

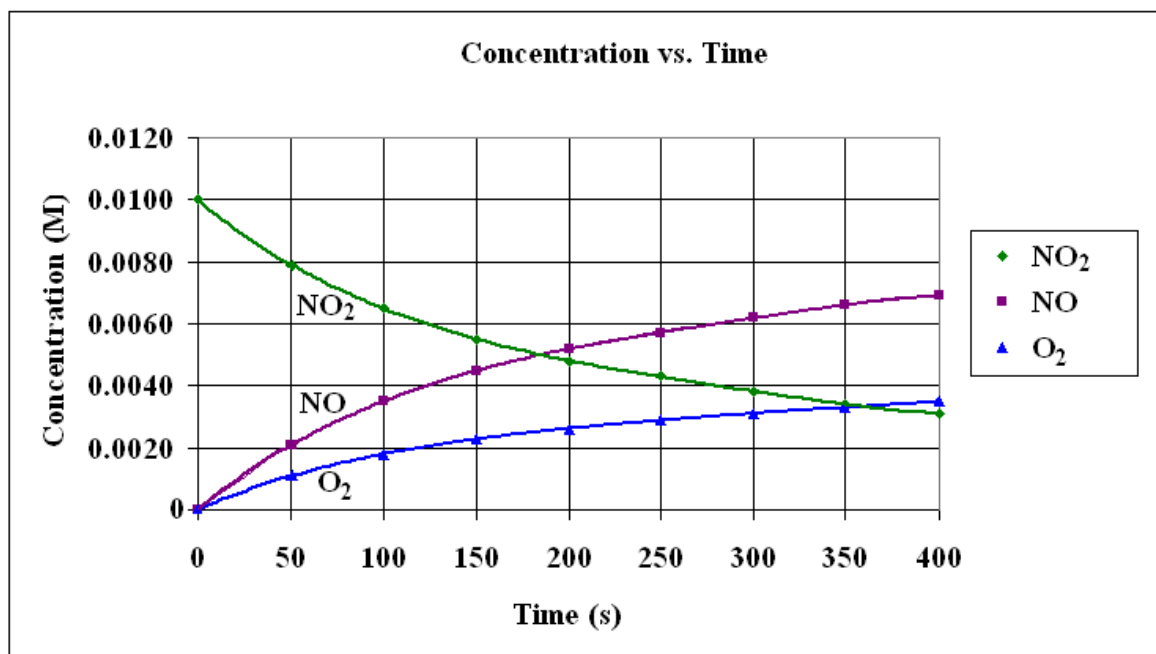
## VII. Reaction Kinetics

**Reaction Rate:** the change in concentration of a reactant or product over time. The study of reaction rates is called reaction kinetics.

$$\text{Rate} = \frac{\Delta[A]}{\Delta t}$$

ex. Consider the reaction:  $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$

Time (s)	[NO <sub>2</sub> ] (mol/L)	[NO] (mol/L)	[O <sub>2</sub> ] (mol/L)
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035



The reaction rate for a chemical at any time can be calculated from the slope of the curve at that time.

Based on the coefficients of the reaction, the following relationship is seen:

Rate of consumption of NO<sub>2</sub> = Rate of production of NO = 2 (Rate of production of O<sub>2</sub>)

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

## Collision Theory

In order for a reaction to occur, the reacting molecules must collide. Furthermore, these collisions must be *effective* collisions. They must have sufficient energy to overcome the repulsive forces of reacting molecules (the minimum amount of energy for a reaction to occur is called the **activation energy**). Molecules must also have the correct collision geometry. The speed of a reaction is called the reaction rate. The more effective collisions there are, the faster the rate. Reaction rate can be measured using the change of any observable property over time. (Most commonly change in concentration over time or change in mass over time)

Factors affecting Reaction Rate:

### (1) Concentration

Increasing concentration increases the reaction rate. When there is a higher concentration there are more collisions resulting in an increased reaction rate.

### (2) Temperature

Increasing temperature increases the reaction rate. Higher temperature causes the molecules to move faster. When molecules move faster, there are more collisions and the collisions have more energy resulting in an increased reaction rate.

### (3) Surface Area

Increasing surface area increases the reaction rate. When there is a greater surface area there are more places for collisions to occur resulting in an increased reaction rate.

### (4) Catalysts

**Catalyst:** a substance that speeds up the rate of a reaction without being used up.

Catalysts make the collisions have a better orientation thereby lowering the activation energy for a reaction and resulting in more effective collisions and an increased reaction rate.

## Reaction Rate and Concentration

An expression, called a **rate law** can be written to show the relationship between the rate of a reaction and the concentration of chemicals.

### Rate Laws

There are two main types of rate laws:

1. Differential Rate Law: shows how the rate of a reaction depends on concentration
2. Integrated Rate Law: shows how the concentration of species in a reaction depend on time

### Differential Rate Laws

A Differential Rate Law can be written as follows:

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

where: k = a proportionality constant, called the specific rate constant

[A] = the concentration of reactant A

n = the order of the reaction (with respect to reactant A)

[B] = the concentration of reactant B

m = the order of the reaction (with respect to reactant B)

(note: the *overall* order of a reaction is the sum of the exponents from the rate law)

ex. For the reaction:  $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$

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

ex. Write a rate law for the reaction:  $\text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

The reaction rate is not constant. In general, as the reaction proceeds, the reaction rate decreases. In addition, since chemical reactions are reversible, as products accumulate, the reverse reaction takes place as well as the forward reaction. In the study of reaction kinetics, it is useful to consider reaction rate during the initial phases of a reaction. At this time, the concentration of the products is not significantly high and therefore, the reverse reaction makes a negligible contribution towards the overall reaction kinetics. Under these conditions, the reaction rate will depend only on the concentration of the reactants.

#### Method of Initial Rates

Several experiments are performed with varying initial concentrations of the reactant chemicals and the initial rate of the reaction is measured. From this information, the order of the reaction with respect to each reactant chemical can be calculated. The rate constant,  $k$ , with appropriate units, can be determined from any of the experiments.

ex. Consider the following reaction:  $\text{NH}_4^+ (\text{aq}) + \text{NO}_2^- (\text{aq}) \rightarrow \text{N}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l})$

The rate of the reaction was measured for various initial concentrations of ammonium and nitrate ion. Determine a rate law based on the experimental data collected. What is the overall order of the reaction?

Experiment	Initial $[\text{NH}_4^+]$ (mol/L)	Initial $[\text{NO}_2^-]$ (mol/L)	Initial Rate (mol/Ls)
1	0.100	0.0050	$1.35 \times 10^{-7}$
2	0.100	0.010	$2.70 \times 10^{-7}$
3	0.200	0.010	$5.40 \times 10^{-7}$

ex. Consider the following reaction:  $2\text{NO}_2 (\text{g}) + \text{O}_3 (\text{g}) \rightarrow \text{N}_2\text{O}_5 (\text{g}) + \text{O}_2 (\text{g})$

Determine a rate law based on the experimental data collected. What is the overall order of the reaction?  
What would the rate be when initially,  $[\text{NO}_2] = 0.200 \text{ mol/L}$  and  $[\text{O}_3] = 0.200 \text{ mol/L}$ ?

Experiment	Initial $[\text{NO}_2]$ (mol/L)	Initial $[\text{O}_3]$ (mol/L)	Initial Rate (mol/Ls)
1	0.100	0.100	0.0250
2	0.100	0.200	0.0500
3	0.200	0.100	0.100

## The Integrated Rate Laws

The integrated rate law of a reaction depends on the order of the reaction.

### First Order Reactions

The integrated rate law for a first order reaction can be written as follows:

$$\ln[A] = -kt + \ln[A]_o$$

where:  $[A]$  = the concentration of chemical A at time  $t$

$k$  = the specific rate constant

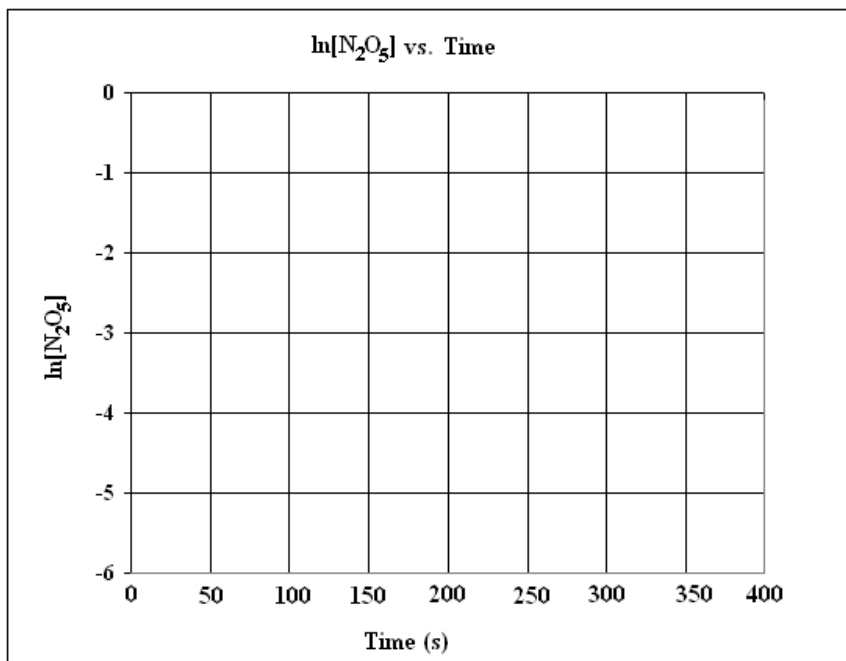
$t$  = time

$[A]_o$  = the initial concentration of chemical A

ex. The compound dinitrogen pentoxide decomposes according to the following reaction:  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

Using the experimental data collected, show that the decomposition of dinitrogen pentoxide is a first order reaction. Determine the specific rate constant and give the integrated rate law. What would be the concentration of  $\text{N}_2\text{O}_5$  after 500 seconds? At what time would the concentration of  $\text{N}_2\text{O}_5$  be 0.00600 mol/L?

Time (s)	$[\text{N}_2\text{O}_5]$ (mol/L)	$\ln[\text{N}_2\text{O}_5]$
0	0.1000	
50	0.0707	
100	0.0500	
200	0.0250	
300	0.0125	
400	0.00625	



Half Life ( $t_{1/2}$ ): The time required for concentration of the reactant to decrease to half of the original amount.

Half Life for a First Order Reaction

$$t_{1/2} = \frac{0.693}{k}$$

## Second Order Reactions

The integrated rate law for a second order reaction can be written as follows:

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

where:  $[A]$  = the concentration of chemical A at time  $t$

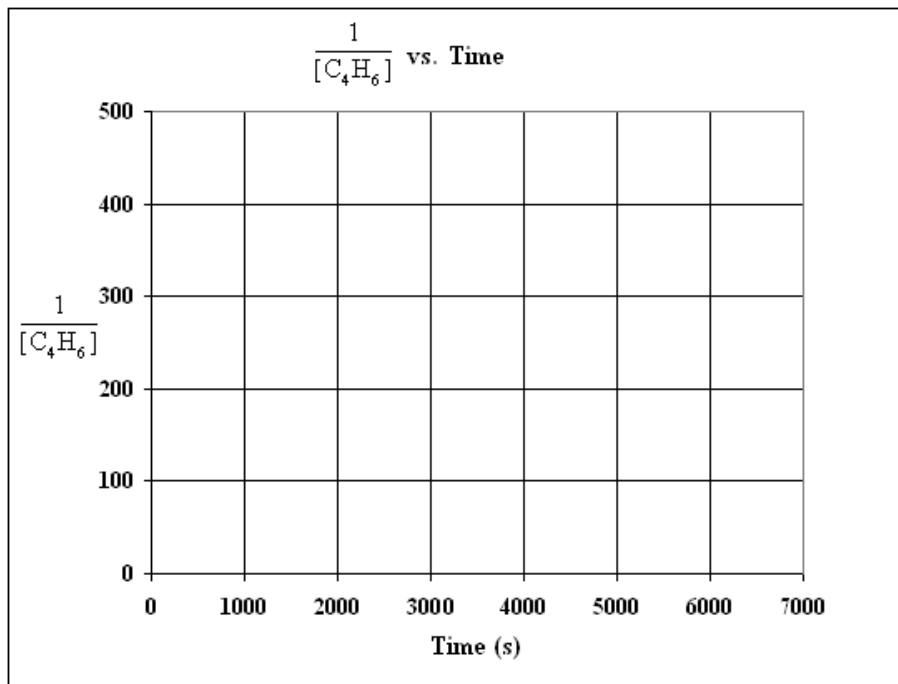
$k$  = the specific rate constant

$t$  = time

$[A]_o$  = the initial concentration of chemical A

ex. The compound butadiene dimerizes according to the following reaction:  $2C_4H_6(g) \rightarrow C_8H_{12}(g)$ . Show that the dimerization is a second order reaction. Determine the specific rate constant and give the integrated rate law. What would be the concentration of  $C_4H_6$  after 7000 seconds? At what time would the concentration of  $C_4H_6$  be 0.00100 mol/L?

Time (s)	$[C_4H_6]$ (mol/L)	$\frac{1}{[C_4H_6]}$
0	0.01000	
1000	0.00625	
1800	0.00476	
2800	0.00370	
3600	0.00313	
4400	0.00270	
5200	0.00241	
6200	0.00208	



Half Life for a Second Order Reaction

$$t_{1/2} = \frac{1}{k[A]_o}$$

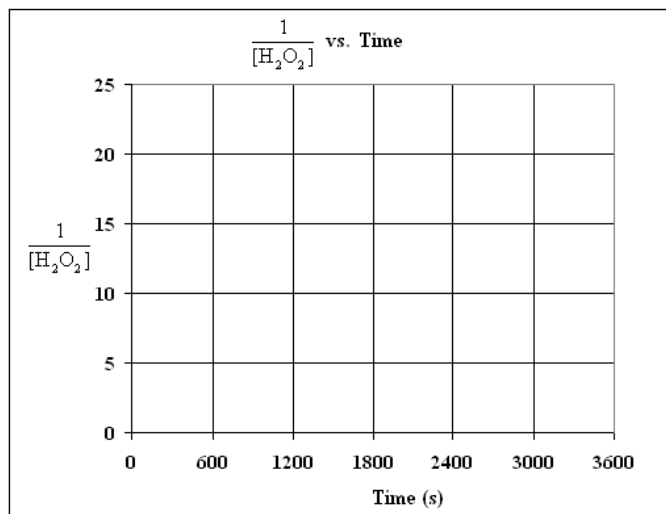
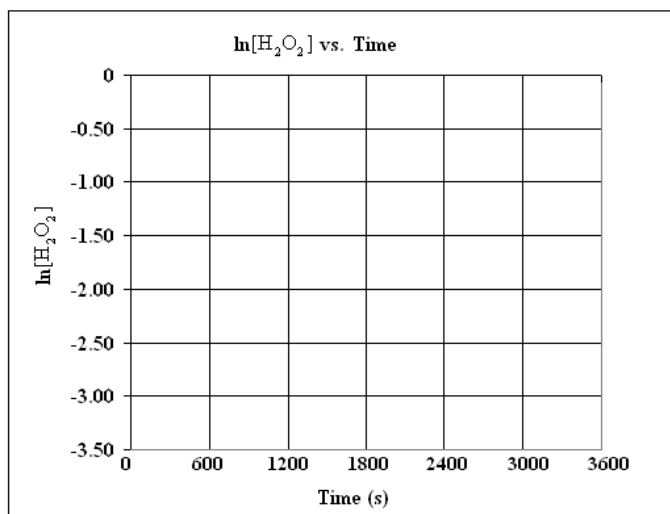
In order to determine the integrated rate law of a reaction from experimental data, two graphs must be created as follows:

1.  $\ln[A]$  vs. *time*
2.  $\frac{1}{[A]}$  vs. *time*

The graph that produces a straight line will indicate the order of the reaction. (ie. If  $\ln[A]$  vs. *time* produces a straight line, then the reaction is first order. If  $\frac{1}{[A]}$  vs. *time* produces a straight line then the reaction is second order.)

ex. Determine the order of the reaction:  $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$  given the following data. Determine the specific rate constant and give the integrated rate law. What is the half life of this reaction?

Time (s)	$[\text{H}_2\text{O}_2]$ (mol/L)	$\ln[\text{H}_2\text{O}_2]$	$\frac{1}{[\text{H}_2\text{O}_2]}$
0	1.0		
120	0.91		
300	0.78		
600	0.59		
1200	0.37		
1800	0.22		
2400	0.13		
3000	0.082		
3600	0.050		



## Reaction Rate and Temperature

Increasing temperature increases the reaction rate. The relationship between reaction rate and temperature can be described according to the Arrhenius Equation:

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

This equation can also be written as follows:

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

Where:  $k$  = rate constant

$A$  = the preexponential factor, called the frequency factor (no units)

$E_a$  = activation energy (J/mol)

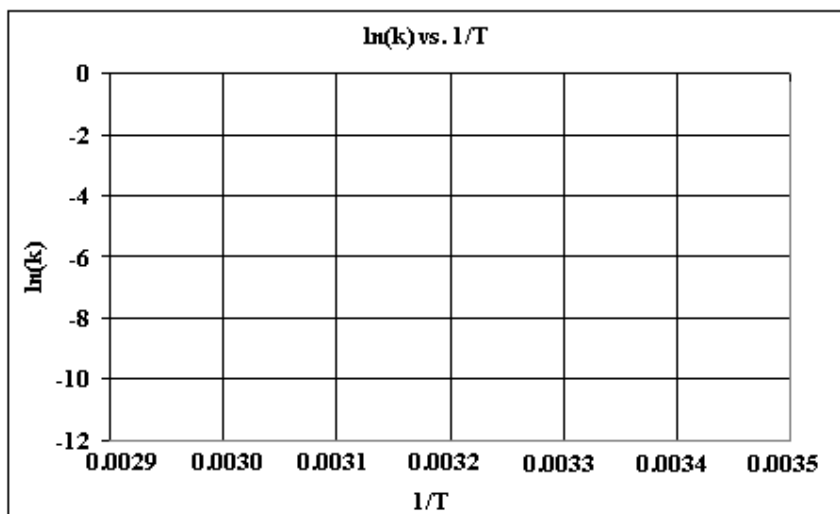
$R$  = gas constant (8.314 J/mol K)

$T$  = temperature (K)

ex. The reaction  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  was studied at several different temperatures and the experimental values of  $k$  were obtained.

Temperature (K)	$k$ ( $\text{s}^{-1}$ )	$\frac{1}{T}$	$\ln(k)$
293	$2.0 \times 10^{-5}$		
303	$7.3 \times 10^{-5}$		
313	$2.7 \times 10^{-4}$		
323	$9.1 \times 10^{-4}$		
333	$2.9 \times 10^{-3}$		

Graph  $\ln(k)$  vs.  $1/T$  and determine the values of  $E_a$  and  $A$ .



ex. Consider the following reaction:  $\text{CH}_4(\text{g}) + 2\text{S}_2(\text{g}) \rightarrow \text{CS}_2(\text{g}) + 2\text{H}_2\text{S}(\text{g})$

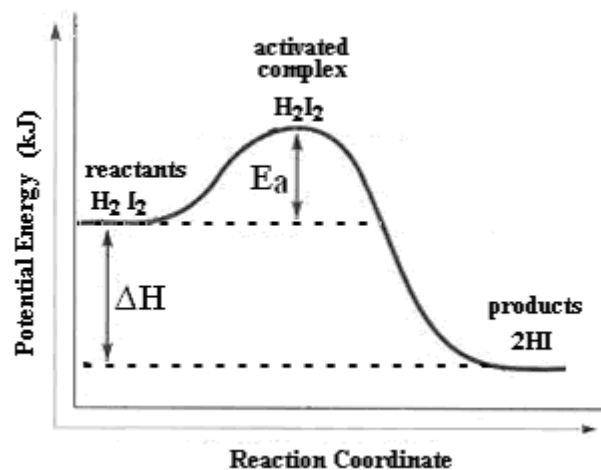
At  $550^\circ\text{C}$ , the rate constant for the reaction is  $1.1 \text{ L/mol s}$ . At  $625^\circ\text{C}$ , the rate constant for the reaction is  $6.4 \text{ L/mol s}$ . Calculate  $E_a$  and  $A$  for the reaction.

## Potential Energy Diagrams

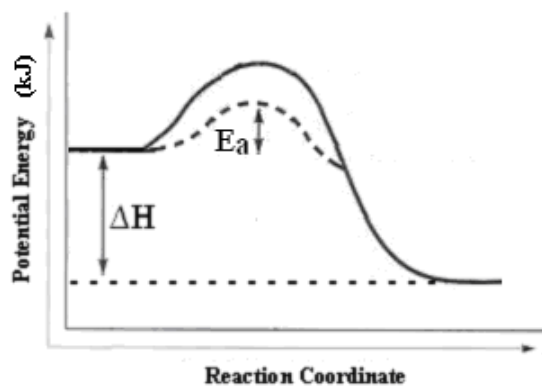
The energy changes in a reaction can be represented by a potential energy diagram.

ex. Consider the following reaction:  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ .

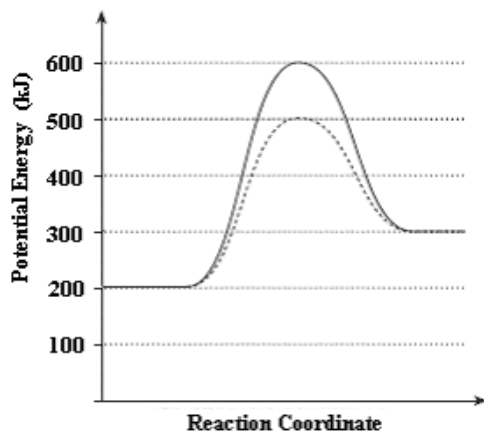
The reactant molecules first collide and form the **activated complex**, a high energy, short-lived, unstable cluster of reacting molecules before the products are formed. The potential energy diagram for this reaction is shown below.



The activation energy for a chemical reaction can be lowered with the addition of a catalyst. The potential energy diagram for the catalyzed reaction is shown below. Note that the heat of the reaction does not change.



ex. The potential energy diagram for a reaction is shown below.

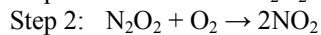
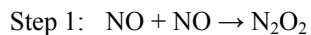


- What is  $E_a$  for the forward, uncatalyzed reaction?
- What is  $E_a$  for the forward, catalyzed reaction?
- What is  $E_a$  for the reverse, uncatalyzed reaction?
- What is  $E_a$  for the reverse, catalyzed reaction?
- What is  $\Delta H$  for the forward, uncatalyzed reaction?
- What is  $\Delta H$  for the forward, catalyzed reaction?
- What is  $\Delta H$  for the reverse, uncatalyzed reaction?
- What is  $\Delta H$  for the reverse, catalyzed reaction?

## Reaction Mechanisms

Most reactions actually occur by a series of steps called a reaction mechanism. Each step in the reaction mechanism is called an *elementary step*.

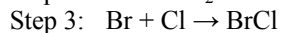
ex. Consider the reaction between nitrogen monoxide and oxygen to form nitrogen dioxide:  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ . This reaction occurs according to the following reaction mechanism:



Overall:

**Reaction Intermediate:** a chemical that is formed in one step and consumed in a subsequent step.

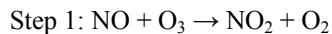
ex. Determine the overall reaction given the following steps:



Overall:

Identify any reaction intermediates.

ex. The following reaction occurs in two steps:  $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$

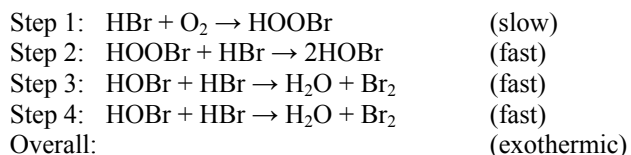


Determine step 2 of this reaction mechanism.

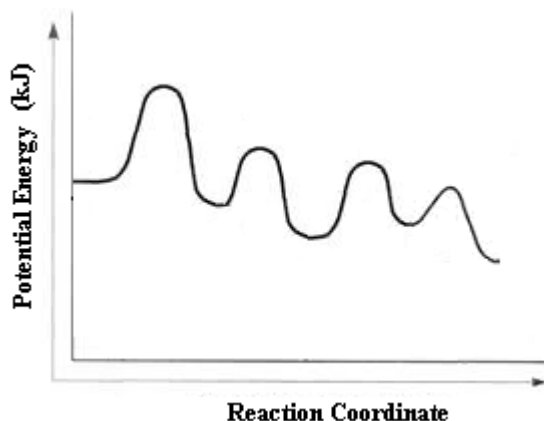
Identify any reaction intermediates.

**Catalysts:** a chemical that is consumed in one step and produced in a subsequent step.

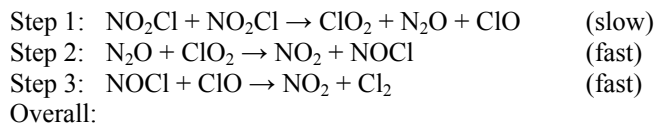
## Potential Energy Diagrams and Reaction Mechanisms



**Rate-Determining Step:** the slowest step in a reaction mechanism. The overall reaction rate depends primarily on the rate of this step. In a potential energy diagram, the rate determining step has the highest activation energy.



ex. Determine the overall reaction given the following steps:



Identify any reaction intermediates.

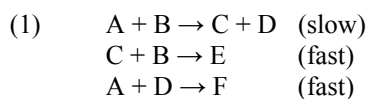
Sketch a potential energy diagram (given that the overall reaction is exothermic) and label the rate determining step.

## Reaction Mechanisms and Rate Laws

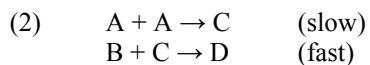
The rate law for a reaction can be written from the *coefficients* of the *rate-determining step*.

The rate law must be written in terms of the reactants in the overall reaction (a substitution may have to be made).

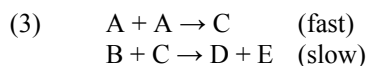
ex. Determine the overall reaction and rate law for each reaction mechanism.



Overall:



Overall:



Overall: