5.1 Rates

Study of reaction rates and what affects reaction rates.

Reaction rates are measured by the change in a measurable quantity divided by time:

$$\text{rate} = \frac{\Delta \text{ quantity}}{\Delta \text{ time}}$$

The quantity measured will depend upon the reaction.

Example 1

Describe a property to measure rate:

$Mg_{(s)} + 2\ HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$

$2\ Fe_{(s)} + 3\ CuCl_{2(aq)} \rightarrow 2\ FeCl_{3(aq)} + 3\ Cu_{(s)}$

$PCl_{3(aq)} + 3\ H_2O_{(l)} \rightarrow H_2PO_3^-{}_{(aq)} + 4\ H^+{}_{(aq)} + 3\ Cl^-{}_{(aq)}$

Example 2

Zinc reacts with hydrochloric acid (HCl) to produce 35 mL of hydrogen gas in 22 s. What is the rate of this reaction?

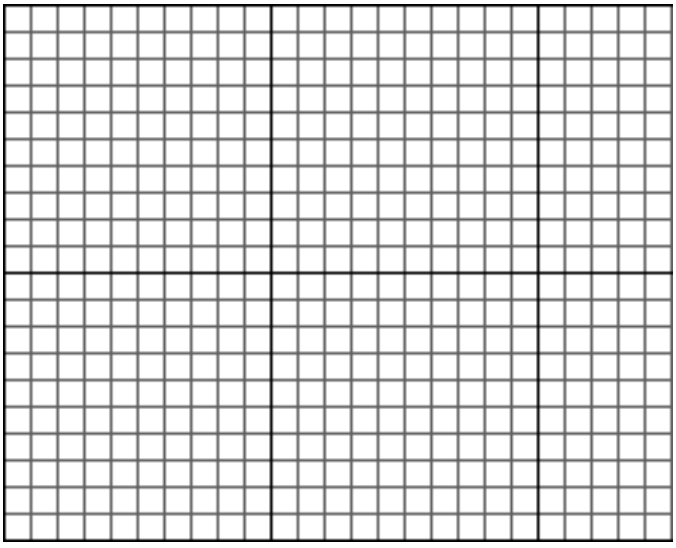
What is the rate of consumption of zinc metal? (Assume STP)

Give the rate calculated for the consumption of zinc, how long to consume 12.0 g of zinc metal?

Example 3

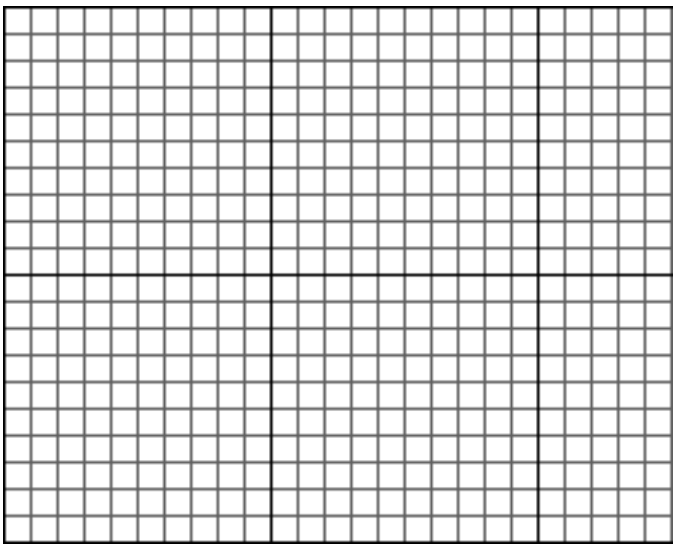
Plot the following data and determine the rate of the reaction by finding the slope of the graph.

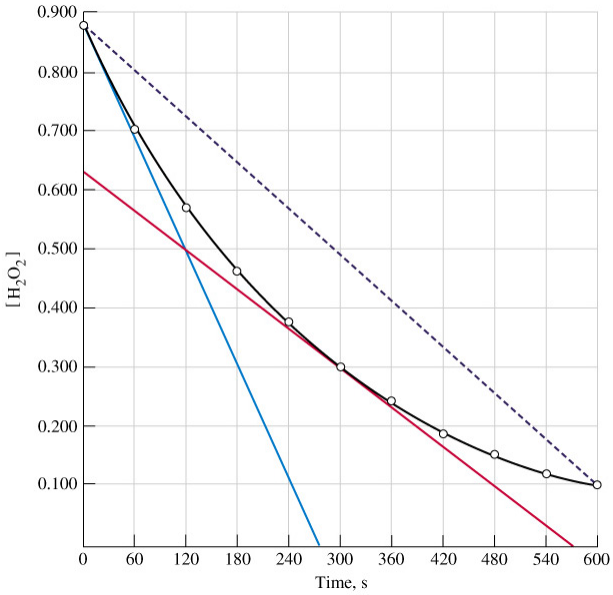
[product] (M)	Time (s)
0.00	0.0
0.11	55
0.19	118
0.30	186



Plot the following data for a reaction:

[product] (M)	Time (s)
0.0	0
0.10	10
0.40	20
0.90	30
1.6	40





Collision Theory

These are necessary conditions for a reaction to occur:

1. There must be a collision or an absorption of energy.
2. Reactant must collide with correct geometry.
3. There must be enough kinetic energy to allow a collision to occur. (or break an initial bond)

Meeting these conditions does not guarantee a reaction, but they are necessary.

Requirement 1: Collisions must occur for a reaction to occur. With more collisions, more reactions are possible.

Requirement 2: For old bonds to break and new bonds form, collisions must occur at the correct part of the molecule, and at the correct angles. This factor will affect some reactant more than others.

Requirement 3: As molecules approach each other, and as their bonds begin to break, they gain potential energy (electrons repel). There must be enough kinetic energy to be converted into potential energy to allow the reaction to proceed.

A successful collision can happen if these conditions are met. The more often these conditions are met, the more reactions that will occur.

Rate $\propto$ ($\#_{collision}$)($\%_{geometry}$)($\%_{energy}$)

Complete the following

Factor	Example	Why does it affect the rate?
Concentration and pressure		
Surface area		
Nature of reactants		
Catalyst		
Temperature		

Example 3 Rank as slow, medium or fast.

a) $H_2(g) + Cl2(g) \text{ ----> } 2HCl(g)$

b) $C6H12O6(s)+ 6O2(g) \rightarrow 6\ CO2(g) + 6\ H2O(l)$

c) $Cu2+(aq) + S2-(aq) \text{ ----> } CuS(s)$

d) A lump of iron in melted sulfur

e) Powdered iron in melted sulfur

f) powdered iron in boiling sulfur

g) $Fe2+(aq) + Ce4^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Ce^{3+}_{(aq)}$

Follow Up Problems 16.1
Problems 16.2, 3, 5, 8, 10, 12, 14, 16, 18

5.2 Kinetics – Energy

Energy in reaction is divided into two categories:
The reaction (system)
The surroundings

We describe energy for the system.

Endothermic — energy into the system
Exothermic — energy exiting the system

The energy of the system is called Enthalpy. (H)
The change in the energy of the system is "delta H" — ΔH
$\Delta H = H_{products} - H_{reactants}$

Exothermic — energy leaving — $\Delta H < 0$

Endothermic — energy entering — $\Delta H > 0$

The following are ways to describe exothermic reactions:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 802\ kJ$

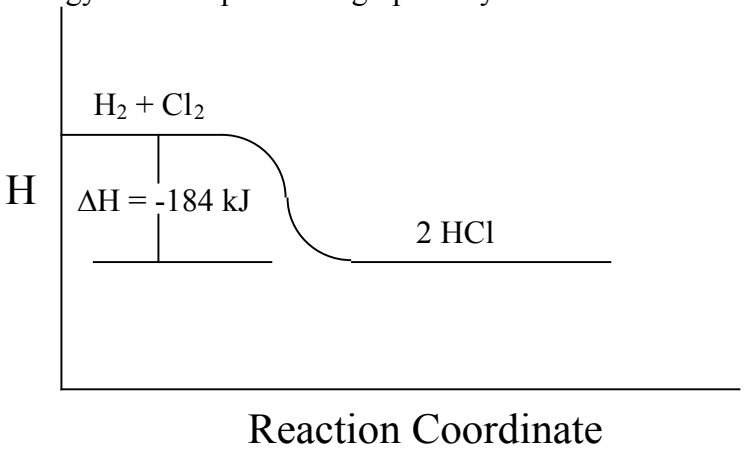
$CH_4 + 2O_2 - 802\ kJ \rightarrow CO_2 + 2H_2O$

$CH_4 + O_2 \rightarrow CO_2 + H_2O \qquad \Delta H = -802\ kJ$

Note on reactions:

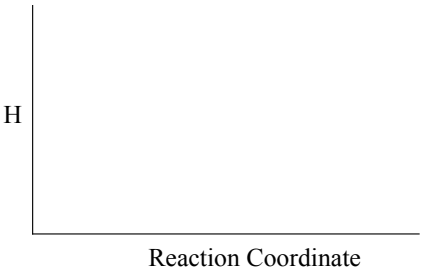
- Most are reversible.
- Reactant are the species to the left of the arrow, product are to the right.
- An exothermic reaction (read left to right) will be an endothermic reaction if reversed (read right to left).

Energy can be represented graphically



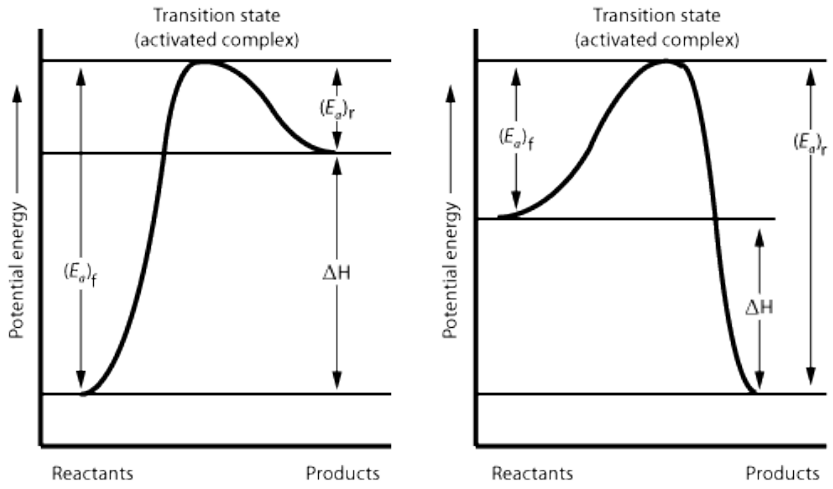
Example 1
Sketch the PE diagram for the following reaction:

$N_{2(g)} + {}^{5}/_{2}O_{2(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(l)}$ $\Delta H = -60.5$ kJ



Systems tend to lower potential energy.
Why are we not dead from nitric acid in our lungs?

A more sophisticated PE diagram shows the change in energy through the process of the reaction, not just initial and final energy.

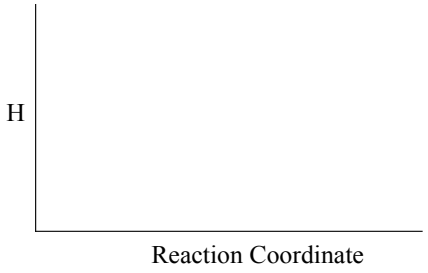


E_a — Activation energy
forward (f) and reverse (r)
Energy required to allow a reaction to proceed. If the colliding particles do not have this energy they will not react.
Activated Complex
Half way between reactants and products
Very unstable
It may become reactants or products.

Example 2
Sketch the changes in potential energy and kinetic energy as a reaction proceeds.

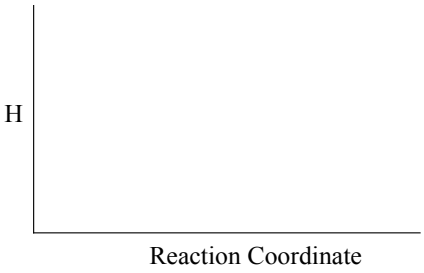
What are the implications of a reaction having a high activation energy?

Example 3
Sketch the PE diagram for the following:
A + B + 150 kJ ⇆ AB
Ea = 250 kJ



Example 4
Sketch the PE diagram for:
$CH_4 + O_2 \rightarrow CO_2 + H_2O$

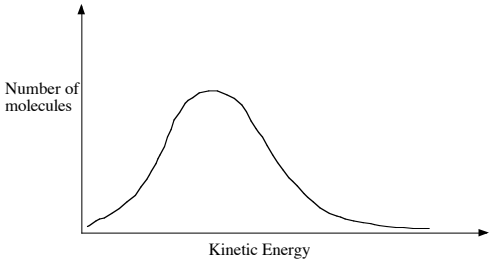
$\Delta H = -802$ kJ
$E_{ar} = 1100$ kJ



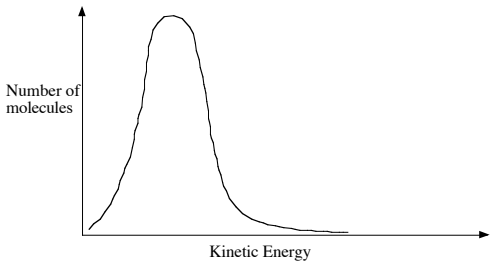
Maxwell-Boltzmann Energy Distribution
Temperature is the average Kinetic energy of the molecules in a sample.
Some particles will have more energy, some will have less.

Following are two samples of energy distributions at different temperatures
Label:
Temperature for each curve.

Which is higher temp?



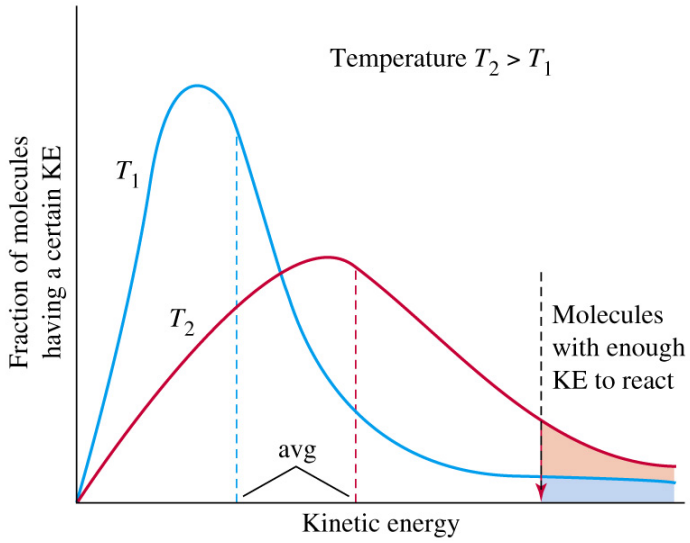
Example 5
How can a glass of water at 20 °C evaporate? Water must be 100 °C to turn into a gas at room temperature.



To react particles at higher kinetic energies must collide.
As there are more particles at the higher energies, more of the collisions can result in reactions

At higher temperatures more particles have enough energy to react.
A slow reaction will about double its rate for a 10°C change in temperature. What is doubled that causes the rate to double?

Example 6
What is the relationship between the energy distribution curve, the activation energy of a reaction, and the rate of a reaction?



Follow Up Problems 16.7
Problems 16.55, 57, 62, 64, handout

5.3 Kinetics — Rate Law

For a generic reaction: A + B → C + D
The rate expression is:

$$\text{rate} = \frac{\Delta[\ ]}{\Delta t} = k[\text{A}]^m[\text{B}]^n$$

The order of the reaction is "*m*" in substance A, and "*n*" in substance B.

The overall order is $m + n$

k is the rate constant. It varies with temperature, but not concentration. Be careful with the units of the rate constant.

The value of "*m*" and "*n*" must be determined experimentally. Experiments are performed with different initial concentrations of the reactants.
The initial rate of the reaction is measured for each trial. The change of the concentration is compared to the effect on the rate. Initial reaction rates are used so that reverse reactions can be ignored.

$$\text{rate} = \frac{\Delta[\ ]}{\Delta t} = k[\text{A}]^m[\text{B}]^n$$

[A] is changed with [B] kept constant.
If [A] was doubled and the rate was doubled, then "*m*" equals 1.
If [A] was doubled and the rate was quadrupled, then "m" equals 2.

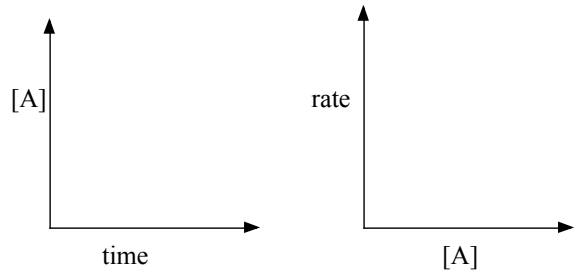
Similar tests are carried out to vary [B] with [A] being constant.

Ex 1: The following data was collected at 25°C for the reaction:
$NH_4^{+}{}_{(aq)} + NO_2^{-}{}_{(aq)} \rightarrow N_{2(g)} + H_2O_{(l)}$

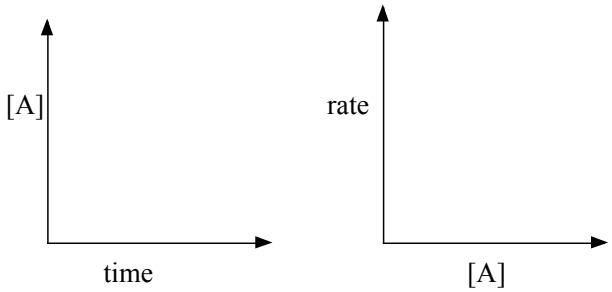
Trial	$[NH_4^+]$	$[NO_2^-]$	Initial rate ($mol \cdot dm^{-3} \cdot s^{-1}$)
1	0.24	0.10	7.2×10^{-6}
2	0.12	0.10	3.6×10^{-6}
3	0.12	0.15	5.4×10^{-6}

Find the rate expression for this reaction.

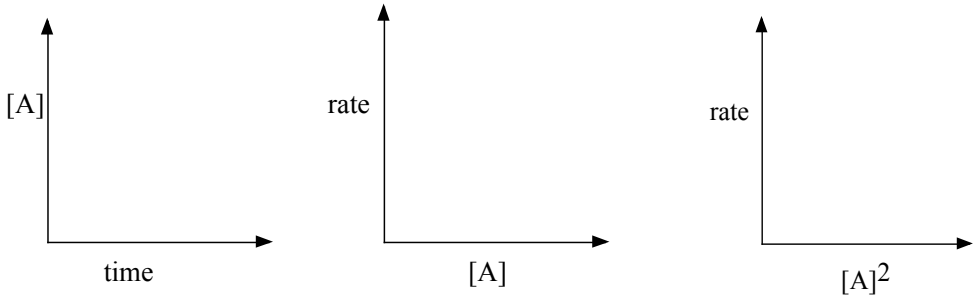
Rate orders in one species are usually zeroth, first, or second order.
Complete the following graphs for a zeroth order reaction



Complete these graphs for a first order reaction.



Complete these graphs for a second order reaction.



Follow Up Problems 16.2, 3
Problems 16.23, 25, 26, 28, 30, 32, 34, 36, 38

5.4 Kinetics — Mechanisms

Reaction Mechanisms
The actual series of steps that result in the overall reaction.
A reaction that involves more than two reactants is very unlikely to occur in one step.
$4HBr + O_2 \rightarrow 2H_2O + 2Br_2$

There must be a series of steps.

1: $HBr + O_2 \rightarrow HOOBr$
2: $HBr + HOOBr \rightarrow 2HOBr$
3: $HBr + HOBr \rightarrow H_2O + Br_2$

Show that this proposed mechanism combines to add to the overall reaction.

Each step in a mechanism is called an *Elementary Process*.
The number of molecules involved in an elementary step is the reactions molecularity.

Elementary processes are usually unimolecular or bimolecular.

Species that are produced in an early step and consumed in a later step are *Reaction Intermediates.*

The slowest step in a mechanism is the *Rate Determining Step*.
It controls the rate of the overall reaction.

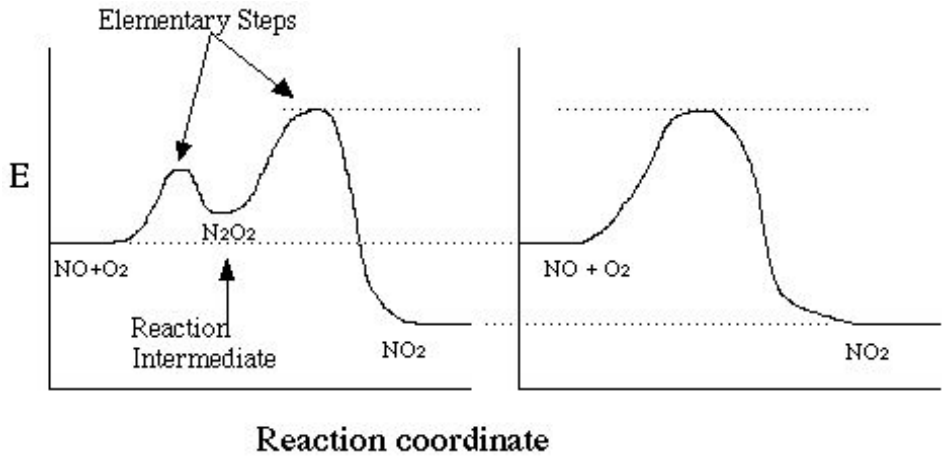
1: $HBr + O_2 \rightarrow HOOBr$ slow
2: $HBr + HOOBr \rightarrow 2HOBr$ fast
3: $HBr + HOBr \rightarrow H_2O + Br_2$ fast

This is determined experimentally.

Ex 1 $OCl^- + I^- \rightarrow IO^- + Cl^-$

A proposed mechanism is:
1: $OCl^- + H_2O \rightarrow ClOH + OH^-$ fast
2: $I^- + ClOH \rightarrow IOH + Cl^-$ fast
3: $IOH + OH^- \rightarrow IO^- + H_2O$ slow
Does this mechanism produce the overall reaction?
What are the intermediates?
What is H_2O in this reaction?

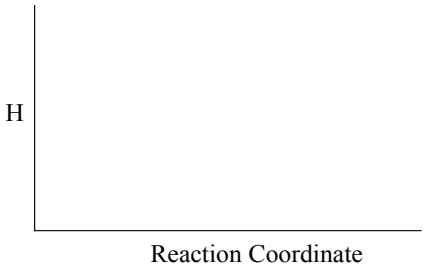
Potential Energy diagrams for Mechanisms
Initial and final Enthalpies are unaffected — ΔH is unaffected.
Each elementary process is a "bump" on the PE curve.
Slowest step has the highest Activation Energy.



Example 2 — Sketch the PE diagram for:

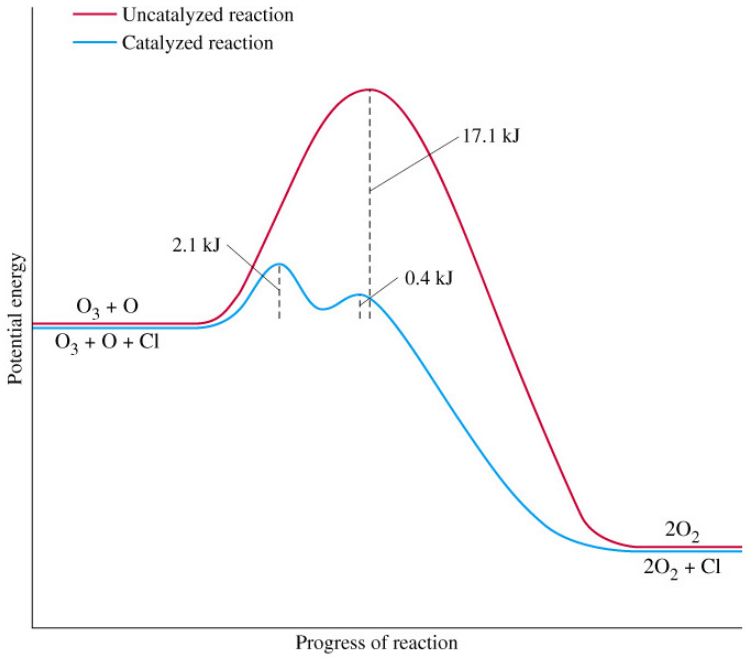
$4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2 + energy$

1: $HBr + O_2 \rightarrow$ HOOBr slow
2: $HBr + HOOBr \rightarrow 2\ HOBr$ fast
3: $HBr + HOBr \rightarrow H_2O + Br_2$ fast



Catalysts increase the rate of a reaction without being consumed in the reaction. They are not represented in the overall reaction as a Reactant or product.
In a mechanism, a catalyst is consumed in an early step and produced in a later step.

The catalyst lowers the amount of energy required for the reaction to proceed.

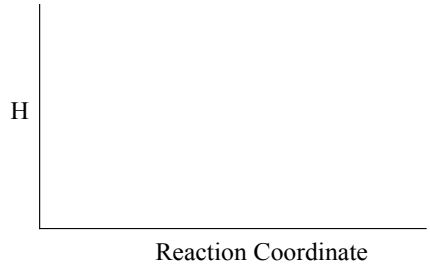


Catalyst:

- Decreases the energy required to react
- Provides an alternate mechanism with a lower energy Activated Complex
- Lowers the forward and reverse Activation Energy
- ΔH is **not** changed

Example 1
Sketch the PE diagram for:

$$2\ H_2O_2 \longrightarrow 2\ H_2O\ +\ O_2 \quad \Delta H = -22\ kJ$$



Now with an I^- catalyst.

$$2\ H_2O_2 \xrightarrow{I^-} 2\ H_2O\ +\ O_2 \quad \Delta H = -22\ kJ$$

Show why the rate increases using the energy distribution curve.

Homogeneous Catalysts

- Same phase as reactants
- Consumed early, reproduced later
- Provide an alternate series of reactions with a lower activation energy.

Heterogeneous Catalysts

- Different phase than reactants
- Usually weaken the bonds in the reactant molecules lowering the energy needed to break them.

Examples of Catalysts:
H+ in esterification and alkene ⇆ alcohol
Contact process:

$$2\ SO_{2(g)} + O_{2(g)} \underset{\leftarrow}{\overset{VO_2}{\rightleftharpoons}} 2\ SO_{3(g)}$$

Nickel used in hydrogenation of unsaturated fats.
Enzymes in living organisms

A mechanism can give us a rate expression.

Remember, mechanisms are often not well known, and can be an experiment in progress

The rate determining step should give us the exponents in the rate expression.

This is the rate expression for each elementary process shown.
$2A \rightarrow B$ rate = $k[A]^2$
$A + B \rightarrow C$ rate = $k[A][B]$
$B \rightarrow C$ rate = $k[B]$

	Reaction: $2A+B \rightarrow C+D$	Rate expression
1	$A + B \rightarrow X + D$ slow $A + X \rightarrow C$ fast	rate = $k[A][B]$
2	$A + B \rightarrow X$ fast $A + X \rightarrow C + D$ slow	rate = $k[A]^2[B]$
3	$A + A \rightarrow X$ slow $B + X \rightarrow C + D$ fast	rate = $k[A]^2$
4	$A + A \rightarrow X$ fast $B + X \rightarrow C + D$ slow	rate = $k[A]^2[B]$
5	$B \rightarrow X$ fast $2A + X \rightarrow C + D$ slow	rate = $k[B]$

Follow Up Problems
16.8
Problems
16.65, 69, 70, 72, 74, 77, 78, 81, 82
Handout (Energy diagrams)

5.5 Kinetics — Mathematics

The mathematical models for reaction kinetics allow for powerful manipulation of kinetics data.

For the first order rate law: rate = k [A]

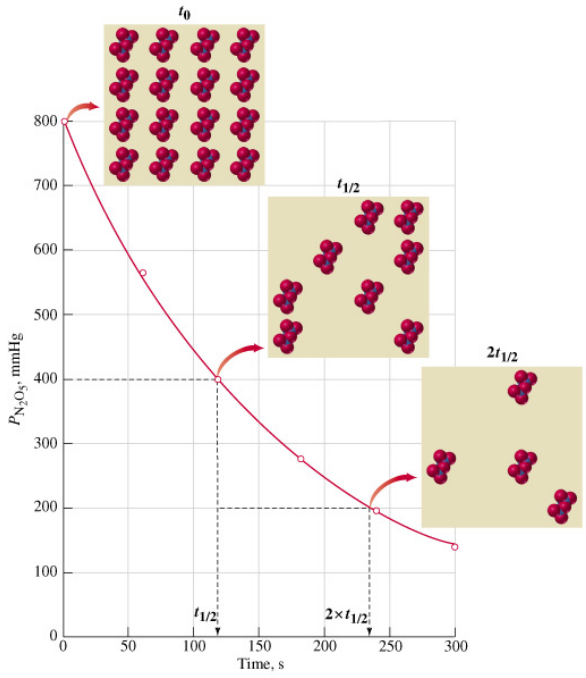
Using calculus, the first order rate law can be integrated to the equation:

$$[A] = [A]_0 e^{-kt} \qquad \ln\frac{[A]_0}{[A]} = kt$$

The advantage of these equations is that the rate does not need to be measured. Only the initial concentration, and the concentration at time *t* need to be measured.

To the right is shown the concentration curve over time for a first order reaction.

Every ~120 s, $[N_2O_5]$ is halved. 120 s is called the half life of this reaction. (For zeroth and second order reactions half life varies.)



Using the integrated form of the rate expression for a half life:

$[A] = 0.5\,[A]_0$

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

$$\ln(2) = kt$$

$$0.693 = kt$$

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

This is the equation in your data booklet.

The other model of kinetics that we will examine is the Arrhenius equation.

$$k = Ae^{\frac{-E_a}{RT}} \qquad \ln k = -\frac{E_a}{RT} + \ln A$$

This equation related the rate constant "k" with the activation energy "E_a" and the temperature "T"

A was a geometrical factor that accounted for the geometry required in the collision.

If reactions are conducted at different temperatures, then k and T are known for several trials.

The unknowns are: E_a and A.

One way to solve for two unknowns is to use two simultaneous equations.

Ex 1: For the following, find E_a and A.

$T_1 = 600$ K; $k_1 = 0.028$

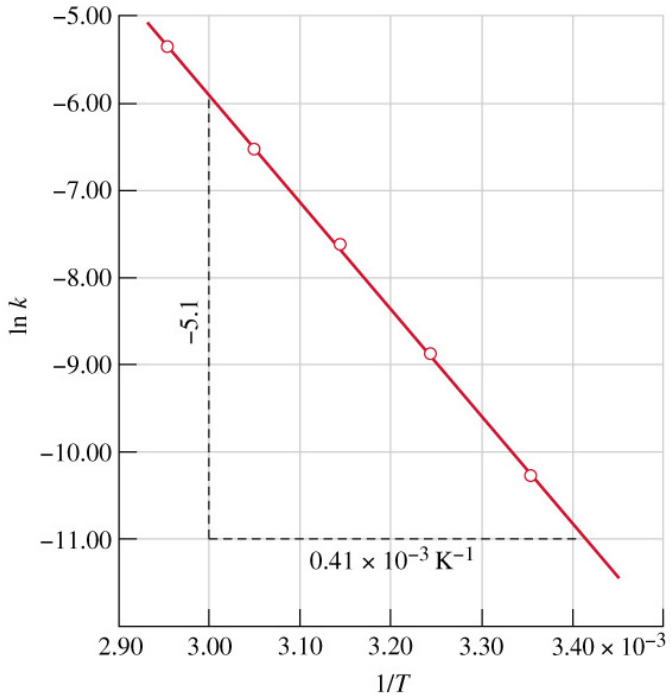
$T_2 = 700$ K; $k_2 = 1.3$

A better way to solve a problem with data that has uncertainties is to graph the results.

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

$$y = mx + b$$

Slope = $-\frac{E_a}{R}$ y intercept = $\ln A$



Sample Problem 16.4
Follow Up Problems 16.5
Problems 16.43, 45, 47, 49
Graphing Exercise.