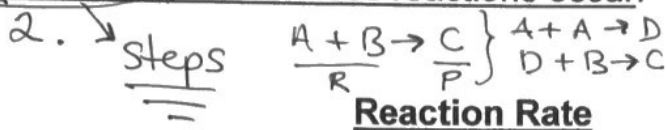


- 1.) catalyst
- 2.) Temp.
- 3.) Conc.
- 4.) surface area (solid)
- 5.) pressure (gas)

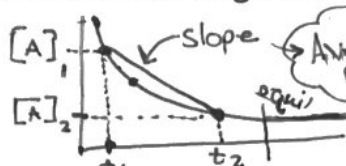
CHEMICAL KINETICS CH 14

Kinetics is the field of chemistry that deals with the rates of reactions and the mechanisms by which these reactions occur.



Reaction rate of a chemical reaction is the change in concentration of a reactant or product per unit time.

Consider the reaction: $A \leftrightarrow B$



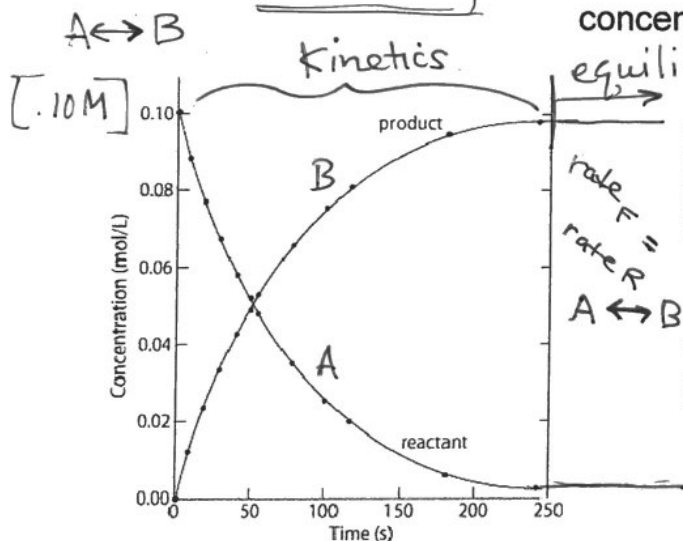
smaller #
bigger #

$$-\frac{[A]_2 - [A]_1}{t_2 - t_1}$$

Rate_{average} = $\frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1}$

Rate_{average} = $-\frac{\Delta[A]}{\Delta t}$

where A is the reactant or product being considered and the brackets indicate concentration in moles per liter Molarity

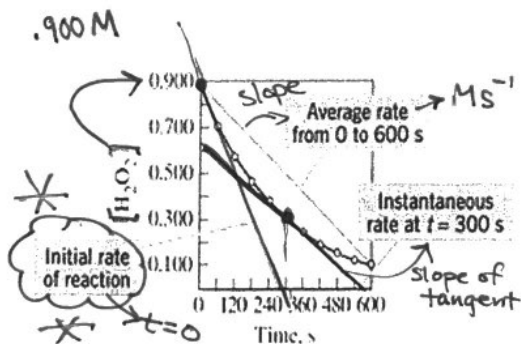


We can measure the rate of the reaction by considering the rate at which A disappears or the rate at which B appears. Since the coefficients of the reaction are both 1, the numerical values of these rates are equal. For this reaction we define the average rate as:

$$\text{Rate}_{\text{average}} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

The negative sign is used to signify that the reactant (A) disappears and the positive sign is used to signify that the product (B) appears. The units of the reaction are generally:

$$\frac{\text{mol/L}}{\text{s}} = \frac{\text{M}}{\text{s}} = \text{Ms}^{-1}$$



Both the average and instantaneous rates of a reaction can be calculated from a concentration vs time graph. This graph tracks the disappearance of H_2O_2 as a function of time and displays average and instantaneous rates for the following reaction: $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$

In order to calculate the average rate over a period of time, a straight line is drawn between two points on the graph, in this case between 0 and 600 seconds. The slope of this line equals the average rate.

In order to calculate the instantaneous rate at a specific moment in time, a tangent line is drawn to the curve at this time. The slope of the tangent line is equal to the instantaneous rate. The instantaneous rate at 0 s and 300 s are shown. (The instantaneous rate at 0 s is called the initial rate: it is the rate that is most often used, since the appearance of products can interfere with the study of a reaction.)

Instantaneous rate - the value of the rate at a particular time (Δt approaches zero)

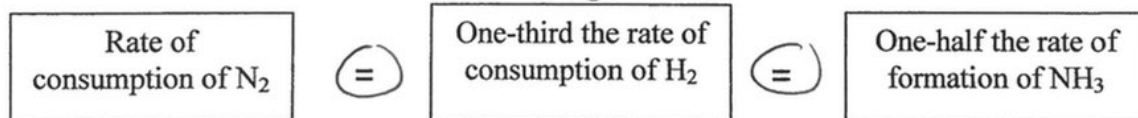
- can be obtained by computing the slope of a line tangent to the curve at that point

Initial rate - the instantaneous rate at 0 seconds; it is the rate most often used since the appearance of products can interfere with the study of a reaction *

- Most reactions are reversible.
- Initially the dominant reaction is the forward reaction. However, after a period of time, enough product accumulates so that the reverse reaction becomes important.
- The change in concentration of reactants depends on the difference in the rates of the forward and reverse reactions.
- Therefore, we must study a reaction at a point soon after the reactants are mixed, before products have had time to build up and significantly affect the rate of the forward reaction.

Method of Initial Rates !!

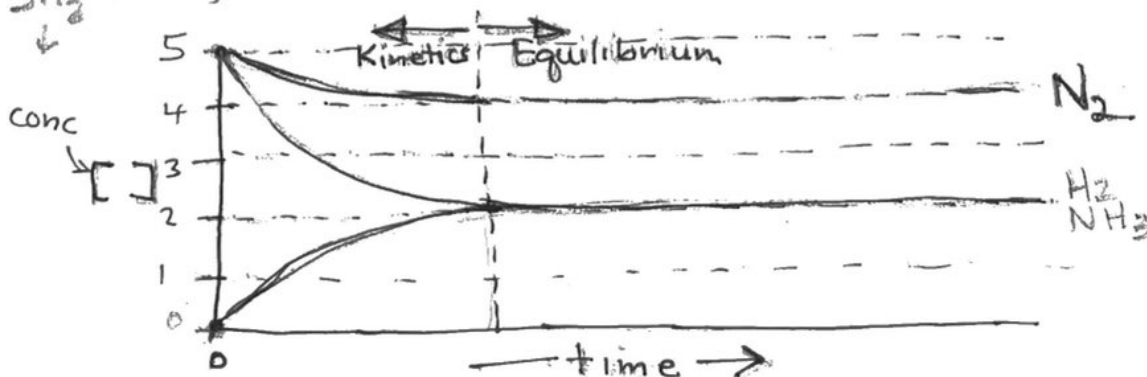
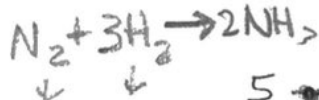
Consider the reaction: $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$



$$-\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$$

The rate of the general reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ is defined as:

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



Concentration and Reaction Rate: Rate Laws

"The Rate Law" The Differential Rate Law

Differential Rate Laws → Integrated Rate Laws

For every chemical reaction it is possible to write a rate law that relates the reaction rate to the concentrations of the reactants. This type of rate law is called a differential rate law.

For the reaction $2A + 3B + 4C \rightarrow \text{products}$,

$$\text{Rate} = k[A]^x[B]^y[C]^z$$

orders
rate constant → units!! Temp dependent!

The terms x, y, and z are known as reaction orders and refer to the reactant with which it is associated. (0, 1, 2)

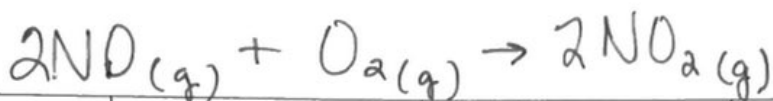
- If a reaction is **zero order** with respect to a reactant, it means the rate does not depend on the concentration of the reactant; for example, doubling the concentration will not increase or decrease the rate.
- If a reaction is **first order** with respect to a reactant, it means that the rate is directly proportional to the concentration of that reactant; for example, doubling the concentration will double the rate.
- If a reaction is **second order** with respect to a reactant, it means that the rate is directly proportional to the square of the concentration of that reactant; for example, doubling the concentration will quadruple the rate.
- * (• The overall order of a reaction is the sum of the individual reaction orders: for the reaction shown above the overall order is $x + y + z$.

The term k is known as the rate constant. It relates the concentrations, and their orders, to the rate of the reaction.

* > **ALL RATE LAWS ARE EXPERIMENTALLY DETERMINED !!!** *

Method of Initial Rates Experiment

Sample Problem 1. Determine the rate law and the rate constant for the following reaction: $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{2(g)}$
The table below lists data for the initial rate of the reaction.



Trial	[NO]	[O ₂]	Initial Rate (M/s)
1	0.0126	0.0125	7.05×10^{-3}
2	0.0252	0.0250	5.64×10^{-2}
3	0.0252	0.0125	2.82×10^{-2}

- 1.) Write a tentative rate law. $\text{Rate} = k [\text{NO}]^x [\text{O}_2]^y$
- 2.) To calculate the order of NO (x), choose two trials in which the concentration of the other reactant (O₂) is constant. Write the rate laws for these trials by substituting values.

Trial 1 Trial 3
 Trial 3 Trial 1

- 3.) Divide the rate law of the trial with the larger values by the rate law of the trial with the smaller values and solve for x.

$$\frac{2.82 \times 10^{-2}}{7.05 \times 10^{-3}} = \frac{k [0.0252]^x [0.0125]^y}{k [0.0126]^x [0.0125]^y}$$

$$4 = 2^x \quad x = 2$$

double [NO] rxn will get 4x faster

This rxn is 2nd order w/ respect to NO. (NO is a 2nd order reactant.)

- 4.) To calculate the order of O₂ (y), choose two trials in which the concentration of NO is constant. Write the rate laws for these trials and divide the larger trial values by the smaller and solve for y.

$$\frac{T_2}{T_3} \quad \frac{5.64 \times 10^{-2}}{2.82 \times 10^{-2}} = \frac{k [0.0252]^2 [0.0250]^y}{k [0.0252]^2 [0.0125]^y}$$

$$2 = 2^y \quad y = 1$$

double [O₂] double rate

This rxn is 1st order w/ respect to O₂ (O₂ is a 1st order reactant.)

- 5.) Write the completed rate law for the reaction.

$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

- 6.) Determine the value of the rate constant, k, by substituting the values and units for any single trial into the rate law. $\frac{1}{s} = s^{-1}$ $\frac{1}{\text{M}^2} = \text{M}^{-2}$

$$k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{O}_2]} = \frac{5.64 \times 10^{-2} \text{ M s}^{-1}}{(\text{M})^2 (\text{M})} = 3520 \text{ M}^{-2} \text{ s}^{-1}$$

3520 $\frac{1}{\text{M}^2 \text{ s}}$ 4

The Integrated Rate Law

The integrated rate law expresses how the concentrations depend on time.

➤ First Order Reactions

Reaction: $aA \rightarrow \text{products}$

Rate Law: $\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$

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

$-(-\text{slope}) = k$

Integrated First Order Rate Law: $\ln[A]_t = -kt + \ln[A]_0$

$y = mx + b$
 \downarrow slope
 \rightarrow y intercept

A reaction is first order in A if a plot of $\ln[A]$ vs t is a straight line with a slope of $-k$.

eg sheet:

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

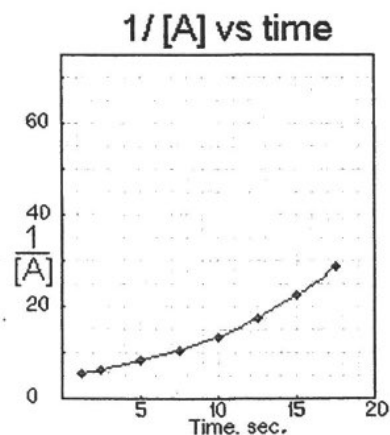
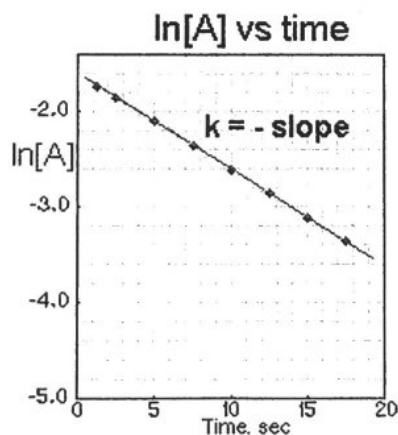
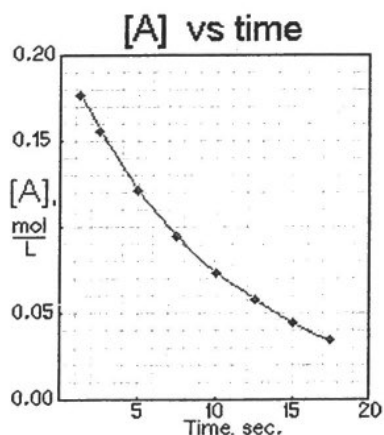
$\ln \frac{[A]_t}{[A]_0} = -kt$

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

$\ln 2 = kt_{1/2}$
 $.693 = kt_{1/2}$

$t_{1/2} = \frac{.693}{k}$

For a first order reaction, as shown in the following figure, the plot of the logarithm of $[A]$ versus time is a straight line with $k = -\text{slope}$ of the line. Other graphs are curved for a first order reaction.



nuclear decay is 1st order Kinetics

The time required for a reactant to reach half its original concentration is called the half-life of the reactant ($t_{1/2}$).

The half-life of a first order reaction: $t_{1/2} = \frac{\ln 2}{k} = \frac{.693}{k}$

For a first order reaction, half-life does not depend on concentration.

Sample Problem 2. A certain first order reaction has a half-life of 20.0 minutes. A.) Calculate the rate constant for this reaction. B.) How much time is required for this reaction to be 75% complete?

$$A.) \quad t_{1/2} = \frac{.693}{k}$$

$$20.0 \text{ min} = \frac{.693}{k}$$

$$k = \frac{.693}{20.0 \text{ min}} = .0347 \frac{1}{\text{min}} = .0347 \text{ min}^{-1}$$

$$B.) \quad \ln [A]_t - \ln [A]_0 = -kt$$

$$\ln [.25]_t - \ln [1]_0 = (-.0347 \text{ min}^{-1})(t)$$

$$\frac{-.0347 \text{ min}^{-1}}{-.0347 \text{ min}^{-1}} = \frac{-0.347}{-.0347}$$

$$t = 39.95 \text{ min} \quad \Rightarrow \quad t = 40.0 \text{ min}$$

Sample Problem 3. A first order reaction has a rate constant of $1.00 \times 10^{-3} \text{ s}^{-1}$ and the initial concentration of the reactant is 1.50 M. What is the concentration of the reactant at 1000. seconds?

$$k = 1.00 \times 10^{-3} \text{ s}^{-1}$$

$$[A]_0 = 1.50 \text{ M}$$

$$[A]_{1000 \text{ s}} = ?$$

$$t = 1000 \text{ s}$$

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

$$\ln [A]_t - \ln(1.50) = \left(\frac{-1.00 \times 10^{-3}}{\cancel{\text{s}^{-1}}} \right) \left(\frac{1000}{\cancel{\text{s}}} \right)$$

$$\ln [A]_t = -.595$$

$$[A]_{1000} = .552 \text{ M}$$

➤ Second Order Reactions

Reaction: $aA \rightarrow \text{products}$

Rate Law: $\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$

Integrated Second Order Rate Law:

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

$$y = mx + b$$

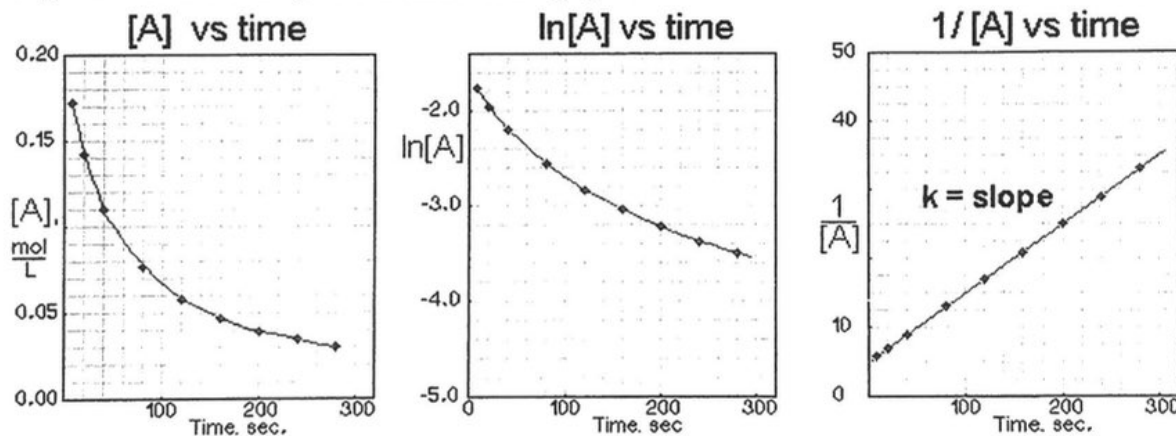
eg
sheet

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

$t_{1/2} \rightarrow \frac{1}{2} \text{ life}$

A reaction is second order in A if a plot of $1/[A]$ vs t is a straight line with a slope of $+k$.

For a second order reaction, as shown in the following figure, the plot of $1/[A]$ versus time is a straight line with $k = \text{slope of the line}$. Other graphs are curved for a second order reaction.



The expression for the half-life of a second order reaction:

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

The half-life of a second order reaction does depend on concentration and therefore changes as time progresses. (Each succeeding half-life doubles in value.)

➤ Zero Order Reactions

Reaction: $aA \rightarrow \text{products}$

$$\text{Rate} = k[A]^0$$

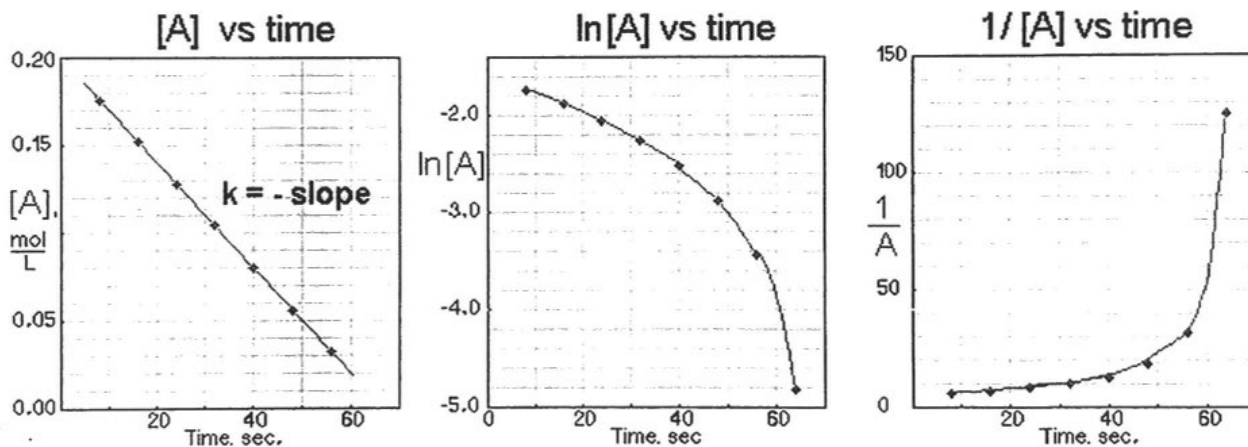
Rate Law: $\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^0 = k(1) = k$ $\text{Rate} = k$

Integrated Zero-Order Rate Law: $[A]_t = -kt + [A]_0$

~~eg/ sheet~~ $[A]_t - [A]_0 = -kt$ $y = mx + b$

A reaction is zero order in A if the plot of [A] vs t gives a straight line with a slope of -k.

For a zero order reaction, as shown in the following figure, the plot of [A] versus time is a straight line with $k = -\text{slope}$ of the line. Other graphs are curved for a zero order reaction.



Solving for $t_{1/2}$ gives: $t_{1/2} = \frac{[A]_0}{2k}$

The half-life of a zero order reaction does depend on concentration of the reactant and therefore changes as time progresses. (Each successive half-life is reduced by a factor of 2.)

Reaction Mechanisms

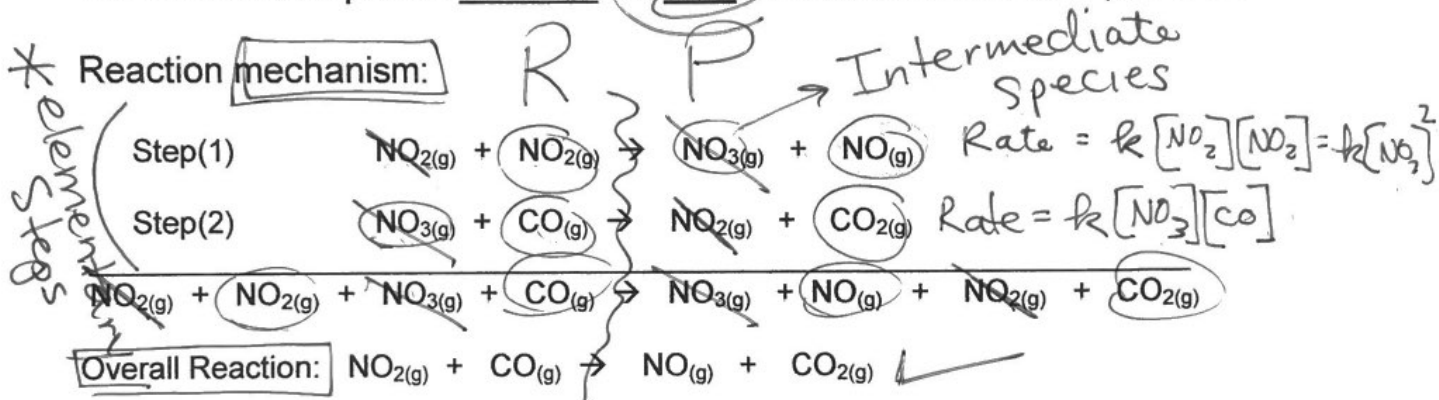
Most chemical reactions occur by a series of steps called the reaction mechanism.

Consider the reaction: $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$

The balanced equation tells us

- the reactants
- the products
- the stoichiometry

The balanced equation does not tell how the reactants become products.



NO_3 is an intermediate species. An intermediate is a particle formed in one step and consumed in a later step and so is never seen as a product.

Each of the two steps is called an elementary step. The rate law for an elementary step can be determined from its molecularity. Molecularity is defined as the number of species that must collide in the reaction indicated by that step.

- Step(1) above involves two molecules and is called a bimolecular step.
- Step(2) above involves two molecules and is also a bimolecular step.
- The rate law for a bimolecular step is always second-order:
 - If a single reactant, $k = [\text{A}]^2$
 - Rate law for Step(1): Rate = $k[\text{NO}_2]^2$
 - If 2 reactants, $k = [\text{A}][\text{B}]$
 - Rate law for Step(2): Rate = $k[\text{NO}_3][\text{CO}]$

The table below summarizes the relationship between molecularity and reaction order.

Molecularity	Elementary Reaction	Rate Law: Rate=	Overall Order of Rxn
Unimolecular	$A \rightarrow \text{products}$	$k[A]$	1 st
Bimolecular	$2A \rightarrow \text{products}$	$k[A]^2$	2 nd
Bimolecular	$A + B \rightarrow \text{products}$	$k[A][B]$	2 nd
Termolecular	$3A \rightarrow \text{products}$	$k[A]^3$	3 rd
Termolecular	$2A + B \rightarrow \text{products}$	$k[A]^2[B]$	3 rd
Termolecular	$A + B + C \rightarrow \text{products}$	$k[A][B][C]$	3 rd

A sequence of elementary reactions will always have one step that is slower than the rest. This slowest step determines the overall rate of the reaction and is called the **rate-determining step**.

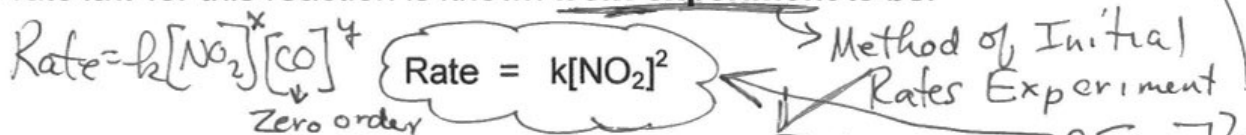
- Since chemists can only measure the overall reaction rate in the laboratory, they are in fact measuring the rate of the rate-determining step!
- Thus the rate law experimentally determined for a reaction is directly related to the rate-determining step.

A possible reaction mechanism must meet two requirements:

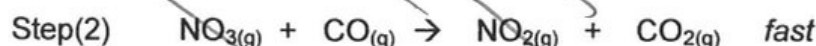
- (1) the sum of the elementary steps must give the overall balanced equation for the reaction
- (2) the mechanism must agree with the experimentally determined rate law

Consider the reaction: $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$

The rate law for this reaction is known from experiment to be:



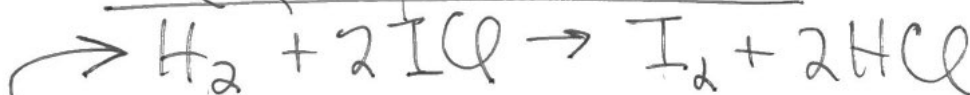
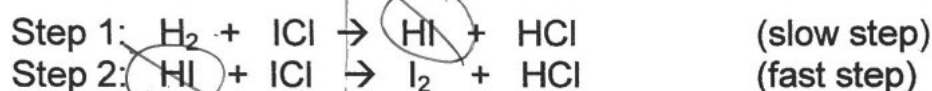
Proposed reaction mechanism is:



- The rate of CO_2 production is controlled by the rate of formation of NO_3 in the first step.
- The bimolecular first step has the rate law: $\text{Rate} = k_1[\text{NO}_2]^2$
- Since the overall reaction rate can be no faster than the slowest step, then the overall rate must be: $\text{Rate} = k_1[\text{NO}_2]^2$
- Therefore, this proposed reaction mechanism satisfies the two rules previously mentioned above.

A reaction mechanism can never be proved absolutely!

Sample Problem 4. The following two-step mechanism has been proposed for a gas-phase reaction:



(a) What is the overall reaction?

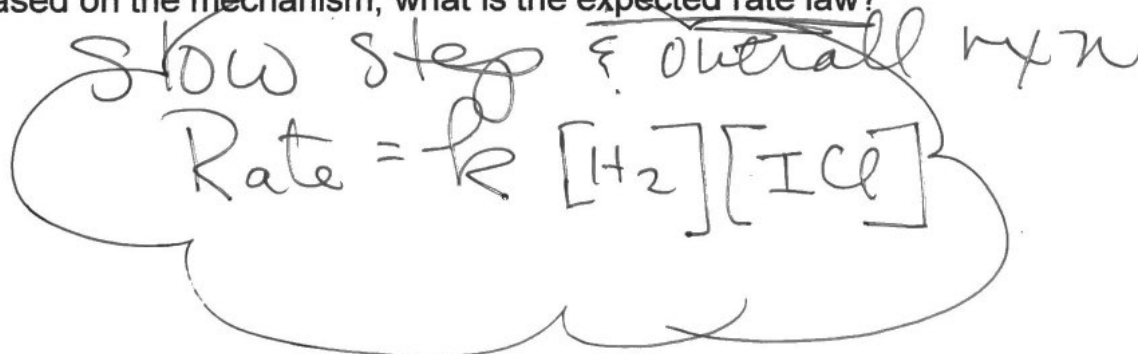
(b) What intermediates are present?



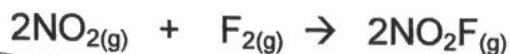
(c) What is the molecularity of each elementary step?

Step 1: bimolecular step
Step 2: bimolecular step

(d) Based on the mechanism, what is the expected rate law?



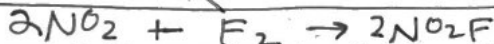
Sample Problem 5. The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is



The experimentally determined rate law is

$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$

A suggested mechanism for this reaction is

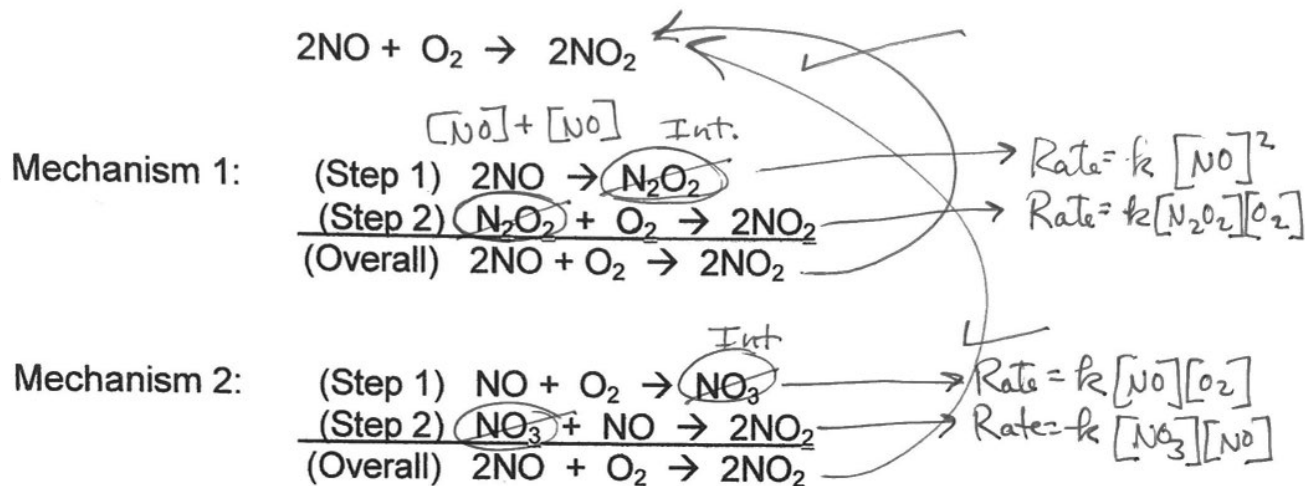


Rate = $k[\text{NO}_2][\text{F}_2]$
based on
molecularity

Is this an acceptable mechanism? Does it meet the two requirements? Explain.

The Steady-State Assumption

Sometimes a reaction may have two possible mechanisms as in the case of the reaction below. When this is the case, how do you determine which mechanism is the most probable?



Both reactions pass the first test – they “add up” to the overall reaction.

Next, determine the rate law for each elementary step. Remember, the rate law is related to the molecularity of the step.

Mechanism 1:

- (1) Rate = $k[\text{NO}]^2$
 (2) Rate = $k[\text{N}_2\text{O}_2][\text{O}_2]$

Mechanism 2:

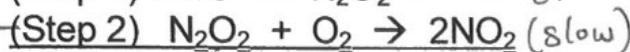
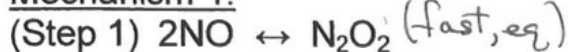
- (1) Rate = $k[\text{NO}][\text{O}_2]$
 (2) Rate = $k[\text{NO}_3][\text{NO}]$

If Step 1 is the rate-determining step, the decision is clear cut because the mechanisms give different rate laws. Remember, the overall rate law and the rate law for the rate-determining step are the same.

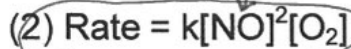
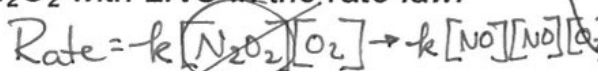
If Step 2 is the rate-determining step, then we must use the steady-state assumption to rewrite these rate laws in terms of measurable reactants. (The second step in each mechanism contains an intermediate product and you cannot use a rate law that contains intermediates.) *If Step 2 is the rate-determining step, then we assume that Step 1 is fast and reversible.*

Rewriting Step 1 for each mechanism gives:

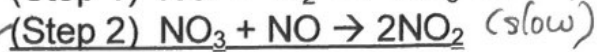
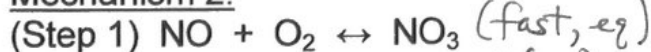
Mechanism 1:



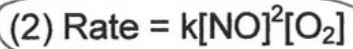
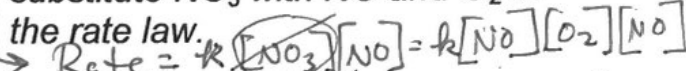
In mechanism 1, it "looks like" 2NO is combining directly with O_2 . Therefore, we can substitute N_2O_2 with 2NO in the rate law.



Mechanism 2:



In mechanism 2, it "looks like" NO and O_2 are combining directly with NO . Therefore, we can substitute NO_3 with NO and O_2 in the rate law.



If Step 2 is the rate-determining step, both mechanisms yield the same rate law. To determine which mechanism is correct, additional experiments must be designed to identify the intermediate, NO_3 or N_2O_5 , that is formed during the reaction.

Stop

Collision Theory and Reaction Profile

- Collision theory states that the frequency of effective collisions between reactants determines the rate of the reaction.
- For a collision to be effective, the molecules must collide with (1) sufficient energy and (2) the proper orientation so that products can form.
- As molecules approach on a collision course, they do not act like billiard balls simply bouncing off each other. Instead, as the molecules get closer, their orbitals interact and distort each other. This distortion weakens bonds within the molecules so that at the moment of collision some bonds are so weak that they break and new bonds may form.
- Activated complex is the term given to the molecules at the moment of collision. You can think of the activated complex as no longer reactants, but not yet product – bonds are partially broken and partially formed. This is a very high energy state.