

Reaction Kinetics

Hebden – Unit 1
(page 1-34)

Reaction Kinetics

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Reaction kinetics is the study of the rates of reactions and the factors which affect the rates.

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What are kinetic studies good for?

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3

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How to speed up:

1. Paint drying
2. Setting of dental fillings
3. Synthesis of pharmaceutical drugs
4. Breakdown of synthetic plastics and other materials in landfills
5. Industrial manufacture of chemicals
6. Destruction of air pollutants in automobile exhaust

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How to slow down:

1. Food decay
2. Rate at which materials burn in fire
3. Rusting of metal objects composed of iron
4. Corrosion
5. Fading of clothes through washing
6. Destruction of the ozone layer

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Factors which influence reaction rates:

1. Chemical nature of the reactants.
 - What are the chemical properties of the reactants.
 - Do the reactants have strong bonds or weak bonds?
 - What about the number of bonds that need to be broken and reformed?

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Factors which influence reaction rates:

2. The ability of the reactants to come in contact with each other.
 - Surface area consideration -
The greater the surface area, the greater the ability the reactants can meet, and therefore, the greater the reaction rate.
 - Phase consideration -
Homogeneous reaction or Heterogeneous reaction

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7

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Factors which influence reaction rates:

2. The ability of the reactants to come in contact with each other.

Aqueous ions > Gases or Liquids > Solids

(Fastest)

(Slowest)

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8

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Factors which influence reaction rates:

- | | |
|-----------------------------------|---|
| 3. Concentration of the reactants | - When the reactant concentration increases, the reaction rate increases. |
|-----------------------------------|---|

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9

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Factors which influence reaction rates:

- | | |
|----------------|--|
| 4. Temperature | - When the temperature increases, the reaction rate increases. |
|----------------|--|

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10

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Factors which influence reaction rates:

5. Pressure

- When the gaseous reactant pressure increases, more reactant is compressed into a given volume (i.e. the reactant concentration increases), the reaction rate increases.

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11

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Factors which influence reaction rates:

6. Presence of Catalysts

- Catalyst is a chemical which can be added to a chemical reaction to increase the rate of the reaction.
- The catalyst is not consumed in the reaction.

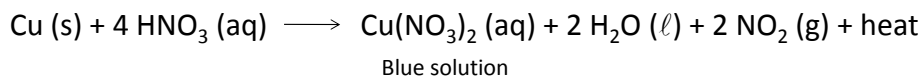
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12

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Possible ways to measure reaction rates:



Method	Observation	Calculation of Rate
1. Mass change	Mass of copper decreases overtime	$\text{Rate} = \frac{\Delta \text{mass}}{\Delta \text{time}}$
2. Temperature change	Exothermic reaction - Temperature rises	$\text{Rate} = \frac{\Delta T}{\Delta \text{time}}$
3. Colour change	- Measure the intensity of the blue colour using colourimetry	$\text{Rate} = \frac{\Delta \text{colour change}}{\Delta \text{time}}$

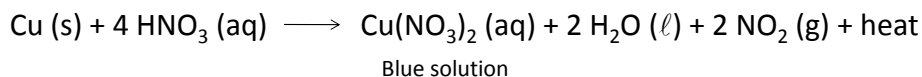
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13

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Possible ways to measure reaction rates:



Method	Observation	Calculation of Rate
4. Pressure change	- Carry out reaction in a sealed vessel equipped with a pressure gauge	$\text{Rate} = \frac{\Delta P}{\Delta \text{time}}$
5. Concentration change	- Reaction will have decreasing $[\text{HNO}_3]$. - Measure pH increasing over time.	$\text{Rate} = \frac{\Delta \text{pH}}{\Delta \text{time}}$

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14

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To measure the reaction rate is the measure of the change in some properties over time.

$$Unit := \frac{moles}{L\ s} = \frac{M}{s} = M\ s^{-1}$$

The change in the measured property can be related back to the change in concentration.

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15

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We will go over Experiment 2: Factors Affecting Reaction Rates in detail.

NOTE: There are a lot of Chemistry 11-type calculations in Experiment 2!

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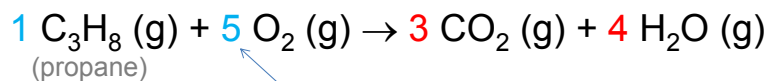
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Relative rates of the disappearance of reactants and appearance of products

Their rates are linked by the reaction stoichiometry, or by the coefficients in the balanced equation.



O₂ is consumed 5x faster than propane.

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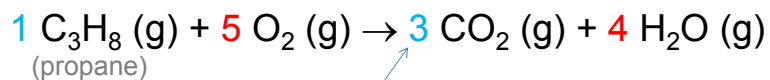
17

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Relative rates of the disappearance of reactants and appearance of products

Their rates are linked by the reaction stoichiometry, or by the coefficients in the balanced equation.



CO₂ is formed 3x faster than propane.

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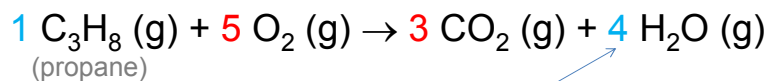
18

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Relative rates of the disappearance of reactants and appearance of products

Their rates are linked by the reaction stoichiometry, or by the coefficients in the balanced equation.



H₂O: is formed 4x faster than propane.

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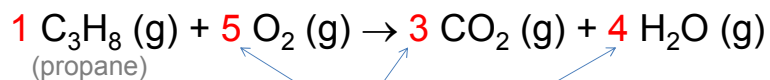
19

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Relative rates of the disappearance of reactants and appearance of products

Their rates are linked by the reaction stoichiometry, or by the coefficients in the balanced equation.



O₂ is consumed 5x faster than propane.

CO₂ is formed 3x faster than propane.

H₂O is formed 4x faster than propane.

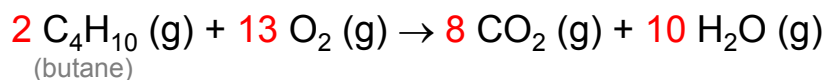
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20

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Experimentally, when butane is burned it decreases at a rate of 0.20 M/s.



- What is the rate at which O_2 concentration is decreasing?
- What are the rates at which the product concentrations are increasing?

Answers:

- $0.20 \text{ M/s} \times 13/2 = 1.3 \text{ M/s}$ is the rate that O_2 is consumed.
- $0.20 \text{ M/s} \times 8/2 = 0.8 \text{ M/s}$ is the rate that CO_2 is produced.
 $0.20 \text{ M/s} \times 10/2 = 1.0 \text{ M/s}$ is the rate that H_2O is produced.

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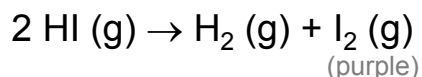
21

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Experimental Measurement of Reaction Rates

The decomposition reaction of hydrogen iodide at 508°C .



- We can study any reactant or products since the rate of decrease of HI and the rates of production of H_2 and I_2 are all related.
- It's easiest to monitor I_2 because it is the only coloured substance. We can use an instrument to monitor the change in colour intensity of the reaction chamber and relate it back to the concentration of I_2 .
- If the concentration of I_2 is known, then we can relate it to the concentration of HI.

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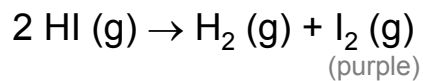
22

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Experimental Measurement of Reaction Rates

The decomposition reaction of hydrogen iodide at 508°C.



Experimental Data:	Time (s)	Concentration of HI (M)
	0	0.1000
	50	0.0716
	100	0.0558
	150	0.0457
	200	0.0387
	250	0.0336
	300	0.0296
	350	0.0265

Easiest way to see the behaviour of the reaction is to plot the data graphically.

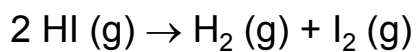
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23

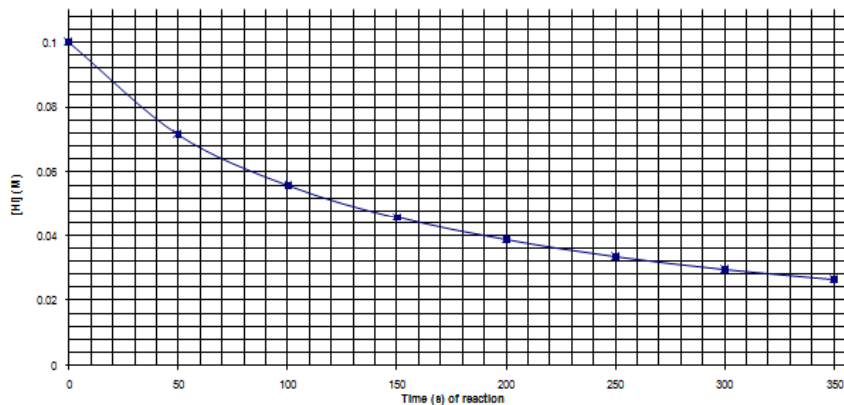
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Experimental Measurement of Reaction Rates



Effect of time on Concentration



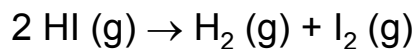
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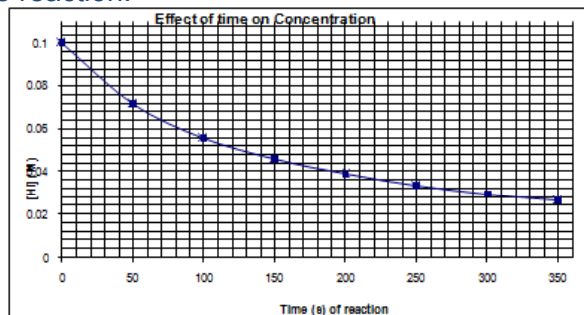
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Experimental Measurement of Reaction Rates



From the graph, we observe that reaction rate is not the same throughout the reaction.



We can draw a tangent line at any time t and determine the slope of the tangent line. This will give us the rate of the reaction at time t .

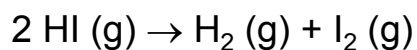
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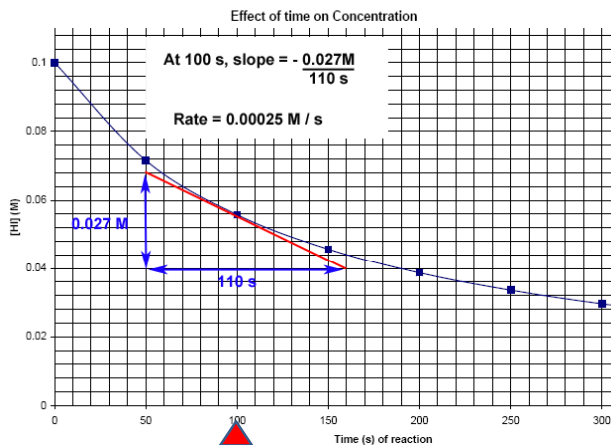
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Experimental Measurement of Reaction Rates



At 100 sec,
the rate of
decrease in HI
is 0.00025 M/s.



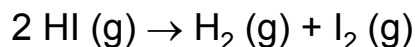
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26

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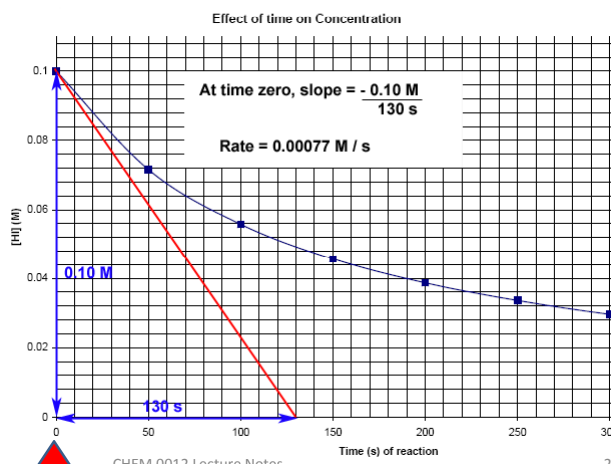
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Experimental Measurement of Reaction Rates



At 0 sec,
the rate of
decrease in HI
is 0.00077 M/s.

The rate of
decrease of HI
is faster at the
beginning of the
reaction.



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Reaction Rate Law

A mathematical equation which relates rate to the
reactant concentrations.

For a general reaction,



where 'a' and 'b' are the coefficients in the balanced chemical equation,
X and Y are the reactants.

$$\text{Rate} \propto [\text{X}]^m [\text{Y}]^n$$

The rate of a reaction is proportional to the products of the
reactants each raised to some power.

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Introduce Logs

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29

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Reaction Rate Law

$a X + b Y \rightarrow \text{products}$

A mathematical equation which relates rate to the reactant concentrations.

$$\text{Rate} \propto [X]^m [Y]^n$$

To remove the proportional symbol, \propto , we introduce a proportionality constant, the rate constant, k .

$$\text{Rate} = k [X]^m [Y]^n$$

k , m , and n are numbers that are determined experimentally!!

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30

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Reaction Rate Law

$a X + b Y \rightarrow \text{products}$

$$\text{Rate} = k [X]^m [Y]^n$$

k , m , and n are numbers that are determined experimentally!!

The reaction is determined to be:

- m^{th} order with respect to X
- n^{th} order with respect to Y

The overall reaction order is $m+n$.

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31

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Reaction Rate Law

$a X + b Y \rightarrow \text{products}$

$$\text{Rate} = k [X]^m [Y]^n$$

k , m , and n are numbers that are determined experimentally!!

k is the rate constant.

- The bigger the rate constant, k , the faster the reaction.
- k is temperature dependent.
- k is reaction dependent.
- k has units.

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32

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Reaction Rate Law



$$\text{Rate} = k [\text{N}_2\text{O}_5] \quad \text{Determined experimentally!!}$$

This reaction is 1st order with respect to N_2O_5 .

The overall reaction order is 1.

Units of k

$$\frac{\text{moles}}{\text{L} \cdot \text{s}} = k \left(\frac{\text{moles}}{\text{L}} \right)$$

$$\frac{\text{moles}}{\text{L} \cdot \text{s}} \left(\frac{\text{L}}{\text{moles}} \right) = k$$

$$k = \frac{1}{\text{s}} = \text{s}^{-1}$$

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33

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Reaction Rate Law



$$\text{Rate} = k [\text{HI}]^2 \quad \text{Determined experimentally!!}$$

This reaction is 2nd order with respect to HI.

The overall reaction order is 2.

$$\text{Units of } k \quad \frac{\text{moles}}{\text{L} \cdot \text{s}} = k \left(\frac{\text{moles}}{\text{L}} \right) \left(\frac{\text{moles}}{\text{L}} \right)$$

$$\frac{\text{moles}}{\text{L} \cdot \text{s}} \left(\frac{\text{L}}{\text{moles}} \right) \left(\frac{\text{L}}{\text{moles}} \right) = k$$

$$k = \frac{\text{L}}{\text{moles} \cdot \text{s}} = \text{M}^{-1} \text{s}^{-1}$$

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34

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Reaction Rate Law $2 \text{ NO (g)} + 2 \text{ H}_2 \text{ (g)} \rightarrow \text{N}_2 \text{ (g)} + 2 \text{ H}_2\text{O (g)}$

$$\text{Rate} = k [\text{NO}]^2 [\text{H}_2] \quad \text{Determined experimentally!!}$$

This reaction is 2nd order with respect to NO,
1st order with respect to H₂.

The overall reaction order is 3.

$$\begin{aligned} \text{Units of } k \quad \frac{\text{moles}}{\text{L} \cdot \text{s}} &= k \left(\frac{\text{moles}}{\text{L}} \right) \left(\frac{\text{moles}}{\text{L}} \right) \left(\frac{\text{moles}}{\text{L}} \right) \\ \frac{\text{moles}}{\text{L} \cdot \text{s}} \left(\frac{\text{L}}{\text{moles}} \right) \left(\frac{\text{L}}{\text{moles}} \right) \left(\frac{\text{L}}{\text{moles}} \right) &= k \\ k &= \frac{\text{L}^2}{\text{moles}^2 \cdot \text{s}} = \text{M}^{-2} \text{s}^{-1} \end{aligned}$$

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35

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Reaction Rate Law

$a \text{ X} + b \text{ Y} \rightarrow \text{products}$

$$\text{Rate} = k [\text{X}]^m [\text{Y}]^n$$

k , m , and n are numbers that are determined experimentally!!

Knowing the rate law allows us to PREDICT the effect
on the rate of the reaction when the concentrations
are changed.

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36

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Reaction Rate Law

$a X + b Y \rightarrow \text{products}$

$$\text{Rate} = k [X][Y]^2$$

Determined experimentally!!

(a) What will happen to the reaction rate when the concentration of Y is tripled?

Rate increases 9x

[i.e. $3^2 = 9$]

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37

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Reaction Rate Law

$a X + b Y \rightarrow \text{products}$

$$\text{Rate} = k [X][Y]^2$$

Determined experimentally!!

(b) What will happen to the reaction rate when the concentration of X is tripled?

Rate increases 3x

[i.e. $3^1 = 3$]

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38

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Reaction Rate Law

$a X + b Y \rightarrow \text{products}$

$$\text{Rate} = k [X][Y]^2 \quad \text{Determined experimentally!!}$$

(c) What will happen to the reaction rate when the concentration of X is tripled and the concentration of Y is halved?

Rate increases $\frac{3}{4} \times$

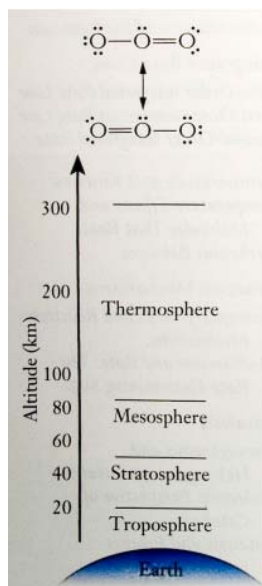
$$[i.e. \quad 3^1 \cdot \left(\frac{1}{2}\right)^2 = 3 \cdot \frac{1}{4} = \frac{3}{4} \times]$$

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39

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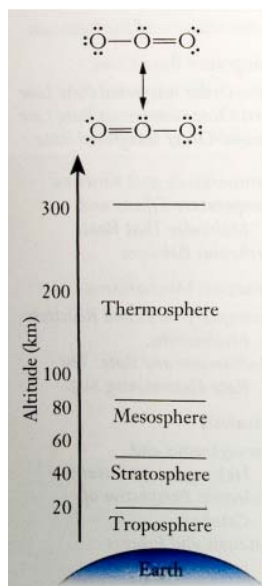
Ozone in the Stratosphere shields life on Earth from the Sun's ultraviolet radiation.

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40

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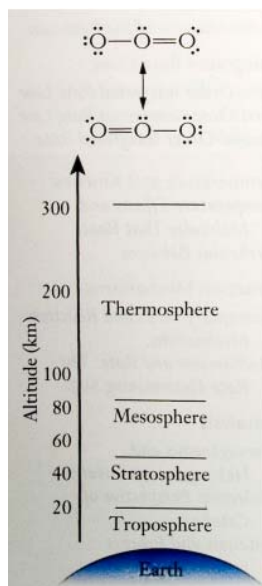
The creation of stratospheric ozone is explained by the “Chapman Cycle”.

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41

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The Chapman Cycle describes the kinetics of ozone using reaction mechanism.

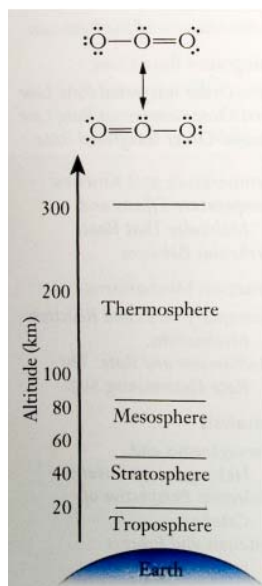
What is *reaction mechanism*?

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42

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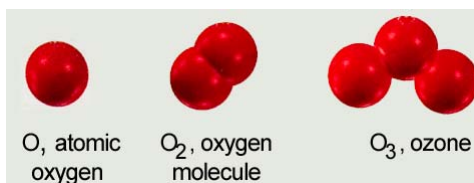
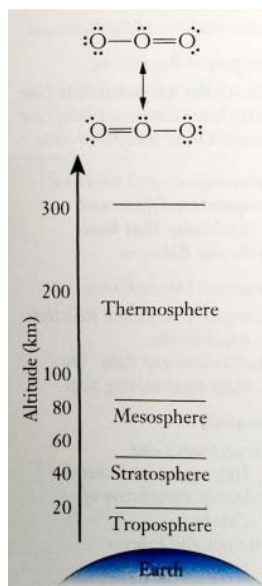
Reaction mechanism is a collection of steps that account for the way the reactants become products.

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43

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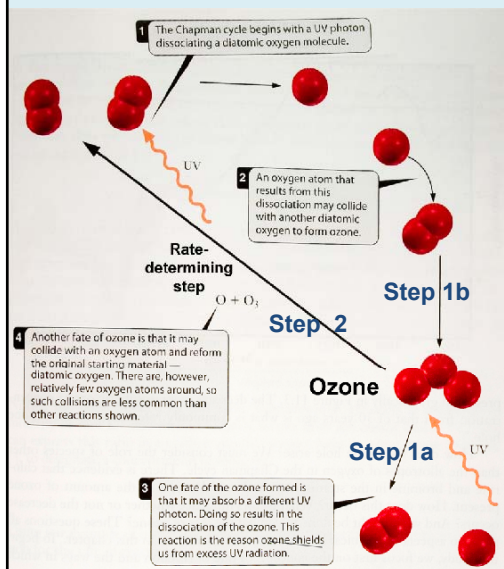


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44

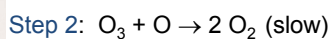
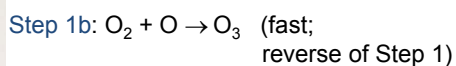
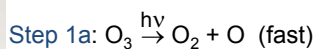
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The Chapman Cycle – the natural creation of ozone in the Stratosphere

Reaction Mechanism:



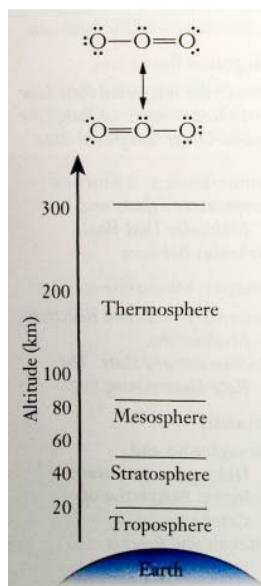
Steps 1b and 2 are a competition between O_2 and O_3 for O atoms. Step 2 is slower since there are relatively few O_3 molecules around.

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45

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Ozone is observed to be depleting in the Stratosphere

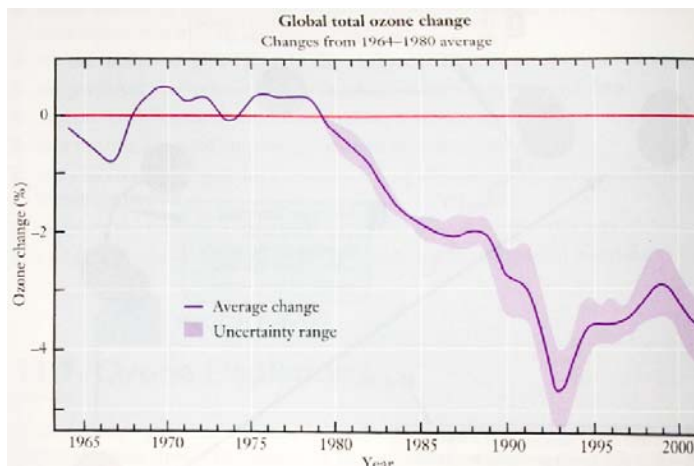
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46

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Problem: Observe a decrease in the overall levels of ozone in the stratosphere in the past decades. We are losing protection from UV light.



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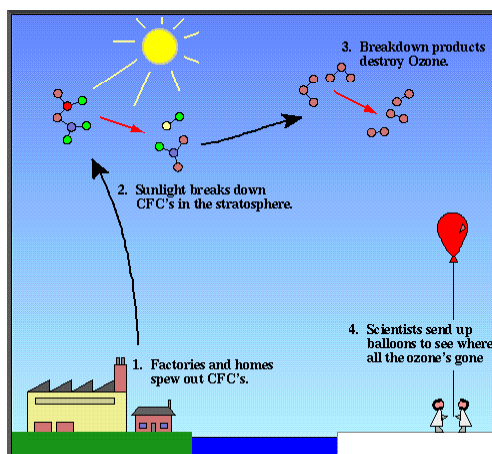
47

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Depletion of ozone:

Ozone depletion in the stratosphere is caused by chemicals that are used in refrigerators and air conditioners, chlorofluorocarbons (CFCs).



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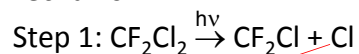
48

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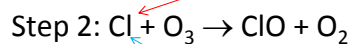
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- The catalytic destruction of ozone in the stratosphere involves chlorine as a catalyst. Released CFC slowly migrate to the stratosphere.

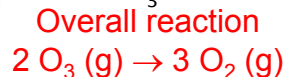
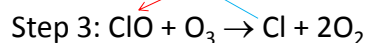
Upon absorption of UV light, the CFCs initiate a catalyzed reaction mechanism:



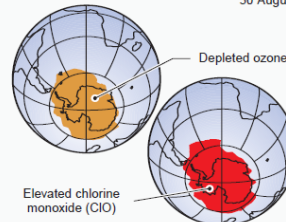
- Step 1 generates Cl, chlorine. Chlorine is the catalyst for Step 2.



- Production of chlorine monoxide



Satellite Observations in the Lower Stratosphere
30 August 1996

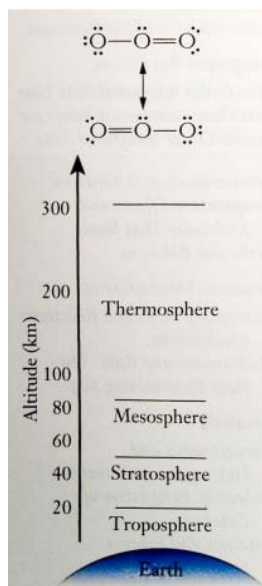


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9

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Reaction mechanism is a collection of steps that account for the way the reactants become products.

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50

Reaction Kinetics

Hebden – Unit 1 (page 1-34)

Reaction mechanism is a collection of steps that account for the way the reactants become products.

The Chapman Cycle:

Step 1a: $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$ (fast)

Step 1b: $\text{O}_2 + \text{O} \rightarrow \text{O}_3$ (fast;
reverse of Step 1)

Step 2: $\text{O}_3 + \text{O} \rightarrow 2 \text{O}_2$ (slow)

The Depletion of Ozone

Step 1: $\text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_2\text{Cl} + \text{Cl}$

Step 2: $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$

Step 3: $\text{ClO} + \text{O}_3 \rightarrow \text{Cl} + 2\text{O}_2$

Each step in a reaction mechanism is called an “elementary step” or an “elementary reaction”.

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51

Reaction Kinetics

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The rate law that governs the Chapman Cycle is

$$\text{Rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} = k[\text{O}_3]^2[\text{O}_2]^{-1}$$

Increase $[\text{O}_3]$ increases the reaction rate.

Increase $[\text{O}_2]$ decreases the reaction rate. ← Negative exponent!

- 2nd order with respect to O_3 .
- Negative 1st order with respect to O_2 .
- Overall reaction order = 1st order.

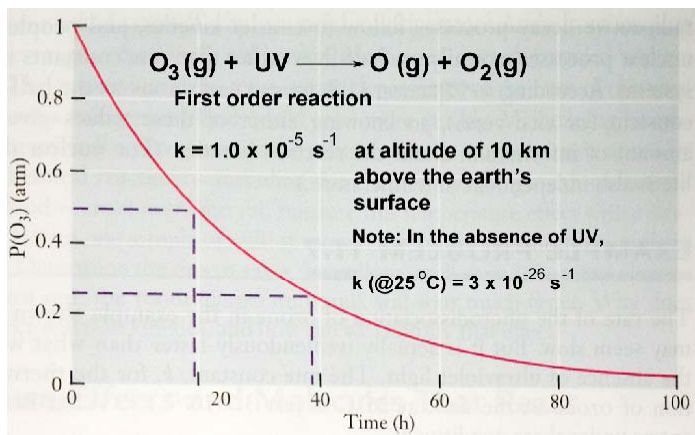
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52

Reaction Kinetics

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Experimental evidence shows that k is large in the presence of UV.



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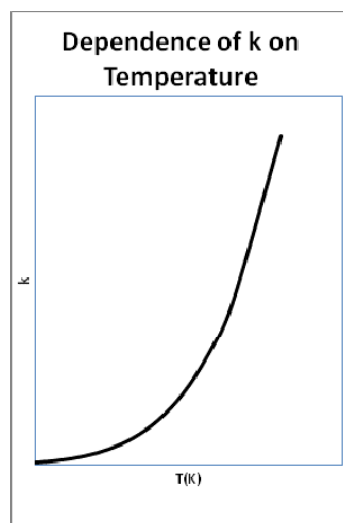
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Reaction Kinetics

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We have seen how the reaction rate depends on the concentration of reactants but how about other parameters such as temperature

The rate constant, k , usually increases exponentially with temperature



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54

Reaction Kinetics

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Reaction rates can be explained using Kinetic Molecular Theory and Collision Theory

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55

Reaction Kinetics

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Kinetic-Molecular Theory

The theory models the behaviour of gas on a microscopic scale.
The theory is based on the following 5 postulates:

1. A gas is made up of a vast number of particles, and these particles are in constant random motion.
2. Particles in a gas are infinitely small; they occupy no volume.
3. Particles in a gas move in straight lines except when they collide with other molecules or with the walls of the container. Collisions with each other and with the walls of the container are elastic, so that the kinetic energy of the particles are conserved.

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56

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Kinetic-Molecular Theory

4. Particles in a gas interact with each other only when collisions occur.
5. The **average kinetic energy** of the particles in a gas is proportional to the **absolute temperature** of the gas and does not depend on the identity of the gas.

Let's take a look to see whether KMT is observed in gases.

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57

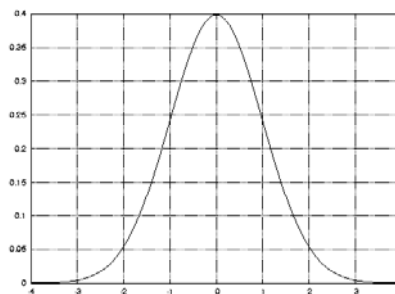
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Let's take a look to see whether KMT is observed in gases.

- Since gases are made up of a collection of gas particles, we will look at them using DISTRIBUTION functions.
- Distribution functions are common mathematical devices used in science, economics, social sciences and education.

Example - Test scores are visualized using distribution function.



Normal distribution or bell curve
Because the shape resembles a bell.

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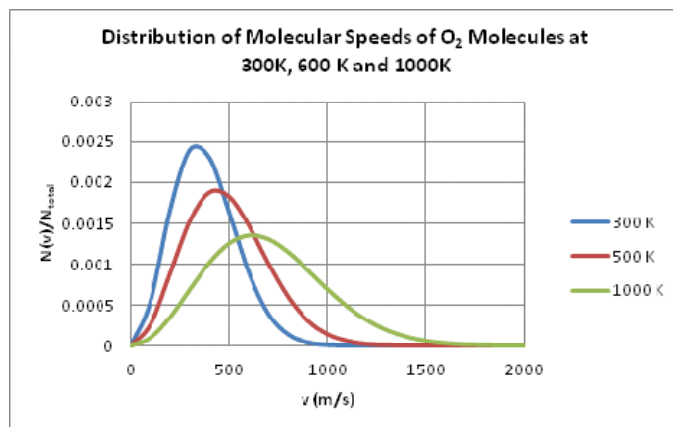


Figure 1: The distributions of molecular speeds of O_2 molecules at three different temperatures.

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59

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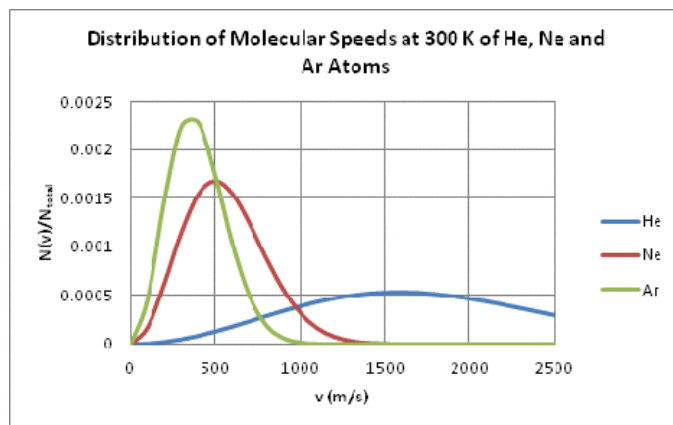


Figure 2: Distributions of molecular speeds for three different gases at the same temperature (300 K). As the molar mass decreases, the fraction of the molecules moving at higher speed increases.

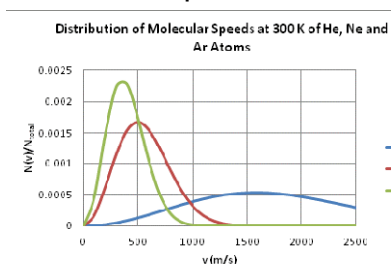
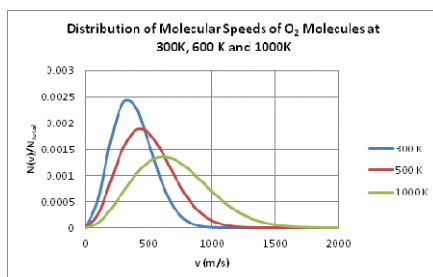
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Figure 1 and 2 are distribution function that describes the speeds of a collection of gas particles. They are known as the **Maxwell-Boltzmann distribution** of speeds.



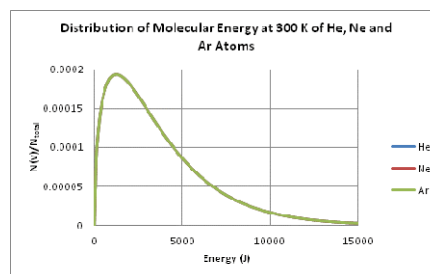
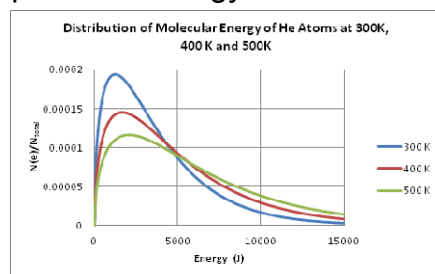
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61

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These distributions can also be plotted as a function of the particle's energy



Note: that the energy distribution does not depend on the mass of the particle. The distribution only depends on the sample's temperature.

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62

Reaction Kinetics

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How does KMT relate to reaction kinetics?

The Kinetic-molecular theory says that:

1. Molecules interact with one another only through collisions (Postulate 4).
 - The greater the number of collisions occurring per second, the greater the **reaction rate**.
2. Increasing the number of collisions can be achieved by
 - increasing the **temperature**, which results in increasing molecular speeds (Postulate 5)
 - increasing the **concentration** of the reactant molecules

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63

Reaction Kinetics

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Collision Theory

Chemical reactions are the result of collisions between reactant particles.

We should not expect that all collisions between molecules would result in chemical reactions.

For most reactions, only a tiny fraction of the collisions leads to a reaction.

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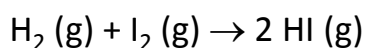
64

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Collision Theory

Example:



At room temperature and pressure - **10^{10} collisions per second**

- If every collision results in the formation of HI, the reaction would be over in much less than a second.
- In reality, at room temperature, this reaction proceeds very slowly. About **one in 10^{13} collisions produces a reaction.**

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Reaction Kinetics

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Collision Theory

What keeps the reaction from occurring more rapidly?

Collision Theory explains what keeps the reaction from occurring more rapidly

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Reaction Kinetics

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Collision Theory

Collision Theory is based on three postulates:

1. Chemical reactions in the gas phase are due to the collision of the reactant particles.
2. A collision only results in a reaction if a certain threshold energy is exceeded.
3. A collision only results in a reaction if the colliding particles are correctly oriented to one another.

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67

Reaction Kinetics

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Collision Theory

1. Chemical reactions result from collision of the reactant particles.

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68

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Collision Theory

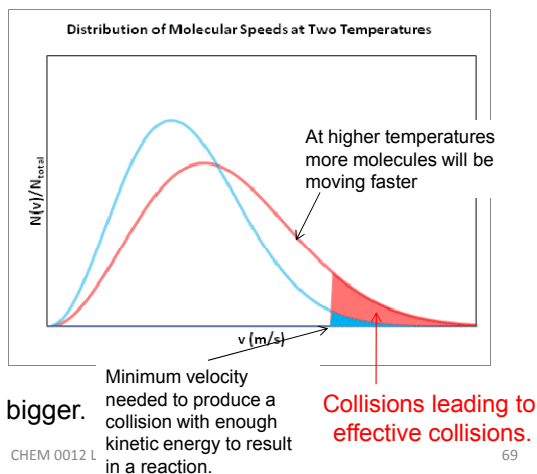
2. A collision only results in a reaction if a certain threshold energy is exceeded.

Activation Energy

The two curves are Maxwell-Boltzmann distribution of molecular speeds for two temperatures.

The shaded area represents the number of molecules traveling fast enough to collide with sufficient energy to react.

The area for the High T curve is bigger.



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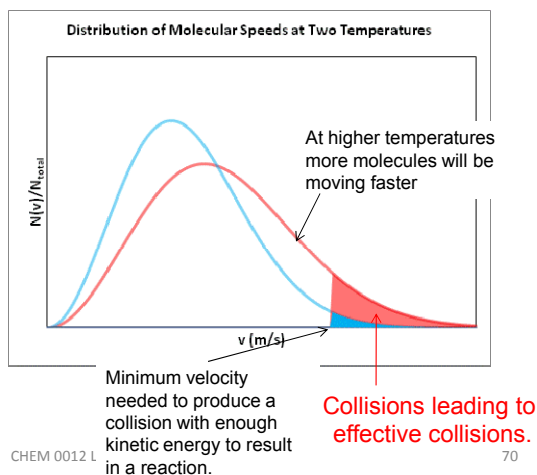
Collision Theory

2. A collision only results in a reaction if a certain threshold energy is exceeded.

Activation Energy

Reaction MUST overcome an energy threshold called the **ACTIVATION ENERGY** or activation barrier.

Only faster moving particles will collide with sufficient KE to overcome the activation barrier.



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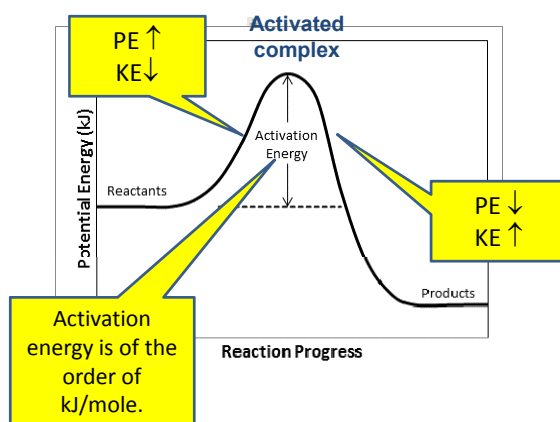
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Collision Theory

2. A collision only results in a reaction if a certain threshold energy is exceeded.

Activation Energy

Potential energy plot for a chemical reaction. To progress from reactants to products, the molecules must collide with enough energy to pass over the activation barrier.



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71

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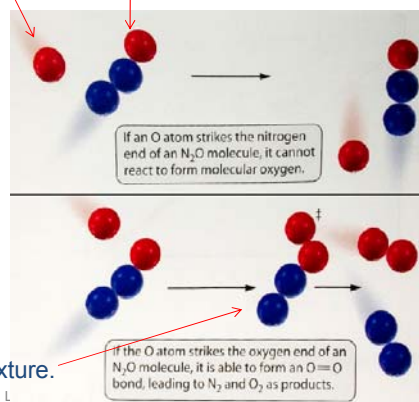
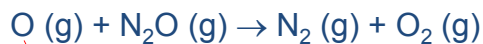
Collision Theory

3. A collision only results in a reaction if the colliding particles are correctly oriented to one another.

Orientation Factor

Oxygen collides with the nitrogen end of N_2O will result in NO REACTION.

Oxygen collides with the oxygen end of N_2O will result in producing the products.



Activation complex forms in the reaction mixture.

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2

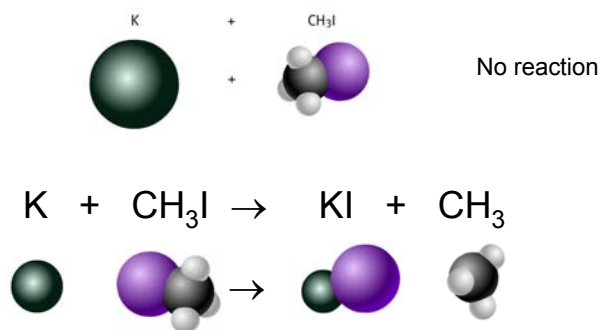
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Collision Theory

3. A collision only results in a reaction if the colliding particles are correctly oriented to one another.

Orientation Factor



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73

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Arrhenius Behaviour

An empirical relationship, called **the Arrhenius equation**, was proposed to describe the **temperature dependence of the rate constant, k** .

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

where E_a is the activation energy,
 R is the universal gas constant,
 T is the temperature (in Kelvin), and
 A is the proportionality constant called the frequency factor, or **pre-exponential factor**.

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74

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Arrhenius Equation – Rate and temperature of the reaction is related

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

In natural logarithmic form,

$$\ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$$

y = m · x + b

Very general rule – a rise of 10 degree will double the rate of a reaction.

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75

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Arrhenius Equation

In natural logarithmic form,

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

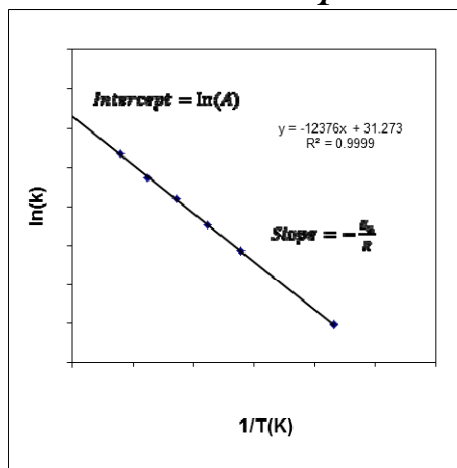
y = m · x + b

Determine E_a from the slope.

Determine A from the intercept.

As E_a increases, k decreases.

$\ln k$ versus $\frac{1}{T}$



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76

Reaction Kinetics

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Catalysts

A catalyst is a substance that increases the rate of the reaction but is neither created nor destroyed in the process. Catalysts can be divided into two broad categories.

Homogeneous catalysts are those that are in the same phase as the reacting substances.

Heterogeneous catalysts are in a different phase from the reacting species.

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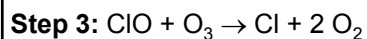
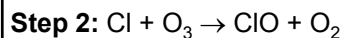
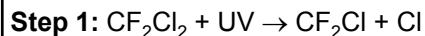
77

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Catalysts

RECALL: The catalytic destruction of ozone in the stratosphere involves chlorine as a catalyst.



Note: The chlorine atoms serve as a catalyst for ozone decomposition because

- They are not part of the reaction stoichiometry
- They are not consumed by the reaction
- They increase the rate of the reaction

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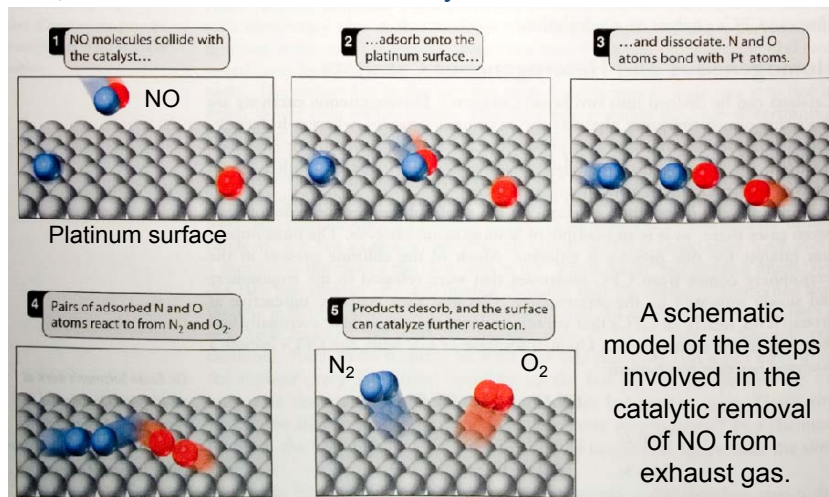
78

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Catalysts

Catalytic converters in automobiles



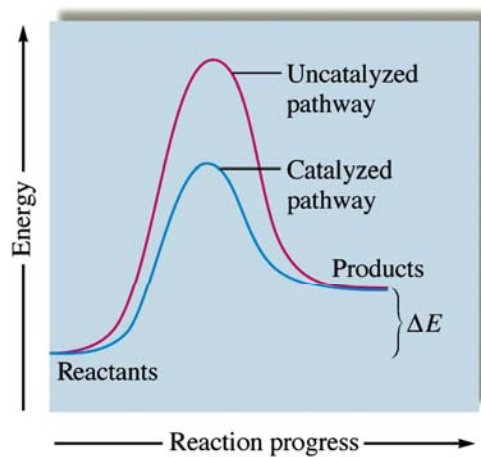
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79

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Catalysts



Catalysts increase the rate of reaction by providing an alternative reaction pathway with lower activation energy.

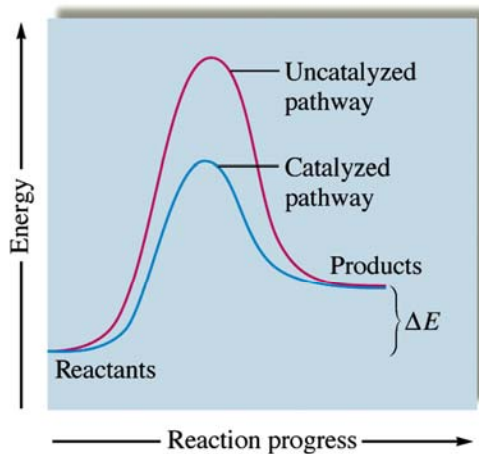
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80

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Catalysts



Eg. – Reaction at 293K

Catalyzed reaction -

$$E_a = 25 \text{ kJ/mole}$$

$$e^{-\frac{E_a}{RT}} = e^{-\frac{25000}{8.314 \cdot 293}} = 3.47 \times 10^{-5}$$

Uncatalyzed reaction -

$$E_a = 50 \text{ kJ/mole}$$

$$e^{-\frac{E_a}{RT}} = e^{-\frac{50000}{8.314 \cdot 293}} = 1.21 \times 10^{-9}$$

Catalyzed reaction speed
Increases.

$$\frac{3.47 \times 10^{-5}}{1.21 \times 10^{-9}} = 28700 \times$$

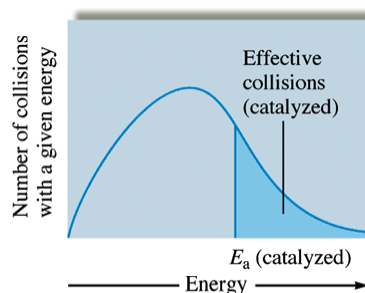
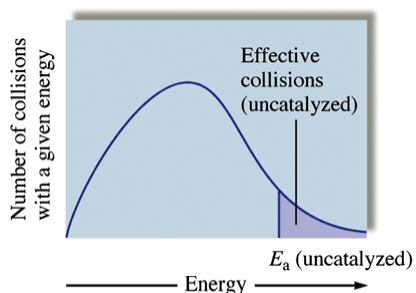
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81

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Catalysts



Effect of a catalyst on the number of reaction-producing collisions.

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82

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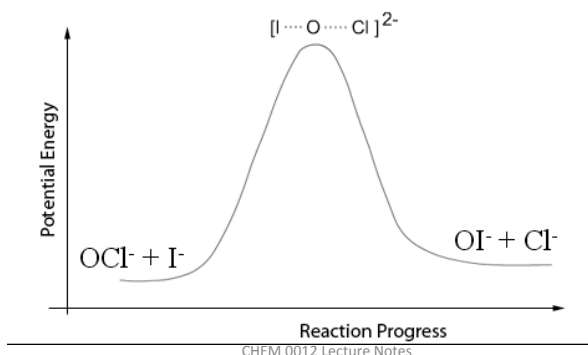
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Catalysts



Uncatalyzed Reaction:

- High E_a (reaction involves two negative ions)
- Requires high energy input



83

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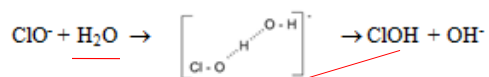
Catalysts



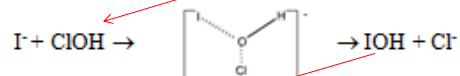
Catalyzed Reaction:

- Water acts as a catalyst for this reaction. It is not consumed in the reaction.
- It provides an alternate mechanism with a lowering of E_a .
- ClOH, IOH and OH⁻ are intermediate species

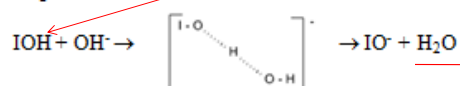
Step 1:



Step 2:



Step 3:



84

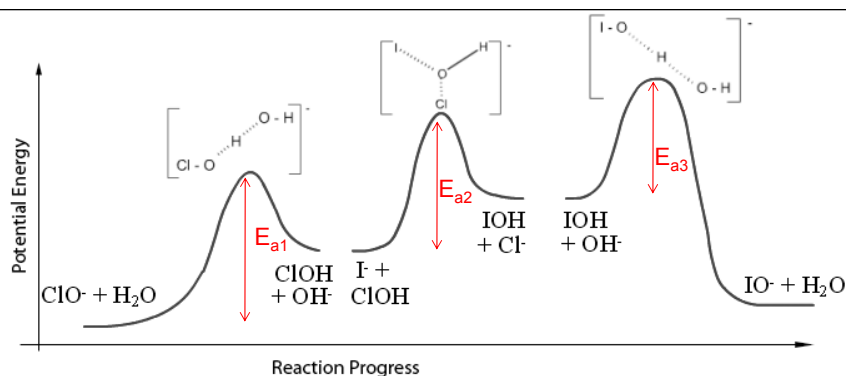
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Catalysts



Catalyzed Reaction:



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85

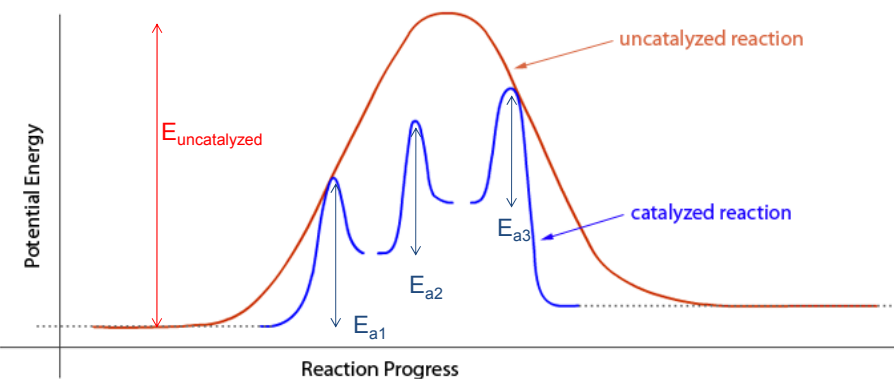
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Catalysts



Compare the Catalyzed and Uncatalyzed Reaction:



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86

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Catalysts

- Important in billion dollar industries such as petroleum refining
- Research of materials and design process for better catalysts
- Selective so that it speeds up one reaction and not all the reactions
- Historically, selection of catalysts is by trial and errors
- Modern days, catalysts are better understood by:
 1. Reaction mechanisms
 2. Molecular structure
 3. Material properties

The importance of Chemistry!!

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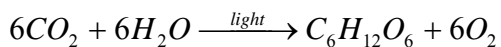
87

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Reaction Mechanism

- A chemical equation does not tell us *how* reactants become products - it is a *summary* of the *overall* process.
- The photosynthesis reaction



occurs in many steps

- The reaction mechanism is the *series of steps* by which a chemical reaction occurs.

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88

Reaction Kinetics

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Reaction Mechanism

- A step-by-step description of a chemical reaction.
- Each step is called an *elementary step*.
 - Any molecular event that significantly alters a molecule's energy or geometry or produces a new molecule.
- Reaction mechanism must be consistent with:
 - Stoichiometry for the overall reaction.
 - The experimentally determined rate law.
- It is only possible to show that a proposed mechanism is consistent with the observed rate law (i.e. it does not prove that the proposed mechanism is correct)

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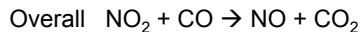
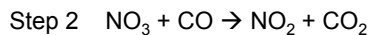
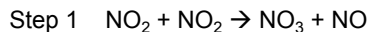
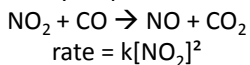
89

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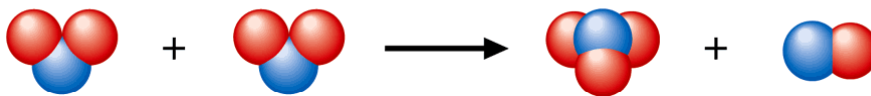
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Reaction Mechanism

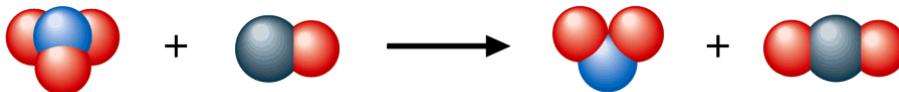
A molecular representation of the elementary steps in the reaction:



Step 1



Step 2



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90

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Reaction Mechanism

Mechanism Terms

- Intermediate: formed in one step and used up in a subsequent step and so is never seen as a product.
- Molecularity: the number of species that must collide to produce the reaction indicated by that step.
- Elementary Step: A reaction whose rate law can be written from its molecularity.

•uni, bi and termolecular

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91

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Reaction Mechanism

Elementary Step

- Unimolecular, bimolecular or trimolecular.
- *Exponents* for concentration terms are the same as the *stoichiometric factors* for the elementary step.
- Elementary steps are reversible.
- *Intermediates* are produced in one elementary step and consumed in another.
- One elementary step is usually slower than all the others and is known as the *rate determining step*. It therefore determines the overall rate of reaction.

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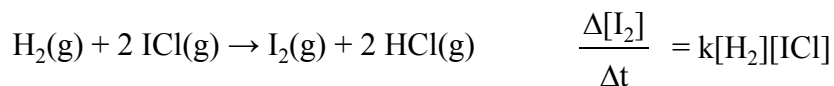
92

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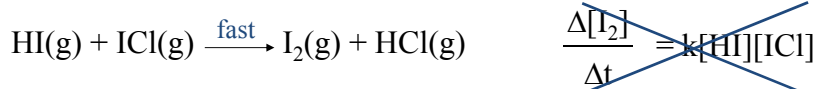
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Reaction Mechanism

Slow Step Followed by a Fast Step



Postulate a mechanism:



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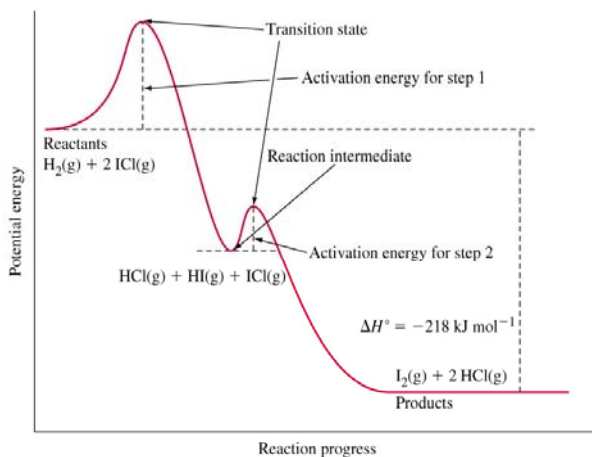
93

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Reaction Mechanism

Slow Step Followed by a Fast Step



Reaction Kinetics

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Reaction Rate Law Example

Using the data provided, establish the order of the reaction with respect to HgCl_2 and $\text{C}_2\text{O}_4^{2-}$, the overall order of the reaction and the value of the rate constant.

What is the rate of reaction when $[\text{HgCl}_2] = 0.10 \text{ M}$ and $[\text{C}_2\text{O}_4^{2-}] = 0.20 \text{ M}$

<u>Experiment</u>	<u>$[\text{HgCl}_2] \text{ (M)}$</u>	<u>$[\text{C}_2\text{O}_4^{2-}] \text{ (M)}$</u>	<u>Initial Rate (M min⁻¹)</u>
1	0.105	0.15	1.8×10^{-5}
2	0.105	0.30	7.1×10^{-5}
3	0.052	0.30	3.5×10^{-5}

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95

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Reaction Rate Law Example

$$\text{Let } R = k [\text{HgCl}_2]^m [\text{C}_2\text{O}_4^{2-}]^n$$

$$R_2 = k [\text{HgCl}_2]^m [\text{C}_2\text{O}_4^{2-}]^n = k (0.105)^m (0.30)^n$$

$$R_1 = k [\text{HgCl}_2]^m [\text{C}_2\text{O}_4^{2-}]^n = k (0.105)^m (0.15)^n$$

$$\frac{R_2}{R_1} = \frac{k (0.105)^m (0.30)^n}{k (0.105)^m (0.15)^n} = \frac{(0.30)^n}{(0.15)^n} = 2^n = \frac{7.1 \times 10^{-5}}{1.8 \times 10^{-5}} = 3.94$$

$$2^n = 3.94 \quad \text{therefore } n = 2$$

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96

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Hebden – Unit 1 (page 1-34)

Reaction Rate Law Example

$$\frac{R_2}{R_3} = \frac{k[\text{HgCl}_2]_2^m [\text{C}_2\text{O}_4^{2-}]_2^2}{k[\text{HgCl}_2]_3^m [\text{C}_2\text{O}_4^{2-}]_3^2} = \frac{k(0.105)^m (0.30)^2}{k(0.052)^m (0.30)^2} = \frac{(0.105)^m}{(0.052)^m}$$

$$\frac{R_2}{R_3} = \left(\frac{0.105}{0.052}\right)^m = (2.0)^m$$

$$\frac{R_2}{R_3} = \frac{7.1 \times 10^{-5}}{3.5 \times 10^{-5}} = 2.0$$

$$2^m = 2.0 \text{ therefore } m = 1$$

CHEM 0012 Lecture Notes

97

Reaction Kinetics

Hebden – Unit 1 (page 1-34)

Reaction Rate Law Example

$$\text{Rate} = k [\text{HgCl}_2]^1 [\text{C}_2\text{O}_4^{2-}]^2$$

Third Order = First Order + Second Order

$$k = \frac{\text{Rate}}{[\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^2}$$

Experiment	$[\text{HgCl}_2] \text{ (M)}$	$[\text{C}_2\text{O}_4^{2-}] \text{ (M)}$	$k \text{ (M}^{-2} \text{ min}^{-1})$
1	0.105	0.15	7.6×10^{-3}
2	0.105	0.30	7.5×10^{-3}
3	0.052	0.30	7.5×10^{-3}

$$\text{Average } k = 7.5 \times 10^{-3} \text{ M}^{-2} \text{ min}^{-1}$$

CHEM 0012 Lecture Notes

98

Reaction Kinetics

Hebden – Unit 1 (page 1-34)

Reaction Rate Law Example

$$\text{Rate} = k [\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^2$$

$$\text{Rate} = (7.5 \times 10^{-3} \text{ M}^{-2} \text{ min}^{-1}) [0.10 \text{ M}] [0.20 \text{ M}]^2$$

$$\text{Rate} = 3.0 \times 10^{-5} \text{ M min}^{-1}$$

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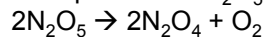
99

Reaction Kinetics

Hebden – Unit 1 (page 1-34)

Effect of Temperature Example

Consider the first-order decomposition of N_2O_5 at several temperatures.



<u>T(°C)</u>	<u>k(s⁻¹)</u>
0	7.87×10^{-7}
25	3.46×10^{-5}
35	1.35×10^{-4}
45	4.98×10^{-4}
55	1.50×10^{-3}
65	4.87×10^{-3}

- What is the activation energy for this reaction?
- What is the value of the pre-exponential factor?
- What is the value of the rate constant at 50.°C?

CHEM 0012 Lecture Notes

100

Reaction Kinetics

Hebden – Unit 1 (page 1-34)

Effect of Temperature Example

$T(^{\circ}\text{C})$	$k(\text{s}^{-1})$	$T(\text{K})$	$1/T(\text{K})$	$\ln(k)$
0	7.87×10^{-7}	273	3.66×10^{-3}	-14.055
25	3.46×10^{-5}	298	3.36×10^{-3}	-10.272
35	1.35×10^{-4}	308	3.25×10^{-3}	-8.910
45	4.98×10^{-4}	318	3.14×10^{-3}	-7.605
55	1.50×10^{-3}	328	3.05×10^{-3}	-6.502
65	4.87×10^{-3}	338	2.96×10^{-3}	-5.325

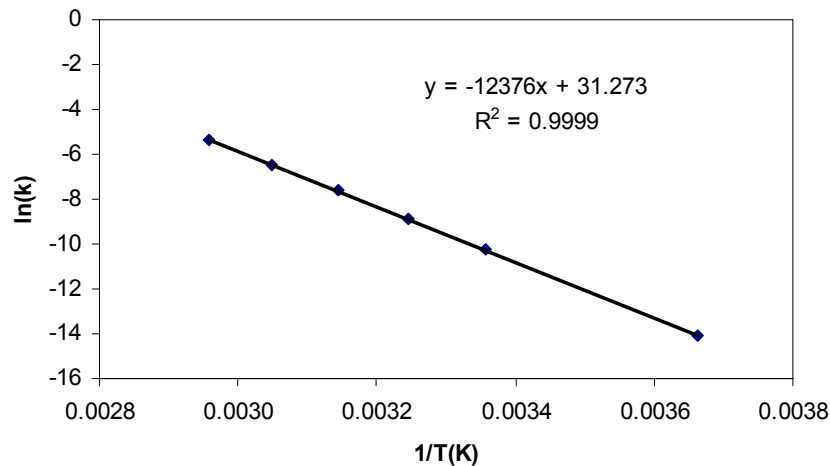
CHEM 0012 Lecture Notes

101

Reaction Kinetics

Hebden – Unit 1 (page 1-34)

Effect of Temperature Example



CHEM 0012 Lecture Notes

102

Reaction Kinetics

Hebden – Unit 1 (page 1-34)

Effect of Temperature Example

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{slope} = -12376 \pm 57 \text{ K}$$

$$\text{y-intercept} = 31.27 \pm 0.18$$

a) $\text{Slope} = -E_a/R$

$$\rightarrow E_a = -\text{slope} \cdot R = -(-12376 \text{ K})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$E_a = 103 \text{ kJ/mol}$$

b) $\text{y-intercept} = \ln(A)$

$$\rightarrow A = e^b = e^{31.27} = 3.82 \times 10^{13} \text{ s}^{-1}$$

CHEM 0012 Lecture Notes

103

Reaction Kinetics

Hebden – Unit 1 (page 1-34)

Effect of Temperature Example

c) $50^\circ\text{C} = (273 + 50) \text{ K} = 323 \text{ K}$

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

$$k_{50^\circ\text{C}} = (3.82 \times 10^{13} \text{ s}^{-1}) e^{-\frac{103 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(323 \text{ K})}}$$

$$k_{50^\circ\text{C}} = 8.4 \times 10^{-4} \text{ s}^{-1}$$

Alternately use equation of best fit line to calculate k

$$\ln(k) = -12376/T + 31.273$$

$$\ln(k) = -(12376 \text{ K})/(323 \text{ K}) + 31.273 = -7.04$$

$$K_{50^\circ\text{C}} = e^{-7.04} = 8.7 \times 10^{-4} \text{ s}^{-1}$$

CHEM 0012 Lecture Notes

104