Chemical Kinetics

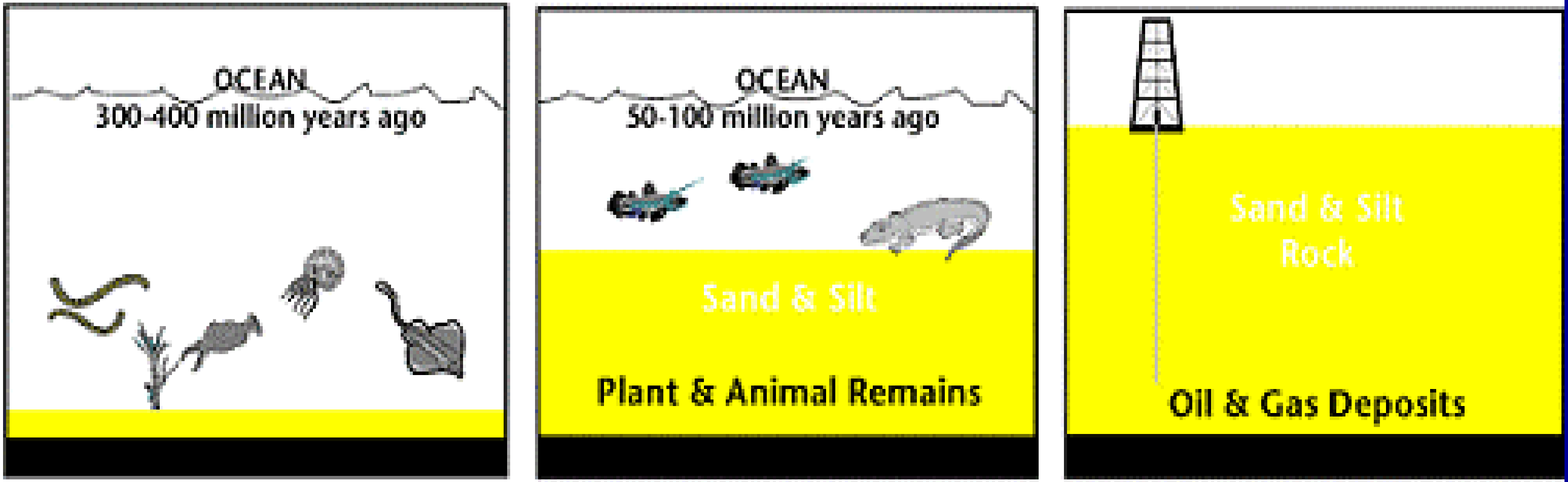
Study of how rapidly reactions proceed - **rate of reaction**

Details of process from reactants to products - **mechanism**

Thermodynamics determines the direction in which reactions proceed spontaneously and equilibrium conditions, but not the rate at which equilibrium is reached.

For a complete picture of a chemical reaction need information on both the thermodynamics and kinetics of a reaction.

PETROLEUM & NATURAL GAS FORMATION



Tiny sea plants and animals died and were buried on the ocean floor. Over time, they were covered by layers of sand and silt.

Over millions of years, the remains were buried deeper and deeper. The enormous heat and pressure turned them into oil and gas.

Today, we drill down through layers of sand, silt, and rock to reach the rock formations that contain oil and gas deposits.

$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ $\Delta G^o = -33.0$ kJ

$K_{298} = 6.0 \times 10^5$

Thermodynamically favored at 298 K

However, rate is slow at 298K

Commercial production of NH_3 is carried out at temperatures of 800 to 900 K, because the rate is faster even though K is smaller.

Thermodynamical functions are state functions (ΔG, ΔH, ΔE)

Thermodynamics does not depend on the mechanism of the reaction.

The rate of the reaction is very dependent on the path of the process or path between reactants and products.

Kinetics reveals information on the mechanism of the reaction.

Thermodynamics vs Kinetics

$A + B \dashrightarrow C + D$ K_1

$A + B \dashrightarrow E + F$ K_2

If $K_1 > K_2$ =>products C & D are thermodynamically favored over E & F.

What about the rates of the two reactions?

If products observed are C & D => reaction is thermodynamically controlled

If products observed are E & F => reaction is kinetically controlled

(1) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

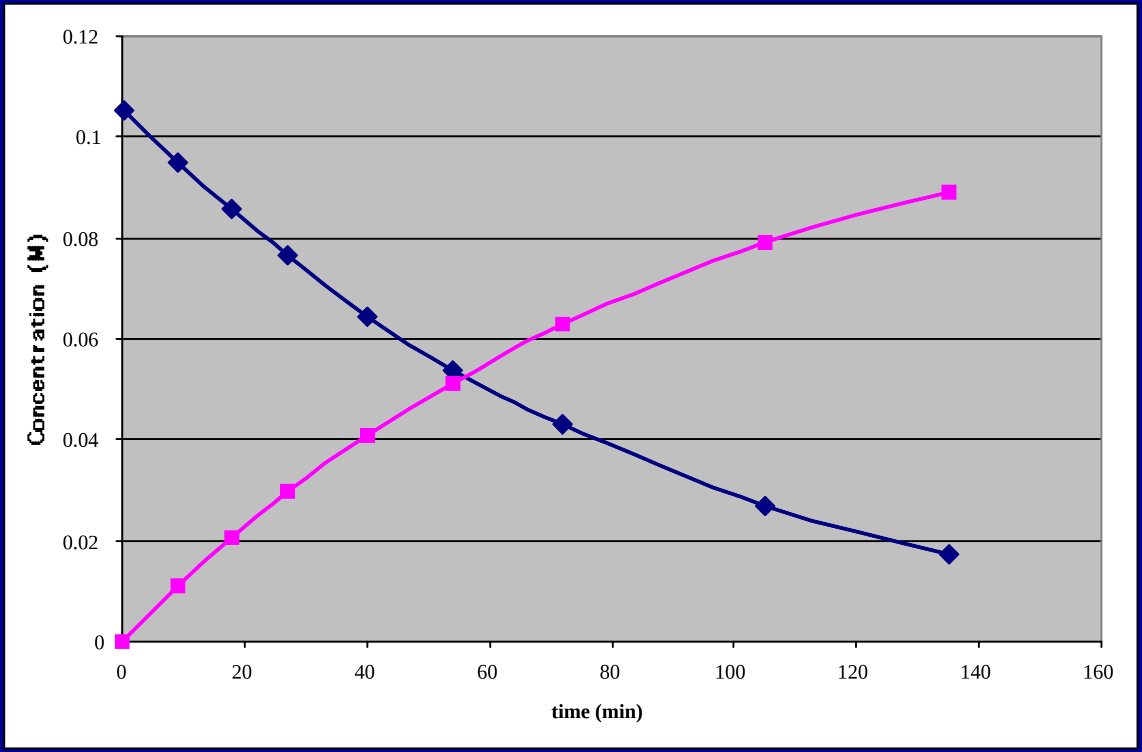
(2) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

Both have large values of K

Reaction (1) is fast; reaction (2) slow

Reactions are kinetically controlled

Rates of Reactions



A -> P

Rate of a reaction: change in concentration per unit time

$$\text{average reaction rate} = \frac{\text{change in concentration}}{\text{change in time}}$$

If concentration is in mol L^{-1}, and time in seconds, the rate has units of mol L^{-1} s^{-1}.

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2\ (g)$

$$\text{average reaction rate} = \frac{[NO]_{final} - [NO]_{initial}}{t_{final} - t_{initial}}$$

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2\ (g)$

Time (s)	[NO] mol L^{-1}
0	0
50	0.0160
100	0.0240
150	0.0288
200	0.0320

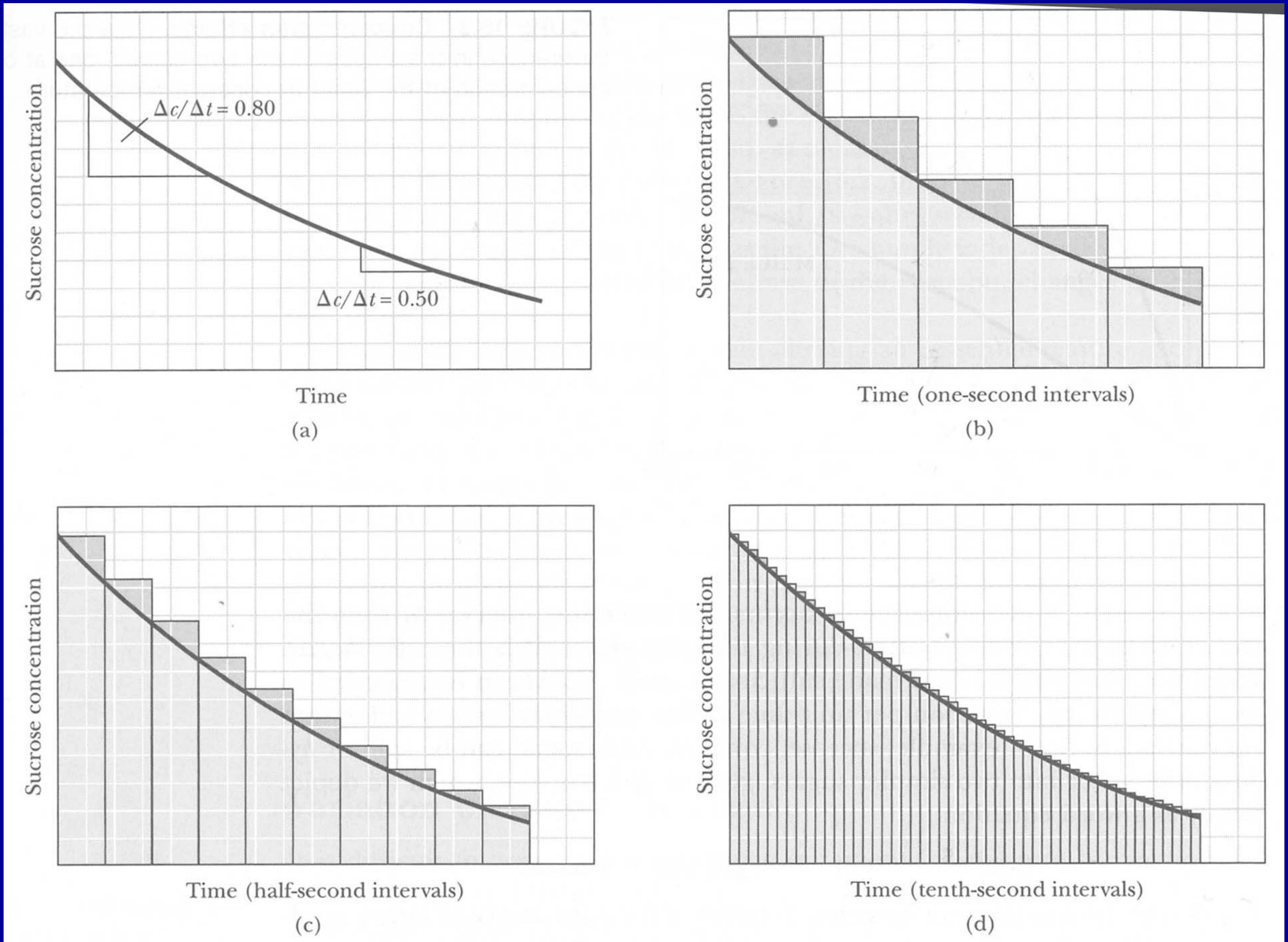
Average rate 1st 50 seconds = 3.2×10^{-4} mol L^{-1}

Average rate 2nd 50 seconds = 1.6×10^{-4} mol L^{-1}

Average rate 3rd 50 seconds = 9.6×10^{-5} mol L^{-1}

Instantaneous Rate - rate at a particular moment in time

Kinetics deals with instantaneous rates, or simply rates



$$NO_2(g) + CO(g) \dashrightarrow NO(g) + CO_2(g)$$

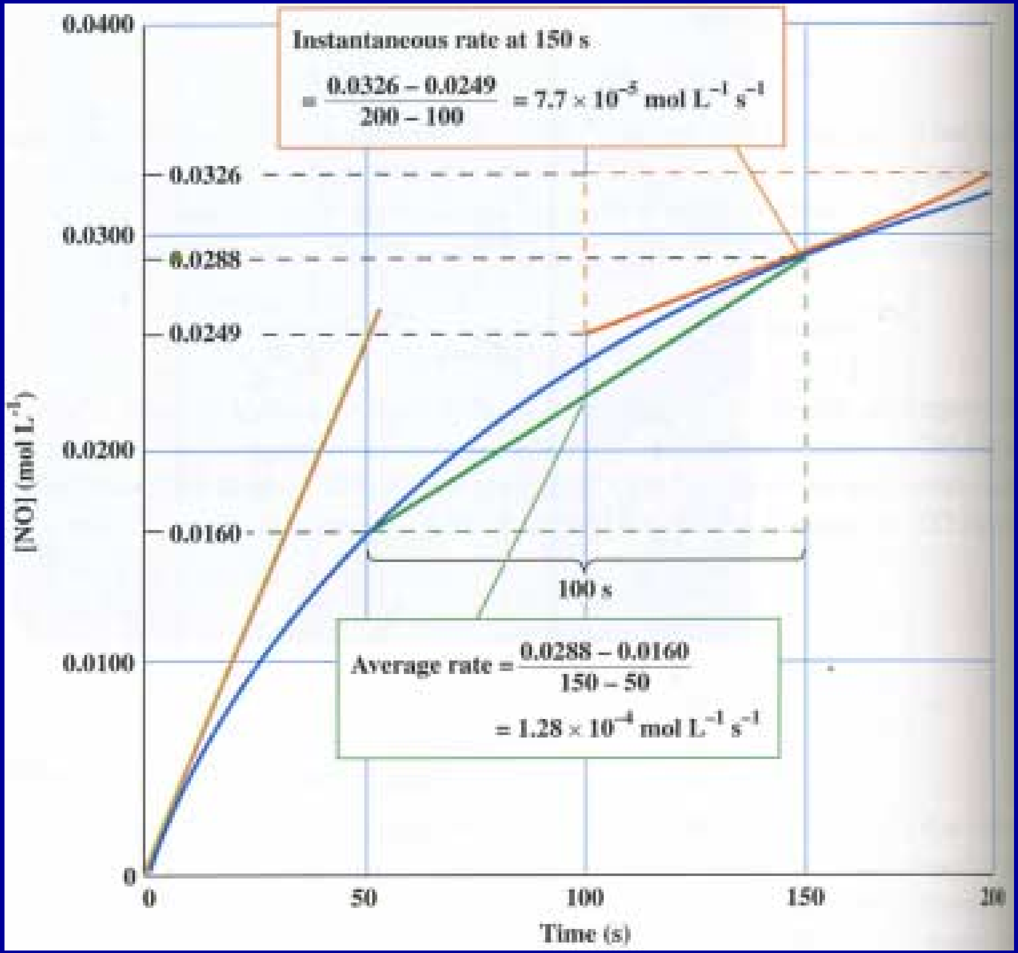
$$\text{rate} = \frac{\Delta[NO]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t} = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[CO]}{\Delta t}$$

which, for infinitesimally small changes, $\frac{d[CO]}{dt}$

For a general reaction:

$$aA + bB \dashrightarrow xC + yD$$

$$\text{rate} = \frac{1}{x}\frac{d[C]}{d\,t} = \frac{1}{y}\frac{d[D]}{d\,t} = -\frac{1}{a}\frac{d[A]}{d\,t} = -\frac{1}{b}\frac{d[B]}{d\,t}$$



Instantaneous rate at 150 s

$$= \frac{0.0326 - 0.0249}{200 - 100} = 7.7 \times 10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$\text{Average rate} = \frac{0.0288 - 0.0160}{150 - 50}$$

$$= 1.28 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Factors affecting rates of reactions

a) Nature of reactants

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ fast

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ slow

b) Concentration of reactants: reactions proceed by collisions between reactants

c) Temperature: In general, as T increases, rate increases

d) Catalyst: increases rate of reaction

e) Surface

f) Nature of solvent

Rate Laws and Rate Constant

$NO_2(g) + CO(g) \dashrightarrow NO(g) + CO_2\,(g)$

$$\text{rate} = \frac{d[NO]}{d\,t} = \frac{d[CO_2]}{dt} = -\frac{d[NO_2]}{dt} = -\frac{d[CO]}{dt}$$

$\text{rate} = k\,[NO_2]\,[CO]$ k is the specific rate constant

For a general reaction:

$$aA + bB \dashrightarrow cC + dD$$

$$\text{rate} = \frac{1}{c}\,\frac{d[C]}{dt} = \frac{1}{d}\,\frac{d[D]}{dt} = -\frac{1}{a}\,\frac{d[A]}{dt} = -\frac{1}{b}\,\frac{d[B]}{dt}$$

$\text{rate} = k\,[A]^m\,[B]^n$ **Rate Law**

For a reaction k has a specific value; k for the reaction changes with temperature

Note: m need not equal a; n need not equal b

Order of a Reaction

rate = k $[A]^m [B]^n$

Order of the reaction = m + n

The reaction order is determined by the experimentally determined rate law

$N_2O_5(g) \rightarrow N_2O_4(g) + 1/2\ O_2(g)$

Rate = k $[N_2O_5]$ reaction is a first order reaction

For a 1st order reaction, units of k: time^{-1}

$C_2H_6(g) \text{-->} 2\ CH_3(g)$

$\text{rate} = k\,[C_2H_6]^2$ second order reaction

$2NO_2(g) \text{-->} 2NO(g) + O_2\ (g)$

$\text{Rate} = k\,[NO_2]^2$ second order reaction

For 2nd order reactions, units of k: $\text{concentration}^{-1}\ \text{time}^{-1}$

Determination of order of a reaction

$2HI(g) \rightarrow H_2(g) + I_2(g)$

At 443°C the rate of the reaction increases with HI concentration as follows:

Data point	1	2	3
[HI] mol L^{-1}	0.0050	0.010	0.020
Rate mol L^{-1} s^{-1}	7.5×10^{-4}	3.0×10^{-3}	1.2×10^{-2}

Determine the order of the reaction and write the rate expression

Calculate the rate constant, and determine its units

Calculate the reaction rate for a concentration of HI = 0.0020M rate = k $[HI]^n$

a) $rate_1 = k ([HI]_1)^n$ $rate_2 = k ([HI]_2)^n$

$rate_2 / rate_1 = ([HI]_2)^n / ([HI]_1)^n$

$3.0 \times 10^{-3} / 7.5 \times 10^{-4} = (0.010/0.0050)^n$

$4 = 2^n$

$n = 2$

rate = k $[HI]^2$

b) 7.5×10^{-4} mol L^{-1} s^{-1} = k (0.0050 mol $L^{-1})^2$

k = 30 L mol^{-1} s^{-1}

c) rate = k $[HI]^2$ = 1.2×10^{-4} mol L^{-1} s^{-1}

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

Determine the rate expression and the value of the rate constant from the data below.

[NO] (mol L^{-1})	[O_2](mol L^{-1})	initial rate (mol L^{-1} s^{-1})
1.0×10^{-4}	1.0×10^{-4}	2.8×10^{-6}
1.0×10^{-4}	3.0×10^{-4}	8.4×10^{-6}
2.0×10^{-4}	3.0×10^{-4}	3.4×10^{-5}

$\text{Rate} = k\,[O_2]^m\,[NO]^n$

To determine the rate law from the data, first determine the dependence of the rate on each reactant separately.

$$\text{rate}_2/\text{rate}_1 = k\,[O_2]_2^m\,[NO]_2^n\ /\ k\,[O_2]_1^m\,[NO]_1^n$$

$$8.4 \times 10^{-6} / 2.8 \times 10^{-6} = (3.0 \times 10^{-4})^m / (1.0 \times 10^{-4})^m$$

$$3 = 3^m \Rightarrow m = 1;\ \text{1st order in } O_2$$

$\text{rate}_3/\text{rate}_2 = k\,[O_2]_3^m\,[NO]_3^n \,/\, k\,[O_2]_2^m\,[NO]_2^n$

$3.4 \times 10^{-5} / 8.4 \times 10^{-6} = (2.0 \times 10^{-4})^n / (1.0 \times 10^{-4})^n$

$4 = 2^n \Rightarrow n = 2$; 2nd order in NO

$\text{Rate} = k\,[O_2][NO]^2$

Order of reaction = 3

$2.8 \times 10^{-6}\ \text{mol L}^{-1}\text{s}^{-1} = k\,[1.0 \times 10^{-4}\ \text{mol L}^{-1}]\,[1.0 \times 10^{-4}\ \text{mol L}^{-1}]^2$

$k = 2.8 \times 10^{6}\ \text{L}^2\ \text{mol}^{-2}\text{s}^{-1}$

First Order Reactions

For the general reaction:

A --> Products

if the experimental rate law is:

Rate = - d[A]/ dt = k [A]   first order reaction

Units of k for a 1st order reaction is time^{-1}

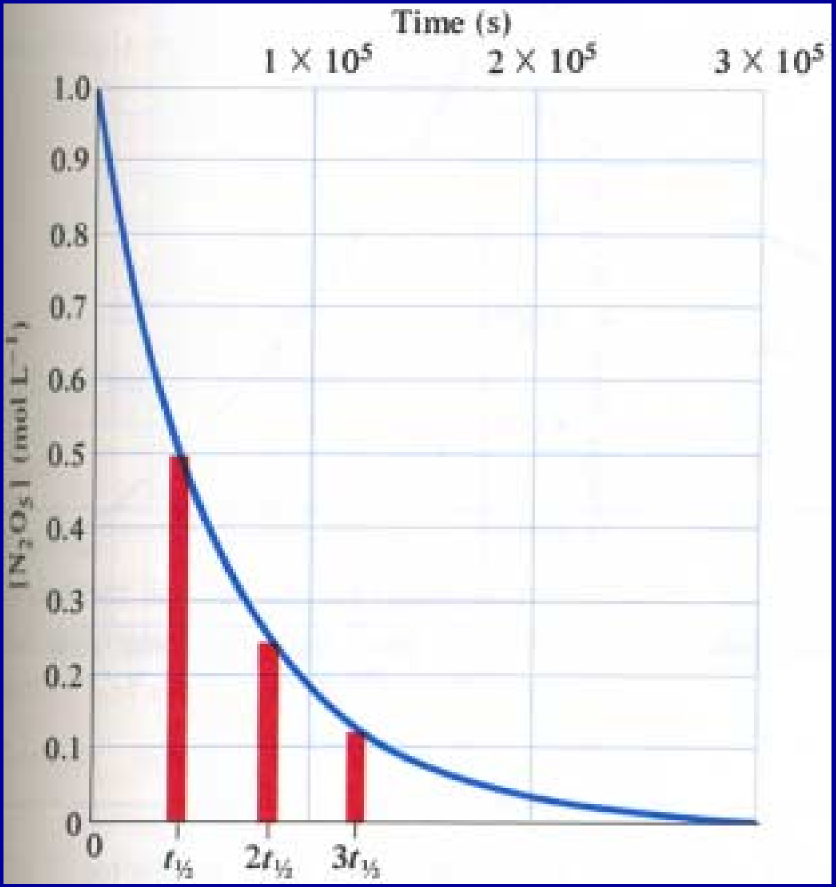
$$d[A]/dt = -k[A]$$

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

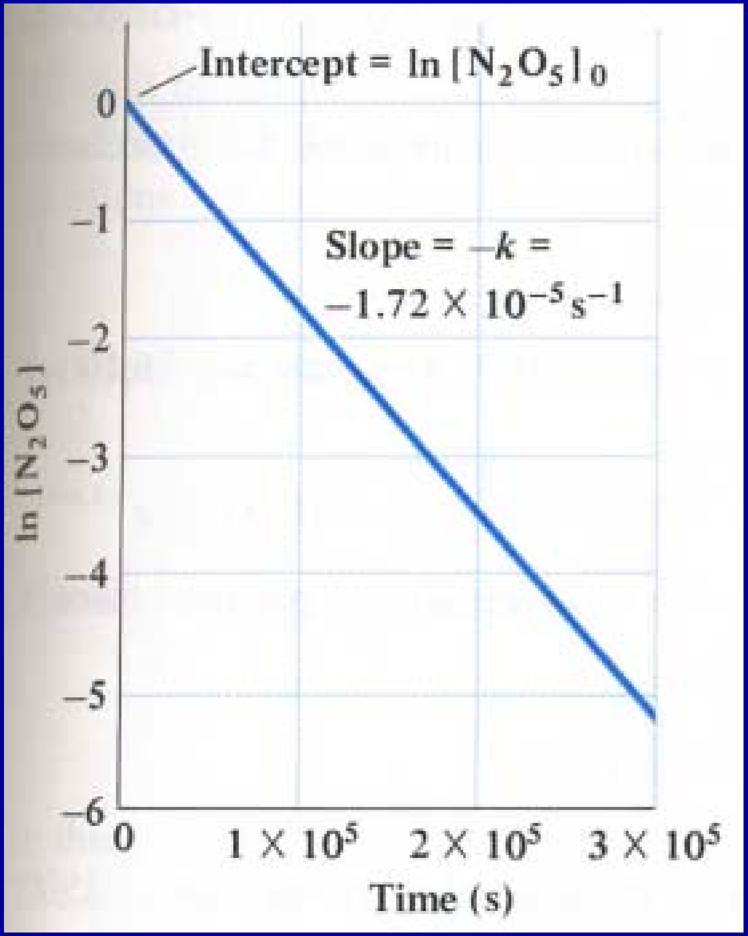
$[A]_o$ where is the initial concentration of A at time t = 0

$N_2O_5(g) \rightarrow N_2O_4(g) + 1/2\ O_2(g)$

$[A] = [A]_o e^{-kt}$



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



rate = $k [N_2O_5]$

Radioactive decay is a first order process

$$N = N_o\, e^{-\lambda t}$$

where N is the number of radioactive nuclei at time t

N_o is the initial number of radioactive nuclei

λ is the decay constant

Half life of a 1st order reaction

Half life : time it takes for the concentration of the reactant A to fall to half its initial value

$t_{1/2}$ when $[A] = [A]_o/2$

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

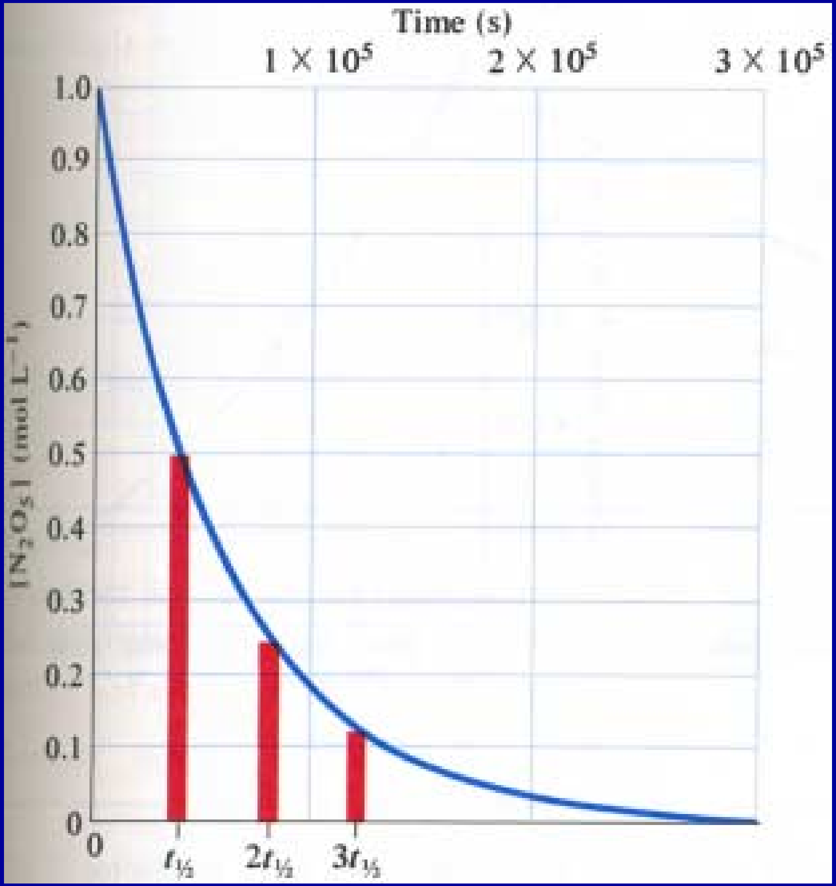
$\ln [A]_o/2 = \ln [A]_o - k\, t_{1/2}$

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

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

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

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



What is the rate constant k for the first order decomposition of $N_2O_5(g)$ at 25°C if the half life at this temperature is 4.03×10^4 s? Under these conditions, what percent of the N_2O_5 molecules have not reacted after one day?

a) $t_{1/2} = 0.6931 / k$

$k = 1.72 \times 10^{-5}\ s^{-1}$

b) $[N_2O_5] = [N_2O_5]_o\ e^{-kt}$

$[N_2O_5]/[N_2O_5]_o = e^{-kt}$

$[N_2O_5]/[N_2O_5]_o = 0.226$

22.6% N_2O_5 molecules have not reacted after one day

Second order reactions

rate = k [A] [B] or rate = k $[A]^2$

Rate = k$[A]^2$

2nd order reaction for which the rate depends on one reactant

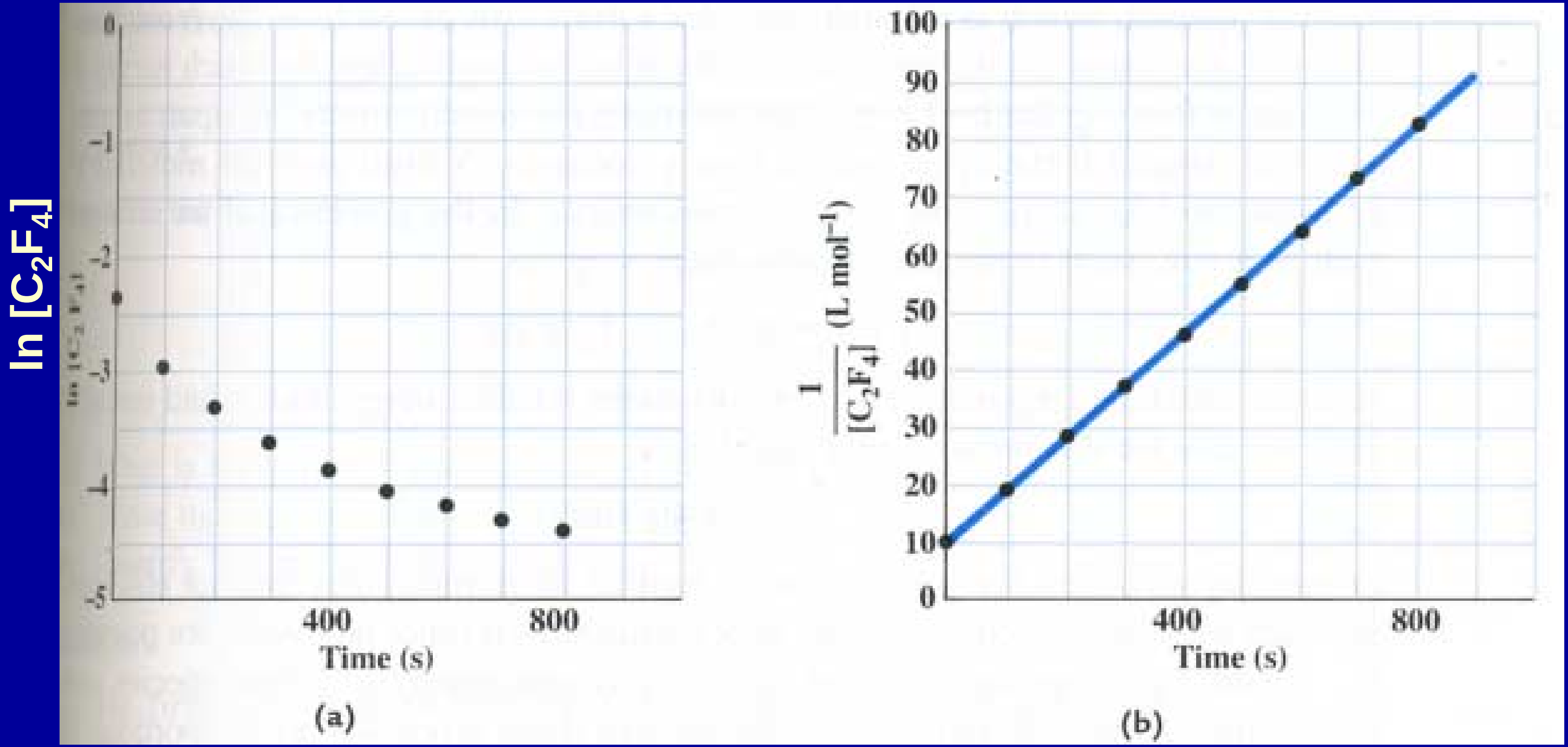
- d[A]/ dt = k $[A]^2$

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

$$t_{1/2} = \frac{1}{k[A]_o}$$

The half-life of a 2nd order reaction can be determined by setting [A] = $[A]_o/2$ at t = $t_{1/2}$

$2C_2F_4$ -> C_4F_8



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

$\ln[C_2F_4]$ vs time is not linear

rate = k $[C_2F_4]^2$

slope = k

Zero order reactions

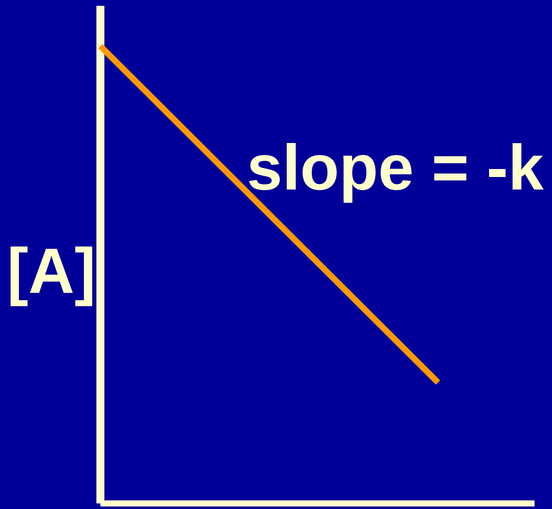
$A \dashrightarrow P$

If the rate law is

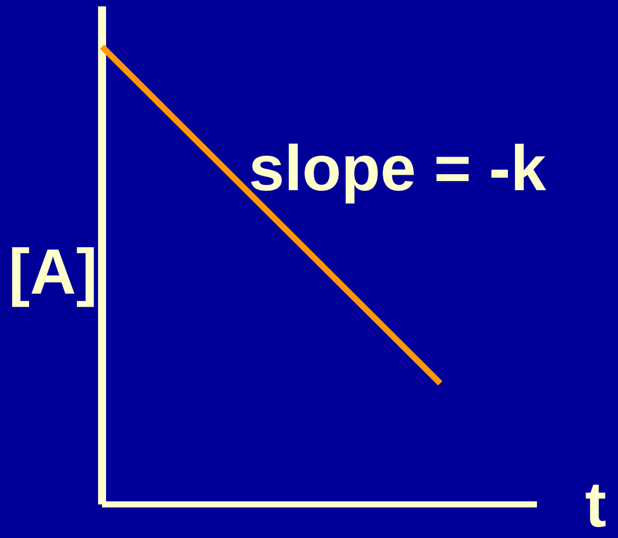
$-d[A]/dt = k$ zero order reaction

For a 0th order reaction: rate is independent of concentration

$[A] = [A]_o - kt$



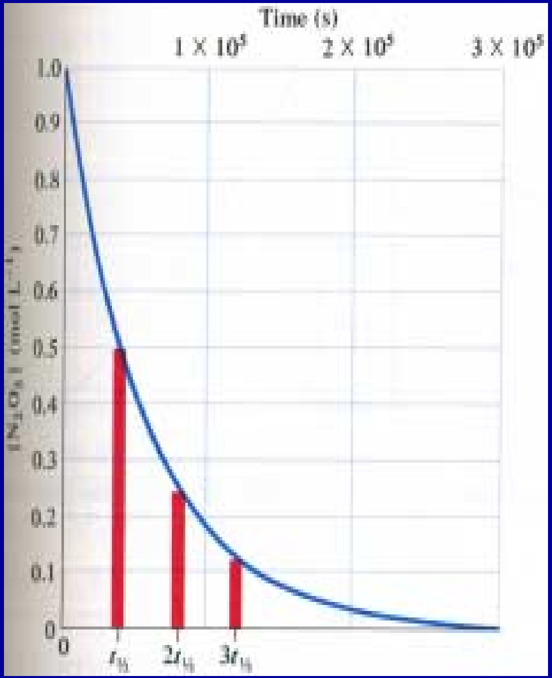
Zero order reaction: $[A] = [A]_o - kt$

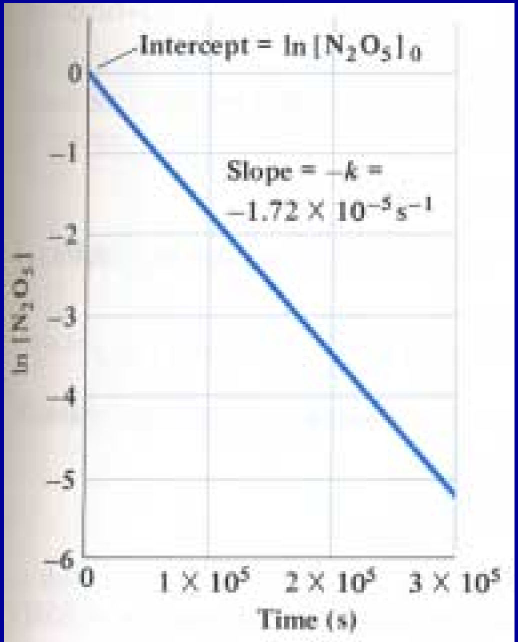


1st order

$[A] = [A]_o e^{-kt}$

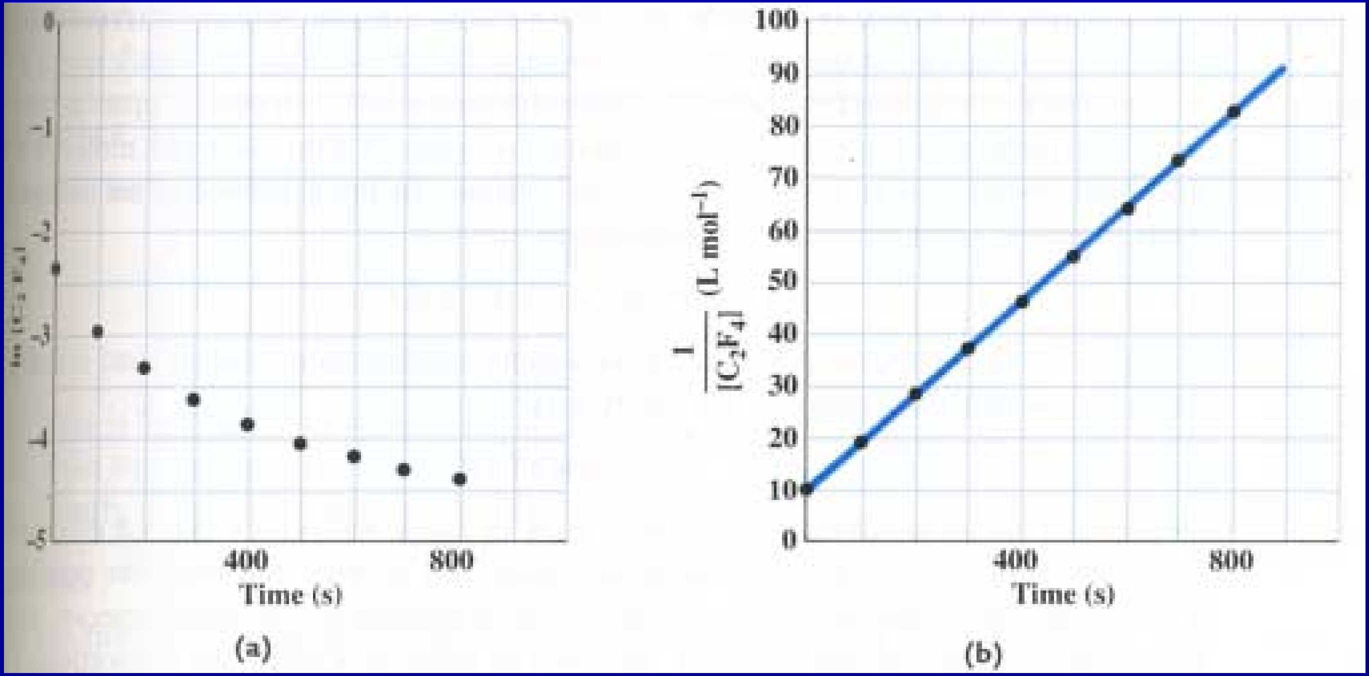
$\ln[A] = \ln [A]_o - kt$





Second order

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



Reaction Mechanisms

Reactions often proceed in a series of steps

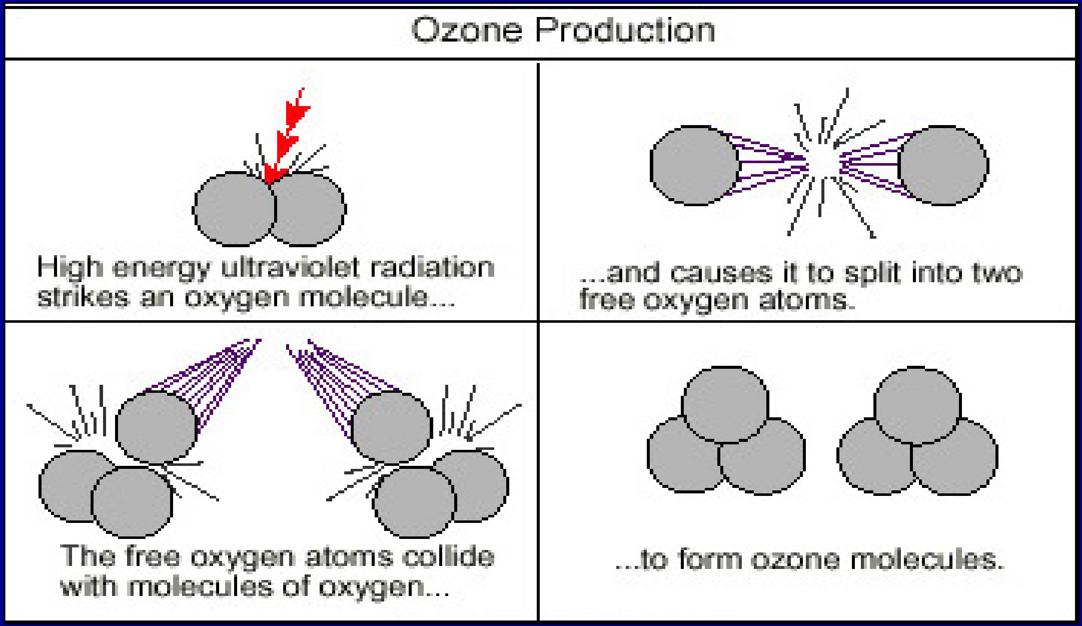
For example:

$O_2 + h\nu \rightarrow O_2^*$

$O_2^* \rightarrow O^{\cdot} + O^{\cdot}$

$2O^{\cdot} + 2O_2 + M \rightarrow 2O_3 + M$

Net: $3O_2 + h\nu \rightarrow 2O_3$



$O^{\cdot}$ is an intermediate species; involved in a step in the mechanism, but does not appear in the overall reaction

Each step is called an elementary reaction

The rate expression for the overall reaction must be determined experimentally

The rate of an elementary reaction is directly proportional to the product of the concentrations of the reactants, each raised to a power equal to its coefficient in the balanced equation for that step

A reaction is not an elementary process if

(i) exponents in the rate law are not the same as the coefficients in a balanced equation

(ii) chemical species in the rate law is not a reactant

Types of elementary reactions

Unimolecular reaction:

$O_2^* \rightarrow O + O$

Rate = $k[O_2^*]$

Bimolecular reaction

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

Rate = $k\,[NO]\,[O_3]$

Termolecular reaction

$O + O_2 + M \rightarrow O_3 + M$

rate = $k\,[O]\,[O_2]\,[M]$

Termolecular reactions are low probability reactions; require three species to come together simultaneously

$2H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$

Experimental rate law: Rate = k $[H_2O_2][I^-]$

(i) $H_2O_2 + I^- \rightarrow H_2O + OI^-$ slow

(ii) $OI^- + H_2O_2 \rightarrow H_2O + O_2 + I^-$ fast

Rate depends on the slow, rate-determining step, (i)

Here, OI^- is the intermediate species

$2NO_2 + F_2 \rightarrow 2\ NO_2F$

Experimental rate expression

rate = $k_{obs}\ [NO_2]\ [F_2]$

Possible mechanism which fits the experimental observation

$NO_2 + F_2 \text{ -----> } NO_2F + F$ slow

$NO_2 + F \text{ -------> } NO_2F$ fast

First step: rate = $k_1\ [NO_2]\ [F_2]$ rate determining step

Second step: rate = $k_2\ [NO_2]\ [F]$

The rate of the first reaction determines the rate of the overall reaction

For the reaction: $2\,H_2(g) + 2NO(g) \rightarrow N_2(g) + H_2O(g)$

The observed rate expression is: rate = $k[NO]^2[H_2]$

The following mechanisms have been proposed. Based on the rate law can any mechanism be ruled out?

Mechanism I $2\,H_2(g) + 2NO(g) \xrightarrow{k_1} N_2(g) + H_2O(g)$

Mechanism II $H_2(g) + NO(g) \xrightarrow{k_2} N(g) + H_2O(g)$ slow

$NO(g) + N(g) \xrightarrow{k_3} N_2(g) + O(g)$ fast

$O(g) + H_2\,(g) \xrightarrow{k_4} H_2O(g)$ fast

Mechanism III $H_2(g) + 2NO(g) \xrightarrow{k_5} N_2O(g) + H_2O(g)$ slow

$H_2(g) + N_2O(g) \xrightarrow{k_6} N_2(g) + H_2O(g)$ fast

Mechanism I	**rate = $k_1[H_2]^2 [NO]^2$**	**not possible**
Mechanism II	**rate = $k_2[H_2] [NO]$**	**not possible**
Mechanism III	**rate = $k_5[H_2] [NO]^2$**	**possible**

If mechanism III is a possible mechanism, try to detect N_2O experimentally to confirm mechanism.

Chain reactions

Reaction which proceeds through a series of elementary steps, some of which are repeated many times.

Steps: initiation, propagation, termination

Free radicals - formed by homolytic cleavage of a bond

Free radicals in the atmosphere - ozone depletion

Free- radicals and biological damage

Explosions

Nuclear fission

Polymerization

Net: $CH_4(g) + F_2(g) \rightarrow CH_3F(g) + HF(g)$

$CH_4(g) + F_2(g) \rightarrow {}^{\bullet}CH_3 + HF + {}^{\bullet}F$ **initiation**

${}^{\bullet}CH_3 + F_2(g) \rightarrow CH_3F + {}^{\bullet}F$ **propagation**

${}^{\bullet}CH_3 + {}^{\bullet}F + M \rightarrow CH_3F + M$ **termination**

$CCl_2F_2 + h\nu$ -> $CF_2Cl + Cl^{\cdot}$

$CCl_2F_2 + O^{\cdot}$ -> $CF_2Cl + ClO^{\cdot}$

reactions which generate free radicals

$Cl + O_3$ -> $ClO + O_2$

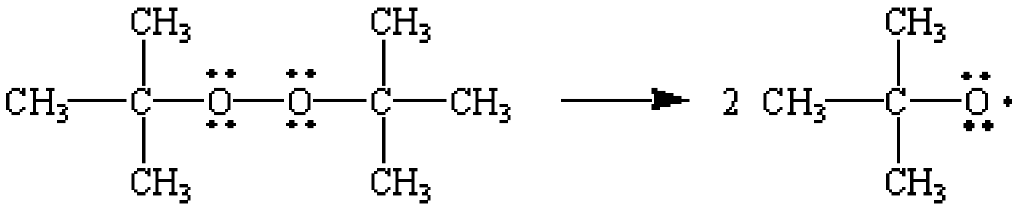
$ClO + O$ -> $Cl + O_2$

Net Reaction

$O + O_3$ -> $2O_2$

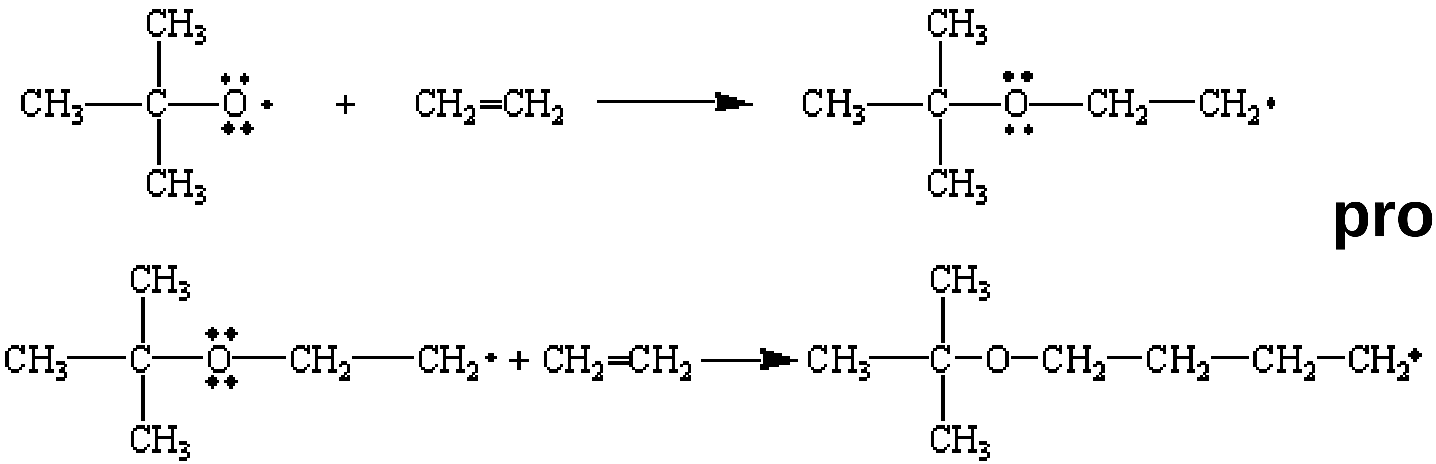
“Ozone Depletion”

1995 Nobel Prize in Chemistry



$$CH_3-C(CH_3)_2-\ddot{O}-\ddot{O}-C(CH_3)_2-CH_3 \longrightarrow 2\ CH_3-C(CH_3)_2-\ddot{O}\cdot$$

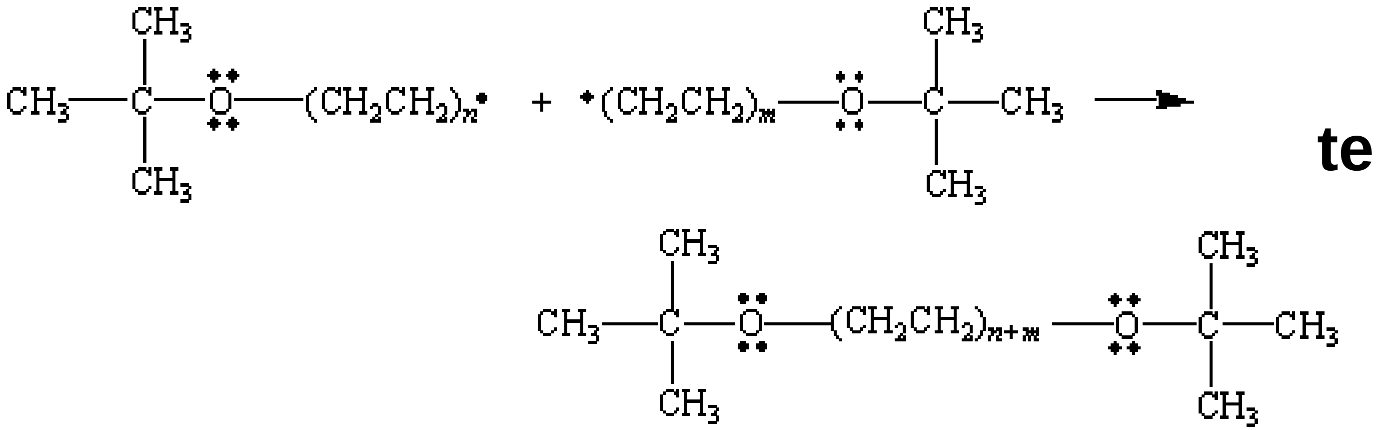
initiation



$$CH_3-C(CH_3)_2-\ddot{O}\cdot + CH_2{=}CH_2 \longrightarrow CH_3-C(CH_3)_2-\ddot{O}-CH_2-CH_2\cdot$$

$$CH_3-C(CH_3)_2-\ddot{O}-CH_2-CH_2\cdot + CH_2{=}CH_2 \longrightarrow CH_3-C(CH_3)_2-O-CH_2-CH_2-CH_2-CH_2\cdot$$

propagation



$$CH_3-C(CH_3)_2-\ddot{O}-(CH_2CH_2)_n\cdot + \cdot(CH_2CH_2)_m-\ddot{O}-C(CH_3)_2-CH_3 \longrightarrow CH_3-C(CH_3)_2-\ddot{O}-(CH_2CH_2)_{n+m}-\ddot{O}-C(CH_3)_2-CH_3$$

termination

Kinetics and Equilibrium

For a reaction which occurs in a single elementary step

$$NO + O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO_2 + O_2$$

Rate of forward reaction = $k_1 [NO] [O_3]$

Rate of reverse reaction = $k_{-1} [NO_2] [O_2]$

At equilibrium:

rate of forward reaction = rate of reverse reaction

$$k_1 [NO]_{eq} [O_3]_{eq} = k_{-1} [NO_2]_{eq} [O_2]_{eq}$$

where the eq denotes equilibrium concentrations

$$\frac{[NO_2]_{eq}[O_2]_{eq}}{[NO]_{eq}[O_3]_{eq}} = \frac{k_1}{k_{-1}} = K$$

K is the equilibrium constant

The reaction: $2NO + 2H_2 \rightleftharpoons N_2 + 2H_2O$

occurs through a series of three elementary reactions

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} N_2O + H_2O$$

$$N_2O + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} N_2 + H_2O$$

At equilibrium

$k_1 [NO]^2_{eq} = k_{-1} [N_2O_2]_{eq}$

$k_2 [N_2O_2]_{eq} [H_2]_{eq} = k_{-2} [N_2O]_{eq} [H_2O]_{eq}$

$k_3 [N_2O]_{eq} [H_2]_{eq} = k_{-3} [N_2]_{eq} [H_2O]_{eq}$

$$K_1 = \frac{[N_2O_2]_{eq}}{[NO]^2_{eq}} = \frac{k_1}{k_{-1}}$$

$$K_2 = \frac{[N_2O]_{eq}[H_2O]_{eq}}{[N_2O_2]_{eq}[H_2]_{eq}} = \frac{k_2}{k_{-2}}$$

$$K_3 = \frac{[N_2]_{eq}[H_2O]_{eq}}{[N_2O]_{eq}[H_2]_{eq}} = \frac{k_3}{k_{-3}}$$

$$K = K_1K_2K_3 = \frac{k_1k_2k_3}{k_{-1}k_{-2}k_{-3}} = \frac{[H_2O]^2_{eq}[N_2]_{eq}}{[NO]^2_{eq}[H_2]^2_{eq}}$$

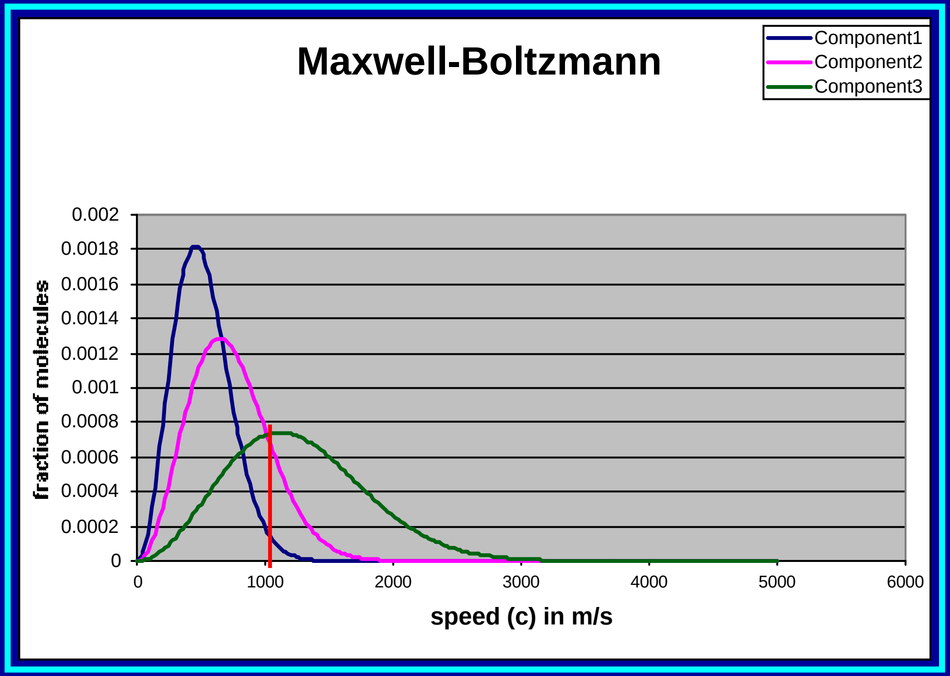
Temperature dependence of reaction rates

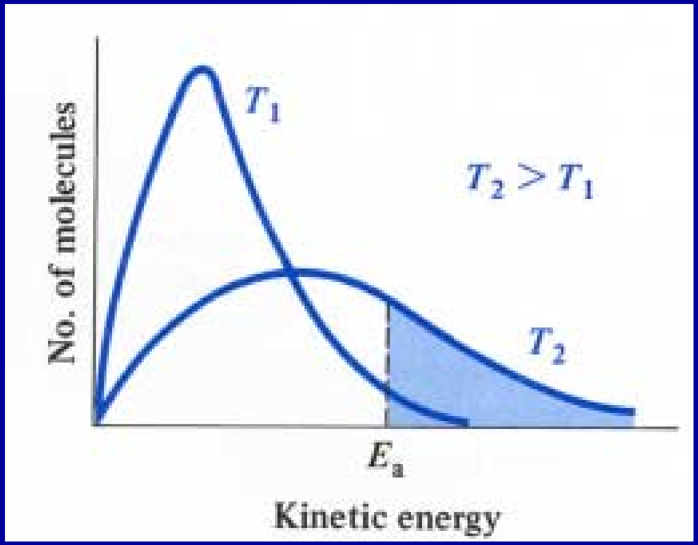
Collisions between two (or more) atoms/molecules required for a reaction.

However, every time two reactants collide they may not react

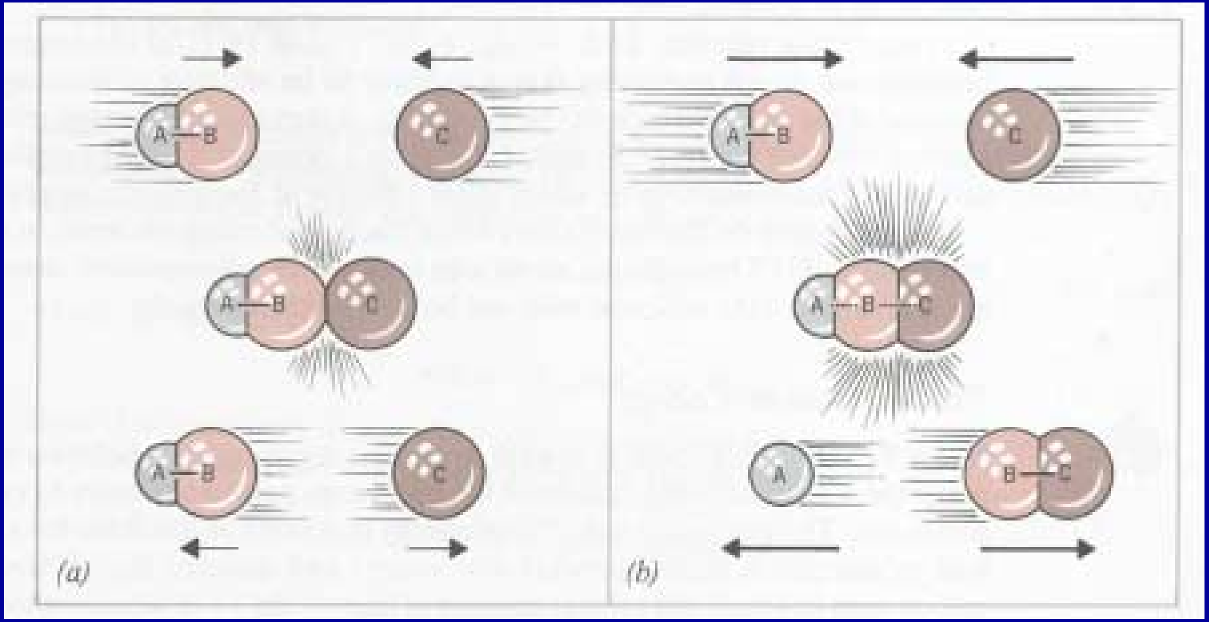
As temperature increases:

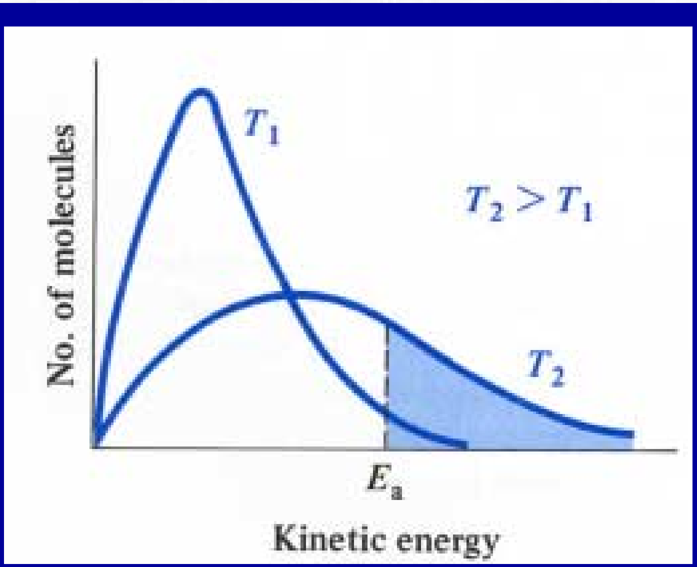
- atoms/molecules collide more frequently
- kinetic energy of atoms/molecules increases


Maxwell-Boltzmann
Component1
Component2
Component3
fraction of molecules
0.002
0.0018
0.0016
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
0
1000
2000
3000
4000
5000
6000
speed (c) in m/s

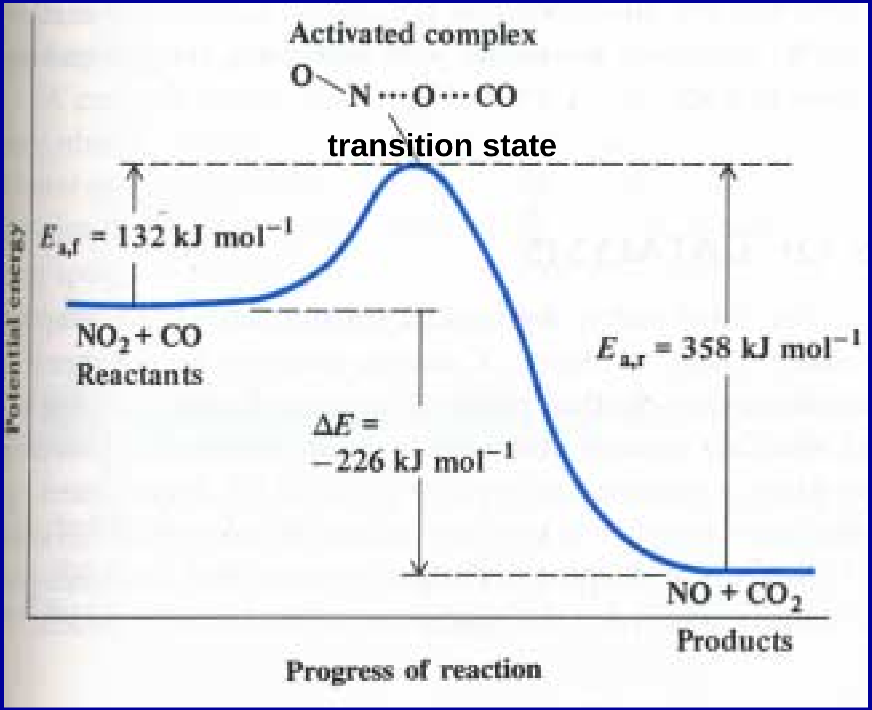

No. of molecules
T_1
$T_2 > T_1$
T_2
E_a
Kinetic energy

Kinetic energy is important





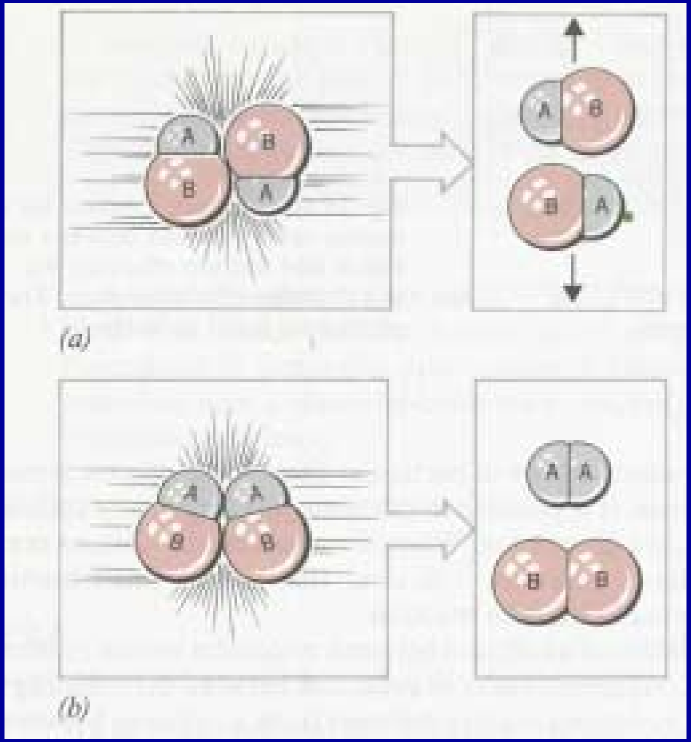
$NO_2(g) + CO(g)$ -> $NO(g) + CO_2(g)$

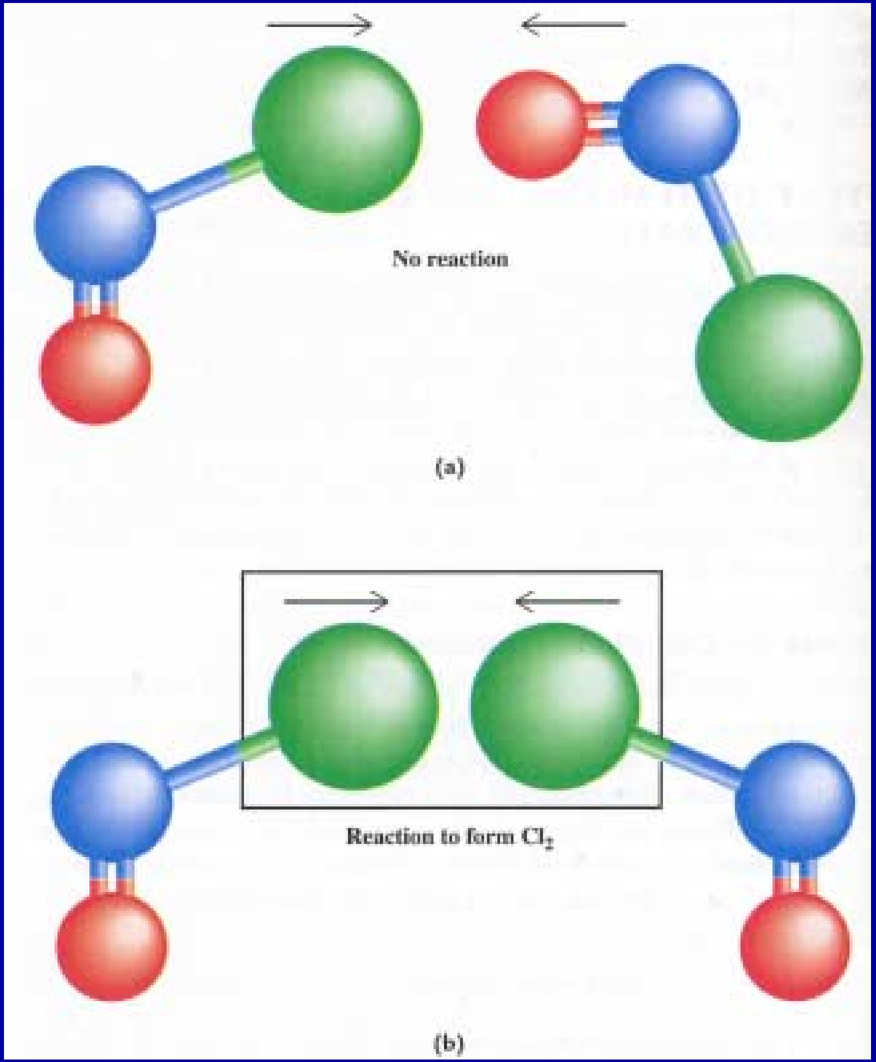


Potential energy

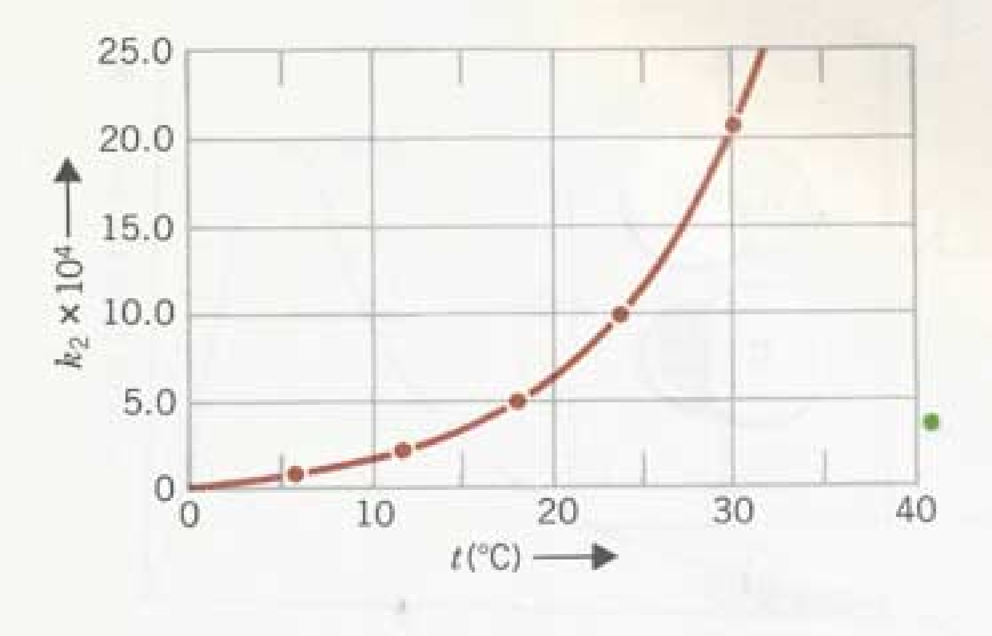
reaction coordinate

Orientation is important





$2 NOCl \rightarrow 2 NO + Cl_2$



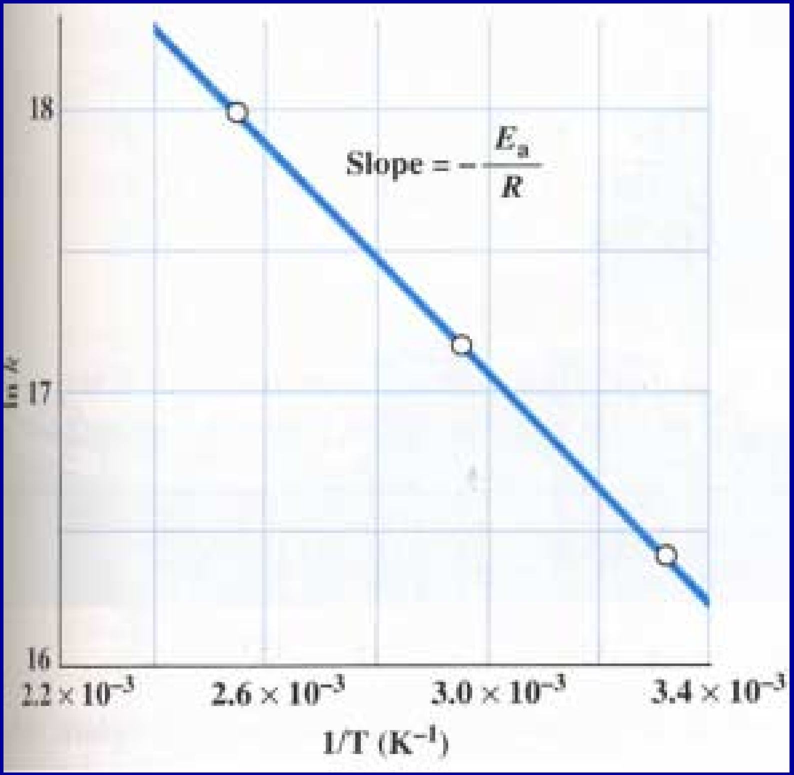
$$k = Ae^{-(E_a/RT)}$$

Arrhenius equation

E_a: activation energy

A: frequency factor

$$\ln k = \ln A - \frac{E_a}{RT}$$



$$\ln k = \ln A - \frac{E_a}{RT}$$

Measuring k as a function of T allows determination of E_a

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

Catalysis

A compound which takes part in a chemical reaction, speeds up the rate, but does not itself undergo a chemical change.

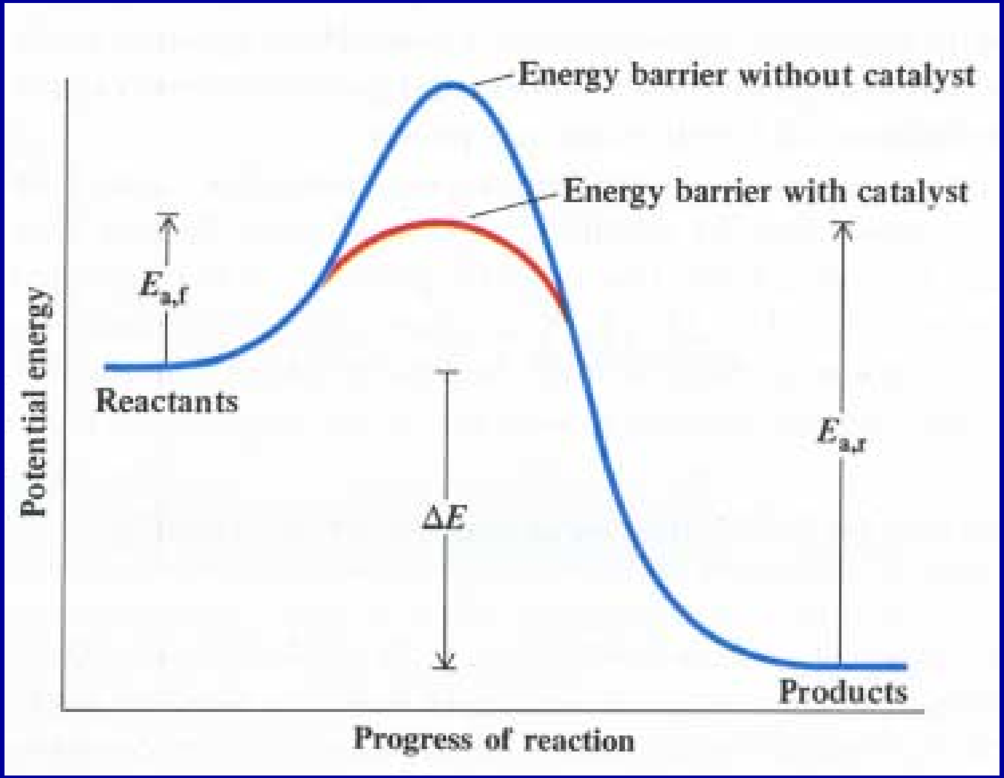
Simple mechanism

A + catalyst -> intermediates

intermediates -> B + catalyst

Overall: A -> B

Concentration of catalyst is included in k; hence k varies with concentration of catalyst



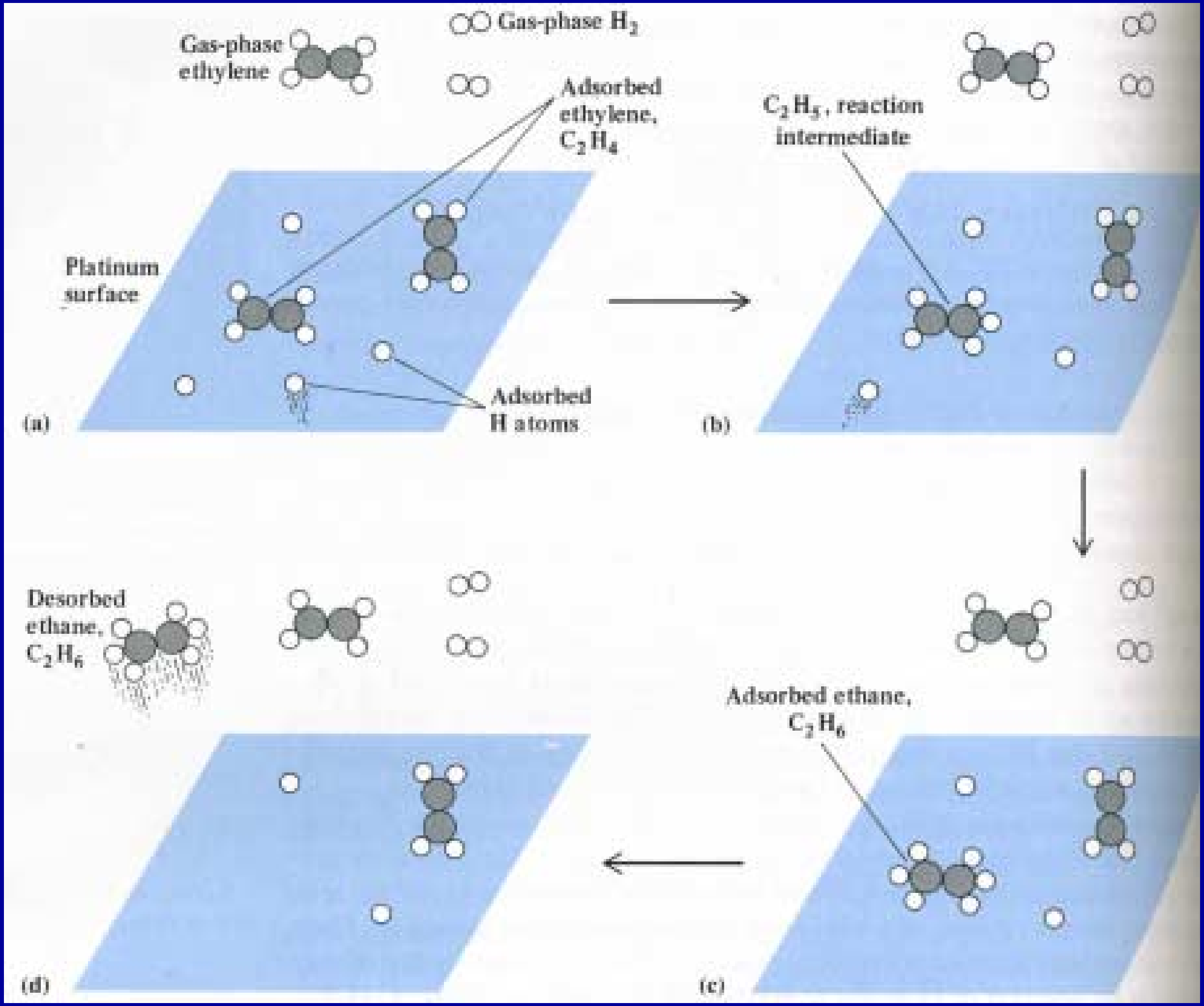
Catalyst speeds up the reaction by lowering E_a

$2H_2O_2(aq) \rightarrow 2H_2O(aq) + O_2(g)$

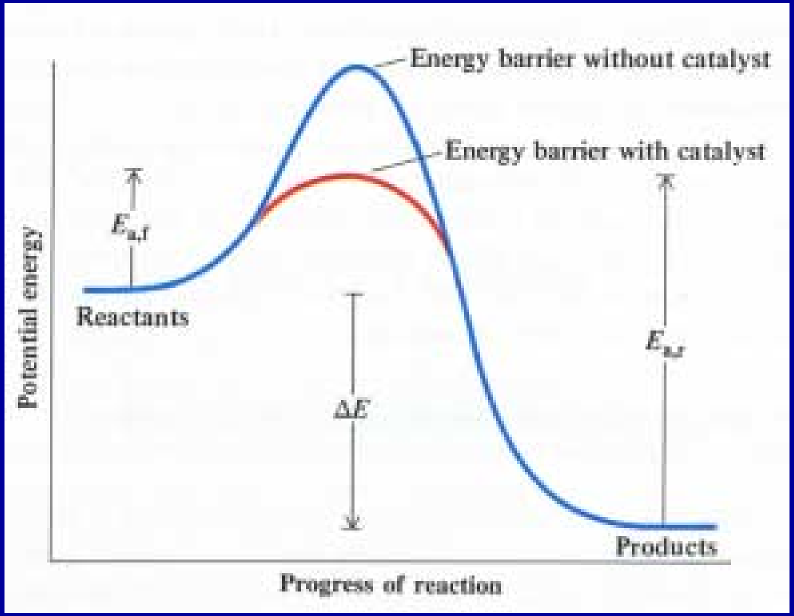
In the absence of a catalyst, E_a = 76 kJ/mol

In the presence of a catalyst (I^-); E_a = 57 kJ/mol; rate constant increases by a factor of 2000

$C_2H_4 + H_2 \xrightarrow{Pt} C_2H_6$



A catalyst does not effect the thermodynamics of the reaction



ΔG is not affected by catalyst and hence neither is K

Equilibrium concentrations are the same with and without catalyst; just the rate at which equilibrium is reached increases in the presence of a catalyst

K = k/k-1; speeds up both the forward and reverse reaction

Enzymes

Practically all living reactions are catalyzed by enzymes; each enzyme specific for a reaction.

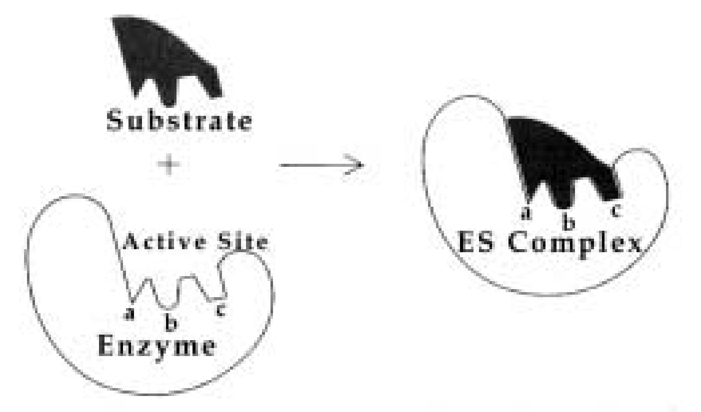
E_a for acid hydrolysis of sucrose: 107 kJ/mol

E_a for catalyzed acid hydrolysis of sucrose: 36 kJ/mol

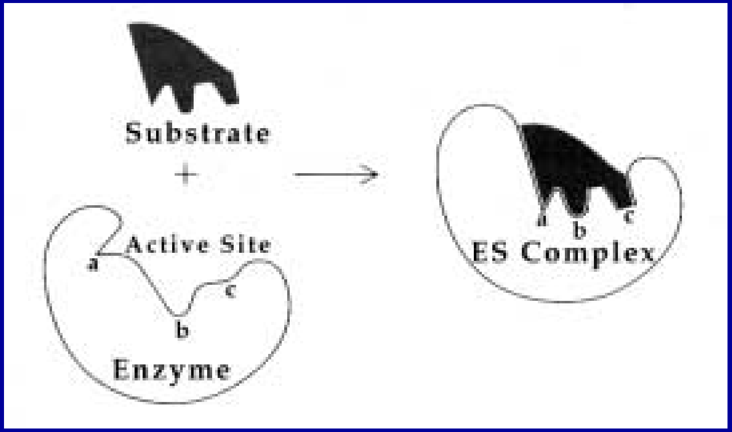
Rate increase of 10^{12} at body temperature

$$E + S \Leftrightarrow ES$$

ES -> P + E



"lock and key" model



"induced-fit" model

Catalytic Converters

Incomplete combustion of gasoline produces CO, hydrocarbon fragments (C_mH_n)

Also, high temperature in the engine causes oxidation of N_2 to NO and NO_2

Introduce catalysts into the exhaust to convert these pollutants to less harmful compounds

Without a catalyst conversion would be very slow

$$CO, C_mH_n, O_2 \xrightarrow{\text{catalyst}} CO_2, H_2O$$

$$NO, NO_2 \xrightarrow{\text{catalyst}} N_2, O_2$$

Catalyst: pellets of Pt, Pd, Rh

Autocatalysis

Catalysis of a reaction by the products

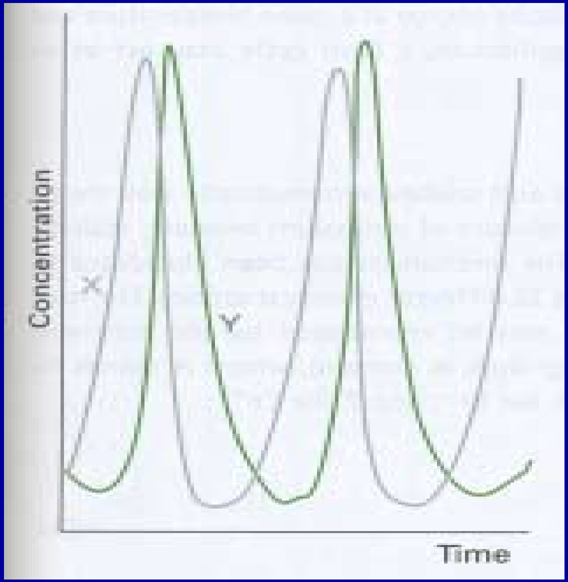
$A \rightarrow P$

Rate = k [A][P] reaction rate increase as P is formed

$BrO_3^- + HBrO_2 + H_3O^+ \rightarrow 2BrO_2 + 2\,H_2O$

$2BrO_2 + 2\,Ce^{3+}\ 2H_3O^+ \longrightarrow 2HBrO_2 + 2\,Ce^{4+} + 2H_2O$

A consequence of autocatalysis is an oscillating reaction



Concentration of reactants, products or intermediates vary periodically with time

Autocatalysis plays the role of “positive feedback”

Briggs-Rauscher Reaction

http://www.chem.leeds.ac.uk/delights/texts/expt_11.html