

Kinetics

Introduction

Chemical Kinetics deals with rate (speed of chemical reactions – how fast?)

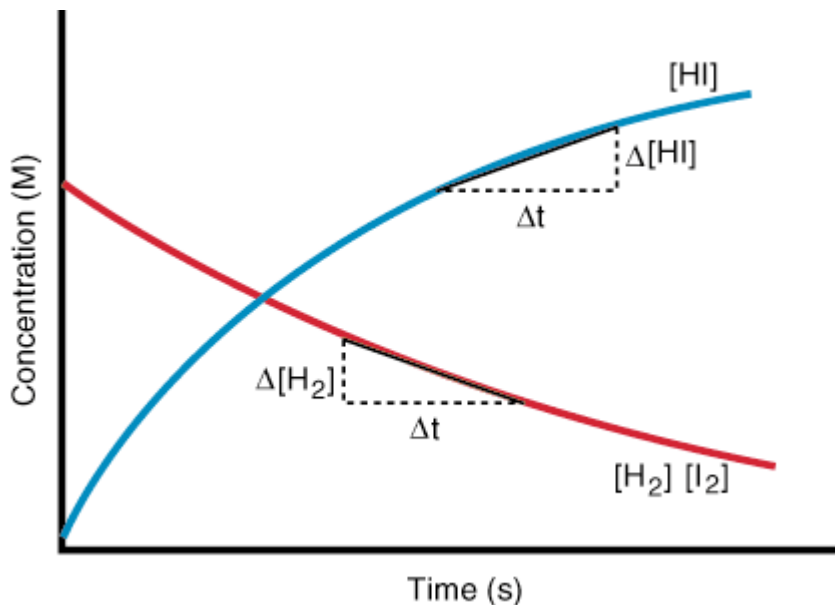
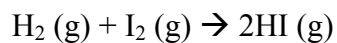
Rate equation represents rate, which depends on various reactants

Reaction mechanism is the details of how atoms are rearranged

Reaction Rate

Hypothetical reaction $A_2(g) + B_2(g) \rightarrow 2AB(g)$

Show change in concentration in graph below



(<http://www.sparknotes.com/chemistry/kinetics/ratelaws/section1.html>)

Slope of line tangent to curve is a measure of rate
steeper slope is greater rate
positive slope means forming product
negative slope means reactant being used up

Consider the reaction $A_2(g) + B_2(g) \rightarrow 2AB(g)$

Indicate change with symbols

$\Delta[AB]/\Delta t$ or $d[AB]/dt$ = rate of formation of AB
rate is change in concentration with time

Units for $d[AB]/dt$ are (mol/ L s)

$-\Delta[A_2]/\Delta t$ or $-d[A_2]/dt$ = rate of loss disappearance of A_2

These changes are opposite in sign but not the same in value

for example: 2AB formed for each A_2 so

$$(1/2) d[AB]/dt = -d[A_2]/dt$$

Rate of reaction may change with time so interested in slope and slope at any time

In experiments scientists follow change in concentration by measuring some property that depends on concentration. Such as: Pressure, acidity, volume, weight, color, etc...

Rate Law

Rate law or rate equation - mathematical expression relating concentration of reactants (or products) to reaction rate

Example- for balanced chemical equation



the rate law is

$$\text{rate} = -d[N_2O_5]/dt = k[N_2O_5] \quad 1^{\text{st}} \text{ order because } [N_2O_5]^1$$

where **k** is called the **rate constant** and k depends on temperature

The rate law cannot be determined from a balanced equation.

It must be determined from experiment.

To write rate law must express what is changing

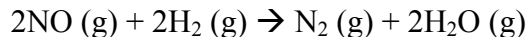
$$-d[N_2O_5]/dt \text{ or } d[O_2]/dt \text{ etc.}$$

For balanced chemical equation



Experiments show that $\text{Rate} = [NO_2][HCl]$ 2nd order overall

For



Experiments show that $\text{rate} = k[\text{NO}]^2[\text{H}_2]$ 3rd order overall

1st order in H_2 2nd order in NO and 3rd order overall

Order is the power that concentration is raised to
[] means concentration in mol/L

Rate laws can have fractional powers but usually will be integers

Experimental methods to determine rate law

- 1) Rate Law from Method of Initial Rates
- 2) Doubling reactant amounts
- 3) Integrated Rate Law
- 4) Isolation Method

1. Rate Law from Method of Initial Rates

How to determine rate law experimentally

For $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ do 5 experiments summarized below:

Experiment	Initial Concentration		Initial Rate
	NO (mol/L)	O ₂ (mol/L)	d[NO ₂]/dt (mmol/Ls) or Δ[NO ₂]/Δt
A	1	1	7
B	1	2	14
C	1	3	21
D	2	3	84
E	3	3	189

then assume rate of formation $d[\text{NO}_2]/dt = k[\text{NO}]^x[\text{O}_2]^y$
and then find x, y, and k

In general $(\text{rate 1} / \text{rate 2}) = (\text{conc 1} / \text{conc 2})^x$ where x is order of reaction with respect to concentration of one reactant. Must keep all other reactants at same amount to compare these two experiments.

Example from experiments in chart above

$$\begin{aligned} & \text{rateB/ rateA} \\ \text{becomes} & \quad 14/7 = k[1]^x [2]^y / k[1]^x [1]^y \\ \text{simplifies to} & \quad 2 = [2]^y/[1]^y \\ \text{or} & \quad 2 = [2/1]^y \\ \text{and solving gives} & \quad 2 = 2^y \quad \text{so } y \text{ must be } y=1 \text{ since } 2^1=2 \end{aligned}$$

$$\begin{aligned} & \text{rateE/rateC} \\ \text{becomes} & \quad 189/21 = k[3]^x [3]^y / k[1]^x [3]^y \\ \text{simplifies to} & \quad 9 = [3]^x/[1]^x \\ \text{or} & \quad 9 = [3/1]^x \\ \text{and solving gives} & \quad 9 = 3^x \quad \text{so } x \text{ must be } x=2 \text{ since } 3^2=9 \end{aligned}$$

And to find k can pick any reaction and sub in

$$\begin{aligned} \text{for example expt D gives} & \quad 84 = k[2]^2[3]^1 \\ & \quad 84 = k (4) (3) \\ & \quad 84 = 12 k \\ & \quad 7 = k \end{aligned}$$

And putting it all together the rate law is expressed as

$$\text{rate} = 7 [\text{NO}]^2 [\text{O}_2]^1 \quad \text{so } 2^{\text{nd}} \text{ order in NO } 1^{\text{st}} \text{ order in O}_2 \text{ and } 3^{\text{rd}} \text{ order overall}$$

Does rate law correctly predict rates? – try expt E put in initial concentrations

$$\text{rate} = 7[3]^2[3]^1 \quad \text{so predict initial rate is 189} \quad \text{see table – correct!}$$

Rate law can predict rate for any concentrations-tells you how fast reaction occurs

2. Doubling

Easy way to use is to look at effect of doubling initial concentration while keeping all other concentrations unchanged. If double concentration then rate will either be unchanged, or double, increase by factor of 4 or factor of 8 and order will be 0,1,2, or 3, respectively.

Order	If Concentration	then and	Rate Increase is
0	1 → 2	$2^0 = 1$	No change
1	1 → 2	$[A]^1 = 2^1$	2
2	1 → 2	$[A]^2 = 2^2$	4
3	1 → 2	$[A]^3 = 2^3$	8

Example if rate of reaction goes eight times faster when concentration of just one reactant doubled then $8 = 2^x$ and $x = 3$ and so this reactant is 3^{rd} order

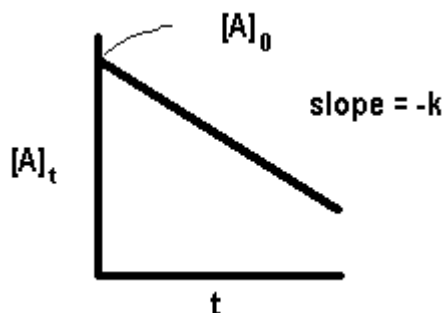
3. Integrated Rate Law

How fast does reactant [A] decrease for different order reactions?

Order: 0

Rate Law
Rate = $-d[A]/dt = k \rightarrow$

Integrated Rate Law
 $[A] = -kt + [A]_0$

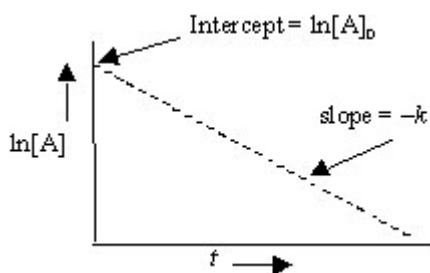


(<http://www.chem.queensu.ca/people/faculty/mombourquette/FirstYrChem/kinetics/>)

Order: 1st

Rate Law
 $-d[A]/dt = k[A] \rightarrow$

Integrated Rate Law
 $\ln[A] = -kt + \ln[A]_0$



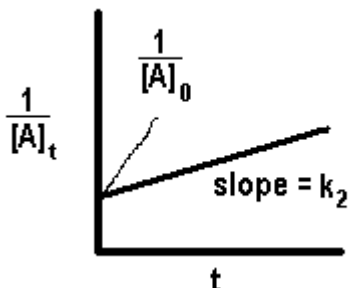
(<http://neon.otago.ac.nz/chemlect/chem201/kinetics/background/background.html>)

Order: 2nd

Rate Law

Integrated Rate Law

$$-d[A]/dt = k[A]^2 \quad \rightarrow \quad 1/[A] = kt + 1/[A]_0$$



(<http://www.chem.queensu.ca/people/faculty/mombourquette/FirstYrChem/kinetics/>)

So experiment collect data for the concentration of a reactant as time passes and try plots of $[A]$, $\ln[A]$ and $1/[A]$ and which ever fits straight line best is the order of reaction so

- if $[A]$ best plot then zero order
- if $\ln[A]$ best plot then first order
- if $1/[A]$ best plot then second order

Can compare visually or calculate r^2 value which is a measure of quality of fit to straight line where $r^2 = 1$ is a perfect straight line and as r^2 gets smaller then fit is worse so that $r^2 = 0$ is completely random scatter. Can use software such as EXCEL to plot data, do linear regression, and calculate r^2 values.

Example:

Plots were made for $[A]$ vs time $\ln[A]$ versus time and $1/[A]$ versus time and r^2 values were found to be 0.965 for $[A]$, 0.989 for $\ln[A]$, and 0.971 for $1/[A]$.

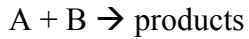
What is the order of the reaction?

Since the $\ln[A]$ versus time gave best fit to a straight line then it must be first order or rate = $k[A]^1$

4. Isolation Method (Integrated Rate Law with more than one reactant)

Make all reactants much larger concentration than just one of reactants

For example if the balanced equation and rate law are



$$\text{Rate} = k[A][B]$$

and you set the initial amounts at

$$[A]_0 = 0.010 \quad \rightarrow 0 \quad \text{decrease 100\%}$$

$$[B]_0 = 1.000 \quad \text{then } \rightarrow 0.990 \quad \text{decrease 1\%}$$

and all of A is used up

$$[A] \ 0.01 \rightarrow 0 \quad \text{decrease by 100\%}$$

then B will only change by small amount

$$[B] \ 1.000 \rightarrow 0.990 \quad \text{decrease by 1\%}$$

So [B] is essentially constant and the rate law can be written as

$$\text{Rate} = k'[A] \quad \text{where } k' \text{ is } k' = k[B]_0$$

and we call $\text{rate} = k'[A]$ Pseudo-first-order rate law

So if multiple reactants can focus on just one at a time by making initial amounts of others in much greater amounts

Example of simple experiment (method of initial rates)

Put one or two identical size pieces of Alka Seltzer tablet in water in plastic film holder and snap on top. Carbon dioxide gas is produced and when enough builds up then the top pops off. The shorter the time to pop the faster the rate of gas production.



(<http://sodiumsymposium.tripod.com/quizzes.html>)

Observe results below and then find ratio as shown

Experiment	Amount	Time to pop (s)	Rate (1/time) s ⁻¹
A	1 piece	20	0.050
B	2 pieces	11	0.091

Ratio of Rates

$$\text{Rate}_B / \text{Rate}_A = (2/1)^x$$

$$.091 / .050 =$$

$$1.82 = 2^x \text{ so } x = 1 \text{ note that there is experimental error so round off}$$

but note that of the choices below only one can fit

$$2^0 = 1$$

$$2^1 = 2 \text{ First Order Reaction}$$

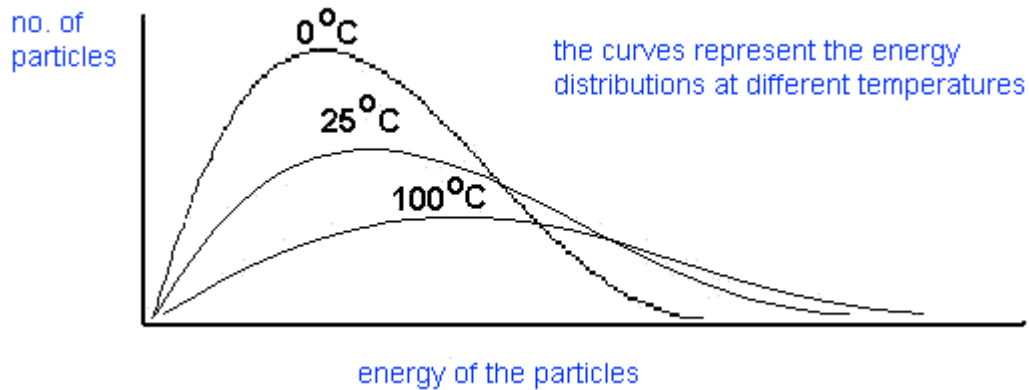
$$2^2 = 4$$

$$2^3 = 8$$

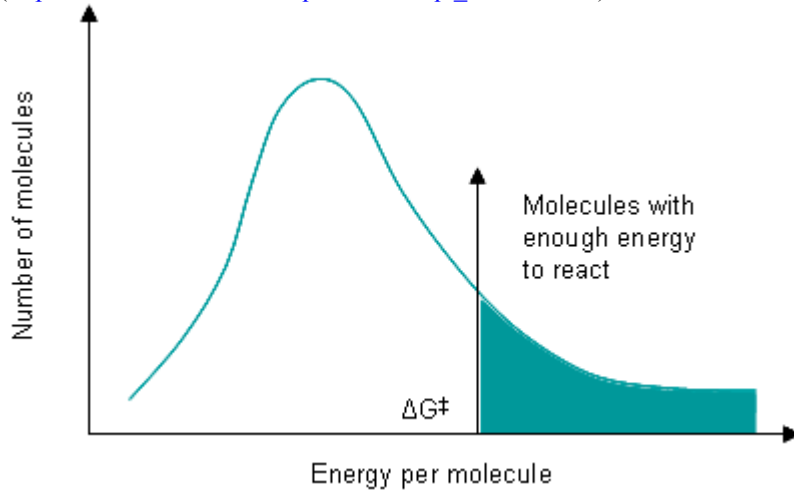
Temperature Effect on Rates

Increase temperature causes increase in rate for exothermic and endothermic reactions

Rough rule for some reactions is that increase 10°C roughly doubles rate



(http://ibchem.com/IB/ibc/equilibrium/equ_htm/8.1.htm)



(http://www.steve.gb.com/science/index.html#enzymes_thermodynamics)

Area under the curve is the minimum energy required for reaction (Activation energy)

There are more collisions but this is a minor factor (few percent)

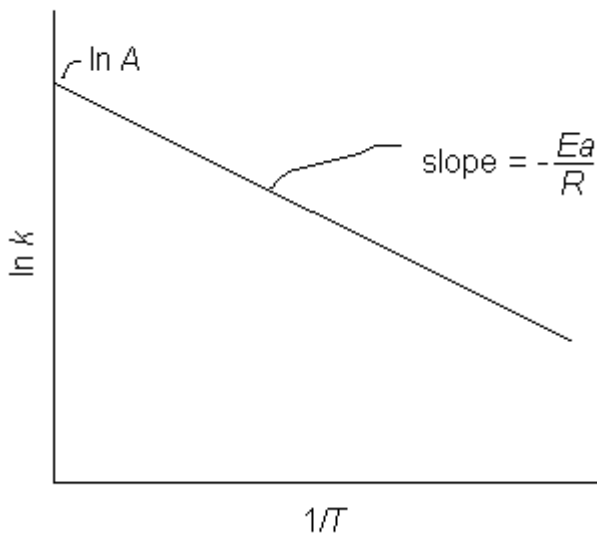
Rate and Temperature

Observe that increase the temperature you increase the rate

Qualitative: higher temperature the faster the reaction

Graphical Representation

Natural log of k versus Reciprocal Temperature



(<http://www.chem.queensu.ca/people/faculty/mombourquette/FirstYrChem/kinetics/>)

Quantitative Relationship

$$k = Ae^{-E_a/RT} \quad \text{Arrhenius Equation}$$

k = rate constant

T = Temperature

A = frequency factor (same units as first order (s^{-1}))

R = gas constant (8.31 J/molK)

E_a = energy of activation (J/mol)

e = 2.718281...

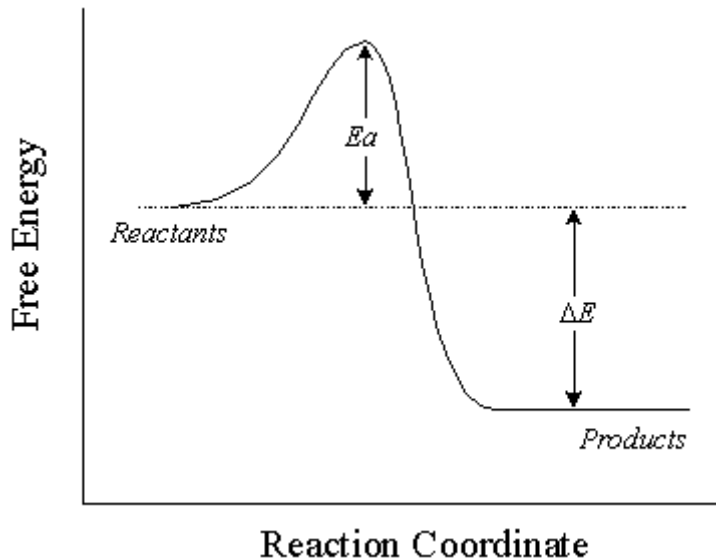
Meaning of equation

Contributions due to:

frequency of collisions and proper **orientation** in A

fraction of molecules with sufficient energy to react are $e^{-E_a/RT}$

Activation energy is a multistep process and is the highest barrier to be overcome



(http://www.ucalgary.ca/~kmuldrew/cryo_course/cryo_chap11_1.html)

Catalysts

Catalyst = substance that increase rate of reaction without being used up

Catalyst change the mechanism of the reaction and lower energy of activation.
This speeds up the reaction

Example:

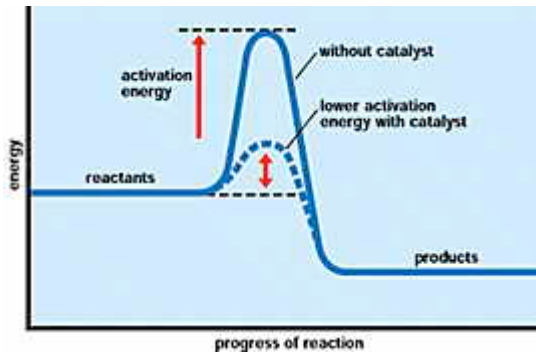
Ea	100kJ/mol	→	50 kJ/mol at T= 400K
	k (without catalyst)		(k with catalyst)
	$e^{-100000/(8.31)(400)} \sim e^{-30}$		$e^{-50000/(8.31)(400)} \sim e^{-15}$

Use $k = Ae^{-Ea/RT}$ and find

$$k(50\text{kJ})/k(100\text{kJ}) = (Ae^{-15}) / (Ae^{-30})$$

$$\begin{aligned} e^{-15}/e^{-30} &= 2.88 \times 10^{-7}/9.36 \times 10^{-14} \\ &= 10^{-6.5}/10^{-13} \\ &= 10^{6.5} \\ &= 3.16 \times 10^6 \sim 3 \times 10^6 = 3 \text{ million} \end{aligned}$$

In this example adding catalyst to lower Energy of Activation from 100 to 50kJ/mol increases rate by factor of 3 million!



(<http://www.tiscali.co.uk/reference/encyclopaedia/hutchinson/m0009937.html>)

A catalyst lowers activation energy but the ΔH remains unchanged.
 ΔH is the difference $E(\text{products}) - E(\text{reactants})$

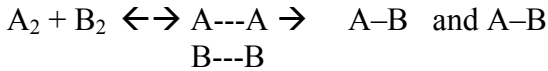
Two types of Catalysis:

Homogenous in phase with reactants

Heterogeneous in different phase than reactants

Energy of Activation (E_a)

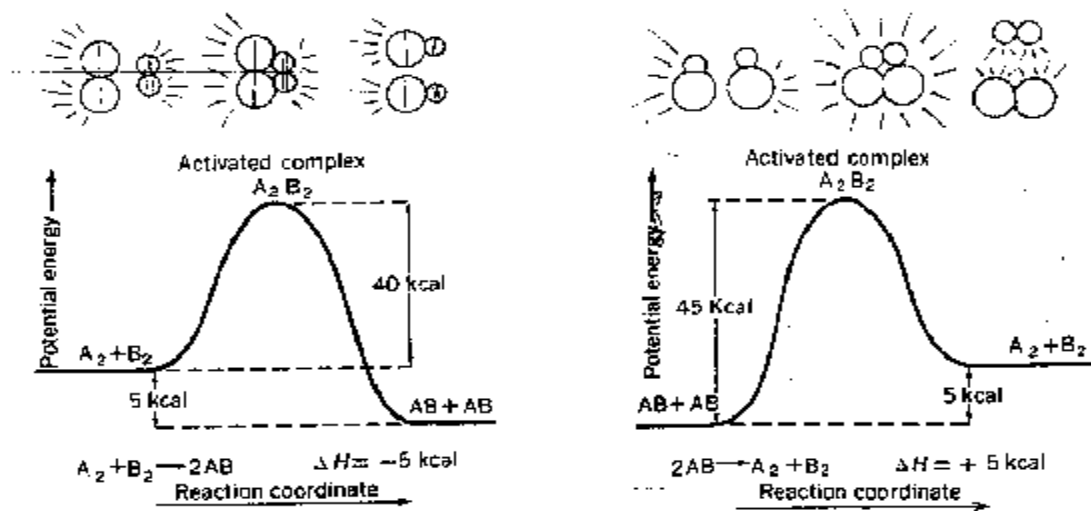
Energy changes associated with reaction described in transition state theory



Activated Complex: Unstable arrangement that exists only for a moment

Also called Transition State

Can either go back to reactants or go on to the products



On the left is a potential energy diagram for the changes occurring in a chemical system during an exothermic reaction. On the right is the same type of diagram for a system undergoing an endothermic reaction.

<http://www.ucdsb.on.ca/tiss/stretton/chem2/rate03.htm>

Energy of Activation (E_a) is the potential energy barrier

The lower the E_a the faster the reaction

The higher the temperature (T) the faster the reaction

so to make reaction go faster can add catalyst or raise temperature

Rate Equations of Single Step Reactions

Molecularity → number of molecules that participate in individual reactions

Unimolecular Step If only one step in reaction
 $A \rightarrow \text{products}$ Rate = $k[A]$

Bimolecular Step
 $A + A \rightarrow \text{products}$ Rate = $k[A]^2$
 $A + B \rightarrow \text{products}$ Rate = $k[A][B]$

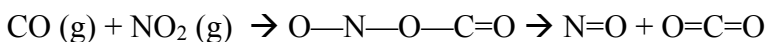
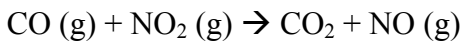
Termolecular Step (unusual for 3 body collisions to occur)
 $A + A + A \rightarrow \text{products}$ Rate = $k[A]^3$
 $A + A + B \rightarrow \text{products}$ Rate = $k[A]^2[B]$
 $A + B + C \rightarrow \text{products}$ Rate = $k[A][B][C]$

In multistep reaction must combine various individual steps

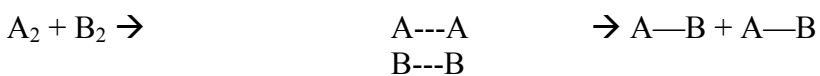
Such a combination of steps is called the mechanism of a reaction

Single Step Reactions

Some reactions occur in single step



Understand single step reaction



Bonds break and form simultaneously

But not all collisions are effective

Factors that affect collision effectiveness

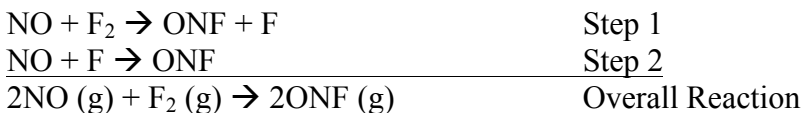
Orientation: Proper position (steric hindrance and factors)

Frequency: Number of collisions

Energy: Minimum energy

Reaction Mechanism

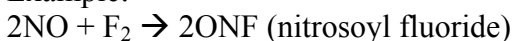
Mechanism is the detailed steps involved in reaction



F is the reaction intermediate which is a substance produced and used up in reaction but not a reactant or product

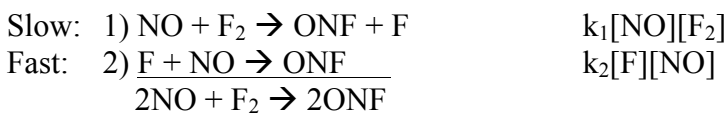
Detailed molecular steps that carry a reaction from reactants to products

Example:



observed experimental rate = $k[\text{NO}][\text{F}_2]$

Mechanism to explain Rate



Note:

Can write rate law if given a step of mechanism

Cannot write rate law for balanced chemical equation

Two bimolecular steps but F reaction intermediate and is used up rapidly so

Step 1 is the slow step

Step 2 is the fast step

Rate = rate 1 + rate 2 and if rate = slow + fast then rate = slow step

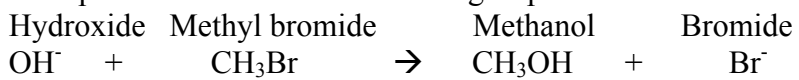
Rate Determining Step



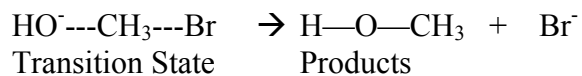
<http://moonie.fccj.org/~ethall/2046/ch12/rdetstep.htm>

Example:

If Step below is the rate determining step of mechanism



then $\text{Rate} = k[\text{OH}^-][\text{CH}_3\text{Br}]$



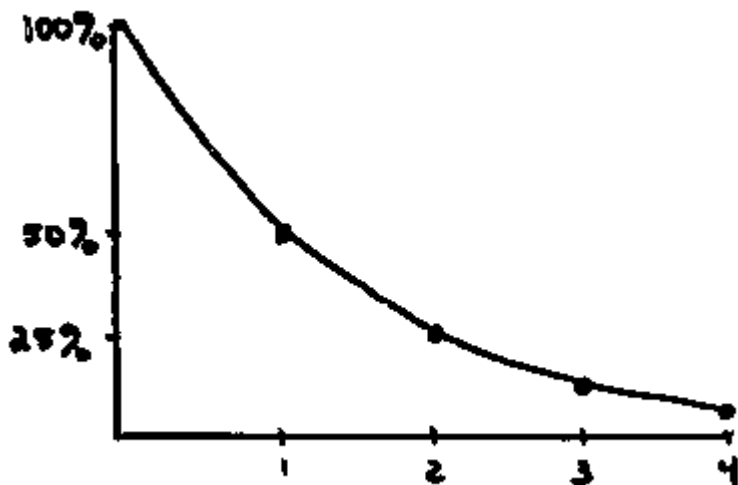
If given balanced chemical equation then **cannot** tell what the mechanism is.

If given mechanism **can** add steps to get balanced chemical equation.

Can guess at mechanism or do more experiments to determine

First Order and Half-life

Half-life normally used for first order - all radioactive decay is first order



(<http://www.osha.gov/SLTC/radiationionizing/introtoionizing/slidepresentation/slide16.html>)

For every half life ($t_{1/2}$) of time that passes, half of concentration disappears

$k t_{1/2} = \ln(2)$ or rearranged to $t_{1/2} = .693/k$

$t_{1/2}$ = half life

k = rate constant

Note - Can derive equation from first order kinetics

$$\ln[A] = -k t + \ln[A_0]$$

$$\ln[A] = -k t_{1/2} + \ln[A_0]$$

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

$$k t_{1/2} = \ln \left(\frac{[A_0]}{[A]} \right) \quad \text{and if } \left(\frac{[A_0]}{[A]} \right) = 2 \text{ then}$$

$$k t_{1/2} = \ln(2)$$

Example:

If half life is 20 seconds then what is rate constant?

$$k t_{1/2} = \ln(2)$$

$$(k) (20 \text{ sec}) = \ln(2)$$

$$k = 0.0347 \text{ s}^{-1}$$

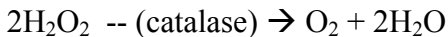
and note that units work out

$$-d[n]/dt = k[A]$$

$$(\text{mol/L s}) = (1/\text{s}) (\text{mol/L}) \text{ units}$$

More in notes on radioactivity but if know $[A]$, k , and $[A_0]$ then use $\ln[A] = -k t + \ln[A_0]$ to find time t that has passed

Example of Enzyme Kinetics



1 molecule of the enzyme catalase (also called peroxidase) can cause 5 million H_2O_2 molecules to break apart every second!

H_2O_2 is formed as a byproduct in cells but is a poison and must be removed or it would oxidize and break apart other molecules in cell.

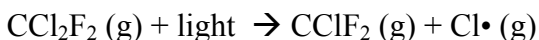
Enzyme = catalyst in living systems made of amino acids that form proteins

Thousands of enzymes in cells enable specific reactions to be carried out millions of times faster than they would without enzyme (biological catalyst)

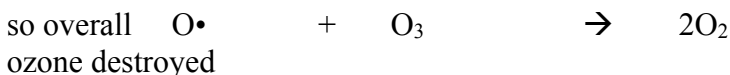
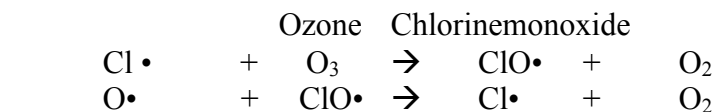
Example Kinetics in the Environment (a chain mechanism)

Ozone (O_3) Layer in upper atmosphere protects us from too much ultraviolet light

Freon-12 and other molecules if released into atmosphere eventually break apart due to exposure to UV light high in atmosphere

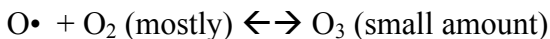


$\text{Cl}\cdot (\text{g})$ is a free radical unpaired electron and very reactive



One $\text{Cl}\cdot$ repeats cycle above over and over and destroys thousands of ozone molecules!

So the Equilibrium in upper atmosphere is shifted and O_3 destroyed



Excess ultraviolet light can cause:

- Skin cancer
- Crop damage
- Cataract (clouding of lens of eye)

Further Information - From Introduction to Ozone website

“Ozone in the Stratosphere

Ozone and oxygen molecules in the stratosphere absorb ultraviolet light from the sun, providing a shield that prevents this radiation from passing to the earth's surface. While both oxygen and ozone together absorb 95 to 99.9% of the sun's ultraviolet radiation, only ozone effectively absorbs the most energetic ultraviolet light, known as UV-C and UV-B, which causes biological damage. The protective role of the ozone layer in the upper atmosphere is so vital that scientists believe life on land probably would not have evolved - and could not exist today - without it.

The term "shield" as a description of ozone in the stratosphere is a bit misleading because the molecules do not form an impermeable sphere around the earth. Ozone continuously breaks apart into its oxygen atoms and reforms as ozone molecules, so a particular ozone molecule doesn't last very long. The "shield" changes constantly, but the atmospheric chemical processes maintain a dynamic equilibrium that keeps the overall amount of ozone constant - that is, it would if humans did not contribute to the chemical processes.

About 90% of the ozone in the earth's atmosphere lies in the region called the stratosphere between 16 and 48 kilometers (10 and 30 miles) above the earth's surface. Ozone forms a kind of layer in the stratosphere, where it is more concentrated than anywhere else, but even there it is relatively scarce. Its concentrations in the ozone layer are typically only 1 to 10 parts of ozone per 1 million parts of air, compared with about 210,000 parts of oxygen per 1 million parts of air.”

http://www.ucar.edu/learn/1_5_1.htm