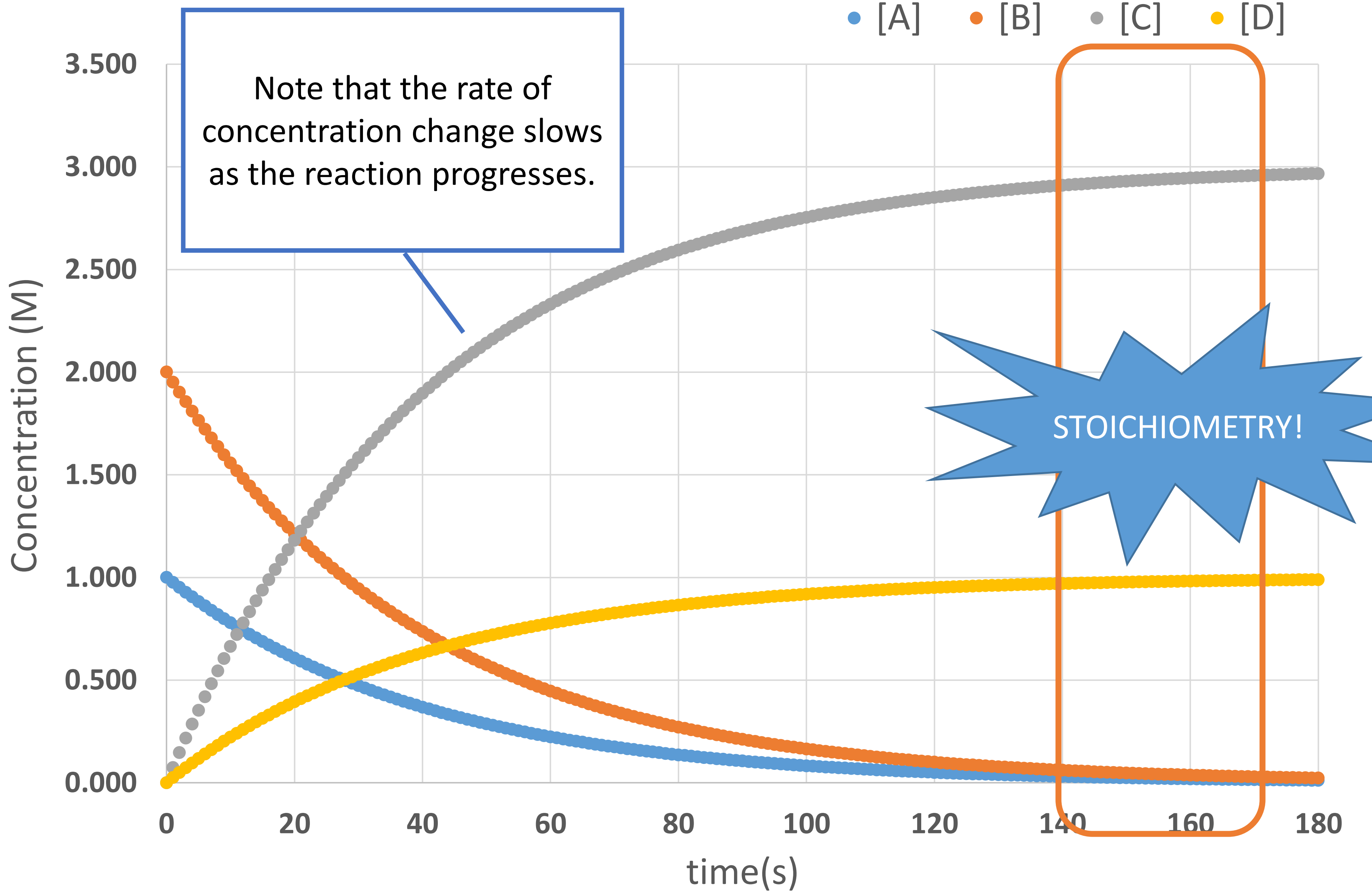
Chapter 13 Slides

SU2014 CHEM1451

Time dependence of component concentration for the reaction:

$A+2B \rightarrow 3C+D$

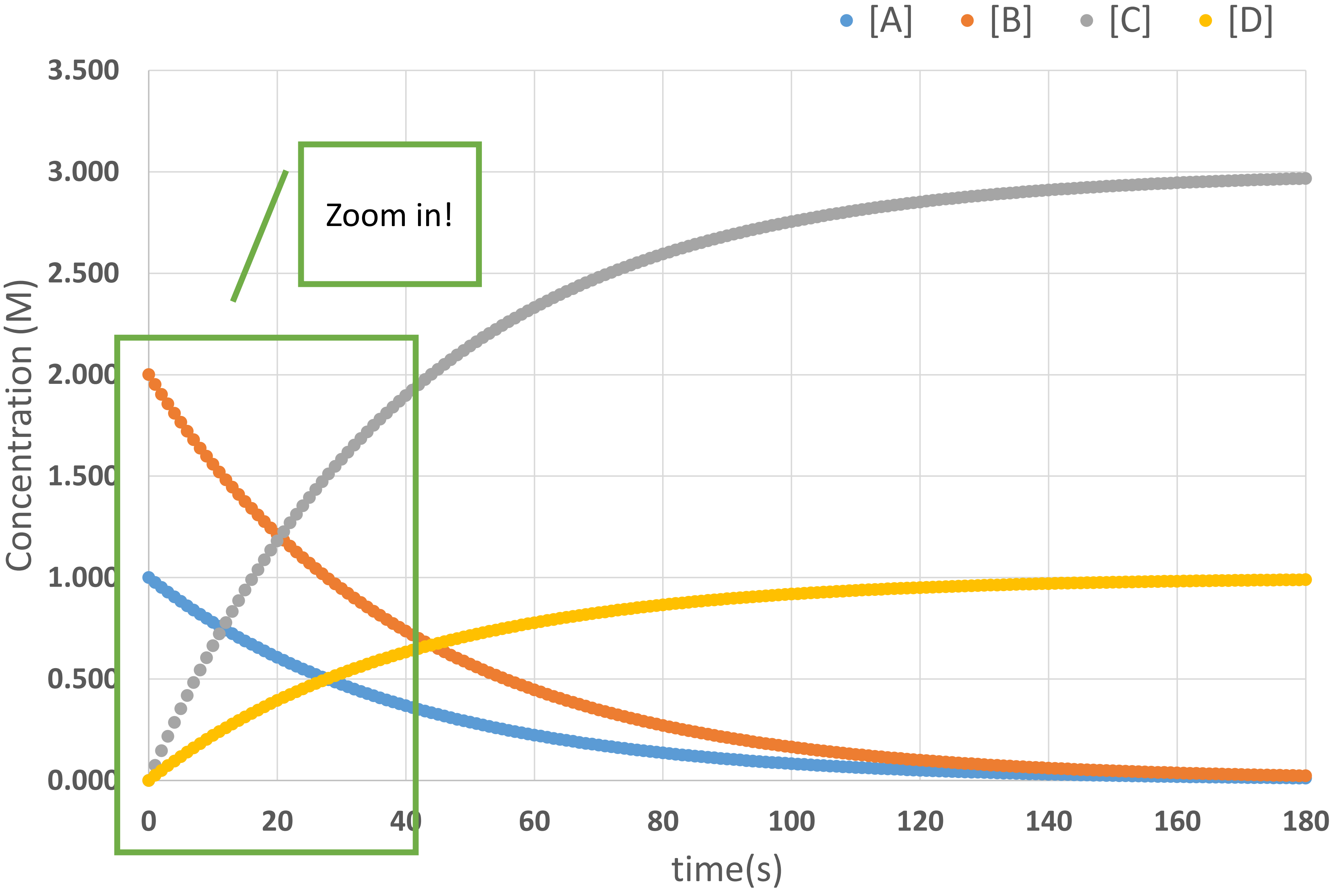


Note that the rate of concentration change slows as the reaction progresses.

STOICHIOMETRY!

Time dependence of component concentration for the reaction:

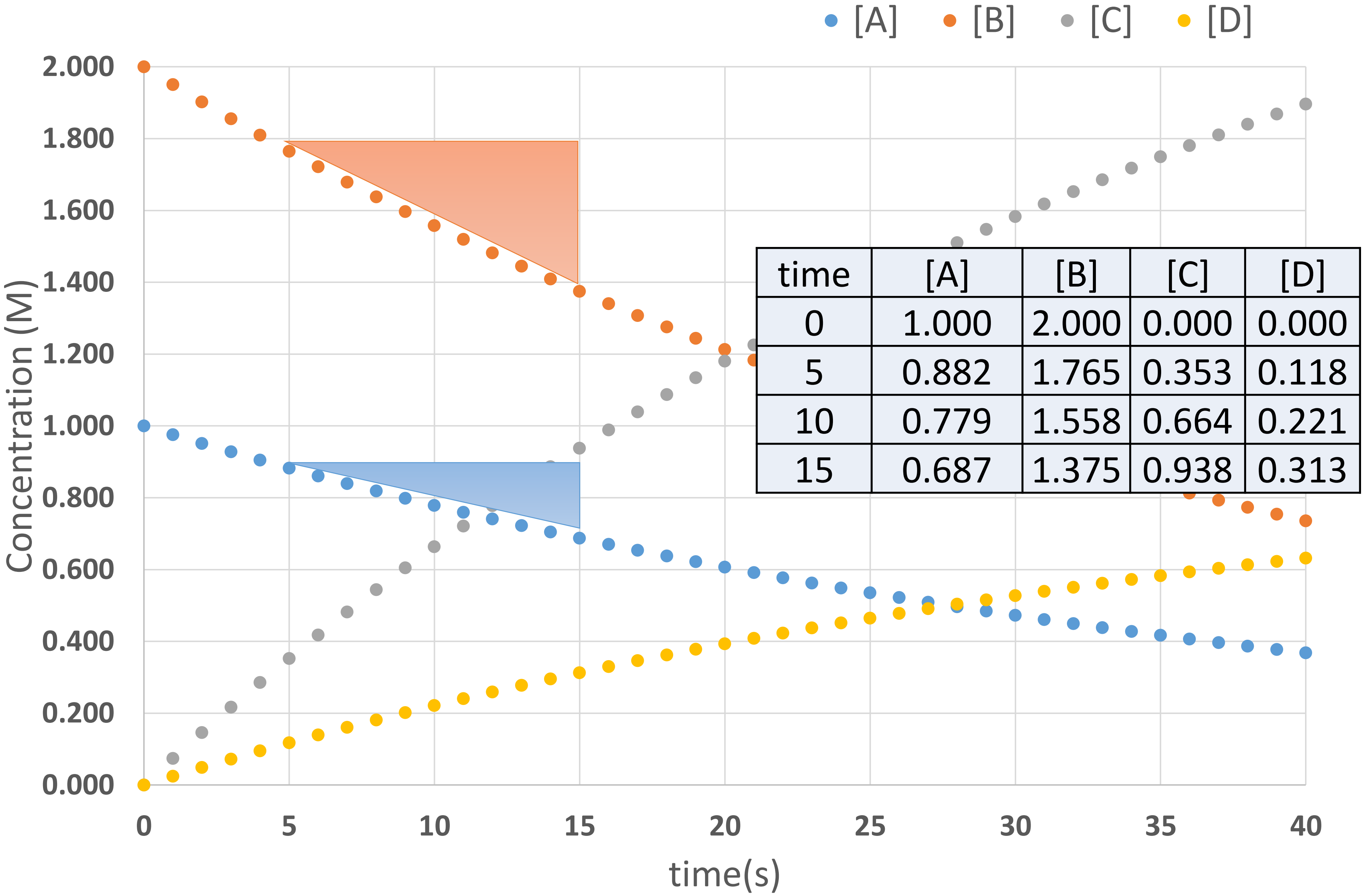
$$A+2B \longrightarrow 3C+D$$



Zoom in!

Time dependence of component concentration for the reaction:

$A+2B \rightarrow 3C+D$



time	[A]	[B]	[C]	[D]
0	1.000	2.000	0.000	0.000
5	0.882	1.765	0.353	0.118
10	0.779	1.558	0.664	0.221
15	0.687	1.375	0.938	0.313

Time dependence of component concentration for the reaction:
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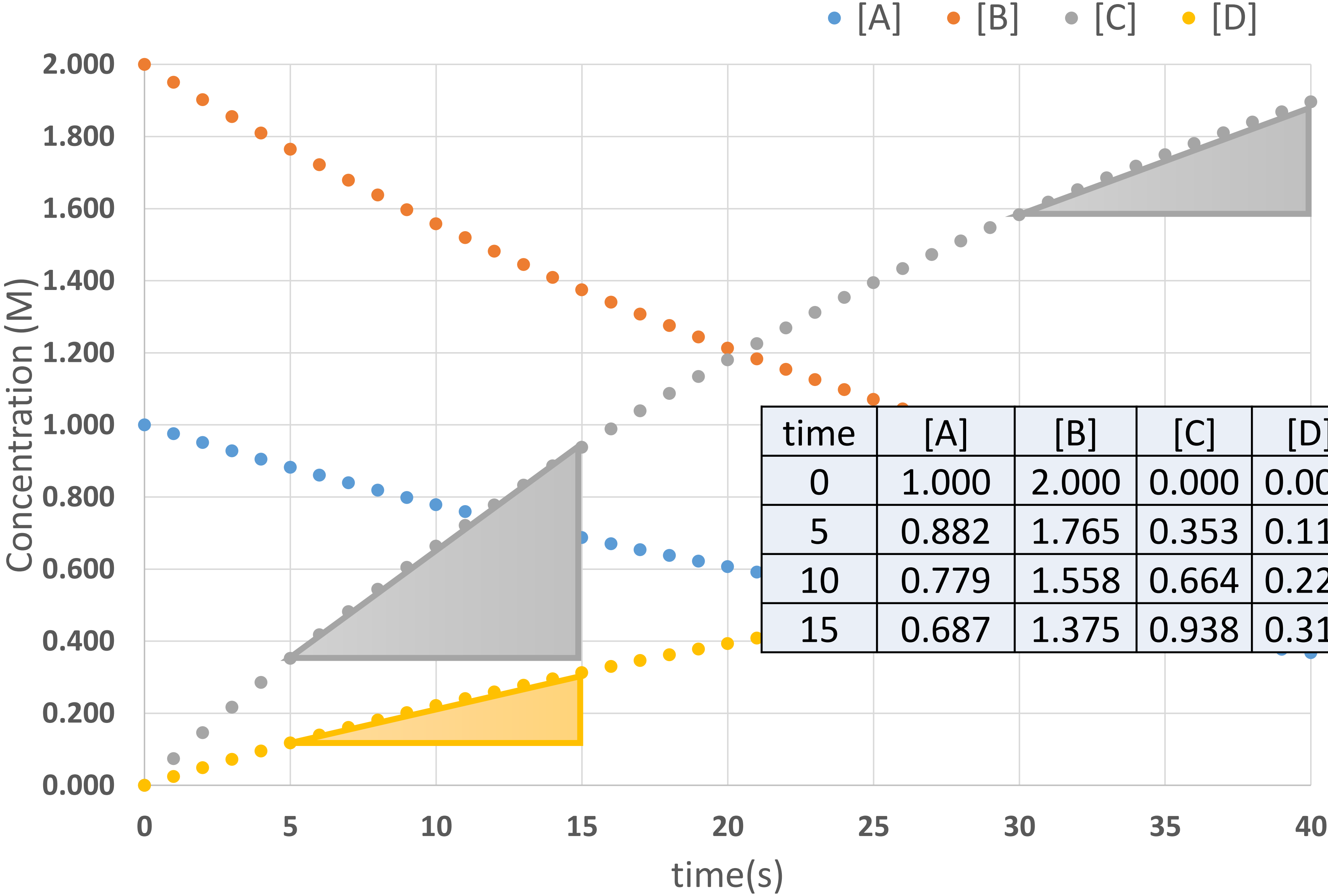

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0	1.000	2.000	0.000	0.000
5	0.882	1.765	0.353	0.118
10	0.779	1.558	0.664	0.221
15	0.687	1.375	0.938	0.313

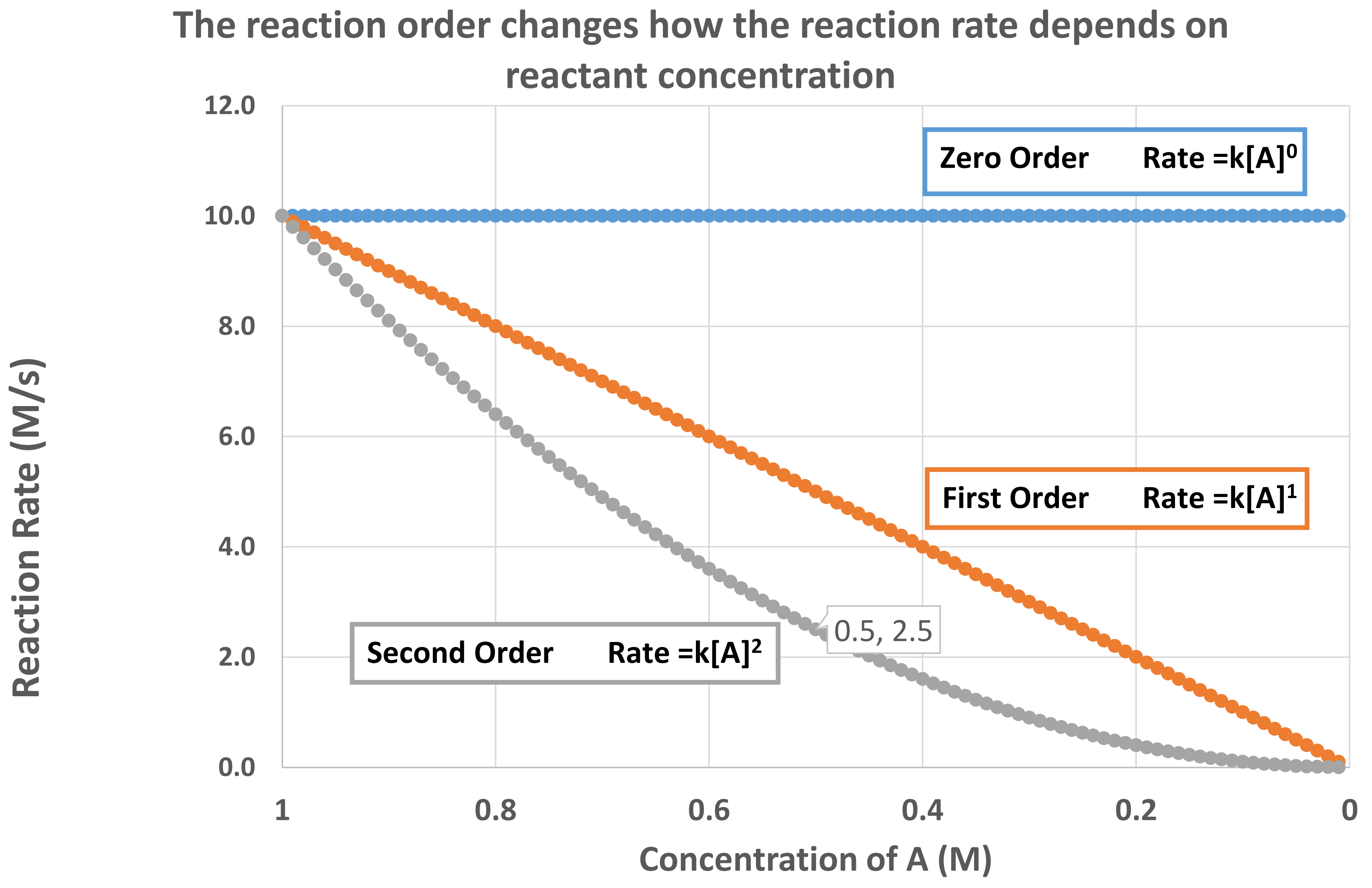
Reaction Rate Terms

- Reaction Rate is one positive number. You can calculate a specific rate of formation or consumption from that number.
  - Always units of concentration per unit time (M/s)
- Average Rate vs. Instantaneous Rate

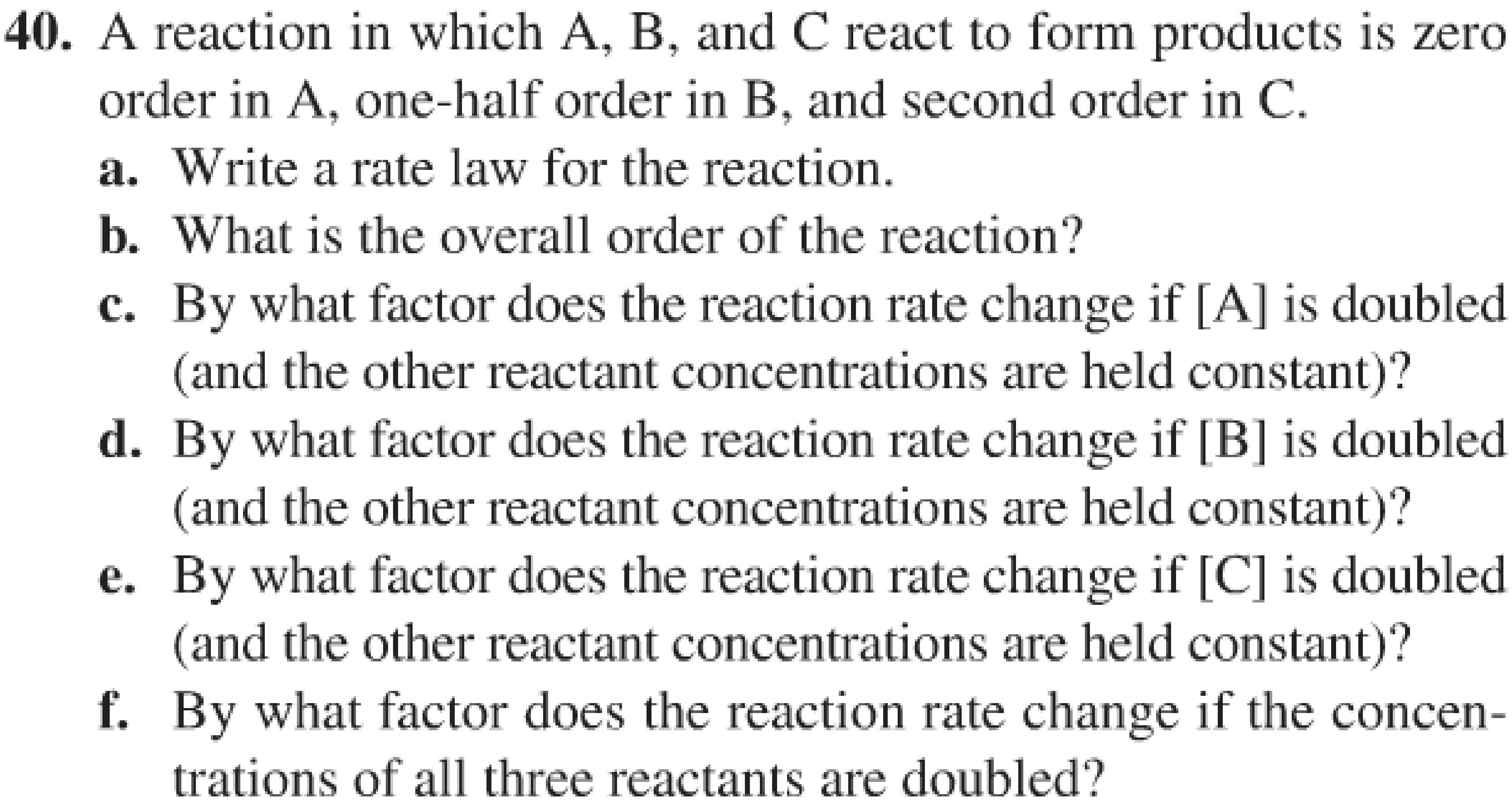
Things that Affect Reaction Rate

- Reactant Concentration
- Temperature

A⟶Products Rate=k[A]^x



Writing a Rate Law

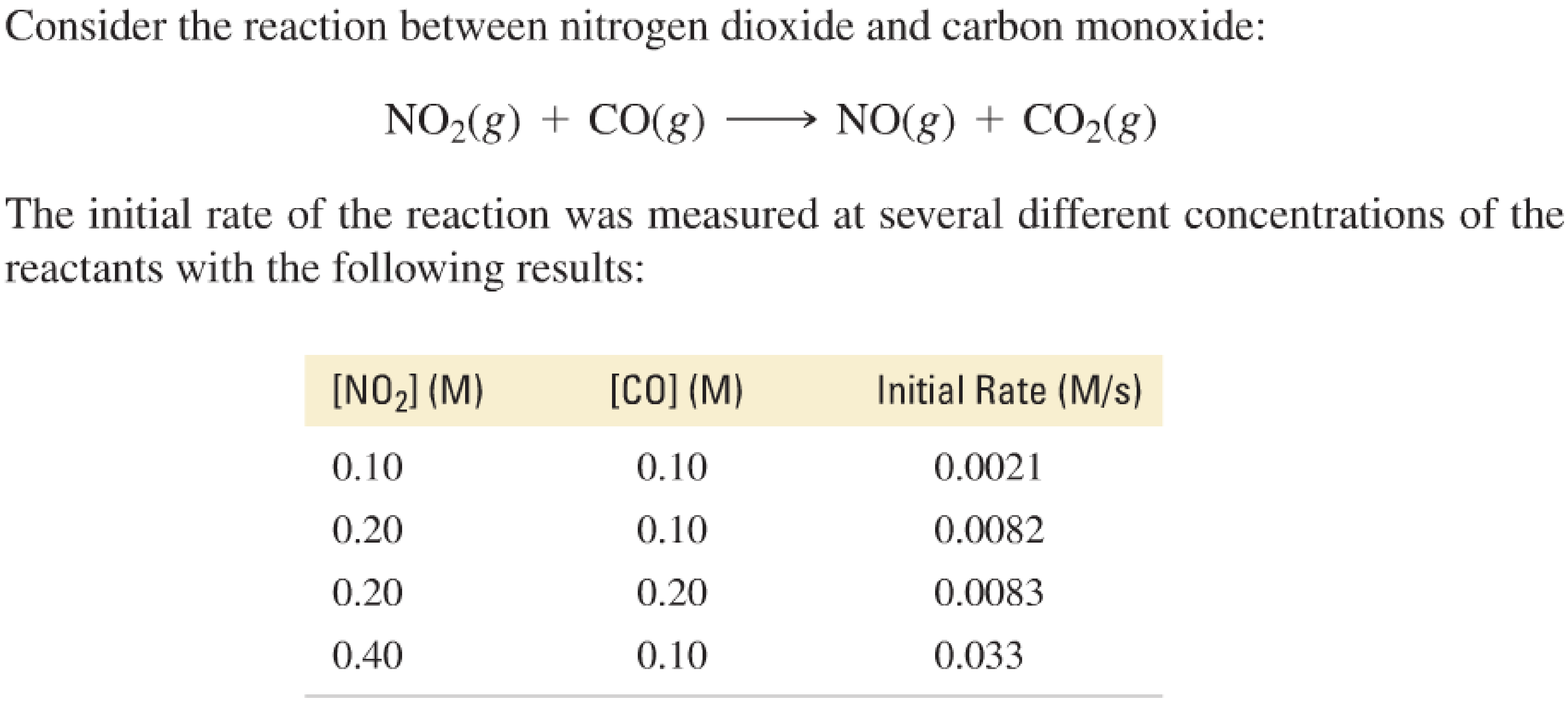


40. A reaction in which A, B, and C react to form products is zero order in A, one-half order in B, and second order in C.

- **a.** Write a rate law for the reaction.
- **b.** What is the overall order of the reaction?
- **c.** By what factor does the reaction rate change if [A] is doubled (and the other reactant concentrations are held constant)?
- **d.** By what factor does the reaction rate change if [B] is doubled (and the other reactant concentrations are held constant)?
- **e.** By what factor does the reaction rate change if [C] is doubled (and the other reactant concentrations are held constant)?
- **f.** By what factor does the reaction rate change if the concentrations of all three reactants are doubled?

How to Determine the Reaction Order

- **You can only determine a reaction rate experimentally!**
- Two common ways:
  1. Method of Initial Rates
     - (Effect of Concentration on the rate)
  2. Integrated Rate Laws
     - (Effect of time on the reactant concentration)



Consider the reaction between nitrogen dioxide and carbon monoxide:

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

The initial rate of the reaction was measured at several different concentrations of the reactants with the following results:

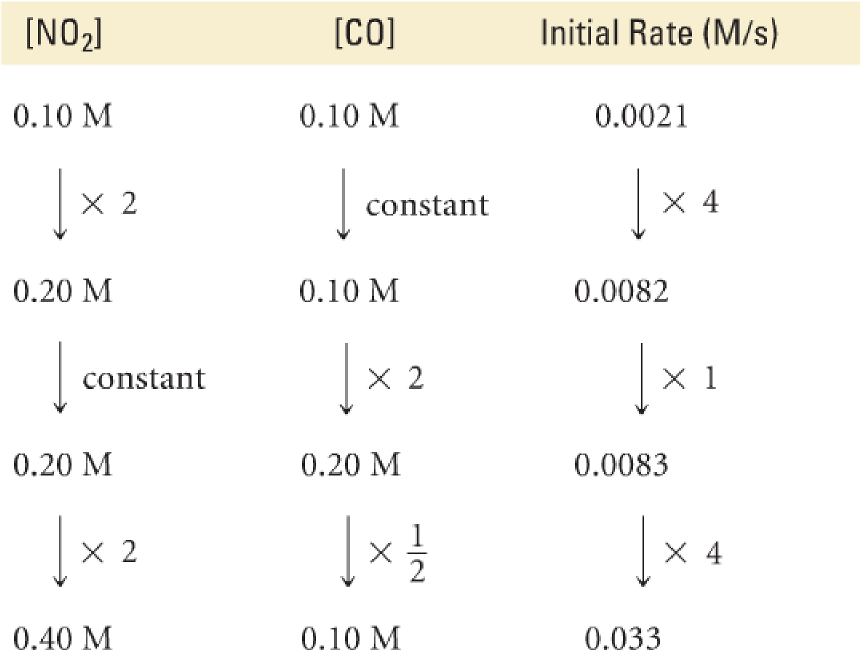
$[NO_2]$ (M)	[CO] (M)	Initial Rate (M/s)
0.10	0.10	0.0021
0.20	0.10	0.0082
0.20	0.20	0.0083
0.40	0.10	0.033

Find the rate law and the value for the rate constant (k) using the data above.

Step 1: Write the rate law for the reaction using place holders for order and for k.

$$\text{Rate} = k[NO_2]^X[CO]^Y$$

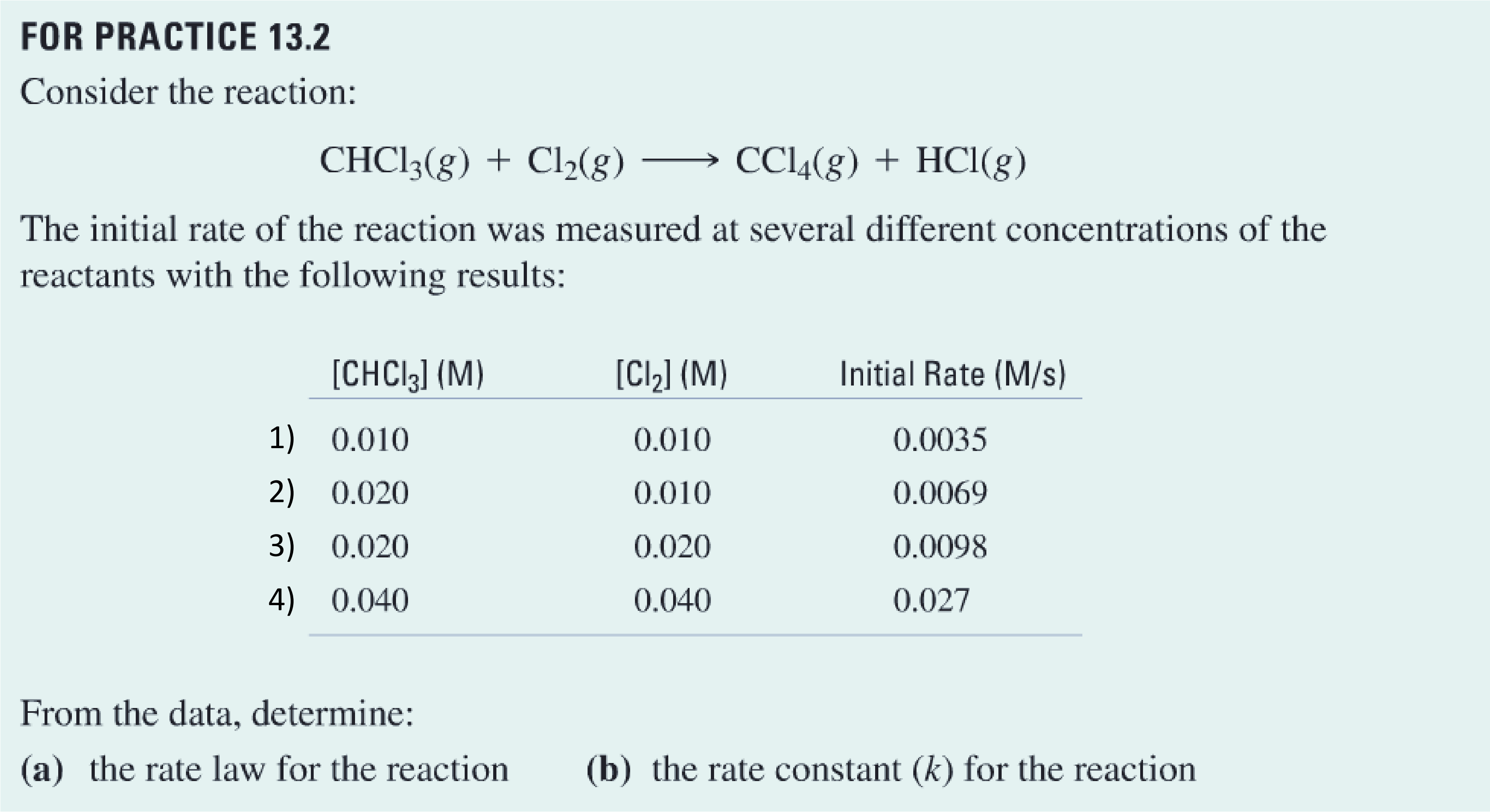
Step 2: Examine the data and determine relationships between the experiments.



$[NO_2]$	[CO]	Initial Rate (M/s)
0.10 M	0.10 M	0.0021
↓ × 2	↓ constant	↓ × 4
0.20 M	0.10 M	0.0082
↓ constant	↓ × 2	↓ × 1
0.20 M	0.20 M	0.0083
↓ × 2	↓ $\times \frac{1}{2}$	↓ × 4
0.40 M	0.10 M	0.033

Step 3: Use those relationships to deduce the values for the orders with respect to the specific reactants. (Solve for X and Y)

Step 4: Determine a value for the rate constant(k) and include units.



FOR PRACTICE 13.2

Consider the reaction:

$$CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g)$$

The initial rate of the reaction was measured at several different concentrations of the reactants with the following results:

	$[CHCl_3]$ (M)	$[Cl_2]$ (M)	Initial Rate (M/s)
1)	0.010	0.010	0.0035
2)	0.020	0.010	0.0069
3)	0.020	0.020	0.0098
4)	0.040	0.040	0.027

From the data, determine:

(a) the rate law for the reaction **(b)** the rate constant (k) for the reaction

44. The data below were collected for this reaction:

$$CH_3Cl(g) + 3\,Cl_2(g) \longrightarrow CCl_4(g) + 3\,HCl(g)$$

$[CH_3Cl]$ (M)	$[Cl_2]$ (M)	Initial Rate (M/s)
0.050	0.050	0.014
0.100	0.050	0.029
[redacted]	[redacted]	[redacted]
0.200	0.200	0.115

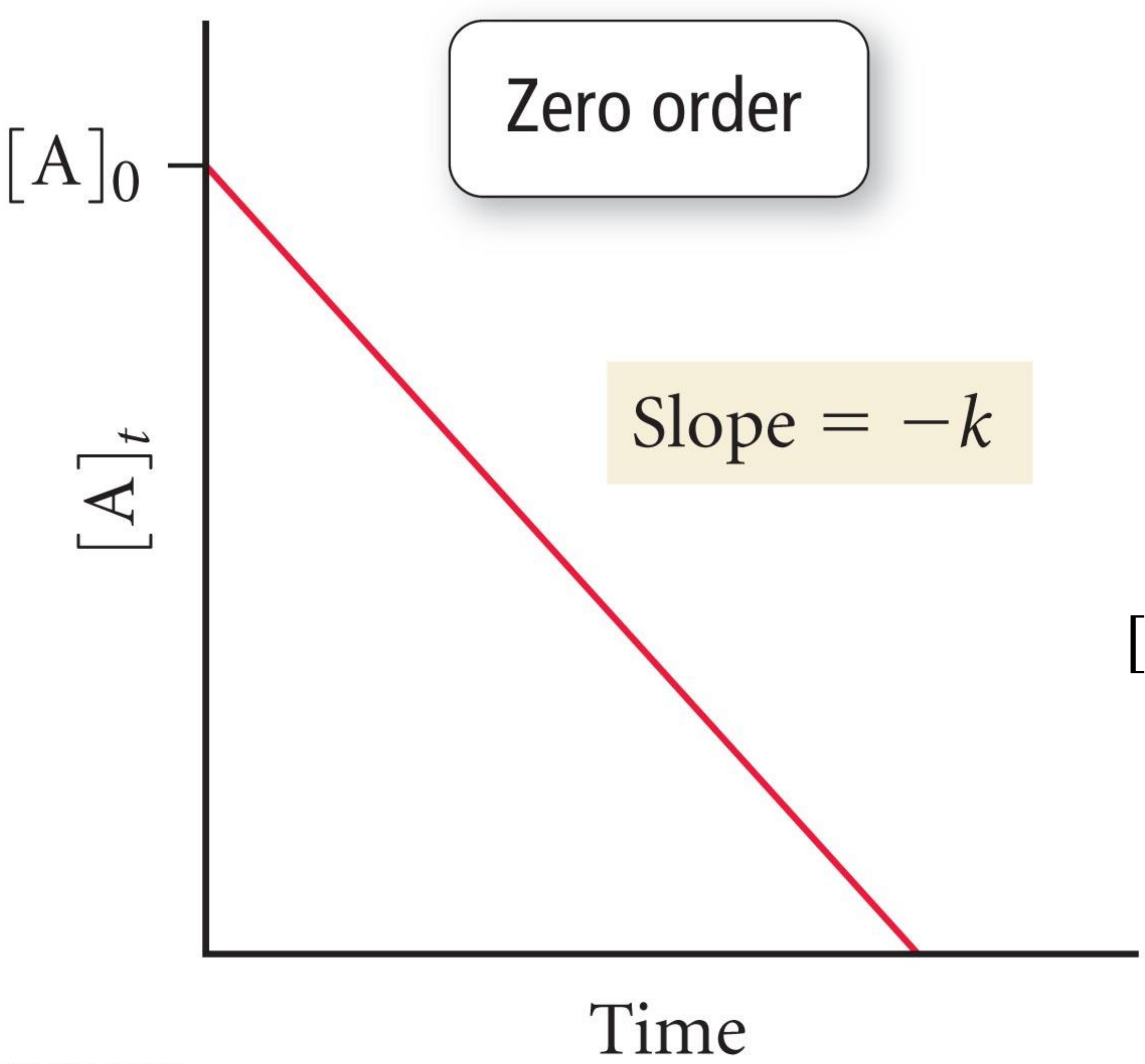
Determine the rate law and the value of k for the following reaction using the data provided.

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

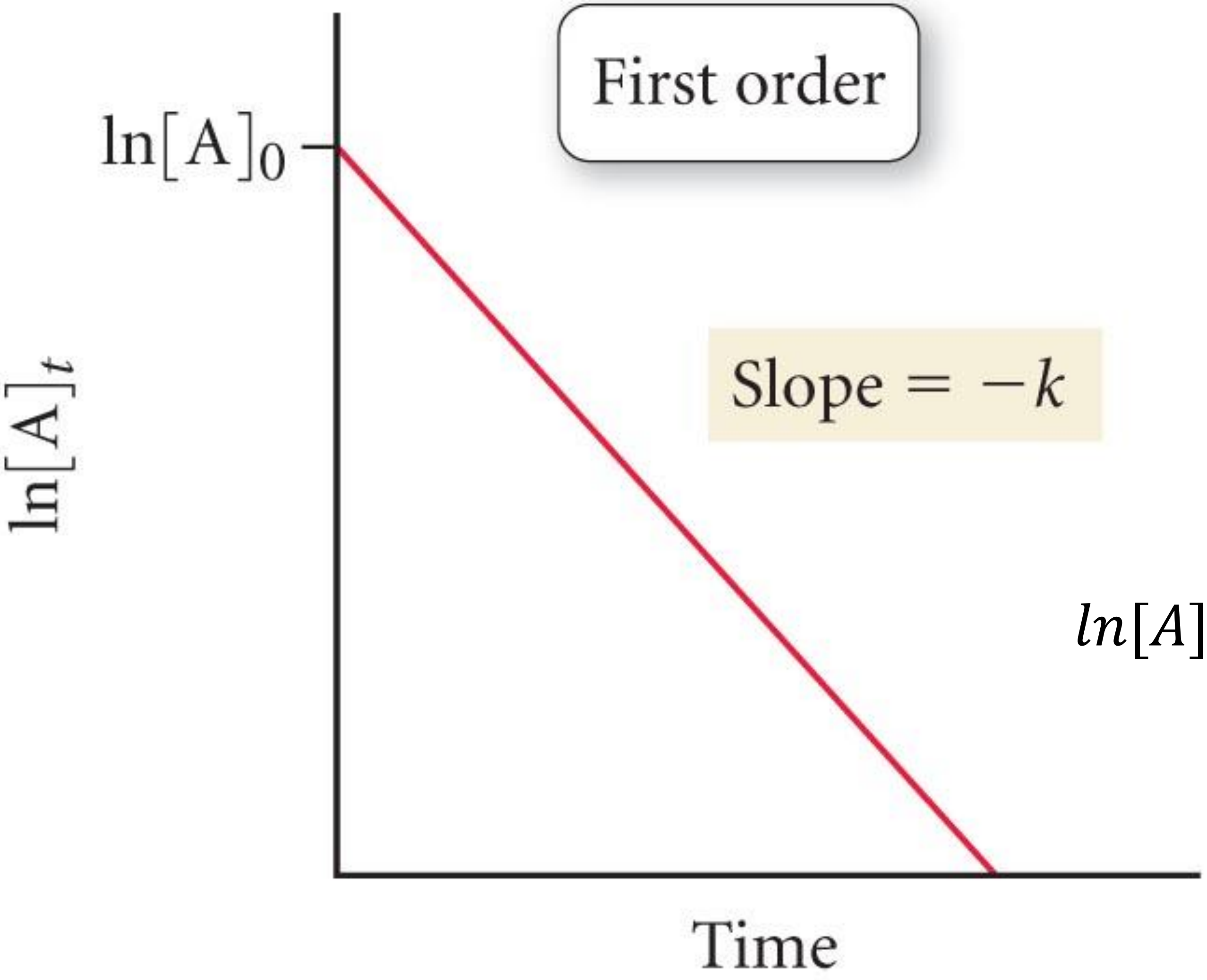
[NO]i (M)	[O2]i (M)	Initial Rate (M/s)
0.030	0.0055	8.55×10^{-3}
0.030	0.0110	1.71×10^{-2}
0.060	0.0055	3.42×10^{-2}

Integrated Rate Laws

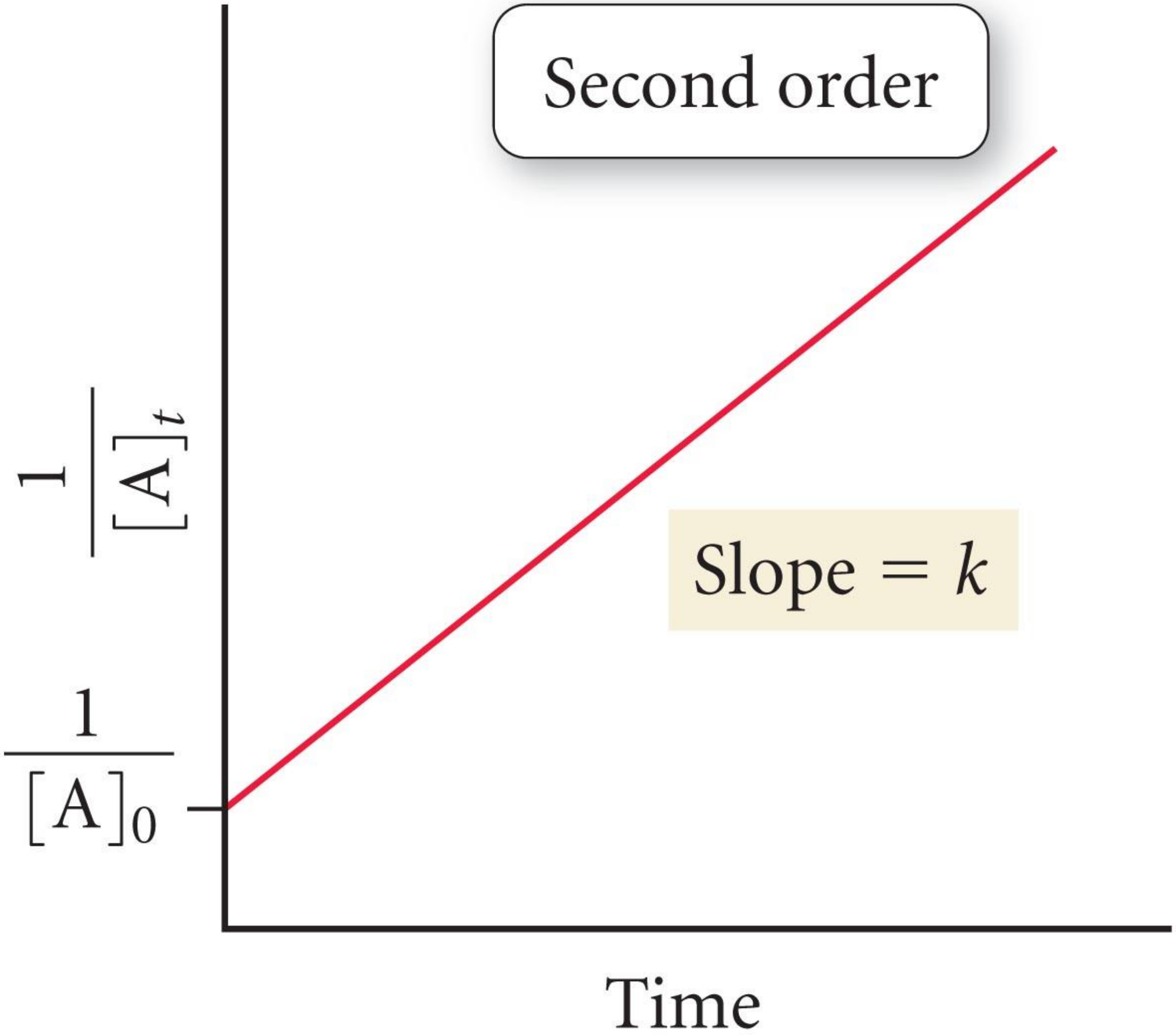
- Experimentally, you follow a concentration of a reactant from the beginning of a reaction until the reaction slows.
- A second method for determining reaction order and k. For the SAME reaction, these methods would produce the SAME results.
  - Why do this another way?
    - Often, it is experimentally easier to do this.
    - Get all the info from one run.



$$[A]_t = -kt + [A]_0$$



$$ln[A]_t = -kt + ln[A]_0$$



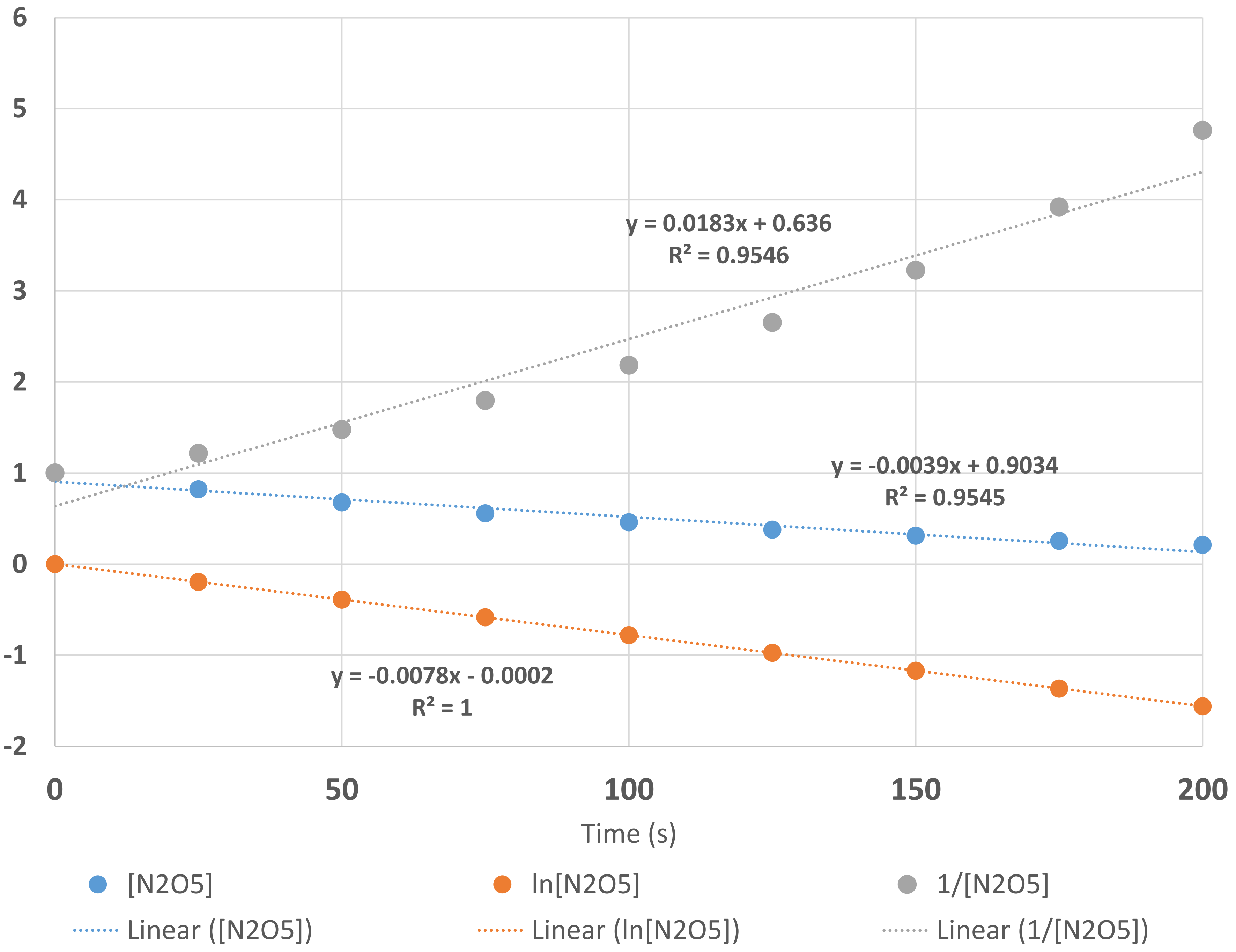
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

48. The data below show the concentration of N_2O_5 versus time for this reaction:

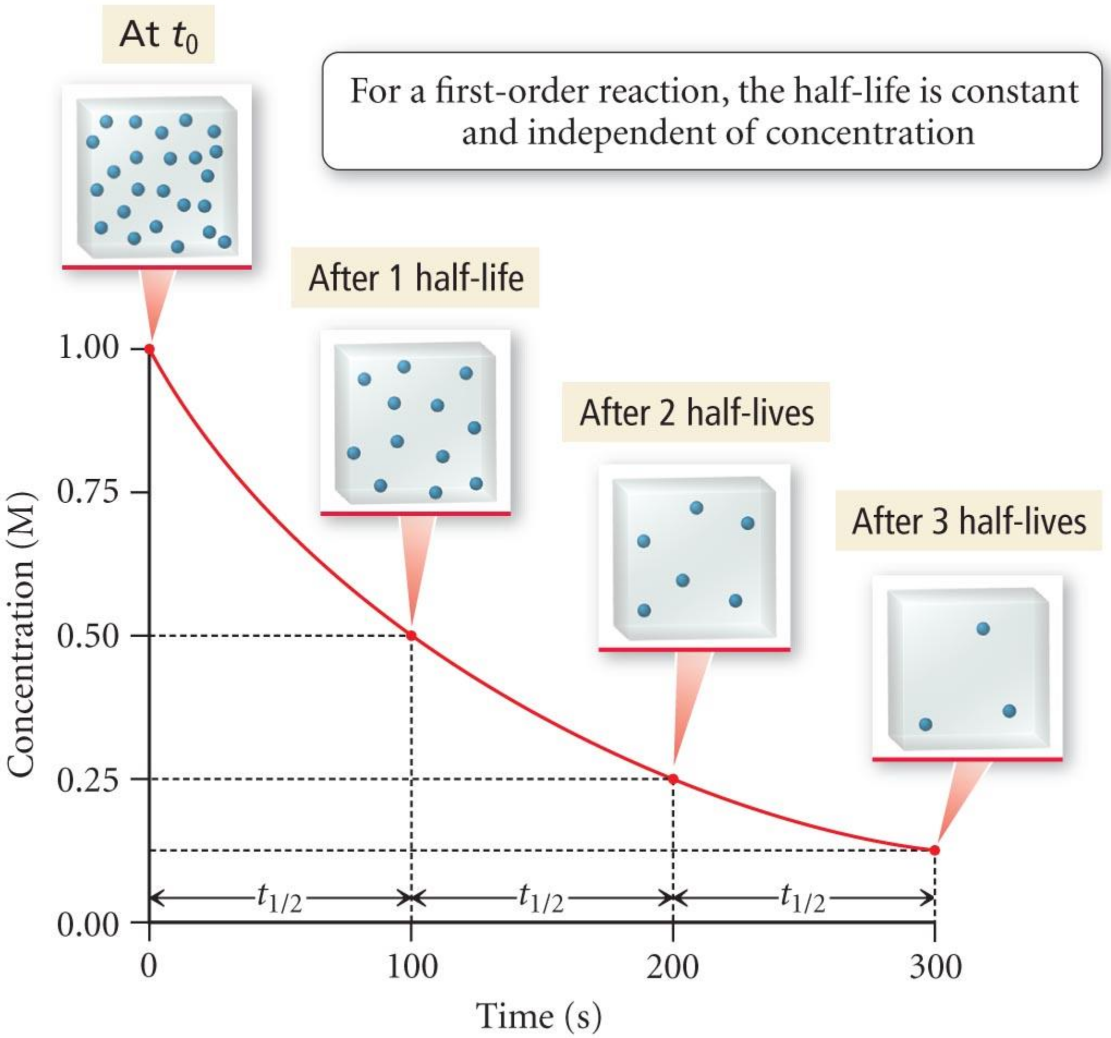
$$N_2O_5(g) \longrightarrow NO_3(g) + NO_2(g)$$

Time (s)	$[N_2O_5]$ (M)
0	1.000
25	0.822
50	0.677
75	0.557
100	0.458
125	0.377
150	0.310
175	0.255
200	0.210

Determine the order of the reaction and the value of the rate constant. Predict the concentration of N_2O_5 at 250 s.


6
5
4
3
2
1
0
-1
-2
0
50
100
150
200
Time (s)
y = 0.0183x + 0.636
R² = 0.9546
y = -0.0039x + 0.9034
R² = 0.9545
y = -0.0078x - 0.0002
R² = 1
[N2O5]
ln[N2O5]
1/[N2O5]
Linear ([N2O5])
Linear (ln[N2O5])
Linear (1/[N2O5])

Half-Life

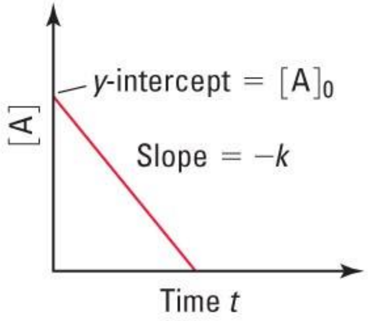
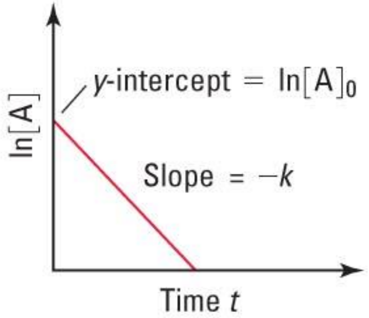
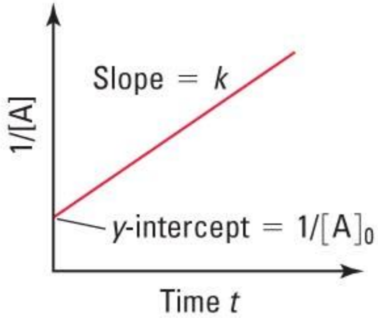


Half-Life for a First-Order Reaction

For a first-order reaction, the half-life is constant and independent of concentration

Equations provided on the exam

TABLE 13.2 Rate Law Summary Table

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate $= k[A]^0$	$M \cdot s^{-1}$	$\boxed{[A]_t = -kt + [A]_0}$		$\boxed{t_{1/2} = \frac{[A]_0}{2k}} = \frac{1}{k}\frac{[A]_0}{2}$
1	Rate $= k[A]^1$	s^{-1}	$\boxed{\ln[A]_t = -kt + \ln[A]_0}$ $\ln\frac{[A]_t}{[A]_0} = -kt$		$\boxed{t_{1/2} = \frac{0.693}{k}} = \frac{1}{k}(0.693)$
2	Rate $= k[A]^2$	$M^{-1} \cdot s^{-1}$	$\boxed{\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}}$		$\boxed{t_{1/2} = \frac{1}{k[A]_0}} = \frac{1}{k}\frac{1}{[A]_0}$

If the concentration of a reactant is 6.25%, how many half-lives has it gone through?
A) 7
B) 6
C) 3
D) 4
E) 5

The rate constant for the first-order decomposition of N2O is 3.40 s-1. What is the half-life of the decomposition?
A) 0.491 s
B) 0.204 s
C) 0.236 s
D) 0.424 s
E) 0.294 s

The half-life for the second-order decomposition of HI is 15.4 s when the initial concentration of HI is 0.67 M. What is the rate constant for this reaction?
A) 1.0 × 10-2 M-1s-1
B) 4.5 × 10-2 M-1s-1
C) 9.7 × 10-2 M-1s-1
D) 2.2 × 10-2 M-1s-1
E) 3.8 × 10-2 M-1s-1

52. This reaction was monitored as a function of time:

$$AB \longrightarrow A + B$$

A plot of 1/[AB] versus time yields a straight line with slope $-0.055/\text{M} \cdot \text{s}$.

a. What is the value of the rate constant (k) for this reaction at this temperature?

b. Write the rate law for the reaction.

c. What is the half-life when the initial concentration is 0.55 M?

d. If the initial concentration of AB is 0.250 M, and the reaction mixture initially contains no products, what are the concentrations of A and B after 75 s?

54. The decomposition of XY is second order in XY and has a rate constant of $7.02 \times 10^{-3}\ M^{-1} \cdot s^{-1}$ at a certain temperature.

a. What is the half-life for this reaction at an initial concentration of 0.100 M?

b. How long will it take for the concentration of XY to decrease to 12.5% of its initial concentration when the initial concentration is 0.100 M? When the initial concentration is 0.200 M?

c. If the initial concentration of XY is 0.150 M, how long will it take for the concentration to decrease to 0.062 M?

d. If the initial concentration of XY is 0.050 M, what is the concentration of XY after 5.0×10^{1} s? After 5.50×10^{2} s?

55. The half-life for the radioactive decay of U-238 is 4.5 billion years and is independent of initial concentration. How long will it take for 10% of the U-238 atoms in a sample of U-238 to decay? If a sample of U-238 initially contained 1.5×10^{18} atoms when the universe was formed 13.8 billion years ago, how many U-238 atoms does it contain today?

The Effect of Temperature on the Reaction Rate

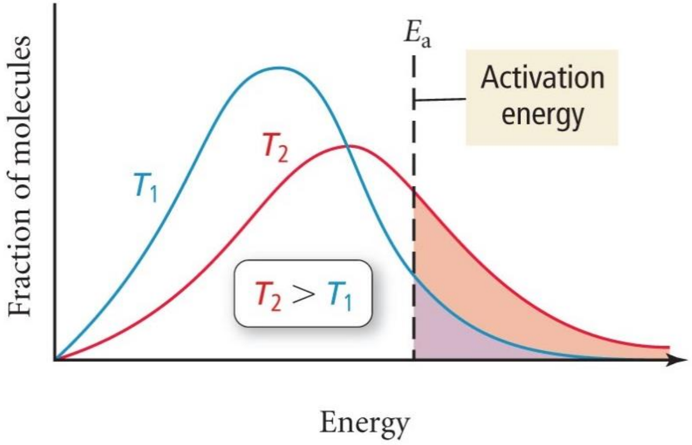
$$k = A \cdot \underbrace{e^{\frac{-E_a}{RT}}}$$

Frequency Factor

Exponential Factor

$$A = p \cdot z$$

- Orientation Factor: “p”
  - the fraction of collisions that are actually successful due to colliding in the correct way.
  - NOT temperature dependent!
- Collision frequency: “z”
  - The number of collisions per unit time. Can be calculated.
  - VERY temperature dependent!



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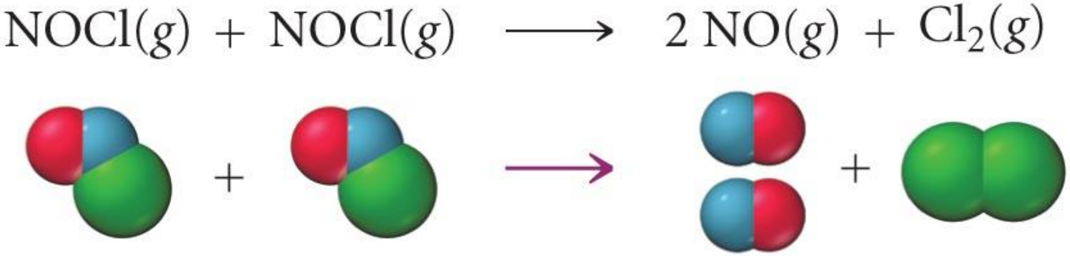
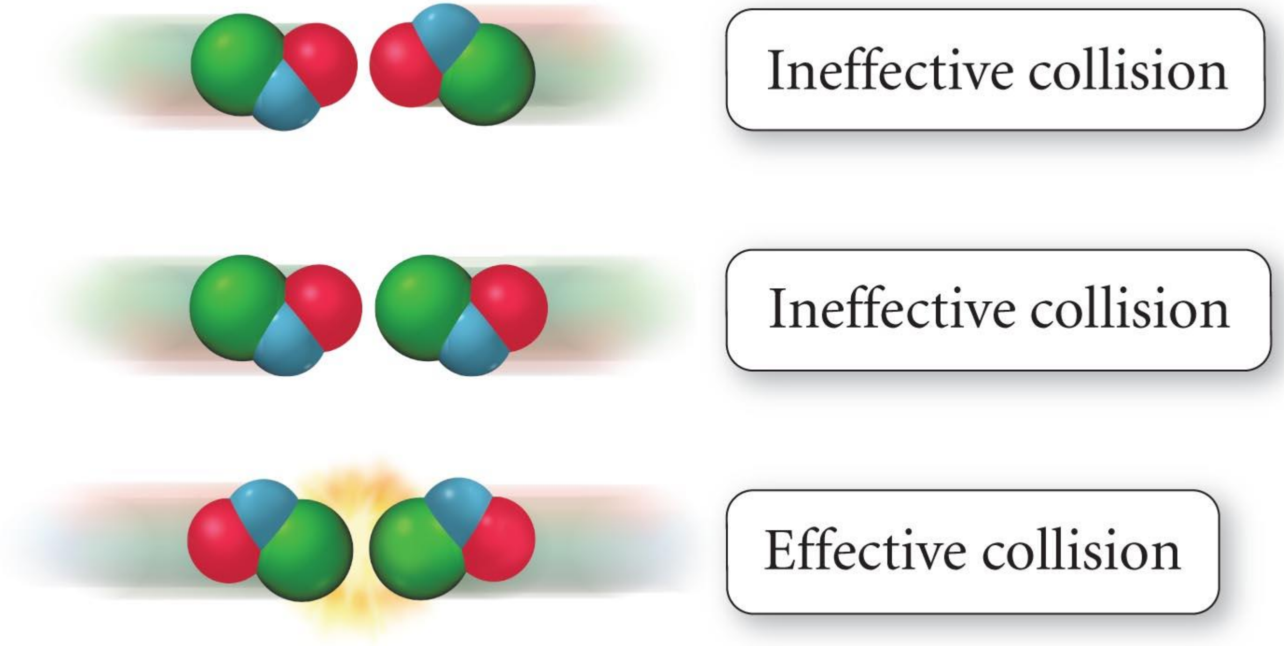
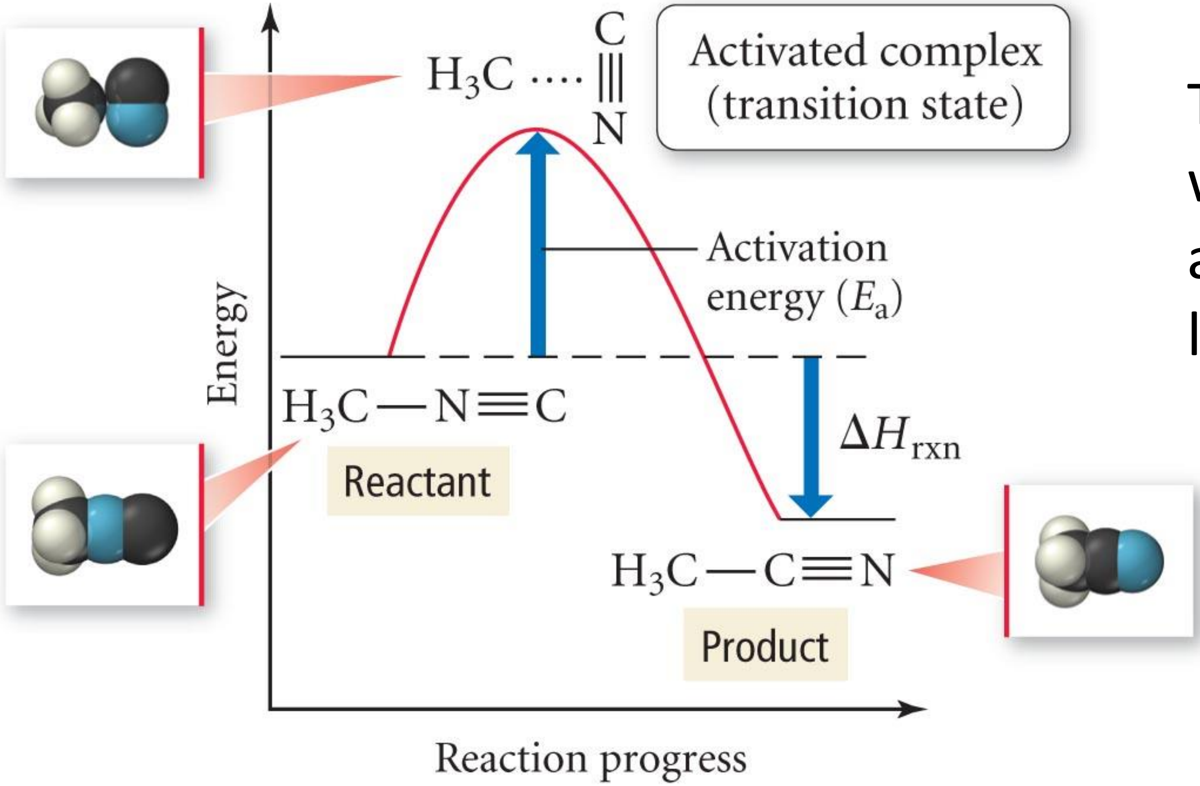
Orientation Factor



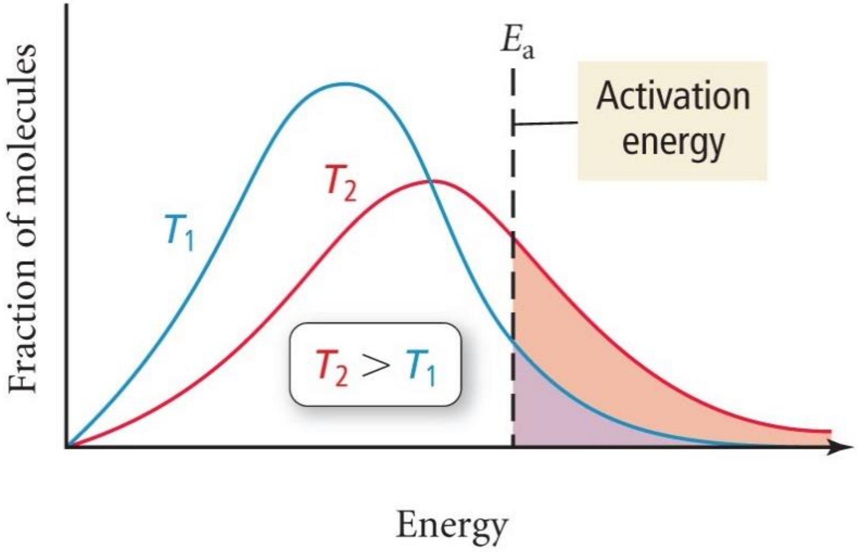
$$NOCl(g) + NOCl(g) \longrightarrow 2\,NO(g) + Cl_2(g)$$





Think about what would make an activation barrier large or small…

The temperature doesn't change the Ea, BUT it changes how many molecules have enough thermal energy to get over the barrier.



58. A chemical reaction is endothermic and has an activation energy that is twice the value of the enthalpy of the reaction. Draw a diagram depicting the energy of the reaction as it progresses. Label the position of the reactants and products and indicate the activation energy and enthalpy of reaction.

The Reaction rate can be related to the rates of formation or consumption of individual species through stoichiometry.

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

- The rate constant is calculated using the Method of Initial Rates or the Integrated rate law.
- BUT, unlike order, these are very temperature dependent!
- After they are measured at many temperatures, you can use the Arrhenius equation to relate temperature to the rate constant.
- The Arrhenius equation describes how increasing thermal energy increases rate by increasing the number of collisions (A), and by increasing the number of collisions that have enough energy to overcome the activation energy.

- Reaction Order can be only be determined experimentally!

  1. Method of Initial Rates
  2. Integrated Rate Laws

- But, either way, these would give you the SAME result.

- Reaction order is Temp-independent.

Mechanisms: One collision at a time…

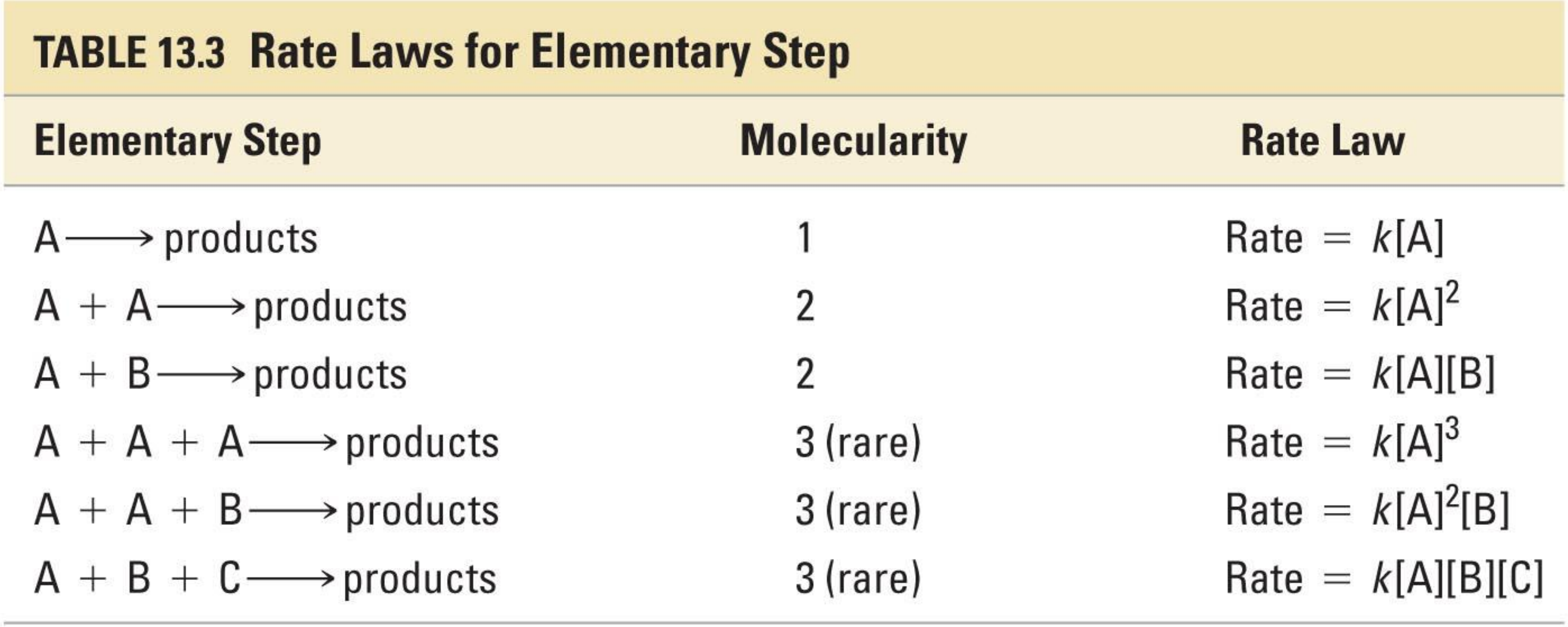
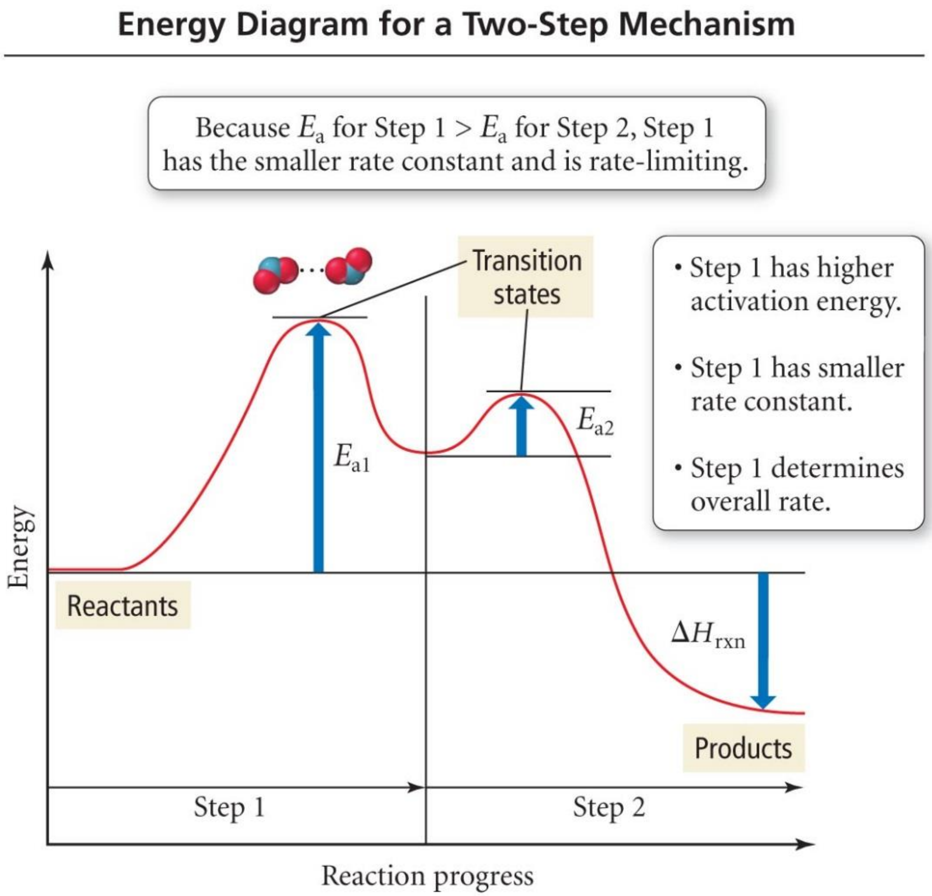


TABLE 13.3 Rate Laws for Elementary Step

Elementary Step	Molecularity	Rate Law
$A \longrightarrow \text{products}$	1	$\text{Rate} = k[A]$
$A + A \longrightarrow \text{products}$	2	$\text{Rate} = k[A]^2$
$A + B \longrightarrow \text{products}$	2	$\text{Rate} = k[A][B]$
$A + A + A \longrightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^3$
$A + A + B \longrightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^2[B]$
$A + B + C \longrightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A][B][C]$

Energy Diagrams for mechanisms



Energy Diagram for a Two-Step Mechanism

Because E_a for Step 1 > E_a for Step 2, Step 1 has the smaller rate constant and is rate-limiting.

- Step 1 has higher activation energy.
- Step 1 has smaller rate constant.
- Step 1 determines overall rate.

74. Consider this overall reaction which is experimentally observed to be second order in X and first order in Y:

$$X + Y \longrightarrow XY$$

a. Does the reaction occur in a single step in which X and Y collide?

b. Is the following two-step mechanism valid?

$$2\,X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X_2 \qquad \text{Fast}$$

$$X_2 + Y \xrightarrow[k_3]{} XY + X \qquad \text{Slow}$$

75. Consider this three-step mechanism for a reaction:

$$Cl_2(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\,Cl(g) \qquad \text{Fast}$$

$$Cl(g) + CHCl_3(g) \xrightarrow[k_3]{} HCl(g) + CCl_3(g) \qquad \text{Slow}$$

$$Cl(g) + CCl_3(g) \xrightarrow[k_4]{} CCl_4(g) \qquad \text{Fast}$$

a. What is the overall reaction?

b. Identify the intermediates in the mechanism.

c. What is the predicted rate law?

103. Consider the gas-phase reaction:

$$H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$$

The reaction was experimentally determined to be first order in H_2 and first order in I_2. Consider the proposed mechanisms.

Proposed mechanism I:

$$H_2(g) + I_2(g) \longrightarrow 2\,HI(g) \qquad \text{Single step}$$

Proposed mechanism II:

$$I_2(g) \underset{k_{-2}}{\overset{k_1}{\rightleftharpoons}} 2\,I(g) \qquad \text{Fast}$$

$$H_2(g) + 2\,I(g) \xrightarrow[k_3]{} 2\,HI(g) \qquad \text{Slow}$$

a. Show that both of the proposed mechanisms are valid.

b. What kind of experimental evidence might lead you to favor mechanism II over mechanism I?

104. Consider the reaction:

$$2\,NH_3(aq) + OCl^-(aq) \longrightarrow N_2H_4(aq) + H_2O(l) + Cl^-(aq)$$

This three-step mechanism is proposed:

$$NH_3(aq)\ OCl^-(aq) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_2Cl(aq) + OH^-(aq) \qquad \text{Fast}$$

$$NH_2CI(aq) + NH_3(aq) \xrightarrow[k_3]{} N_2H_5^+(aq) + Cl^-(aq) \qquad \text{Slow}$$

$$N_2H_5^+(aq) + OH^-(aq) \xrightarrow[k_4]{} N_2H_4(aq) + H_2O(l) \qquad \text{Fast}$$

a. Show that the mechanism sums to the overall reaction.
b. What is the rate law predicted by this mechanism?

105. The proposed mechanism for the formation of hydrogen bromide can be written in a simplified form as:

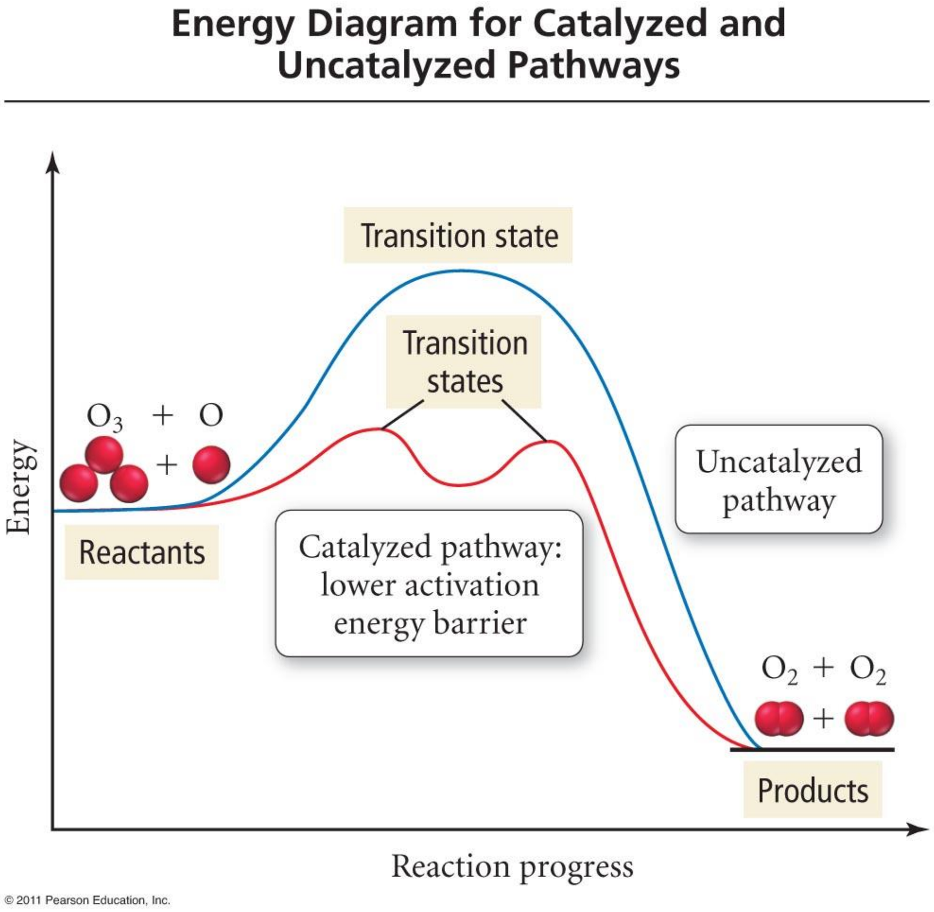
$$Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Br(g) \qquad \text{Fast}$$

$$Br(g) + H_2(g) \xrightarrow{k_2} HBr(g) + H(g) \qquad \text{Slow}$$

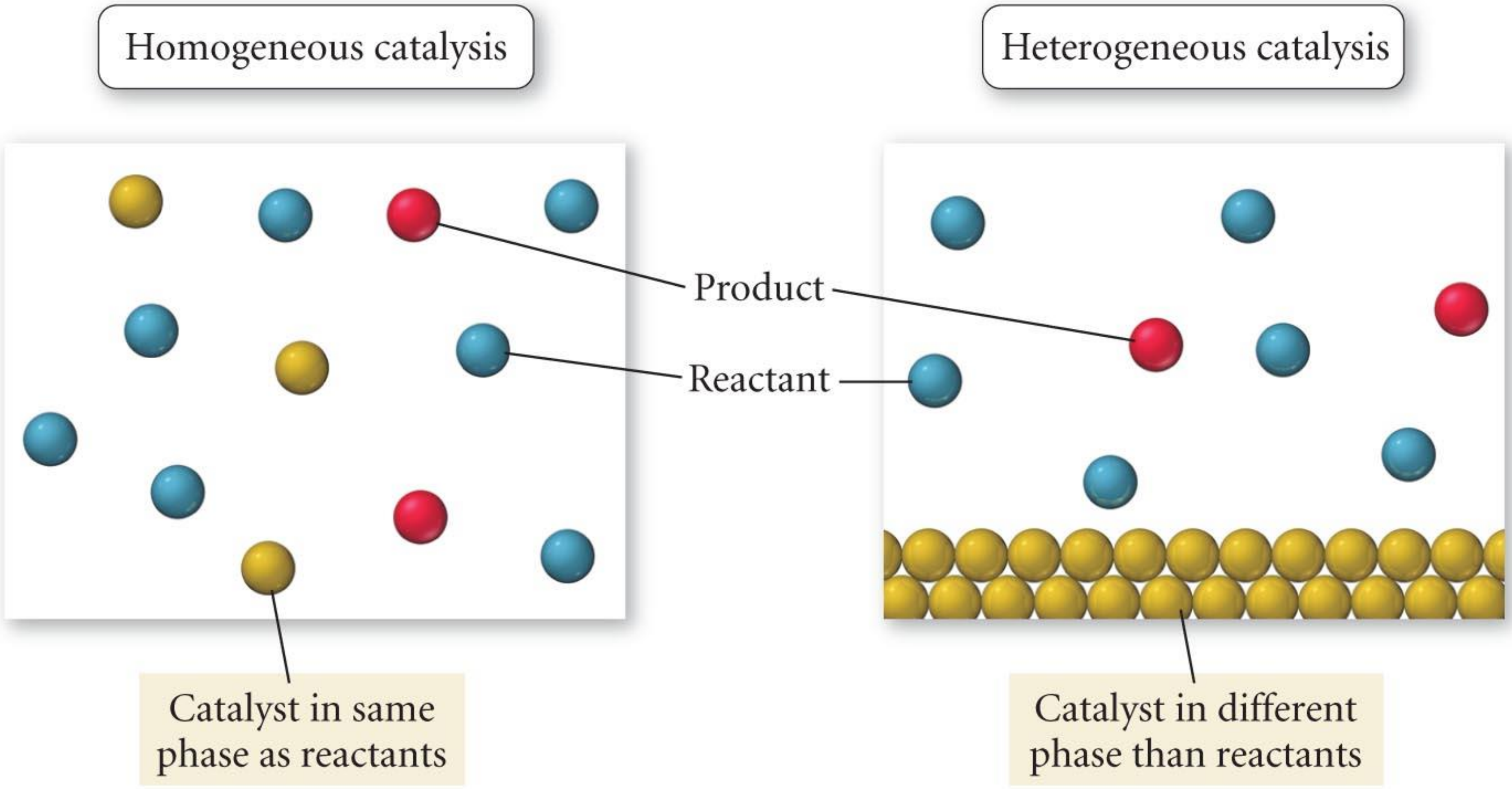
$$H(g) + Br_2(g) \xrightarrow{k_3} HBr(g) + Br(g) \qquad \text{Fast}$$

What rate law corresponds to this mechanism?

The effect of a Catalyst



Types of Catalysts



Homogeneous catalysis

Heterogeneous catalysis

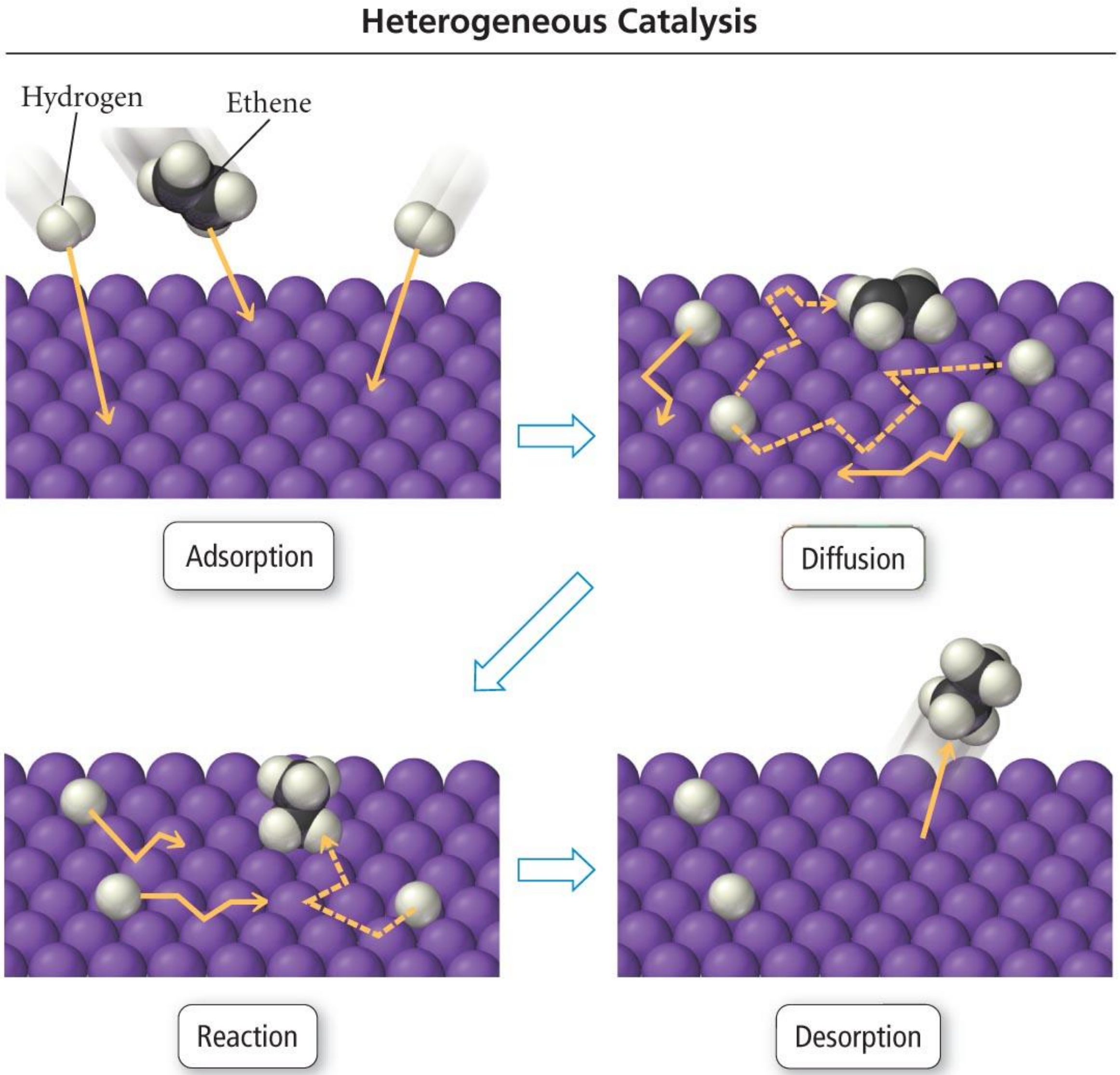
Product

Reactant

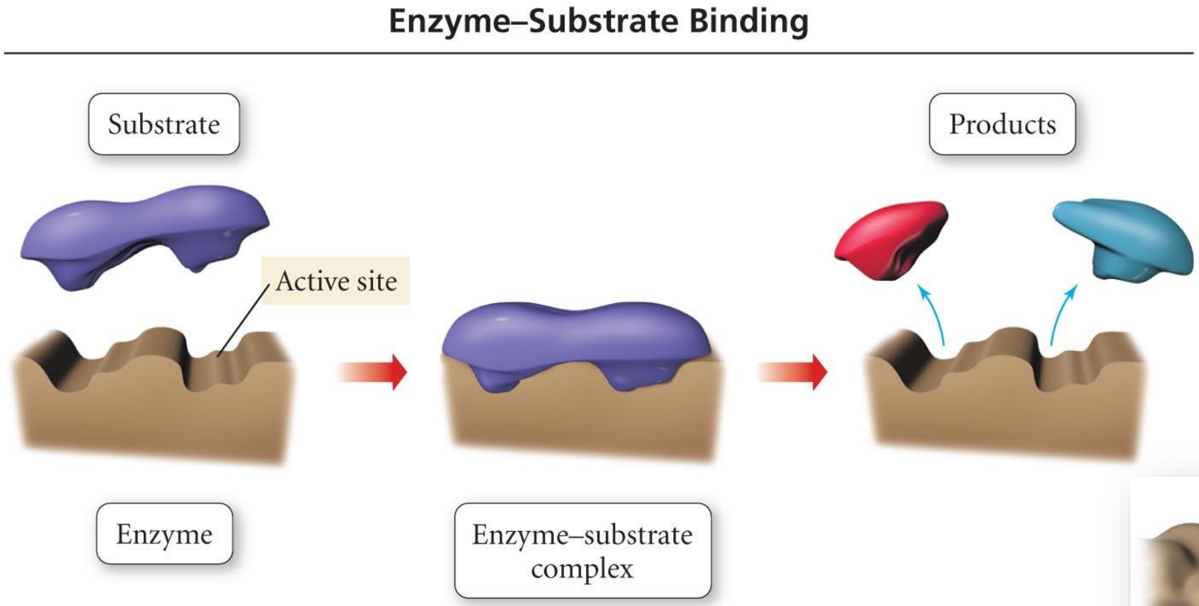
Catalyst in same phase as reactants

Catalyst in different phase than reactants

Hydrogenation of ethene



Biological Catalysts: Enzymes



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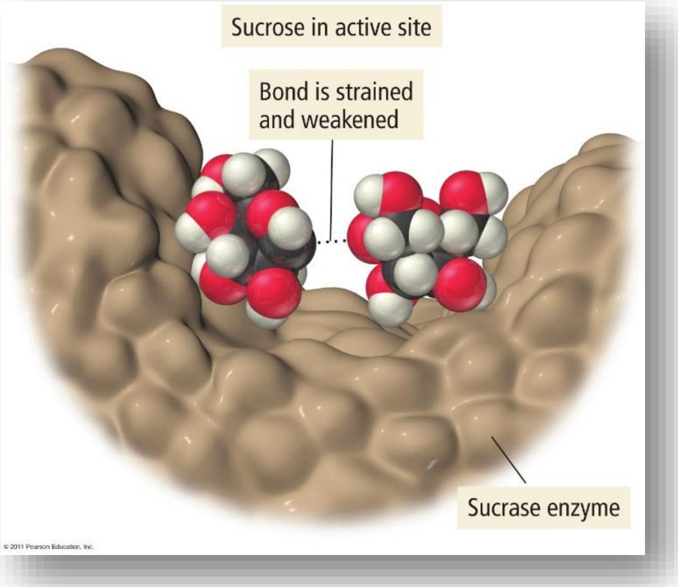

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