Kinetics

Unit 5

12.1 Reaction Rates

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Reaction rate is defined as the change in concentration of a reactant or product per time.

$2NO_2 \rightarrow 2NO + O_2$

In terms of reactants:

The rate will be _negative_ because the reaction used up reactants and the concentration will _decrease_. So to keep the rate positive you need to use a _negative sign_ in the equation.

2NO$_2$ → 2NO + O$_2$

Rate = -Δ[NO$_2$]/Δt

In terms of products:

   Since more product is being made the rate can be kept
   Positive.

NO: Rate = Δ[NO]/Δt   Rate= (2)Δ[O$_2$]/Δt

     Production of NO is twice that of O$_2$. (Coefficients)

Example

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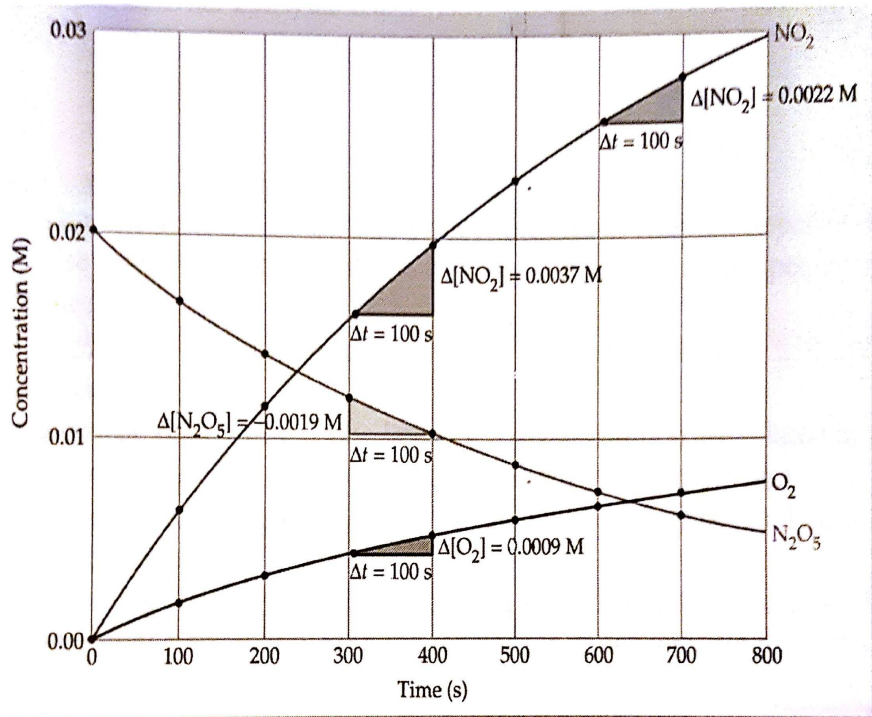
What is the chemical reaction?

Write the reaction rates:

12.2 Rate Laws: An Introduction

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Chemical reactions are reversible. If we choose conditions where the reverse reaction is neglected, the reaction rate will depend only on the concentrations of the reactants.

For the decomposition of nitrogen dioxide we can write:

$$2NO_2 \rightarrow 2NO + O_2 \qquad\qquad Rate= k[NO_2]^n$$

k= rate constant   n= order of the reaction

Two Important Points

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1. The concentration of the products do not appear in the rate law because the reaction rate is being studied under the conditions were the reverse reaction does not contribute to the overall rate.

2. The value of the exponent (n) must be determined by the experiment; it cannot be written from the balanced equation.

Summary of Rate Laws

- The *differential rate law* shows how the *rate* of the reaction *depends on concentration*.
- The *integrated rate law* show how *concentrations* of species in the reaction *depend on time*.
- Since only the forward reactions are considered, the rate laws will involve only concentrations of *reactants.*
- Both must be determined experiementally.

12.3 Determinations of the Rate Law

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- Write the rate with respect to the reactants (Rate=$k[A]^n$)

- Pick 2 trials and solve for the orders R_1/R_2

- Take one trial and solve for k.

- Use the units to solve for the unit of k.

Example 1

Example:

Initial Concentration and Rate Data for the Reaction

$$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$$
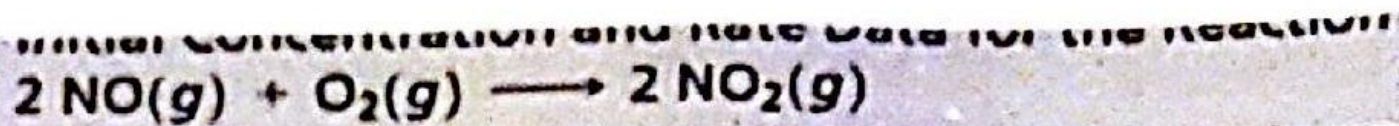
Experiment	Initial [NO]	Initial [O$_2$]	Initial Rate of For... (M/s)
1	0.015	0.015	0.048
2	0.030	0.015	0.192
3	0.015	0.030	0.096
4	0.030	0.030	0.384

Example 2

Example:

Experiment	Initial [CH_3COCH_3]	Initial Rate of Decomposition of CH_3COCH_3 (M/s)
1	6.0×10^{-3}	5.2×10^{-5}
2	9.0×10^{-3}	7.8×10^{-5}

Example 3

Example:

Experiment	Initial [CH$_3$NNCH$_3$]	Initial Rate of Decomposition of CH$_3$NNCH$_3$ (M/s)
1	2.4 × 10^{-2}	6.0 × 10^{-6}
2	8.0 × 10^{-3}	2.0 × 10^{-6}

Example 4

Example:

Experiment	Initial $[NH_4^+]$	Initial $[NO_2^-]$	Initial Rate of Consumption of NH_4^+ (M/s)
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}

Example 5

Example:

Experiment	Initial [NO]	Initial $[Cl_2]$	Initial Rate of Consumption of Cl_2 (M/s)
1	0.13	0.20	1.0×10^{-2}
2	0.26	0.20	4.0×10^{-2}
3	0.13	0.10	5.0×10^{-3}

Example 6

Example:

Experiment	Initial $[C_2H_4Br_2]$	Initial $[I^-]$	Initial Rate of Formation of I_3^- (M/s)
1	0.127	0.102	6.45×10^{-5}
2	0.343	0.102	1.74×10^{-4}
3	0.203	0.125	1.26×10^{-4}

12.4 Integrated Rate Law– First Order Rate Laws

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For first order reactions, if the concentration of the reactant is doubled, the rate of production will also be doubled.

Integrated rate law" $\ln[A]= -kt + \ln[A]_0$

The graph of this equation is a straight line for first order reactions.

y= $\ln[A]$ x= t   m=-k   b= $\ln[A]_0$

Graph of Rate Law
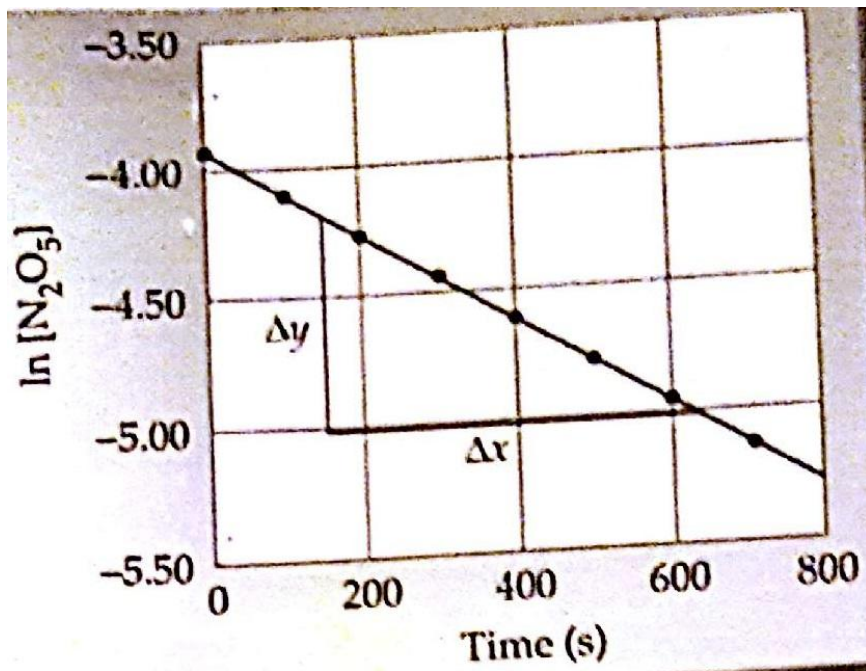
- - -

$$\ln[N_2O_5] = -kt + \ln [N_2O_5]_0$$

(a)
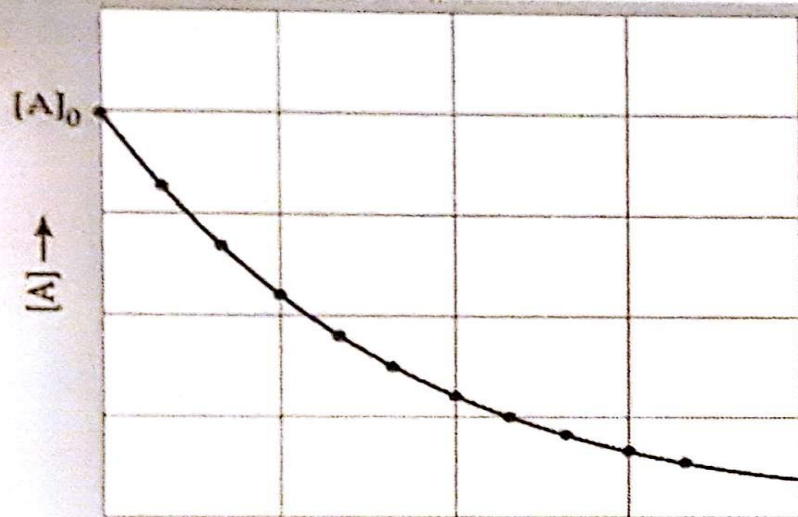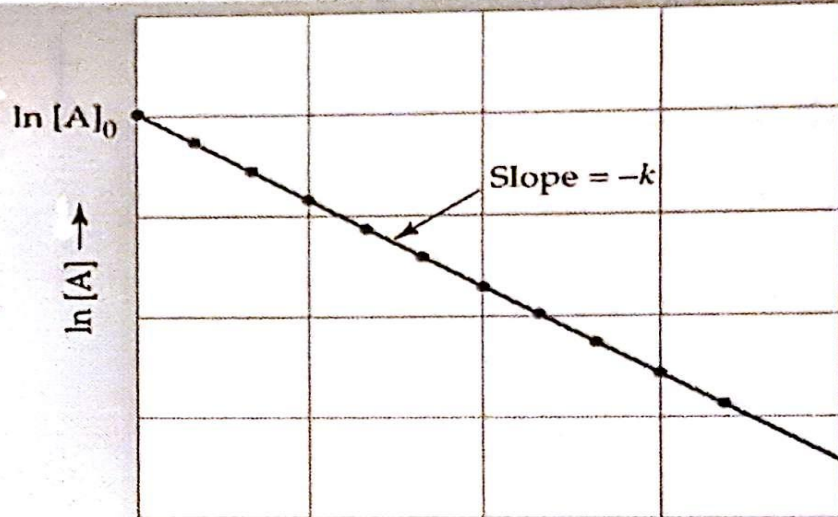
(b)

Example 7

1. What is k for this reaction?

2. Calculate the concentration of the reactant at 150s after the start of the reaction.

Half-life of a first order reaction
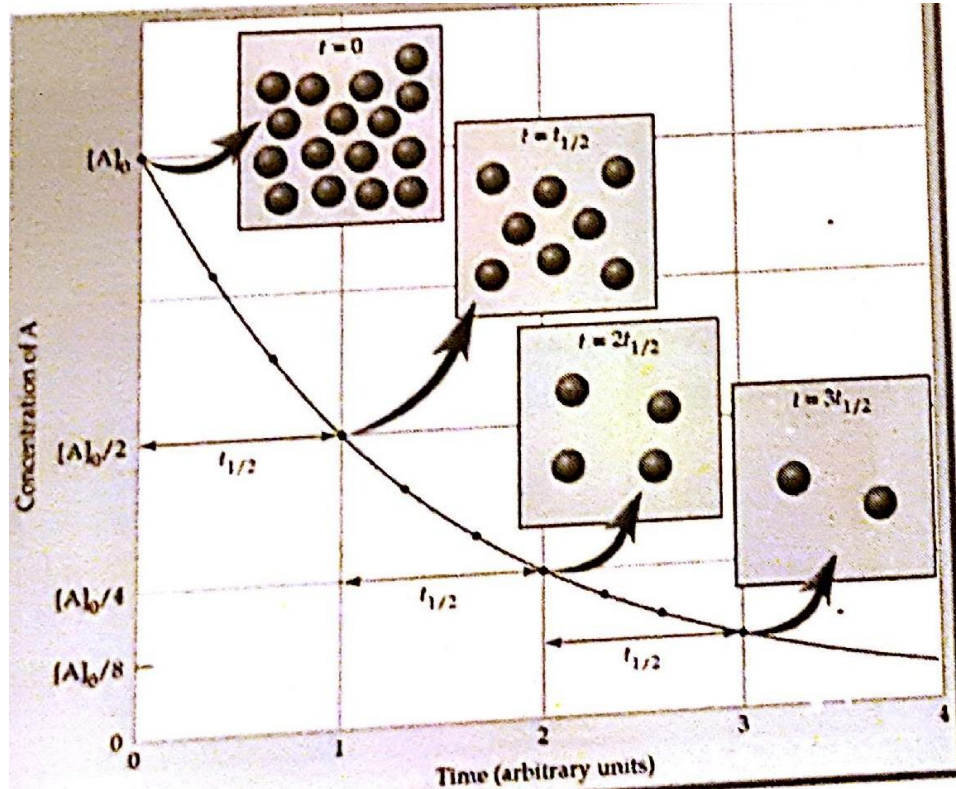
Half life– time it takes the reacts to react half its concentration

It takes 100s for [A] to be halved in this reaction.

When t=$t_{1/2}$ [A]=[A]$_0$/2

When integrated t1/2 = 0.693/k because the ln2 is 0.693

Example 8

A certain first-order reaction has a half-life of 20.0min.

Calculate the rate constant for this reaction.

How much time is required for this reaction to be 75% completed?

Second Order Rate Law

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Integrated 2nd order rate law:

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

$$\underset{y}{\uparrow} \qquad \underset{mx}{\uparrow\uparrow} \qquad \underset{b}{\uparrow}$$

2nd Order Rate Law Explained

Doubling the concentration of A quadruples the rate of reaction. For second order reactions the plot of 1/[A] vs t is linear.

2nd Order Rate Law- Half Life

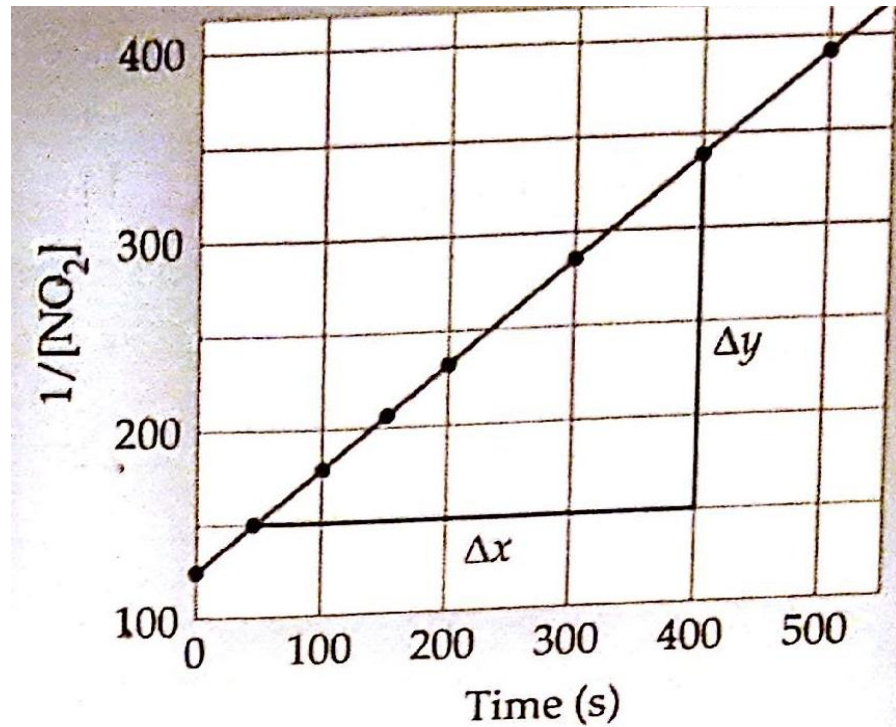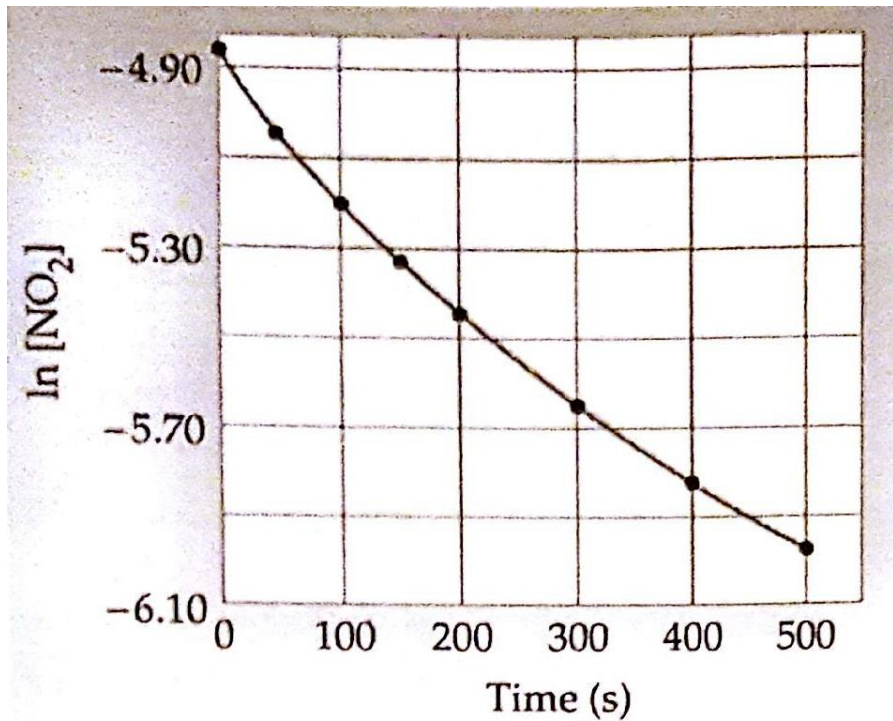
When $t-t_{1/2}$,
$[A] = [A]_0/2$

A bunch of calculus...

$t_{1/2} = 1/(k[A]_0)$
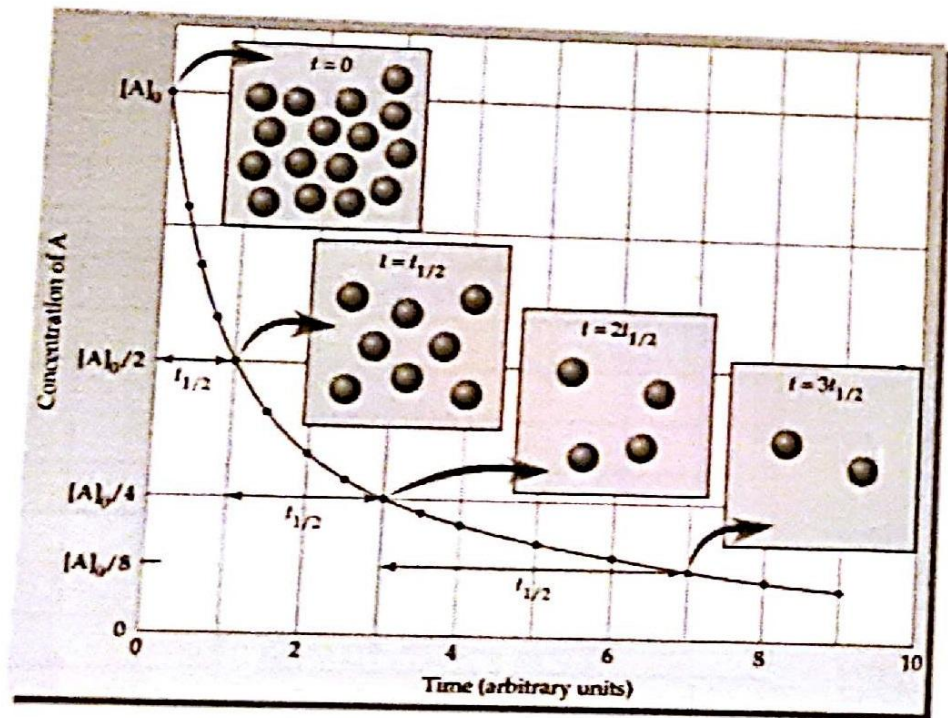
First Order   vs.   Second Order

Example 9

[C_4H_6] (M)	Time (s)	1/[C_4H_6]	ln[C_4H_6]
0.01000	0		
0.00625	1000		
0.00476	1800		
0.00370	2800		
0.00313	3600		
0.00270	4400		
0.00241	5200		
0.00208	6200		

Half- Live (First Order vs Second Order)

First Order:

- Depends on k
- Constant time is required to reduce the concentration by half.

Second Order:

- Depends on k and $[A]_0$
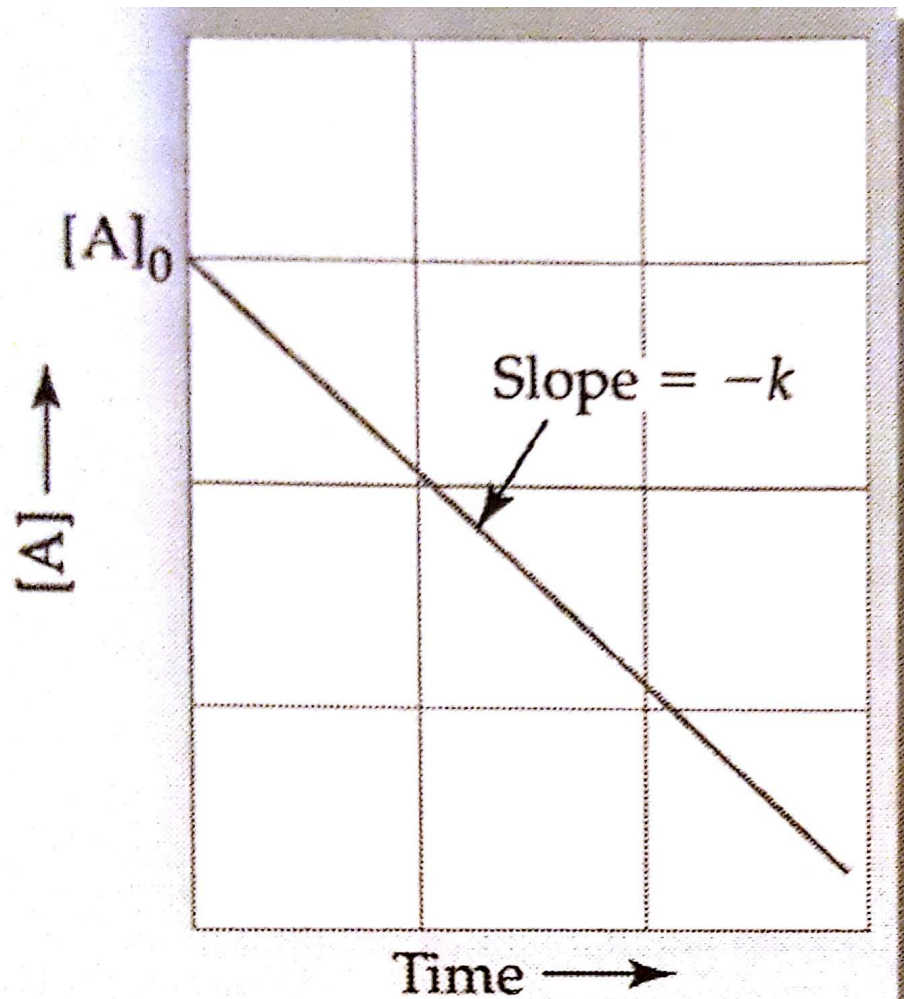- Each successive half life is double the preceding one.

Zero Order Rate Law

Rate = $k[A]_0$ = k

Integrated rate law:

$[A] = -kt + [A]_0$

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

Step 1. $N_2O(g) \longrightarrow N_2(g) + O(g)$

Step 2. $N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g)$

In the first step N_2O breaks apart

In the second step oxygen breaks away from N_2O

The second reaction the first O pulls away another O from the N_2O

O is an intermediate which means that it is produced in the first reaction and used up in the second reaction.
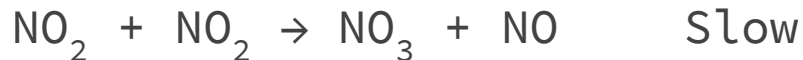
Reaction Mechanism

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A reaction mechanism is a series of elementary steps that must satisfy two requirements:

1. The sum of the elementary steps must give the overall balanced equation for the reaction.
2. The mechanism must agree with the experimentally determined rate law.

Molecularity- number of species that collide

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| Elementary Step	Molecularity	Rate Law
A $\longrightarrow$ product	Unimolecular	Rate $= k[A]$
2A $\longrightarrow$ product	Bimolecular	Rate $= k[A]^2$
A + B $\longrightarrow$ product	Bimolecular	Rate $= k[A][B]$
2A + B $\longrightarrow$ product	Termolecular	Rate $= k[A]^2[B]$

Rate Determining Step (aka: The SLOW step)

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$NO_2 + NO_2 \rightarrow NO_3 + NO$ Slow

$+ \ NO_3 + Co \rightarrow NO_2 \ + CO_2$ Fast

$NO_2 + CO \rightarrow NO_2 + CO_2$

A multi-step reaction has one step that is the rate determining step. The overall rate cannot be faster than the SLOW step.
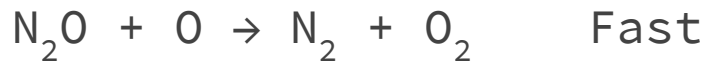
Example 10

The balanced equation for the reaction of the gaes nitrogen dioxide and fluorine is $2NO_2 + F_2 \rightarrow 2NO_2F$. The experimentally determined rate law is Rate=$k[NO_2][F_2]$ A suggested mechanism for this reaction is:

$2NO_2 + F_2 \text{ --} > NO_2F + F$ Slow

$+ \;\; F + NO_2 \rightarrow NO_2F$ Fast
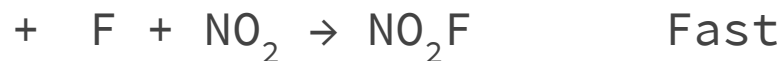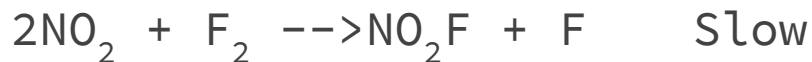
Is this an acceptable mechanism? Does it satisfy the 2 requirements?

Example 11

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The decomposition of nitrous oxide is believed to occur by a two-step mechanism:
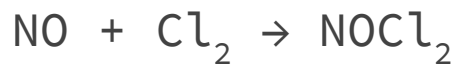
$N_2O \rightarrow N_2 + O$ Slow

$N_2O + O \rightarrow N_2 + O_2$ Fast

Write the equation for the overall reaction.

Write the rate law for the overall reaction.

Example 12

The reaction $2NO + Cl_2 \rightarrow 2NOCl$, obeys the rate law, Rate= $k[NO]^2[Cl_2]$. The following mechanism has been proposed for this reaction:

$NO + Cl_2 \rightarrow NOCl_2$

$NOCl_2 + NO \rightarrow 2NOCl$

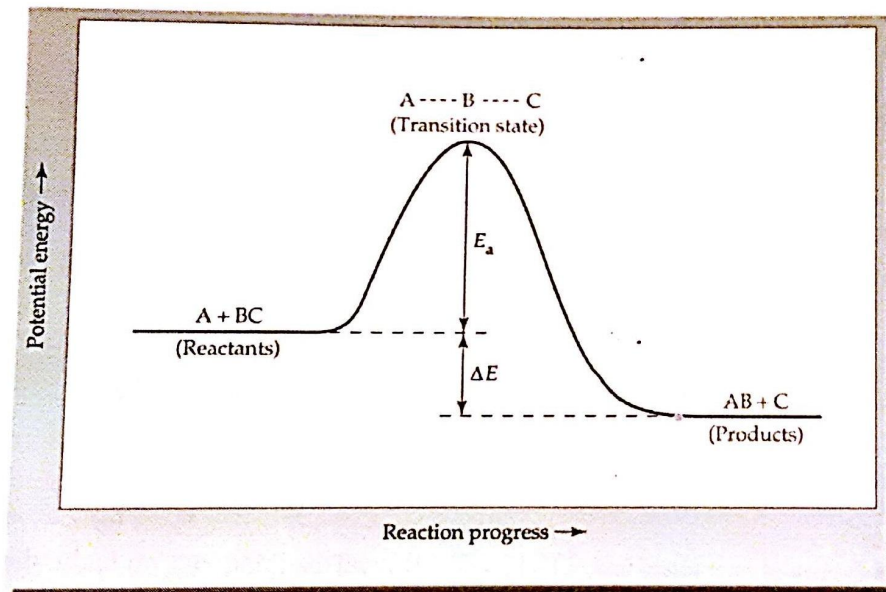What would the rate law be if the first step were rate determining?

Based on the observed rate law, what can we conclude about the relative rates of the two steps?

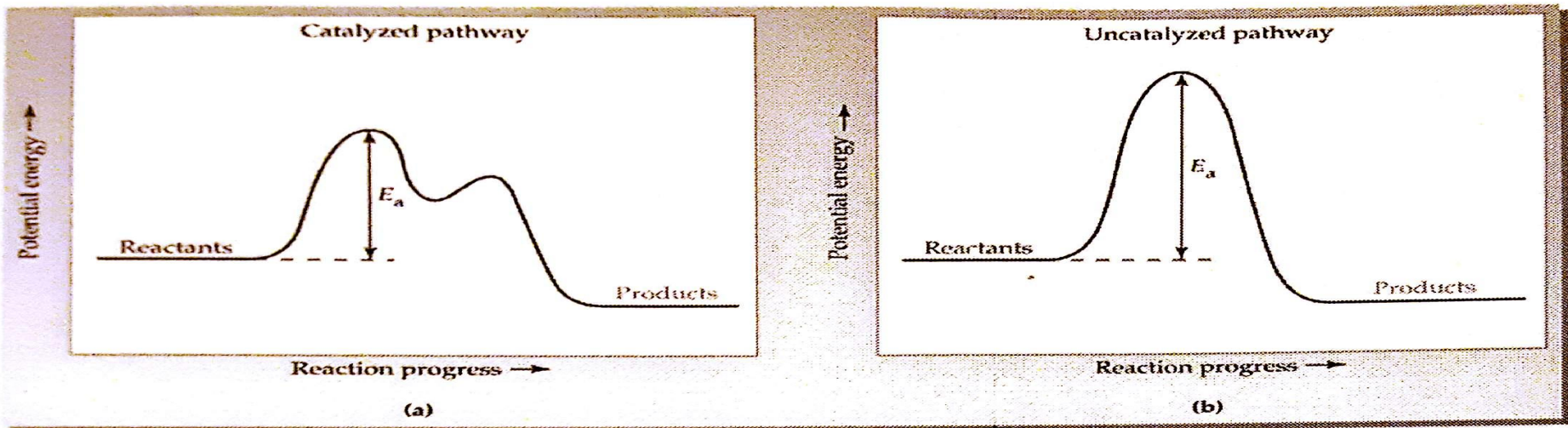# 12.7 A Model for Chemical Kinetics

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For the graph to the right:

The reaction is exothermic

And ΔH is negative.

Catalyst

A substance that speeds up the reaction by lowering the activation energy, but does not participate in the reaction.