3 => N_2 + 3H_2$ rate =  $k[NH_3]^0 = k$  0<sup>th</sup> order

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Chapter 12



# 12.2 Rate Law Summary

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.

$$F_{2}(g) + 2CIO_{2}(g) \longrightarrow 2FCIO_{2}(g)$$
  
rate = k [F<sub>2</sub>][CIO<sub>2</sub>]<sup>1</sup>



# 12.3 Determination of the Form of Rate Law

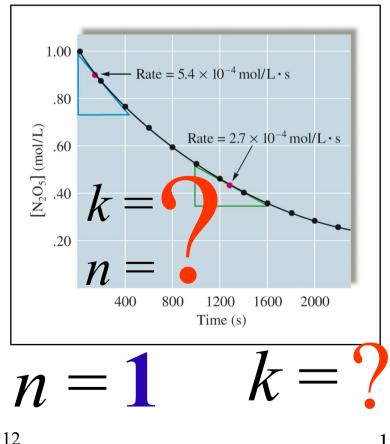
Figure 12.3 A Plot of the Concentration of  $N_2O_5$  as a Function of Time for the Reaction

$$2N_2O_5(soln) \rightarrow 4NO_2(soln) + O_2(g)$$

$$rate = -\frac{\Delta[N_2O_5]}{\Delta t} = k[N_2O_5]^n$$
at  $M_1$ =0.90 Mol/L ...  $r_1 = 5.4 \ge 10^{-4}$  Mol/L.s

at 
$$M_2$$
=0.45 Mol/L ...  $r_2$  = 2.7 x 10<sup>-4</sup> Mol/L.s

Exponent Value	[conc]	rate	
0	double	same	
1	double	double	
2	double	x 4	
3	double	x 8	
4	double	x 16	
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# 12.3 Determination of the Form of Rate Law



 $F_2(g) + 2CIO_2(g) \longrightarrow 2FCIO_2(g)$ 

rate =  $k [F_2]^x [CIO_2]^y$ k =x =

#### Initial Rates Method

v =

Table 13.2Rate Data for theReaction between F2 and CIO2



Double  $[F_2]$  with  $[CIO_2]$  constantRate doublesQuadruplx = 1Rate quadrupl

rate = 
$$k [F_2][CIO_2]$$

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Determine the rate law and calculate the rate constant for the following reaction from the following data:  $S_2O_8^{2-}(aq) + 3I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$ 

Experiment	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ]	[I-]	Initial Rate ( <i>M</i> /s)
1	0.08	0.034	2.2 x 10 <sup>-4</sup>
2	0.08	0.017	1.1 x 10 <sup>-4</sup>
3	0.16	0.017	2.2 x 10 <sup>-4</sup>

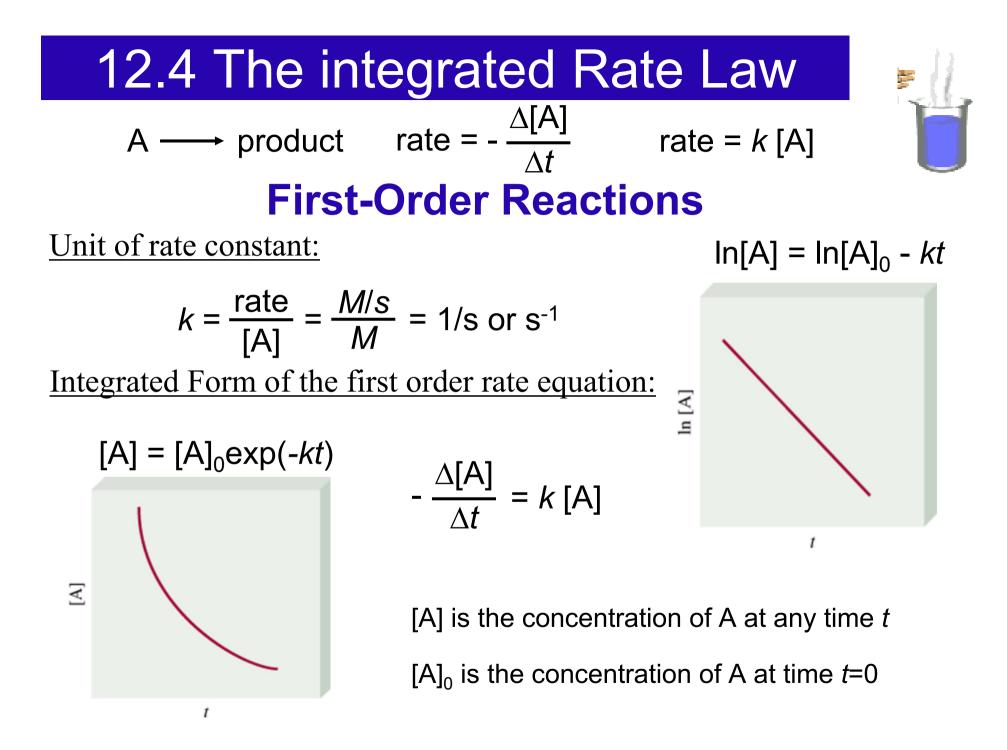
rate = 
$$k [S_2O_8^{2-}]^x[I^-]^y$$
  
 $y = 1$   
 $x = 1$   
rate =  $k [S_2O_8^{2-}][I^-]$ 

Double [I-], rate doubles (experiment 1 & 2)

Double  $[S_2O_8^{2-}]$ , rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[S_2 O_8^{2}][I]} = \frac{2.2 \times 10^{-4} \, \text{M/s}}{(0.08 \, \text{M})(0.034 \, \text{M})} = 0.08 / \text{M} \cdot \text{s}$$

20

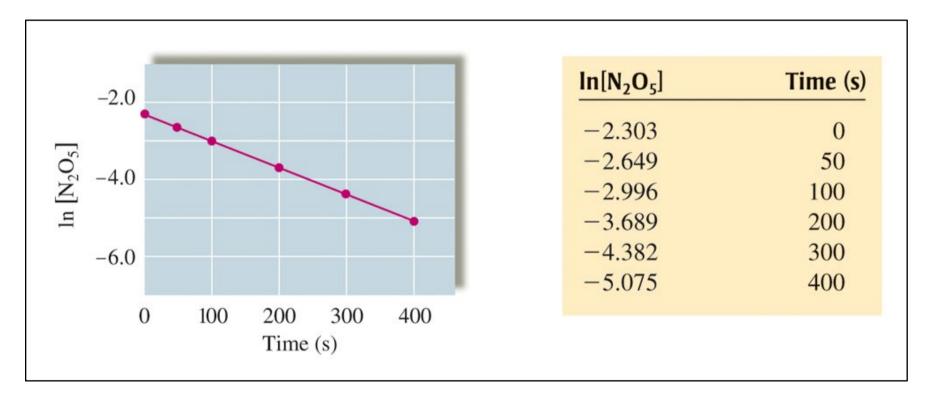


**First-Order Reactions** 



Figure 12.4 A Plot of In[N<sub>2</sub>O<sub>5</sub>] versus Time

 $2N_2O_5(soln) \rightarrow 4NO_2(soln) + O_2(g)$ 



## **First-Order Reactions**



The reaction  $2A \longrightarrow B$  is first order in A with a rate constant of 2.8 x  $10^{-2}$  s<sup>-1</sup> at 80<sup>o</sup>C. How long will it take for A to decrease from 0.88 *M* to 0.14 *M*?

$$\ln[A] = \ln[A]_0 - kt$$
 [A]<sub>0</sub> = 0.88 M

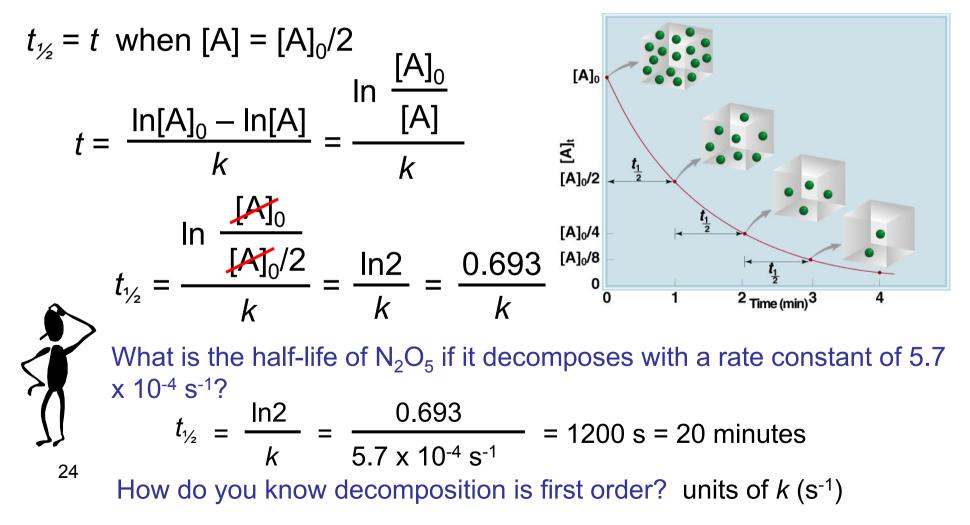
$$kt = \ln[A]_0 - \ln[A] \qquad [A] = 0.14 M$$

$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \frac{[A]_0}{[A]}}{k} = \frac{\ln \frac{0.88 M}{0.14 M}}{2.8 \times 10^{-2} \text{ s}^{-1}} = 66 \text{ s}$$

#### Half-life time of the First-Order Reactions

The **half-life**,  $t_{1/2}$ , is the time required for the concentration of a reactant to decrease to half of its initial concentration.

20



$$A \longrightarrow \text{product} \quad \text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = k [A]^2$$
$$A \longrightarrow \text{product} \quad \text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = k [A]^0$$

÷

Second-Order Reactions Zero-Order Reactions Unit of rate constant

$$k = \frac{\text{rate}}{[A]^2} = \frac{M/s}{M^2} = 1/M \cdot s$$
  $k = \frac{\text{rate}}{[A]^0} = M/s$ 

Integrated Form of the first order rate equation

$$-\frac{\Delta[A]}{\Delta t} = k [A]^{2} \qquad -\frac{\Delta[A]}{\Delta t} = k$$

$$\frac{1}{[A]} = \frac{1}{[A]_{0}} + kt \qquad [A] = [A]_{0} - kt$$

$$t_{\frac{1}{2}} = t \quad \text{when} \qquad [A] = [A]_{0}/2$$

$$t_{\frac{1}{2}} = \frac{1}{k[A]_{0}} \qquad t_{\frac{1}{2}} = \frac{[A]_{0}}{2k}$$

25

## **Graphical Methods**

P.

#### **Equation for a Straight Line**

У	=	bx	+	a	<pre>{ b = slope   a = y intercept   x = time</pre>
$\ln[A]_t$	=	- kt	+	$\ln[A]_0$	1st order

1	=	kt	+	1	2nd order
$[A]_t$				$[A]_0$	

 $[A]_t = kt + [A]_0 \qquad \text{Zero order}$ 

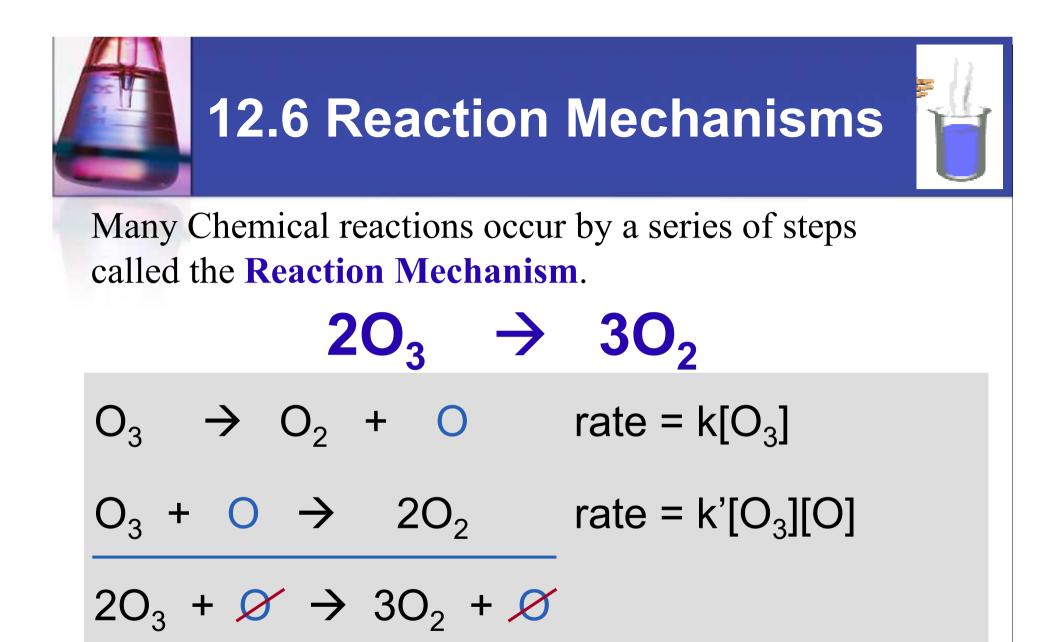


## 12.5 Rate Laws: A Summary

- The used laws contain reactant concentration only
- Rate types: Differential or Integral rate laws
- The common experimental methods:
  - For differential rate law is the initial concentration method
  - For integral rate law graphical method
- For reactions with several reactants the integral method can be applied only if the concentration of one reactant only can be treated (Pseudo rate law), i.e.
   Rate = k[A]<sup>n</sup>[B]<sup>m</sup>[C]<sup>p</sup>

To be reduced to Rate =  $k'[A]^n$ 

			Concentration-Time Equation	
	Order	Rate Law	•	Half-Life
	0	rate = <i>k</i>	[A] = [A] <sub>0</sub> - <i>kt</i>	$t_{\frac{1}{2}} = \frac{[A]_0}{2}$
	1	rate = <i>k</i> [A]	$\ln[A] = \ln[A]_0 - kt$	$\frac{2k}{t_{1/2}} = \frac{2k}{\ln 2}$
	2	rate = $k [A]^2$	$\frac{1}{1} = \frac{1}{1} + kt$	<i>k</i> 1
	-			$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$



*Intermediates* are species that appear in a reaction mechanism **but not** in the overall balanced equation.

### **Reaction Mechanisms**

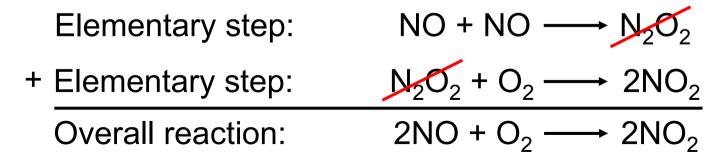
1-

The overall progress of a chemical reaction can be represented at the molecular level by a series of simple *elementary steps* or *elementary reactions.* 

The sequence of **elementary steps** that leads to product formation is the *reaction mechanism*.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

 $N_2O_2$  is detected during the reaction!





## **12.6 Reaction Mechanisms**



Elementary Step

equation describing a single molecular event

#### Molecularity

- Unimolecular rate = k[A]
- Bimolecular rate = k[A][B] or rate = k[A]<sup>2</sup>
- Termolecular rate = k[A

rate = 
$$k[A][B]$$
 or rat  
rate =  $k[A]^2[B]$ 

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## **12.6 Reaction Mechanisms**



The proposed **Reaction Mechanism** will be coorected if it satisfy the following two requirements:

- The sum of the elementary steps give the overall balanced equation.
- The rate of the mechanism agrees the experimental rate law.

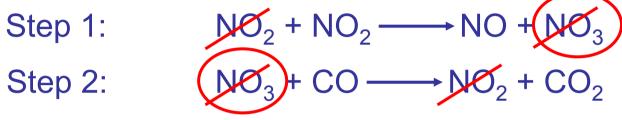
For example: Given the following reaction and rate law:

 $NO_{2(g)} + CO_{(g)} => CO_{2(g)} + NO_{(g)}$  rate = k[NO<sub>2</sub>]<sup>2</sup>

 Does the reaction occur in a single step?
 Which of the following two mechanisms is most likely: <u>Mechanism A:</u> NO<sub>2</sub> + NO<sub>2</sub>  $\rightarrow$  NO<sub>3</sub> + NO

 NO<sub>3</sub> + CO  $\rightarrow$  NO<sub>2</sub> + CO<sub>2</sub>

 DE MORY
 CO + O  $\rightarrow$  CO<sub>2</sub>
 The experimental rate law for the reaction between NO<sub>2</sub><sup>2</sup> and CO to produce NO and CO<sub>2</sub> is rate =  $k[NO_2]^2$ . The reaction is believed to occur via two steps:



What is the equation for the overall reaction?

$$NO_2 + CO \longrightarrow NO + CO_2$$

What is the intermediate?

#### NO<sub>3</sub>

What can you say about the relative rates of steps 1 and 2?





# **Temperature Effects**

- Rates typically increase with T increase
- Collisions between molecules increase
- Energy of collisions increase
- Even though only a small fraction of collisions lead to reaction
- Minimum Energy necessary for reaction is the Activation Energy



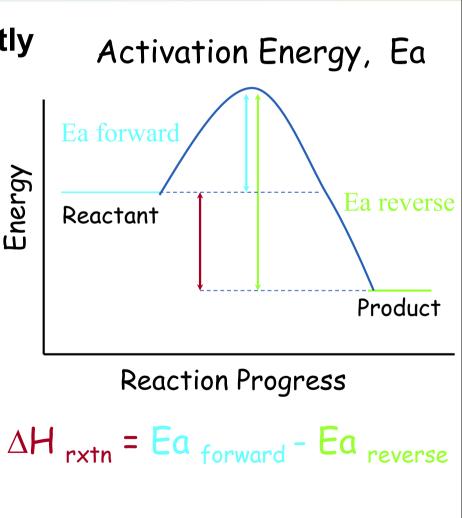
#### Molecular Theory (Collision Theory)

#### Activation Energy varies greatly

- almost zero to hundreds of kJ
- size of E<sub>a</sub> affects reaction rates

#### Concentration

- more molecules, more collisions
- Molecular Orientation
  - collisions must occur "sterically"



Chapter 12



# **The Arrhenius Equation**



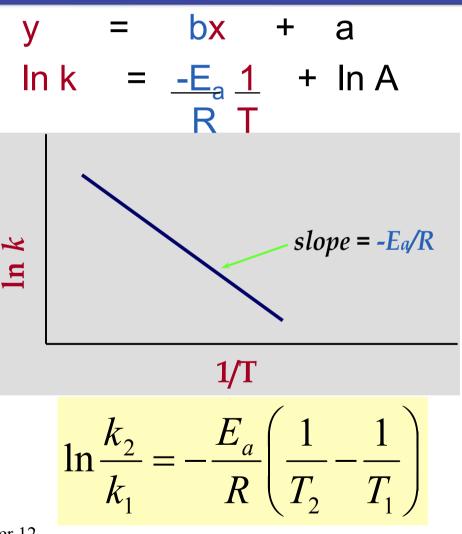
 increase temperature, increase reaction rates

 reaction rates are α to energy, collisions, temperature & orient

$$k = A e^{-Ea/RT}$$

k = rate constant

A = frequency of collisions - $E_a/RT$  = fraction of molecules with energy necessary for reaction





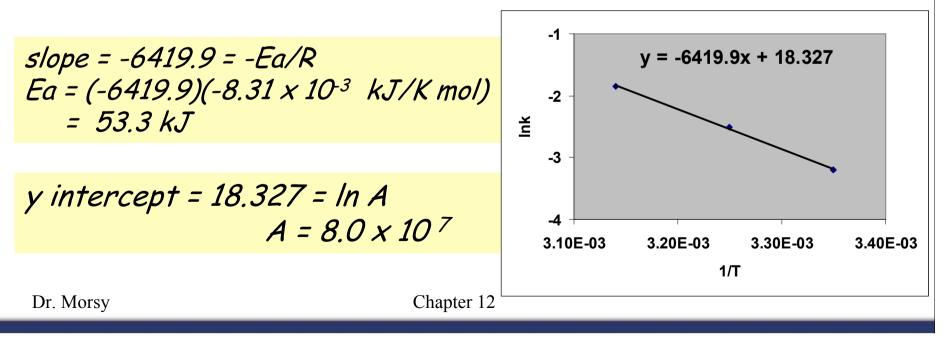
#### **Problem:**



Data for the following reaction are listed in the table. Calculate  $E_a$  graphically, calculate A and find k at 311 K.

ln k	k, min <sup>-1</sup>	T (K)	1/T x 10 <sup>-3</sup>
-3.20	0.0409	298	3.35
-2.50	0.0818	308	3.25
-1.85	0.157	318	3.14

 $Mn(CO)_{5}(CH_{3}CN)^{+} + NC_{5}H_{5} => Mn(CO)_{5}(NC_{5}H_{5})^{+} + CH_{3}CN$ 





#### **Problem:**



The energy of activation for

 $C_4H_{8(g)} \implies 2C_2H_{4(g)}$ is 260 kJ/mol at 800 K and k = 0.0315 sec Find k at 850 K.

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$
  
k at 850 K = 0.314 sec<sup>-1</sup>

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Chapter 12



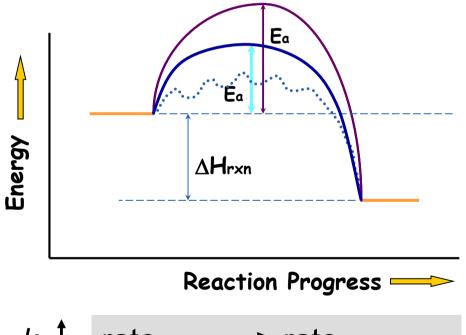
# 12.8 Catalysis

A *catalyst* is a substance that increases the rate of a chemical reaction without itself being consumed.

homogeneous

Heterogeneous

Facilitates the progress of a reaction by lowering the overall activation energy



 $k = A \cdot \exp(-E_a/RT)$   $E_a \downarrow k \uparrow rate_{catalyzed} > rate_{uncatalyzed}$ 

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Chapter 12



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# **12.8 Catalysis**

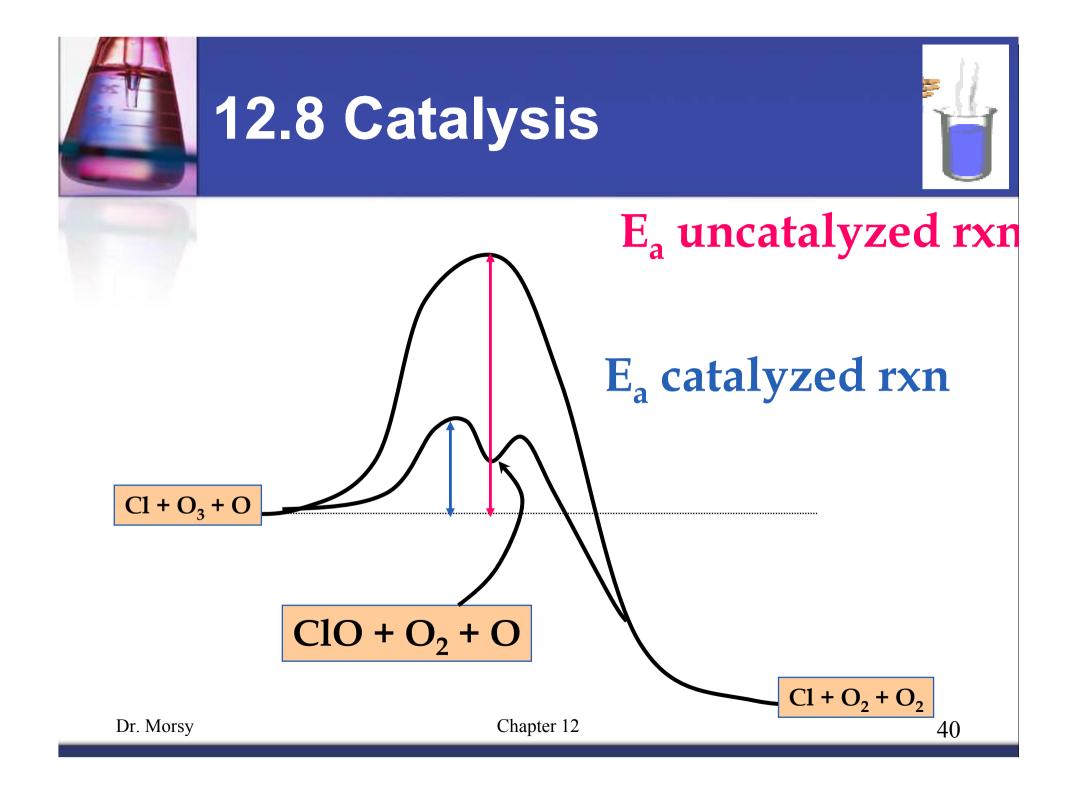
**Uncatalyzed Reaction:** 

$$O_{3(g)} \iff O_{2(g)} + O_{(g)}$$
  
 $O_{(g)} + O_{3(g)} \implies 2O_{2(g)}$   
Catalyzed Reaction:

Step 1: 
$$Cl_{(g)} + O_{3(g)} + O_{(g)} => ClO_{(g)} + O_{2(g)} + O_{(g)}$$

Step 2: 
$$ClO_{(g)} + O_{2(g)} + O_{(g)} => Cl_{(g)} + 2O_{2(g)}$$

=> 2O<sub>2(g)</sub> **O**<sub>3(g)</sub> **Overall rxn:** ╋ )<sub>(g)</sub> Chapter 12





# 12.8 Examples

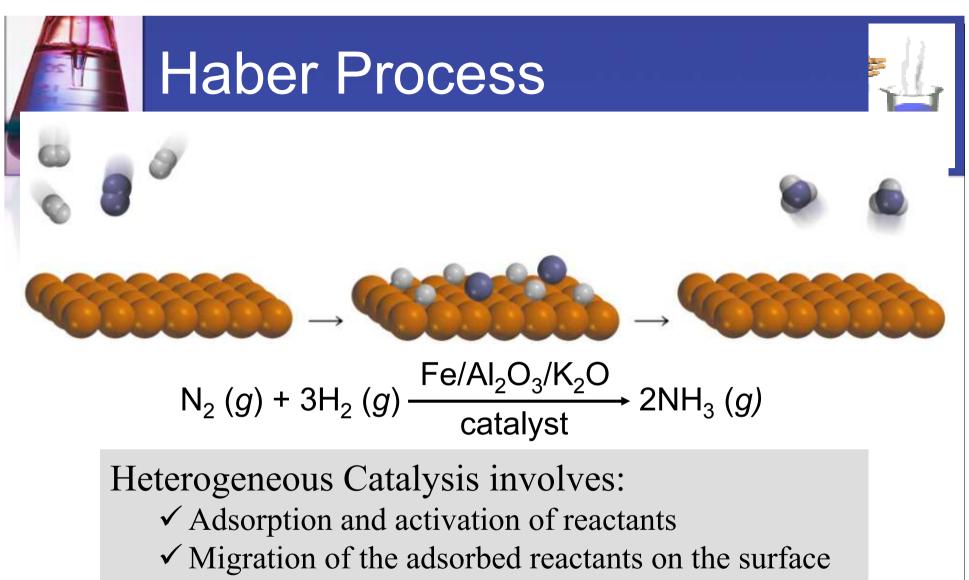


In *heterogeneous catalysis*, the reactants and the catalysts are in different phases.

- Haber synthesis of ammonia
- Ostwald process for the production of nitric acid
- Catalytic converters

In *homogeneous catalysis*, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
- Base catalysis

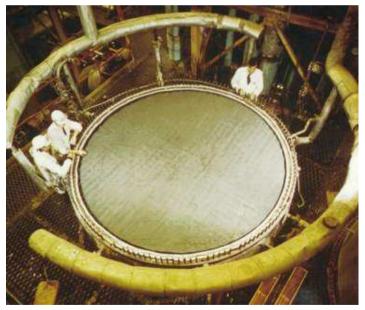


- $\checkmark$  Reaction of the adsorbed substances
- $\checkmark$  Escape, or desorption, of the product

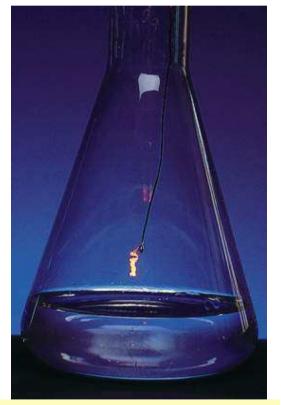


### **Ostwald Process**

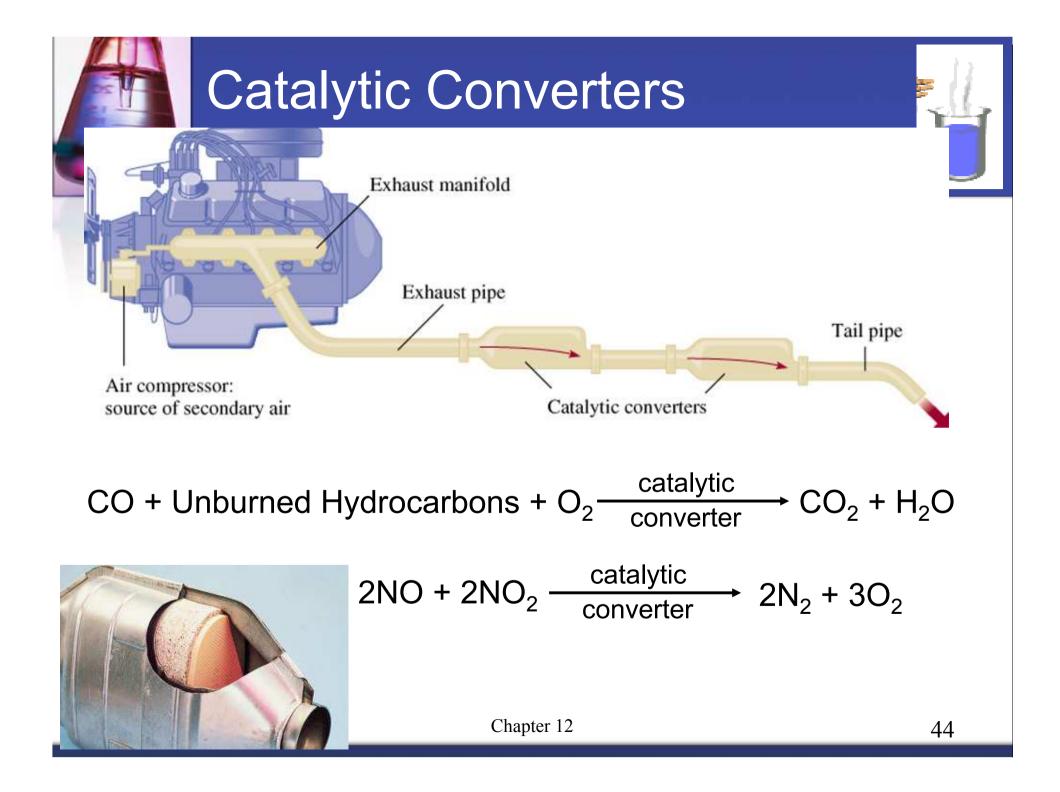
 $4NH_{3}(g) + 5O_{2}(g) \xrightarrow{Pt \text{ catalyst}} 4NO(g) + 6H_{2}O(g)$  $2NO(g) + O_{2}(g) \longrightarrow 2NO_{2}(g)$  $2NO_{2}(g) + H_{2}O(l) \longrightarrow HNO_{2}(aq) + HNO_{3}(aq)$ 

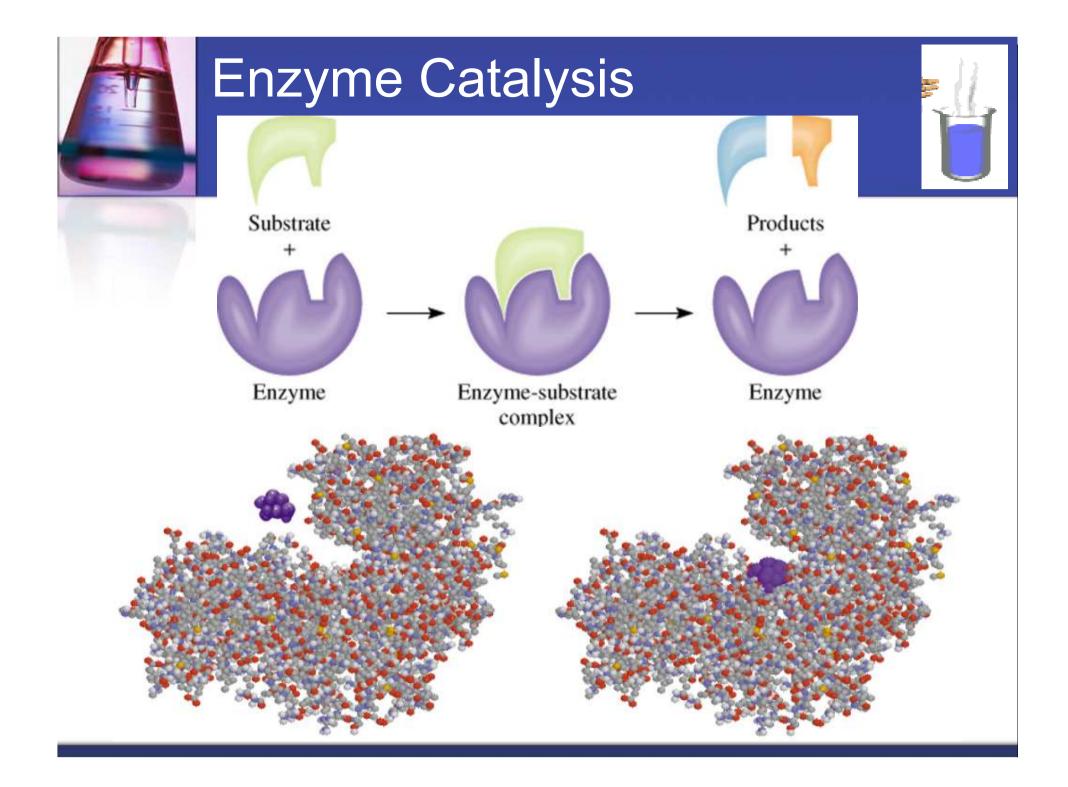


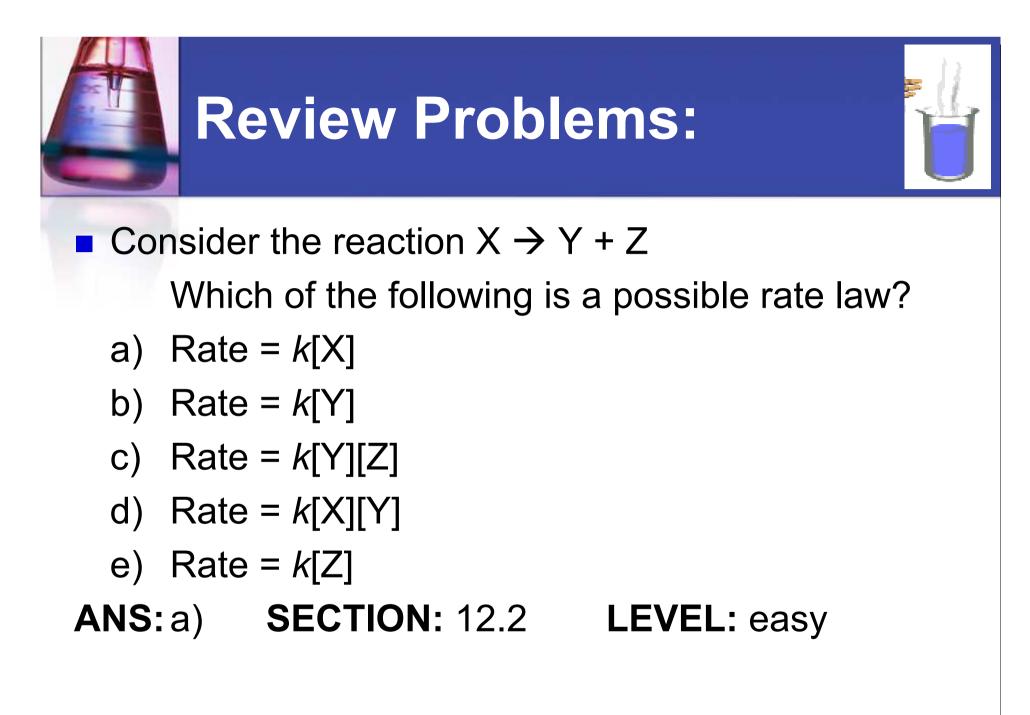
Pt-Rh catalysts used in Ostwald process Chapter 12

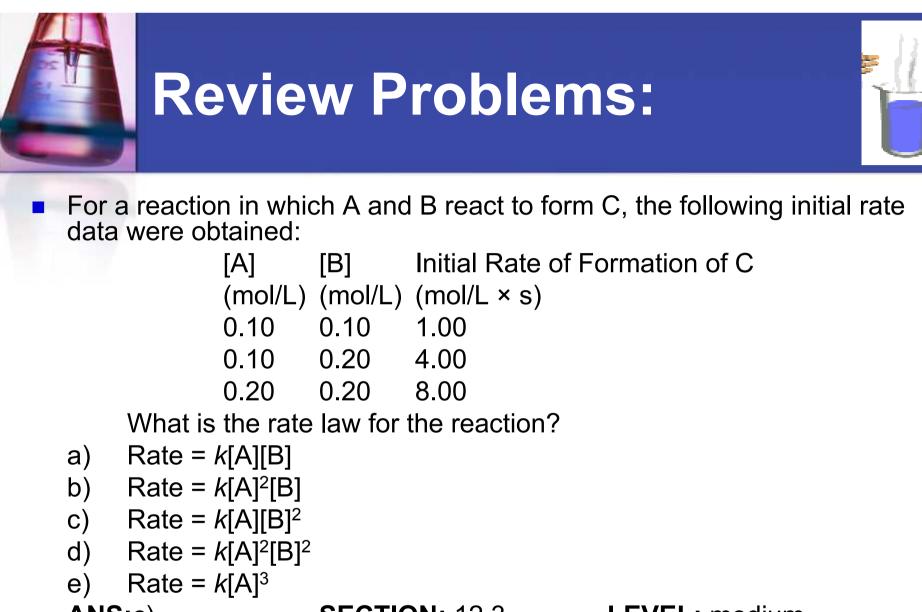


# Hot Pt wire over NH<sub>3</sub> solution









ANS:c)

**SECTION:** 12.3

LEVEL: medium



# **Review Problems:**



- A first-order reaction is 45% complete at the end of 35 minutes. What is the length of the half-life of this reaction?
  - a) 41 min
  - b) 39 min
  - c) 30. min
  - d) 27 min
  - e) none of these

#### **ANS:**a) **SECTION:** 12.4 **LEVEL:** medium



# **Review Problems:**



The reaction 2NO → N<sub>2</sub> + O<sub>2</sub> has the following rate law:

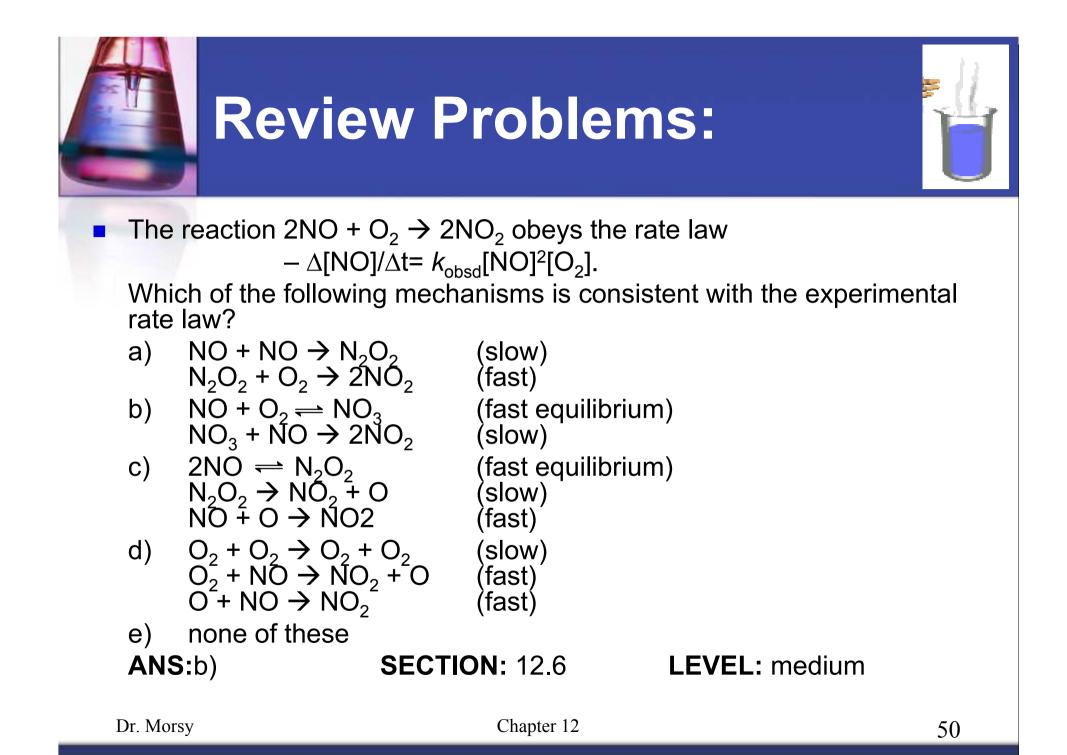
 $-\Delta[NO]/\Delta t = 2k[NO]^2.$ 

After a period of 2.0 x  $10^3$  s, the concentration of NO falls from an initial value of 2.8 x  $10^{-3}$  mol/L to 2.0 x  $10^{-3}$  mol/L. What is the rate constant, *k*?

- c)  $4.0 \times 10^{-4} \text{ M}^{-1}/\text{s}$
- d) 4.0 x 10<sup>-7</sup> M<sup>-1</sup>/s
- e) 3.6 x 10<sup>-2</sup> M<sup>-1</sup>/s

ANS:e) SECTION: 12.4

**LEVEL:** medium





Use the following information to determine the activation energy for the reaction shown here:

 $2NO \rightarrow N_2 + O_2$ 

Temperature (K) 1400 1500

a) 3.2 x 10<sup>4</sup> J/mol

- b) 9.5 x 10<sup>6</sup> J/mol
- c) 2.8 x 10<sup>4</sup> J/mol
- d) 6.8 x 10<sup>5</sup> J/mol

e) 2.7 x 10<sup>5</sup> J/mol **SECTION:** 12.7

Rate Constant (L/mol × s) 0.143 0.659

**LEVEL:** easy

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Chapter 12

