

Chemical Kinetics

What factors affect the rate of a reaction?

Reaction Rate Factors

-Concentration of reactants

-Temperature (Increasing temperature increases the reaction rates. In what direction is a different question.)

-Surface Area

-Catalysis (Substance that participates but is not changed by the reaction. It is not included in the balanced equation. Inhibitors slow down reactions.)

Plotting the concentration of a chemical in a reaction as a function of time is called a **Kinetic Curve** or **Concentration vs. Time Curve**

Calculate the slope at a given time (Instantaneous rate) by drawing a tangent at that point and calculating the slope (derivative) of the line.

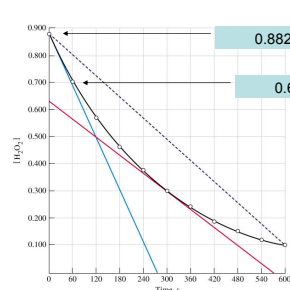
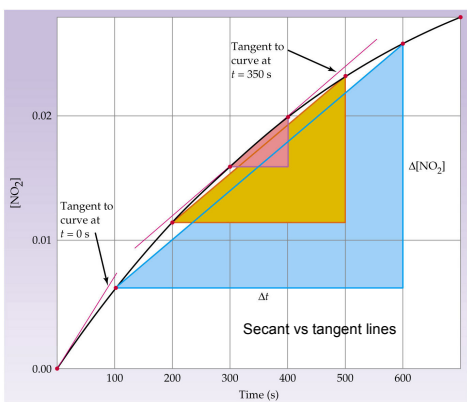
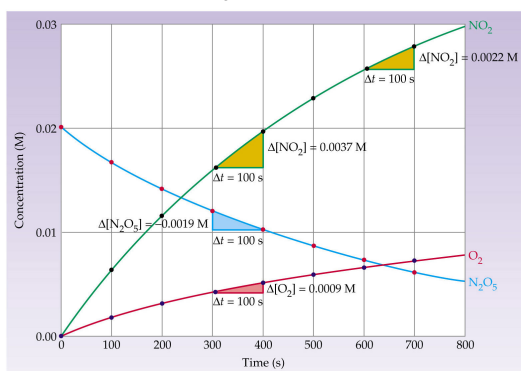
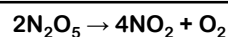
Always use a positive value for rate

$$\text{Rate} = \Delta C_{\text{products}} / \Delta t \quad \text{Rate} = -\Delta C_{\text{reactants}} / \Delta t$$

Where C is the concentration

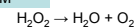
Once the rate of one component is determined, others can be determined (i.e. the rate of appearance and disappearance) using stoichiometric ratios. (More on this in a moment)

Units: mol/Ls or M/s



Question:

This picture shows the decomposition of hydrogen peroxide by the reaction



a. Use the diagram to determine the initial rate of the reaction by

-Using the first two concentration measurement points

-Estimating the slope of the line at $t = 0$ (the blue line)

b. Once you have done this, calculate $[\text{H}_2\text{O}_2]$ at $t = 30\text{sec}$ using the value from above you feel is best for this measurement.

(remember brackets means concentration (molarity))

Results:

a. Using the first two data points (Secant):

$$-\Delta[\text{H}_2\text{O}_2]/\Delta t = (0.697\text{M} - 0.882\text{M})/(60\text{s} - 0\text{s}) = \mathbf{3.08 \times 10^{-3}\text{M/s}}$$

Using the estimated slope of the tangent (best for initial rate):

$$\text{Slope} = (0 - 0.882\text{M})/(275 - 0)\text{s} = -3.21 \times 10^{-3}\text{M/s}$$

The initial rate is the negative of the slope of the tangent line = $\mathbf{3.21 \times 10^{-3}\text{M/s}}$

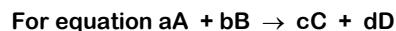
b. Initial Rate = $-\Delta[\text{H}_2\text{O}_2]/\Delta t$

$$3.08 \times 10^{-3} = -\Delta[\text{H}_2\text{O}_2]/30\text{s} \text{ (The "average" is better)}$$

$$\Delta[\text{H}_2\text{O}_2] = -0.092\text{M}$$

$$[\text{H}_2\text{O}_2]_{30\text{s}} = 0.882\text{M} - 0.092\text{M} = \mathbf{0.790\text{M}}$$

The **general rate** of reaction is obtained by dividing the rate of disappearance of a reactant or the rate of formation of a product by the stoichiometric coefficient of that reactant or product in the balanced chemical equation.



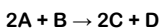
The **general rate of reaction** is:

$$\text{Rate} = -(1/a) \Delta[\text{A}]/\Delta t = -(1/b) \Delta[\text{B}]/\Delta t = (1/c) \Delta[\text{C}]/\Delta t = (1/d) \Delta[\text{D}]/\Delta t$$

This represents the average rate of a reaction over a time interval, as the rate is generally greater when the concentration of reactants are greater.

Question:

Consider the following hypothetical reaction:



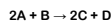
Suppose that at some point during the reaction $[\text{D}] = 0.2885\text{M}$ and that 2.55min (that is, 2min 33s) later $[\text{D}] = 0.3546\text{M}$

a. What is the average rate of reaction during this time period, expressed in Mmin^{-1} ?

b. What is the rate of formation of C, expressed in Ms^{-1} ?

Question:

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a. What is the average rate of reaction during this time period, expressed in Mmin^{-1} ?

b. What is the rate of formation of C, expressed in Ms^{-1} ?

Result:

$$\text{a. } (1/d) \Delta[\text{D}]/\Delta t = (0.3546 - 0.2885)\text{M}/(2.55\text{min}) = \mathbf{.0259\text{M/min}}$$

$$\text{b. } (1/c) \Delta[\text{C}]/\Delta t = (1/d) \Delta[\text{D}]/\Delta t$$

$$\frac{1}{2} \Delta[\text{C}]/\Delta t = .0259\text{M/min}$$

$$\Delta[\text{C}]/\Delta t = .0259\text{M/min} (2)(1\text{min}/60\text{s}) = \mathbf{8.63 \times 10^{-4}\text{M/s}}$$

The Rate Law (How is the rate affected by concentration?)

Relates the rate of a reaction to the concentration of the reactants

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y[\text{C}]^z \quad (\text{A, B and C are Reactants})$$

k = rate constant whose units depend on the "order" of the reaction

-Exponents are usually small whole numbers but may be negative or rational fractions

-They are **NOT** stoichiometric coefficients.

-The exponents of the rate law must be determined experimentally.

The rate law is determined by taking the ratios of experimental results on a reaction such that one or more of the concentrations cancel out leaving one to be determined

Ex:

$$\begin{array}{l} \text{Rate}_2 = k[.1]^x[.2]^y \quad \text{This concentration is} \\ \text{Rate}_1 = k[.05]^x[.2]^y \quad \text{kept constant in this} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{example.} \end{array}$$

After the exponents are determined, k may be determined from any of the reactions (see section in text for examples)

The order of the reaction

Either: 1. refers to the individual exponents of each component

Or 2. refers to the sum of all of them for the overall reaction

The units of the rate **constant k** vary with the order of the rate law, however they **must be** such that the overall rate is given in units of **concentration per unit time**.

If the concentration of a component has no effect on the reaction rate (i.e. zeroth order) it is not included in the rate law

Example: Determining the rate law through the method of initial rates:

Given:

Initial Rates of the Reaction $2\text{NO}_{(g)} + \text{Cl}_{2(g)} \rightarrow 2\text{NOCl}_{(g)}$

| Exp. | Init. [NO] | Init. [Cl ₂] | Init. Rate (M/s) |
|------|------------|--------------------------|-----------------------|
| 1 | 0.0125M | 0.0255M | 2.27×10^{-5} |
| 2 | 0.0125M | 0.0510M | 4.55×10^{-5} |
| 3 | 0.0250M | 0.0255M | 9.08×10^{-5} |

Question:

Determine the rate law for this reaction

$$\frac{\text{InitialRate}_3}{\text{InitialRate}_1} = \frac{k[\text{NO}]_3^m [\text{Cl}_2]_3^n}{k[\text{NO}]_1^m [\text{Cl}_2]_1^n}$$

Using the reactions 1 and 3, the Cl₂ cancels out because they are both .0255M

$$(9.08 \times 10^{-5} \text{M/s}) / (2.27 \times 10^{-5} \text{M/s}) = k(.0250\text{M})^m / k(.0125\text{M})^m$$

$$4 = (.0250\text{M} / .0125\text{M})^m$$

$$4 = 2^m \quad m = 2 \quad \text{The reaction is 2}^{\text{nd}} \text{ order in NO}$$

Doing the same thing for NO

$$(\text{InitialRate})_2 / (\text{InitialRate})_1 = k[\text{NO}]_2^m [\text{Cl}_2]_2^n / k[\text{NO}]_1^m [\text{Cl}_2]_1^n$$

The NO cancels out because they are both .0125M

$$(4.55 \times 10^{-5} \text{M/s}) / (2.27 \times 10^{-5} \text{M/s}) = k(.0510\text{M})^n / k(.0255\text{M})^n$$

$$2 = (.0510\text{M} / .0255\text{M})^n$$

$$2 = 2^n \quad n = 1 \quad \text{The reaction is 1}^{\text{st}} \text{ order in Cl}_2$$

The reaction is 3rd order overall.

Solution:

Solving for k, we can use any one of the experimental results

$$2.27 \times 10^{-5} \text{M/s} = k[0.0125\text{M}]^2 [0.0255\text{M}]$$

$$k = 5.697 = 5.7$$

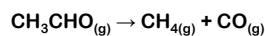
Since the rate must be in M/s, k's units must be 1/M²s

Note:

| <u>Zero order</u> | <u>No effect on the rate</u> |
|-----------------------|------------------------------|
| 1 st order | The rate doubles |
| 2 nd order | The rate quadruples |
| 3 rd order | The rate increases eightfold |

Follow up question:

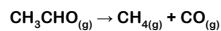
In the thermal decomposition of acetaldehyde,



The rate of reaction increases by a factor of about 2.8 when the initial concentration of acetaldehyde is doubled. What is the order of the reaction? (Hint: Recall that a reaction order can be noninteger.)

Result:

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$$2.8/1 = (2/1)^m$$

$$2.8 = 2^m$$

$$m = 1.48543 = 1.5$$

The Integrated Rate Law

What concentration will exist at some time, t?

In the last section we were concerned with how the rate of a reaction was affected by the initial concentrations of the reactant(s).

In this section we derive equations for some specific reaction orders to be able to determine the concentration at some time, t.

What will the concentration of a reactant be at a later time if we know its concentration initially?

First-Order Reactions

Of the type: $A \rightarrow \text{Products}$

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

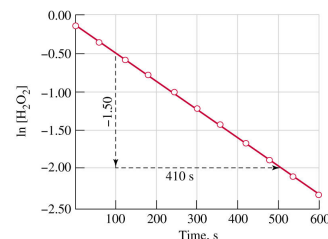
If this equation is integrated with respect to time the equation becomes

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

Writing this in line equation form:

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

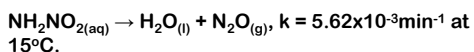
Note that the slope of the line is $-k$



Note that mass and partial pressure are proportional to the molarity and are sometimes substituted into the integrated rate-law equation.

Question:

The decomposition of nitroamide, NH_2NO_2 , is a first-order reaction:



Starting with 0.105M NH_2NO_2 ,

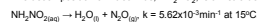
a. At what time will $[\text{NH}_2\text{NO}_2] = 0.0250\text{M}$?

b. What is $[\text{NH}_2\text{NO}_2]$ after 6.00hr?

c. What is the **rate** of the reaction after 35.0min?

Solution:

The decomposition of nitroamide, NH_2NO_2 , is a first-order reaction:



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c. What is the **rate** of the reaction after 35.0min?

$$\ln[A]_t = -kt + \ln[A]_0 \quad \ln[0.0250\text{M}] = -5.62 \times 10^{-3} \text{min}^{-1}(t) + \ln(0.105\text{M})$$

$$t = 255.353\text{min} = \mathbf{255\text{min}}$$

$$\ln[\text{NH}_2\text{NO}_2] = -5.62 \times 10^{-3} \text{min}^{-1}(6.00\text{hr} (60\text{min/hr})) + \ln(0.105\text{M})$$

$$x = .013884\text{M} = \mathbf{.0139\text{M}}$$

c. After 35.0min, the concentration is .0863M. Using this as the "initial" concentration

$$\text{Rate} = k[\text{NH}_2\text{NO}_2] = 5.62 \times 10^{-3} \text{min}^{-1}(.0863\text{M}) = \mathbf{4.85 \times 10^{-4} \text{M/min}}$$

Reaction half-life: The time for one-half of the initial concentration of a reactant to be consumed.

For first order reactions:

Using

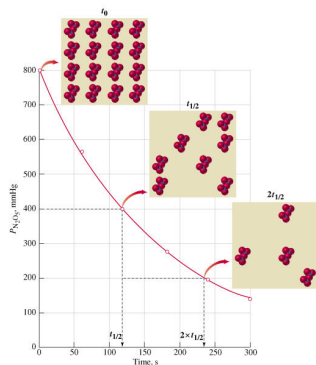
$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$t_{1/2} = \ln \frac{1/2[A]_0}{[A]_0} = -kt$$

$$\ln(1/2) = -kt_{1/2}$$

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

Note that $t_{1/2}$ is independent of the initial concentration of A.



Note that 1st order reactions are similar to that of radioactive decay reactions.

Reactions of Other Orders:

Zeroth Order: Rates are independent of initial concentration (such as those dependent upon the absorption of light or surface-catalyzed reaction).

$$\text{Rate} = k$$

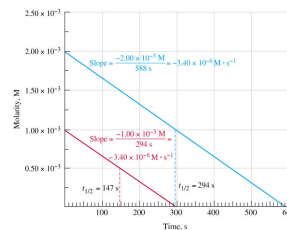
Second Order: Those of the type

$$\text{Rate} = k[A][B] \quad \text{or} \quad k[A]^2 \quad (\text{which is the form we will focus on})$$

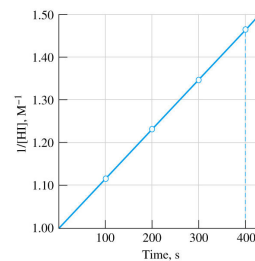
Summary of Reactions of Type: A → Products

| Order | Rate Law | Integrated Rate Law | Straight-Line Plot | k = | Units of k | Half-life |
|-------|-----------------|---|--------------------|--------|----------------|--------------|
| 0 | Rate = k | $[A]_t = -kt + [A]_0$ | $[A]$ vs. t | -slope | $M s^{-1}$ | $[A]_0/2k$ |
| 1 | Rate = $k[A]$ | $\ln[A]_t = -kt + \ln[A]_0$ $\ln([A]_t/[A]_0) = -kt$ | $\ln[A]$ vs. t | -slope | s^{-1} | $0.693/k$ |
| 2 | Rate = $k[A]^2$ | $1/[A]_t = kt + 1/[A]_0$ | $1/[A]$ vs. t | slope | $M^{-1}s^{-1}$ | $1/(k[A]_0)$ |

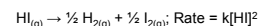
Examples of zeroth and 2nd Order Reactions



Decomposition of ammonia on tungsten surface is zeroth order



Second-order decomposition of HI(g) given by:



Theories of Chemical Kinetics (Collision Theory and Transition State Theory)

1. Collision Theory:

Factors affecting reaction progress

- KE of colliding particles
- Orientation of particles
- Frequency of Collisions
- Activation Energy (E_a) (minimum energy that must be supplied by collisions for a reaction to occur).

Theories of Chemical Kinetics

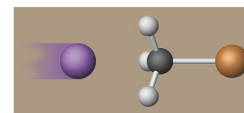
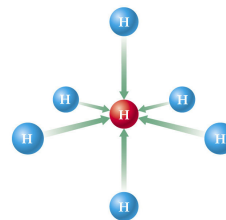
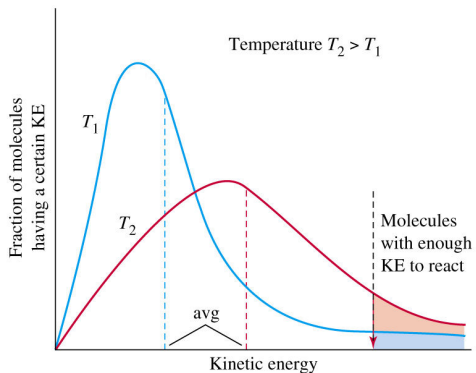
Fraction of molecules or atoms with sufficient reaction energy is related to the Kinetic Molecular Theory

$$\text{Reaction Rate} = N f_e f_o$$

N = number of collisions per second (temperature and concentration dependent).

f_e = fraction of collisions with minimum required energy (increases with increasing temperature)

f_o = fraction of collisions with correct orientation (constant for a given reaction)

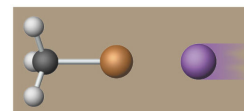


(a)

H attempting to react with H to form H_2

Note differences in spatial orientation requirements.

I attempting to react with CH_3Br



(b)

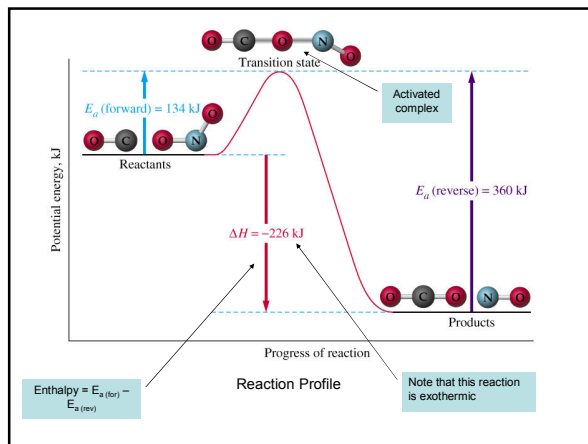
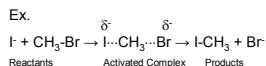
Transition State Theory

Envisions systematic breaking and forming of bonds.

Whether the reaction goes to completion depends on the species reaching the "transition state" of the reaction where it is known as the "activated complex"

This is the point of no return for the reaction (imagine a roller coaster going up a hill. Once it just barely gets over the top, it is going down the other side, not back the way it came.)

The transition state occurs where the system has achieved activation energy
(See Reaction profile on the next slide)



Effect of Temperature on Rates of Reactions



How fast does charcoal react with air (combust) with and without elevated temperatures?

Increased temperatures not only increase the frequency of collisions (i.e. increased K.E.), but increase the number of particles with sufficient energy for a reaction to take place.

The Arrhenius Equation (Svante Arrhenius, 1889)

Arrhenius equation **relates the rate constant to the temperature**

$$k = Ae^{-E_a/RT} \quad E_a = \text{activation energy}$$

$$R = 8.314 \text{ J/molK (or } 8.314 \times 10^{-3} \text{ kJ/molK)}$$

$$T = \text{temperature in K}$$

Note units of R from kinetic molecular theory

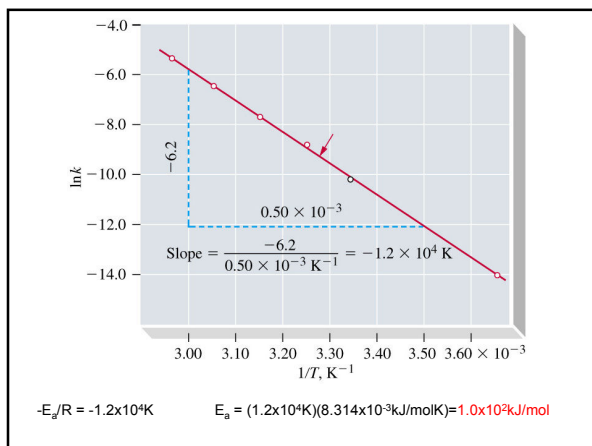
A is known as the **frequency factor** (product of the collision frequency (Z) and a probability factor (p)) Amounts to the number of collision/time capable of leading to a reaction. It is temperature dependent and has units of L/mol-s

Taking the natural log of both sides and using the rules of logarithms gives

$$\ln k = (-E_a/R)(1/T) + \ln A$$

we can plot $\ln k$ vs. $1/T$ after determining the rate constant (k) at different temperatures

Slope = $-E_a/R$, from this you can determine the activation and also the rate constant at other temperatures (from the plot)

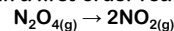


Alternate useful form of the equation:

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

Sample Problem:

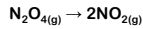
The colorless gas N_2O_4 decomposes to the brown gas NO_2 in a first-order reaction:



The rate constant $k = 4.5 \times 10^3 \text{ s}^{-1}$ at 274K and $k = 1.00 \times 10^4 \text{ s}^{-1}$ at 283K. What is the activation energy, E_a ?

Answer:

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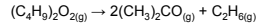
$$\ln(1.00 \times 10^4 s^{-1} / 4.5 \times 10^3 s^{-1}) = (E_a/R)(1/274 - 1/283)$$

$$.7985 = (E_a/8.314 \times 10^{-3} kJ/molK)(1.16 \times 10^{-4} K^{-1})$$

$$E_a = 57.2 kJ/mol$$

Example:

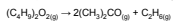
Di-tert-butyl peroxide (DTBP) is used as a catalyst in the manufacture of polymers. In the gaseous state, DTBP decomposes to acetone and ethane by a first-order reaction,



The half-life of DTBP is 17.5h at 125°C and 1.67h at 145°C. What is the activation energy E_a , of the decomposition reaction?

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The half-life of DTBP is 17.5h at 125°C and 1.67h at 145°C. What is the activation energy E_a , of the decomposition reaction?

Answer:

$$t_{1/2} = .693/k \text{ for } 1^{st} \text{ order reactions}$$

$$k_1 = .693/17.5h = .0396 \text{ @ } 125^\circ C = 398.15K$$

$$k_2 = .693/1.67h = .41497 \text{ @ } 145^\circ C = 418.15K$$

$$\ln(.41497/.0396) = [E_a/8.3145J/molK](1/398.15K - 1/418.15K)$$

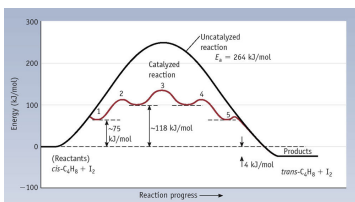
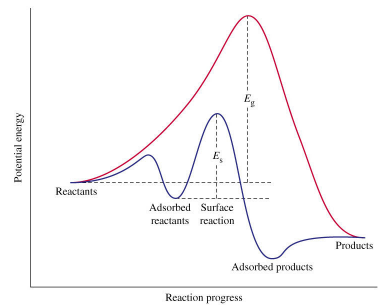
$$2.34938 = [E_a/8.3145J/molK] .0012K^{-1}$$

$$E_a = 162606J/mol = 163kJ/mol$$

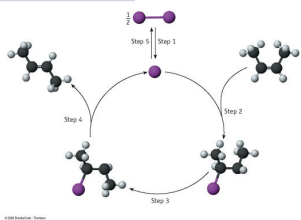
Catalysts

Increases the rate of the reaction without being "changed" overall

Usually creates alternate pathway (mechanism) for the reaction with lower E_a



The five step iodine catalyzed conversion of cis-2-butene to trans-2-butene

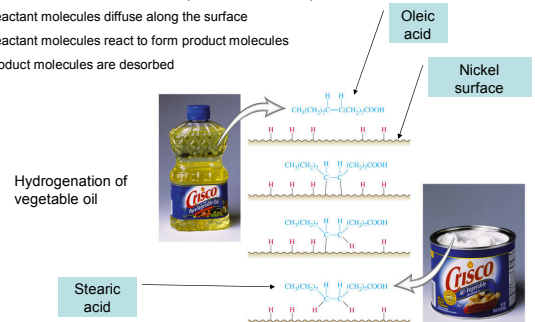


Catalysts

Catalysts can be homogeneous (one-phase) or heterogeneous

Heterogeneous catalysis generally requires four steps:

1. Reactant molecules are adsorbed (bound to the surface)
2. Reactant molecules diffuse along the surface
3. Reactant molecules react to form product molecules
4. Product molecules are desorbed



Enzyme Catalysis

Usually high molecular mass proteins with a specific catalytic function.

Some enzymes require a medium of specific pH for optimal performance.

Others are temperature sensitive and the active site can be "warped" out of shape.

Lock and key model for enzyme catalysis

Enzyme inhibitors make an enzyme less active or completely inactive.

Some attach to the active site

Some react with other molecules in the enzyme distorting and deactivating it

(ex. Hg^{2+} and Pb^{2+} reacting with sulfhydryl groups in the amino acid cysteine.)

Many poisons (e.g. insecticides) and warfare agents (e.g. sarin) create convulsions and death by interruption of acetylcholine (neutral transmitter) breakdown by cholinesterase (known as cholinesterase inhibitors) between nerve cells (see below)

Reaction Mechanisms

Reaction Mechanism: Series of simple steps that ultimately lead from the initial reactants to the final products of a reaction.

Elementary Reaction: A single step in the reaction mechanism process

More than one plausible reaction mechanism for a reaction may be possible.

Molecularity: Number of molecules involved in the elementary step

- Unimolecular:** 1 molecule (dissociation)
- Bimolecular:** 2 molecules
- Termolecular:** 3 molecules (much less likely)

The exponents in the rate law for an elementary reaction **are the coefficients of the chemical equation**.

Rate-determining step: The slowest step in a multi-step reaction mechanism. This is the "bottleneck" of the reaction.

Overall Reaction: $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{FNO}_2(\text{g})$

Experimental rate law: $\text{Rate} = k[\text{NO}_2][\text{F}_2]$

Elementary Step 1 Slow $\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \xrightarrow{k_1} \text{FNO}_2(\text{g}) + \text{F}(\text{g})$

Elementary Step 2 Fast $\text{NO}_2(\text{g}) + \text{F}(\text{g}) \xrightarrow{k_2} \text{FNO}_2(\text{g})$

Overall Reaction $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{FNO}_2(\text{g})$

Question:

The Raschig reaction produces hydrazine, N_2H_4 , an industrially important reducing agent, from NH_3 and OCl^- in basic, aqueous solution. A proposed mechanism is

Step 1 (fast) $\text{NH}_3(\text{aq}) + \text{OCl}^-(\text{aq}) \rightarrow \text{NH}_2\text{Cl}(\text{aq}) + \text{OH}^-(\text{aq})$

Step 2 (slow) $\text{NH}_2\text{Cl}(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{N}_2\text{H}_5^+(\text{aq}) + \text{Cl}^-(\text{aq})$

Step 3 (fast) $\text{N}_2\text{H}_5^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{N}_2\text{H}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$

- What is the overall stoichiometric equation?
- Which step of the three is rate-determining?
- Write the rate equation for the rate-determining step.
- What reaction intermediates are involved?

Reaction Mechanisms

The reaction mechanism must:

- Account for the experimentally determined rate law.
- Be consistent with the stoichiometry of the overall or net reaction.

Example of iodide catalyzed decomposition of hydrogen peroxide:

$$2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$$

Slow step: $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{OI}^-$

Fast Step: $\text{H}_2\text{O}_2 + \text{OI}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{I}^-$

Net: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

I⁻ is an intermediate

I⁻ is the catalyst (remains unchanged overall: consumed in the first step and produced in the second step)

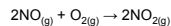
Writing the rate law in terms of the rate determining step:

Rate = k[H₂O₂][I⁻] but the concentration of I⁻ remains fixed

k' = k[I⁻] (Absorbs [I⁻] into the constant)

Rate = k'[H₂O₂] which is consistent with the observed rate.

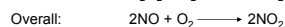
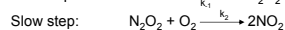
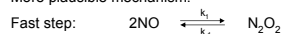
Example: Mechanism with a fast reversible step followed by a slow step:



Although observed rate law is Rate = k[NO]²[O₂]

This would be an unlikely termolecular reaction.

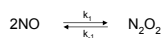
More plausible mechanism:



Rate law becomes Rate = k₂[N₂O₂][O₂]

However, the rate law cannot **contain any intermediates**.

The equation **must be written in terms of reactants**



Forward rate = Reverse rate

Writing their own "rate laws" equal to one another:

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

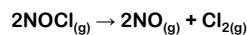
$$(k_1/k_{-1})[\text{NO}]^2 = [\text{N}_2\text{O}_2]$$

Substituting this in gives

$$(k_2 k_1/k_{-1})[\text{NO}]^2[\text{O}_2] = k[\text{NO}]^2[\text{O}_2]$$

Question:

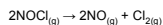
The decomposition of nitrosyl chloride is a first-order reaction



Propose a mechanism for this reaction consisting of one fast step and one slow step.

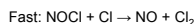
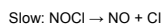
Question:

The decomposition of nitrosyl chloride is a first-order reaction



Propose a mechanism for this reaction consisting of one fast step and one slow step.

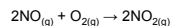
Result:



$$\text{Rate} = k[\text{NOCl}]$$

Question:

An alternative mechanism to the one described earlier for the reaction



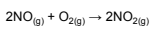
Involves NO₃ as an intermediate instead of N₂O₂.

a) Write the steps for this alternative mechanism

b) Show that the alternative mechanism is also consistent with the observed rate law of Rate = k[NO]²[O₂]

Question:

An alternative mechanism to the one described earlier for the reaction

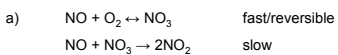


Involves NO_3 as an intermediate instead of N_2O_2 .

a) Write the steps for this alternative mechanism

b) Show that the alternative mechanism is also consistent with the observed rate law of $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$

Result:



b)

Rate law for RDS: $\text{Rate} = k_2[\text{NO}][\text{NO}_3]$

$$k_1[\text{NO}][\text{O}_2] = k_{-1}[\text{NO}_3]$$

$$[\text{NO}_3] = (k_1/k_{-1})[\text{NO}][\text{O}_2]$$

$$(k_2 k_1/k_{-1})[\text{NO}][\text{NO}][\text{O}_2] = k[\text{NO}]^2[\text{O}_2]$$