# MINISTRY OF HEALTH REPUBLIC OF BELARUS GOMEL STATE MEDICAL UNIVERSITY

Department of general and bioorganic chemistry

Philippova V.A., Lusenkova A.V., Chernishova L.V.

# **CHEMICAL KINETICS**

Laboratory manual

Gomel 2005

УДК 57.037+54 ББК 24.54 Ф 53

Рецензент: заведующий кафедрой биологической химии, профессор, доктор медицинских наук А.И. Грицук.

Авторы-составители: Филиппова В.А., Лысенкова А.В., Чернышева Л.В.

# Филиппова В.А.

Ф 52 Chemical kinetics: Методическое пособие к лабораторно-практическим занятиям к курсу по общей химии для студентов лечебного факультета, обучающихся на английском языке / Авт.-сост.: В.А. Филиппова, А.В. Лысенкова, Л.В. Чернышева. — Гомель: Учреждение образования «Гомельский государственный медицинский университет», 2005. — 19 с.

ISBN 985-6779-39-1

Методическое пособие призвано помочь студентам, обучающимся на английском языке, овладеть основами знаний о скорости и механизме химических реакций. Особое внимание уделено вопросам кинетики ферментативных реакций, вопросам, играющим важную роль в формировании мировоззрения будущего врача. Приведенные задачи и упражнения помогут приобрести студентам практические навыки по выполнению кинетических расчетов.

Утверждено и рекомендовано к изданию Центральным учебным научно-методическим Советом Учреждения образования «Гомельский государственный медицинский университет» 09 ноября 2005 г., протокол № 11.

ISBN 985-6779-39-1

УДК 57.037+54 ББК 24.54

© Коллектив авторов, 2005 © Учреждение образования «Гомельский государственный медицинский университет», 2005

# **Chapter 1**

# **The Rates of Chemical Reactions**

The rate of chemical reactions is a very complicated subject. This statement is to be interpreted as a challenge to enthusiastic and vigorous chemists; it is not to be interpreted as a sad sigh of defeat.

Harold S. Johnston

# After reading this chapter, you should be able to:

- Define rates of homogeneous and heterogeneous reactions;
- Describe mechanism and molecularity of chemical reactions;
- Discuss rate laws and rate constants;
- Describe temperature dependence of the reactions rate.

# **1.1. RATE AND MECHANISM OF CHEMICAL REACTIONS**

Chemical kinetics is a branch of chemistry dealing with the rates and mechanisms of chemical reactions.

Rate of homogeneous reactions (reactions preceding in a uniform medium) is defined as the change in the concentration of reactants or products per unit time:

Rate 
$$(\mathcal{G}) = \pm \frac{[A] - [A]_0}{\tau},$$
 (1)

where  $\tau$  — time, s., min., hours;

 $[A]_0$  — initial molar concentration, mol/L;

[A] — final molar concentration.

A negative sign appears in the equation to make the rate positive, even though substance A concentration decreases with time.

For a chemical reaction  $2 \text{ NO}_2 \rightarrow 2 \text{ NO} + \text{O}_2$ Rate ( $\mathcal{G}$ ) of NO<sub>2</sub> consumption =  $-\frac{[NO_2] - [NO_2]_0}{\tau}$ Rate ( $\mathcal{G}$ ) of O<sub>2</sub> production =  $\frac{[O_2] - [O_2]_0}{\tau}$ 

In general, for the reaction  $\mathbf{aA} + \mathbf{bB} \rightarrow \mathbf{cC} + \mathbf{dD}$ the rate is given by

rate 
$$(\mathcal{G}) = -\frac{1}{a} \frac{d[A]}{d\tau} = -\frac{1}{b} \frac{d[B]}{d\tau} = \frac{1}{c} \frac{d[C]}{d\tau} = \frac{1}{d} \frac{d[D]}{d\tau},$$
 (2)

where the expressions in brackets refer to the concentrations of the reactants and products at time  $\tau$  after the start of the reaction. For heterogeneous reactions (reactions proceeding in non uniform medium) rate is defined as a change in moles of reactants and products per unit time per unit area of an interface surface:

Rate 
$$(\mathcal{G}) = \pm \frac{\upsilon(A) - \upsilon_0(A)}{\tau \times S}$$
, (3)

where  $\tau$  — time, s., min., hours;

 $v_0(A)$  — initial quantity of a substance, mol;

v(A) — final quantity of a substance, mol.

#### EXAMPLE 1

Write the rates for the following reactions in terms of the disappearance of reactants and appearance of products:

 $3~O_2 \rightarrow 2~O_3$ 

## **ANSWER:**

Rate 
$$(\mathcal{G}) = -\frac{1}{3} \frac{d[O_2]}{d\tau} = \frac{1}{2} \frac{d[O_3]}{d\tau},$$

The rate of chemical reactions depends upon:

Nature of reactants;

Their concentrations;

➤ Temperature;

➤ Catalyst;

Many other external factors.

The rates of chemical processes in vivo differ greatly. The time of the total renewal of bone tissue is 4–7 years, the time of a half proteins renewal — 70 days, chemical reactions responsible for neural activity run instantly.

A reaction mechanism is a sequence of simple molecular processes (elementary steps). Each step in such a sequence is called an elementary reaction. Elementary reactions may be:

(a) Unimolecular: an elementary step involves one molecule

$$N_2O_4 \rightarrow 2 NO_4$$

(b) Bimolecular: an elementary step involves two molecules

$$H_2 + I_2 \rightarrow 2 HI$$

(c) Termolecular: an elementary step involves three molecules

$$2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2$$

р

If a reaction mechanism involves only one elementary reaction it is known as a simple, but most reactions involve several elementary reactions (they are complex by mechanism). The types of complex reactions are:

 $\succ \text{Reversible} \quad A \leftrightarrow B$ 

➤ Parallel

 $\succ \text{Consecutive } A \rightarrow B \rightarrow C$ 

≻ Radical (chain).

## **1.2. RATE LAWS AND RATE CONSTANTS**

The relationship between the rate of a chemical reaction and the concentrations of the reactants is a complex one that must be determined experimentally. Referring to the general equation of a chemical reaction rate can be expressed as

$$Rate(\mathcal{G}) = k \times [A]^{x} \times [B]^{y}, \qquad (4)$$

This equation, known as the *rate law*, tells us that the rate of a reaction is not constant; its value at any time  $(\tau)$  is proportional to the concentrations of A and B raised to some powers. These powers are the orders of a reaction by reactants. The sum of powers is called the overall reaction order (n): n = x + y.

Only for simple reactions their order coincides with coefficients in chemical equations.

#### **Zero-Order Reactions**

The rate law for a zero-order reaction of the type  $\mathbf{A} \rightarrow \mathbf{product}$  is given by

Rate 
$$(\mathcal{G}) = -\frac{d[A]}{d\tau} = = \mathbf{k} \times [\mathbf{A}]^0 = \mathbf{k},$$
 (5)

#### **First-Order Reactions**

A first-order reaction is one in which the rate of the reaction depends only on the concentration of the reactant raised to the first power:

Rate 
$$(\mathcal{G}) = -\frac{d[A]}{d\tau} = -k \times [A],$$
 (6)  
where  $k = \frac{1}{\tau} \times \ln \frac{[A]_0}{[A]}$ 

A measure of considerable practical importance in kinetic studies is the *half-life*  $(\tau_{\frac{1}{2}})$  of a reaction. The *half-life* of a reaction is defined as the time it takes for the concentration of the reactant to decrease by half of its original value. For the first-order reactions

$$\pi_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0,693}{k},\tag{7}$$

Biochemical reactions catalyzed by enzymes, radioactive decay and many other natural processes fit first order kinetics.

## EXAMPLE 2

In healing some forms of cancer a medicine, containing radioisotope Ir-192 is used (its half-life is 74.08 days). Calculate what a part of Ir-192 will be contained in a human body through 10 days.

$$\frac{\text{ANSWER:}}{\tau_{\gamma_2} = \frac{\ln 2}{k} = \frac{0,693}{k},$$

$$k = \frac{0,693}{74,08} = 9,35 \times 10^{-3} \text{ day}^{-1}$$
$$\frac{[A]}{[A]_{o}} = e^{-0,00935 \times 10 \text{ days}} = 0,91 \text{ or } 91\%$$

# **Second-Order Reactions**

We consider two types of second-order reactions here. In one type, there is just one reactant. The second type involves two different reactants. The first type is represented by the general reaction  $2 A \rightarrow product$ 

and that rate is

rate 
$$(\mathcal{G}) = k [A]^2$$
, (8)

where  $\mathbf{k} = \frac{1}{\tau} \times \frac{[A]_0 - [A]}{[A]_0 \times [A]}$ 

 $\tau_{\frac{1}{2}} = \frac{1}{k[A]_0},$ (9)

The second type of second order reactions is represented by

2

## $A + B \rightarrow products$

This reaction is the first order in A, first order in B, and second order overall. Below are a few examples of a second-order reactions:

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

$$CH_3COCl (aq) + H_2O (L) \rightarrow CH_3COOH (aq) + HCl (aq)$$

# **1.3. THE TEMPERATURE DEPENDANCE OF REACTION RATES**

Fig.1 shows four types of temperature dependence for reaction rate constants. Type (a) represents normal reactions whose rates increase with increasing temperature. Type (b) shows a rate that initially increases with temperature, reaches a maximum, and finally decreases with further temperature rise. It is typical for enzyme-catalyzed reaction. When the enzyme is in the native state, the reaction rate does increase with temperature. At higher temperatures, the enzyme molecule may undergo denaturation, thereby losing its effectiveness as a catalyst. Type (c) shows a steady decrease of rate with temperature. It corresponds to termolecular reactions. The behavior shown in (d) corresponds to chain reaction. At first, the rate rises gradually with temperature. At a particular temperature, the chain propagation reactions become significant, and the reaction is literally explosive.

The normal reactions obey the Van't Hoff's rule: for every 10 Kelvin's of temperature elevation, the rate of most reactions increases from 2 to 4 times.

$$k_2 = k_1 \times \gamma^{\frac{T_2 - T_1}{10}}$$
, (10)

where  $\gamma$  — is the temperature coefficient of the chemical reaction,  $2 \le \gamma \le 4$  for most reactions and  $1,5 \le \gamma \le 3,0$  for biochemical reactions.





The more accurate description of how reactions' rates depend upon temperature is given in the Arrhenius equation (1889):

$$k = k_0 \times e^{\frac{-E_a}{RT}}, \qquad (11)$$

where  $k_0$  — pre-exponential factor,

Ea — activation energy, kJ/mol.

The activation energy is a minimum amount of energy required to initiate a chemical reaction. In other words, it's an amount of energy necessary to form an activated complex from reactants according to the scheme:

$$A + B \leftrightarrow A \dots B \rightarrow AB$$
  
activated  
complex

A following graph represents the pathway of a chemical reaction:





We may think of activation energy as a barrier that prevents less energetic molecules from reacting. Normally, only a small fraction of the reacting molecules have enough kinetic energy to exceed the activation energy. The higher the temperature the greater the kinetic energy of reacting molecules and the more is a fraction of active molecules in a mixture. Thus increase in temperature accelerates most chemical reactions.

If we know rate constants at two different temperatures we may use them to calculate activation energy according to the formula:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{T_1 - T_2}{T_2 \times T_2} \right),$$
 (12)

# EXAMPLE 3

The rate constant of a first-order reaction is  $4.60 \times 10^{-4} \text{ s}^{-1}$  at  $350^{\circ}$ C. Its activation energy is 104 kJ/mol. Calculate the temperature at which rate constant of a reaction is  $8,80 \times 10^{-4} \text{ s}^{-1}$ .

ANSWER:  

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

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

$$\ln 4.6 \times 10^{-4} - \ln 8.8 \times 10^{-4} = \frac{104000}{8.314} \times \left( \frac{350 - T_2}{350 \times T_2} \right),$$

$$\left( \frac{350 - T_2}{350 \times T_2} \right) = \frac{\ln \frac{4.6 \times 10^{-4}}{8.8 \times 10^{-4}} \times 8.314}{104000},$$

$$\left( \frac{350 - T_2}{350 \times T_2} \right) = -5.18 \times 10^{-5},$$

$$350 - T_2 = -0.018 \times T_2,$$

$$0.98 \times T_2 = 350,$$

$$T_2 = 356.5 \text{ K}.$$

# CHAPTER 2 ENZYME KINETICS

In recent years there has been some controversy about how enzymes manage to catalyze chemical reactions as fast as they do. Lost sight of in these arguments, however, has been the fact that the actual chemical reaction is seldom what limits the rate of an enzymatic reaction.

W.W. Cleland

After reading this chapter, you should be able to: Define catalysis and it's general principles; Describe the characteristics of enzymatic reactions from the viewpoint of energy and equilibrium; Discuss enzyme kinetics based on the Michaelis-Menten equation and the significance of the Michaelis constant;

■Define the enzyme activity or turnover number;

**Describe the factors affecting enzymatic reactions.** 

# 2.1. GENERAL PRINCIPLES OF CATALYSIS

General principles of catalysis are:

 $\succ$  A catalyst is a substance that changes the rate of a reaction without itself being consumed by the process. A reaction in which a catalyst is involved is a catalyzed reaction, and a process is called catalysis.

 $\succ$  A small quantity of a catalyst should be able to affect the rate of a reaction for a large amount of reactants.

> Catalysts do not change the equilibrium constant of chemical reactions.

Catalysts may affect rates of chemical reactions by decreasing or increasing their activation energies. They are classified as heterogeneous, homogeneous and enzymatic.

The phenomenon of enzyme catalysis usually results in a very large increase in reaction rate and high specificity.

## **2.2 THE EQUATION OF ENZYME KINETICS**

Almost all biological functions are supported by chemical reactions catalyzed by biological catalysts, enzymes. Efficient metabolism is controlled by orderly, sequential, and branching metabolic pathways. Enzymes accelerate chemical reactions under physiologic conditions: 37°C and neutral pH. However, an enzyme cannot alter the equilibrium of a concentration, but can only accelerate the reaction rate, by decreasing the activation energy of the reaction (fig. 3).



Fig. 3. Reaction profile for enzymatic and nonenzymatic reactions

Regulation of enzymatic activities allows metabolism to adapt to rapidly changing conditions. Nearly all enzymes are proteins are proteins, although some ribonucleic acid molecules, termed ribozymes, also have catalytic activity.

In 1913, the German biochemist Leonor Michaelis and the Canadian biochemist Maud L.Menten proposed a mechanism to explain the dependence of the initial rate of enzyme-catalyzed reactions on concentration. They considered the following scheme, in which ES is the enzyme-substrate complex:

$$S + E \leftrightarrow ES \rightarrow P + E$$

where S — a substrate;

E — an enzyme;

P — a product of a reaction.

The initial rate of product formation is given by

$$\mathcal{G} = \mathbf{k}_2 \,[\mathrm{ES}] \,, \tag{13}$$

where  $k_2$  is a first-order rate constant, known as molar enzyme activity or turnover number, expressed in min<sup>-1</sup>. It's the number of substrate molecules processed by an enzyme molecule per second when the enzyme is saturated with the substrate.

To derive the expression for the rate in terms of the more easily measurable substrate concentration, Michaelis and Menten assumed that

$$\mathcal{G} = \frac{k_2 \times [E]_0 \times [S]}{K_M + [S]},\tag{14}$$

Substituting equation (14) with equation (13) yields

$$\mathcal{G} = \frac{k_2 \times [E] \times [S]}{K_M + [S]} = \frac{\mathcal{G}_{\max} \times [S]}{K_M + [S]},$$
(15)

where  $K_M$  is the equilibrium constant, known as Michaelis constant; it characterizes stability of enzyme-substrate complexes,

 $\mathcal{G}_{\mathrm{max}}$  is a maximum rate, corresponding to the zero-order enzymatic reaction.

Equation (15) is a rate law of enzymatic reaction, which is known as the Michaelis-Menten equation.

At low substrate concentrations [S] << K<sub>M</sub> equation (15) becomes

$$\mathcal{G} = \frac{\mathcal{G}_{\max}}{K_m} \times [S], \tag{16}$$

it's a first reaction in [S]. This rate law corresponds to the initial linear portion of the plot in fig. 3.

At high substrate concentrations, [S]>>K<sub>M</sub>, equation (15) can be written as  $\mathcal{G} = \mathcal{G}_{max}$ ; (17)

It's a zero order in [S] and corresponds to the horizontal portion of the plot in fig.3. Now consider what happens when  $[S] = K_M$ . From equation (15) we find that this condition gives  $\mathcal{P} = \mathcal{P}_{max}/2$ , so  $K_M$  equals the concentration of S when the rate is half its maximum value.

A kinetic curve of an enzymatic reaction is given in fig. 3. We may use it for graphical determination of v max and  $K_M$ .



**Fig. 3.** Kinetic curve of enzymatic reactions

Factors affecting enzymatic reactions are:

- ✓ Temperature;
- ✓ Acidity and basicity of medium;
- ✓ Enzyme inhibitors.

Enzymes work best at an optimum pH value, which varies from enzyme to enzyme. Most enzymes that are active within cells have a pH optimum fairly close to the range of pH within which cells normally function. For example, the pH optima of two digestive enzymes, pepsin and trypsin, occur at about pH 2 and pH 8 respectively.

We will consider two forms of inhibition (there are others):

- Competitive inhibition
- Noncompetitive inhibition

Competitive inhibitors generally structurally similar to substrate and bind to active site — keeping out the substrate:



Original (uninhibited) Vmax can be attained by increasing [S] (competes out the inhibitor).

• K<sub>M</sub> increases (apparent loss of affinity for substrate).

• Noncompetitive inhibitors bind away from the catalytic site but cause a conformational change to be transmitted to the active site:



**3. LABORATORY WORK «CHEMICAL KINETICS»** 

# 3.1. Experiment № 1

# Affect of the reactants concentrations on the reaction rate

The aim of the experiment is to determine a linkage between reactants concentrations and the rate for the following chemical reaction:

$$Na_{2}S_{2}O_{3} + H_{2}SO_{4} \rightarrow Na_{2}SO_{4} + H_{2}S_{2}O_{3}$$
$$H_{2}S_{2}O_{3} \rightarrow H_{2}O + SO_{2} + S \downarrow$$

The end of the reaction is identified by evident appearance of sulfur precipitate.

Fill 10 test tubes with solution of sodium tiosulfate, sulfuric acid and water according to the scheme, given in a table  $N_{2}$  1.

Table 1

№ of a test tube	1	2	3	4	5	6	7	8	9	10
Initial solutions										
1 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , mL	1		2		3		4		5	
Water, mL	4		3		2		1		0	
1 M <b>H<sub>2</sub>SO<sub>4</sub>,</b> mL				5		5		5		5
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> initial concentration,		5								
mol/L	0,1		0,2		0,3		0,4		0,5	

Time after which sulfur precipitate appears, s.

Rate of a chemical reaction: 
$$\mathcal{G} = \frac{1}{\tau}$$
, (18)

Mix solutions of  $Na_2S_2O_3$  and  $H_2SO_4$ , contained in test tubes 1 and 2, 3 and 4, 5 and 6, 7 and 8, 9 and 10 correspondently. Mark the time of solutions' mixing, and the time, when sulfur precipitate appears.

Calculate rates of a chemical reaction using formula (1) and  $\mu$  represent the obtained data in a graph form (a plot of rates against Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> concentrations).

# 3.2. Experiment № 2

## Affect of the Temperature on the reaction rate

In this experiment we shall use the same  $Na_2S_2O_3$  and  $H_2SO_4$  solutions as in the experiment 1 were used. Pour 5 mL of  $Na_2S_2O_3$  solution into four test tubes, and 5 mL of  $H_2SO_4$  solution into another four test tubes. Organize these test tubes into four couples. Mark the room temperature of in a laboratory, and mix solutions of the first couple. Determine a time of a reaction under this temperature. Immerse all other test tubes into a chemical glass with water and heat them by ten degrees. Mix solutions of the second couples of test tubes and measure a time of a reaction. Repeat the experiment when a temperature will be increased by the next ten degrees and so on. Write the obtained data into the table  $N_2$  2.

No of a test tube	Volume of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , mL	Volume of H <sub>2</sub> SO <sub>4</sub> , mL	Temperature, °C	Time after which sulfur precipitate appears , s.	$\mathcal{G} = \frac{1}{\tau}$
1					
2					
3					
4					

Calculate temperature coefficients of an examined reaction. Does the reaction obey the Van't Hoff's rule or not?

Table 2

# 4. EXERCISES FOR THE SELF CONTROL

## **Reaction Order, Rate Law**

1. Write the rates for the following reactions in terms of the disappearance of reactants and appearance of products:

(a)  $C_2H_6 \rightarrow C_2H_4 + H_2$ (b)  $ClO^- + Br^- \rightarrow BrO^- + Cl^-$ (c)  $(CH_3)_3CCl + H_2O \rightarrow (CH_3)_3 + H^+ + Cl^-$ 

(d)  $2 \operatorname{AsH}_3 \rightarrow 2 \operatorname{As} + 3\operatorname{H}_2$ 

2. The rate law for the reaction

# $NH_4^+$ (aq) + $NO_2^- \rightarrow N_2$ (g) + 2 H<sub>2</sub>O (l)

Is given by rate -  $k[\mathbf{NH_4}^+][\mathbf{NO_2}^-]$ . At 25°C, the rate is  $3.0 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ . Calculate the rate of the reaction at this temperature if  $[\mathbf{NH_4}^+] = 0.26 \text{ M}$  and  $[\mathbf{NO_2}^-] = 0.080 \text{ M}$ 

3. Certain of first-order reaction is 34,5% complete in 49 min at 298 K. What is its rate constant?

4. What is the half-life of a compound if 75% of given sample of the compound decomposes in 60 min? Assume first-order kinetics.

5. The half-life for the (first-order) radioactive decay of  ${}^{14}C$  is 5730 years. An archaeological sample contained wood that had only 72 per cent of the  ${}^{14}C$  found in living trees. What is its age?

6. One of the hazards of nuclear explosions is the generation of  $^{90}$ Sr and its subsequent incorporation in place of calcium in bones. This nuclide has a half-life of 28,1 years. Suppose 1.00 µg was absorbed by a newly born child. How much will remain after (a) 18 years, (b) 70 years if none is lost metabolically?

7. Consider the following nuclear decay

 ${}^{64}Cu \rightarrow {}^{64}Zn + {}^{0}_{-1}\beta, t_{\frac{1}{2}} = 12.8 \text{ hr}$ 

Starting with one mole of <sup>64</sup>Cu, calculate the number of grams of <sup>64</sup>Zn formed after 25,6 hours.

## **Activation Energy**

8. Use reaction:

# $3 O_2(g) \rightarrow 2 O_3(g)$

to calculate the rate constant at 300 K for  $E_a = 0,2$  and 50 kJ mol<sup>-1</sup>. Assume that  $A = 10^{11}$  s<sup>-1</sup> in each case.

9. Many reactions double their rates with every  $10^{\circ}$  rise in temperature. Assume that such a reaction takes place at 305 K and 315 K. What must its activation energy be for this statement to hold?

10. The rate of bacterial hydrolysis of fish h muscle is twice as great at 2,2°C as at -1.1°C. Estimate an E<sub>a</sub> value for this reaction. Is there any relation to the problem of storing fish for food?

# **Catalysis. Michaelis-Menten Kinetics**

11. Activation energy of hydrogen peroxide decomposition

$$2 \operatorname{H}_2\operatorname{O}_2 \rightarrow 2 \operatorname{H}_2\operatorname{O} + \operatorname{O}_2$$

proceeds without a catalyst is 750 kJ/mol. Activation energy of the same reaction catalyzed by free iodine is much lower, only 55 kJ/mol. Calculate how much times a catalyst can accelerate a reaction.

12. The hydrolysis of acetylcholine is catalyzed by the enzyme acetyl cholinesterase, which has a turnover rate of  $25,000 \text{ s}^{-1}$ . Calculate how long it takes for the enzyme to cleave one acetylcholine molecule.

13.An enzyme that has a K<sub>M</sub> value of  $3.9 \times 10^{-5}$ M is studied at an initial substrate concentration of 0.035 M. After 1 min, it is found that 6.2 µM of a product has been produced. Calculate the value of  $\mathcal{G}_{max}$  and the amount of product formed after 4.5 min.

14. The initial rate of  $O_2$  production by the action of an enzyme on a substrate was measured for a range of substrate concentrations; the data are below. Evaluate the Michaelis constant for the reaction.

$[S] (mol L^{-1})$	0,050	0,017	0,010	0,0050	0,0020
$\mathcal{G}(\mathrm{mm}^3\mathrm{min}^{-1})$	16,6	12,4	10,3	6,6	3,3

# LITERATURE

1. Chang Raymond. Chemistry.: 4-th ed.

2. Olmsted, John 111 Chemistry, the molecular science.

3. Leo J. Malone Basic concepts of chemistry.: 4 th ed. — P. 360–366.

4. Chang Raymond. Physical chemistry for chemical and biological sciences. 3-d ed.

## Glossary

Activated complex An energetically excited state that is intermediate between reactants and products in a chemical reaction. Also called a transition state.

Activation energy The minimum energy required to initiate a chemical reaction.

**Arrhenius equation** An equation that relates the rate constant to the preexponential factor and the activation energy:

$$k = k_0 \times e^{\frac{-E_a}{RT}}$$

Bimolecular reaction An elementary step that involves two molecules.

**Catalyst** A substance that changes the rate of a reaction without itself being consumed.

**Cain reaction** A reaction in which an intermediate generated in one step attacks another species to produce another intermediate, and so on.

**Consecutive reactions** Consecutive reactions are reactions of the type  $A \rightarrow B \rightarrow C$ .

**Elementary step** A reaction that represents the progress at the molecular level. **Enzyme** A biological catalyst that is either the protein or an RNA molecule.

**First-order reaction** A reaction whose rate depends on the reactant concentration raised to the first power.

**Half-life** The time required for the concentration of a reactant to decrease to half of its initial concentration.

**Inhibitor** A substance that is capable of stopping or retarding an enzymecatalyzed reaction.

Maximum rate  $(V_{max})$  The rate of enzyme catalyzed reaction when all the enzymes are bound to substrate molecules.

**Michaelis-Menten kinetics** A mathematical treatment that assumes the initial step in enzyme catalysis is a pre-equilibrium between the substrate and the enzyme, followed by the conversion of the enzyme-substrate complex to product.

Molecularity The number of molecules reacting in an elementary step.

**Rate constant** Constant of proportionality between the reaction rate and the concentration of reactants.

**Rate-determining step** The slowest elementary step in the sequence of steps leading to formation of products.

**Rate law** An expression relating the rate of a reaction to the rate constant and the concentrations of the reactants.

**Reaction mechanism** The sequence of elementary steps that leads to product formation.

**Reaction order** The sum of the powers to which all reactant concentrations appearing in the rate law are raised.

**Second-order reaction** A reaction whose rate depends on the reaction concentration raised to the second power or on the concentrations of two different reactants, each raised to the first power. Termolecular reaction An elementary step that involves three molecules.

**Turnover number** The number of substrate molecules processed by an enzyme molecule per second when the enzyme is saturated with the substrate. Also referred to as  $k_2$ , the catalytic rate constant

Unimolecular reaction An elementary step that involves one molecule.

**Zero-order reaction** A reaction whose rate is independent of the concentrations of the reactants.

# CONTENT

Chapter 1. The Rates of Chemical Reactions	. 3
1.1. Rate and mechanism of chemical reactions	. 3
1.2. Rate laws and rate constants	. 5
1.3. The temperature dependence of reaction rates	. 6
Chapter 2. Enzyme Kinetics	. 9
2.1. General principles of catalysis	. 9
2.2. The Equation of Enzyme Kinetics	. 9
3. Laboratory Work «Chemical kinetics»	. 12
3.1. Experiment № 1. Affect of the reactants concentrations	
on the reaction rate	. 12
3.2. Experiment № 2. Affect of the Temperature on the reaction rate	. 13
4. Exercises for the self control	. 14
Literature	. 16
Glossary	. 17

Учебное издание

## ХИМИЧЕСКАЯ КИНЕТИКА (на английском языке)

Методическое пособие к лабораторно-практическим занятиям к курсу по общей химии для студентов лечебного факультета, обучающихся на английском языке

Редактор Лайкова В.Г.

Подписано в печать 05. 12. 2005 Формат 60×84<sup>1</sup>/<sub>16</sub>. Бумага офсетная 65 г/м<sup>2</sup>. Гарнитура «Таймс» Усл. печ. л. 1,16. Тираж 120 экз. Заказ № 223

Издатель и полиграфическое исполнение Учреждение образования «Гомельский государственный медицинский университет» 246000, г. Гомель, ул. Ланге, 5 ЛИ № 02330/0133072 от 30. 04. 2004