

Chapter 12

In-Class Problems

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Introduction

Chemical kinetics is the study of:

1. The rate at which reactants are converted to products during the course of a chemical reaction.
2. The factors, which include temperature, pressure, concentration, catalyst and surface area that affect the rate of a chemical reaction.
3. The sequence of steps, or the mechanism, which we believe occurs when reactants are converted to products.

The four factors that affect the rates of reactions are:

1. **Temperature:** the rate of a reaction increases with increasing temperature.
2. **Concentration:** the rate of a reaction increases with increasing concentration of reactants (pressure changes behave in the same way as concentration).
3. **Catalyst:** the rate of a reaction increases with addition of a catalyst.
4. **Surface area:** the rate of a reaction increases with increased surface area of the reactant.

For a chemical reaction its rate, or rate of reaction, is expressed in terms of how fast the concentration of a substance changes in the course of a chemical reaction.

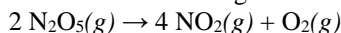
$$\text{Rate of reaction} = \frac{\Delta[\text{product}]}{\text{time}} \quad \text{or} \quad \text{Rate of reaction} = -\frac{\Delta[\text{reactant}]}{\text{time}}$$

One symbol you should become familiar with is the []. Brackets from here on out will mean "the concentration of in molarity"

Relative Rates

Notice the rates above only differ in a '–' sign. This is there because rates must be positive, and the change of your reactants is negative, so you must have a negative sign.

Consider the following reaction:



The rate can be expressed the following ways:

$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = 2 \frac{\Delta[\text{O}_2]}{\Delta t}$$

Rate Laws

This is an example of the general form of a rate law.

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

k is the rate constant in the mathematical equation.

The exponents 'm' and 'n' represent the order of the reaction with respect to NO and Cl₂, respectively. The sum of m + n represents the **order of the reaction**.

"rate" generally refers to the initial rate. The initial rate is the fastest rate of the reaction and occurs at the very beginning of the reaction. At this point there are few competing reactions. It should be noted when using the initial rate, the concentration of the reactants are initial concentrations. $\text{rate} = k[\text{NO}]_{t=0}^m [\text{Cl}_2]_{t=0}^n$

1. Given the hypothetical reaction: $2\text{A} + n\text{B} \rightarrow q\text{C} + r\text{D}$

If: $\frac{-\Delta[\text{A}]}{\Delta t} = 0.050 \text{ mol/L}\cdot\text{s}$

$$\frac{-\Delta[\text{B}]}{\Delta t} = 0.150 \text{ mol/L}\cdot\text{s}$$

$$\frac{+\Delta[\text{C}]}{\Delta t} = 0.075 \text{ mol/L}\cdot\text{s}$$

$$\frac{+\Delta[\text{D}]}{\Delta t} = 0.025 \text{ mol/L}\cdot\text{s}$$

What are the coefficients of n, q and r?

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Reaction Mechanisms: *the first way to find a rate law!!!!*

A reaction mechanism attempts to describe the stepwise sequence of elementary reactions that take reactants to products. The mechanism describes in detail the bonds that are broken and formed as the reaction proceeds.

Every mechanism consists of a series of stepwise reactions. Each reaction in the mechanism has a rate associated with it. The overall speed of the reaction depends upon the slowest step of the mechanism. The rate law of this step is identical to the experimental rate law. The slow step of the mechanism is also called the rate determining step of the mechanism. The sum of all the steps of the mechanism must equal the overall balanced chemical equation.

Each elementary step of a mechanism typically involves one, two or three reactants combining to form products. The steps of a mechanism must add together to yield the overall balanced chemical equation. The coefficients of the reactants in the rate determining step of the mechanism must correspond to the exponents, or order of the reactants in the experimental rate law.

A catalyst is a substance that acts to increase the speed of a chemical reaction without itself undergoing a permanent change in the process. Catalysts increase the rate of a reaction by providing an alternate path for the reaction to occur. This means that there will be a change in the magnitude of the rate constant and possibly a change in the order of the reaction. A catalyst can be distinguished from an intermediate in a mechanism. An intermediate is produced early in the reaction (product) and used up (reactant) in a subsequent step. A catalyst is used up early in a reaction (reactant) and is regenerated (product) in a subsequent step.

2. In one of the labs you *attempted* recently, you ran the following reaction: $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$
Consider the following mechanism for this reaction:

$\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{HOI} + \text{OH}^-$	slow
$\text{HOI} + \text{I}^- \rightarrow \text{I}_2 + \text{OH}^-$	fast
$2\text{OH}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}$	fast

- What rate law would be expected if this mechanism is correct? That is, will it be zero-order, first-order or second-order with respect to H_2O_2 ? Zero-order, first-order or second-order with respect to I^- ? Explain briefly.
- What species are intermediates in the above mechanism? Any catalysts?
- Sketch an energy profile for the three-step mechanism and clearly label the rate determining step in your diagram.

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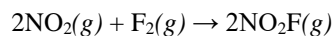
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3.

$\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$	
$\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$	
$\text{HBr} + \text{O}_2 \rightarrow \text{HOBr}$	(slow)
$\text{HOBr} + \text{HBr} \rightarrow 2 \text{HOBr}$	

- What is the overall reaction of the above rate law?
- What species are intermediates in the above mechanism? Any catalysts?
- Sketch an energy profile for the three-step mechanism and clearly label the rate determining step in your diagram.
- What rate law would be expected if this mechanism is correct?

4. The rate law for following reaction was experimentally determined to be $\text{rate} = k[\text{NO}_2]^1[\text{F}_2]^1$:



Which of the following mechanisms is the most reasonable? Explain your reasoning for making the choice you did.

- | | |
|---|---|
| a. $2\text{NO}_2(g) + \text{F}_2(g) \rightarrow 2\text{NO}_2\text{F}(g)$ | c. $\text{NO}_2(g) + \text{F}_2(g) \rightarrow \text{NO}_2\text{F}(g) + \text{F}(g)$ (slow)
$\text{NO}_2(g) + \text{F}(g) \rightarrow \text{NO}_2\text{F}(g)$ (fast) |
| b. $\text{NO}_2(g) + \text{F}_2(g) \rightarrow \text{NO}_2\text{F}(g) + \text{F}(g)$ (fast)
$\text{NO}_2(g) + \text{F}(g) \rightarrow \text{NO}_2\text{F}(g)$ (slow) | |

5. When a certain substance's concentration is doubled, the initial rate of a reaction proceeds eight times as fast. What is the order with respect to this substance? _____

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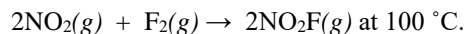
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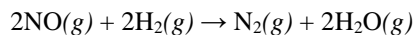
Method of Initial Rates: *the second way to find a rate law!!!*

6. The following initial rate data were collected for the reaction:



Experiment	[NO ₂]	[F ₂]	initial rate (M/sec)
1	0.0482 M	0.0318 M	1.90 x 10 ⁻³
2	0.0120 M	0.0315 M	4.69 x 10 ⁻⁴
3	0.0480 M	0.127 M	7.57 x 10 ⁻³

- a. Determine the reaction order for NO₂ and F₂. (Let's use UGLY ALGEBRA to find the orders.)
- b. Determine the overall order of the reaction. _____
- c. Write the specific rate law for the reaction. _____
- d. Determine the rate constant for the reaction (include units).
7. Consider the reaction and the following initial rate data.



Experiment	PNO(mmHg)	PH ₂ (mmHg)	Initial Rate (mmHg • s ⁻¹)
1	400	150	0.66
2	400	300	1.34
3	150	400	0.25
4	300	400	1.03

- a. Determine the reaction order for NO and H₂. (this one is cleaner so let's do it by table logic instead!)
- b. Determine the overall order of the reaction. _____
- c. Write the specific rate law for the reaction. _____
- d. Determine the rate constant for the reaction (include units).

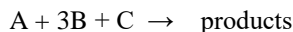
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8. For the reaction:



and the following initial rate data. This one is a nightmare. If you can do it, you can do ANY of these things!

Experiment	[A]	[B]	[C]	Rate of formation of products (M/s)
1	1.05×10^{-2}	2.50×10^{-2}	4.00×10^{-3}	1.74×10^{-4}
2	8.71×10^{-2}	2.50×10^{-2}	4.00×10^{-3}	1.19×10^{-2}
3	2.10×10^{-2}	2.10×10^{-2}	2.10×10^{-2}	1.34×10^{-3}
4	4.20×10^{-2}	2.10×10^{-2}	4.20×10^{-2}	7.58×10^{-3}

- Determine the reaction order for A, B and C.
- Determine the overall order of the reaction. _____
- Write the specific rate law for the reaction. _____
- Determine the rate constant for the reaction (include units).

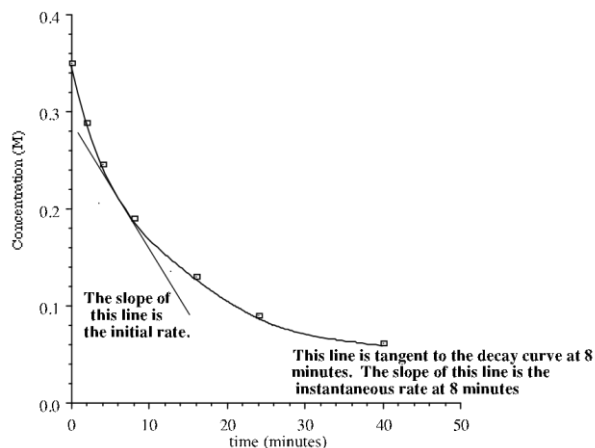
Graphical Rate Law Determination: *the final way to find a rate law!!!*

Since rate is defined as $-\Delta[\text{reactant}]/\Delta\text{time}$, the concentration of reacting species must be followed over time. Typically, two experiments, each with different initial concentrations, are required. After collecting the experimental data, the initial rate is determined. The order of the reaction with respect to a particular reactant is obtained by comparing the ratio of the initial concentrations of the reactant with the ratio of their initial rates.

Instantaneous Rate

Instantaneous rate is the rate at any one point in time during the experiments. To find instantaneous rate you find the slope of the curve at the time in question (aka a derivative).

- Notice that the rate (which is the slope of the tangent line at any point) is constantly decreasing.
- This is because the concentration of reactants is constantly decreasing as the reaction proceeds.



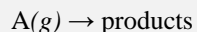
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For **zero order reactions** of the type:



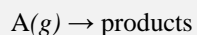
we can write the differential form of the rate law (which is useful in describing how the rate of disappearance of reactant is proportional to the concentration of the reactant) as:

$$\text{rate} = k[A]^0$$

When this relationship is integrated from t_0 to t_t we obtain the relationship:

The half-life of a chemical reaction is defined as the time required for the initial concentration, $[A]_0$, to fall to half its value. This can be described using the mathematical equation:

For **first order reactions** of the type:



we can write the differential form of the rate law (which is useful in describing how the rate of disappearance of reactant is proportional to the concentration of the reactant) as:

$$\text{rate} = k[A]^1$$

When this relationship is integrated from t_0 to t_t we obtain the relationship:

The half-life of a chemical reaction is defined as the time required for the initial concentration, $[A]_0$, to fall to half its value. This can be described using the mathematical equation:

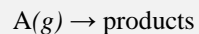
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For **second order reactions** of the type:



we can write the differential form of the rate law (which is useful in describing how the rate of disappearance of reactant is proportional to the concentration of the reactant) as:

$$\text{rate} = k[A]^2$$

When this relationship is integrated from t_0 to t_t we obtain the relationship:

The half-life of a chemical reaction is defined as the time required for the initial concentration, $[A]_0$, to fall to half its value. This can be described using the mathematical equation:

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Summary of Graphical Methods of Analysis

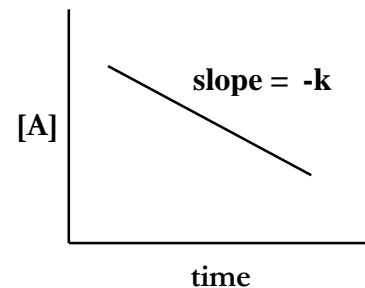
For zero order reactions:

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

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

this equation fits the general equation for a line, $y = mx + b$, where:

$$y = [A] : m = -k : x = t$$



For first order reactions:

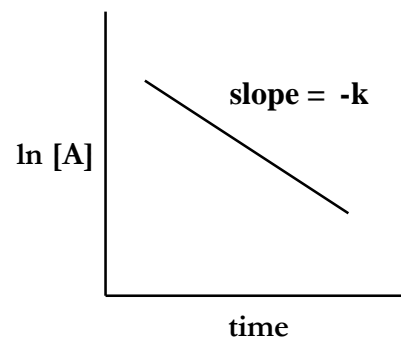
$$\ln \left(\frac{[A]}{[A]_0} \right) = -kt$$

$$\ln[A] - \ln[A]_0 = -kt$$

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

this equation fits the general equation for a line, $y = mx + b$, where:

$$y = \ln[A] : m = -k : x = t$$



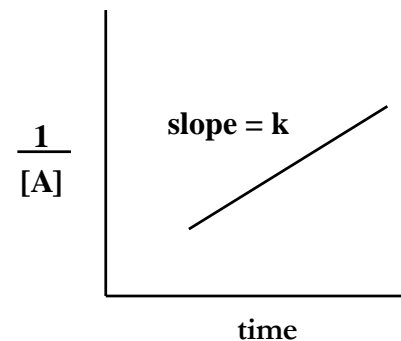
For second order reactions:

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

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

this equation fits the general equation for a line, $y = mx + b$, where:

$$y = 1/[A] : m = k : x = t$$



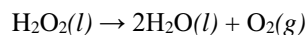
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9. The decomposition of H_2O_2 to H_2O and O_2 follows first order kinetics with a rate constant of 0.0410 min^{-1} at a particular temperature.



Calculate the $[\text{H}_2\text{O}_2]$ after 10 min if $[\text{H}_2\text{O}_2]_0$ is 0.200 M .

10. The decomposition of N_2O_5 to O_2 and NO_2 follows first order kinetics. If a sample at 25°C with the initial concentration of N_2O_5 of $1.25 \times 10^{-3} \text{ M}$ falls to $1.02 \times 10^{-3} \text{ M}$ in 100. minutes, calculate the rate constant (k) for the reaction.

11. In Problem 9, how long would it take for half of the H_2O_2 to decompose?

12. The decomposition of $\text{NOCl}(g)$: $2\text{NOCl}(g) \rightarrow 2\text{NO}(g) + \text{Cl}_2(g)$ is a second order reaction with a rate constant of $0.0480 \text{ M}^{-1}\cdot\text{s}^{-1}$ at 200°C . In an experiment at 200°C , the initial concentration of NOCl was 0.400 M . What is the concentration of NOCl after 15.0 min have elapsed?

13. The initial concentration of NOCl , described in 12 above, is 0.400 M . Calculate the half-life for the decomposition reaction.

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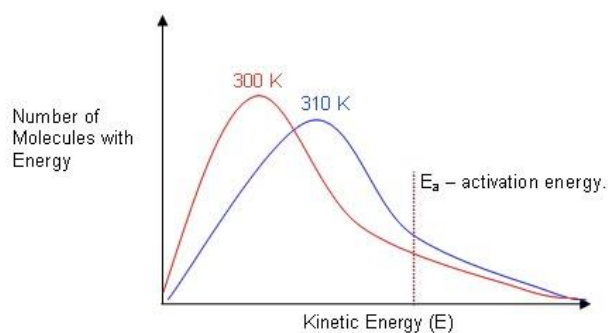
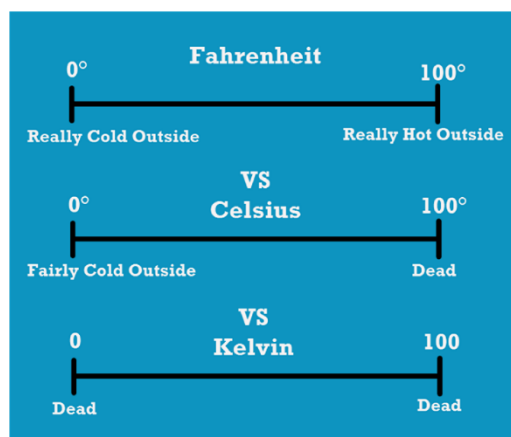
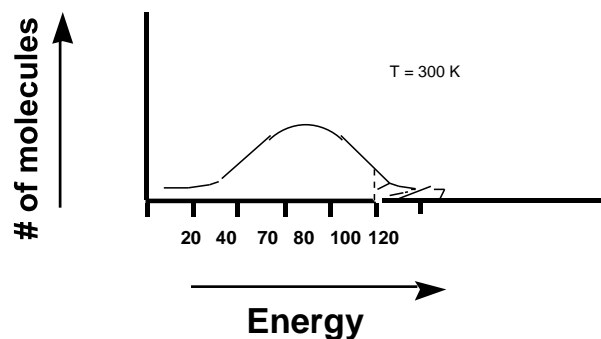
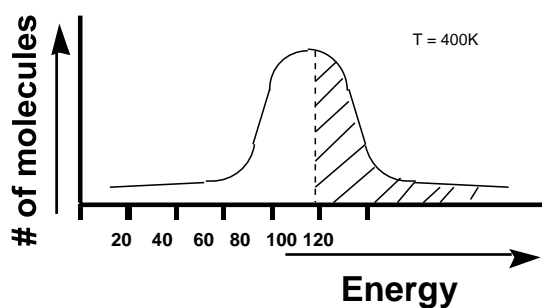
14. Given the following data use your calculator and graphical methods to determine the order of the reactions, the k 's with units and the rate laws.

$2\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$	
Time (sec)	$[\text{N}_2\text{O}_5]$ (M)
0	1.50×10^{-3}
2000	1.40×10^{-3}
5000	1.27×10^{-3}
7000	1.18×10^{-3}
11000	1.03×10^{-3}
15000	9.00×10^{-4}

$2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$	
Time (sec)	$[\text{NO}_2]$ (M)
0	0.0100
25	0.0088
50	0.0079
75	0.0071
100	0.0065
150	0.0055
175	0.0051
200	0.0048
250	0.0042
300	0.0038

How does temperature affect the reaction rate?

Molecules have a range of energies that can be described by an energy distribution diagram. Notice that it has a bell-shaped curve, and most of the molecules have an average of 100 kJ/mol, although some have more, and some have less. If the reaction we're discussing has an E_a of 100 kJ/mol, then about half of the molecules will have enough energy to reach the activated complex, therefore half of collisions will be effective with respect to energy.



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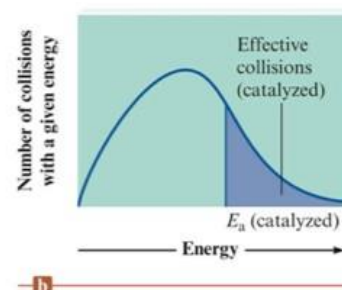
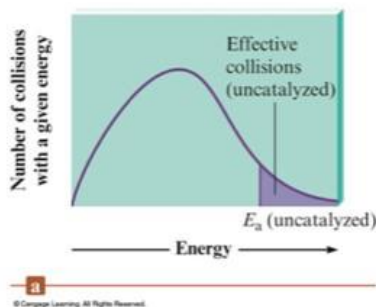
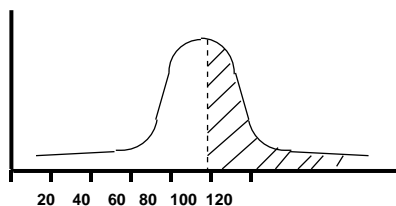
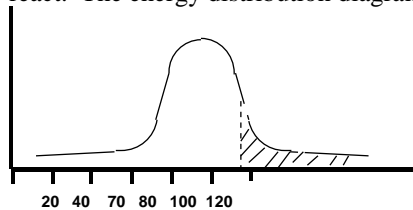
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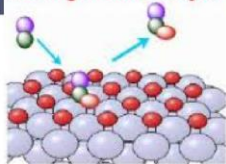
How does a catalyst affect the rate of the reaction?

This can best be shown using both progress of reaction diagrams and progress of reaction diagrams. The catalyst for a certain reaction lowers the E_a for that particular reaction from 118 kJ/mol to only 99 kJ/mol. Looking at the energy distribution diagrams, this means that a larger fraction of molecules will have the energy to reach the activated complex and will be able to react. The energy distribution diagrams are shown on the following page.



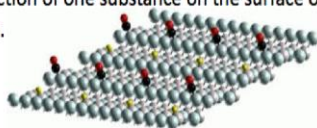
Section 12.7

Heterogeneous catalysis



Heterogeneous Catalyst

- Most often involves gaseous reactants being adsorbed on the surface of a solid catalyst.
- Adsorption – collection of one substance on the surface of another substance.

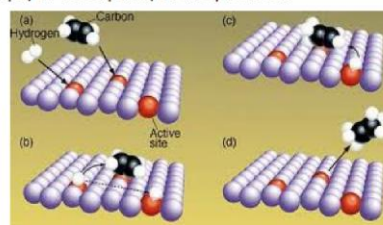


Section 12.7

Catalysis

Heterogeneous Catalyst

- Adsorption and activation of the reactants.
- Migration of the adsorbed reactants on the surface.
- Reaction of the adsorbed substances.
- Escape, or desorption, of the products.

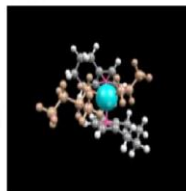
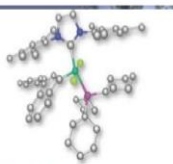
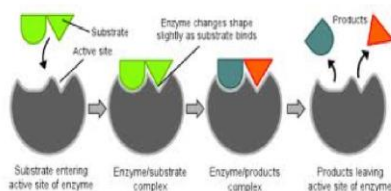


Section 12.7

Catalysis

Homogeneous Catalyst

- Exists in the same phase as the reacting molecules.
- Enzymes are nature's catalysts.

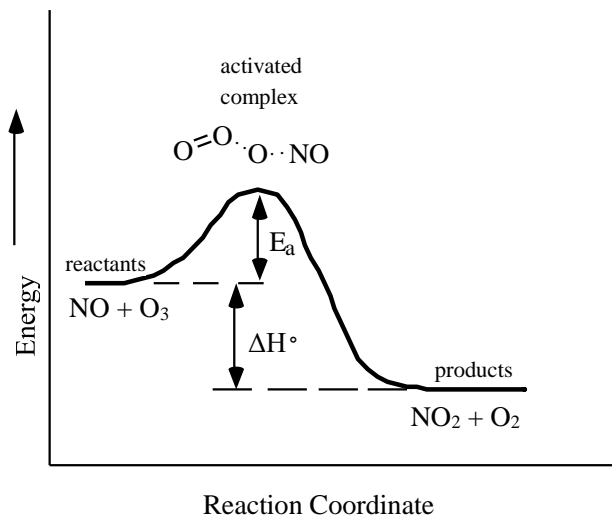


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The activation energy, E_a , represents a measure of the energy barrier colliding molecules must surmount if they are to react rather than to recoil from one another. It is assumed that every pair of molecules with energy less than E_a will not react and every pair with energy greater than E_a and the proper orientation will react.

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

k_1 and k_2 are both rate constants at T_1 and T_2 , respectively. E_a is the activation energy for the reaction and R is the ideal gas constant. The value of R is $8.314 \text{ J}/(\text{mol}\cdot\text{K})$.

Collision Theory

Collision theory says that for a reaction to happen two things must occur:

1. To react molecules must collide with sufficient energy to react --- they must collide with enough kinetic energy to cause them to reach the activation energy barrier.
2. The molecules must collide with the appropriate orientation for a reaction to occur.

These two factors are summarized in the single temperature Arrhenius equation:

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

This factor takes into account
particle orientation.

This factor takes into account
energy of collisions.

A is the Arrhenius constant and tells how many collisions have the appropriate orientation. Two simple atoms that can collide in any orientation will have a very high A value, while two very complex molecules that must collide in a very specific way will have a very small A value.

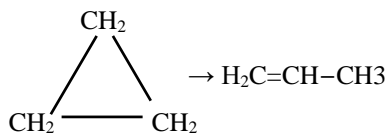
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15. At 300°C the rate constant for the reaction



is $2.41 \times 10^{-10} \text{ s}^{-1}$. At 400 °C the rate constant is $1.16 \times 10^{-6} \text{ s}^{-1}$. Calculate the activation energy for the reaction.

16. If the activation energy for the decomposition of N_2O_5 is $1.0 \times 10^2 \text{ kJ/mol}$, calculate the temperature change necessary to double the rate at room temperature.