ZAPOROZHYE STATE MEDICAL UNIVERSITY

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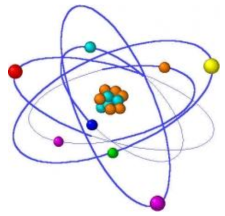
CHEMICAL KINETICS

Teaching and methodical manual
for foreign student



Zaporozhye, 2016

ЗАПОРІЗЬКИЙ ДЕРЖАВНИЙ МЕДИЧНИЙ УНІВЕРСИТЕТ

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ХІМІЧНА КІНЕТИКА

Навчально-методичний посібник для студентів англомовної форми навчання

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Навчальний посібник розглянуто та затверджено:

Цикловою методичною комісією з фармацевтичних дисциплін
(протокол №__ від ________р.),
Центральною методичною радою ЗДМУ
(протокол №__ від ________р.)

CONTENTS

PREFACE

Medicinal Chemistry is one of the most rapidly developing areas within the discipline of Chemistry, both globally and locally. It is the study of the design, biochemical effects, regulatory and ethical aspects of drugs for the treatment of disease.

The aim of this discipline is to produce graduates with an appropriate background in biology and pharmacology, built upon a strong chemistry foundation.

Methodical recommendation of Medicinal Chemistry is designed to equip students with strong grounding in biological and chemical technique which is relevant to the pharmaceutical world.

The discipline gives an in-depth coverage of the chemical techniques required and relates these to the relevant pharmacology, anatomy, biochemistry and molecular biology.

The whole course of Medical chemistry which consists of ten topics is studied by students-physicians during the first year. Lecturer staff of department has prepared an educational and methodical recommendation in which the theoretical material is stated in the concise and available form.

The distribution of material on each of ten topics that are studied is set according to training program, the thematic plan of lectures and practical training.

The material of each topic is stated in such way that performance of practical work and the solution of situational tasks are preceded by theoretical part in which questions of medicine and biological value and also connection with other disciplines (biological chemistry, normal physiology, pathophysiology and others) are included.

Offered laboratory works and situational tasks will give students the chance to understand theoretical material fully and to use this knowledge in practice.

The experience of teaching medical chemistry shows that it is not always possible to coordinate an order of laboratory works realization with sequence of lecture course statement. That is why students usually have to prepare for practical work performance independently before the lesson. Therefore the theoretical part (in which the necessary volume of knowledge for conscious performance of experiment is given) precedes to each section of these Methodical recommendations.

Increasing of level of seminar and laboratory works is reached by use of such forms of occupations which open and consolidate theoretical knowledge, train scientific thinking, develop creative initiative and impart skills of handling devices and chemicals, chemical ware.

The structures, figures and schemes are clear and easy to follow and color is used well, highlighting main points without being distracting.

Chapters are helpfully signposted throughout, informing the reader how topics are related, which is especially important in such a multidisciplinary subject.

Topics are also presented clearly and with a logical progression culminating in the main points, questions and reading sections at the beginning of each chapter.

An assortment of case studies is provided and the authors work through each one in great detail, giving an overall perspective on the science.

Finally, very useful and informative appendices and a glossary are provided together with a comprehensive index that is good enough to rival any search engine!

There are many books that describe medicinal chemistry and its uses, but these methodological recommendations present medicinal chemistry and its related topics in a clear, informative and interesting way that really demonstrates the application and impact of this fundamental subject in society.

INTRODUCTION

Targets:

- The expressions of rate of reaction and types of rates;
- Stoichiometric relationships between the rates of appearance or disappearance of components in a given reaction;
- Determination of rate orders and rate law using the kinetic data of a reaction;
- The graphical method to determine a first-order and second-order reaction.
- The meaning and calculation half-life of a first order reaction;
- Determination of the activation energy, E_a, either graphically or from rate constants at different temperatures.
- Derive rate law from reaction mechanism.
- The role of catalyst
- Homogenous and heterogeneous catalyst

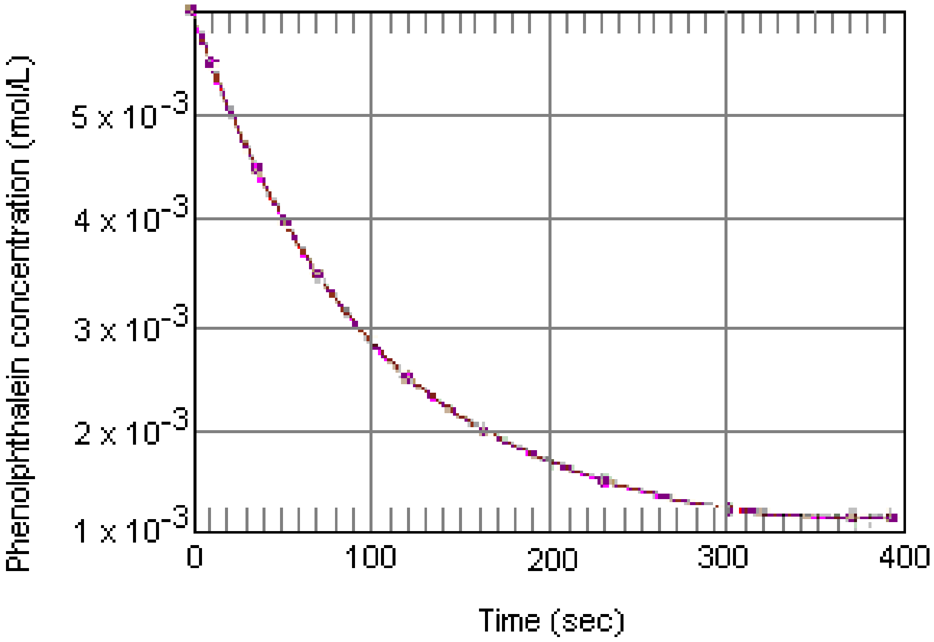
CONCISE THEORETICAL MATERIAL

Chemical Kinetics is *the study of reaction rates*; that is, how fast a given reaction does proceeds. It is a measure of the change of the concentration of reactants (or products) as a function of time.

Reaction rates provide information regarding how fast a chemical process occurs as well as the mechanism by which a reaction occurs at molecular level.

You may be familiar with acid-base titrations that use phenolphthalein as the endpoint indicator. You might not have noticed, however, what happens when a solution that contains phenolphthalein in the presence of excess base is allowed to stand for a few minutes. Although the solution initially has a pink color, it gradually turns colorless as the phenolphthalein reacts with the OH^- ion in a strongly basic solution.

The table below shows what happens to the concentration of phenolphthalein in a solution that was initially 0.005 M in phenolphthalein and 0.61 M in OH^- ion. As you can see when these data are plotted in the graph below, the phenolphthalein concentration decreases by a factor of 10 over a period of about four minutes.



Experimental Data

for the Reaction Between Phenolphthalein and Excess Base

Concentration of Phenolphthalein (M)	*Time (s)*
0.0050	0.0
0.0045	10.5
0.0040	22.3
0.0035	35.7
0.0030	51.1
0.0025	69.3
0.0020	91.6
0.0015	120.4
0.0010	160.9
0.00050	230.3
0.00025	299.6
0.00015	350.7
0.00010	391.2

Experiments such as the one that gave us the data in the above table are classified as measurements of chemical kinetics (from a Greek stem meaning "to move"). One of the goals of these experiments is to describe the rate of reaction — the rate at which the reactants are transformed into the products of the reaction.

The term *rate* is often used to describe the change in a quantity that occurs per unit of time. The rate of inflation, for example, is the change in the average cost of a collection of standard items per year.

The rate at which an object travels through space is the distance traveled per unit of time, such as miles per hour or kilometers per second. In chemical kinetics, the distance traveled is the change in the concentration of one of the components of the reaction.

The rate of a reaction is therefore the change in the concentration of one of the reactants — $\Delta(X)$ — that occurs during a given period of time — Δt.

$$Rate\ of\ reaction = \frac{\Delta\ X}{\Delta\ t}$$

1. Instantaneous Rates of Reaction and the Rate Law for a Reaction

The rate of the reaction between phenolphthalein and the OH^- ion isn't constant; it changes with time.

Like most reactions, the rate of this reaction gradually decreases as the reactants are consumed. This means that the rate of reaction changes while it is being measured.

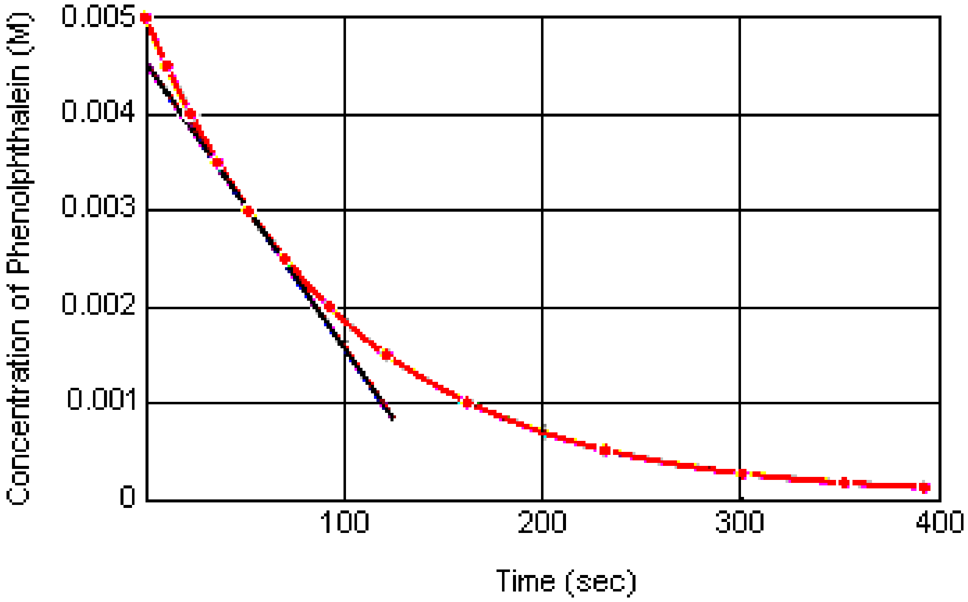
To minimize the error this introduces into our measurements, it seems advisable to measure the rate of reaction over periods of time that are short compared with the time it takes for the reaction to occur.

We might try, for example, to measure the infinitesimally small change in concentration — $d(X)$ — that occurs over an infinitesimally short period of time — dt. The ratio of these quantities is known as the instantaneous rate of reaction.

$$Rate = \frac{d(X)}{dt}$$

The instantaneous rate of reaction at any moment in time can be calculated from a graph of the concentration of the reactant (or product) versus time.

The graph below shows how the rate of reaction for the decomposition of phenolphthalein can be calculated from a graph of concentration versus time. The rate of reaction at any moment in time is equal to the slope of a tangent drawn to this curve at that moment.



The instantaneous rate of reaction can be measured at any time between the moment at which the reactants are mixed and the reaction reaches equilibrium.

Extrapolating these data back to the instant at which the reagents are mixed gives the *initial instantaneous rate of reaction*.

2. Rate Laws and Rate Constants

An interesting result is obtained when the instantaneous rate of reaction is calculated at various points along the curve in the graph in the previous section. The rate of reaction at every point on this curve is directly proportional to the concentration of phenolphthalein at that moment in time.

Rate = k(phenolphthalein)

Because this equation is an experimental law that describes the rate of the reaction, it is called the rate law for the reaction. The proportionality constant, *k*, is known as the rate constant.

3. Different Ways of Expressing the Rate of Reaction

There is usually more than one way to measure the rate of a reaction. We can study the decomposition of hydrogen iodide, for example, by measuring the rate at which either H_2 or I_2 is formed in the following reaction or the rate at which HI is consumed.

$$2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Experimentally we find that the rate at which I_2 is formed is proportional to the square of the HI concentration at any moment in time.

$$\frac{d(I_2)}{dt} = k\ (HI)^2$$

What would happen if we studied the rate at which H_2 is formed? The balanced equation suggests that $H_2$and I_2 must be formed at exactly the same rate.

$$\frac{d(H_2)}{dt} = \frac{d(I_2)}{dt}$$

What would happen, however, if we studied the rate at which HI is consumed in this reaction? Because HI is consumed, the change in its concentration must be a negative number. By convention, the rate of a reaction is always reported as a positive number. We therefore have to change the sign before reporting the rate of reaction for a reactant that is consumed in the reaction.

$$-\frac{d(HI)}{dt} = k'\ (HI)^2$$

The negative sign does two things.

- ✓ Mathematically, it converts a negative change in the concentration of HI into a positive rate.
- ✓ Physically, it reminds us that the concentration of the reactant decreases with time.

What is the relationship between the rate of reaction obtained by monitoring the formation of H_2 or I_2 and the rate obtained by watching HI disappear?

The stoichiometry of the reaction says that two HI molecules are consumed for every molecule of H_2 or I_2 produced. This means that the rate of decomposition of HI is twice as fast as the rate at which H_2 and I_2 are formed.

We can translate this relationship into a mathematical equation as follows.

$$-\frac{d(HI)}{dt} = 2[\frac{d(H_2)}{dt}] = 2[\frac{d(I_2)}{dt}]$$

As a result, the rate constant obtained from studying the rate at which H_2 and I_2 are formed in this reaction (k) is not the same as the rate constant obtained by monitoring the rate at which HI is consumed (k')

4. The Rate Law Versus the Stoichiometry of a Reaction

In the 1930s, Sir Christopher Ingold and coworkers at the University of London studied the kinetics of substitution reactions such as the following.

$CH_3Br(aq) + OH^-(aq) \rightleftharpoons CH_3OH(aq) + Br^-(aq)$

They found that the rate of this reaction is proportional to the concentrations of both reactants.

Rate = $k(CH_3Br)(OH^-)$

When they ran a similar reaction on a slightly different starting material, they got similar products.

$(CH_3)_3CBr(aq) + OH^-(aq) \rightleftharpoons (CH_3)_3COH(aq) + Br^-(aq)$

But now the rate of reaction was proportional to the concentration of only one of the reactants.

Rate = $k((CH_3)_3CBr)$

These results illustrate an important point: The rate law for a reaction cannot be predicted from the stoichiometry of the reaction; it must be determined experimentally. Sometimes, the rate law is consistent with what we expect from the stoichiometry of the reaction.

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

Rate = $k(HI)^2$

Often, however, it is not.

$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

Rate = $k(N_2O_5)$

5. Order of Molecularity

Some reactions occur in a single step. The reaction in which a chlorine atom is transferred from $ClNO_2$ to NO to form NO_2 and ClNO is a good example of a one-step reaction.

$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$

Other reactions occur by a series of individual steps. N_2O_5, for example, decomposes to NO_2 and O_2 by a three-step mechanism.

Step 1:

$N_2O_5 \rightleftharpoons NO_2 + NO_3$

Step 2:

$NO_2 + NO_3 \rightleftharpoons NO_2 + NO + O_2$

Step 3:

$NO + NO_3 \rightleftharpoons 2\ NO_2$

The steps in a reaction are classified in terms of molecularity, which describes the number of molecules consumed. When a single molecule is consumed, the step is called unimolecular. When two molecules are consumed, it is bimolecular.

Reactions can also be classified in terms of their order. The decomposition of N_2O_5 is a first-order reaction because the rate of reaction depends on the concentration of N_2O_5 raised to the first power.

Rate = $k(N_2O_5)$

The decomposition of HI is a second-order reaction because the rate of reaction depends on the concentration of HI raised to the second power.

Rate = $k(HI)^2$

When the rate of a reaction depends on more than one reagent, we classify the reaction in terms of the order of each reagent.

The difference between the molecularity and the order of a reaction is important. The molecularity of a reaction, or a step within a reaction, describes what happens on the molecular level.

The order of a reaction describes what happens on the macroscopic scale. We determine the order of a reaction by watching the products of a reaction appear or the reactants disappear.

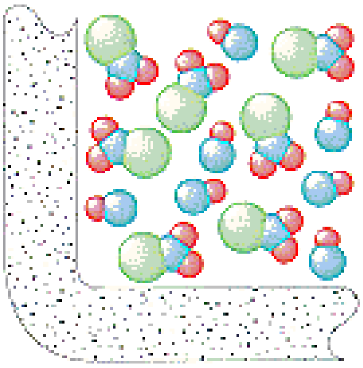
The molecularity of the reaction is something we deduce to explain these experimental results.

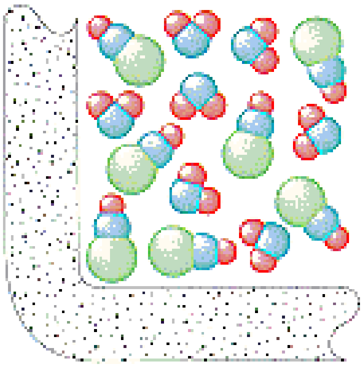
6. Collision Theory Model of Chemical Reactions

The collision theory model of chemical reactions can be used to explain the observed rate laws for both one-step and multi-step reactions. This model assumes that the rate of any step in a reaction depends on the frequency of collisions between the particles involved in that step.

The figure below provides a basis for understanding the implications of the collision theory model for simple, one-step reactions, such as the following.

$$\mathrm{ClNO_2}(g) + \mathrm{NO}(g) \rightleftharpoons \mathrm{NO_2}(g) + \mathrm{ClNO}(g)$$





The kinetic molecular theory assumes that the number of collisions per second in a gas depends on the number of particles per liter. The rate at which NO_2 and ClNO are formed in this reaction should therefore be directly proportional to the concentrations of both $ClNO_2$ and NO.

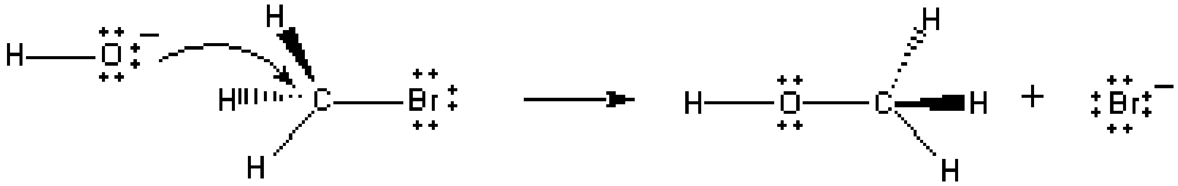
Rate = $k(ClNO_2)(NO)$

The collision theory model suggests that the rate of any step in a reaction is proportional to the concentrations of the reagents consumed in that step. The rate law for a one-step reaction should therefore agree with the stoichiometry of the reaction.

The following reaction, for example, occurs in a single step.

$CH_3Br(aq) + OH^-(aq) \rightleftharpoons CH_3OH(aq) + Br^-(aq)$

When these molecules collide in the proper orientation, a pair of nonbonding electrons on the OH^- ion can be donated to the carbon atom at the center of the CH_3Br molecule, as shown in the figure below.



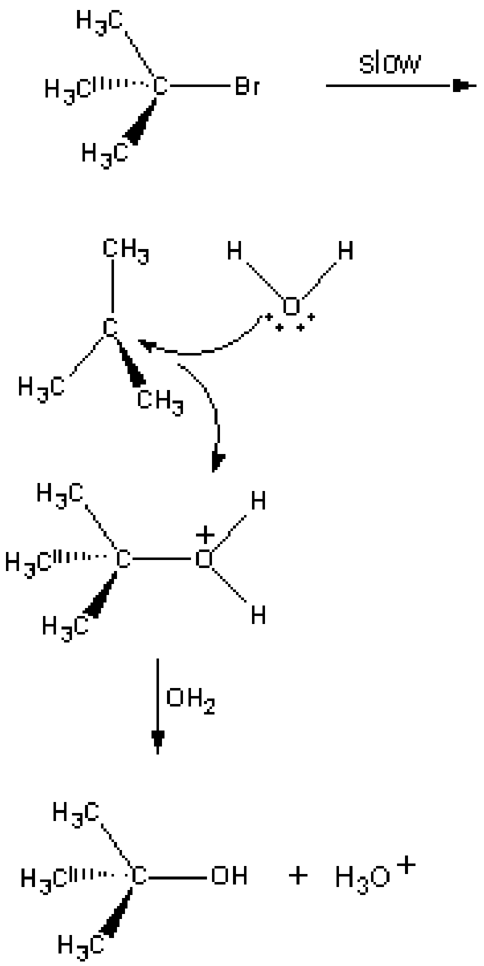
When this happens, a carbon-oxygen bond forms at the same time that the carbon-bromine bond is broken.

The net result of this reaction is the substitution of an OH^- ion for a Br^- ion. Because the reaction occurs in a single step, which involves collisions between the two reactants, the rate of this reaction is proportional to the concentration of both reactants.

Rate = $k(CH_3Br)(OH^-)$

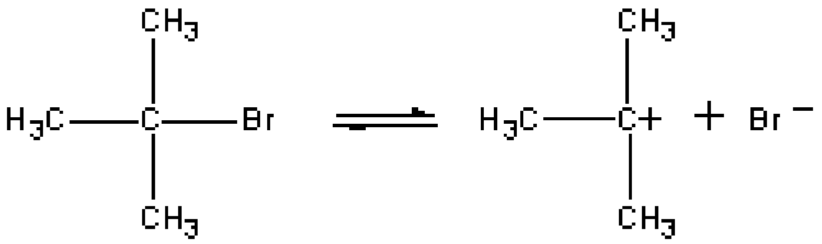
Not all reactions occur in a single step. The following reaction occurs in three steps, as shown in the figure below.

$(CH_3)_3CBr(aq) + OH^-(aq) \rightleftharpoons (CH_3)_3COH(aq) + Br^-(aq)$



In the first step, the $(CH_3)_3CBr$ molecule dissociates into a pair of ions.

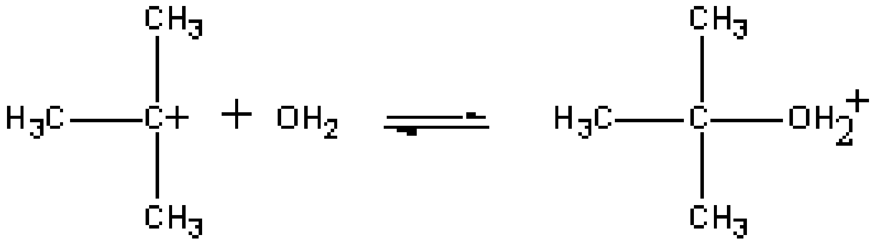
First step



$$H_3C-C(CH_3)_2-Br \rightleftharpoons H_3C-C^+(CH_3)_2 + Br^-$$

The positively charged $(CH_3)_3C^+$ ion then reacts with water in a second step.

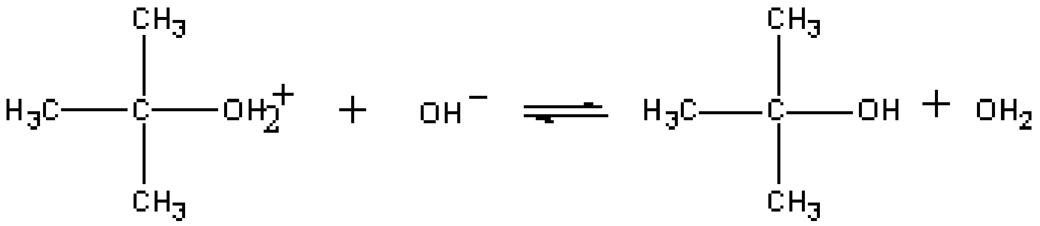
Second step



$$H_3C-C^+(CH_3)_2 + OH_2 \rightleftharpoons H_3C-C(CH_3)_2-OH_2^+$$

The product of this reaction then loses a proton to either the OH^- ion or water in the final step.

Third step



The second and third steps in this reaction are very much faster than first.

Slow step

$(CH_3)_3CBr \rightleftharpoons (CH_3)_3C^+ + Br^-$

Fast step

$(CH_3)_3C^+ + H_2O \rightleftharpoons (CH_3)_3COH_2{}^+$

Fast step

$(CH_3)_3COH_2{}^+ + OH^- \rightleftharpoons (CH_3)_3COH + H_3O$

The overall rate of reaction is therefore more or less equal to the rate of the first step. The first step is therefore called the rate-limiting step in this reaction because it literally limits the rate at which the products of the reaction can be formed. Because only one reagent is involved in the rate-limiting step, the overall rate of reaction is proportional to the concentration of only this reagent.

Rate = $k((CH_3)_3CBr)$

The rate law for this reaction therefore differs from what we would predict from the stoichiometry of the reaction. Although the reaction consumes both $(CH_3)_3CBr$ and OH^-, the rate of the reaction is only proportional to the concentration of $(CH_3)_3CBr$.

The rate laws for chemical reactions can be explained by the following general rules.

- The rate of any step in a reaction is directly proportional to the concentrations of the reagents consumed in that step.

- The overall rate law for a reaction is determined by the sequence of steps, or the mechanism, by which the reactants are converted into the products of the reaction.
- The overall rate law for a reaction is dominated by the rate law for the slowest step in the reaction.

7. The Mechanisms of Chemical Reactions

What happens when the first step in a multi-step reaction is not the rate-limiting step? Consider the reaction between NO and O_2 to form NO_2, for example.

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

This reaction involves a two-step mechanism. The first step is a relatively fast reaction in which a pair of NO molecules combine to form a dimer, N_2O_2. The product of this step then undergoes a much slower reaction in which it combines with O_2 to form a pair of NO_2 molecules.

Step 1: $2\ NO \rightleftharpoons N_2O_2$ (fast step)

Step 2: $N_2O_2 + O_2 \rightleftharpoons 2\ NO_2$ (slow step)

The net effect of these reactions is the transformation of two NO molecules and one O_2 molecule into a pair of NO_2 molecules.

$$2\ NO \rightleftharpoons \cancel{N_2O_2}$$

$$\cancel{N_2O_2} + O_2 \rightleftharpoons 2\ NO_2$$

$$\overline{\qquad\qquad\qquad\qquad}$$

$$2\ NO + O_2 \rightleftharpoons 2\ NO_2$$

In this reaction, the second step is the rate-limiting step. No matter how fast the first step takes place, the overall reaction cannot proceed any faster than the second step in the reaction. As we have seen, the rate of any step in a reaction is directly proportional to the concentrations of the reactants consumed in that step. The rate law for the second step in this reaction is therefore proportional to the concentrations of both N_2O_2 and O_2.

Step 2: $Rate_{2nd} = k(N_2O_2)(O_2)$

Because the first step in the reaction is much faster, the overall rate of reaction is more or less equal to the rate of this rate-limiting step.

Rate $\approx k(N_2O_2)(O_2)$

This rate law is not very useful because it is difficult to measure the concentrations of intermediates, such as N_2O_2, that are simultaneously formed and consumed in the reaction. It would be better to have an equation that related the overall rate of reaction to the concentrations of the original reactants.

Let's take advantage of the fact that the first step in this reaction is reversible.

Step 1: $2\ NO \rightleftharpoons N_2O_2$

The rate of the forward reaction in this step depends on the concentration of NO raised to the second power.

Step 1: $Rate_{forward} = k_f(NO)^2$

The rate of the reverse reaction depends only on the concentrations of N_2O_2.

Step 1: $Rate_{reverse} = k_r(N_2O_2)$

Because the first step in this reaction is very much faster than the second, the first step should come to equilibrium. When that happens, the rate of the forward and reverse reactions for the first step are the same.

$k_f(NO)^2 = k_r(N_2O_2)$

Let's rearrange this equation to solve for one of the terms that appears in the rate law for the second step in the reaction.

$(N_2O_2) = (k_f/k_r)\ (NO)^2$

Substituting this equation into the rate law for the second step gives the following result.

$\text{Rate}_{2nd} = k\,(k_f/k_r)\,(NO)^2(O_2)$

Since k, k_f, and k_r are all constants, they can be replaced by a single constant, k', to give the experimental rate law for this reaction described in Exercise 22.6.

$\text{Rate}_{overall} \approx \text{Rate}_{2nd} = k'(NO)^2(O_2)$

8. The Relationship Between the Rate Constants and the Equilibrium Constant for a Reaction

There is a simple relationship between the equilibrium constant for a reversible reaction and the rate constants for the forward and reverse reactions if the mechanism for the reaction involves only a single step. To understand this relationship, let's turn once more to a reversible reaction that we know occurs by a one-step mechanism.

$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$

The rate of the forward reaction is equal to a rate constant for this reaction, k_f, times the concentrations of the reactants, $ClNO_2$ and NO.

$\text{Rate}_{forward} = k_f(ClNO_2)(NO)$

The rate of the reverse reaction is equal to a second rate constant, k_r, times the concentrations of the products, NO_2 and ClNO.

$\text{Rate}_{reverse} = k_r(NO_2)(ClNO)$

This system will reach equilibrium when the rate of the forward reaction is equal to the rate of the reverse reaction.

$\text{Rate}_{forward} = \text{Rate}_{reverse}$

Substituting the rate laws for the forward and reverse reactions when the system is at equilibrium into this equation gives the following result.

$k_f[NO][ClNO_2] = k_r[ClNO][NO_2]$

This equation can be rearranged to give the equilibrium constant expression for the reaction.

$$\frac{k_f}{k_r} = \frac{[ClNO][NO_2]}{[NO][ClNO_2]}$$

Thus, the equilibrium constant for a one-step reaction is equal to the forward rate constant divided by the reverse rate constant.

$$K_c = \frac{k_f}{k_r}$$

9. Determining the Order of a Reaction from Rate of Reaction Data

The rate law for a reaction can be determined by studying what happens to the initial instantaneous rate of reaction when we start with different initial concentrations of the reactants. To show how this is done, let's determine the rate law for the decomposition of hydrogen peroxide in the presence of the iodide ion.

$$2\ H_2O_2(aq) \xrightarrow{I^-} 2\ H_2O(aq) + O_2(g)$$

Data on initial instantaneous rates of reaction for five experiments run at different initial concentrations of H_2O_2 and the I^- ion are given in the table below.

Rate of Reaction Data for the Decomposition of H_2O_2 in the Presence of the I^- Ion

	Initial (H_2O_2) (M)	Initial (I^-) (M)	Initial Instantaneous Rate of Reaction (M/s)
Trial 1:	1.0×10^{-2}	2.0×10^{-3}	2.3×10^{7}
Trial 2:	2.0×10^{-2}	2.0×10^{-3}	4.6×10^{7}
Trial 3:	3.0×10^{-2}	2.0×10^{-3}	6.9×10^{7}

Trial 4:	1.0 x 10^{-2}	4.0 x 10^{-3}	4.6 x 10^{7}
Trial 5:	1.0 x 10^{-2}	6.0 x 10^{-3}	6.9 x 10^{7}

The only difference between the first three trials is the initial concentration of H_2O_2. The difference between Trial 1 and Trial 2 is a two-fold increase in the initial H_2O_2 concentration, which leads to a two-fold increase in the initial rate of reaction.

$$\frac{Rate\ \ for\ \ trial\ \ 2}{Rate\ \ for\ \ trial\ \ 1} = \frac{4.6\ \text{x}\ 10^{-7}\ M/s}{2.3\ \text{x}\ 10^{-7}\ M/s} = 2$$

The difference between Trial 1 and Trial 3 is a three-fold increase in the initial H_2O_2 concentration, which produces a three-fold increase in the initial rate of reaction.

$$\frac{Rate\ \ for\ \ trial\ \ 3}{Rate\ \ for\ \ trial\ \ 1} = \frac{6.9\ \text{x}\ 10^{-7}\ M/s}{2.3\ \text{x}\ 10^{-7}\ M/s} = 3$$

The only possible conclusion is that the rate of reaction is directly proportional to the H_2O_2 concentration.

Experiments 1, 4, and 5 were run at the same initial concentration of H_2O_2 but different initial concentrations of the I^- ion. When we compare Trials 1 and 4 we see that doubling the initial I^-concentration leads to a twofold increase in the rate of reaction.

$$\frac{Rate\ \ for\ \ trial\ \ 4}{Rate\ \ for\ \ trial\ \ 1} = \frac{4.6\ \text{x}\ 10^{-7}\ M/s}{2.3\ \text{x}\ 10^{-7}\ M/s} = 2$$

Trials 1 and 5 show that tripling the initial I^- concentration leads to a three-fold increase in the initial rate of reaction. We therefore conclude that the rate of the reaction is also directly proportional to the concentration of the I^- ion.

The results of these experiments are consistent with a rate law for this reaction that is first-order in both H_2O_2 and I^-.

Rate = $k(H_2O_2)(I^-)$

10.The Integrated Form of First-Order and Second-Order Rate Laws

The rate law for a reaction is a useful way of probing the mechanism of a chemical reaction but it isn't very useful for predicting how much reactant remains in solution or how much product has been formed in a given amount of time. For these calculations, we use the integrated form of the rate law.

Let's start with the rate law for a reaction that is first-order in the disappearance of a single reactant, X.

$$-\frac{d(X)}{dt} = k(X)$$

When this equation is rearranged and both sides are integrated we get the following result.

Integrated form of the first-order rate law:

$$\ln[\frac{(X)}{(X)_0}] = -kt$$

In this equation, (X) is the concentration of X at any moment in time, $(X)_0$ is the initial concentration of this reagent, k is the rate constant for the reaction, and t is the time since the reaction started.

To illustrate the power of the integrated form of the rate law for a reaction, let's use this equation to calculate how long it would take for the ^{14}C in a piece of charcoal to decay to half of its original concentration. We will start by noting that ^{14}C decays by first-order kinetics with a rate constant of 1.21×10^{-4} yr^{-1}.

$$-\frac{d(^{14}C)}{dt} = k(^{14}C)$$

The integrated form of this rate law would be written as follows.

$$\ln[\frac{(^{14}C)}{(^{14}C)_0}] = -kt$$

We are interested in the moment when the concentration of ^{14}C in the charcoal is half of its initial value.

$$({}^{14}C) = 1/2\ ({}^{14}C)_o$$

Substituting this relationship into the integrated form of the rate law gives the following equation.

$$\ln\left[\frac{1/2\ ({}^{14}C)}{({}^{14}C)_o}\right] = -kt$$

We now simplify this equation

$$\ln\ [1/2] = -kt$$

and then solve for t.

$$t = \frac{\ln(1/2)}{k} = \frac{0.693}{1.21\ x\ 10^{-4}\ y^{-1}} = 5730\ y$$

It therefore takes 5730 years for half of the ${}^{14}C$ in the sample to decay. This is called the half-life of ${}^{14}C$. In general, the half-life for a first-order kinetic process can be calculated from the rate constant as follows.

$$t_{1/2} = -\frac{\ln(1/2)}{k} = \frac{0.693}{k}$$

Let's now turn to the rate law for a reaction that is second-order in a single reactant, X.

$$-\frac{d(X)}{dt} = k(X)^2$$

The integrated form of the rate law for this reaction is written as follows.

Integrated form of the second-order rate law:

$$\frac{1}{(X)} - \frac{1}{(X)_o} = kt$$

Once again, (X) is the concentration of X at any moment in time, $(X)_0$ is the initial concentration of X, k is the rate constant for the reaction, and t is the time since the reaction started.

The half-life of a second-order reaction can be calculated from the integrated form of the second-order rate law.

$$\frac{1}{(X)} - \frac{1}{(X)_o} = kt$$

We start by asking: "How long it would take for the concentration of X to decay from its initial value, $(X)_0$, to a value half as large?"

$$\frac{1}{1/2\ (X)_o} - \frac{1}{(X)_o} = kt_{1/2}$$

The first step in simplifying this equation involves multiplying the top and bottom halves of the first term by 2.

$$\frac{2}{(X)_o} - \frac{1}{(X)_o} = kt_{1/2}$$

Subtracting one term on the left side of this equation from the other gives the following result.

$$\frac{1}{(X)_o} = kt_{1/2}$$

We can now solve this equation for the half-life of the reaction.

$$t_{1/2} = \frac{1}{k(X)_o}$$

There is an important difference between the equations for calculating the half-life of first order and second-order reactions. The half-life of a first-order reaction is a constant, which is proportional to the rate constant for the reaction.

first-order reaction:

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

The half-life for a second-order reaction is inversely proportional to both the rate constant for the reaction and the initial concentration of the reactant that is consumed in the reaction.

second-order reaction:

$$t_{1/2} = \frac{1}{k(X)_o}$$

Discussions of the half-life of a reaction are therefore usually confined to first-order processes.

11.Determining the Order of a Reaction with the Integrated form of Rate Laws

The integrated form of the rate laws for first- and second-order reactions provides another way of determining the order of a reaction. We can start by assuming, for the sake of argument, that the reaction is first-order in reactant X.

Rate = k(X)

We then test this assumption by checking concentration versus time data for the reaction to see whether they fit the first-order rate law.

$$\ln\left[\frac{(X)}{(X)_o}\right] = -kt$$

To see how this is done, let's start by rearranging the integrated form of the first-order rate law as follows.

$\ln (X) - \ln (X)_0 = - kt$

We then solve this equation for the natural logarithm of the concentration of X at any moment in time.

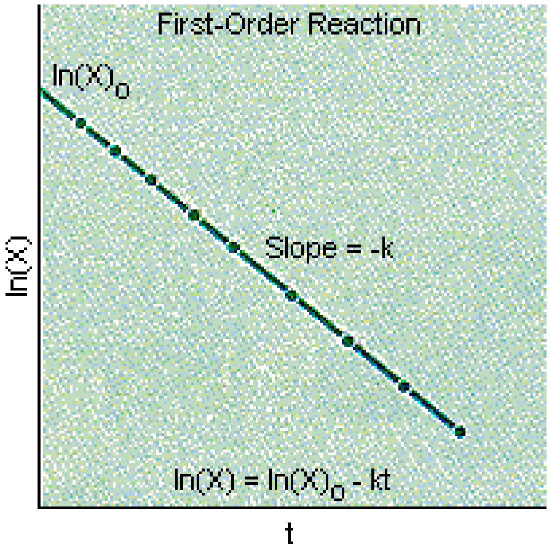
$\ln (X) = \ln (X)_0 - kt$

This equation contains two variables — ln (X) and t — and two constants — ln $(X)_0$ and k. It can therefore be set up in terms of the equation for a straight line.

$y = mx + b$

$\ln (X) = -kt + \ln (X)_0$

If the reaction is first-order in X, a plot of the natural logarithm of the concentration of X versus time will be a straight line with a slope equal to -k, as shown in the figure below.



If the plot of ln (X) versus time is not a straight line, the reaction can't be first-order in X. We therefore assume, for the sake of argument, that it is second-order in X.

Rate = k$(X)^2$

We then test this assumption by checking whether the experimental data fit the integrated form of the second-order rate law.

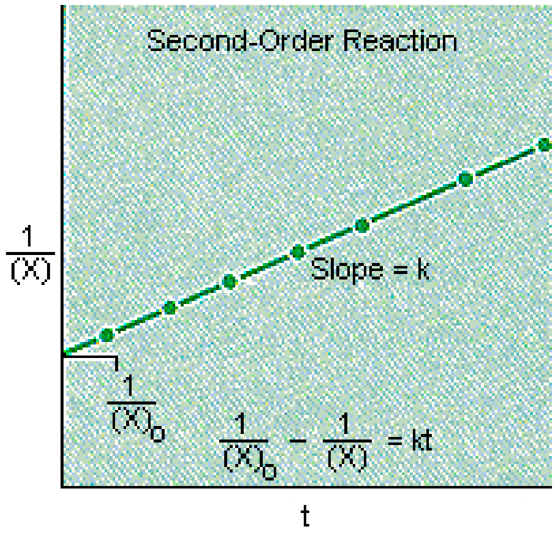
$$\frac{1}{(X)} - \frac{1}{(X)_o} = kt$$

This equation contains two variables — (X) and t — and two constants — $(X)_0$ and k. Thus, it also can be set up in terms of the equation for a straight line.

y = mx + b

$$\frac{1}{(X)} = kt + \frac{1}{(X)_o}$$

If the reaction is second-order in X, a plot of the reciprocal of the concentration of X versus time will be a straight line with a slope equal to k, as shown in the figure below.



12. Reactions That are First-Order in Two Reactants

What about reactions that are first-order in two reactants, X and Y, and therefore second-order overall?

Rate = k(X)(Y)

A plot of 1/(X) versus time won't give a straight line because the reaction is not second-order in X. Unfortunately, neither will a plot of ln (X) versus time, because the reaction is not strictly first-order in X. It is first-order in both X and Y.

One way around this problem is to turn the reaction into one that is pseudofirst-order by making the concentration of one of the reactants so large that it is effectively constant. The rate law for the reaction is still first-order in both reactants. But the initial concentration of one reactant is so much larger than the other that the rate of reaction seems to be sensitive only to changes in the concentration of the reagent present in limited quantities.

Assume, for the moment, that the reaction is studied under conditions for which there is a large excess ofY. If this is true, the concentration of Y will remain essentially constant during the reaction. As a result, the rate of the reaction will not depend on the concentration of the excess reagent. Instead, it will appear to be first order in the other reactant, X. A plot of ln (X) versus time will therefore give a straight line.

Rate = k'(X)

If there is a large excess of X, the reaction will appear to be first-order in Y. Under these conditions, a plot of log (Y) versus time will be linear.

Rate = k'(Y)

The value of the rate constant obtained from either of these equations – k' – won't be the actual rate constant for the reaction. It will be the product of the rate constant for the reaction times the concentration of the reagent that is present in excess.

In our discussion of acid-base equilibria, we argued that the concentration of water is so much larger than any other component of these solutions that we can build it into the equilibrium constant expression for the reaction.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

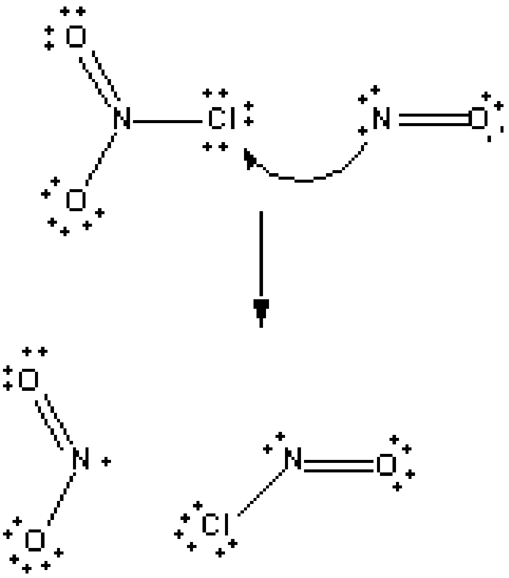
We now understand why this is done. Because the concentration of water is so large, the reaction between an acid or a base and water is a pseudo-first-order reaction that only depends on the concentration of the acid or base.

13. The Activation Energy of Chemical Reactions

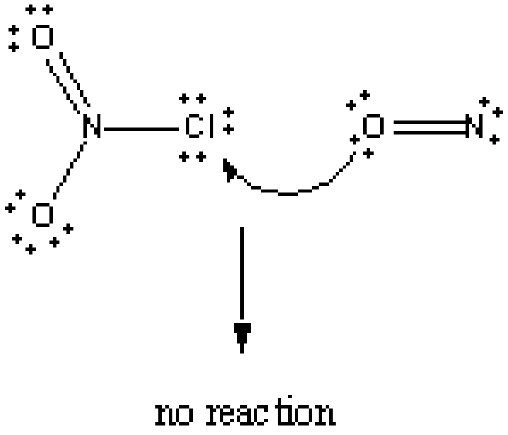
Only a small fraction of the collisions between reactant molecules convert the reactants into the products of the reaction. This can be understood by turning, once again, to the reaction between $ClNO_2$ and NO.

$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$

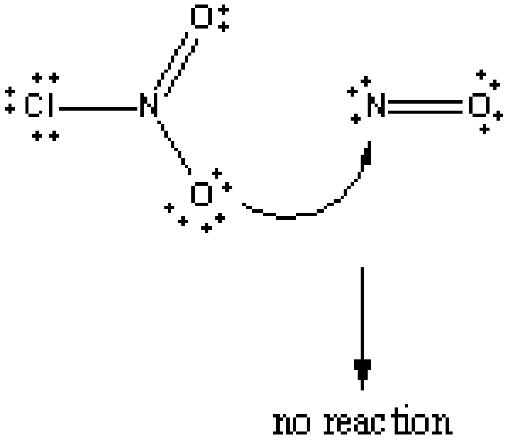
In the course of this reaction, a chlorine atom is transferred from one nitrogen atom to another. In order for the reaction to occur, the nitrogen atom in NO must collide with the chlorine atom in $ClNO_2$.



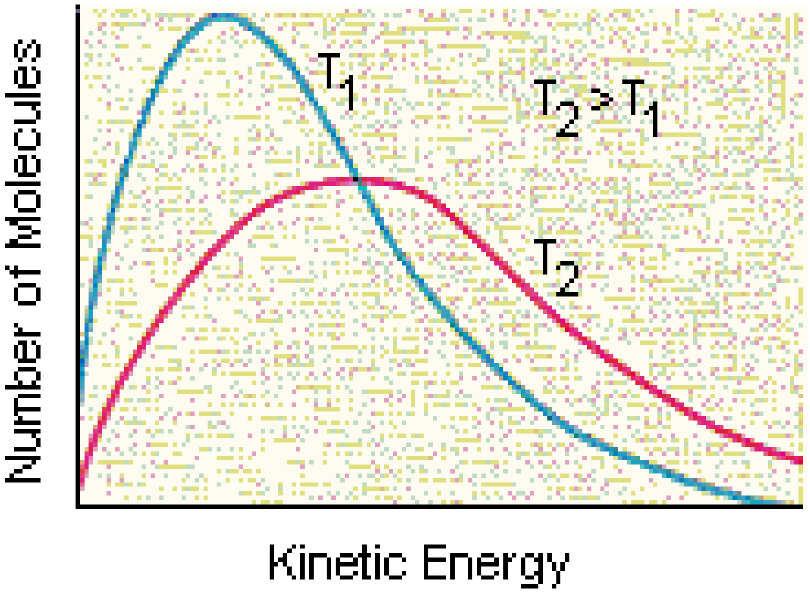
Reaction won't occur if the oxygen end of the NO molecule collides with the chlorine atom on $ClNO_2$.



Nor will it occur if one of the oxygen atoms on $ClNO_2$ collides with the nitrogen atom on NO.



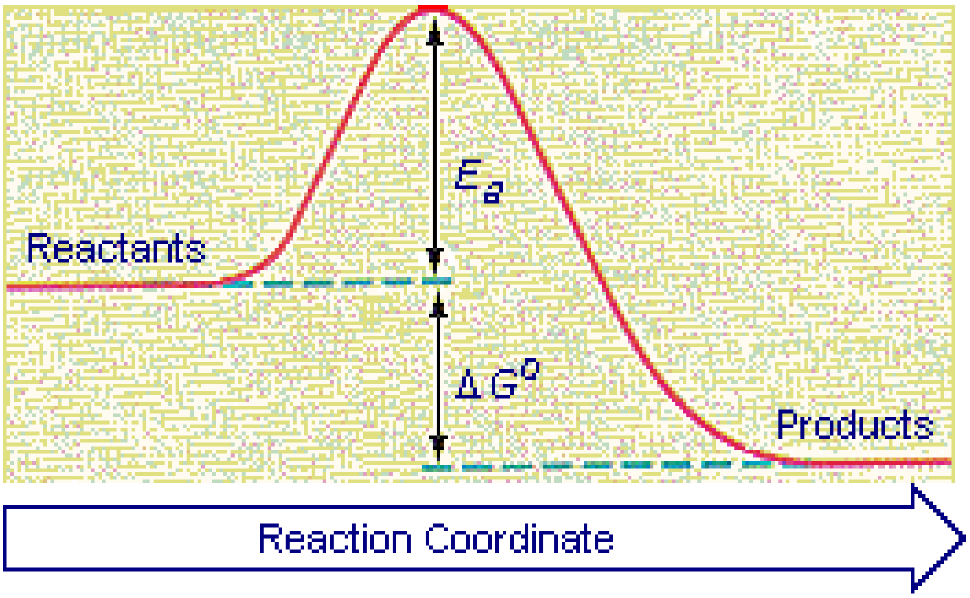
Another factor that influences whether reaction will occur is the energy the molecules carry when they collide. Not all of the molecules have the same kinetic energy, as shown in the figure below. This is important because the kinetic energy molecules carry when they collide is the principal source of the energy that must be invested in a reaction to get it started.



The overall standard free energy for the reaction between $ClNO_2$ and NO is favorable.

$$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g) \qquad \Delta G^o = -23.6 \text{ kJ/mol}$$

But, before the reactants can be converted into products, the free energy of the system must overcome the activation energy for the reaction, as shown in the figure below. The vertical axis in this diagram represents the free energy of a pair of molecules as a chlorine atom is transferred from one to the other. The horizontal axis represents the the sequence of infinitesimally small changes that must occur to convert the reactants into the products of this reaction.



To understand why reactions have an activation energy, consider what has to happen in order for $ClNO_2$ to react with NO. First, and foremost, these two molecules have to collide, thereby organizing the system. Not only do they have to be brought together, they have to be held in exactly the right orientation relative to each other to ensure that reaction can occur.

Both of these factors raise the free energy of the system by lowering the entropy.

Some energy also must be invested to begin breaking the $Cl\text{-}NO_2$ bond so that the Cl-NO bond can form.

NO and $ClNO_2$ molecules that collide in the correct orientation, with enough kinetic energy to climb the activation energy barrier, can react to form NO_2 and ClNO.

As the temperature of the system increases, the number of molecules that carry enough energy to react when they collide also increases. The rate of reaction therefore increases with temperature.

As a rule, the rate of a reaction doubles for every 10^oC increase in the temperature of the system.

Purists might note that the symbol used to represent the difference between the free energies of the products and the reactants in the above figure is ΔG^o, not ΔG^o.

A small capital "G" is used to remind us that this diagram plots the free energy of a pair of molecules as they react, not the free energy of a system that contains many pairs of molecules undergoing collision. If we averaged the results of this calculation over the entire array of molecules in the system, we would get the change in the free energy of the system, ΔG^o.

Purists might also note that the symbol used to represent the activation energy is written with a capital "E". This is unfortunate, because it leads students to believe the activation energy is the change in the internal energy of the system, which is not quite true. E_a measures the change in the potential energy of a pair of molecules that is required to begin the process of converting a pair of reactant molecules into a pair of product molecules.

14. Catalysts and the Rates of Chemical Reactions

Aqueous solutions of hydrogen peroxide are stable until we add a small quantity of the I^- ion, a piece of platinum metal, a few drops of blood, or a freshly cut slice of turnip, at which point the hydrogen peroxide rapidly decomposes.

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

This reaction therefore provides the basis for understanding the effect of a catalyst on the rate of a chemical reaction. Four criteria must be satisfied in order for something to be classified as catalyst.

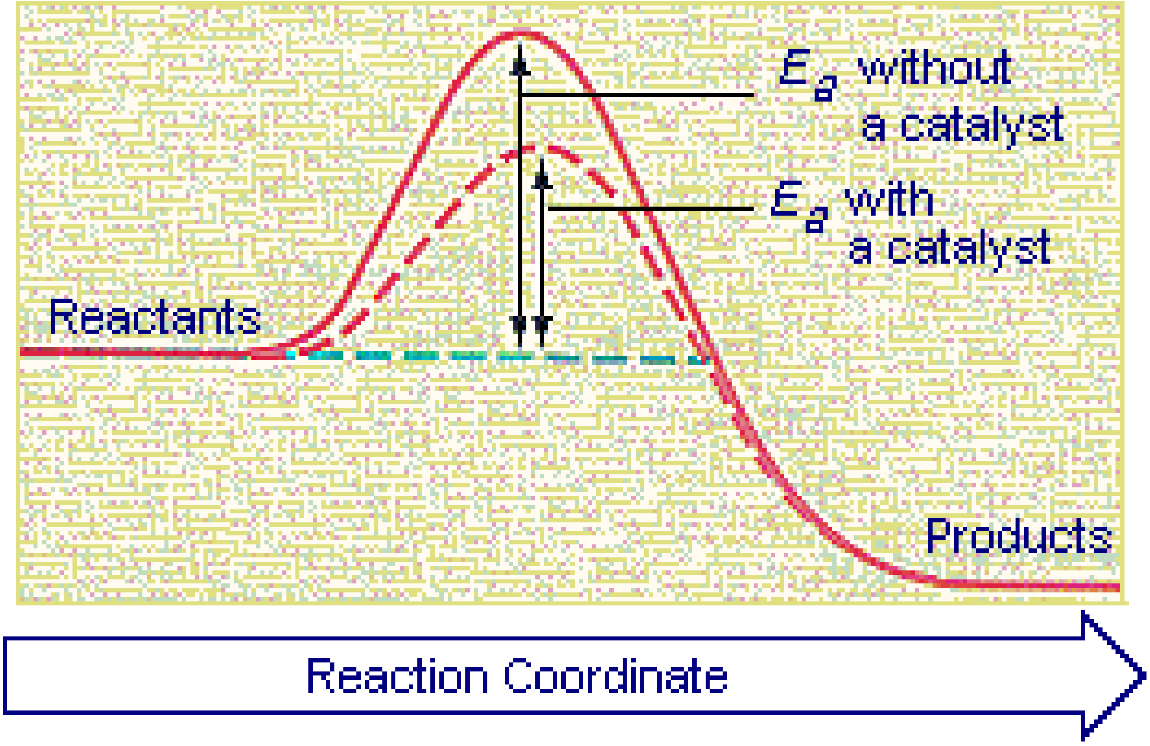
- Catalysts increase the rate of reaction.
- Catalysts are not consumed by the reaction.
- A small quantity of catalyst should be able to affect the rate of reaction for a large amount of reactant.
- Catalysts do not change the equilibrium constant for the reaction.

The first criterion provides the basis for defining a catalyst as something that increases the rate of a reaction.

The second reflects the fact that anything consumed in the reaction is a reactant, not a catalyst.

The third criterion is a consequence of the second; because catalysts are not consumed in the reaction, they can catalyze the reaction over and over again. The fourth criterion results from the fact that catalysts speed up the rates of the forward and reverse reactions equally, so the equilibrium constant for the reaction remains the same.

Catalysts increase the rates of reactions by providing a new mechanism that has a smaller activation energy, as shown in the figure below. A larger proportion of the collisions that occur between reactants now have enough energy to overcome the activation energy for the reaction. As a result, the rate of reaction increases.



To illustrate how a catalyst can decrease the activation energy for a reaction by providing another pathway for the reaction, let's look at the mechanism for the decomposition of hydrogen peroxide catalyzed by the I^- ion. In the presence of this ion, the decomposition of H_2O_2 doesn't have to occur in a single step. It can occur in two steps, both of which are easier and therefore faster. In the first step, the I^- ion is oxidized by H_2O_2 to form the hypoiodite ion, OI^-.

$H_2O_2(aq) + I^-(aq) \rightleftharpoons H_2O(aq) + OI^-(aq)$

In the second step, the OI^- ion is reduced to I^- by H_2O_2.

$OI^-(aq) + H_2O_2(aq) \rightleftharpoons H_2O(aq) + O_2(g) + I^-(aq)$

Because there is no net change in the concentration of the I^- ion as a result of these reactions, the I^- ion satisfies the criteria for a catalyst. Because H_2O_2 and I^- are both involved in the first step in this reaction, and the first step in this reaction is the rate-limiting step, the overall rate of reaction is first-order in both reagents.

15. Determining the Activation Energy of a Reaction

The rate of a reaction depends on the temperature at which it is run. As the temperature increases, the molecules move faster and therefore collide more frequently. The molecules also carry more kinetic energy. Thus, the proportion of collisions that can overcome the activation energy for the reaction increases with temperature.

The only way to explain the relationship between temperature and the rate of a reaction is to assume that the rate constant depends on the temperature at which the reaction is run. In 1889, Svante Arrhenius showed that the relationship between temperature and the rate constant for a reaction obeyed the following equation.

$$k = Ze^{-E_a/RT}$$

In this equation, k is the rate constant for the reaction, Z is a proportionality constant that varies from one reaction to another, E_a is the activation energy for the reaction, R is the ideal gas constant in joules per mole kelvin, and T is the temperature in kelvin.

The **Arrhenius equation** can be used to determine the activation energy for a reaction. We start by taking the natural logarithm of both sides of the equation.

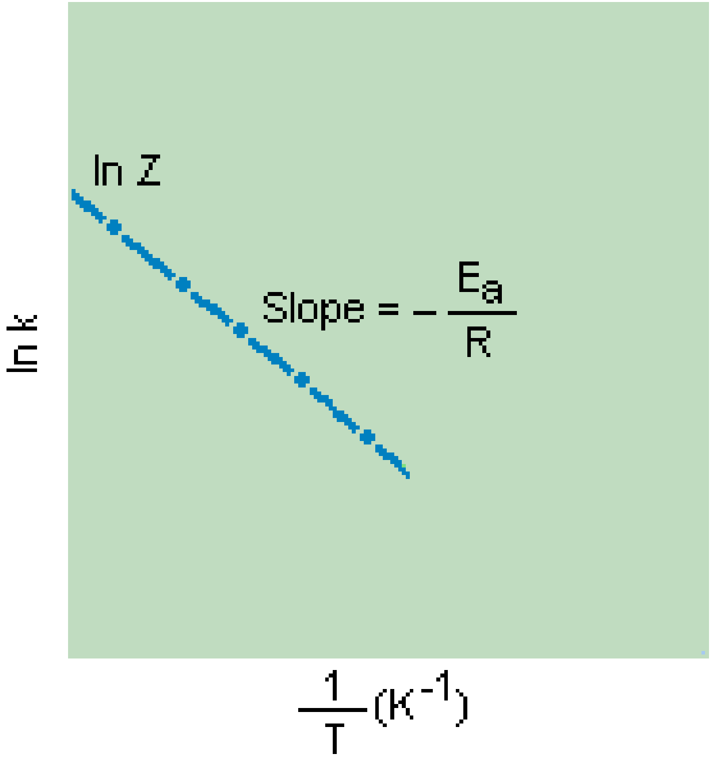
$$\ln k = \ln Z - \frac{E_a}{RT}$$

We then rearrange this equation to fit the equation for a straight line.

y = mx + b

$$\ln k = \frac{E_a}{RT} \left[\frac{1}{T}\right] + \ln Z$$

According to this equation, a plot of ln k versus 1/T should give a straight line with a slope of - E_a/R, as shown in the figure below.



By paying careful attention to the mathematics of logarithms, it is possible to derive another form of the Arrhenius equation that can be used to predict the effect of a change in temperature on the rate constant for a reaction.

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

The Arrhenius equation can also be used to calculate what happens to the rate of a reaction when a catalyst lowers the activation energy.

16.Catalysis

Catalysts are substances that increase the rate of reactions, but do not get used up by the reactions. A catalyst functions by providing an *alternative reaction pathway with lower activation energy*. It increases the reaction rate, but does not affect the reaction enthalpy or the equilibrium position.

Homogeneous Catalysis

These are catalysts that have the same phase as the reactants. For example, nitric oxide (NO) catalyzes the reaction between SO_2 and O_2:

$$2SO_2(g) + O_2(g) \xrightarrow{\text{NO catalyst}} 2SO_3(g)$$

The above reaction, though spontaneously and highly exothermic, is very slow because of the very high activation energy. NO molecules provide an alternative pathway that has a lower E_a.

Step-1: $2NO + O_2 \rightarrow 2NO_2$

Step-2: $2NO_2 + 2SO_2 \rightarrow 2NO + 2SO_3$

Overall: $2 SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

Some catalysts may be involved in the reaction kinetics and the concentration appears in the rate law. For example, iodine which catalyzes the *isomerization* of *cis*-2-butene to *trans*-2-butene is included in the rate law expression.

Heterogeneous Catalysis

These are catalysts which have a different physical state from the reactants. Most reactions involving gases use inert metals or metal oxides as catalysts. These solid catalysts provide surface areas for molecules to interact effectively. The metal surface also facilitates the breaking and formation of bonds. Ni, Pd and Pt are often used in the hydrogenation of vegetable oil to make margarine and “Crisco oil”, where a hydrogen molecule is added to each carbon-carbon double bond in the unsaturated fatty acid chains.

Heterogeneous catalyses are used in automobile catalytic converters, which consist of Pt, Pd and Rh mixture embedded in ceramic honeycombs. The metals catalyze the following reaction:

$$2NO(g) + 2CO(g) \xrightarrow{(Pt+Pd+Rh)} N_2(g) + 2CO_2(g)$$

Catalytic converters reduce the emission of toxic exhaust gases

Some reactions require specific catalysts. For example, Nickel catalyzes the reaction:

$$CO(g) + 3H_2(g) \xrightarrow{\text{Ni-catalyst}} CH_4(g) + H_2O(g)$$

Whereas $ZnO\text{-}Cr_2O_3$ mixture catalyzes the formation of methanol from the same reactants:

$$CO(g) + 2H_2(g) \xrightarrow{ZnO\text{-}Cr_2O_3} CH_3OH(g)$$

QUESTIONS FOR SELF-TRAINING

1. Explain the term chemical kinetics, and describe factors that influence rate of chemical reactions
2. Define and use proper units for chemical reaction rates.
3. Give the conditions for homogeneous and heterogeneous reactions.
4. The expressions of rate of reaction and types of rates;
5. Stoichiometric relationships between the rates of appearance or disappearance of components in a given reaction;
6. Determination of rate orders and rate law using the kinetic data of a reaction;
7. The graphical method to determine a first-order and second-order reaction.
8. The meaning and calculation half-life of a first order reaction;
9. Determination of the activation energy, E_a, either graphically or from rate constants at different temperatures.
10. Derive rate law from reaction mechanism.
11. The role of catalyst

TASKS

Task 1

The activation energy of an elementary chemical reaction is 30 kcal mol-1. Determine:

a) The increase in the reaction rate when the temperature increases from 300ºC· to 360ºC

b) The increase in temperature necessary to double the rate of the reaction at 300ºC

Task 2

The following reaction A → B + C has a rate constant of 0.02 L mol-1 min-1. A daily production of 9000 mol/day is aimed for, using a batch reactor. To avoid secondary reactions the maximum conversion of 75% is the limit. Knowing that the initial concentration of A is 1 mol·L-1 and the conditioning time for the reactor is 1.5 h, calculate the minimum volume of the reactor.

Task 3

In a batch reactor of 18 L volume an isothermal irreversible reaction takes place R→P, in liquid phase. The kinetic constant is expressed as $k = 4.48\times10^6$ exp(-7000/T), in s-1, where T is the process temperature expressed in Kelvin.

a) Calculate the time required to reach a conversion of 80% at 40 ºC if [R]o = 3 mol/L.

b) Indicate the daily molar production of P under the conditions in section (a), knowing that the load, unload and conditioning time is 22 minutes (assume 24 working h/day).

c) If the conversion desired is 95%, without changing the operating conditions in section (a), calculate the time necessary to achieve it.

d) What should be the temperature of the process for a conversion rate of 95% without changing the time of the reaction determined in (a)?

Task 4

Half-life time for substance A in a second order reaction A→ Products at 20 ºC is 25 seconds when [A]0=0.8 mol/L.

a) Calculate the time required so that the concentration of A is reduced to one fifth of its initial value.

b) If the rate of the reaction is doubled when temperature increases from 20ºC to 30ºC, calculate the activation energy of the process.

Task 5

A reaction is 50% complete in 10 minutes. It is allowed to proceed another 5 minutes. How much of the reaction would be complete at the end of these 15 minutes if the reaction follows zero order kinetics?

Task 6

Half-life for disintegration of radium is 1590 years. Calculate the rate constant in s^{-1} and also how many years will be taken for the disintegration of 80% of the material?

THE STANDARD ANSWERS

Exercise #1

Use the data in the above table to calculate the rate at which phenolphthalein reacts with the OH^- ion during each of the following periods:

(a) During the first time interval, when the phenolphthalein concentration falls from 0.0050 *M* to 0.0045 *M*.

(b) During the second interval, when the concentration falls from 0.0045 *M* to 0.0040 *M*.

(c) During the third interval, when the concentration falls from 0.0040 *M* to 0.0035 *M*.

Solution

The rate of reaction is equal to the change in the phenolphthalein concentration divided by the length of time over which this change occurs.

(a) During the first time period, the rate of the reaction is 4.8 x 10^{-5} moles per liter per second:

$$\text{Rate} = \frac{\Delta(X)}{\Delta t} = \frac{(0.0050\ M) - (0.0045\ M)}{(10.5\ s - 0\ s)} = 4.8 \times 10^{-5}\ M/s$$

(b) During the second time period, the rate of reaction is slightly smaller:

$$\text{Rate} = \frac{\Delta(X)}{\Delta t} = \frac{(0.0045\ M) - (0.0040\ M)}{(22.3\ s - 10.5\ s)} = 4.2 \times 10^{-5}\ M/s$$

(c) During the third time period, the rate of reaction is even smaller:

$$\text{Rate} = \frac{\Delta(X)}{\Delta t} = \frac{(0.0040\ M) - (0.0035\ M)}{(35.7\ s - 22.3\ s)} = 3.7 \times 10^{-5}\ M/s$$

Exercise #2

Calculate the rate constant for the reaction between phenolphthalein and the OH^- ion if the instantaneous rate of reaction is 2.5 x $10^{-}5$ mole per liter per second when the concentration of phenolphthalein is 0.0025 *M*.

Solution

We start with the rate law for this reaction:

Rate = k(phenolphthalein)

We then substitute the known rate of reaction and the known concentration of phenolphthalein into this equation:

$$\frac{2.5 \times 10^{-5}\ \text{mol/L}}{1\ \text{s}} = k(0.0025\ \text{mol/L})$$

Solving for the rate constant gives the following result:

$$k = 0.010\ \text{s}^{-1}$$

Exercise #3

Use the rate constant for the reaction between phenolphthalein and the OH^- ion to calculate the initial instantaneous rate of reaction for the experimental data listed in the preceding table.

Solution

Substituting the rate constant for the reaction from the preceding problem and the initial concentration of phenolphthalein into the rate law for this reaction gives the following:

Rate = k(phenolphthalein) = (0.010 s^{-1})(0.0050 mol/L) = 5.0 x 10^{-5} (mol/L)/s

Because the rate of reaction is the change in the concentration of phenolphthalein divided by the time over which the change occurs, it is reported in units of moles per liter per second. Because the number of moles of phenolphthalein per liter is the molarity of this solution, the rate can also be reported in terms of the change in molarity per second: *M*/s.

Exercise #4

Calculate the rate at which HI disappears in the following reaction at the moment when I_2 is being formed at a rate of 1.8 x 10^{-6} moles per liter per second:

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

Solution

The balanced equation for the reaction shows that 2 moles of HI disappear for every mole of I_2 formed. Thus, HI is consumed in this reaction twice as fast as I_2 is formed:

$$-\frac{d(\mathrm{HI})}{dt} = 2\left[\frac{d(\mathrm{I_2})}{dt}\right] = \frac{2(1.8 \times 10^{-6})\ \mathrm{mol/L}}{1\ \mathrm{s}} = 3.6 \times 10^{-6}\ M/s$$

Students sometimes get the wrong answer to this exercise because they become confused about whether the equation for the calculation should be written as:

$$-\frac{d(\mathrm{HI})}{dt} = 2\left[\frac{d(\mathrm{I_2})}{dt}\right]$$

or as:

$$\frac{d(\mathrm{I_2})}{dt} = 2\left[-\frac{d(\mathrm{HI})}{dt}\right]$$

You can avoid mistakes by checking to see whether your answer makes sense. The balanced equation states that 2 moles of HI are consumed for every mole of I_2produced. HI should therefore disappear ($3.6 \times 10^{-6}\ M$/s) twice as fast as I_2 is formed ($1.8 \times 10^{-6}\ M$/s).

Exercise #5

Determine the molecularity of each step in the reaction by which N_2O_5 decomposes to NO_2 and O_2.

Solution

All we have to do is count the number of molecules consumed in each step in this reaction to decide that the first step is unimolecular and the other two steps are bimolecular:

Step 1: $N_2O_5 \rightleftharpoons NO_2 + NO_3$

Step 2: $NO_2 + NO_3 \rightleftharpoons NO_2 + NO + O_2$

$$\text{Step 3:} \quad NO + NO_3 \rightleftharpoons 2\ NO_2$$

Exercise #6

The rate constants for the forward and reverse reactions in the following equilibrium have been measured. At 25°C, k_f is 7.3×10^3 liters per mole-second and k_r is 0.55 liters per mole-second. Calculate the equilibrium constant for this reaction:

$$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$$

Solution

We start by assuming that the rates of the forward and reverse reactions at equilibrium are the same:

$$\text{At equilibrium:} \quad \text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$

We then substitute the rate laws for these reactions into this equality:

$$\text{At equilibrium:} \quad k_f[ClNO_2][NO] = k_r[NO_2][ClNO]$$

We then rearrange this equation to get the equilibrium constant expression for the reaction :

$$K_c = \frac{k_f}{k_r} = \frac{[NO_2][ClNO]}{[ClNO_2][NO]}$$

The equilibrium constant for the reaction is therefore equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction:

$$K_c = \frac{k_f}{k_r} = \frac{7300\ \text{L/mol-s}}{0.55\text{L/mol-s}} = 1.3 \times 10^4$$

Exercise #7

Hydrogen iodide decomposes to give a mixture of hydrogen and iodine:

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

Use the following data to determine whether the decomposition of HI in the gas phase is first order or second order in hydrogen iodide.

	Initial (HI) (M)	Initial Instantaneous Rate of Reaction (M/s)
Trial 1:	1.0×10^{-2}	4.0×10^{-6}
Trial 2:	2.0×10^{-2}	1.6×10^{-5}
Trial 3:	3.0×10^{-2}	3.6×10^{-5}

Solution

We can start by comparing trials 1 and 2. When the initial concentration of HI is doubled, the initial rate of reaction increases by a factor of 4:

$$\frac{\text{Rate for trial 2}}{\text{Rate for trial 1}} = \frac{1.6 \times 10^{-5}\ M/s}{4.0 \times 10^{-6}\ M/s} = 4$$

Now let's compare trials 1 and 3. When the initial concentration of HI is tripled, the initial rate increases by a factor of 9:

$$\frac{\text{Rate for trial 3}}{\text{Rate for trial 1}} = \frac{3.6 \times 10^{-5}\ M/s}{4.0 \times 10^{-6}\ M/s} = 9$$

The rate of this reaction is proportional to the square of the HI concentration. The reaction is therefore second order in HI, as noted in a previous section:

$$\text{Rate} = k(\text{HI})^2$$

Exercise #8

Acetaldehyde, CH_3CHO, decomposes by second-order kinetics with a rate constant of 0.334 $M^{-1}s^{-1}$ at 500°C. Calculate the amount of time it would take for 80% of the acetaldehyde to decompose in a sample that has an initial concentration of 0.00750 *M*.

Solution

We start with the rate law for the decomposition of acetaldehyde, which follows second-order kinetics:

$$\text{Rate} = k(\text{CH}_3\text{CHO})^2$$

We then write the integrated form of this rate law:

$$\frac{1}{(CH_3CHO)} - \frac{1}{(CH_3CHO)_0} = kt$$

The initial concentration of acetaldehyde is 0.00750 *M*. The final concentration is only 20% as large, or 0.00150 *M*:

$$\frac{1}{(0.00150)} - \frac{1}{(0.00750)} = kt$$

Substituting the rate constant for this reaction (k= 0.334) into this equation and then solving for t gives the following result:

$$t = 1600 \text{ s}$$

It therefore takes slightly less than one-half of an hour for 80% of the acetaldehyde to decompose at this temperature.

Exercise #9

Use the experimental data found in the table at the beginning of this lesson to determine whether the reaction between phenolphthalein (PHTH) and the OH^- ion is a first-order or a second-order reaction.

Answer

The first step in solving this problem involves calculating the natural log of the phenolphthalein concentration, ln (PHTH), and the reciprocal of the concentration, 1/(PHTH), for each point at which a measurement was taken:

(PHTH) (mol/L)	ln (PHTH)	1/(PHTH)	Time (s)
0.0050	-5.30	200	0.0
0.0045	-5.40	222	10.5
0.0040	-5.52	250	22.3
0.0035	-5.65	286	35.7
0.0030	-5.81	333	51.1
0.0025	-5.99	400	69.3
0.0020	-6.21	500	91.6

0.0015	-6.50	667	120.4
0.0010	-6.91	1000	160.9
0.00050	-7.60	2000	230.3
0.00025	-8.29	4000	299.6
0.00015	-8.80	6670	350.7
0.00010	-9.21	10,000	391.2

We then construct graphs of ln (PHTH) versus time (Figure 1)and 1/(PHTH) versus time (Figure 2). Only one of these graphs, Figure 1, gives a straight line. We therefore conclude that these data fit a first-order kinetic equation, as noted in the beginning of this lesson.

Rate = *k*(phenolphthalein)

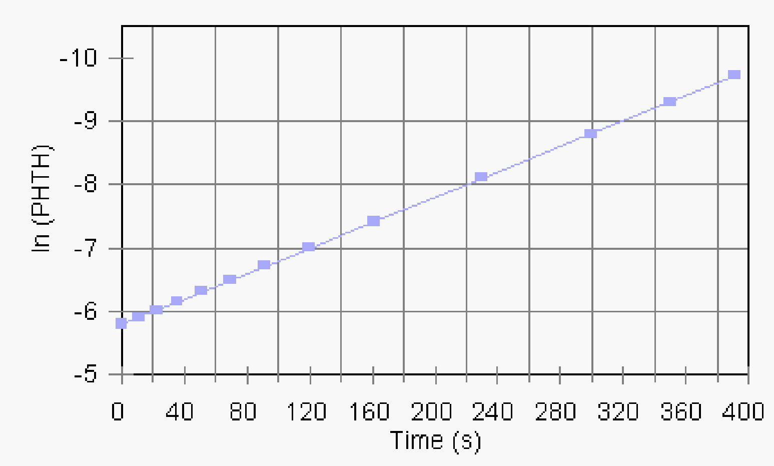


Figure 1. A plot of the natural log of the concentration of phenolphthalein versus time for the reaction between phenolphthalein and excess OH^- ion is a straight line, which shows that this reaction is first order in phenolphthalein.

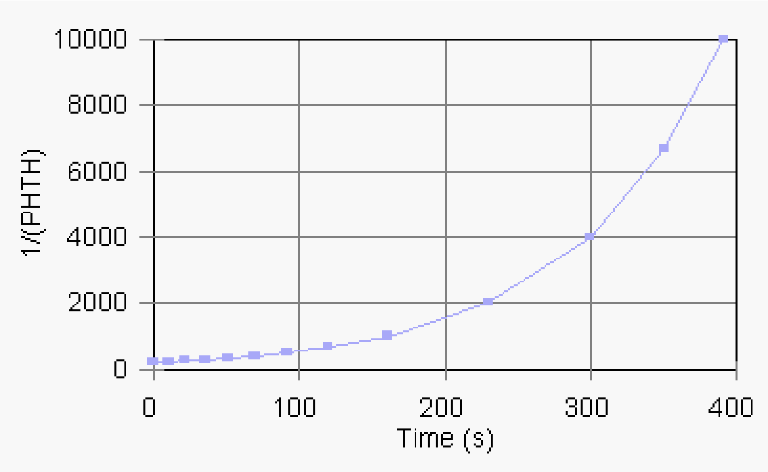


Figure 2. A plot of the reciprocal of the concentration of phenolphthalein versus time for the reaction between phenolphthalein and excess OH^- ion *is not* a straight line, which shows that this reaction is not second order in phenolphthalein.

Exercise #10

Use the following data to determine the activation energy for the decomposition of HI:

Temperature (K)	Rate Constant (*M*/s)
573	2.91×10^{-6}
673	8.38×10^{-4}
773	7.65×10^{-2}

Solution

We can determine the activation energy for a reaction from a plot of the natural log of the rate constants versus the reciprocal of the absolute temperature. We therefore start by calculating 1/T and the natural logarithm of the rate constants:

ln k	1/T (K^{-1})
-12.75	0.00175
-7.08	0.00149
-2.57	0.00129

When we construct a graph of these data, we get a straight line with a slope of -22,200 K, as seen in Figure 1.

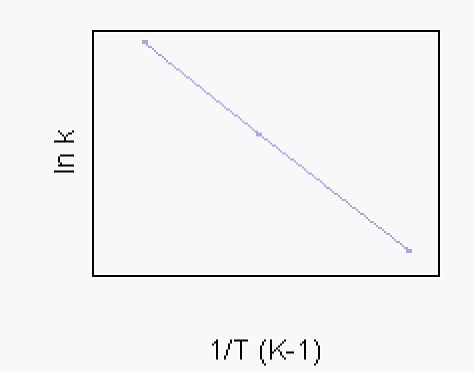


Figure 1. A plot of the natural log of the rate constant for the reaction at different temperatures versus the inverse of the temperature in kelvin is a straight line with a slope equal to $-E_a/R$.

According to the Arrhenius equation, the slope of this line is equal to $-E_a/R$:

$$-22,200\ \text{K} = -\frac{E_a}{8.314\ \text{J/mol-K}}$$

When this equation is solved, we get the follwoing value for the activation energy for this reaction:

$$E_a = 183\ \text{kJ/mol}$$

Exercise #11

Calculate the rate of decomposition of HI at 600°C.

Solution

We start with the following form of the Arrhenius equation:

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

We then pick any one of the three data points used in the preceding practice problem as T_1 and allow the value of T_2 to be 873 K:

$T_1 = 573$ K $k_1 = 2.91$ x 10-6 M/s

$T_2 = 873$ K $k_2 = ?$

Substituting what we know about the system into the equation given above gives the following result:

$$\ln\left[\frac{2.91 \times 10^{-6}\ M/s}{k_2}\right] = \frac{183,000\ \text{J/mol}}{8.314\ \text{J/mol-K}}\left[\frac{1}{873\ \text{K}} - \frac{1}{573\ \text{K}}\right]$$

We can simplify the right-hand side of this equation as follows:

$$\ln\left[\frac{2.91 \times 10^{-6}\ M/s}{k_2}\right] = -13.20$$

We then take the antilog of both sides of the equation:

$$\frac{2.91 \times 10^{-6}\ M/s}{k_2} = 1.85 \times 10^{-6}$$

Solving for k_2 gives the rate constant for this reaction at 600°C:

$$k_2 = 1.6\ M/\mathrm{s}$$

Increasing the temperature of the reaction from 573 K to 873 K therefore increases the rate constant for the reaction by a factor of almost a million.

EXPERIMENTAL PART

Laboratory work: The determination of rate constant and reaction order

Put 0,05N sodium thiosulfate ($Na_2S_2O_3$) in the burette. Measure 25 ml of 0,4N potassium iodide (KI) and 25 ml of ammonium persulfate ($(NH_4)_2S_2O_8$). Mix both solutions and record the start time of the experiment. Measure 50 ml of distilled water in a clean flask cylinder. In three minutes from the start of the experiment put 5 ml of mixture into the flask with distilled water. Add 3 drops of 1% starch solution (indicator). Titrate with 0,05N solution of $Na_2S_2O_3$ to discoloration. Write the amount of sodium thiosulfate (ml), departed for titration, in a table. Repeat the same on the fifth, tenth, etc. minutes (see the time specified in the table).

Attention: Last titration gives the value of the initial concentration of "a." Put the value of $Na_2S_2O_3$, which was used for the titration of 5 ml of a mixture (in accordance of the time) into the formula instead of "x".

Table with results:

Time from start of the experiment, min	Value of 0,05 н. Na2S2O3, ml	$\frac{a}{a-x}$	$\lg\frac{a}{a-x}$	$K=\frac{2.3}{t}\cdot\lg\frac{a}{a-x}$
3				
5				
10				
15				
20				
30				
45				
60				
90		-	-	-

Write the chemistry of the reaction and the reaction order in case when KI is in excess.

$KI+(NH_4)_2S_2O_8 \rightarrow$

Calculate the rate constant for each time value.

$$K = \frac{2.3}{t} \cdot \lg \frac{a}{a-x}$$

K_1=

K_2=

K_3=

K_4=

K_5=

K_6=

K_7=

K_8=

K_9=

Explain why the order and molecularity of reaction are not the same in this case.

TESTS

Please indicate dimension of a reaction’s velocity of the 2nd order:

a) *Mole^{-1}*dm^{3}*c^{-1}

b) Mole*dm^{3}*C^{-1}

c) C^{-1}

d) Mole^{2}*dm^{6}*C^{-1}

Please indicate dimension of a reaction’s velocity of an order zero:

a) *Mol*dm^{-3}*sec

b) C^{-1}

c) Mole*dm^{3}*sec^{-1}

d) Mole^{-2}*dm^{6}*sec^{-1}

The half-life of what reaction expresses by an equation T=1/kc(0):

a) *The second order;

b) The third order;

c) The fractional order;

d) An order zero;

e) The first order.

The half-life of what reaction expresses by an equation T=C(0)/2k:

a) *An order zero;

b) The third order;

c) The fractional order;

d) The first order;

e) The second order.

Temperature coefficient of velocity of reaction = 3. In how many of times the velocity of this reacting will be changed at a temperature variation on 30?

a) *In 27 times;

b) In 9 times;
c) In 18 times;
d) In 36 times;
e) In 45 times.

The reaction $2NO+Cl_2=2NOCl$ is composite. It is possible to assert, that it is 3-molecular?

a) *No.
b) Yes.

Whether the following expression is correct: “ Velocity of particular chemical reaction is a constant “?

a) *No.
b) Yes.

Whether the following expression is correct: “ A constant of velocity of chemical reaction is a constant “?

a) *Yes.
b) No.

What formula reflects true velocity of chemical reaction:

a) *V=dc/dt
b) V=?C/?T

How the order of reaction is determined?

a) *By method of determination of dependence of half-life of reaction from initial concentration of reactants;
b) By a method of gradual dissolution;
c) By a method of determination of an activation energy;
d) On determination of isotonic and isothermal factor of Vant-Hoff;

e) By a method of weighing.

How the order of reacting is determined?
a) *By graphic method on dependence of concentration on time;
b) By a method of determination of isothermal factor of Vant-Hoff;
c) On an equation of Nernst; D. On an equation Colerauche;
d) On significance of an equilibrium constant of chemical reaction.

The empiric rule, according to which the velocity of chemical reaction increases in 2-4 times at temperature rise on 10 has formulated by:
a) *Vant-Hoff.
b) Ostwald;
c) Kirchhoff;
d) Hess;
e) Henry;

Temperature coefficient of velocity of chemical reaction = 4. In how many of times the velocity of this reaction will be changed at a temperature variation on 30?
a) *In 64 times.
b) In 16 times;
c) In 24 times;
d) In 32 times;
e) In 48 times;

Please indicate exponential form of an equation of the Arrhenius:
a) *$K=A*e-E/RT$
b) $dlnK/dT=E/RT^2$
c) $lgK=lgA-E/RT$

What is activation energy?

a) *It is energy of molecules entering chemical interplay;
b) It is energy of molecules;
c) It is energy of molecules before reacting;
d) It is energy of molecules after reacting;
e) It is a differential of energy of molecules before and after reacting;

Influencing of the catalyzer on activation energy:

a) *Decreases;
b) Does not influence;
c) Increases;

Temperature influence on activation energy:

a) *Decreases;
b) Does not influence;
c) Increases;

Increasing of activation energy:

a) *Decreases velocity of chemical reaction;
b) Increases velocity of chemical reaction;
c) Does not influence on velocity of chemical reaction;
d) Promotes formation of a fissile complex.

Please indicate dimension of a reaction velocity of the 1st order:

a) *C^{-1}
b) Mol*dm $^{-3}$*C^{-1}
c) Mole^{-1}*dm^{3}*C^{-1}
d) Mole^{-2}*dm^{6}*C^{-1}

Please indicate the order and molecularity of reaction of a hydrolysis of saccharose $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6$ (glucose) + $C_6H_{12}O_6$ (fructose):

a) *Bimolecular, first order;

b) Monomolecular, first order;

c) Bimolecular, second order;

d) Monomolecular, second order;

e) Bimolecular, third order.

What determines molecularity of reaction?

a) *Amount of molecules, which one participate in the elementary act of reacting;

b) An amount of molecules of agents, according to stoichiometric factors of reacting;

c) An amount of molecules of reaction products.

d) In what case the equation of velocity of chemical reaction, according to a law of mass action, is fair:

e) *For single-stage reactions;

f) For multiphase reactions.

What formula reflects an average velocity of chemical reaction:

a) *$V=\Delta C/\Delta T$

b) $V=dc/dt$

What value gives the comparative performance of velocity of chemical reaction:

a) *Value of a constant of velocity (K).

b) Value of reaction velocity (V);

Half-life of what reaction expresses by an equation $T = 1*3/k_2C(0)$:

a) *The third order;

b) The first order;

c) The second order;
d) The fractional order;
e) An order zero.

Please indicate for reaction of what order a constant of velocity expresses by the following equation: k=1/t(C(0)-C):

a) *An order zero;
b) The third order;
c) The second order;
d) The first order;
e) The fractional order.

The half-life of what reaction expresses by an equation T(1/2) = 1/K*ln2:

a) *The first order;
b) An order zero;
c) The second order;
d) The third order;
e) The fractional order.

Please indicate, for reaction of what order the constant of velocity expresses by the following equation: K=1/tlnC(0)/C:

a) *The first order;
b) An order zero;
c) The second order;
d) The third order;
e) The fractional order.

Please indicate, for reaction of what order the constant of velocity expresses by the following equation: $K=1/2t(1/C^2-1/C(0)^2)$:

a) *The third order.

b) The fractional order;
c) An order zero;
d) The first order;
e) The second order;

Kinetic equation of reaction velocity of what order is the expression K=1/t (1/C-1/C (0))?

a) *2nd order;
b) 1st order;
c) 3rd order;
d) An order zero;
e) The fractional order.

What is a catalysis?

a) *This is an alteration of velocity of chemical reaction;
b) This is an increasing of velocity of chemical reaction;
c) This is an decreasing of velocity of chemical reaction;
d) It is an industrial synthesizing of chemical agents;
e) It is a laboratory synthesizing of chemical agents.

Catalyzers:

a) *Do not influence on value of an equilibrium constant of chemical reaction;
b) Increases velocity of direct reacting in a reversible reaction;
c) Increases velocity of reverse reaction in a reversible process;
d) Do not influence on velocity of reversible reactions.

The molecularity of reaction is determined by:

a) *Number of molecules sharing in the elementary act of reacting;

b) Number of molecules which are generated as a result of the elementary act of reacting;

c) Total number of all molecules before and after reacting.

If the reaction velocity does not depend on concentration of reactants, it is a reaction:

a) *The order zero;

b) The first order;

c) The second order;

d) The third order;

e) The fractional order.

How the order of reaction is determined?

a) *By trial and error method of a kinetic equation of the miscellaneous orders;

b) By a method of weighing;

c) By a method of determination of an activation energy of reacting;

d) On determination of an isotonic coefficient of reacting.

Whether the molecularity and order of reacting coincides?

a) *Only for simple single-stage reactions;

b) Coincide always;

c) Do not coincide never;

d) Only for composite reactions;

e) Only for enzymatic reactions.

The velocity of what reaction is determined by the formula $V=KC_1^2 C_2$:

a) *$2H_2 + O_2 = 2H_2O$

b) $C + O_2 = CO_2$

c) $2N_2 + 3H_2 = 2NH_3$

d) $S + O_2 = SO_2$
e) $H_2 + Cl_2 = 2HCl$

Whether the expression is correct: The constant of velocity of chemical reaction is reaction velocity at concentration of reactants, equal to 1:

a) *Yes.
b) No.
c) Yes, if the concentrations of reactants are not equal to 1.

According to what law the velocity of chemical reaction is determined by expression V=KC(1)^3 C(2):

a) *The law of mass action;
b) The law of Vant Hoff;
c) The law of partial pressures;
d) The law of the Arrhenius;
e) The law of ionic strength.

Please indicate an equation expressing a half-life of chemical reaction of the 3rd order:

a) $*T=3/2KC_0^2$
b) $T=1/2C_0$
c) $T=C_0/2K$
d) $T=\ln 2/K$

According to the law of mass action, the velocity of chemical reaction is determined by expression:

a) $*V = KC_1C_2$
b) $V = -dc/dt$
c) $V=S/t$
d) $V=ezdt/kl$

Please indicate an equation which reflects a half-life of reaction of 1st order:

a) *T=1/K*Ln2
b) $T=1/K*3/2C_0^2$
c) T=1/KC(0)
d) T=C (0)/2K

Please indicate a kinetic equation of a constant of velocity of chemical reaction of 2nd order:

a) *K=1/t(1/C-1/C(0))
b) K=1/t*Ln(C(0)/C)
c) $K=1/t(1/C^2-1/C_0^2)$
d) $K=1/t(C_0-C)$

Please indicate a kinetic equation of a constant of velocity of chemical reaction of 3d order:

a) $*K=1/t(1/C^2-1/C_0^2)$
b) $K=1/t*\ln C_0/C$
c) $K=1/t\ (1/C-1/C_0)$
d) $K=1/t\ (C_0\ -C)$

Please indicate an equation which reflects a half-life of reaction of 2nd order:

a) $*T=1/KC_0$
b) T=1/K*ln2
c) $T=C_0/2K$
d) T=1/K*3/2C(0)^2

Please indicate an equation of a constant of velocity of chemical reaction of 1 order:

a) $*K=1/t*\ln(C_0/C)$

b) $K=1/t(1/C-1/C_0)$

c) $K=1/2t(1/C^2-1/C_0^2)$

d) $K=1/t(C_0-C)$

On what value we can compare velocities of chemical reactions:

a) *On value of a reaction velocity constant;

b) On value of reaction velocity;

c) On time of the termination of reaction;

d) On concentration of reactants.

Temperature coefficient of velocity of chemical reaction = 4. In how many of times the velocity of this reaction will be changed at a temperature variation on 20?

a) In 64 times.

b) *In 16 times;

c) In 24 times;

d) In 32 times;

e) In 48 times;

Does the catalyzer nfluence activation energy:

a) *Yes

b) No;

Does temperature influence activation energy:

a) *Yes

b) No

Decreasing of activation energy:

a) Decreases velocity of chemical reaction;

b) *Increases velocity of chemical reaction;

c) Does not influence on velocity of chemical reaction;
d) Promotes formation of a fissile complex.

Please indicate for reaction of what order a constant of velocity expresses by the following equation: k=1/t(C(0)-C):

f) *An order zero;
g) The third order;
h) The second order;
i) The first order;
j) The fractional order.

The half-life of what reaction expresses by an equation T(1/2) = 1/K*ln2:

f) *The first order;
g) An order zero;
h) The second order;
i) The third order;
j) The fractional order.

Please indicate, for reaction of what order the constant of velocity expresses by the following equation: K=1/tlnC(0)/C:

f) *The first order;
g) An order zero;
h) The second order;
i) The third order;
j) The fractional order.

Please indicate, for reaction of what order the constant of velocity expresses by the following equation: $K=1/2t(1/C^2-1/C(0)^2)$:

f) *The third order.
g) The fractional order;

h) An order zero;

i) The first order;

j) The second order;

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