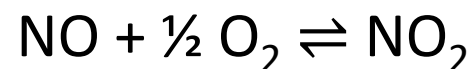


# Effect of Concentration on Rate

Increasing concentration of reactants will (generally) increase the reaction rate.

But by how much?



(When  $[\text{NO}] = 0.020 \text{ M}$ )

Trial A:  $[\text{O}_2] = 0.020 \text{ M}$  Rate =  $0.057 \text{ M/s}$

Trial B:  $[\text{O}_2] = 0.040 \text{ M}$  Rate =  $0.114 \text{ M/s}$

(When  $[\text{O}_2] = 0.020 \text{ M}$ )

Trial A:  $[\text{NO}] = 0.020 \text{ M}$  Rate =  $0.057 \text{ M/s}$

Trial B:  $[\text{NO}] = 0.040 \text{ M}$  Rate =  $0.227 \text{ M/s}$

# Expressing Rates: Rate Laws

We can express the dependence of rate on concentration using a **rate law**. For the generic reaction:



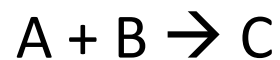
$[A]^1$  : *first-order* rates

$[A]^2$ : *second-order* rates

$[A]^0$ : *zero-order* rates



The rate law for the reaction:

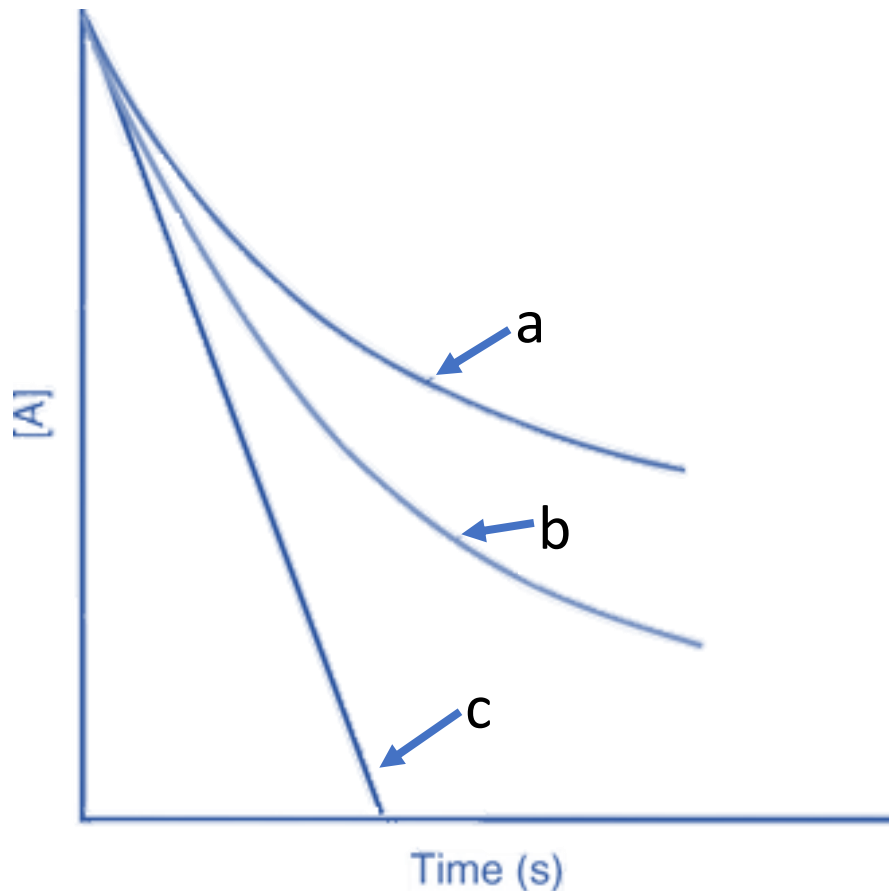


is:  $\text{rate} = k[A]^2[B]^0$

The lines below represent 3 different reactions - one each of a 0<sup>th</sup>, 1<sup>st</sup>, and 2<sup>nd</sup> order.

Which line best represents [A] during the reaction above?

(note: the example reactions have been chosen so that they have a *similar initial rate*.)



$$[A]^1[B]^1 :$$

When  $[A] \gg [B]$ :

# Experiment 2 & Pseudo-order kinetics

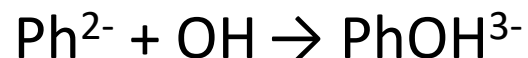
Observe reaction of phenolphthalein with  $\text{OH}^-$  :

$$\text{Rate} = k[\text{Ph}^{2-}]^p[\text{OH}^-]^n$$

$$[\text{Ph}^{2-}] = 0.00003 \text{ M}, [\text{OH}^-] = 0.3 \text{ M}$$

Even if all  $[\text{Ph}^{2-}]$  was consumed,  $[\text{OH}^-]$  would essentially remain the same throughout the reaction. Changes in rate over time during the reaction are due to decrease in  $[\text{Ph}^{2-}]$  only – find reaction order with respect to  $[\text{Ph}^{2-}]$  and the pseudo-rate constant  $k'$ .

How do we determine  $[\text{Ph}^{2-}]$ ? Absorbance (colourimetry):



# How can we explain these observations at the molecular level?

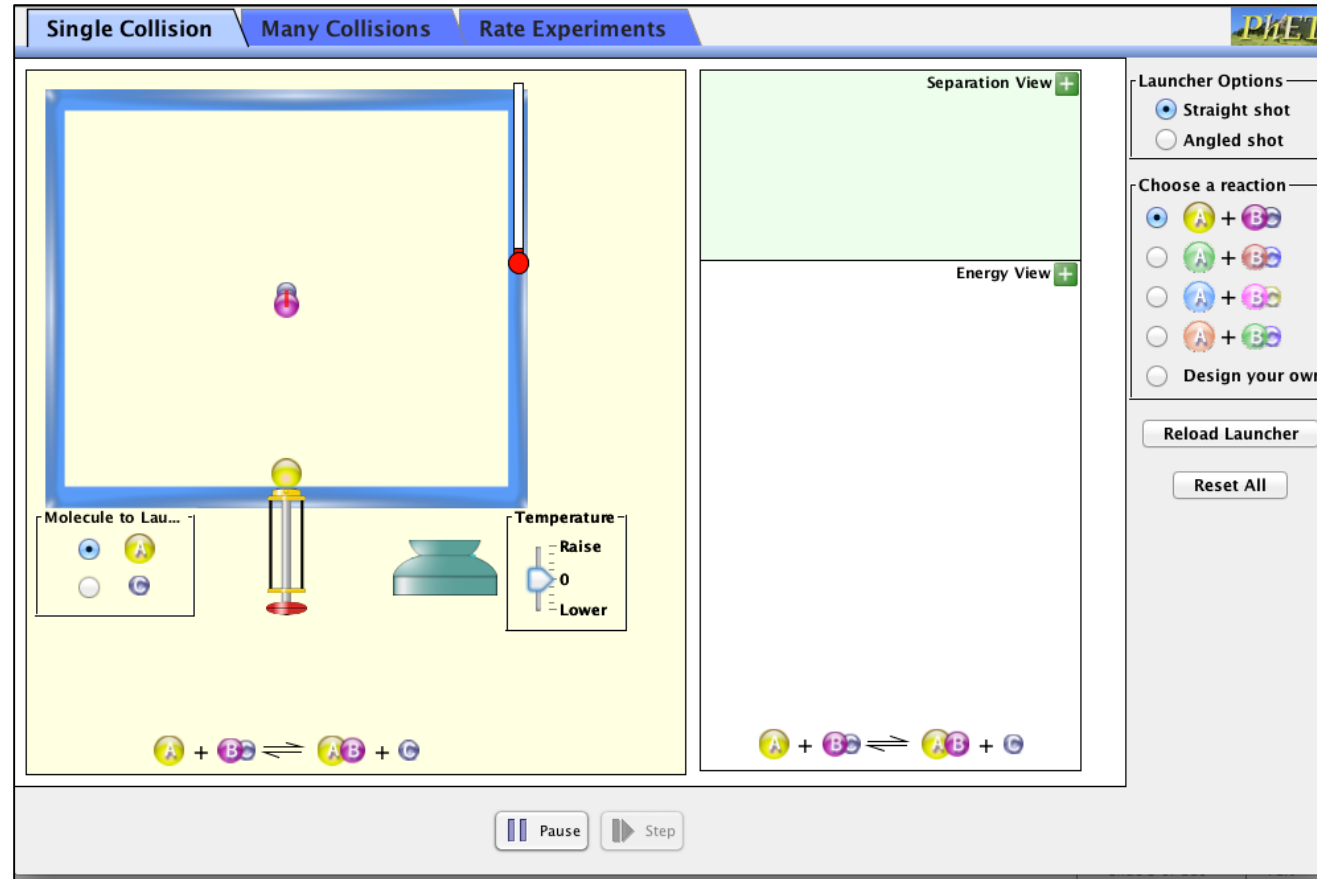
## COLLISION THEORY (for chemical reactions)

In order to react, particles must collide with each other.

*BUT* – particles are colliding all the time (e.g.  $\text{H}_2$  and  $\text{O}_2$  in air) without reacting! What needs to happen in order for two molecules or atoms to react with each other?

Let's make some observations of a simplified system...

<http://phet.colorado.edu/en/simulation/reactions-and-rates>



✓ Qualitatively *describe* what the speed of a reaction depends upon.



Let's make some observations of a simplified system...



SCENARIO			Observations
Atom launched	Launch speed	Launch direction	
A	LOW	DIRECT	
A	HIGH	DIRECT	
A	HIGH	ANGLED	
C	HIGH	DIRECT	
C	LOW	DIRECT	

<http://phet.colorado.edu/en/simulation/reactions-and-rates>

✓ Qualitatively *describe* what the speed of a reaction depends upon.

# How can we explain these observations at the molecular level?

## COLLISION THEORY (for chemical reactions)

In order for a chemical reaction to occur between two atoms or molecules, they must...

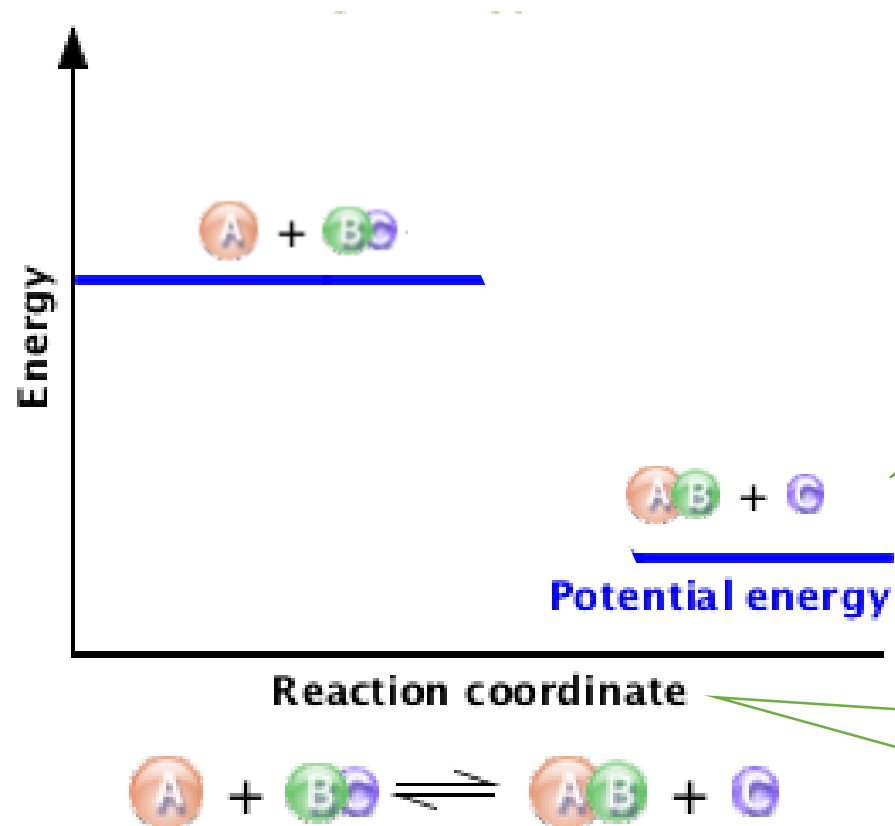
(1)

(2)

# How can we explain these observations at the molecular level?

Why did it matter which atom we launched?

Let's look at a *reaction coordinate diagram*:



This reaction is **exothermic**:

What's a **reaction coordinate**?

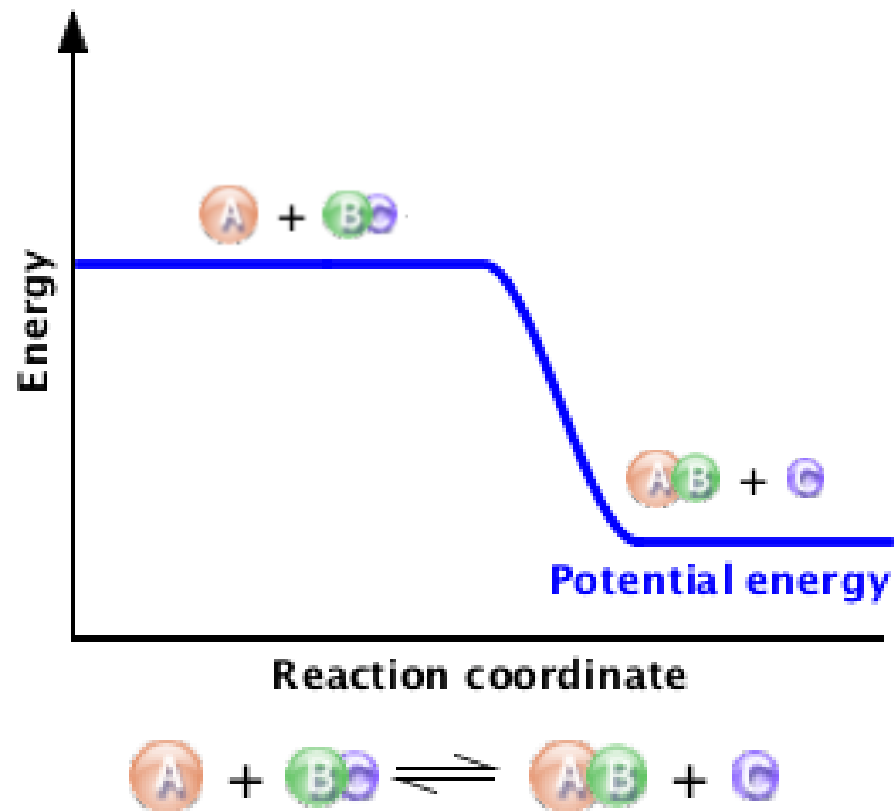
# How can we explain these observations at the molecular level?

Why did it matter which atom we launched?

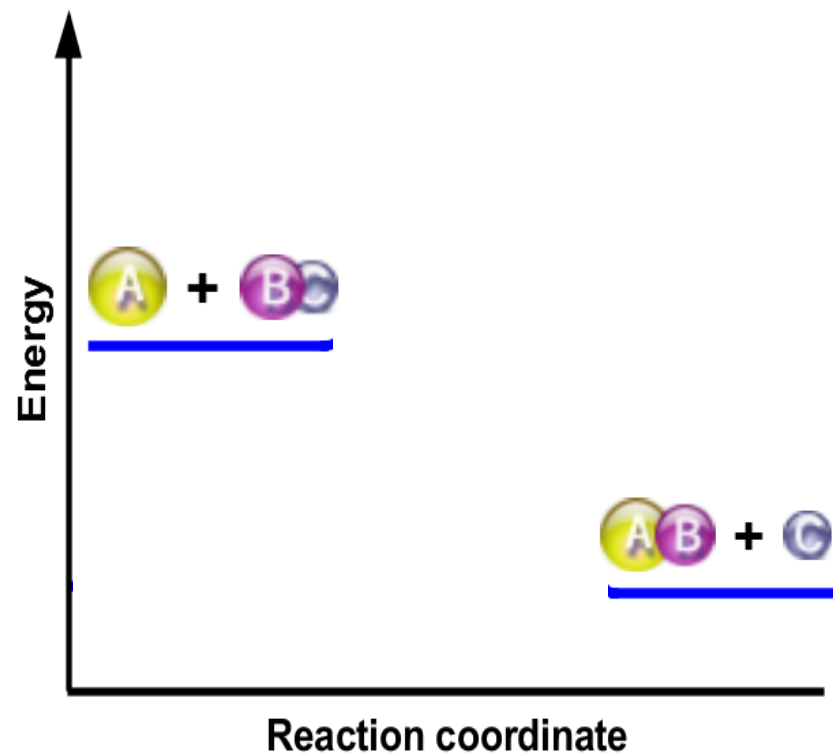
Let's look at a *reaction coordinate diagram*:

Potential energy:

Kinetic energy:



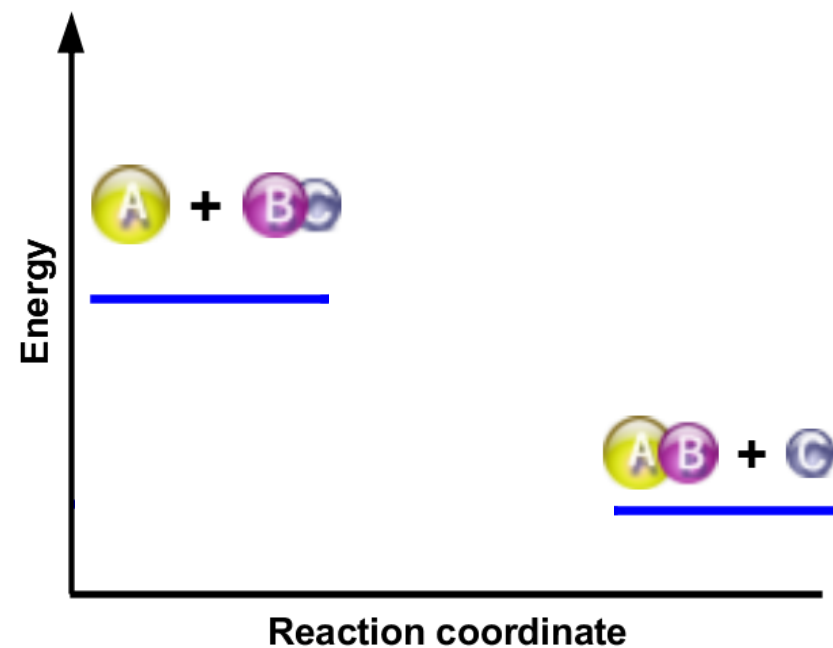
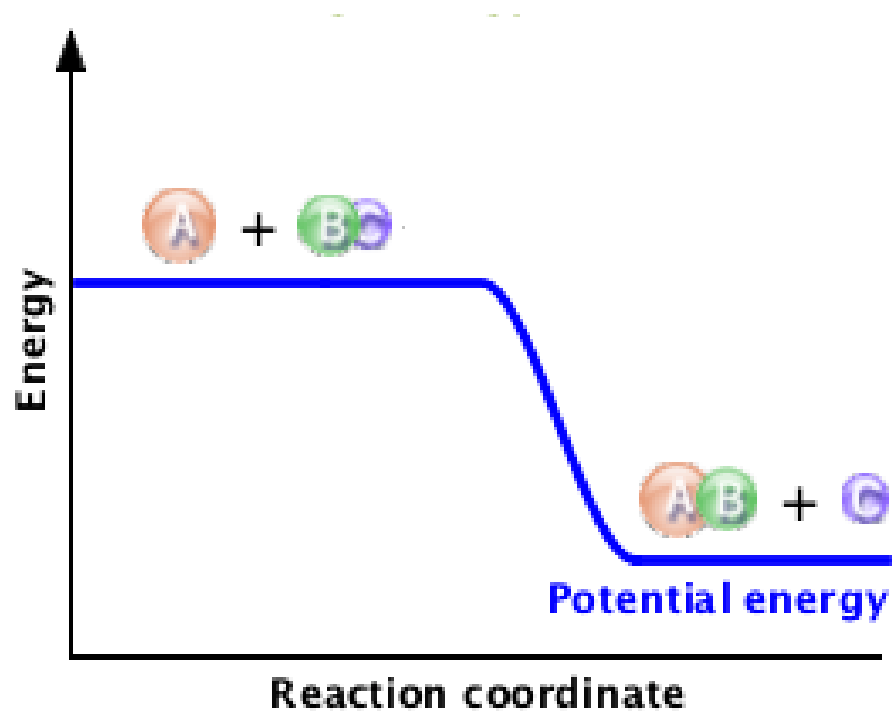
# Let's try another exothermic reaction:



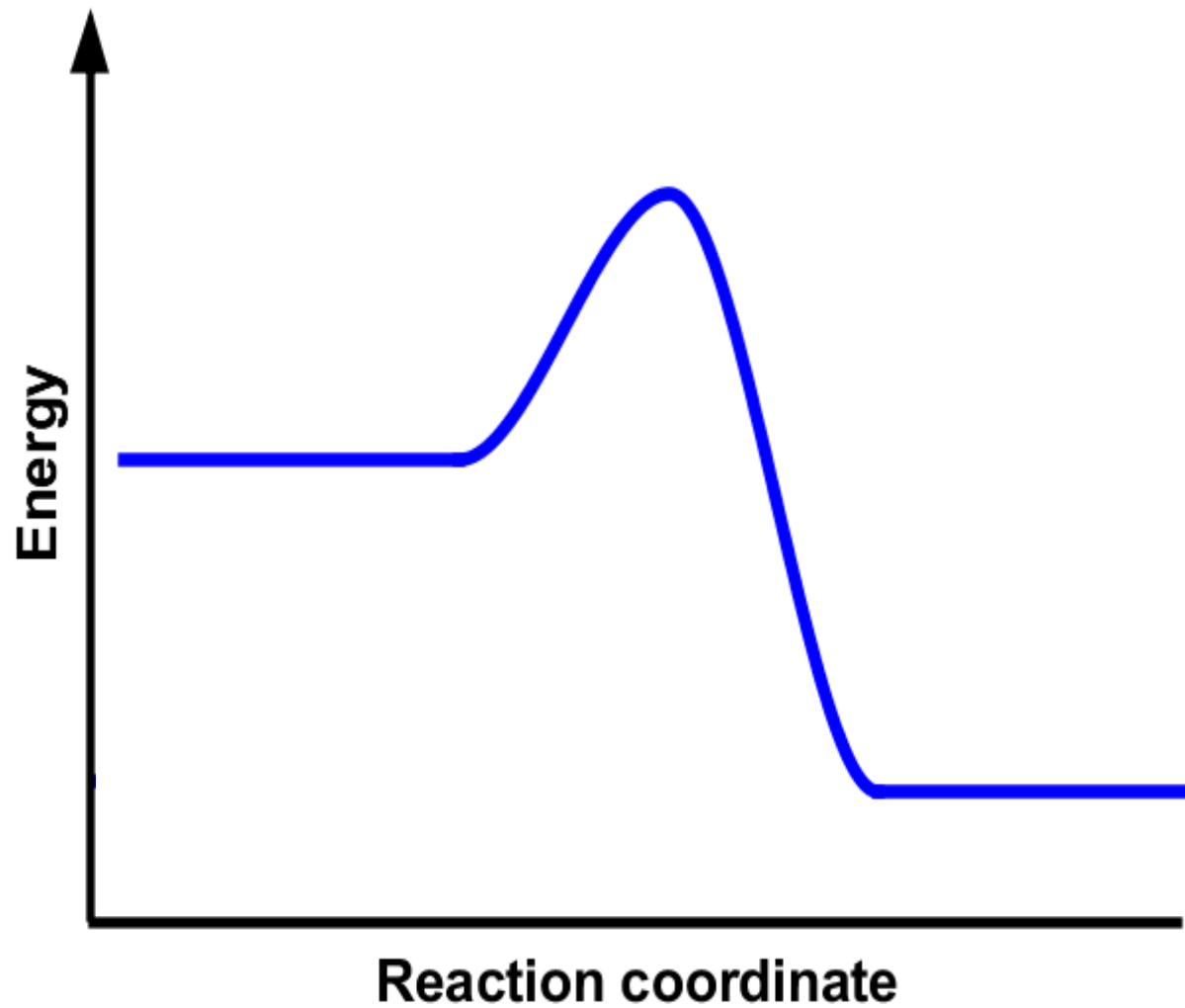
SCENARIO			Observations
Atom launched	Launch speed	Launch direction	
A	LOW	DIRECT	
A	HIGH	DIRECT	
C	HIGH	DIRECT	
C	LOW	DIRECT	

✓ Qualitatively *describe* what the speed of a reaction depends upon.

# But what's the difference?



# Reaction Profiles & $E_a$



# Activation Energy ( $E_a$ )

- The **activation energy** is the minimum energy required in order to result in a chemical reaction.
- Controlling temperature is one way to change how many collisions will result in a successful reaction.
- A large  $E_a$  is generally harder to achieve, so the reaction would be slower at a given temperature.

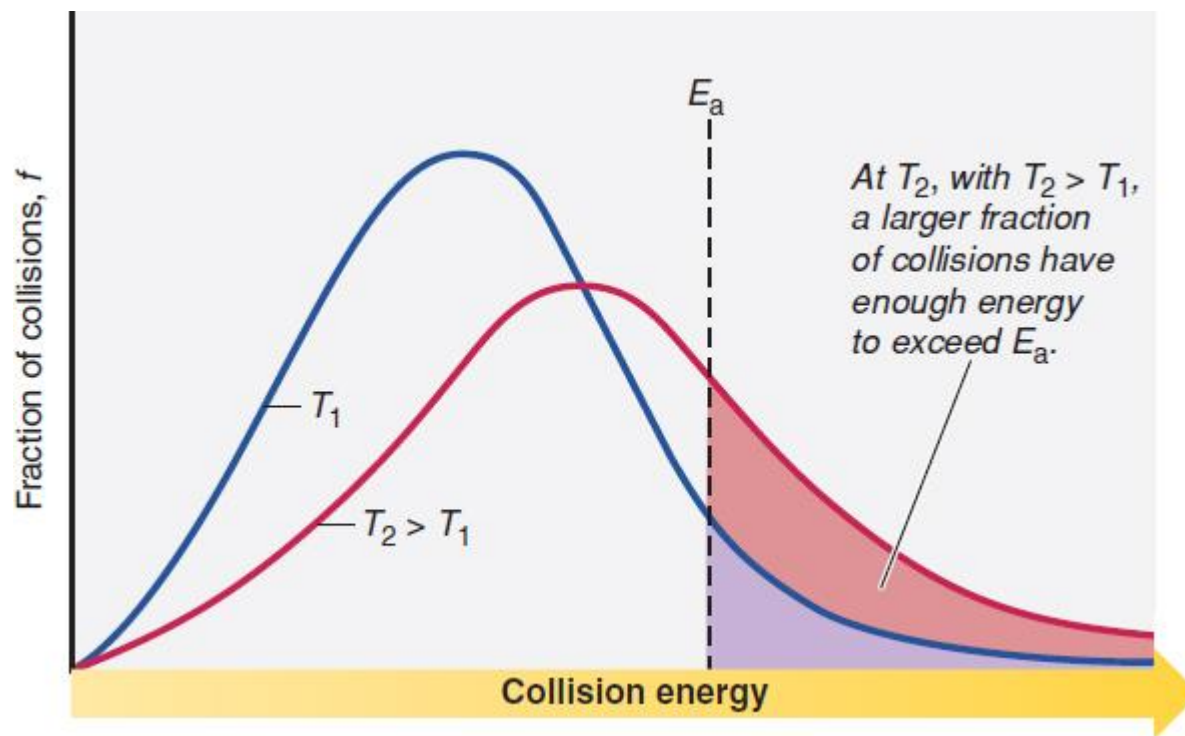
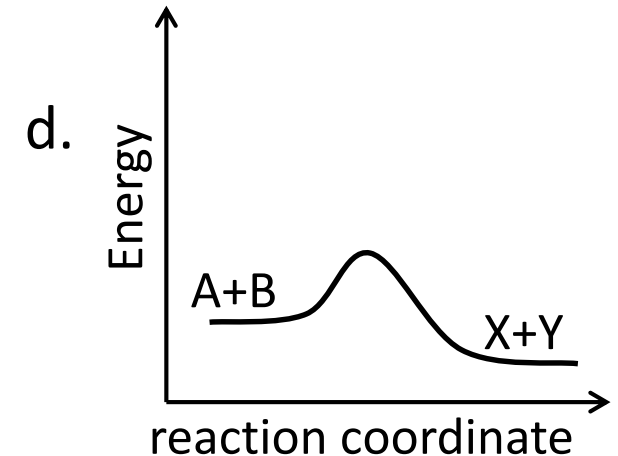
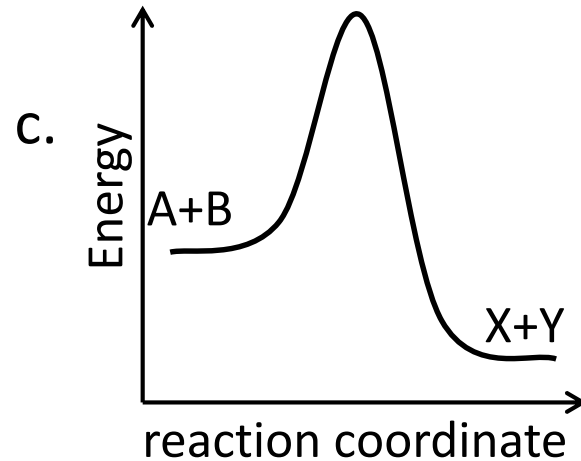
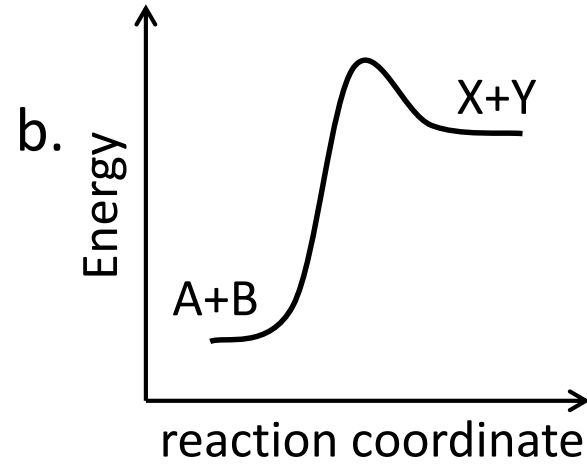
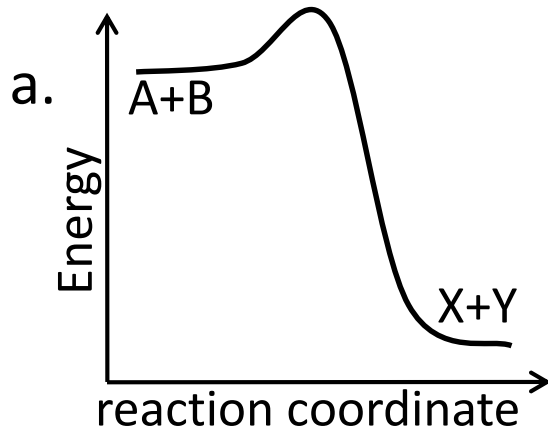


Fig. 14.16



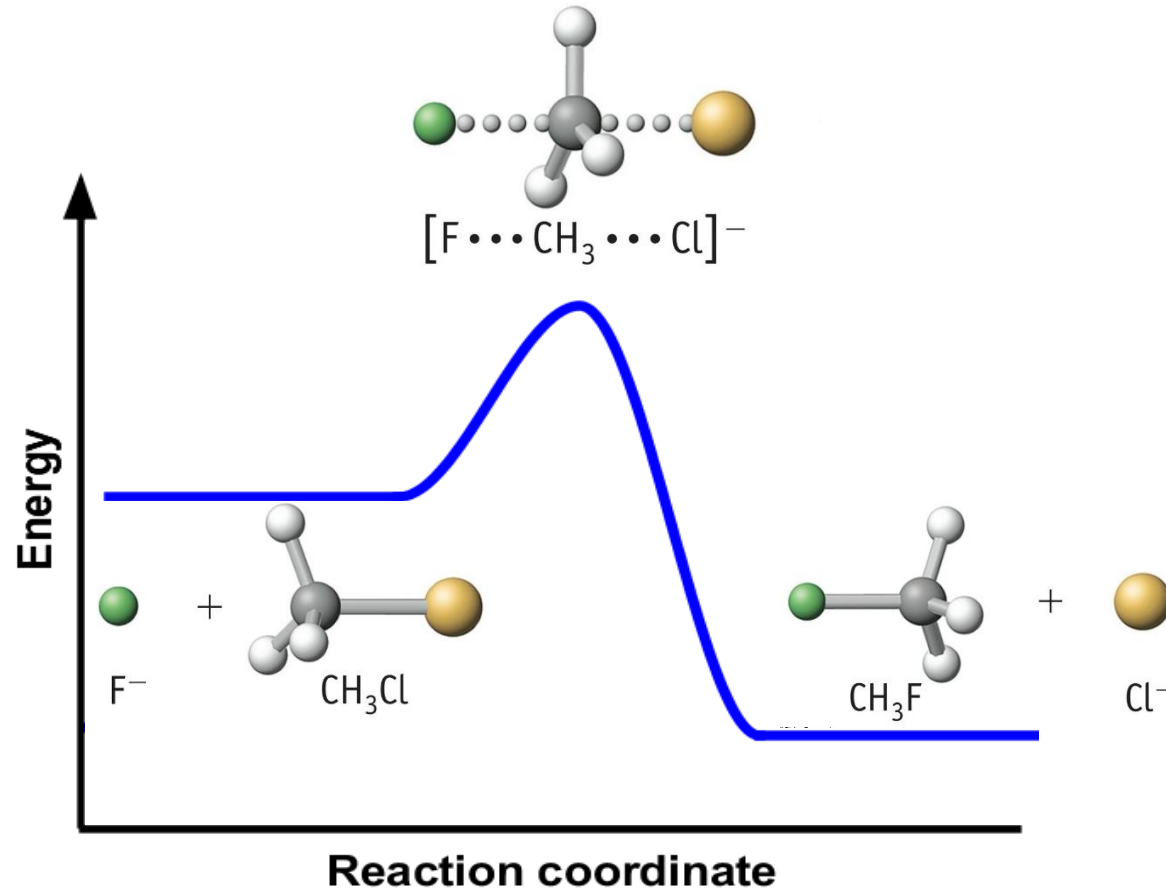


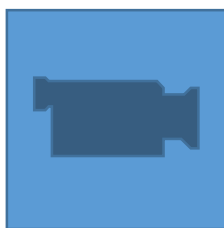
The reaction between A and B is determined to be a fairly fast reaction and slightly exothermic. Which of the following reaction profiles best fits this description?



# Transition States

- A high-energy, short-lived state where the molecular configuration is somewhere between the reactants and products
- You cannot isolate the transition state in a reaction – it doesn't last long enough.





# Reaction Mechanisms

A reaction **mechanism** is a step-by step explanation of the process of a chemical reaction.

Each step in a mechanism is called an **elementary step** – these describe an individual event in the reaction.

For example, the mechanism of the reaction of  $\text{NO}_2$  with  $\text{CO}$  ( $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ ) has two elementary steps:

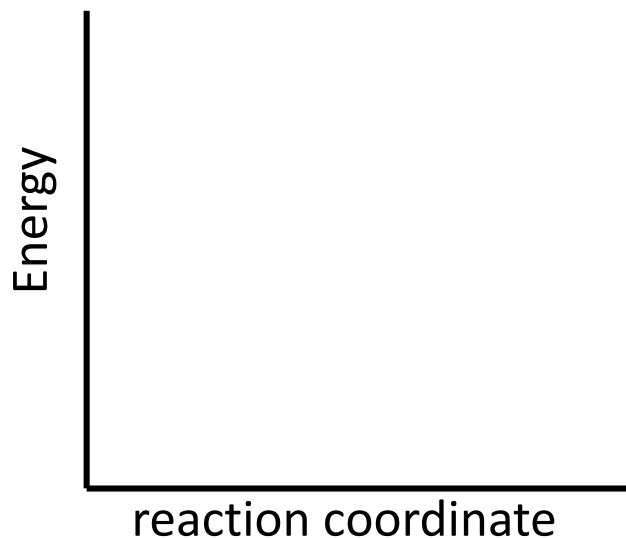
- An oxygen is transferred from  $\text{NO}_2$  to a second  $\text{NO}_2$ , forming a molecule of  $\text{NO}$  and a molecule of  $\text{NO}_3$
- An oxygen is transferred from  $\text{NO}_3$  to  $\text{CO}$ , producing a molecule of  $\text{NO}_2$  and a molecule of  $\text{CO}_2$
- Note that  $\text{NO}_3$  was formed, although it does not appear in the overall reaction. It is a **reactive intermediate**.

# Transition States vs. Reactive Intermediates

**Transition states** are short-lived, not isolatable, and contain partially formed bonds.

**Reactive Intermediates** can be longer-lived, are usually fairly stable – at least surviving long enough to detect with standard techniques – and contain only fully formed bonds.

Additionally, intermediates usually are found in a “well” in the reaction profile, while transition states are at a peak energy.

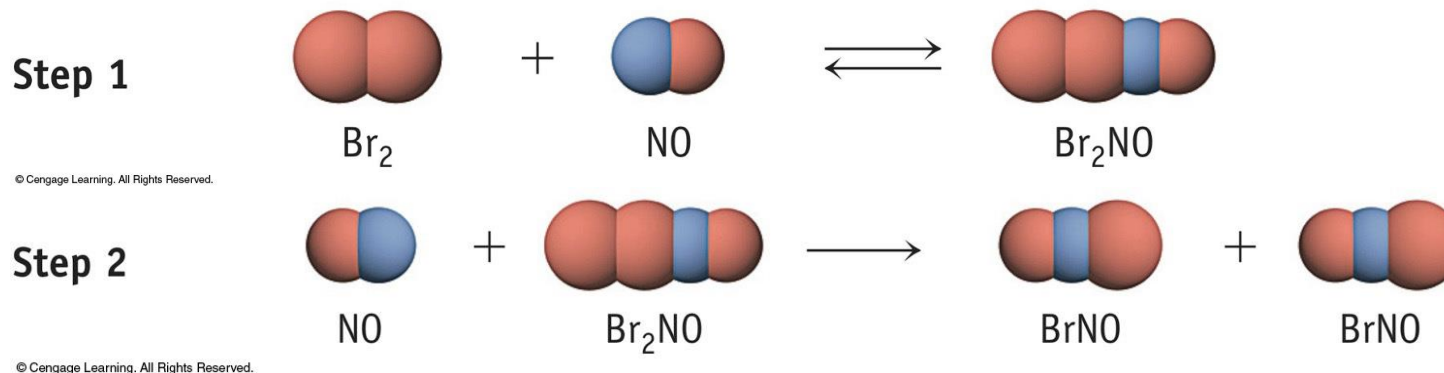


- ✓ Determine the rate law given the mechanism of a reaction, and vice versa - for reactions with a slow first step.
- ✓ Draw and interpret a reaction energy diagram for a given reaction.





The reaction between  $\text{Br}_2$  and  $\text{NO}$  is described by the mechanism below. What, if any, are the **reactive intermediates** in this reaction?



a)  $\text{Br}_2$

b)  $\text{NO}$

c)  $\text{Br}_2\text{NO}$

d)  $\text{BrNO}$

e)  $\text{Br} \cdots \text{BrNO}$

f)  $\text{Br}_2 \cdots \text{NO}$

g)  $\text{NO}$  &  $\text{Br}_2\text{NO}$

h)  $\text{Br}_2$  &  $\text{NO}$

# Elementary Processes

Elementary processes represent each step in a mechanism – i.e. the actual molecular event. (collision or separation)

Characteristics of elementary processes:

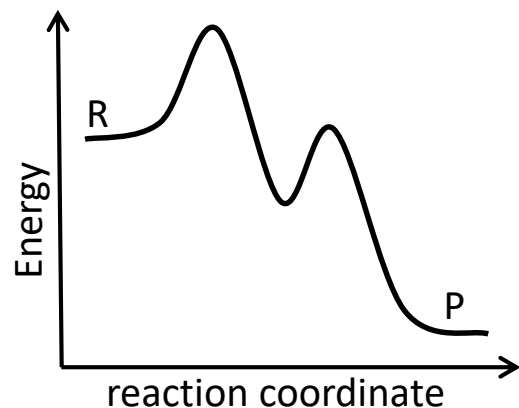
- **Unimolecular** or **bimolecular**. Termolecular or higher are very rare.
- **Intermediates** may be produced in one elementary process but must be consumed in another.
- One elementary step is usually slower than all the others and is known as the **rate determining step**.



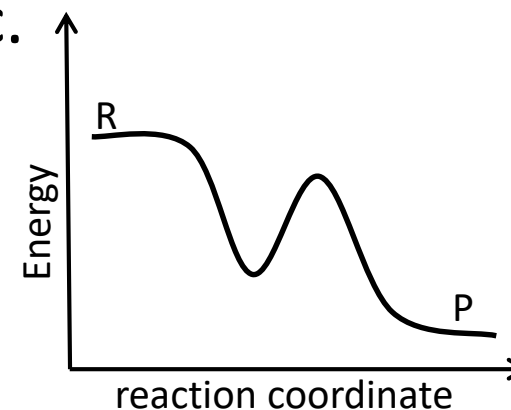


The iodide catalyzed decomposition of peroxide (“Elephant’s Toothpaste”) occurs via two separate steps, in which the first step is the rate determining step. Which of the following three reaction profiles best describes this reaction?

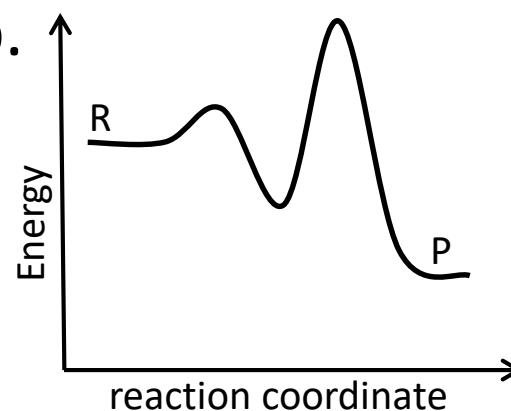
a.



c.



b.



- ✓ Determine the rate law given the mechanism of a reaction, and vice versa - for reactions with a slow first step.
- ✓ Draw and interpret a reaction energy diagram for a given reaction.

# Rate Laws and Elementary Steps

The **rate-determining step** of a mechanism determines the rate law, *not* the overall reaction.

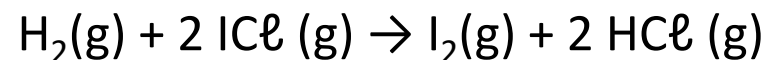
For the generic (overall) reaction  $2A + B \rightarrow C$

If the rate-determining step is:	The rate law will be:
$A + B \rightarrow \text{Products}$	
$A + A \rightarrow \text{Products}$	
$A \rightarrow \text{Products}$	
$2A + B \rightarrow \text{Products}$	

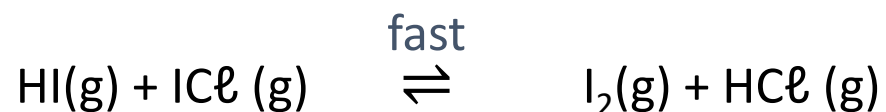
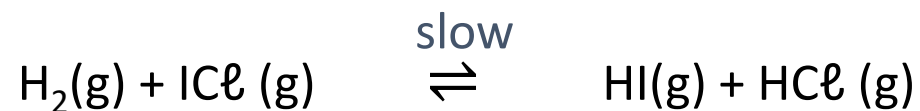


✓ Determine the rate law given the mechanism of a reaction, and vice versa - for reactions with a slow first step.

e.g. for the exothermic reaction:



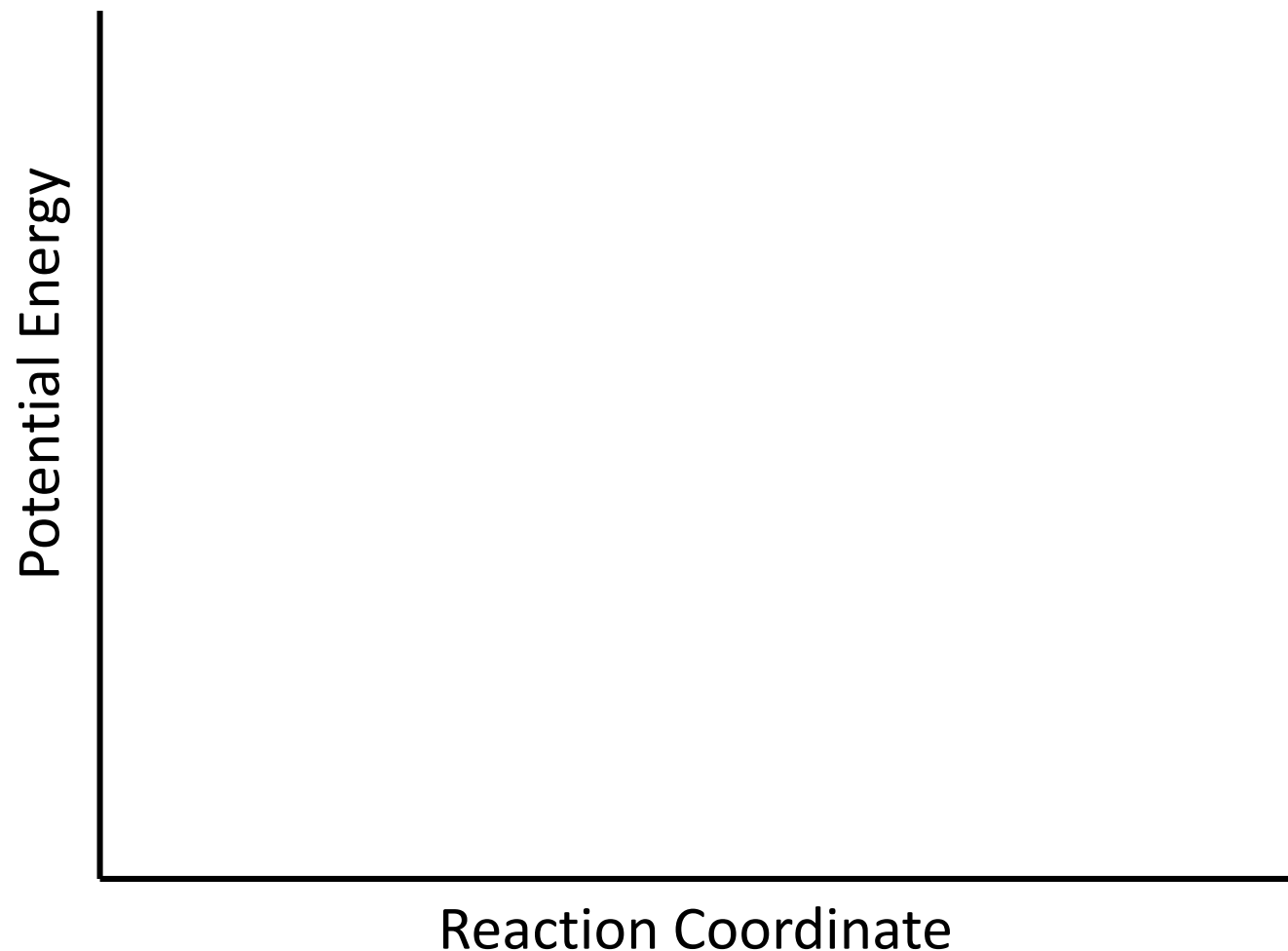
The mechanism is:



And the rate law is:

$$\text{rate} = k[\text{H}_2][\text{ICl}]$$

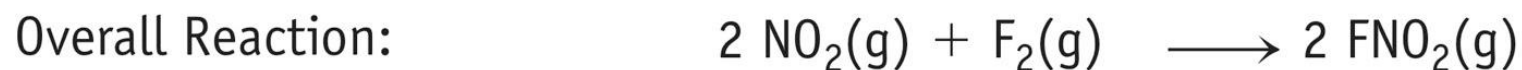
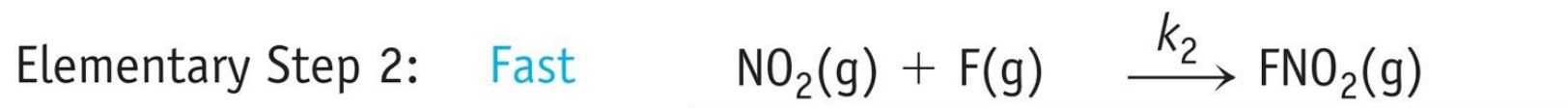
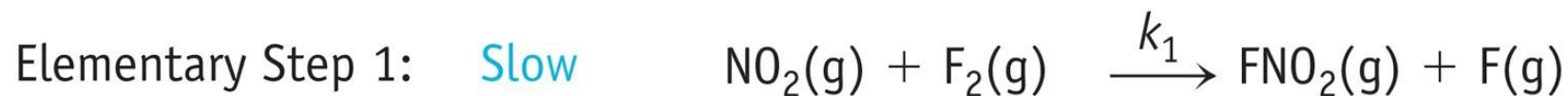
The reaction profile for this reaction looks like:



- ✓ Determine the rate law given the mechanism of a reaction, and vice versa - for reactions with a slow first step.
- ✓ Draw and interpret a reaction energy diagram for a given reaction.



A proposed mechanism for the reaction between  $\text{NO}_2$  and  $\text{F}_2$  is shown below. What is the rate law and over all order for this reaction?



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### Part 1

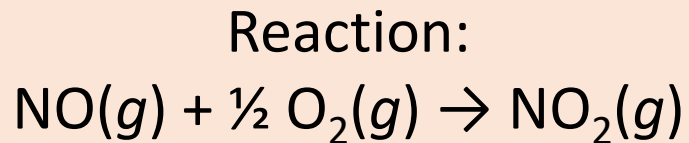
- a)  $\text{Rate} = k[\text{NO}_2]^2[\text{F}_2]$
- b)  $\text{Rate} = k[\text{NO}_2]^2[\text{F}_2] / [\text{FNO}_2]^2$
- c)  $\text{Rate} = k_1[\text{NO}_2][\text{F}_2]$
- d)  $\text{Rate} = k_2[\text{NO}_2][\text{F}]$
- e)  $\text{Rate} = k_1[\text{NO}_2][\text{F}_2] / [\text{FNO}_2][\text{F}]$

### Part 2

- a) Zero order
- b) First order
- c) Second order
- d) Third order
- e) 3/2 order

# Determining Rate Laws: Initial Rates

We can control the initial concentration of the reactants – studying the initial rate with varying initial concentrations can help determine a rate law:



EXPERIMENT	INITIAL CONCENTRATIONS (mol/L)		INITIAL RATE (mol NO/L · s)
	[NO]	[O <sub>2</sub> ]	
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

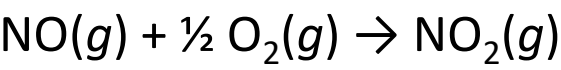
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If the concentration of reactant “A” is **doubled**, AND

- The reaction is **first order** (  $[\text{A}]^1$  ) – the reaction rate should:
- The reaction is **second order** (  $[\text{A}]^2$  ) – the reaction rate should:

✓ Given experimental data, quantitatively determine the components of a rate law (k and order), using the method of initial rates.

What is the rate law for this reaction?



EXPERIMENT	INITIAL CONCENTRATIONS (mol/L)		INITIAL RATE (mol NO/L · s)
	[NO]	[O <sub>2</sub> ]	
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

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✓ Given experimental data, quantitatively determine the components of a rate law (k and order), using the method of initial rates.



What is the rate law and rate constant?

What will the initial rate of reaction be if  $[\text{NO}_2]=0.10\text{ M}$  and  $[\text{CO}] = 0.30\text{ M}$ ?

Expt.	Initial Rate (mol/L·s)	Initial $[\text{NO}_2]$ (mol/L)	Initial $[\text{CO}]$ (mol/L)
1	0.0050	0.10	0.10
2	0.080	0.40	0.10
3	0.0050	0.10	0.20



# Effect of temperature on rates

We know that temperature affects the rate of reaction, but how is that included in the expression for a rate law?

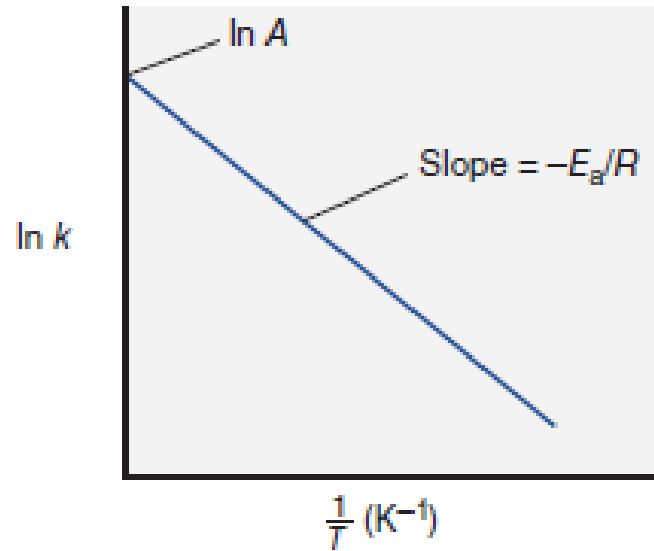
The relationship between  $k$ ,  $E_a$  and  $T$  is the **Arrhenius equation**:

$$k = Ae^{-E_a/RT}$$

When we compare the rate of a reaction under two sets of conditions we can use:

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

# Using Arrhenius Eq. to find $E_a$



Linearizing the Arrhenius Equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

$$\ln(k) = \ln\left(A e^{\frac{-E_a}{RT}}\right) = \ln(A) + \ln\left(e^{\frac{-E_a}{RT}}\right)$$

$$\ln(k) = \ln(A) + \frac{-E_a}{RT}$$

$$\ln(k) = \ln(A) + \left(\frac{-E_a}{R}\right) * \left(\frac{1}{T}\right)$$

Fig. 14.17

Plot to determine  $E_a$  (Arrhenius plot)

✓ Qualitatively *describe* what the speed of a reaction depends upon.

# Determining Rates: Integrated Rate Laws

Differential Rate Laws (“regular” rate laws):

- Measures rate as it varies with reactant concentration

Integrated Rate Laws:

- Measure change in concentration with time, and relate this back to the rate
- Easier & more convenient experimentally
- Goal: Make a plot with a straight line
- Works best for 0, 1, or 2 order (since the integral is well defined)

# Zero-order Integrated Rate Law

For the reaction:

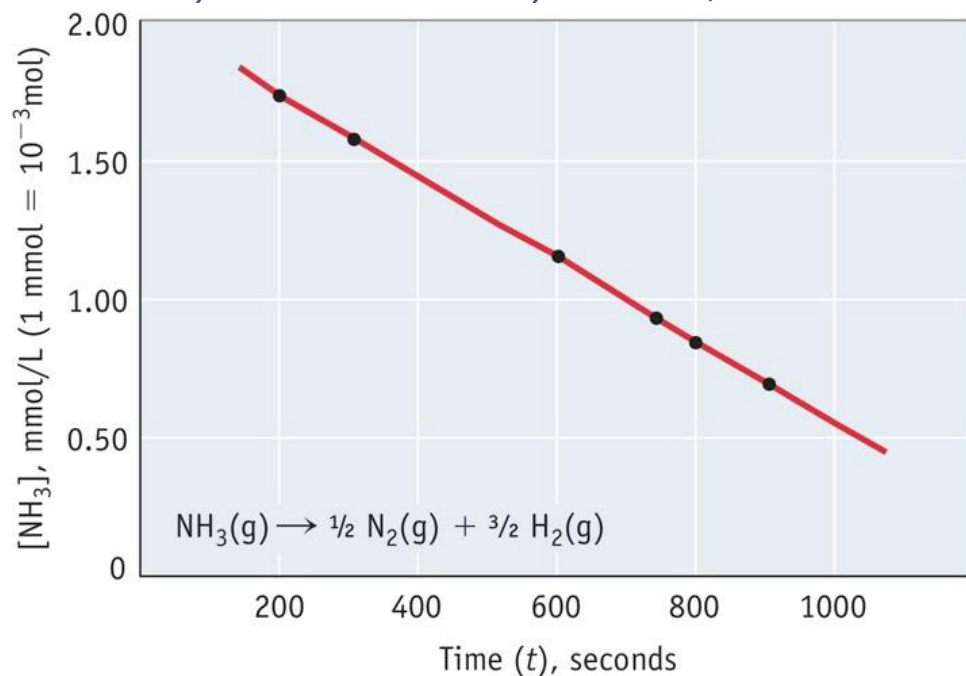


Differential rate law:  $\text{Rate} = k[A]^0$

Integrated rate law:  $[A]_t = -kt + [A]_0$

For the decomposition of  $\text{NH}_3$ :

Figure 14.6 from *Chemistry & Chemical Reactivity 9<sup>th</sup> Edition*, Kotz et al. 2012



$$\text{Rate} = k[\text{NH}_3]^0$$

$$\text{Slope} = -k$$

$$= \frac{(0.540 - 1.29) \text{ mmol/L}}{(1000 - 500) \text{ s}}$$

$$= -1.5 \times 10^{-3} \text{ mmol/L} \cdot \text{s}$$

$$k = 1.5 \times 10^{-3} \text{ mmol/L} \cdot \text{s}$$

✓ Use integrated rate laws to determine the amount of product produced (or reactant remaining) at any given point within a reaction

# First-order Integrated Rate Law

For the reaction:

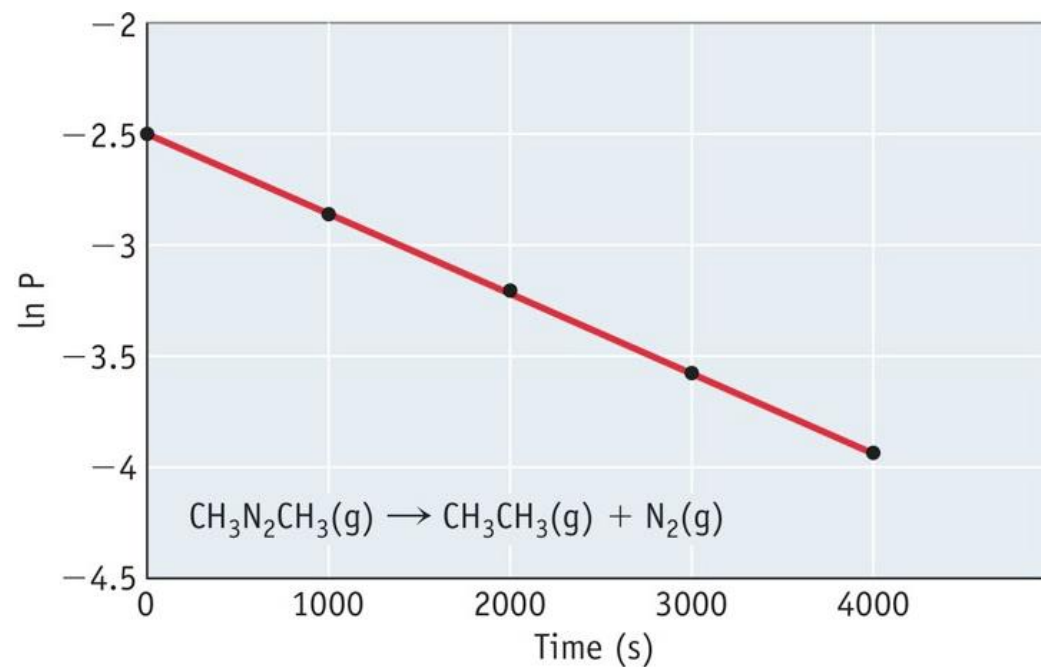


Differential rate law:  $\text{Rate} = k[A]$

Integrated rate law:  $\ln \left( \frac{[A]_0}{[A]_t} \right) = kt$

For the decomposition of  $\text{CH}_3\text{N}_2\text{CH}_3$ :

Figure 14.6 from *Chemistry & Chemical Reactivity 9<sup>th</sup> Edition*, Kotz et al. 2012



$$\text{Rate} = k[\text{CH}_3\text{N}_2\text{CH}_3]$$

$$\text{Slope} = -k$$

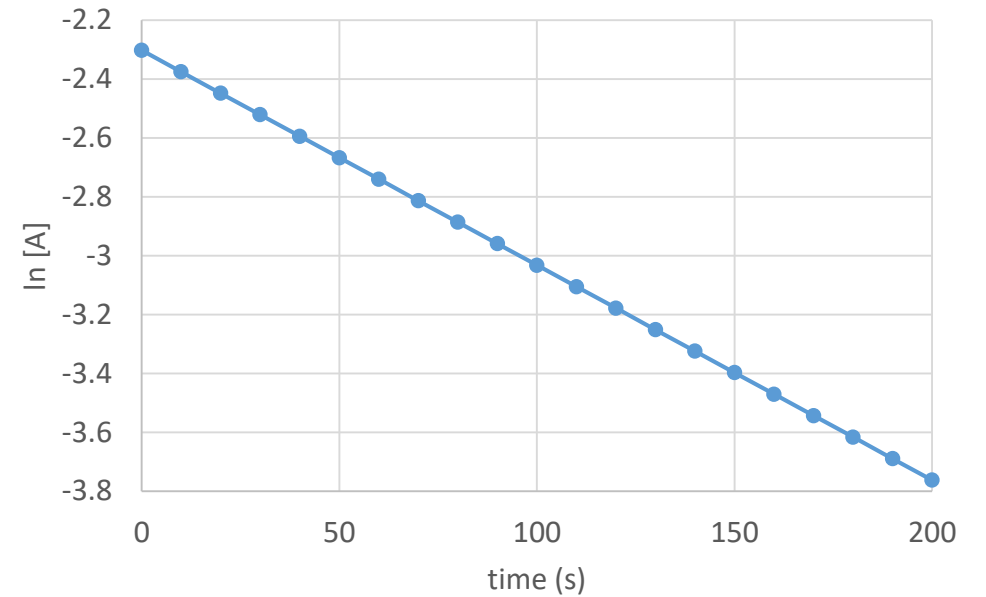
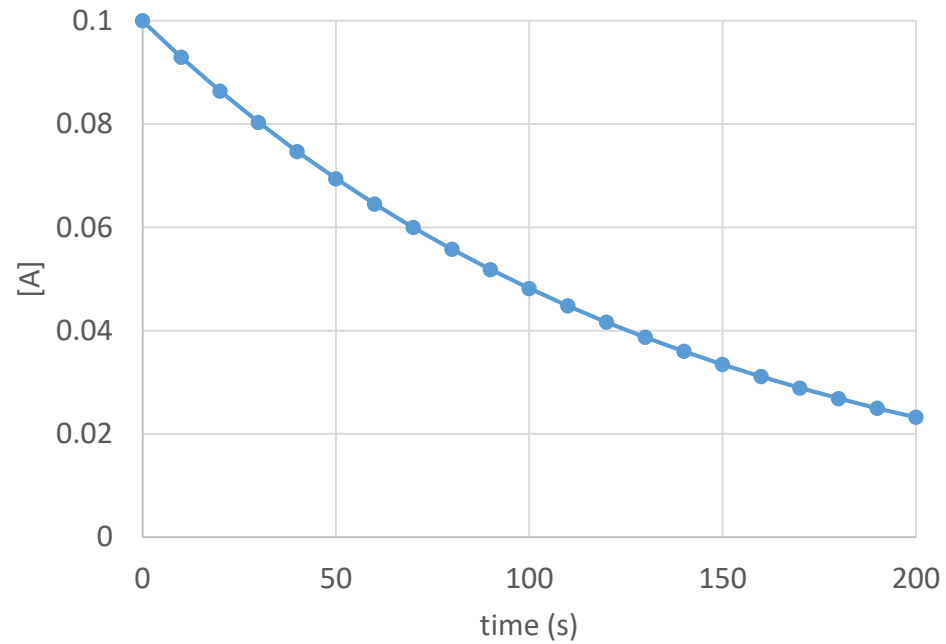
$$= \frac{[(-3.76) - (-3.04)]}{(3500 - 1500) \text{ s}}$$

$$k = 3.6 \times 10^{-4} \text{ s}^{-1}$$

✓ Use integrated rate laws to determine the amount of product produced (or reactant remaining) at any given point within a reaction

# First-Order Reactions

First-Order Reaction



✓ Use integrated rate laws to determine the amount of product produced (or reactant remaining) at any given point within a reaction

# Second-order Integrated Rate Law

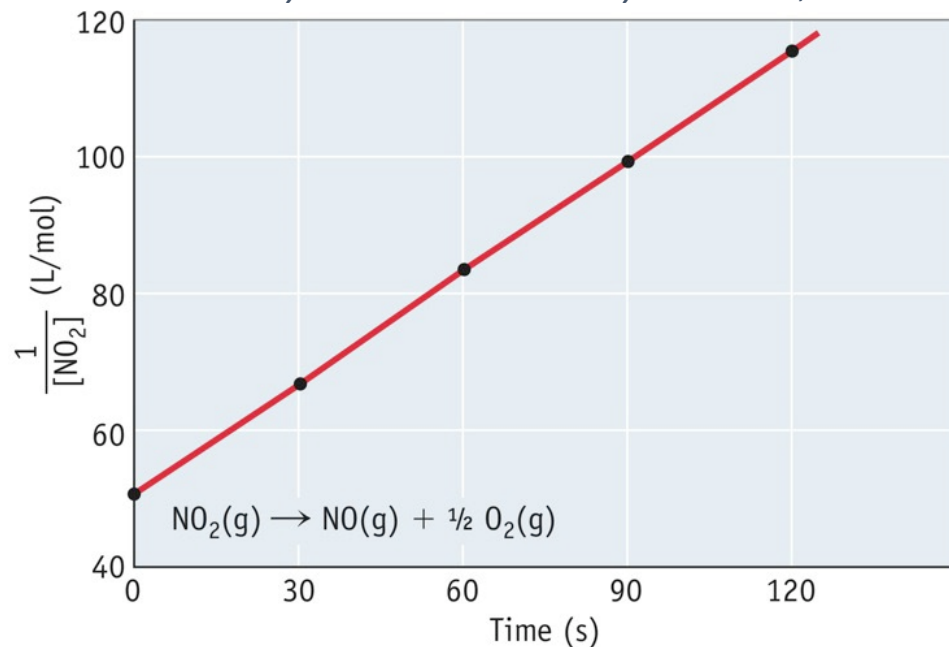
For the reaction:  $aA \rightarrow \text{products}$

Differential rate law:  $\text{Rate} = k[A]^2$

Integrated rate law:  $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

For the decomposition of  $\text{NO}_2$ :

Figure 14.6 from *Chemistry & Chemical Reactivity 9<sup>th</sup> Edition*, Kotz et al. 2012



$$\text{Rate} = k[\text{NO}_2]^2$$

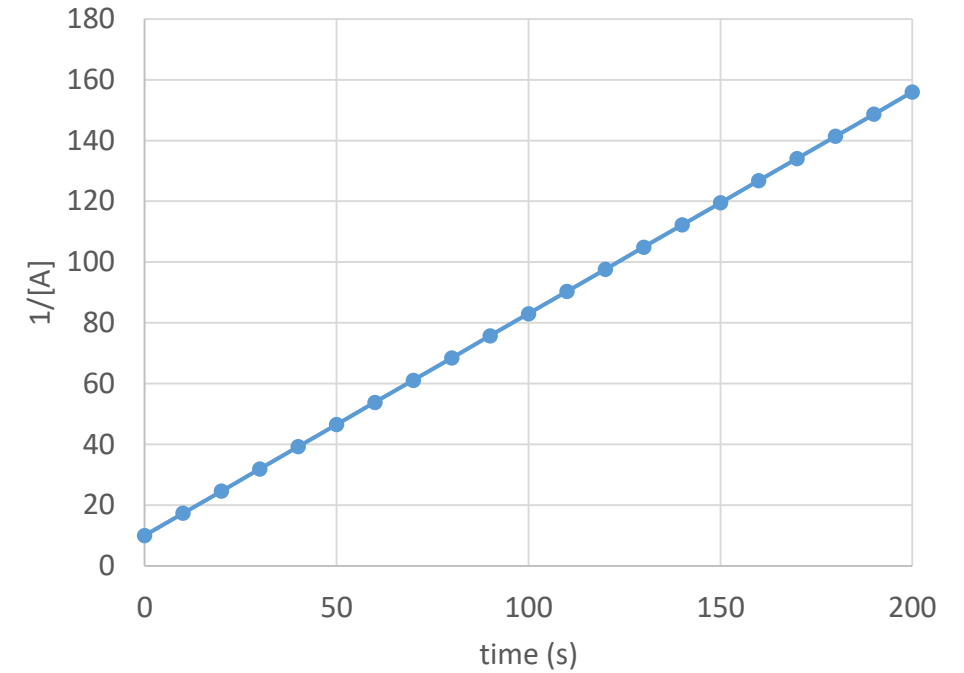
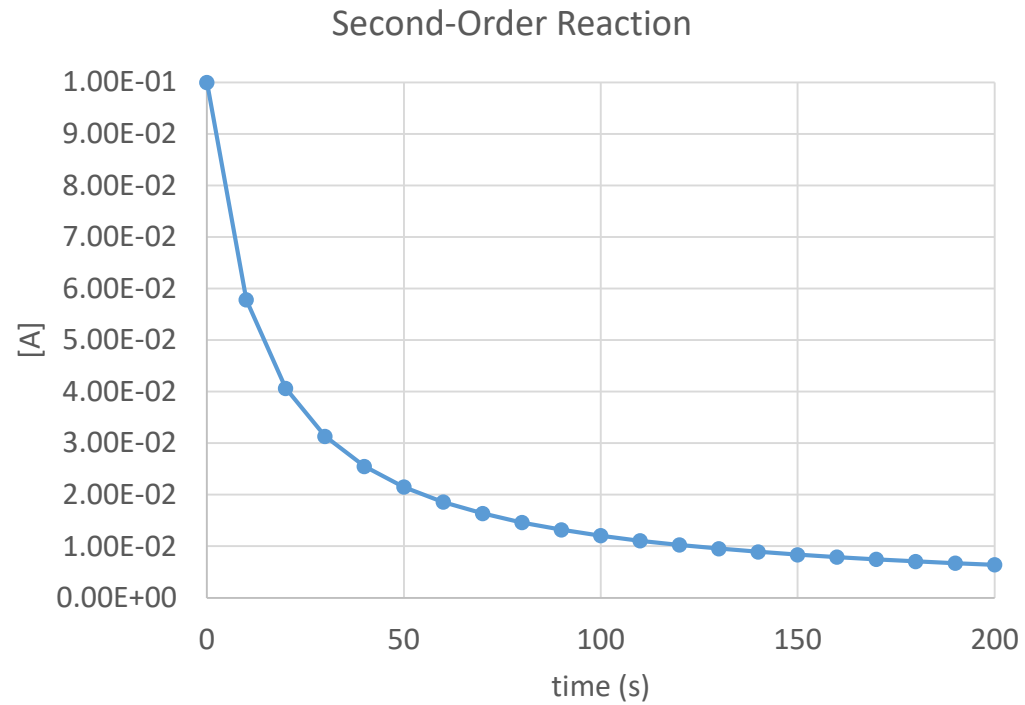
Slope =  $k$

$$= \frac{(105 - 61) \text{ mol/L}}{(100 - 20) \text{ s}}$$

$$k = 0.55 \text{ L/mol} \cdot \text{s}$$

✓ Use integrated rate laws to determine the amount of product produced (or reactant remaining) at any given point within a reaction

# Second-Order Reactions



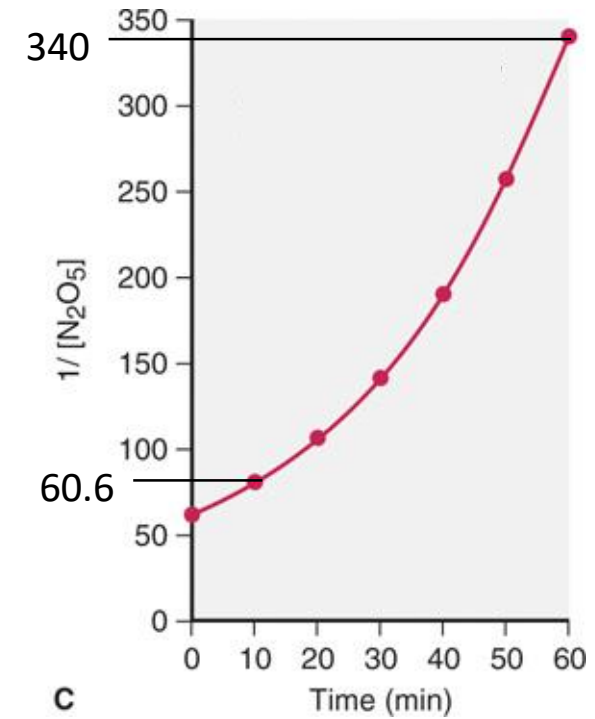
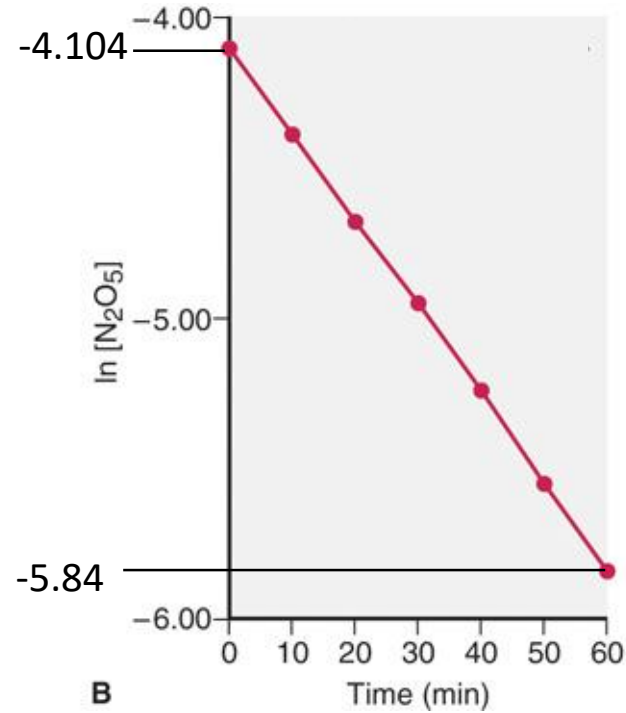
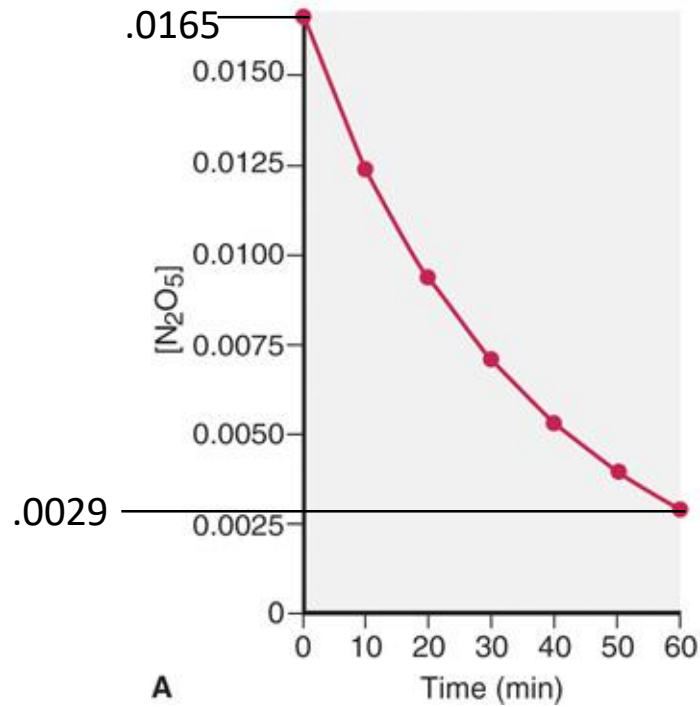
✓ Use integrated rate laws to determine the amount of product produced (or reactant remaining) at any given point within a reaction





Below are 3 plots obtained using data from the reaction of  $\text{N}_2\text{O}_5$ . Using these plots:

1. Determine the order of the reaction with respect to  $\text{N}_2\text{O}_5$ . (answer: 0, 1, 2)
2. Determine a value for  $k$ . (*at home*)



✓ Use integrated rate laws to determine the amount of product produced (or reactant remaining) at any given point within a reaction

# Half-Life

Time taken to go from initial state to  $\frac{1}{2}$  the initial concentration

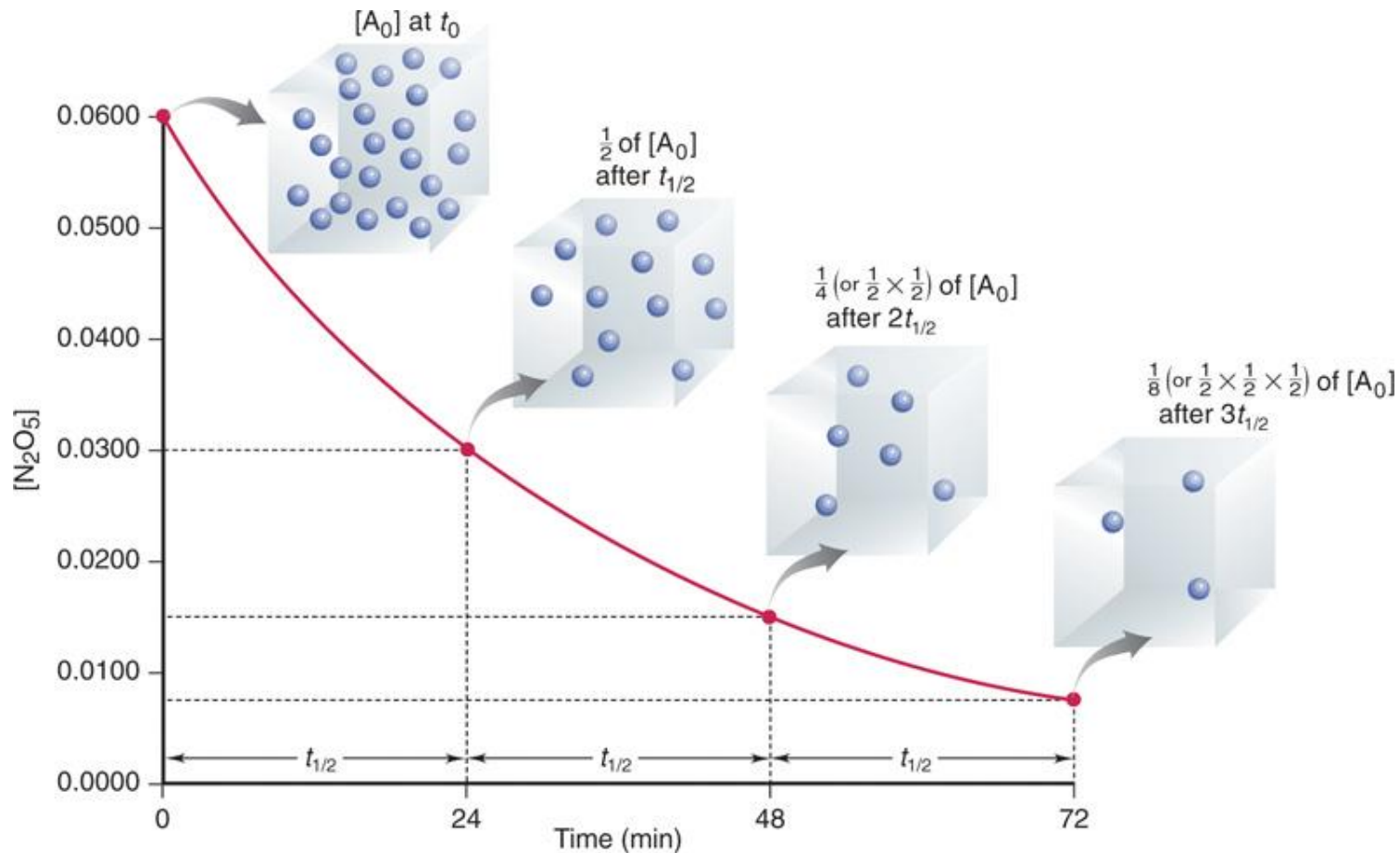


Fig. 14.12

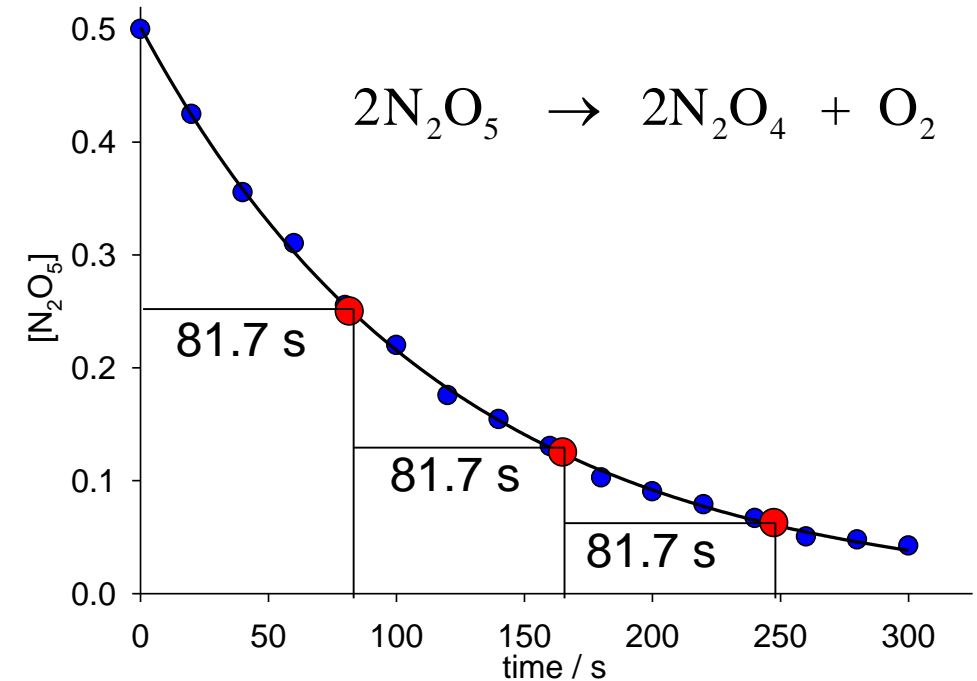
✓ Use integrated rate laws to determine the half-life of a reaction

- Half life for 0<sup>th</sup> order reaction:
- Half life for 1<sup>st</sup> order reaction:
- Half life for 2<sup>nd</sup> order reaction:



Some data for the decomposition of dinitrogen pentoxide are plotted to the right. Which of the following statements is correct?

- A. The rate constant is 81.7 s.
- B. The rate constant is  $\frac{1}{81.7 \text{ s}}$ .
- C. The units of the rate constant are s.
- D. The reaction is first order in  $\text{N}_2\text{O}_5$ .
- E. The reaction is third order in  $\text{N}_2\text{O}_5$ .



# Summary:

## Determination of rate Law from $[A]$ and time

1. Prepare 3 plots:
  1.  $[A]$  vs  $t$
  2.  $\ln[A]$  vs  $t$
  3.  $1/[A]$  vs  $t$
2. Which plot is linear?
3. Calculate  $k$  based on the linear plot

If 2 plots appear linear, check y-intercept: does it best match  $[A]_0$ ,  $-\ln [A]_0$ , or  $1/[A]_0$  ?

A 2.32 M solution of hydrogen peroxide is allowed to decompose. After 1200s, what will  $[\text{H}_2\text{O}_2]$  be, if  $k = 7.30 \times 10^{-4} \text{s}^{-1}$  for the decomposition?

# Catalysts

- Catalysts increase the **rate** of a chemical reaction, without changing the reaction outcome.
- They provide an alternate reaction mechanism that has a lower-energy transition state.
- This lowers the activation energy, increasing the rate of reaction.
- If a reaction is reversible, the catalyst will increase the rate of **both** the forward and reverse reactions!

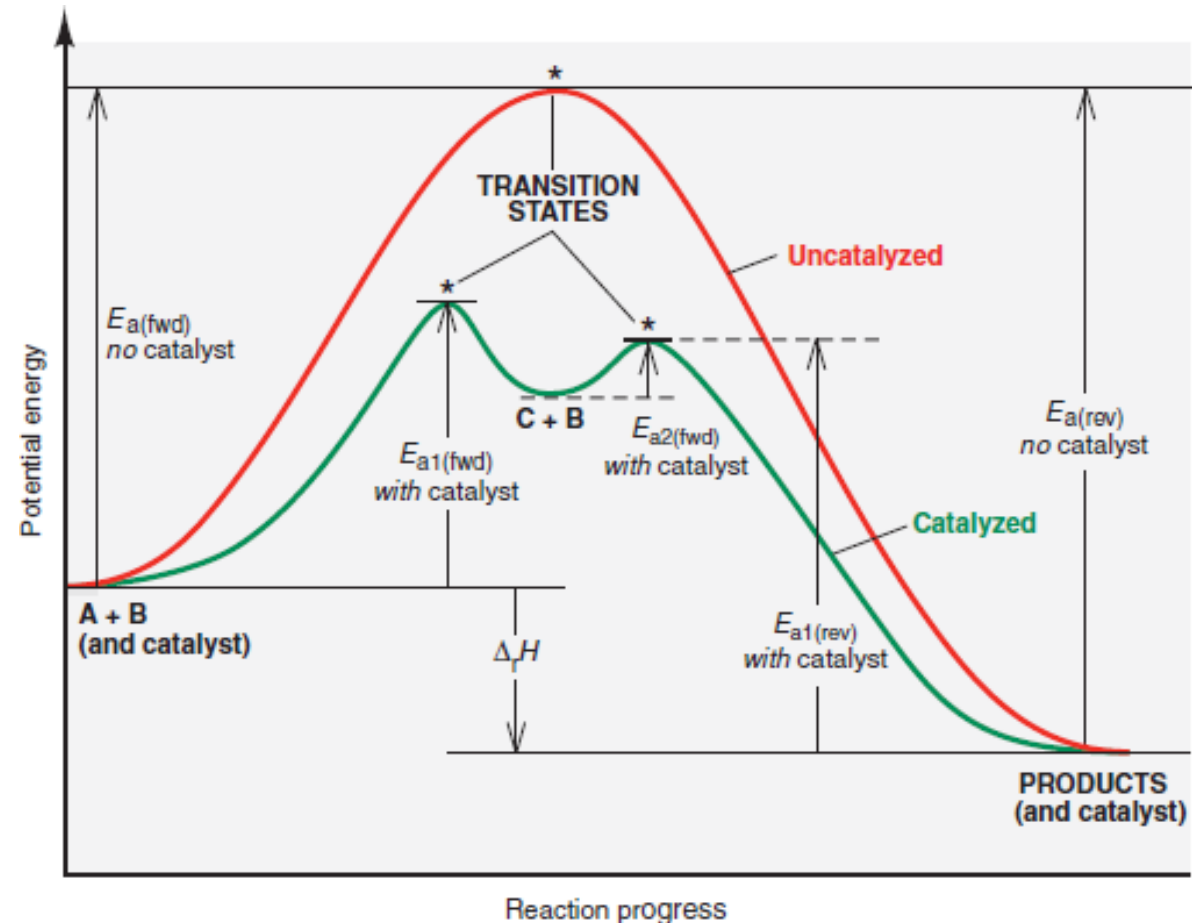
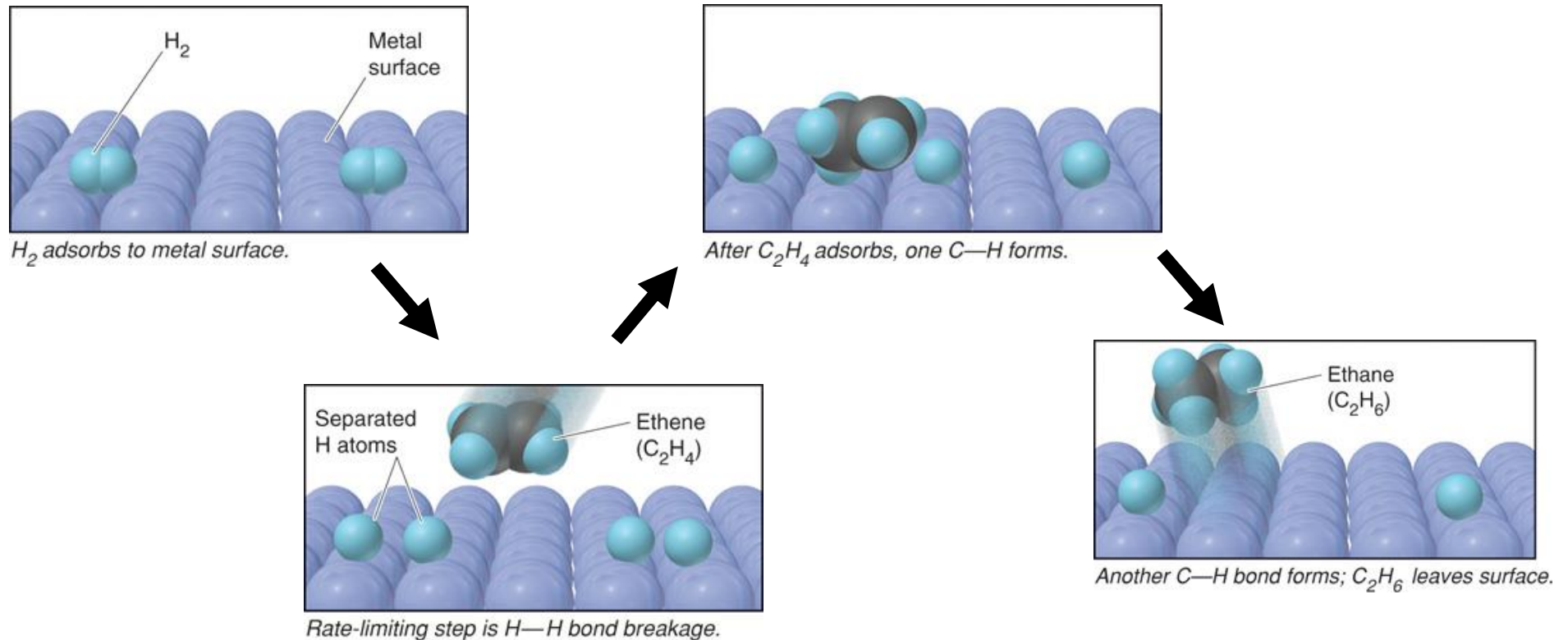


Fig. 14.23

**Homogenous** catalysts are in the same phase as the reaction (usually, in solution) and distributed throughout the reaction mixture. **Heterogeneous** catalysts are (usually) solids that facilitate a reaction by adsorbing the reactants onto their surface.

e.g. metal-catalyzed hydrogenation of ethene (heterogeneous catalysis):

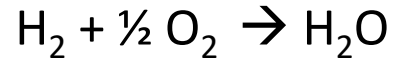


✓ Qualitatively *describe* what the speed of a reaction depends upon.

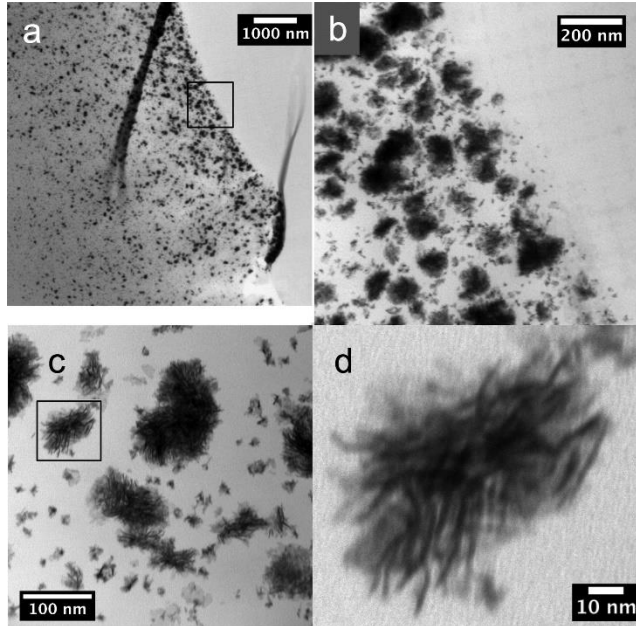


# Fuel Cells & Catalysis

Proton exchange membrane fuel cells capture energy released by the reaction:



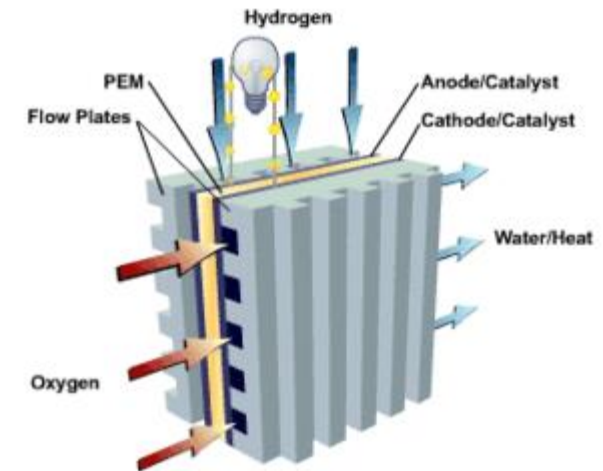
The polymer membrane separates the  $\text{H}_2$  and  $\text{O}_2$  gases, and provides a place to house Pt nanoparticles that catalyze the breakdown of  $\text{O}_2$  in the reaction.



DOI: 10.1021/la403399y



<http://gizmodo.com/391963/>



[https://en.wikipedia.org/wiki/Proton\\_exchange\\_membrane\\_fuel\\_cell](https://en.wikipedia.org/wiki/Proton_exchange_membrane_fuel_cell)