

**„NICOLAE TESTEMITANU”
STATE UNIVERSITY OF MEDICINE AND PHARMACY**

**FACULTY OF PHARMACY
DEPARTMENT OF GENERAL CHEMISTRY**

**MÎRZAC VIORICA
JORA ELENA**

PHYSICAL CHEMISTRY
Methodological guidelines for laboratory and practical work

Chisinau 2026

**„NICOLAE TESTEMITANU”
STATE UNIVERSITY OF MEDICINE AND PHARMACY**

**FACULTY OF PHARMACY
DEPARTMENT OF GENERAL CHEMISTRY**

**MÎRZAC VIORICA
JORA ELENA**

PHYSICAL CHEMISTRY
Methodological guidelines for laboratory and practical work

**Chisinau
Centrul Editorial-Poligrafic *Medicina*
2026**

CZU 544(076.5)
M 78

Approved by the Council of the Quality Management of „Nicolae Testemitanu” SUMPh (Minutes No.12 of June 19, 2026).

Authors:

Viorica Mîrzac, PhD, assistant lecturer, Department of general chemistry, „Nicolae Testemitanu” State University of Medicine and Pharmacy

Elena Jora, assistant lecturer, Department of general chemistry, „Nicolae Testemitanu” State University of Medicine and Pharmacy

Reviewers:

Constantin Cheptanaru, PhD, associate professor, Department of general chemistry, „Nicolae Testemitanu” State University of Medicine and Pharmacy.

Pavel Globa, PhD, associate professor, Department of biochemistry and clinical biochemistry, „Nicolae Testemitanu” State University of Medicine and Pharmacy.

DESCRIEREA CIP A CAMEREI NAȚIONALE A CĂRȚII
DIN REPUBLICA MOLDOVA

Mîrzac, Viorica.

Physical chemistry: Methodological guidelines for laboratory and practical work / Mîrzac Viorica, Jora Elena; „Nicolae Testemitanu” State University of Medicine and Pharmacy, Faculty of Pharmacy, Department of General Chemistry. – Chișinău: CEP *Medicina*, 2026. – 123 p.: fig., tab.

Ref. bibliogr.: p. 123 (4 tit.). – 50 ex.

ISBN 978-9975-82-512-2.

Text: nemediat.

544(076.5)
M 78

ISBN 978-9975-82-512-2

© CEP *Medicina*, 2026

© Viorica Mîrzac, Elena Jora, 2026

Contents

Preface	5
Laboratory rules in chemistry	6
Rules for plotting graphs	7
Laboratory and practical work No. 1	
Elements of chemical thermodynamics. Thermochemical equations. Hess's law	8
Laboratory and practical work No. 2	
The First Law of thermodynamics and its application to biosystems. Determination of the enthalpy change of a salt hydration	10
Laboratory and practical work No. 3	
The Second Law of thermodynamics. Thermodynamic state functions	20
Laboratory and practical work No. 4	
Thermodynamics of chemical equilibrium. Study of the chemical equilibrium of a homogeneous reaction	24
Assignment No. 1	31
Laboratory and practical work No. 5	
Thermodynamics of phase equilibria. Phase diagram of the aspirin–phenacetin binary system	33
Laboratory and practical work No. 6	
Thermodynamics of phase equilibria. Boiling point diagram for a binary liquid system	39
Laboratory and practical work No. 7	
Partially miscible liquid systems. Distribution Law. Study of the extraction process	45
Laboratory and practical work No. 8	
Colligative properties of electrolyte and nonelectrolyte solutions. Determination of the isotonic coefficient and the degree of ionization of a weak electrolyte solution using cryoscopy	52

Laboratory and practical work No. 9

Electrical conductivity of electrolyte solutions. Conductometric determination of the degree of ionization and the ionization constant of a weak electrolyte 60

Assignment No. 2 69

Laboratory and practical work No. 10

Thermodynamics of electrode processes. Potentiometric determination of solution pH. Potentiometric titration of hydrochloric and acetic acids 71

Laboratory and practical work No. 11

Thermodynamics of electrode processes. Oxidation–reduction systems. Concentration galvanic cells. Determination of the electrode potential and standard electrode potential of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox system 82

Laboratory and practical work No. 12

Chemical kinetics and kinetic equations. Kinetic study of sucrose hydrolysis 91

Laboratory and practical work No. 13

Chemical kinetics and kinetic equations. Kinetic study of the alkaline hydrolysis of acetylsalicylic acid 99

Laboratory and practical work No. 14

Mechanism of chemical reactions. Determination of the rate constant for the catalytic decomposition of hydrogen peroxide in the presence of MnO_2 106

Laboratory and practical work No. 15 113

Mechanism of chemical reactions. Determination of the rate constant for the oxidation of iodide ions by hydrogen peroxide... 113

Assignment No. 3 117

Appendices 119

Further reading 123

Preface

Physical chemistry is the science that studies chemical phenomena and the principles governing them through the laws of physics. Its main objective is to explain and predict the course and outcomes of chemical processes based on the structure and properties of matter.

The study of physical chemistry course at the Faculty of Pharmacy provides students with fundamental theoretical knowledge and practical skills required for disciplines such as pharmacognosy, pharmaceutical chemistry, toxicological chemistry, and pharmaceutical technology.

Laboratory and practical sessions are designed to consolidate theoretical knowledge of physical chemistry, familiarize students with physicochemical methods widely used in pharmaceutical practice, and develop skills in conducting experiments, processing experimental results, and interpreting data. These activities promote analytical thinking and the practical application of acquired knowledge.

Modern physical chemistry includes fields such as electrochemistry, photochemistry, and chemical kinetics. Its principles are essential for understanding and optimization processes involved in the production of metals, polymers, chemical fibres, pharmaceuticals, inorganic compounds, and food products.

Physical chemistry methods are widely applied in the pharmaceutical industry in processes such as evaporation, separation, distillation, drying, extraction, crystallization, and dissolution. They are also used to determine quality parameters, including acidity, moisture, and the content of sugars, fats, proteins, and vitamins.

This methodological guideline is intended for second-year students of the Faculty of Pharmacy. It includes descriptions of laboratory and practical sessions, control questions, and tasks for independent study. The theoretical introductions support a clear understanding of fundamental concepts and support the successful completion of practical tasks. The experimental sections provide detailed procedures, instructions for data processing, calculation formulas, guidelines for graphical representation of results, and recommendations for report preparation.

The guideline is designed to ensure a systematic approach to the educational process, supports the practical training of students, promotes the development of analytical skills, and facilitates independent learning.

Laboratory rules in chemistry

1. Wear a fastened cotton laboratory coat to ensure personal protection and prevent contamination of clothing.
2. Begin laboratory work only after thoroughly understanding the experimental procedure. If you have any doubts regarding the correct performance or safety of the experiment, consult the instructor.
3. Maintain the cleanliness of laboratory glassware and reagents. Do not use the same pipette for different substances, and never return excess reagent to its original container.
4. Do not use contaminated glassware; clean it immediately after completing the experiment.
5. Never taste chemical substances. To detect odours, cautiously waft vapours or gases toward your nose with your hand, avoiding direct or deep inhalation.
6. Use a rubber pipette bulb when drawing liquids into pipettes.
7. Avoid direct contact of chemicals with the skin to prevent irritation or chemical burns.
8. Do not heat, mix, or shake reagents near your face. When heating substances, never point the opening of a test tube or flask toward yourself or others.
9. Eating, drinking, smoking, or engaging in activities unrelated to laboratory work is prohibited in the chemical laboratory.
10. Do not dispose of broken glass, paper, or cotton wool in the sink.
11. At the end of the laboratory session, turn off electricity, gas and water supplies, and fume hoods.

Rules for plotting graphs

Graphical methods of data representation and analysis are widely used in the processing of physicochemical measurement results.

When plotting graphs, the following basic rules should be observed:

1. Graphs should be drawn on graph paper using a pencil (not a pen) or created using a computer software and inserted into the laboratory journal.
2. The origin of the coordinate system should coincide with a major grid line on the graph paper.
3. The independent variable should be plotted on the x-axis (horizontal axis) and the dependent variable on the y-axis (vertical axis). Each axis must be labelled with the corresponding quantity and its units of measurement.
4. The scale should be selected so that the coordinates of any point can be determined directly without additional calculations.
5. Experimental points should be marked with circles, crosses, or other clearly distinguishable symbols.
6. A smooth best-fit curve should be drawn through the experimental points. If justified, some points may be excluded from the fit. The curve should represent the average trend of the experimental data. The curve should be thin but clearly visible and should occupy most the plotting area. The axis scales should start and end at rounded value close to the minimum and maximum measured values.
7. In some experiments (e.g., adsorption or electrical conductivity measurements), very small values such as 4.5×10^{-10} , 1.2×10^{-5} , or 1.35×10^{-5} may be encountered. In such cases, the scale should be expressed using convenient whole-number intervals. The scales should be selected so that the curve is inclined at approximately 45° to the x-axis.
8. Numerical experimental data should not be written directly on the graph.
9. The relationship represented should be indicated below the graph. Graphical methods provide a clear visual representation of relationships between variables and allow certain calculations to be performed directly from the graph.

Laboratory and practical work No. 1

Elements of chemical thermodynamics

Thermochemical equations. Hess's law

Significance of the topic

Chemical thermodynamics is the science that studies the conditions of system stability and the laws governing their behaviour. It deals with macroscopic systems and enables the prediction of whether a given process is thermodynamically feasible. Physical and chemical phenomena are interpreted on the basis of the fundamental laws of thermodynamics.

The state of a system is described by measurable thermodynamic properties (state functions) that characterize the system independently of the path of the process or its molecular structure.

An important application of thermodynamics in medicine is the study of heat exchange in the human body. The maintenance of normal body temperature, regulation of heat production and dissipation, and uniform heat distribution are essential for normal physiological function. Thermodynamic principles help explain the body's response to environmental changes and the mechanisms for maintaining thermal equilibrium.

Thermodynamic analysis is essential for understanding biochemical reactions in the body. Most biological processes involve energy transformation, and the application of thermodynamic principles allows the mechanisms of their regulation and control to be explained.

In pharmacy, thermodynamics plays a critical role. Processes such as mixing, dissolution, and drug release are governed by thermodynamic laws. Understanding these principles enables the development of stable and effective pharmaceutical systems and helps prevent undesirable chemical reactions.

Applications of thermodynamics in pharmacy include the evaluation of drug stability and the determination of optimal storage conditions. The preservation of efficacy and safety is based on thermodynamic parameters such as enthalpy, entropy, and heat capacity.

Thermodynamic analysis is also used in studying the thermal effects of medical procedures, including laser therapy and magnetic resonance

imaging. Their safety and effectiveness depend on the thermodynamic characteristics of both the equipment and the applied methods.

Integral heat values reported in reference literature are widely used to calculate enthalpies changes of formation and reaction enthalpies in accordance with Hess's law. Differential heats of dissolution characterize the thermodynamic properties of solutions and the processes involved in their formation.

Thermodynamics plays a significant role in medicine and pharmacy by enabling a deeper understanding and optimization of physical and chemical processes occurring in the human body and in drug manufacturing. This knowledge supports the development of safer and more effective methods for diagnosis, treatment, and drug production.

Learning objectives

1. To acquire knowledge of:
 - a) the classification of thermodynamic systems;
 - b) thermochemical processes and reactions;
 - c) standard enthalpies of reactions;
 - d) thermochemical equations.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Control questions

1. Hess's law. Thermochemical equations.
2. Standard enthalpies changes. Standard enthalpies of formation.
3. Calculation of reaction enthalpy using standard enthalpies of formation and combustion.
4. Enthalpy changes of neutralization, dissolution, and hydration.

Session overview

1. Introduction to laboratory rules and procedures, graph plotting, and the preparation of laboratory reports in physical chemistry.
2. Review of the theoretical aspects of „Elements of chemical thermodynamics” studied in the General and inorganic chemistry course.
3. Problem-solving related to the topic: „Thermochemical equations. Hess's law”.

Laboratory and practical work No. 2

The First Law of thermodynamics and its application to biosystems Determination of the enthalpy change of salt hydration

Significance of the topic

The First Law of thermodynamics is a fundamental law that describes the transformation and conservation of energy in physical and chemical systems.

Thermodynamic principles are widely applied in pharmacy, biochemistry, and medicine to address a variety of theoretical and practical problems. They enable the description and explanation of processes occurring in the human body, as well as those involved in the production of pharmaceutical products. These principles also provide insight into the body's responses to environmental changes and the mechanisms responsible for maintain thermal balance.

Food intake supplies the body with energy, which is either utilized to perform physiological functions or stored for future use. This energy is released through biological oxidation, a multistep process. At the cellular level, it is first used for the synthesis of high-energy compounds such as adenosine triphosphate (ATP), which serves as the primary energy carrier for most cellular processes.

Calorimetric studies have established the average physiologically available energy content of the major nutrients (in kilocalories per gram): carbohydrates, 4.1; proteins, 4.1; and fats, 9.3.

Thus, nearly all energy expended by the body is ultimately converted into heat, except when muscles perform mechanical work on external objects.

Thermodynamic analysis is widely used in biophysical research to study parameters such as affinity and entropy. These parameters help explain interactions among proteins, enzymes, and other biomolecules, as well as identify energetic barriers in biochemical processes. Because many biological processes involve energy transformations, thermodynamics provides a fundamental basis for their analysis, regulation, and control.

In pharmaceutical practice, thermodynamics plays an essential role in evaluating drug stability and determining the conditions required to preserve their efficacy and safety. Knowledge of thermal effects and reaction mechanisms supports the rational selection of synthesis conditions and facilitates the assessment of product quality.

Calculations of thermodynamic functions are an important tool for predicting the feasibility and direction of chemical reactions and for studying solutions and complex physicochemical systems.

Thermochemical data are also indispensable for engineering calculations involved in the design of equipment and technological installations used in the chemical and pharmaceutical industries. For example, in the development of medical inhalers and mechanical ventilation devices, thermodynamic parameters must be carefully controlled to maintain specific pressure and temperature conditions, thereby ensuring operational safety and the effectiveness of therapeutic procedures.

Learning objectives

1. To acquire knowledge of:
 - a) the subject matter and significance of physical chemistry;
 - b) the First Law of thermodynamics;
 - c) the relationship between enthalpy change and internal energy change;
 - d) the dependence of reaction enthalpy on temperature.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Thermochemical equations of reactions. Hess's law.
2. Standard enthalpies of formation and combustion.
3. Calculation of reaction enthalpy using standard enthalpies of formation and combustion.
4. Enthalpy changes of neutralisation, dissolution, and hydration.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „The First Law of thermodynamics and its application to biosystems”.
3. Study of problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Determination of the enthalpy change of salt hydration”.

Control questions

1. Scope, objectives, and methods of physical chemistry. The significance of physical chemistry in medicine and pharmacy.
2. Key stages in the development of physical chemistry and the contributions of scientists to its development.
3. The First Law of thermodynamics and its mathematical representation.
4. Enthalpy and its relationship to internal energy changes.
5. Dependence of reaction enthalpy on temperature.
6. Kirchhoff's equation and its significance.

Self-assessment questions

1. What problems does physical chemistry address?
2. What is the role of physical chemistry in the development of medicine and pharmacy?
3. Describe the main stages in the development of physical chemistry.
4. Which scientific achievements contributed to the development of physical chemistry?
5. What topics are studied in thermodynamics?
6. What is a thermodynamic system? Which systems are considered isolated, closed, and open?
7. Define the internal energy of a system, work, and heat.
8. State the zeroth law of thermodynamics.
9. What are specific, molar, and differential heat capacities?
10. State the First Law of thermodynamics and write its mathematical expressions.

11. Write expressions for the expansion work of one mole of an ideal gas in isobaric, isothermal, and adiabatic processes. What is the work in an isochoric process?
12. What is meant by the heat effect of a reaction under isochoric and isobaric conditions?
13. Define enthalpy. Why is enthalpy considered a state function?
14. Write the relationship between changes in enthalpy and internal energy.
15. Which equations are referred to as thermochemical equations? Give examples.
16. Define Hess's law and write its mathematical expression.
17. Explain why Hess's law is a consequence of the first law of thermodynamics. Show that at constant pressure the heat of a reaction $Q_p = \Delta H$ and at constant volume $Q_v = \Delta U$, and deduce that the enthalpy change of a reaction is independent of the reaction pathway.
18. Define standard enthalpies of formation and combustion.
19. Write equations for calculating the enthalpy change of reaction using standard enthalpies of formation and combustion.
20. Define the enthalpy of neutralisation, dissolution, and hydration?
21. Explain integral and differential heats of dissolution and how they are determined.
22. Describe the temperature dependence of reaction enthalpy and write Kirchhoff's equation.

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (75 minutes).

Laboratory work

Determination of the enthalpy change of salt hydration

Laboratory objectives

To develop practical skills in:

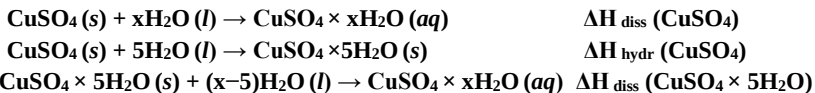
- determining the calorimeter heat constant;
- calculating the enthalpy of dissolution of an anhydrous salt and its crystalline hydrate;
- determining the enthalpy change of hydration of an anhydrous salt from experimental data.

Theoretical background

The enthalpy of hydration of an anhydrous salt is the enthalpy associated with the formation of a crystalline hydrate (i.e. incorporation of water of crystallisation). It can be determined using Hess's law, based on the enthalpies of dissolution of the anhydrous salt and the corresponding hydrate.

The enthalpy of dissolution of an anhydrous salt is equal to the sum of the enthalpy of hydration and the enthalpy of dissolution of the corresponding crystalline hydrate.

For copper(II) sulphate, the dissolution of the anhydrous salt, hydration, and dissolution of the resulting crystalline hydrate may be represented by the following thermochemical equations:



The reactions described above can be represented by the following scheme:



According to Hess's law:

$$\Delta H_{\text{diss}}(\text{CuSO}_4) = \Delta H_{\text{hydr}}(\text{CuSO}_4) + \Delta H_{\text{diss}}(\text{CuSO}_4 \times 5\text{H}_2\text{O})$$

ΔH_{hydr} – enthalpy of hydration;

ΔH_{diss} – enthalpy of dissolution.

Hence,

$$\Delta H_{\text{hydr}}(\text{CuSO}_4) = \Delta H_{\text{diss}}(\text{CuSO}_4) - \Delta H_{\text{diss}}(\text{CuSO}_4 \times 5\text{H}_2\text{O}) \quad (1)$$

Therefore, the enthalpy of hydration of anhydrous CuSO_4 can be determined from the enthalpies of dissolution of the anhydrous salt (CuSO_4) and its crystalline hydrate ($\text{CuSO}_4 \times 5\text{H}_2\text{O}$).

The enthalpy changes are measured using a calorimeter. The enthalpy changes of dissolution of an anhydrous salt and its crystalline hydrate are calculated from experimental calorimetric data:

$$\Delta H = -K \frac{\Delta T \times M(B)}{m(B)} \quad (2)$$

where:

$m(B)$ – mass of the substance, g;

$M(B)$ – molar mass, $\text{g} \times \text{mol}^{-1}$;

ΔT – temperature change, K;

K – calorimeter constant, $\text{kJ} \times \text{K}^{-1}$.

Experimental procedure

Apparatus and reagents

1. calorimeter;
2. graduated cylinder, 200 mL;
3. thermometer ($\pm 0.01^\circ\text{C}$);
4. glass stirring rod;
5. stopwatch;
6. analytical and technical balances;
7. substances for determining the calorimeter constant: KNO_3 , KCl , KBr , CuCl_2 , NH_4NO_3 , NH_4Cl ;
8. anhydrous salts: CuSO_4 , CuCl_2 , Na_2CO_3 , Na_2SO_4 , Na_2HPO_4 , MgSO_4 , ZnSO_4 , and their crystalline hydrates;
9. distilled water.

Experiment 1. Determination of the calorimeter constant

As follows from equation (2), the calculation of the enthalpy of dissolution of an anhydrous salt and its crystalline hydrate requires prior determination of the calorimeter.

The calorimeter constant characterizes the amount of heat required to raise the temperature of the calorimeter by 1 °C. Its value depends on the heat capacities of all calorimeter components involved in the heat exchange process.

Method 1

The calorimeter constant is calculated as the sum of the products of the masses and specific heat capacities of the individual components of the calorimetric system.

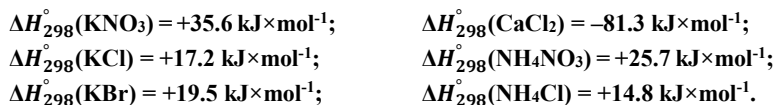
$$K = \sum m_i \times c_i \quad (3)$$

where:

m_i – mass of each component of the apparatus and the liquid, kg;
 c_i – specific heat capacity of each component, $\text{kJ} \times \text{kg}^{-1} \times \text{K}^{-1}$.

In practice, K can be approximated as the sum of the heat capacities of the beaker, stirrer, and water (or solution). The following specific heat capacities are typically used: $0.753 \text{ kJ} \times \text{kg}^{-1} \times \text{K}^{-1}$ for glass, $4.184 \text{ kJ} \times \text{kg}^{-1} \times \text{K}^{-1}$ for the solution, and $0.462 \text{ kJ} \times \text{kg}^{-1} \times \text{K}^{-1}$ for steel.

The calorimeter constant may also be determined experimentally using substances with known standard enthalpies of dissolution, for example:



The value of the calorimeter constant remains valid only for a given calorimeter setup and a fixed volume of the liquid used.

Method 2

To determine the calorimeter constant using one of the salts listed, proceed as follows. Assemble the calorimeter as shown in Figure 1.

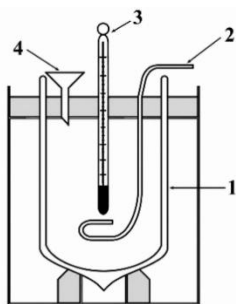


Fig. 1. Schematic diagram of a classical calorimeter

Using a graduated cylinder, transfer 150 mL of distilled water into the inner vessel (1), then insert the stirrer (2) into the vessel. Cover the vessel with the lid and insert a thermometer (3) with an accuracy of 0.01 °C, ensuring that the mercury bulb is positioned approximately 1 cm below the liquid surface.

Weigh the salt sample using an analytical balance and record the mass in Table 1.

Preliminary period. Start the stopwatch and gently stir the water while recording the thermometer readings every 30 seconds for 5 minutes. Record all temperature measurements in Table 2.

Main period. After 5 minutes, without stopping the stopwatch, quickly add the weighed salt sample into the water through the funnel opening (4), then immediately seal with a stopper. Continue stirring and record the temperature every 30 seconds until the salt has completely dissolved, which typically takes 1-2 minutes. The exact duration of the main period should be determined from the temperature-time graph.

Final period. After the salt has completely dissolved, continue stirring and record the temperature every 30 seconds for 5 minutes.

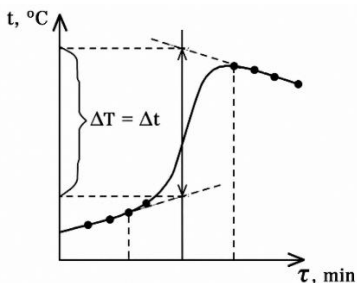


Fig. 2. Temperature-time graph for the dissolution of the salt in water

Based on the experimental data, construct a temperature-time graph. Determine the temperature change (ΔT) from the graph, as shown in Figure 2. Calculate the calorimeter's thermal constant using the formula derived from equation (2):

$$K = -\Delta H(B) \frac{m(B)}{\Delta T \times M(B)} \quad (4)$$

Experiment 2. Determination of the enthalpy change of dissolution of an anhydrous salt

After determining the temperature change required to calculate the calorimeter constant, determine the enthalpy change of dissolution of an anhydrous salt assigned by the instructor (e.g., CuSO_4 , CuCl_2 , Na_2CO_3 , Na_2SO_4 , Na_2HPO_4 , MgSO_4 , ZnSO_4). The mass of the salt sample should be 3-5 g. Record all weighing data and calorimetric measurements in Tables 1 and 2.

Experiment 3. Determination of the enthalpy change of dissolution of a hydrated salt

First, calculate the required mass of the hydrated salt so that the resulting solution has the same concentration as that prepared from the corresponding anhydrous salt. For example, if 4 g of CuSO_4 is used for the anhydrous salt, a larger mass of $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ is required to account for the water of crystallisation.

Example calculation:

160 g CuSO_4 corresponds to 250 g $\text{CuSO}_4 \times 5\text{H}_2\text{O}$

4.00 g CuSO_4 corresponds to x g $\text{CuSO}_4 \times 5\text{H}_2\text{O}$

$$x(\text{CuSO}_4 \times 5\text{H}_2\text{O}) = \frac{250 \text{ g} \times 4.00 \text{ g}}{160 \text{ g}} = 6.25 \text{ g}$$

The volume of water used for dissolution should be reduced by the amount of water of crystallisation contained in the hydrate:

$$m(\text{H}_2\text{O}) = m(\text{CuSO}_4 \times 5\text{H}_2\text{O}) - m(\text{CuSO}_4) = 6.25 \text{ g} - 4.00 \text{ g} = 2.25 \text{ g},$$

which corresponds to a volume of $V(\text{H}_2\text{O}) \approx 2.25 \text{ mL}$, assuming a water density $\rho(\text{H}_2\text{O}) \approx 1.0 \text{ g} \times \text{mL}^{-1}$.

Measure 150 mL of distilled water in a graduated cylinder, then remove 2.25 mL with a pipette to compensate for the water of crystallization present in the hydrate. Transfer the remaining water to the calorimeter vessel and perform the experiment as described in Experiment 1.

Using the calorimeter constant K and the results obtained in Experiments 2 and 3, calculate the enthalpy change of dissolution of the

anhydrous salt and its hydrate using equation (2), and determine the enthalpy change of hydration using equation (1).

Table 1. Salt samples used in the experiments

	Experiment 1 Determination of the calorimeter constant	Experiment 2 Determination of the enthalpy of dissolution of an anhydrous salt	Experiment 3 Determination of the enthalpy of dissolution of a hydrated salt
Salt used			
Sample mass, g			

Table 2. Calorimetric measurements used to determine the calorimeter constant and the enthalpy of dissolution of a salt and its hydrate

Calorimetric period	Time from the start of the experiment, τ , min	Temperature measurement, °C		
		Experiment 1 Calorimeter constant	Experiment 2 Dissolution of anhydrous salt	Experiment 3 Dissolution of hydrated salt
Preliminary period (5 min)				
Main period (salt dissolution)				
Final period (5 min)				

Independent study

1. Analysis of the experimental data and plotting of the graphs.
2. Preparation of the laboratory report: „Determination of the enthalpy change of salt hydration”.
3. Problem-solving related to the topic: „The First Law of thermodynamics and its application to biosystems”.

Laboratory and practical work No. 3

The Second Law of thermodynamics

Thermodynamic state functions

Significance of the topic

Most chemical reactions are characterized by the fundamental thermodynamic state functions – enthalpy, entropy, and Gibbs free energy. Thermodynamic analysis has wide application in biology and medicine, particularly in evaluating the energy expenditure of living organisms, determining the caloric value of food, and studying the energetics of muscle contraction, metabolism, and other physiological processes.

A comparison of the energetic characteristics of healthy and diseased cells makes it possible to investigate various pathological phenomena and contributes to the development of diagnostic and therapeutic approaches at different stages of disease progression. Thus, knowledge of the theoretical principles and practical aspects of chemical thermodynamics is essential for the study of biochemistry, pharmaceutical chemistry, pathology, and other related disciplines.

The Second Law of thermodynamics is of fundamental importance. The increase in entropy reflects the irreversible evolution of isolated systems and, on a cosmological scale, the gradual progression of the Universe toward thermodynamic equilibrium, where spontaneous processes eventually cease.

W. Ostwald considered that the essence of living matter is reflected in the specific manifestation of the law of energy dissipation: living systems differ from non-living ones by a higher rate of entropy increase. The Russian physicist N. Umov noted that the sensory organs of living organisms perceive signals from the external environment due to the action of the law of energy dissipation.

Critical discussions of the Second Law of thermodynamics contributed to the development of nonequilibrium thermodynamics and synergetic and also drew attention to fundamental issues in ecology and evolution.

Learning objectives

1. To acquire knowledge of:
 - a) the Second Law of thermodynamics as a statistical law;
 - b) entropy changes in various processes;
 - c) thermodynamic state functions under isobaric-isothermal and isochoric-isothermal conditions;
 - d) the criteria governing the spontaneity of processes;
 - e) the thermodynamic conditions of equilibrium.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. The Second Law of thermodynamics.
2. Energy changes and the direction of chemical reactions.
3. The Carnot cycle.

Homework assignment

1. Review the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „The Second Law of thermodynamics. Thermodynamic state functions”.
3. Study of the problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.

Control questions

1. The Second Law of thermodynamics and its mathematical formulation.
2. Entropy and entropy changes in isolated systems.
3. Thermodynamic probability and its relationship to entropy. The statistical nature of the Second Law of thermodynamics.
4. The Third Law of thermodynamics. Absolute and standard entropy.
5. Helmholtz free energy (isochoric-isothermal potential).
6. Gibbs free energy (isobaric-isothermal potential).
7. Changes in Helmholtz and Gibbs free energies during spontaneous processes.
8. Thermodynamic conditions of equilibrium. The concept of chemical potential.

Questions self-assessment

1. What are reversible and irreversible processes in thermodynamic and chemical terms?
2. Which formulations of the Second Law of thermodynamics are known?
3. Write the mathematical expression of the Second Law of thermodynamics for reversible and irreversible processes.
4. Write the combined mathematical expression of the First and Second Laws of thermodynamics for reversible and irreversible processes.
5. How is the entropy change determined during phase transitions (evaporation, melting, and sublimation)?
6. Write the mathematical relationship between entropy and enthalpy changes for an irreversible process.
7. What is the relationship between the molar entropies of a substance in the gaseous, liquid, and solid states? Which state has the highest molar entropy?
8. How can the equilibrium state of an isolated system be determined from the entropy change?
9. Can the direction of a process in a non-isolated system be predicted based on the entropy change?
10. What is the thermodynamic probability of a system and how is it related to entropy? State the Boltzmann-Planck equation.
11. Why does the Second Law of thermodynamics have a statistical nature?
12. Name the thermodynamic state functions and thermodynamic potentials.
13. What is Helmholtz free energy?
14. What are Gibbs free energy and standard Gibbs free energy?
15. Under what conditions can internal energy serve as a criterion for the direction of a process?
16. Under what conditions can enthalpy serve as a criterion for the spontaneity of a process? What is its change under these conditions?
17. In a spontaneous isobaric-isothermal process, entropy decreases. Compare the changes in Gibbs free energy and enthalpy of the process. Which change is greater?

18. Which thermodynamic state functions determine the direction of a process in a non-isolated system at constant volume and temperature (V, T), and at constant pressure and temperature (P, T)?
19. What is the relationship between the changes in Gibbs free energy and Helmholtz free energy for one mole of an ideal gas during isothermal expansion from volume V_1 to V_2 ?
20. Write the equations relating Helmholtz free energy and Gibbs free energy to the maximum useful work.
21. How does Helmholtz free energy change during the dissolution of sugar in water?
22. Explain how enthalpic and entropic factors influence the magnitude of Gibbs free energy and the direction of a process.
23. To what value does the entropy of a perfect crystal tend as the temperature approaches absolute zero?
24. What are absolute entropy and standard entropy?
25. Write the formulas for calculating the absolute entropy of a substance in the solid, liquid, and gaseous states.
26. What is chemical potential? Write all its expressions in terms of thermodynamic potentials.
27. Write the equation expressing the dependence of chemical potential on concentration.
28. Write the equations relating changes in Helmholtz free energy, Gibbs free energy, internal energy, and enthalpy to chemical potential.
29. State the conditions for chemical equilibrium.

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (30 minutes).

Laboratory and practical work No. 4

Thermodynamics of chemical equilibrium Study of chemical equilibrium in a homogeneous reaction

Significance of the topic

Chemical equilibrium plays an important role in medicine and pharmacy, as it underlies numerous biochemical and pharmacological processes. Understanding the principles of chemical equilibrium contributes to the development of medicinal products, prediction of their behaviour in the body, and optimization of conditions for their storage and administration.

Chemical equilibrium determines the solubility of substances in biological fluids, which is essential for the transport and delivery of active pharmaceutical ingredients to organs and tissues. In particular, the equilibrium between the ionized and non-ionized forms of a drug affects its absorption in the gastrointestinal tract.

The concept of chemical equilibrium is also of major importance in pharmacokinetics, as it affects the distribution, metabolism, and excretion of medicinal products. The equilibrium between a drug bound to plasma proteins and its free form determines the bioavailability to interact with receptors.

In the liver and other organs, drug biotransformation involves enzymes catalysed reactions that modify the chemical structure of medicinal substances. The dynamic equilibrium between metabolic and excretory processes makes it possible to predict the drug's half-life and to determine the optimal dosing regimen.

Chemical equilibrium plays a key role in the mechanisms underlying the development of microbial resistance to antibiotics, since changes in environmental conditions may shift the equilibrium in favour of resistant strains.

Thus, knowledge of the principles of chemical equilibrium is essential for the development of safer and more effective medicinal products, the optimization of drug delivery, and the improvement of therapeutic efficacy.

The theory of chemical equilibrium is essential for calculating equilibrium constants, which can be expressed in various forms. This is of great importance for assessing the feasibility of chemical synthesis, estimating yields of drug substances with desired properties, selecting analytical methods, and studying pharmacological processes.

If a system at equilibrium is subjected to external factors, such as changes in concentration, temperature, or pressure, the system tends to counteract this influence. As a result, the chemical equilibrium shifts in the direction that opposes the imposed change.

Similarly, living systems exposed to external factors reorganize to minimize their impact. This principle ensures the maintenance of homeostasis – a dynamic steady state far from chemical equilibrium – which enables adaptation and survival of living organisms.

Many reversible biochemical processes proceed with the participation of biocatalysts – enzymes. These substances accelerate reaction rates by lowering the time required to reach equilibrium, which is essential for the proper functioning of living systems.

Learning objectives

1. To acquire knowledge of:
 - a) the law of mass action for homogeneous and heterogeneous chemical equilibria;
 - b) the equations of the chemical reaction isotherm, isochore, and isobar.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Reversible and irreversible chemical reactions. Chemical equilibrium and the equilibrium constant. The law of mass action for reversible reactions.
2. Calculation of the equilibrium constant from the standard Gibbs free energy change.
3. Prediction of the equilibrium shift under changing reaction conditions using Le Chatelier's principle.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Thermodynamics of chemical equilibrium”.
3. Study of the problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Study of chemical equilibrium in a homogeneous reaction”.

Control questions

1. The law of mass action for homogeneous and heterogeneous equilibria.
2. The equilibrium constant and its forms of expression: K_p , K_c , K_a , and K_x .
3. The reaction isotherm equation and its analysis.
4. The reaction isobar and isochore equations and their analysis.
5. Calculation of the equilibrium constant using standard enthalpies and standard entropies of formation of the reaction components.

Self-assessment questions

1. Explain the conditions for chemical equilibrium from both kinetic and thermodynamic perspectives. What are the similarities and differences between these approaches?
2. Define chemical equilibrium and describe its dynamic nature and characteristic features. What are reversible reactions, and how does reaction reversibility differ from thermodynamic reversibility?
3. Can constant concentrations of reacting substances be regarded as evidence of chemical equilibrium? Justify your answer based on the principles of chemical equilibrium.
4. Express the equilibrium constant in terms of the degree of dissociation and pressure. Give examples of situations in which different equilibrium characteristics, such as the degree of dissociation, mole fractions, molar concentrations, and pressure, are used.
5. Express the equilibrium constant of a reaction in solution in terms of activity and mole fractions. Do these equilibrium constants differ?

6. State the equilibrium conditions for heterogeneous reactions. Write the expression for the equilibrium constant of a reaction involving substances in different phases.
7. The equilibrium constants for the reactions $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ and $\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$ have the same mathematical form. Explain why their numerical values are different at the same temperature.
8. What thermodynamic and molecular-kinetic characteristics define the equilibrium state of a system?
9. Which factors influence the values of the equilibrium constants K_p and K_c ?
10. How can the effect of temperature on the equilibrium constant be predicted using Le Chatelier's principle?
11. An inert gas is added to an equilibrium reaction mixture at constant pressure or at constant volume. Does the equilibrium constant change in either case?
12. Write the relationship between the equilibrium constants K_p and K_c for the reaction $2\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{O}_2(\text{g})$.
13. Express the equilibrium constant K_p for the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ in terms of the equilibrium partial pressures of the components.
14. How can the direction of a chemical reaction under given conditions be determined? What is the criterion for the direction of a chemical reaction? What are the conditions for establishing equilibrium?
15. Write the isotherm equation for the reaction $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$, assuming that all substances behave as ideal gases.
16. How does the direction of a chemical reaction depend on the concentrations or partial pressures of the reacting substances?
17. How does temperature affect the position of equilibrium in exothermic and endothermic reactions?
18. Write and analyse the differential equation describing the dependence of the equilibrium constant on temperature.
19. How can the equilibrium constant of a reaction at different temperatures be determined from experimental data?

20. How can the enthalpy change of a reaction be calculated using the values of K_p and K_c at different temperatures?
21. In which coordinates is the dependence of the equilibrium constant on temperature represented by a straight line?
22. By what methods can the equilibrium of a chemical reaction be shifted at constant temperature?
23. How does a decrease in pressure affect the equilibrium position of the reaction $2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 4\text{HCl}(\text{g}) + \text{O}_2(\text{g})$, assuming that all substances behave as ideal gases?
24. How is the equilibrium constant calculated using standard enthalpies and standard entropies of formation of the reaction components?
25. In what units should the pressure of CO_2 be expressed for the reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ so that the value of ΔG^0_T , calculated from the equation $\Delta G^0_T = -RT \ln P(\text{CO}_2)$, corresponds to the standard state?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (60 minutes).

Laboratory work

Study of chemical equilibrium in a homogeneous reaction

Laboratory objectives

To develop practical skills in evaluating the effect of reactant concentration and temperature on the chemical equilibrium.

Theoretical background

The formation of iron(III) thiocyanate complexes is commonly used to study the effect of reactant concentration on the position of chemical equilibrium.

This process proceeds stepwise through the successive coordination of thiocyanate ions to the iron(III) ion:

1. $\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons [\text{Fe}(\text{SCN})]^{2+}$,
2. $[\text{Fe}(\text{SCN})]^{2+} + \text{SCN}^- \rightleftharpoons [\text{Fe}(\text{SCN})_2]^+$, etc.,

up to the formation of saturated complex ions, for example:



The complex ions $[\text{Fe}(\text{SCN})]^{2+}$, $[\text{Fe}(\text{SCN})_2]^+$, and related species exhibit an intense red colour, whereas aqueous iron(III) ions are yellow. Potassium, ammonium, chloride, and thiocyanate ions are colourless.

Changes in the concentration of the iron(III) thiocyanate complexes are accompanied by changes in the intensity of the red colour, providing a visual indication of shifts in chemical equilibrium.

Experimental procedure

Apparatus and reagents

1. FeCl_3 and KSCN (or NH_4SCN), saturated solutions;
2. KCl (or NH_4Cl) crystals;
3. aqueous iodine solution, molar concentration $0.1 \text{ mol} \times \text{L}^{-1}$;
4. starch solution;
5. alcohol burner;
6. distilled water.

Experiment 1. Effect of reactant concentration on the chemical equilibrium

Pour 20 mL of water into a small beaker and add a few drops of saturated FeCl_3 and KSCN (or NH_4SCN) solutions. Mix thoroughly and divide the resulting solution equally among four test tubes.

Add a few drops of concentrated FeCl_3 solution to the first test tube, concentrated KSCN (or NH_4SCN) solution to the second test tube, and a small amount of solid KCl (or NH_4Cl) to the third test tube. Leave the fourth test tube unchanged as a reference sample.

Using the law of mass action and Le Chatelier's principle, explain the colour changes observed in the first three test tubes. Record your observations in the Table 3.

Table 3. Influence of reactant concentration on chemical equilibrium

Added substance	Change in colour intensity	Direction of equilibrium shift
FeCl ₃ solution		
KSCN solution		
KCl crystals		

Experiment 2. Effect of temperature on the chemical equilibrium

When iodine reacts with starch, a blue-coloured iodine–starch complex is formed:



Pour 4-5 mL of starch solution into each of two test tubes and add 3-4 drops of iodine solution to each. Heat one test tube in a water bath and then allow it to cool. Leave the second test tube at room temperature as a reference.

Observe the changes that occur during heating and subsequent cooling of the solution. Determine whether the formation of the iodine–starch complex is an exothermic or an endothermic process, and explain the observed changes using Le Chatelier’s principle.

Independent study

1. Analysis of the experimental observations and writing the chemical equations for the performed experiments.
2. Preparation of the laboratory report: „Study of the chemical equilibrium of a homogeneous reaction”.
3. Problem-solving related to the topic: „Thermodynamics of chemical equilibrium”.

Assessment No. 1

Learning objectives

Based on the above topics, to assess:

- a) the level of assimilation of theoretical knowledge;
- b) the practical skills and competencies acquired during laboratory sessions;
- c) the ability to solve applied problems.

Written test on the topics

1. Elements of chemical thermodynamics.
2. The First and Second Laws of thermodynamics.
3. Thermodynamic state functions.
4. Thermodynamics of chemical equilibrium.

Control questions

1. Scope, objectives, and methods of physical chemistry. The significance of physical chemistry in medicine and pharmacy.
2. Key stages in the development of physical chemistry and the contributions of scientists to its development.
3. The First Law of thermodynamics and its mathematical formulation.
4. Enthalpy and its relationships to internal energy change.
5. The dependence of reaction enthalpy on temperature.
6. Kirchhoff's equation and its significance.
7. Hess's law.
8. Thermochemical equations.
9. Standard enthalpies of formation and combustion.
10. Calculation of reaction enthalpy using standard enthalpies of formation and combustion.
11. Enthalpy changes in neutralization, dissolution, and hydration processes.
12. The Second Law of thermodynamics and its mathematical formulation.
13. Entropy and entropy changes in isolated systems.
14. Thermodynamic probability and its relationship to entropy. Statistical interpretation of the Second Law of thermodynamics.

15. The Third Law of thermodynamics. Absolute and standard entropy.
16. Helmholtz free energy (isochoric-isothermal potential).
17. Gibbs free energy (isobaric-isothermal potential).
18. Changes in Helmholtz and Gibbs free energies in spontaneous processes.
19. Thermodynamic conditions of equilibrium. The concept of chemical potential.
20. The law of mass action for homogeneous and heterogeneous chemical equilibria.
21. The chemical equilibrium constant and its forms of expression: K_p , K_c , K_a , and K_x .
22. The reaction isotherm equation and its analysis.
23. The reaction isobar and isochore equations and their analysis.
24. Calculation of the chemical equilibrium constant using standard enthalpies and standard entropies of formation of the reactants and products.

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment based on control questions and problems analogous to those previously solved (60 minutes).
3. Analysis of errors made in the written test.

Laboratory and practical work No. 5

Thermodynamics of phase equilibria

Phase diagram of the aspirin-phenacetin binary system

Significance of the topic

Knowledge of phase equilibria is essential for ensuring the quality, stability, and efficacy of pharmaceutical products. It enables the optimization of dosage forms (solutions, ointments, tablets) and the selection of appropriate conditions for combining active ingredients.

In pharmacy, incompatibility refers to changes in the chemical, physical, or pharmacodynamic properties of substances that may reduce product quality. Phase diagrams help predict and prevent both physical incompatibilities (e.g., caking, phase separation) and chemical interactions between components.

Physical incompatibility of pharmaceutical substances is often related to eutectic formation. However, eutectic mixtures may improve the quality and technological properties of pharmaceutical products. For example, in powders containing thymol and menthol, eutectic mixtures form finer particles than non-eutectic mixtures, promoting more uniform distribution of components within the dosage form.

Phase diagrams are also important in pharmaceutical quality control. They allow prediction of the effects of temperature and pressure changes on drug stability and efficacy. In pharmaceutical manufacturing, phase equilibria are essential for controlling crystallization processes and the formation of polymorphic forms of active ingredients, thereby ensuring the desired physicochemical and therapeutic properties.

The study of phase equilibria also facilitates the optimal selection of solvents and excipients to ensure sufficient solubility of active substances and stability of the final product.

Phase diagrams of binary mixtures are used to determine optimal component ratios, preparation and storage conditions, and shelf life of pharmaceutical products.

Learning objectives

1. To acquire knowledge of:
 - a) phase transitions and phase equilibria;
 - b) Gibbs' phase rule;
 - c) phase diagrams of single-component systems;
 - d) melting diagrams of binary systems;
 - e) methods of thermal analysis.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Concepts of phase and component.
2. Phase transitions.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Thermodynamics of phase equilibria”.
3. Study of the problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Phase diagram of the aspirin-phenacetin binary systems”.

Control questions

1. Concepts of phase, system constituents, components, and degrees of freedom.
2. Phase transitions and phase equilibria.
3. Clausius-Clapeyron equation and its application to evaporation, sublimation, and melting processes.
4. Gibbs' phase rule.
5. Phase diagrams of single-component systems.
6. Phase diagrams of binary systems.
7. Thermal analysis. Concept of physicochemical analysis.

Self-assessment questions

1. Formulate the general thermodynamic condition for phase equilibrium.
2. Define the concepts of phase, component, and degrees of freedom of a system.
3. How is the number of components in a thermodynamic system determined?
4. What does the number of degrees of freedom of a system indicate?
5. How many phases and degrees of freedom are present in the regions, along the curves, and at the triple point of the water phase diagram?
6. What is the triple point in a single-component phase diagram?
7. Write the Gibbs phase rule for a system influenced only by temperature and pressure.
8. What is the number of degrees of freedom in a single-component system with coexisting liquid and solid phases?
9. What is the maximum number of phases that can coexist in equilibrium in a single-component system?
10. Sketch the phase diagram of water in $P=f(T)$ coordinates and indicate the phase regions.
11. Derive the Clausius-Clapeyron equation from the equality of the specific (or molar) Gibbs energy of a substance in coexisting phases at equilibrium, and analyse the equation.
12. Using the Clausius-Clapeyron equation, explain why vapour pressure increases with temperature.
13. At which coordinates does the vapour pressure-temperature relationship become linear?
14. What is the typical relationship between melting temperature and pressure for most substances? Why does water behave differently?
15. Write and analyse the Clausius-Clapeyron equation based on the equality of molar
16. Write the equation used to calculate the enthalpy of vaporization over a small temperature interval.
17. Draw and explain the melting diagram of a simple eutectic system.
18. What is thermal analysis, and what are its application?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (75 minutes).

Laboratory work

Phase diagram of the aspirin-phenacetin binary system

Laboratory objectives

To develop practical skills in:

- a) determining the melting temperatures of pure substances and their mixtures;
- b) constructing and interpret the phase diagrams of binary systems;
- c) calculating the degrees of freedom of different systems.

Theoretical background

Thermal analysis is widely used to investigate phase transitions in binary pharmaceutical mixtures. In this experiment, a simplified method is used in which the onset and completion of melting are observed in small samples packed into narrow capillary tubes. For pure substances, the melting temperature is identical to the crystallization temperature. In contrast, binary mixtures generally melt and crystallize over a temperature range.

When solid mixtures of different compositions are heated, melting begins at the eutectic temperature, which is identical for all mixtures in the system. Complete melting occurs at different temperatures corresponding to the disappearance of the last remaining solid phase in each mixture.

Upon cooling, melts of different compositions begin to crystallize at different temperatures, whereas crystallization is completed at the same temperature – the eutectic temperature.

Experimental procedure

Equipment and reagents

1. Aspirin-phenacetin mixtures in the following ratios: 1:0, 4:1, 7:3, 3:2, 1:1, 2:3, 3:7, 1:4, and 0:1;

2. capillary tubes (1 mm internal diameter, 4 cm in length);
3. melting point apparatus;
4. electric heating plate;
5. glass rods;
6. mortar and pestle.

Prepare seven 1 g mixtures of aspirin and phenacetin according to the proportions indicated in Table 4. Thoroughly grind each mixture in a mortar until homogeneous. Fill capillary tubes sealed at one end with the prepared mixtures, packing the powder tightly. Glass rods may be used to facilitate compaction.

To ensure uniform packing, repeatedly tap the capillary through a glass tube against a hard surface. The packed sample should occupy approximately 0.5-1.0 cm of the capillary length.

Attach the capillary to a thermometer (range up to 200 °C) using a rubber band, ensuring that the sealed end containing the sample is positioned level with the thermometer bulb (Fig. 3).

Place the thermometer with the attached capillary into a test tube serving as an air jacket. Immerse the test tube in a glycerol bath and heat it at a constant rate of approximately 4 °C per minute.

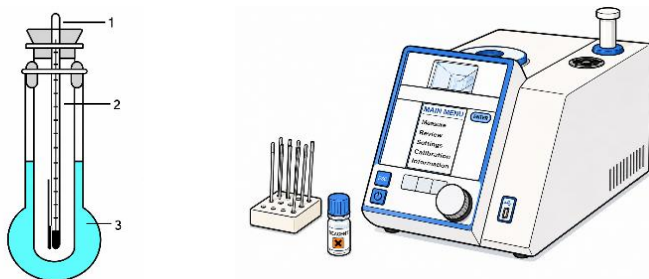


Fig. 3. Apparatus for determining the melting temperature

Observe the sample under good illumination throughout heating. Record the thermometer readings at the onset of melting (eutectic temperature) and at the completion of melting (liquids temperature). Perform the measurements for all prepared mixtures and record the experimental data in Table 4.

Table 4. Composition of aspirin-phenacetin mixtures and their melting temperatures

Mixture composition, %	Aspirin	100	80	70	60	50	40	30	20	0
	Phenacetin	0	20	30	40	50	60	70	80	100
Melting onset temperature, °C										
Melting completion temperature, °C										

Using the experimental data, construct the phase diagram of the aspirin–phenacetin system and determine the eutectic point and the composition of the eutectic mixture.

For this system, the eutectic point is 102.5 °C, and the eutectic composition is 47 % aspirin and 53 % phenacetin.

Construct similar phase diagrams for the binary pharmaceutical mixtures listed in Table 5.

Table 5. Eutectic characteristics of selected binary pharmaceutical mixtures

Mixture composition		Eutectic temperature, °C	Eutectic composition	
Component 1	Component 2		Component 1	Component 2
Pyramidon	Aspirin	73.0	47	53
Pyramidon	Phenacetin	86.0	64	36
Luminal	Phenacetin	122.5	40	60

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Phase diagram of the aspirin–phenacetin binary system”.
3. Solving exercises on determining the number of components, phases, and degrees of freedom in the phase diagrams of one- and two-component systems, as well as calculating the mass of the solid phase and melt composition using the phase diagram.
4. Problem-solving related to the topic: „Thermodynamics of phase equilibria”.

Laboratory and practical work No. 6

Thermodynamics of phase equilibria Boiling point diagram for a binary liquid system

Significance of the topic

Temperature – composition (boiling point) diagrams for binary liquid system are of great importance in medicine and pharmacy, particularly in the development, production, and quality control of pharmaceutical products. These diagrams describe the relationship between the boiling temperature and the composition of binary liquid systems, making it possible to determine the conditions under which the liquid and vapour phases coexist in equilibrium. Such information is essential for preparing homogeneous mixtures and for optimizing separation and purification processes.

In pharmaceutical practice, such diagrams are widely used in the optimization of distillation, extraction, and purification of active pharmaceutical ingredients. During the development of liquid dosage forms, it is important to establish the temperature conditions and component ratios required to obtain stable mixtures that ensure the efficacy and safety of pharmaceutical products.

In medical practice, an understanding of phase equilibria in liquid mixtures contributes to the accurate preparation of solutions containing precisely defined concentrations of active substances. This is essential for ensuring correct therapeutic dosages, maintaining product quality, and enhancing patient safety.

Learning objectives

1. To acquire knowledge of:
 - a) the mutual solubility of liquids;
 - b) ideal solutions and Raoult's law;
 - c) Konovalov's laws;
 - d) methods of distillation.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Concepts of solutions and the solubility of gases in liquids.
2. Solution concentration and methods of expressing concentration.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Thermodynamics of phase equilibria”.
3. Study of problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Boiling point diagram for a binary liquid system”.

Control questions

1. Mutual solubility of liquids. Ideal solutions. Raoult's law.
2. Positive and negative deviations from Raoult's law.
3. The composition of liquid and vapour phases at equilibrium. Konovalov's first law.
4. Pressure – composition and temperature – composition diagrams. Lever rule.
5. Azeotropic mixtures. Konovalov's second law.
6. Simple and fractional distillation.

Self-assessment questions

1. Define the term „solution”.
2. Solution concentration and methods of its expression. Relationships between different methods of expressing solution concentration.
3. What types of mutual solubility exist for liquid-liquid systems?
4. What is an ideal solution? Describe its main characteristics and the conditions under which it is formed.
5. What is the saturated vapour pressure of a liquid? Provide examples and explain the concept.
6. State Raoult's law and write its mathematical expression.
7. Why is the saturated vapour pressure of a solvent above a solution always lower than over the pure solvent?

8. What is the relationship between the relative lowering of the vapour pressure and the mole fraction of the solute?
9. Construct and analyse a graph illustrating the dependence of total and partial vapour pressures on the composition of a binary mixture.
10. Explain the origin of positive and negative deviations from Raoult's law. Provide appropriate examples.
11. Why do electrolyte solutions deviate from Raoult's law?
12. State Konovalov's first law and analyse it using phase diagrams in the coordinates $P = f(\text{composition})$ at constant T and $T = f(\text{composition})$ at constant P .
13. Explain the application of the lever rule for determining quantitative phase ratios.
14. State Konovalov's second law and analyse it using phase diagrams in the coordinates $P = f(\text{composition})$ at constant T and $T = f(\text{composition})$ at constant P , including the interpretation of minimum and maximum points.
15. What are azeotropic mixtures?
16. What is distillation, and on what principle is it based?
17. What is fractional distillation? Explain the operating principle of a fractionating column.
18. Explain the distillation process using a $T = f(\text{composition})$ phase diagram at constant pressure for systems following Konovalov's first law.
19. According to what principle are the components separated during the distillation of mixtures whose $T = f(\text{composition})$ diagrams exhibit minimum or maximum points at constant pressure?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 min).
3. Performance of the laboratory work (75 min).

Laboratory work

Boiling point diagram for a binary liquid system

Laboratory objectives

To develop practical skills in:

- a) determining the boiling temperature of solutions;
- b) constructing temperature-composition (boiling point) diagrams;
- c) interpreting pressure-composition and temperature-composition diagrams for binary liquid systems that are completely miscible in all proportions.

Theoretical background

Boiling temperature is an important parameter, widely used for the quality control of liquid pharmaceutical preparations and their components. Knowledge of the boiling temperature allows for the selection of optimal conditions for storage, stabilization, and administration of active pharmaceutical ingredients.

In the production of pharmaceuticals such as syrups, tinctures, and inhalation solutions, control of the boiling temperature is essential for determining of distillation points and for obtaining products with the required concentration and properties.

In addition, boiling temperature plays a central role in distillation processes used for the purification and separation of components in pharmaceutical mixtures.

The determination of the boiling temperature of solutions is based on the use of a short-sealed capillary tube, with its open end immersed in the test liquid. The capillary acts as a manometer, allowing determination of the temperature at which the vapour pressure of the liquid equals the atmospheric pressure, i.e., the boiling temperature.

Experimental procedure

Apparatus and reagents

1. apparatus for determining the boiling point;
2. capillary tubes;

3. electric heating plate;
4. thermometer (100-150 °C range);
5. ethanol solutions, mass fractions 80 %, 60 %, 50 %, 40 %, and 20 %;
6. ethanol solutions of unknown concentration.

The apparatus consists of an outer wide vessel (1) fitted with a stirrer (2) and an inner glass tube (3) ending in a thin-walled bulb with a diameter of 20-25 mm (Fig. 4).

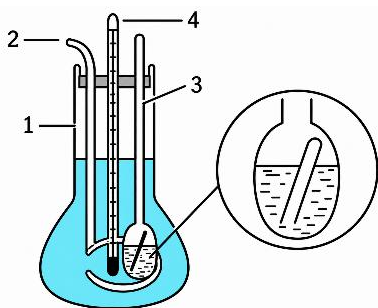


Fig. 4. Apparatus for determining boiling temperature

Fill the outer vessel with water to three-quarters of its volume and fix it on a stand. Install the stirrer. Place the test liquid in the inner tube to approximately half of its volume, then insert a sealed capillary (about 30 mm in length, with the open end down) into the tube.

Attach the thermometer so that its bulb is at the same level as the bulb of the inner tube. Continuously stir the liquid while heating the outer vessel and observe the behaviour of the liquid in the capillary. As the temperature increases, observe the formation of gas bubbles emerging from the lower end of the capillary. When the boiling temperature is slightly exceeded, observe an intensive stream of vapour bubbles.

At this point, stop heating and allow the system to cool while continuing to stir. When bubble formation ceases and the liquid begins to rise in the capillary, record the thermometer reading. Take this temperature as the boiling temperature of the liquid.

After cooling, repeat the experiment with other samples, gradually decreasing the ethanol concentration. Determine the boiling temperatures for tinctures with ethanol mass fractions of 80 %, 60 %, 50 %, 40 %, and 20 %.

Finally, measure the boiling temperature of a sample with unknown ethanol concentration. Before each measurement, rinse the inner tube with a fresh portion of the solution, and use a new capillary. Record the experimental data in Table 6.

Table 6. Boiling temperature of tinctures as a function of ethanol concentration

Ethanol concentration, %	Boiling temperature, °C
80	
60	
50	
40	
20	
ω_X (unknown)	

Based on the obtained data, construct a graph showing the dependence of boiling temperature on ethanol concentration. Determine the unknown ethanol concentration from the experimentally measured boiling temperature using this calibration curve.

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Boiling point diagram for a binary liquid system”.
3. Solving exercises related to the determination of the number of components, phases, and degrees of freedom in various phase diagrams.

Laboratory and practical work No. 7

Partially miscible liquid systems. Distribution law Study of the extraction process

Significance of the topic

Extraction, based on the distribution law, is of major importance in medicine and pharmacy and is widely used in both laboratory practice and pharmaceutical production. It is particularly used in the preparation of extracts, tinctures, and concentrates due to its efficiency in isolating and purifying active substances from complex multicomponent systems.

In pharmaceutical analysis, partition chromatography – also based on the distribution law – is widely employed for the analysis of medicinal preparations, identification of components, and quality control. Knowledge of critical dissolution temperatures and mutual solubility limits in binary liquid systems allows the determination of optimal compositions, as well as appropriate storage and application conditions.

In pharmaceutical technology, pharmaceutical chemistry, and pharmacognosy, extraction is used to obtain biologically active compounds from plant and animal sources, such as alkaloids, glycosides, and vitamins. This enables the production of extracts, tinctures, concentrates, and other dosage forms containing active substances.

Extraction is also essential for purification and concentration of target compounds, which is particularly important in the production of pharmaceuticals. For example, antibiotics such as penicillin cannot be concentrated by evaporation of dilute solutions due to their thermal instability. In such cases, extraction with solvents such as ethyl or butyl acetate is used to obtain concentrated solutions without degradation.

Extraction is essential in the development, production, and analysis of medicinal products. In drug development, it enables the investigation of the structure and biological activity of natural compounds. In biopharmaceutical production, it is used to isolate and purify substances from microbial cultures or cell systems, ensuring high-quality and effective products.

Thus, extraction represents an essential integrated process linking drug development, production, and quality control, and serves as a fundamental tool for ensuring the efficacy and safety of medicinal products.

Learning objectives

1. To acquire knowledge of:
 - a) the mutual solubility of liquids and the factors affecting it;
 - b) the distribution of a substance between two immiscible liquid phases;
 - c) steam distillation;
 - d) extraction methods.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Theory of extraction methods and the distribution law.
2. The distribution coefficient and its significance.
3. Conditions for the extraction of organic and inorganic compounds.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Partially miscible liquid systems. Distribution law”.
3. Study of problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Study of the extraction process”.

Control questions

1. Mutual solubility of liquids. Partially miscible liquids. Upper and lower critical solution temperatures (V. F. Alekseev).
2. Vapour pressure and composition above immiscible liquids. Principles of steam distillation.
3. Distribution of a substance between two liquid phases. Distribution coefficient. Nernst distribution law.

4. Extraction processes. Calculation of the mass of substance extracted and the mass remaining in the solution after single, double, and multiple extractions.

Self-assessment questions

1. Provide examples of liquids with different degrees of mutual solubility.
2. Construct a phase diagram for partially miscible liquids, indicating the upper and lower critical solution temperatures.
3. What factors influence the mutual solubility of partially miscible liquids?
4. What are liquid phases? Illustrate using phase diagrams of partially miscible systems.
5. What are the pressure and composition of the vapour above immiscible liquids?
6. What is extraction and which law underlies the extraction process?
7. What are the pressure and composition of the vapour in equilibrium with a partially miscible liquid system?
8. What is steam distillation, and when is it applied? Give examples.
9. Write the quantitative relationship between the mass of the distilled substance and the amount of water during steam distillation.
10. State the general form of the Nernst distribution law.
11. What causes deviations from the distribution law?
12. Write the formulas used to calculate the mass of substance extracted and the mass remaining in solution after single, double, triple, and multiple extractions.
13. What are the optimal conditions for performing an efficient extraction?
14. How can complete extraction be achieved using a given volume of solvent?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (75 minutes).

Laboratory work

Study of the extraction process

Laboratory objectives

To develop practical skills in:

- a) selecting optimal extraction conditions;
- b) determining the distribution coefficient;
- c) calculating the amount of substance extracted and the amount remaining in solution after single, double, and multiple extractions.

Theoretical background

The study of extraction involves understanding and optimizing methods for isolating components from complex mixtures using immiscible solvents. The process is based on the distribution law (Nernst's law), which states that a solute distributes between two mutually immiscible liquid phases at constant temperature.

This law enables the calculation of both the amount of substance transferred into the extractant and the amount remaining in the original phase after single or multiple extractions using a given solvent volume.

Extraction principles are based on differences in the solubility of a substance in two immiscible liquids. Depending on the nature of the phases, extraction can be classified as liquid-liquid, liquid-solid, or solid-liquid extraction.

The distribution coefficient, defined as the ratio of the equilibrium concentrations of a solute in the two phases, characterizes the efficiency of extraction and is used to select optimal extraction conditions.

Experimental procedure

Equipment and reagents

1. iodine solution in benzene, mass fraction 4 %;
2. separatory funnels, 50 mL and 100 mL;
3. 4 conical flasks, 50 or 100 mL;
4. standard sodium thiosulfate solution, molar concentration $0.01 \text{ mol} \times \text{L}^{-1}$;

5. starch solution, mass fraction 0.5 %;
6. pipettes, 1 mL, 5 mL, 10 mL;
7. burettes, 25 mL;
8. graduated cylinder, 50 mL.

Using a pipette, transfer 5 mL of 4 % iodine solution in benzene into two separatory funnels. Add 45 mL of distilled water to the first funnel and 15 mL to the second using a graduated cylinder. Shake the funnels vigorously for 10 minutes, then allow the phases to separate.

Transfer the aqueous layers into separate conical flasks. To the second funnel, add an additional 15 mL of distilled water, shake, allow phase separation, and combine the aqueous layer with the previous one. Repeat this procedure once more to obtain a total of 45 mL of aqueous iodine solution in each flask.

From each flask, take 15 mL of the aqueous phase, add 2-3 drops of starch solution, and titrate with $0.01 \text{ mol} \times \text{L}^{-1}$ sodium thiosulfate until the blue colour disappears.

From each separatory funnel, take 1 mL of the benzene layer, transfer it into separate flasks, dilute with 20 mL of distilled water, add starch solution, and titrate slowly with sodium thiosulfate, continuously shaking until decolourization occurs.

Repeat each titration 2-3 times for both the aqueous and benzene solution, and record the average values. Summarize the experimental results in Table 7.

Table 7. Results of titration of aqueous and benzene layers

	Aqueous layer		Benzene layer	
	1st funnel	2nd funnel	1st funnel	2nd funnel
Volume of solution taken for titration, mL				
Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for titration, mL				
Average volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution, mL				

Calculate the molar concentrations ($\text{mol} \times \text{L}^{-1}$) of iodine in the benzene and aqueous phases from the titration results using the corresponding equations:

$$c_{I_2}^b = \frac{V_2(\text{Na}_2\text{S}_2\text{O}_3) \times 0.01}{1}$$

$$c_{I_2}^a = \frac{V_1(\text{Na}_2\text{S}_2\text{O}_3) \times 0.01}{15}$$

where $V_1(\text{Na}_2\text{S}_2\text{O}_3)$ and $V_2(\text{Na}_2\text{S}_2\text{O}_3)$ are the volumes (in mL) of $0.01 \text{ mol} \times \text{L}^{-1}$ sodium thiosulfate solution used for titrating 15 mL of the aqueous phase and 1 mL of the benzene phase, respectively.

Define the distribution coefficient in extraction processes as the ratio of the solute concentration in the original phase to that in the extracting phase. For the extraction of iodine from benzene with water, express it as:

$$K = \frac{c_{I_2}^b}{c_{I_2}^a}$$

Calculate the mass of iodine remaining in the benzene phase after a single extraction with a given volume of water at a specified temperature using the equation:

$$m_1(I_2) = m_0(I_2) \left[\frac{K \times V(C_6H_6)}{K \times V(C_6H_6) + V_1(H_2O)} \right]$$

For triple extraction, calculate the mass using the equation:

$$m_3(I_2) = m_0(I_2) \left[\frac{K \times V(C_6H_6)}{K \times V(C_6H_6) + V_2(H_2O)} \right]^3$$

where $V_1(H_2O)$ and $V_2(H_2O)$ are the volumes of water used for extraction in the first and second separatory funnels, respectively.

Determine the mass of iodine extracted after a single extraction as the difference between the initial mass of iodine in the solution and the mass remaining after extraction:

$$m_2(I_2) = m_0(I_2) - m_1(I_2)$$

Alternatively:

$$m_{\text{extr.}}(I_2) = m_0(I_2) \left[1 - \frac{K \times V(C_6H_6)}{K \times V(C_6H_6) + V_1(H_2O)} \right]$$

Calculate the mass of iodine extracted after three successive extractions using the equation:

$$m_{\text{extr.}}(I_2) = m_0(I_2) - m_3(I_2)$$

Alternatively:

$$m_{\text{extr.}}(I_2) = m_0(I_2) \left[1 - \left(\frac{K \times V(C_6H_6)}{K \times V(C_6H_6) + V_2(H_2O)} \right)^3 \right]$$

At the end of the experiment, compare the amounts of iodine extracted by single and multiple (triple) extraction, and formulate a conclusion regarding the most efficient extraction conditions.

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Study of the extraction process”.
3. Problem-solving related to the topic: „Partially miscible liquid systems. Distribution law”.

Laboratory and practical work No. 8

Colligative properties of electrolyte and nonelectrolyte solutions Determination of the isotonic coefficient and the degree of ionization of a weak electrolyte solution using cryoscopy

Significance of the topic

Colligative properties of solutions depend only on the number of the solute particles in an ideal solution, and allow the determination of the molar mass of substances based on experimental data. For this purpose, a suitable solvent with a known cryoscopic (or ebullioscopic) constant is selected, and a dilute solution is prepared from accurately measured amounts of solvent and solute. The freezing point depression or boiling point elevation is then measured. In practice, the cryoscopy is most commonly used due to its relative experimental simplicity.

The cryoscopy is widely applied in pharmacy for determining the molar mass of new pharmaceutical compounds and for estimating their isotonicity. The isotonic concentration is evaluated through the freezing point depression (ΔT) of a solution, which should correspond to the freezing point depression of biological fluids in the human body.

Osmotic pressure plays a vital role in living organisms, governing the movement of water and dissolved substances across biological membranes. For example, the osmotic pressure of human blood is approximately 8.1×10^5 Pa (~ 8 atm). A decrease in water content leads to thirst, which restores the water-salt balance and normal osmotic pressure.

Osmotic pressure also determines cell turgor. In seeds with a moisture content of about 6 %, it may reach approximately 4.04×10^7 Pa (~ 400 atm), enabling water absorption even from dry soil, which is essential for germination.

The osmotic method is used to determine the molar mass of macromolecules, such as proteins and polysaccharides, by measuring the osmotic pressure of dilute solutions of known concentration.

In pharmaceutical practice, mixtures of essential and non-essential amino acids are used in parenteral nutrition solutions. These formulations

typically include eight essential amino acids (valine, isoleucine, leucine, lysine, methionine, threonine, tryptophan, phenylalanine), six amino acids synthesized from carbohydrates (alanine, glycine, serine, proline, glutamic acid, aspartic acid), and four amino acids synthesized in limited amounts (arginine, histidine, tyrosine, cysteine). The osmolarity of such solutions must be adjusted to match that of blood plasma.

Understanding the colligative properties of electrolyte and nonelectrolyte solutions enables the determination of osmotic concentration, the isotonic coefficient (van't Hoff factor), and the degree of ionization of weak electrolytes. These parameters are essential for the formulation of injectable and ophthalmic preparations, ensuring their safety and physiological compatibility.

Learning objectives

1. To acquire knowledge of:
 - a) thermodynamic properties of dilute solutions;
 - b) cryoscopy, ebullioscopy, and osmometry for determining molar mass, osmotic concentration, and isotonic and osmotic coefficients;
 - c) relationships between the colligative properties of solutions.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Concentration of solutes and methods of expressing concentration.
2. Freezing point depression, osmosis, and osmotic pressure of dilute nonelectrolyte solutions.
3. van't Hoff law, degree of ionization, and isotonic coefficient.
4. Plasmolysis, haemolysis, and turgor. Isotonic, hypotonic, and hypertonic solutions.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Colligative properties of electrolyte and nonelectrolyte solutions”.

3. Study of problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Determination of the isotonic coefficient and the degree of ionization of a weak electrolyte solution using cryoscopy”.

Control questions

1. Freezing point depression of dilute solutions. Cryoscopy.
2. Cryoscopic constant and its relation to the enthalpy of fusion of the solvent.
3. Boiling point elevation of dilute solutions. Ebullioscopy.
4. Osmotic properties of electrolyte and nonelectrolyte solutions. Isotonic and osmotic coefficients.
5. Relationships among colligative properties: relative vapour pressure lowering, freezing point depression, boiling point elevation, and osmotic pressure of dilute solutions.
6. Cryoscopy, ebullioscopy, and osmometry for determining molar mass, osmotic concentration, isotonic coefficient, and osmotic coefficient.

Self-assessment questions

1. What is a solution? Provide relevant examples.
2. In which units can solution concentration be expressed, and how are different concentration units related?
3. Why is the term melting point used for pure substances, whereas terms such as crystallization temperature and freezing point are applied to solutions?
4. Plot the dependence of the saturated vapour pressure of dilute solutions of different concentrations on temperature, and analyse the effect of concentration on phase equilibrium.
5. Plot the dependence of freezing point depression (ΔT_f) and boiling point elevation (ΔT_b) on concentration, and analyse the influence of concentration on the colligative properties of solutions.
6. For which component (solute or solvent) and which property change are cryoscopic and ebullioscopic constants determined?

7. Which experimental and theoretical methods are used to determine the cryoscopic and ebullioscopic constants?
8. Which methods are used to determine the molar mass of nonelectrolytes, the degree of ionization, and the isotonic coefficient of electrolytes?
9. What criteria should be considered when selecting a solvent for cryoscopic and ebullioscopic methods?
10. Will $0.1 \text{ mol} \times \text{kg}^{-1}$ solutions of glucose, sucrose, urea, NaCl, and Na_2SO_4 freeze at the same temperature? Justify your answer and illustrate it graphically.
11. What are the degree of ionization (α) and the isotonic coefficient (i), and how are they related?
12. Does the association of non-volatile solute molecules affect the vapour pressure of the solvent? If so, explain how?
13. Formulate the condition of phase equilibrium at the melting point and at the onset of crystallization.
14. What is osmotic pressure and how is it measured?
15. Define osmosis and identify the factors on which osmotic pressure depends.
16. Will 5 % (by mass) sucrose and glucose solutions be isosmotic at the same temperature? Justify your answer.
17. What laws describe osmotic pressure in dilute solutions of nonelectrolytes and electrolytes?
18. Identify the factors affecting the van't Hoff isotonic coefficient.
19. What is the osmotic coefficient and how is it determined?
20. Explain the relationships among the following colligative properties:
 - a) vapour pressure lowering and freezing point depression;
 - b) vapour pressure lowering and boiling point elevation;
 - c) vapour pressure lowering and osmotic pressure;
 - d) freezing point depression and osmotic pressure;
 - e) boiling point elevation and osmotic pressure.
21. Determine the cryoscopic constant of water if a nonelectrolyte solution with a molality $0.001 \text{ mol} \times \text{kg}^{-1}$ freezes at -0.00186°C .
22. What is osmotic concentration and how can it be determined?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (75 minutes).

Laboratory work

Determination of the isotonic coefficient and the degree of ionization of a weak electrolyte solution using cryoscopy

Laboratory objectives

To develop practical skills in:

- a) determining the freezing points of solvent and dilute solutions of electrolytes and nonelectrolytes;
- b) calculating the molar mass of dissolved substances;
- c) calculating the isotonic coefficient, degree of ionization, osmotic concentration, osmotic pressure, and relative lowering of vapour pressure above the solution.

Theoretical background

Certain properties of solutions depend only on the number of dissolved particles rather than on their chemical nature. Such properties, known as colligative properties, include osmotic pressure, lowering of solvent vapour pressure, boiling point elevation, and freezing point depression. Methods based on the measurement of freezing point depression are referred to as cryoscopy.

For dilute solutions of nonelectrolytes, the freezing point depression is given by:

$$\Delta T_f = K \times c_m(B) \quad (1)$$

where:

K – the cryoscopic constant of the solvent, $^{\circ}\text{C} \times \text{kg} \times \text{mol}^{-1}$;

$c_m(B)$ – the molality of the solute, $\text{mol} \times \text{kg}^{-1}$.

The molality is calculated using the equation:

$$c_m = \frac{m(B) \times 1000}{M(B) \times m(A)} \quad (2)$$

where:

$m(A)$ – the mass of the solvent, g;

$m(B)$ – the mass of the solute, g;

$M(B)$ – the molar mass of the solute, $\text{g}\cdot\text{mol}^{-1}$.

Combining Eqs. (1) and (2), the molar mass of the dissolved substance can be determined:

$$M(B) = K \frac{m(B) \times 1000}{m(A) \times \Delta T_f} \quad (3)$$

For electrolyte solutions, the increase in the number of dissolved particles due to electrolytic dissociation must be taken into account. This effect is described by the van't Hoff isotonic coefficient i , which represents the factor by which the number of particles in solution increases:

$$\Delta T_f = i K c_m(B) = i K \frac{m(B) \times 1000}{M(B) \times m(A)} \quad (4)$$

For weak electrolytes, the isotonic coefficient can be used to determine the degree of ionization:

$$\alpha = \frac{i - 1}{n - 1} \quad (5)$$

where n is the number of ions formed by the dissociation of one molecule of the electrolyte.

The osmotic concentration is calculated as:

$$c_{m,osm} = c_m(B) [1 + (n - 1) \times \alpha] = i \times c_m(B) \quad (6)$$

For strong electrolytes, an apparent degree of dissociation may be considered. Although strong electrolytes are almost completely dissociated in dilute solutions, electrostatic interactions between ions reduce the effective number of independently moving particles. Therefore, the experimentally observed freezing point depression is smaller than the theoretical value predicted for complete dissociation:

$$\Delta T_f = n \times K \times c_m(B) \quad (7)$$

The osmotic coefficient, f is defined as the ratio of the experimentally determined osmotic pressure to the theoretical osmotic pressure:

$$f = \frac{\pi_{exp}}{\pi_{theor}} \quad (8)$$

where π_{exp} and π_{theor} are the experimental and theoretical osmotic pressure, respectively.

Experimental procedure

Apparatus and reagents

1. cryoscopic apparatus (cryoscope);
2. Beckmann thermometer or a thermometer with a scale division 0.01 °C;
3. test tubes;
4. ice and sodium chloride;
5. chloroacetic, oxalic, aminoacetic, malonic, and dichloroacetic acids;
6. distilled water;
7. pipette, 20 mL;
8. analytical balance.

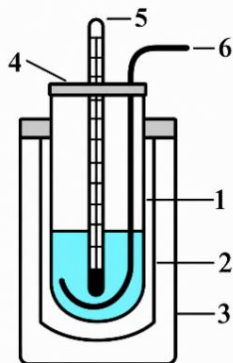


Fig. 5. Schematic diagram of a cryoscope

Use a cryoscope (Fig. 5) to determine the freezing point of the pure solvent and dilute solutions. Assemble the cryoscope by placing test tube 1 inside the wider test tube 2, which serves as an air jacket to prevents excessively rapid cooling of the liquid in test tube 1. Close the upper opening of test tube 1 with stopper 4, and insert thermometer 5 and stirrer 6 through it. Fix the entire assembly in the opening of a thick-walled beaker 3 containing a cooling mixture of ice and sodium chloride.

Using a pipette, transfer 20 mL of distilled water into test tube 1. Insert the thermometer and stirrer, then place the tube into the air jacket immersed in the cooling mixture. Stir the liquid continuously by moving the stirrer up and down.

As cooling proceeds, the thermometer reading decreases and may fall below 0 °C, indicating supercooling. When the first ice crystals appear, the temperature rapidly rises due to the release of the heat of

crystallization. Record the highest stable temperature reached as the freezing point of pure water.

Remove the test tube from the cryoscope and melt the ice crystals by gently warming the tube with the hand. After the crystals have completely melted, repeat the measurement. The difference between the two measurements should not exceed 0.010 °C.

To determine the freezing point of a solution, weigh 0.4-0.8 g of the investigated substance using an analytical balance and add it to the water used in the previous experiment. Stir until the substance has dissolved completely and a homogeneous solution is obtained. Determine the freezing point of the solution following the same procedure used for pure water.

Table 8. Results of cryoscopy measurements

Mass of water: _____ g			
Mass of the investigated substance: _____ g			
Parameter	t ₁ , °C	t ₂ , °C	t _{aver} , °C
Freezing point of water			
Freezing point of the solution			

Using the obtained experimental data, calculate:

- the isotonic coefficient;
- the degree of ionization;
- the osmotic concentration;
- the osmotic pressure of the solution;
- the relative lowering of the solvent vapour pressure;
- the boiling point elevation of the solution.

Independent study

- Analysis of the experimental observations and processing of the obtained data.
- Preparation of the laboratory report: „Determination of the isotonic coefficient and the degree of ionization of a weak electrolyte solution using cryoscopy”.
- Problem-solving related to the topic: „Colligative properties of electrolytes and nonelectrolytes solutions”.

Laboratory and practical work No. 9

Electrical conductivity of electrolyte solutions Conductometric determination of the degree of ionization and the ionization constant of a weak electrolyte

Significance of the topic

Conductometric methods are widely used in medicine and pharmacy to measure the electrical conductivity of solutions, enabling the determination of ion concentrations, investigation of solution properties, and the quality of pharmaceutical products. These methods are applicable to a wide variety of pharmaceutical preparations, including aqueous, non-aqueous, and mixed aqueous-organic systems, as well as transparent, coloured, and turbid solutions containing oxidizing or reducing agents.

Conductometry is commonly employed to assess the purity of water and pharmaceutical solutions, determine the concentration of active pharmaceutical ingredients, and study the kinetics of chemical reactions.

In medical diagnostics, conductometric methods are used to evaluate electrolyte balance by measuring the electrical conductivity of biological fluids such as blood, plasma, and urine. The conductivity of these fluids depends primarily on the concentration and mobility of dissolved ions, including Na^+ , K^+ and Cl^- . Changes in electrical conductivity may indicate pathological conditions such as dehydration, renal failure, acid-base imbalance, and cardiovascular disorders. Conductometry therefore provides a rapid and accurate means for clinical diagnosis and patient monitoring.

These methods are characterized by high sensitivity, accuracy, and rapid execution, making them indispensable in pharmaceutical analysis, clinical diagnostics, and laboratory practice.

Learning objectives

1. To acquire knowledge of:
 - a) specific and equivalent electrical conductivity and their dependence on solution concentration;
 - b) ionic mobility, absolute ionic velocity, and Kohlrausch's law of independent ionic migration;

- c) the applications of conductometry in medicine and pharmacy.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Electrical conductivity and specific electrical conductivity of conductors of the first kind.
2. Measurement of the electrical resistance of conductors of the first kind for the evaluation of their electrical properties.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Electrical conductivity of electrolyte solutions”.
3. Study of problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Conductometric determination of the degree of ionization and the ionization constant of a weak electrolyte”.

Control questions

1. Electrolyte solutions as conductors of the second kind. Electrical conductivity of aqueous and non-aqueous electrolyte solutions.
2. Specific and equivalent electrical conductivity of electrolyte solutions. Equivalent electrical conductivity at infinite dilution.
3. Absolute ionic velocity, ionic mobility, and Kohlrausch's law of independent ion migration.
4. Conductometric determination of:
 - a) the degree of ionization and the ionization constant of a weak electrolyte;
 - b) the conductivity coefficient of a strong electrolyte;
 - c) the ionic product of water;
 - d) the solubility of sparingly soluble electrolytes and the application of conductometric titration in aqueous solutions.

Self-assessment questions

1. What are conductors of the first and second kinds? What is ionic electrical conductivity?
2. Which quantity characterizes the ability of a medium to conduct electricity? What is the specific electrical resistance of electrolyte solutions?
3. What is specific electrical conductivity? On which factors does it depend, and in what units is it expressed?
4. How does the radius of the ionic atmosphere depend on ion concentration, the nature of the ions, the solvent, and temperature?
5. Why does the curve of specific electrical conductivity versus concentration exhibit a maximum for both weak and strong electrolytes?
6. What is equivalent electrical conductivity? Which factors influence it, and in what units is it measured?
7. What is meant by dilution of a solution, and how is it related to molar concentration and equivalent concentration?
8. On the same scale, plot the dependence of equivalent electrical conductivity on dilution for KCl, KOH, HCl, and CH_3COOH solutions.
9. What relationship connects specific electrical conductivity and equivalent electrical conductivity?
10. What is molar electrical conductivity?
11. How are the degree of ionization of a weak electrolyte, the equivalent electrical conductivity, and the equivalent electrical conductivity at infinite dilution related?
12. What relationship exists between the ionization constant of a weak electrolyte, the equivalent electrical conductivity, and the equivalent electrical conductivity at infinite dilution?
13. How is the degree of ionization related to the isotonic coefficient?
14. Why does electrical conductivity measurement provide the true degree of ionization for weak electrolytes but only the apparent degree of ionization for strong electrolytes? Why does dilution increase the true degree of ionization for weak electrolytes, whereas for strong electrolytes only the apparent degree increases?

15. What is the absolute ionic velocity, and which factors affect it?
16. What is ionic mobility, and how is it related to the absolute ionic velocity?
17. What is the essence of Kohlrausch's law? What are ion hydration (solvation)?
18. How is the equivalent electrical conductivity of an electrolyte at infinite dilution related to the mobilities of its cations and anions?
19. What is conductometry and what is this method based on?
20. What is the cell constant and how is it determined?
21. How can the degree of ionization and the ionization constant of a weak electrolyte be determined from conductometric measurements?
22. How can conductometric data be used to determine:
 - a) the conductivity coefficient (apparent degree of ionization) of a strong electrolyte;
 - b) the ionic product of water;
 - c) the solubility of sparingly soluble electrolytes?
23. How can the concentration of electrolytes be determined by conductometric titration? Provide examples.

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 min).
3. Performance of the laboratory work (75 min).

Laboratory work

Conductometric determination of the degree of ionization and the ionization constant of a weak electrolyte

Laboratory objectives

To develop practical skills in:

- a) measuring the resistance of electrolyte solutions;
- b) determining the cell constant;

- c) calculating the specific conductivity and equivalent conductivity of electrolyte solutions;
- d) determining the degree of ionization and the ionization constant of a weak electrolyte.

Experimental procedure

Instruments and reagents

1. R-38 rheochord bridge;
2. conductometric cell;
3. alternating current (AC) power supply (220 V);
4. standard electrolyte solutions;
5. distilled water;
6. graduated cylinder, 50 mL.

Measurement of the resistance of electrolyte solutions using the R-38 rheochord bridge

The R-38 rheochord bridge is a balanced bridge with a stepwise adjustable comparison arm (5) and a continuously adjustable rheochord arm (6). The instrument operates on alternating current supplied from a 127 or 220 V mains source (Fig. 6).

To measure the resistance of an electrolyte solutions, proceed as follows:

1. Connect the electrodes of the conductometric cell to terminals (4).
2. Connect the instrument to a 220 V AC power supply with a frequency of 50-500 Hz. The indicator lamp (8) should light up.
3. Set the power switch (9) to the „~” position.
4. Set the comparison arm switch (5) to the „zero setting” position.
5. Set the galvanometer switch (3) to the „fine” position and adjust the galvanometer needle to zero using the corrector (2).

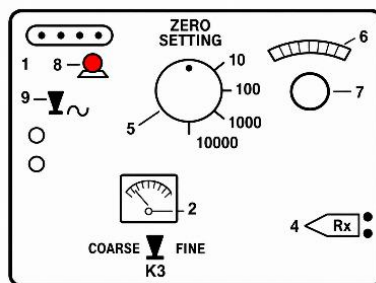


Fig. 6. Diagram of the R-38 rheochord bridge

6. Switch the galvanometer (3) to the „coarse” position and balance the bridge by adjusting the comparison arm (5) and the rheochord (7) until the galvanometer needle returns to zero.
7. Switch the galvanometer (3) back to the „fine” position and balance the bridge by rotating the rheochord knob (7) until the galvanometer needle again indicates zero.
8. Turn off the galvanometer by setting it to the „K3” position.
9. Determine the resistance of the standard or test solution by multiplying the reading of the comparison arm (5) - (R_m) by the reading of the rheochord scale (6).
10. Calculate the solution resistance using equation (1):

$$R_x = \frac{b}{a} R_m = BR_m \quad (1)$$

11. Repeat the measurements several times and calculate the average resistance.

After completing the resistance measurements, turn off the instrument as follows:

- a) set the galvanometer switch to the „K3” position;
- b) set the comparison arm switch (5) to the „zero setting” position;
- c) return the rheochord scale to zero;
- d) switch off the instrument using the power switch (9), and disconnect it from the AC mains supply.

Determination of the cell constant

Determine the cell constant (D) using standard potassium chloride (KCl) solutions with concentrations of 0.01, 0.02, and 0.10 mol×L⁻¹ prepared with double-distilled water. The corresponding values of their specific electrical conductivity at different temperatures are presented in Table 9.

Prepare the standard KCl solutions from chemically pure potassium chloride that has been recrystallized twice and calcined to constant mass. Alternatively, use an analytical standard (ampoule) to prepare the standard solution.

Table 9. Specific electrical conductivity of KCl solutions at different temperatures

KCl concentration, $\text{mol} \times \text{L}^{-1}$	Temperature							
	273 K	278 K	283 K	288 K	291 K	293 K	298 K	303 K
	$\chi, \text{S} \times \text{m}^{-1}$							
0.01	0.0776	0.0896	0.1020	0.1147	0.1224	0.1278	0.1413	0.1552
0.02	0.1521	0.1752	0.1994	0.2243	0.2399	0.2501	0.2765	0.3036
0.10	0.7150	0.8220	0.9330	1.0480	1.1200	1.1670	1.2880	1.4120
1.00	6.5410	7.4140	8.3190	9.2520	9.8300	10.207	11.180	–

Pour the standard KCl solution into the conductometric cell until the platinum electrodes are completely immersed. Mark the solution level to ensure identical filling volumes for all subsequent measurements.

Use distilled water with a specific electrical conductivity not exceeding $2 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$ for preparing standard solutions.

To determine the resistance of the standard solutions, connect the conductometric cell to the R-38 rheochord bridge operating with alternating current (see Fig. 6).

Calculate the conductometric cell constant using equation (2):

$$D = \chi(\text{KCl}) \times R(\text{KCl}) \quad (2)$$

where:

$R(\text{KCl})$ – the average resistance of the standard KCl solution, Ω ;

$\chi(\text{KCl})$ – the specific electrical conductivity of the standard KCl solution, $\text{S} \times \text{m}^{-1}$.

When calculating the specific electrical conductivity of the solutions, take into account the specific electrical conductivity of the water used for their preparation at the given temperature.

Determination of the resistance of acetic acid solutions

After determining the cell constant, measure the resistance of acetic acid solutions of different concentrations using the same procedure.

Before each measurement, rinse the conductometric cell with distilled water and then with a small amount of the test solution. Fill the cell to the previously marked level.

The resistance of each solution is calculated using equation (1).

Using the measured solution resistance R and the cell constant D , calculate the specific electrical conductivity of the solution using equation:

$$\chi_{\text{sol}} = \frac{D}{R_{\text{sol}}} \quad (3)$$

After determining the specific electrical conductivity of each test solution, calculate the equivalent electrical conductivity λ_c using equation (4):

$$\lambda_c = \frac{\chi_{\text{sol}}}{1000 \times c (f_{\text{eq}}(x) \times)} \quad (4)$$

where c_{eq} is the equivalent concentration, $\text{mol} \times \text{L}^{-1}$.

Use the factor 1000 to convert the concentration from $\text{mol} \times \text{L}^{-1}$ to $\text{mol} \times \text{m}^{-3}$, ensuring consistency with SI units. Express the unit of equivalent electrical conductivity (λ_c) as $\text{S} \times \text{m}^2 \times \text{mol}^{-1}$.

Using the tabulated limiting ionic equivalent electrical conductivities of the cation and anion of the studied electrolyte, calculate the equivalent electrical conductivity at infinite dilution using Equation (5):

$$\lambda_0 = \lambda_+^0 + \lambda_-^0 \quad (5)$$

Using the values of the equivalent electrical conductivity of the electrolyte solution (λ_c) and the limiting equivalent electrical conductivity (λ_0), determine the degree of ionization of the electrolyte at each concentration using equation (6):

$$\alpha = \frac{\lambda_c}{\lambda_0} \quad (6)$$

Using the calculated degree of ionization, determine the ionization constant using equation (7):

$$K = \frac{\alpha^2 \times c}{1 - \alpha} = \frac{c \times \lambda_c^2}{\lambda_0 (\lambda_0 - \lambda_c)} \quad (7)$$

Record the experimental data and the calculated results in Tables 10 and 11.

Table 10. Determination of the conductometric cell constant

Standard electrolyte solution	Concentration, $\text{mol} \times \text{L}^{-1}$	t , $^{\circ}\text{C}$	χ , $\text{S} \times \text{m}^{-1}$	R_m , Ω	B	$R(\text{KCl})$, Ω	D, m^{-1}
KCl	0.01						
	0.02						
	0.10						

Table 11. Experimental data and calculated results for the test electrolyte

Test electrolyte solution	Concentration, $\text{mol} \times \text{L}^{-1}$	R_m , Ω	B	R_x , Ω	χ , $\text{S} \times \text{m}^{-1}$	$\lambda_c \times 10^4$, $\text{S} \times \text{m}^2 \times \text{mol}^{-1}$	α	$K \times 10^5$, $\text{mol} \times \text{L}^{-1}$

After completing the tables, analyse the results and draw conclusions regarding the dependence of the solution resistance (R_x), specific electrical conductivity (χ), equivalent electrical conductivity (λ_c), degree of ionization (α), and ionization constant (K) on the concentration of the electrolyte under study.

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Conductometric determination of the degree of ionization and the ionization constant of a weak electrolyte”.
3. Problem-solving related to the topic: „Electrical conductivity of electrolyte solutions”.

Assessment No. 2

Learning objectives

Based on the above topics, to assess:

- a) the level of assimilation of theoretical knowledge;
- b) the practical skills and competencies acquired during laboratory sessions;
- c) the ability to solve applied problems.

Written test on the topics

1. Thermodynamics of phase equilibria.
2. Colligative properties of electrolytes and nonelectrolytes solutions.
3. Electrical conductivity of electrolyte solutions. Conductometry.

Control questions

1. Concepts of phase, system constituents, components, and degrees of freedom.
2. Phase transitions and phase equilibria.
3. The Clausius-Clapeyron equation and its application to evaporation, sublimation, and melting processes.
4. Gibbs phase rule.
5. Phase diagrams of one-component systems (using water as an example).
6. Liquid-solid phase diagrams of binary systems. Eutectics.
7. Thermal analysis and the concept of physicochemical analysis.
8. Mutual solubility of liquids. Ideal solutions. Raoult's law.
9. Positive and negative deviations from Raoult's law.
10. Composition of liquid and vapour phases at equilibrium. Kononov's first law.
11. Vapour pressure-composition and temperature-composition diagrams. The lever rule.
12. Azeotropes: the limits of distillation. High- and low-boiling azeotrope. Kononov's second law.
13. Distillation and fractional distillation.
14. Partially miscible liquids. Upper and lower critical solution temperatures.
15. Temperature and composition of vapour above mutually immiscible liquids. Steam distillation.
16. Distribution of a substance between two liquid phases. Distribution coefficient. The Nernst distribution law.

17. Extraction. Quantitating single extraction. Quantitating multiple extraction.
18. Freezing point depression of dilute solutions. Cryoscopy.
19. The cryoscopic constant and its relationship to the enthalpy of fusion of the solvent.
20. Boiling point elevation of dilute solutions. Ebullioscopy.
21. Osmotic properties of electrolytes and nonelectrolytes solutions. Isotonic and osmotic coefficients.
22. Relationship among colligative properties: relative lowering of vapour pressure, freezing-point depression, boiling-point elevation and osmotic pressure of dilute solutions.
23. Cryoscopy, ebullioscopy and osmometry in determining molar mass, osmotic concentration of solutions, and isotonic and osmotic coefficients.
24. Electrolytic dissociation of water. The ionic product of water.
25. The hydrogen ion exponent (pH) as a measure of acidity/basicity. The empirical pH scale.
26. Electrolyte solutions as conductors of the second kind. Electrical conductivity of aqueous electrolyte solutions.
27. Specific and equivalent electrical conductivity of electrolyte solutions. Equivalent conductivity at infinite dilution.
28. Ionic drift velocity and ionic mobility. Kohlrausch's law of independent ion migration.
29. Conductometric determination of:
 - a) the degree of ionisation and the ionisation constant of a weak electrolyte;
 - b) the electrical conductivity coefficient (apparent degree of ionisation) of a strong electrolyte;
 - c) the ionic product of water;
 - d) the solubility of sparingly soluble electrolytes;
 - e) the concentration of electrolytes in solutions by conductometric titration.

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of the material based on control questions and problems analogous to those previously solved (60 minutes).
3. Analysis of errors made in the written test.

Laboratory and practical work No. 10

Thermodynamics of electrode processes

Potentiometric determination of solution pH

Potentiometric titration of hydrochloric and acetic acids

Significance of the topic

Electrochemistry is a branch of physical chemistry that studies the interconversion of chemical and electrical energy. These processes occur at the interface between a metal electrode (electronic conductor) and an electrolyte solution (ionic conductor) – and involve electron transfer between the electrode and ions in solution.

The potentiometric method of analysis is based on measuring electrode potential and establishing its relationship with the concentration, more precisely the activity, of the potential-determining ions in solution.

Potentiometric methods are widely used both for the direct determination of ion activity in solutions (direct potentiometry or ionometry) and for identifying the equivalence point in titration by monitoring changes in the potential of an indicator electrode (potentiometric titration).

Examples of applications of electrochemical analytical methods in medicine and pharmacy include:

Determination of blood glucose concentration

Electrochemical glucometers are widely used to measure blood glucose levels and enable patients with diabetes mellitus to perform regular self-monitoring.

Electrolyte analysis

Electrochemical methods, particularly those employing ion-selective electrodes, are used to determine the concentrations of sodium, potassium, and other electrolyte ions in blood, urine, and other biological fluids.

Determination of medicinal substances

In pharmaceutical laboratories, voltametric and amperometric methods are applied for the quantitative analysis of active pharmaceutical ingredients in medicinal products.

Oxygen monitoring

Electrochemical sensors are used to measure the partial pressure of oxygen in blood, which is essential in anaesthesiology and intensive care medicine.

Analysis of toxic substances

Electrochemical analytical methods enable the detection of trace amounts of toxic substances, such as heavy metals and pesticides, in biological samples and environmental objects.

Sensors for the diagnosis of infectious diseases

Electrochemical sensors are used for the rapid detection of pathogens and antibodies in biological samples, facilitating the early diagnosis of infectious diseases.

These examples demonstrate the important role of electrochemical analyses methods for diagnosis and treatment in medicine and pharmacy.

Learning objectives

1. To acquire knowledge of:
 - a) electrode potentials and their dependence on ion activity in solution;
 - b) reference and indicator electrodes;
 - c) galvanic cells and their electromotive force (EMF);
 - d) the potentiometric method for the determination of pH;
 - e) potentiometric titration;
 - f) the potentiometric method for determining equilibrium constants, activity coefficients and thermodynamic functions.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. The concept of electrodes and galvanic cells.
2. The Jacobi-Daniell galvanic cell and the electrode processes at the cathode and anode.
3. Determination of electromotive force by the compensation method.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Thermodynamics of electrode processes”.

3. Study of problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Potentiometric determination of solution pH. Potentiometric titration of hydrochloric and acetic acids”.

Control questions

1. Electrode potential and electromotive force (EMF) of galvanic cells.
2. Electrodes and their classification.
3. The Nernst equation for the electrode potential.
4. Measurement of electromotive force and electrode potentials.
5. Reference electrodes:
 - a) the standard hydrogen electrode;
 - b) the calomel electrode;
 - c) the silver-silver chloride electrode.
6. Indicator electrodes. Ion-selective electrodes (e.g., the glass electrode).
7. Potentiometric methods for pH measurement.
8. Potentiometric titration.
9. Potentiometric determination of ion activity and activity coefficients.
10. Potentiometric determination of Gibbs free energy change (ΔG) and the equilibrium constant (K_p).
11. Importance of potentiometry in pharmaceutical practice.

Self-assessment questions

1. What processes occur at the metal-solution interface that lead to the formation of electrode potential? On what factors does its magnitude depend?
2. What are an electrode and a standard electrode?
3. What is electrode potential and how is it determined?
4. What is the standard electrode potential, and how is the series of standard electrode potentials established?
5. According to which principles are electrodes classified? Provide their classification.
6. What are electrodes of the first and second kind? Give examples.

7. Describe the structure of the hydrogen electrode. Which process determines its potential? Write the equation used to calculate the hydrogen electrode potential.
8. How does the potential of the hydrogen electrode change with increasing hydrogen pressure?
9. What is the standard hydrogen electrode, and what is the value of its potential?
10. Describe the structure of the silver-silver chloride electrode. Which reaction occurs at the electrode during operation, and what equation defines its potential?
11. Describe the structure of the calomel electrode. Which reaction occurs at the electrode, and how is its potential calculated?
12. What is a galvanic cell? Define electromotive force (EMF) and standard EMF?
13. Describe the Daniell-Jacobi cell and explain the mechanism of EMF generation. Apply the Nernst equation to calculate its EMF.
14. Which galvanic cells are called reversible and which are irreversible? Provide examples.
15. What rule should be followed when writing the electrochemical scheme of a galvanic cell for EMF calculations? Justify your answer.
16. Present the scheme and explain the principle of the compensation method for EMF measurement.
17. What is an ion-selective electrode, and what types exist?
18. What is a glass electrode and what are its applications?
19. List the advantages and limitations of the glass electrode.
20. How is solution pH measured using a glass electrode?
21. What is the principle of potentiometric pH determination?
22. Which electrodes are used for pH measurement, and which serve as reference electrodes?
23. What is potentiometric titration and what is its principle?
24. What are simple and differential titration curves and for what purpose are they constructed?
25. How is the concentration of acids and bases determined by potentiometric titration?

26. Which factors affect the magnitude of the potential (pH) jump on a potentiometric titration curve?
27. Under what conditions can mixtures of acids or bases be subjected to sequential titration?
28. How are ion activity and activity coefficients determined by the potentiometric method?
29. How are the Gibbs free energy change (ΔG) and the equilibrium constant (K) determined by potentiometry?
30. What is the significance of potentiometry in pharmaceutical practice?
31. Draw and write the schemes of the following galvanic cells:
 - a) hydrogen – hydrogen galvanic cell;
 - b) hydrogen – calomel galvanic cell;
 - c) hydrogen – silver-silver chloride galvanic cell;
 - d) glass – hydrogen galvanic cell;
 - e) glass – calomel galvanic cell;
 - f) glass – silver-silver chloride galvanic cell.

How can the pH of a solution be determined using these cells?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (60 minutes).

Laboratory work

Potentiometric determination of solution pH

Potentiometric titration of hydrochloric and acetic acids

Laboratory objective

To develop practical skills in:

- a) assembling galvanic cells;
- b) measuring the electromotive force (EMF) of galvanic cells;
- c) measuring electrode potentials and standard electrode potentials;
- d) performing potentiometric titration;
- e) determining the concentrations of strong acids and bases from potentiometric data.

Experimental procedure

Instruments and reagents

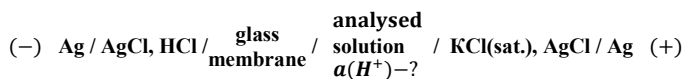
1. magnetic stirrer;
2. glass electrode and silver–silver chloride electrode;
3. solutions with unknown pH;
4. hydrochloric acid solution of unknown concentration;
5. standard sodium hydroxide solution, molar concentration $0.1 \text{ mol} \cdot \text{L}^{-1}$;
6. microburette, 2 or 5 mL;
7. pipette, 20 or 25 mL;
8. distilled water;
9. filter paper.

Experiment 1. Potentiometric determination of solution pH

One of the principal methods for determining the pH of solutions is the potentiometric method, which is based on measuring the electromotive force (EMF) of an electrochemical cell composed of an indicator electrode, whose potential depends on the activity of hydrogen ions, and a reference electrode immersed in the test solution.

Indicator electrodes include hydrogen, quinhydrone, and glass electrodes. In practice, the glass electrode is most widely used due to its convenience, stability, and high selectivity toward hydrogen ions.

For pH measurement, an electrochemical cell is assembled using a glass indicator electrode and a silver-silver chloride reference electrode.



The EMF of this cell is measured using potentiometric instruments (ionometers or pH meters), to which the electrodes are connected. Modern ionometers allow direct pH readings, as their scales are calibrated both in millivolts and in pH units.

Prior to measurement, the glass electrode is conditioned in $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl solution, while the silver-silver chloride electrode is stored in saturated KCl solution for 2-3 days. The ionometer is then calibrated using two or three buffer solutions with known pH values. Only after calibration can the pH of the test solutions be measured.

Connect the ionometer to the power supply and prepare it for operation according to the manufacturer's instructions. Transfer 20-30 mL of the test solution into a 50 mL beaker. Immerse the electrodes in the solution and measure the pH according to the procedure described in the instrument manual. Refer to this method as potentiometric pH determination.

After completing the measurements, remove the electrodes, rinse them with distilled water, and gently blot them with filter paper. Prepare the electrodes for subsequent pH measurement.

Attention!

Do not wipe the glass bulb of the electrode, as this may damage its hydrated gel layer. The electrode should not be touched with sharp objects, since the glass membrane is extremely thin (fractions of a millimetre) and can be easily damaged.

Experiment 2. Potentiometric titration of hydrochloric acid

Potentiometric pH determination is used to determine the concentrations of strong acids and bases. For this purpose, potentiometric titration is applied, which is analogous to classical acid-base titration.

The main difference is that, instead of visual acid-base indicators, a glass electrode is used to record changes in the pH of the solution during titration with a standard alkali or acid solution.

Transfer 20 or 25 mL of hydrochloric acid of unknown concentration into a 50 mL beaker using a pipette. Fill the microburette with a standard sodium hydroxide solution. Connect the glass and silver-silver chloride electrodes to the ionometer and immerse them in the HCl solution, then record the initial pH value.

Perform the titration by adding portions of the standard NaOH solution according to the instructor's guidance. After each addition, thoroughly mix the solution using a magnetic stirrer and measure the pH value. Near the equivalence point, where a sharp change in pH (or EMF) is observed, add the titrant in smaller increments. After passing the equivalence point, continue adding NaOH until the pH reaches approximately 11.5-12.0.

Record the experimental data in Table 12.

Table 12. Potentiometric titration data

No	V(NaOH), mL	pH

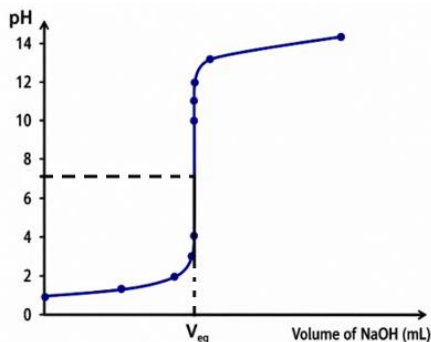


Fig. 7. Titration curve of hydrochloric acid

Plot a graph of pH versus the volume of added NaOH based on the potentiometric titration data (Fig. 7). The equivalence point is identified by drawing a perpendicular from the midpoint of the pH jump to the abscissa axis, which allow determination of the equivalent volume of the standard solution consumed during titration.

When titrating a hydrochloric acid solution with a standard NaOH solution, the equivalence point corresponds to $\text{pH} = 7$ and coincides with the midpoint of the pH jump.

Calculate the concentration of hydrochloric acid based on the obtained data using the law of equivalents:

$$n(\text{HCl}) = n(\text{NaOH})$$

that is,

$$c(\text{NaOH}) \times V(\text{NaOH}) = c(\text{HCl}) \times V(\text{HCl})$$

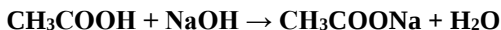
from which:

$$c(\text{HCl}) = \frac{c(\text{NaOH}) \times V(\text{NaOH})}{V(\text{HCl})}$$

Experiment 3. Potentiometric titration of acetic acid

The potentiometric method is widely used not only for the quantitative determination of acids and bases but also for evaluating the ionization (dissociation) constants of weak acids and bases. In this experiment, the method is demonstrated using acetic acid as a model weak acid.

A standard sodium hydroxide or potassium hydroxide solution is used as the titration. During the potentiometric titration of acetic acid with a standard alkali solution, the pH of the solution changes gradually according to the neutralization reaction:



Before the equivalence point is reached, the solution contains both unneutralized acetic acid and the sodium acetate formed during neutralization. Therefore, the pH depends on the ratio of the concentrations of the acid and its salt.

The mixture of CH_3COOH and CH_3COONa constitutes an acetate buffer solution, whose pH is described by the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{c(\text{salt})}{c(\text{acid})} \quad (1)$$

According to equation (1), when exactly one-half of the acetic acid has been neutralized, the concentrations of the acid and its salt are equal, the logarithmic term becomes zero, and the pH is equal to the acid dissociation constant expressed as pK_a .

Therefore, the ionization constant of acetic acid can be determined by measuring the pH at the half-equivalence point, where 50 % of the acid has been neutralized.

To locate this point, the equivalent volume of the standard alkali solution required for complete neutralization of the acid is first determined. Half of this volume is then calculated, and the corresponding pH value is obtained graphically from the potentiometric titration curve. The pK_a value is subsequently used to calculate the ionization constant of acetic acid.

Perform a potentiometric titration of acetic acid with a standard sodium hydroxide solution for this purpose. Transfer 20 or 25 mL of the acetic acid solution of the concentration specified by the instructor into a 50 mL titration beaker using a pipette. Fill the microburette with $0.1 \text{ mol} \times \text{L}^{-1}$ standard NaOH solution. Connect the glass indicator electrode and the silver-silver chloride reference electrode to the ionometer according to the operating instructions. Immerse the electrodes in the acetic acid solution and measure the initial pH.

Titrate the acetic acid solution with a standard NaOH solution. To minimize dilution during titration, use a standard alkali concentration at least ten times greater than that of the acetic acid solution.

After each addition of NaOH, thoroughly mix the solution using a magnetic stirrer and record the pH after the reading stabilizes. Add the standard NaOH solution in portions of 0.1 mL. Record the results of the titration in Table 13.

Table 13. Potentiometric titration data

No	V(NaOH), mL	pH	$\Delta V(\text{NaOH}),$ mL	ΔpH	$\frac{\Delta \text{pH}}{\Delta V(\text{NaOH})}$	pK	K (CH ₃ COOH)

Method I for determining the ionization constant (K_a) of acetic acid

Using the experimental data, construct both the simple and differential titration curves. Determine the equivalence volume of the NaOH solution (V_{eq}) from the differential titration curve and calculate the half-equivalence volume $V_{eq}/2$.

On the simple titration curve, locate the point corresponding to $V_{eq}/2$ on the abscissa axis. Draw a vertical line to intersect the titration curve, and from this point draw a horizontal line to the ordinate. The corresponding pH value is equal to the acid dissociation constant expressed as pK_a .

Calculate the ionization constant of acetic acid using the following equation:

$$K_a = 10^{-pK_a} \quad (2)$$

Method II for determining the ionization constant (K_a) of acetic acid

Using the experimental titration data, calculate the number of mole-equivalents of the added NaOH and determine the ratio of the mole-equivalents of alkali to those of acetic acid.

The pK_a values are calculated for the titration region in which this ratio is close to 0.5, corresponding to the half-neutralization point:

$$\frac{n_{eq}(\text{NaOH})}{n_{eq}(\text{CH}_3\text{COOH})} = 0.5 \quad (3)$$

Within the buffer region, where the mole-equivalent ratio of salt to acid ranges from approximately 0.3 to 0.7, the pH varies only slightly and

remains close to the pK_a value. At the half-neutralization point, where the ratio is exactly 0.5, the following relationship applies:

$$pH = pK_a \quad (4)$$

Example calculation

Assume that 25.0 mL of a CH_3COOH solution with a concentration of $5.0 \times 10^{-3} \text{ mol} \times L^{-1}$ is used for the titration. The number of mole-equivalents of acetic acid is:

$$\begin{aligned} n_{eq}(CH_3COOH) &= c(CH_3COOH) \times V(CH_3COOH) \\ &= 5.0 \times 10^{-3} \text{ mol} \times L^{-1} \times 25.0 \times 10^{-3} L = 1.25 \times 10^{-4} \text{ mol} \end{aligned}$$

Suppose that 0.50 mL of $0.1 \text{ mol} \times L^{-1}$ NaOH has been added. The number of mole-equivalents of sodium hydroxide is:

$$\begin{aligned} n_{eq}(NaOH) &= c(NaOH) \times V(NaOH) = 0.1 \text{ mol} \times L^{-1} \times 0.5 \times 10^{-3} L \\ &= 5.0 \times 10^{-5} \text{ mol} \end{aligned}$$

Then the ratio of the number of mole-equivalents of alkali to that of the acid is:

$$\frac{n(NaOH)}{n(CH_3COOH)} = \frac{5.0 \times 10^{-5}}{1.25 \times 10^{-4}} = 0.40$$

The pK_a value is calculated using the equation derived from the Henderson-Hasselbalch equation:

$$pK(CH_3COOH) = pH + \log \frac{n_{eq}(CH_3COOH) - n_{eq}(NaOH)}{n_{eq}(NaOH)}$$

The obtained experimental and calculated data record in Table 14.

Table 14. Potentiometric titration data

No	V(NaOH), mL	pH	$n_{eq}(NaOH)$	$n_{eq}(CH_3COOH)$	$\frac{n_{eq}(NaOH)}{n_{eq}(CH_3COOH)}$	$pK(CH_3COOH)$	K

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Potentiometric determination of solution pH. Potentiometric titration of hydrochloric and acetic acids”.
3. Problem-solving related to the topic: „Thermodynamics of electrode processes”.

Laboratory and practical work No. 11

Thermodynamics of electrode processes

Oxidation-reduction systems. Concentration galvanic cells

Determination of the electrode potential and the standard electrode potential of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox system

Significance of the topic

Understanding oxidation-reduction potentials is essential for studying and interpreting the redox processes that occur in living organisms. Biological oxidation is the primary source of metabolic energy and proceeds through a series of electron and proton-transfer reactions. During this process, hydrogen is transferred stepwise from substrate molecules to oxygen through a series of intermediate carriers.

Knowledge of redox chains involved in biological oxidation provides a quantitative basis for understanding the individual stages of oxidative phosphorylation and cellular energy production.

Redox potentials are of fundamental importance in medicine and pharmacy because they are closely related to numerous physiological and biochemical processes. Measurement of the redox potentials of biological fluids, such as blood and plasma, is used in the diagnosis of various diseases and facilitates the detection of metabolic disturbances associated with oxidative stress.

Redox potentials are also important in antioxidant therapy, as the assessment of cellular redox balance contributes to the development and evaluation of therapeutic agents designed to protect cells against oxidative damage caused by reactive oxygen species and free radicals.

In addition, the pharmacological activity of many medicinal substances, including anti-inflammatory and antitumor agents, is associated with changes in the redox state of cells.

In pharmaceutical analysis and manufacturing, redox potentials measurements are employed to evaluate the stability of pharmaceutical formulations, monitor redox processes during production, and assess the biocompatibility of materials intended for medical and pharmaceutical applications.

Thus, the study of oxidation-reduction potentials is of considerable interdisciplinary importance, linking fundamental principles of physical chemistry and biochemistry with practical applications in medicine and pharmaceutical science.

Learning objectives

1. To acquire knowledge of:
 - a) oxidation-reduction systems, electrodes, and electrode potentials;
 - b) the quinhydrone electrode;
 - c) redox galvanic cells and their electromotive force (EMF);
 - d) concentration galvanic cells and diffusion potential.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Redox reactions and methods for balancing redox equations.
2. Measurement of electrode potentials and the electromotive force (EMF) of galvanic cells (see laboratory and practical session No. 10).

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Thermodynamics of electrode process. Oxidation-reduction systems. Concentration galvanic cells”.
3. Study of problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Determination of the electrode potential and the standard electrode potential of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox system”.

Control questions

1. Redox electrodes and redox galvanic cells.
2. Electrode potentials and standard electrode potentials of redox electrodes. Electromotive force (EMF) of redox galvanic cells. The Nernst-Peters equation.

3. The quinhydrone electrode and its application.
4. Concentration galvanic cells.
5. Diffusion and membrane potentials.

Self-assessment questions

1. What is a redox system and what is a redox electrode?
2. Which electrodes are referred to as redox electrodes? Provide examples.
3. On which factors does the potential of a redox electrode depend? Which equation is used to calculate it?
4. Write the Nernst-Peters equation for the redox electrode in which the following half-reaction occurs: $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$.
5. Draw the experimental setup for measuring the potential of the $\text{Pt}/\text{Sn}^{4+}, \text{Sn}^{2+}$ redox electrode and describe the measurement procedure.
6. Which reference electrodes are commonly used for determining the potential of a redox electrode?
7. Define the standard electrode potential of a redox electrode and provide examples.
8. Which galvanic cells are classified as redox cells? Provide examples.
9. What is a quinhydrone electrode and which redox process occurs at this electrode?
10. What are the characteristic features, advantages, and limitations of the quinhydrone electrode?
11. Which galvanic cells are classified as concentration cells? Provide examples.
12. Write the equation used to calculate the electromotive force (EMF) of a concentration galvanic cell.
13. Define the diffusion potential and write the equation used for its calculation.
14. Write the equation for calculating the EMF of a concentration galvanic cell when the diffusion potential is taken into account.
15. What is the membrane potential, and what role does it play in the generation of bioelectric potentials?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (60 minutes).

Laboratory work

Determination of the electrode potential and the standard potential of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox system

Laboratory objectives

To develop practical skills in:

- a) measuring the electrode potential and determining the standard electrode potential of a redox electrode;
- b) determining the equilibrium constant of a redox reaction and the standard Gibbs free energy change.

Theoretical background

To determine the electrode potential of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$, redox system, the electromotive force (EMF) of an electrochemical cell is measured. The cell consists of a platinum indicator electrode and a silver-silver chloride reference electrode immersed in a solution containing the redox couple $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$.

The electrochemical cell is represented by the following notation:



For simplicity, the oxidized form $[\text{Fe}(\text{CN})_6]^{3-}$ will be denoted as Ox, and the reduced form $[\text{Fe}(\text{CN})_6]^{4-}$ as Red.

The electromotive force of the galvanic cell is given by:

$$E = \varphi_{\text{ox/red}} - \varphi_{\text{AgCl/Ag, Cl}^-} \quad (1)$$

where:

E – the electromotive force of the galvanic cell, V;

$\varphi_{\text{ox/red}}$ – the electrode potential of the redox system $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox system, V;

$\varphi^0_{\text{AgCl/Ag, Cl}^-}$ – the electrode potential of the silver-silver chloride electrode, V.

For a silver-silver chloride electrode containing saturated KCl solution, the electrode potential at 298 K is 0.201 V. When the activity of chloride ions is $1 \text{ mol} \times \text{L}^{-1}$, the electrode potential corresponds to the standard electrode potential of the silver-silver chloride electrode, which is 0.222 V.

According to the Nernst-Peters equation, the electrode potential of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}/\text{Pt}$ redox electrode is:

$$\varphi_{\text{ox/red}} = \varphi^0_{\text{ox/red}} + \frac{RT}{zF} \ln \frac{a(\text{ox})}{a(\text{red})} \quad (2)$$

where:

$\varphi^0_{\text{Ox/Red}}$ – standard electrode potential of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ system, V;

R – the universal gas constant;

T – the absolute temperature, K;

z – the number of electrons transferred in the electrode process ($z = 1$);

F – the Faraday constant, $96485 \text{ C} \times \text{mol}^{-1}$;

a(ox) and a(red) – the activities of the oxidized and reduced forms of the redox system, $\text{mol} \times \text{L}^{-1}$.

Substituting equation (2) into equation (1) gives:

$$E = \varphi^0_{\text{ox/red}} + 0.0591 \log \frac{a(\text{ox})}{a(\text{red})} - \varphi_{\text{AgCl/Ag, Cl}^-} \quad (3)$$

The relationship between activity, concentration, and activity coefficient is:

$$a(\text{ox}) = c(\text{ox}) \times f(\text{ox}) \quad (4)$$

$$a(\text{red}) = c(\text{red}) \times f(\text{red}) \quad (5)$$

Substituting equations (4) and (5) into equation (3) yields:

$$E = E^0 + 0.0591 \log \frac{c_m(\text{ox})}{c_m(\text{red})} + 0.0591 \log \frac{f(\text{ox})}{f(\text{red})} \quad (6)$$

where:

$$E^0 = \varphi^0_{\text{ox/red}} - \varphi_{\text{AgCl/Ag, Cl}^-} \quad (7)$$

The activity coefficients of the oxidized and reduced forms are calculated using the Debye-Hückel equation for dilute electrolyte solutions:

$$\log f = - \frac{0.508 \times z^2 \times \sqrt{I}}{1 + \sqrt{I}} \quad (8)$$

where:

z – the ionic charge;

I – the ionic strength of the solution.

The ionic strength of the solution is calculated according to the Lewis equation:

$$I = \frac{1}{2} \sum c_i(x) \times z_i^2 \quad (9)$$

where:

$C_i(x)$ – the molal concentration of the ion, mol $\times$ kg $^{-1}$.

Using equation (8), the activity-coefficient term in equation (6) becomes:

$$\log \frac{f(ox)}{f(red)} = - \frac{0.508(-3)^2\sqrt{I}}{1+\sqrt{I}} + \frac{0.508(-4)^2\sqrt{I}}{1+\sqrt{I}} = \frac{3.556\sqrt{I}}{1+\sqrt{I}} \quad (10)$$

Substituting equation (10) into equation (6) gives:

$$E = E^0 + 0.0591 \left(\log \frac{c_m(ox)}{c_m(red)} + \frac{3.556\sqrt{I}}{1+\sqrt{I}} \right) \quad (11)$$

From equation (11), the standard EMF E^0 can be determined:

$$E^0 = E - 0.0591 \left(\log \frac{c_m(ox)}{c_m(red)} + \frac{3.556\sqrt{I}}{1+\sqrt{I}} \right) \quad (12)$$

Finally, from equation (7), the standard potential of the redox system is calculated:

$$\varphi_{ox/red}^0 = E^0 + \varphi_{AgCl/Ag, Cl^-} \quad (13)$$

Experimental procedure

Apparatus and reagents

1. universal ionometer EV-74;
2. magnetic stirrer;
3. platinum and silver-silver chloride electrodes;

4. $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ solutions, molal concentrations $0.01 \text{ mol} \times \text{kg}^{-1}$;
5. two pipettes, 10 mL;
6. beaker, 50 mL;
7. distilled water;
8. filter paper.

Connect the ionometer to the power supply and prepare it for operation according to the manufacturer's operating instructions.

Prepare a series of mixtures of $0.01 \text{ mol} \times \text{kg}^{-1}$ of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ solutions in a 50 mL beaker using the volume ratios specified by the instructor (Table 15). Immerse the platinum indicator electrode and the silver-silver chloride reference electrode into each prepared mixtures and measure the electromotive force (EMF) of the electrochemical cell.

Table 15. Values of electromotive force (EMF) and electrode potential

No	V ($K_3[Fe(CN)_6]$), ml	V ($K_4[Fe(CN)_6]$), ml	E , V	$C_m(\text{ox})$, $\text{mol} \times \text{kg}^{-1}$	$C_m(\text{red})$, $\text{mol} \times \text{kg}^{-1}$	I , $\text{mol} \times \text{kg}^{-1}$	E^0 , V	φ^0 , ox/red
1	18	2						
2	14	6						
3	10	10						
4	6	14						
5	2	18						

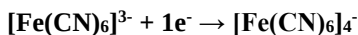
To determine the standard electromotive force, E^0 , using equation (12), calculate the logarithm of the concentration ratio of the oxidized and reduced forms and the ionic strength of each solution. Because both stock solutions have the same initial concentration, the concentration ratio may be replaced by the corresponding ratio of the mixed solution volumes.

After determining E^0 , calculate the standard electrode potential of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox system using equation (13) and compare the experimental value.

Using the relationship:

$$E^0 = \frac{RT}{Z F} \ln K$$

calculate the equilibrium constant, K, of the corresponding redox reaction:



Calculate the standard Gibbs free energy change (ΔG^0) from the thermodynamic equilibrium constant using the equation:

$$G_{298}^0 = -RT \ln K$$

where:

R – the universal gas constant;

T – the temperature, K;

K – the equilibrium constant.

Record all experimental and calculated data in the table, analyse the results, and formulate conclusions.

Example of calculation of $\log \frac{c_m(\text{ox})}{c_m(\text{red})}$ and the ionic strength

The following example illustrates the calculation for a mixture prepared by combining 18 mL of a 0.01 mol×kg⁻¹ K₃[Fe(CN)₆] solution with 2 mL of 0.01 mol×kg⁻¹ K₄[Fe(CN)₆] solution.

Since both stock solutions have the same molal concentration, the concentration ratio is equal to the ratio of the mixed solution volumes:

$$\log \frac{c_m(\text{ox})}{c_m(\text{red})} = \log \frac{V(\text{ox})}{V(\text{red})} = \log \frac{18}{2} = \log 9 = 0.95$$

The ionic strength of the solution is determined by the concentrations and charges of all ions present in the solution. The molal concentrations of the two salts in the final mixture are calculated first.

For K₃[Fe(CN)₆]:

$$c_{m1}(\text{K}_3[\text{Fe}(\text{CN})_6]) \times V_1(\text{K}_3[\text{Fe}(\text{CN})_6]) = c_{m2}(\text{K}_3[\text{Fe}(\text{CN})_6]) \times V_{\text{tot}}$$

Therefore,

$$c_{m_2}(K_3[Fe(CN)_6]) = \frac{c_{m_1}(K_3[Fe(CN)_6]) \times V_1(K_3[Fe(CN)_6])}{V_{tot}}$$

$$= \frac{0.01 \text{ mol} \times \text{kg}^{-1} \times 18 \text{ mL}}{20 \text{ mL}} = 9 \times 10^{-3} \text{ mol} \times \text{kg}^{-1}$$

Similarly, the molal concentration for $K_4[Fe(CN)_6]$ is calculated:

$$c_{m_2}(K_4[Fe(CN)_6]) = \frac{0.01 \text{ mol} \times \text{kg}^{-1} \times 2 \text{ mL}}{20 \text{ mL}} = 10^{-3} \text{ mol} \times \text{kg}^{-1}$$

The ionic strength of the mixture is then calculated using the Lewis equation:

$$I = \frac{1}{2} \{ 9 \times 10^{-3} [3 \times 1^2 + 1(-3)^2] + 10^{-3} [4 \times 1^2 + 1(-4)^2] \}$$

$$= 6.4 \times 10^{-2}$$

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Determination of the electrode potential and the standard electrode potential of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox system”.
1. Problem-solving related to the topic: „Oxidation-reduction systems. Concentration galvanic cells”.

Laboratory and practical work No. 12

Chemical kinetics and kinetic equations

Kinetic study of sucrose hydrolysis

Significance of the topic

Chemical kinetics is a branch of physical chemistry that studies the rates of chemical reactions, the factors influencing these rates, and the mechanisms by which reactions proceed. Knowledge of the theoretical foundations of chemical kinetics enables pharmacists to interpret kinetic data, provide a scientific basis for determining the shelf life of medicinal substances, identify factors that improve their stability, and conduct biopharmaceutical studies on the transformations of medicinal substances in the body. Based on this knowledge, an independent field of medical science – pharmacokinetics – has been developed.

The laws of chemical kinetics play an important role in medicine and pharmacy, as they allow for a deeper understanding of the processes affecting medicinal substances within the body. They are essential for the study of biochemistry, pharmaceutical technology, pharmaceutical chemistry, and pharmacology, all of which are closely related to the rates and dynamics of drug absorption, stability, efficacy, and storage. The application of chemical kinetics in pharmaceutical practice supports the development of safer and more effective medicines and the optimization of their storage and use, ultimately enhancing therapeutic outcomes and the quality of healthcare.

Learning objectives

1. To acquire knowledge of:
 - a) reaction rates and methods for their determination;
 - b) molecularity and the order of chemical reactions;
 - c) kinetic equations for zero-, first-, and second-order reactions.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Average and instantaneous reaction rates.
2. Dependence of reaction rate on reactant concentration (the law of mass action).
3. Elementary and complex reactions.
4. Polarized light.
5. Structure and operating principle of a polarimeter.
6. Optically active substances.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Chemical kinetics and kinetic equations”.
3. Study of problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Kinetic study of sucrose hydrolysis”.

Control questions

1. The subject and significance of chemical kinetics.
2. Homogeneous and heterogeneous reactions. Elementary and complex reactions.
3. Reaction rates and methods for their measurement. Factors affecting reaction rates. First-order reactions.
4. Molecularity and reaction order. Kinetic equations for irreversible zero-, first-, and second-order reactions. Half-life.
5. Kinetic equation of a reversible first-order reaction.
6. Methods for determining the reaction order.

Self-assessment questions

1. What does chemical kinetics study? Define the average and instantaneous reaction rates. Based on the concentration change of which component is the reaction rate typically determined? In what units is the reaction rate expressed?

2. How do the reaction rate and reactant concentrations change over time? Illustrate the corresponding graphical relationships.
3. Why are the terms „reaction rate” and „reaction rate with respect to a given substance” both used?
4. Which reactions are classified as elementary and which as complex? What types of complex reactions are known?
5. What factors influence the reaction rate? What is the fundamental kinetic law for elementary reactions (the Guldberg-Waage law)?
6. What is the physical meaning of the reaction rate constant, and which factors influence its value?
7. What is the molecularity of a chemical reaction? List the kinetic classification of reactions according to molecularity.
8. What is meant by the reaction order with respect to a substance and the overall reaction order? How does molecularity differ from reaction order?
9. Which reactions are classified as pseudo-first-order reactions? Provide examples.
10. Write the equation used to calculate the rate constant of a zero-order reaction.
11. Write and analyse the kinetic equations describing the change in reactant concentrations for a first-order reaction.
12. Write and analyse the kinetic equations describing the change in reactant concentrations for a second-order reaction.
13. Under identical initial concentrations and equal rate constants, which irreversible reaction proceeds faster: a first-order or a second-order reaction?
14. What is the half-life of a reaction, and how is it related to the rate constant for first- and second-order reactions?
15. Does the half-life of first- and second-order reactions depend on the initial reactant concentrations? If so, how?
16. What methods are used to determine the reaction order?
17. How can the rate constant of zero-, first-, and second-order reactions be determined graphically?

18. What are the units of the rate constants for zero-, first-, and second-order reactions?
19. What is polarized light? Describe the structure and operating principle of a polarimeter.
20. Which substances are optically active? Provide examples.
21. How is the angle of rotation of the plane of polarized light measured using a polarimeter?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (75 minutes).

Laboratory work

Kinetic study of sucrose hydrolysis

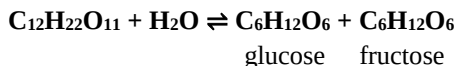
Laboratory objectives

To develop practical skills in:

- a) determining the reaction rate constant;
- b) calculating the reaction order and the half-life of sucrose hydrolysis.

Theoretical background

The hydrolytic cleavage of cane sugar (sucrose) yields glucose and fructose according to the reaction:



This bimolecular reaction is a classic example of a pseudo-first-order reaction. Sucrose hydrolysis is typically carried out in dilute aqueous solutions, in which the concentration of water remains essentially constant and can be neglected. Under these conditions, the reaction rate depends only on the concentration of sucrose:

$$\vartheta = -\frac{dc}{d\tau} = K c (\text{C}_{12}\text{H}_{22}\text{O}_{11}) \quad (1)$$

In neutral aqueous solution, sucrose hydrolysis proceeds very slowly and is catalysed by hydrogen ions. The rate of this homogeneous catalytic process is directly proportional to the concentration of the hydrogen ions in the solution.

Sucrose and its hydrolysis products are optically active due to the presence of asymmetric carbon atoms in their molecules. Therefore, changes in the concentration of the reacting substance can be conveniently monitored by measuring changes in the optical activity of the solution.

Natural light is characterized by electromagnetic oscillations occurring in all planes perpendicular to the direction of propagation, whereas polarized light oscillates in only one such plane. When polarized light passes through a solution of an optically active substance, the plane of polarization is rotated by an angle known as the angle of rotation.

Sucrose rotates the plane of polarized light to the right ($\alpha = +66.55^\circ$), whereas the mixture of its hydrolysis products rotates it to the left. This is due to the stronger laevorotation of fructose ($\alpha = -99.9^\circ$), which exceeds the dextrorotation of glucose ($\alpha = +52.5^\circ$). As a result, during hydrolysis the angle of rotation decreases, passes through zero, and becomes negative. Thus, dextrorotation is replaced by laevorotation. At the end of inversion, the angle reaches a limiting negative value.

The angle of rotation is measured using a polarimeter – an optical instrument consisting of two main components: a polarizer, which produces polarized light, and an analyser, which allows determination of the rotation angle.

Based on the kinetic equation of a first-order reaction (1), the following expression is obtained:

$$K = \frac{1}{\tau} \ln \frac{c_0 (C_{12}H_{22}O_{11})}{c_\tau (C_{12}H_{22}O_{11})} \quad (2)$$

Since the concentration of the reacting substance is proportional to the angle of rotation of the plane of polarization, equation (2) can be written as:

$$K = \frac{2.303}{\tau} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_\tau - \alpha_\infty} \quad (3)$$

From the initial moment to the completion of the reaction, the change in the angle of rotation ($\alpha_0 - \alpha_\infty$) is proportional to the initial sucrose concentration $c_0(\text{C}_{12}\text{H}_{22}\text{O}_{11})$. The difference between the angle of rotation at time τ and at the end of inversion ($\alpha_\tau - \alpha_\infty$) is proportional to the sucrose concentration at that time $c_\tau(\text{C}_{12}\text{H}_{22}\text{O}_{11})$.

Experimental procedure

Apparatus and reagents

1. polarimeter;
2. sucrose solutions, mass fractions 16 %, 20 % and 24 %;
3. hydrochloric acid solutions, molar concentrations 2.0, 2.5, and 3.0 $\text{mol} \times \text{L}^{-1}$;
4. two pipettes, 25 mL;
5. water bath;
6. distilled water;
7. two conical flasks, 100 mL;
8. filter paper;
9. thermometer (upper limit 100 °C).

The experiment is conducted at room temperature. The sucrose concentration is varied within the range of 16-24 %, and the catalyst concentration within 2.0-3.0 $\text{mol} \times \text{L}^{-1}$. The exact values are assigned by the instructor.

Transfer 25 mL of the sucrose solution into one conical flask and 25 mL of hydrochloric acid solution of the required concentration into another. Allow both solutions to equilibrate to room temperature. Meanwhile, prepare the polarimetric tube by thoroughly rinsing it with distilled water and carefully drying the end windows with filter paper.

Determine the initial angle of rotation of the sucrose solution. Rinse the polarimetric tube twice with small portions of the sucrose solution, then fill it completely so that a convex meniscus forms. Carefully apply the cover glass from the side to avoid trapping air bubbles, and secure the cap tightly, ensuring the rubber gasket is properly positioned. Wipe the exterior of the tube dry, paying particular attention to the cleanliness of the optical windows.

Place the tube in the polarimeter near the eyepiece and measure the initial angle of rotation. Since subsequent measurements are performed with a solution diluted twofold, the initial angle is taken as $\alpha_0 = \alpha/2$.

To study the kinetics of sucrose hydrolysis catalysed by hydrogen ions, mix equal volumes of the prepared sucrose and hydrochloric acid solutions. The moment of mixing is taken as the start of the reaction. Rinse the polarimetric tube twice with the resulting mixture, fill it, and measure the angle of rotation at specified time intervals (e.g., 5, 10, 20, 30, 40, and 60 minutes). Record all measurements in a table. After each measurement, switch off the polarimeter light source.

At room temperature, sucrose inversion is completed within 2-5 days. To accelerate the process, place the remaining reaction mixture (after filling the polarimetric tube) in a water bath at 60-65 °C (not higher, to prevent thermal degradation of sucrose) for 30 minutes. Subsequently, allow the mixture to cool to room temperature without removing the thermometer.

After completing measurements at all specified time intervals, remove the working solution from the polarimetric tube, rinse the tube with distilled water followed by the cooled reaction mixture. Refill the tube and measure the final angle of rotation (α_∞).

The final angle of rotation is negative, since the solution contains glucose and fructose. The overall optical rotation is dominated by the stronger laevorotation of fructose.

After completion of the experiment, thoroughly rinse the polarimetric tube with tap water and then with distilled water.

Calculate the reaction rate constant at each time point using equation (3). Draw conclusions regarding the reaction order based on the obtained values.

Calculate the half-life of sucrose hydrolysis using the average reaction rate constant:

$$\tau_{1/2} = \frac{0.6932}{K_{av}}$$

Record all experimental and calculated data in Table 16.

Table 16. Experimental and calculated data

Time from start, τ min	α_{τ}	$\alpha_0 - \alpha_{\infty}$	$\alpha_{\tau} - \alpha_{\infty}$	K, min^{-1}	$\bar{k}, \text{min}^{-1}$
0					
5					
10					
20					
30					
40					
60					
after heating					

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Kinetic study of sucrose hydrolysis”.
3. Problem-solving related to the topic: „Chemical kinetics and kinetic equations”.

Laboratory and practical work No. 13

Chemical kinetics and kinetic equations

Kinetic study of the alkaline hydrolysis of acetylsalicylic acid

Significance of the topic

Acetylsalicylic acid (aspirin) is a widely used medicinal substance with analgesic and antipyretic properties. In aqueous media, it undergoes hydrolysis to yield salicylic acid and acetic acid.

The kinetic study of the alkaline hydrolysis of acetylsalicylic acid is essential for understanding the chemical stability of pharmaceutical substances during storage and in biological environments. Determination of the rate constant, reaction order, half-life, and activation energy allows a quantitative assessment of the drug degradation rate and the influence of temperature on this process. This knowledge is fundamental for predicting the shelf life of medicinal products and is widely applied in the development and quality control of pharmaceutical dosage forms.

Although the hydrolysis reaction may appear to follow first-order kinetics, its mechanism is strongly dependent on the pH of the medium. As a result, the apparent reaction order may vary under different experimental conditions.

Learning objectives

1. To acquire knowledge of:
 - a) the van't Hoff temperature coefficient;
 - b) activation energy;
 - c) collision theory;
 - d) the relationship between reaction rate and activation energy;
 - e) transition state theory.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Average and instantaneous reaction rates.
2. Temperature dependence of reaction rates. The van 't Hoff rule.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Chemical kinetics and reaction mechanisms”.
3. Study of problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Kinetic study of the alkaline hydrolysis of acetylsalicylic acid”.

Control questions

1. The van 't Hoff rule.
2. Activation energy. The Arrhenius equation and the relationship between the rate constant and activation energy.
3. Methods for determining activation energy.
4. Collision theory.
5. Express methods for determining the shelf life of medicinal substances.
6. Fundamentals of transition state theory.

Self-assessment questions

1. How does temperature affect the rate of chemical reactions? What changes should be taken into account?
2. How is the van 't Hoff rule for the temperature dependence of reaction rate formulated? What is the van't Hoff temperature coefficient? What are its typical values for most reactions at room temperature?
3. Who first established the quantitative relationship between the reaction rate constant and temperature, and on what basis?
4. What assumptions did Arrhenius make when deriving the equation describing the temperature dependence of the reaction rate constant?
5. What is activation energy? What is its physical significance?
6. How is the Arrhenius equation expressed, and what information does it provide?

7. Which methods can be used to determine the activation energy of a reaction?
8. What are the main postulates of the collision theory? Explain the concept of an active molecule.
9. How are the reaction rate and the number of effective collisions related?
10. What is the steric factor and what causes its occurrence?
11. What are the fundamental principles of the transition state theory that allow derivation of the reaction rate equation?
12. What occurs to reacting molecules when the activated complex passes through the potential barrier? What is the lifetime of the activated complex?
13. What is the physical meaning of activation entropy in the transition state theory?
14. What is the principle of express methods for determining the shelf life of medicinal substances?
15. How are kinetic parameters used to assess the stability of medicinal products?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (75 minutes).

Laboratory work

Kinetic study of the alkaline hydrolysis of acetylsalicylic acid

Laboratory objectives

To develop practical skills in:

- a) determining the rate constant, reaction order, and half-life of the alkaline hydrolysis of acetylsalicylic acid;
- b) determining the activation energy of the investigated process.

Theoretical background

Hydrolysis is carried out using a strictly defined amount of an ethanoic solution of acetylsalicylic acid in the presence of a known excess of standardized sodium hydroxide solution. At specified time intervals, the reaction is stopped by adding a known excess of hydrochloric acid solution. The resulting solution is then titrated with sodium hydroxide to determine the residual amount of alkali and, consequently, the extent of the reaction.

Based on these measurements, the amount of hydrolysed acetylsalicylic acid is determined, and the reaction order and activation energy of the investigated process are calculated.

Experimental procedure

Apparatus and reagents

1. analytical balance;
2. burette, 25 mL;
3. volumetric flask, 250 mL;
4. Erlenmeyer flasks, 100 mL;
5. volumetric pipettes, 5 mL;
6. thermometer (0-50 °C);
7. water bath;
8. stopwatch;
9. acetylsalicylic acid (aspirin);
10. ethanol;
11. sodium hydroxide solution, molar concentration $0.1 \text{ mol} \times \text{L}^{-1}$;
12. hydrochloric acid solution, molar concentration $0.1 \text{ mol} \times \text{L}^{-1}$;
13. phenolphthalein alcoholic solution;
14. distilled water.

Dissolve a sample of acetylsalicylic acid with a mass of $m_{\text{sample}} = 4.5 \text{ g}$ in ethanol in a 250 mL volumetric flask. Transfer 5 mL of this solution into a 100 mL Erlenmeyer flask. Add four drops of phenolphthalein and titrate the solution with NaOH from a burette. This step corresponds to the neutralization of the acidic group of acetylsalicylic acid. Record the volume of NaOH solution consumed during titration as $V(\text{NaOH})$.

Determination of the reaction order

Transfer 2.5 mL of the ethanoic acetylsalicylic acid solution into an Erlenmeyer flask, avoiding contact with the neck walls. While stirring continuously, add 5 mL of NaOH solution from the burette. The moment when the entire volume of NaOH solution has been added is taken as the start of the reaction ($\tau=0$). Maintain the reaction mixture for exactly 2 minutes.

After the specified time, add 5 mL of $0.1 \text{ mol} \times \text{L}^{-1}$ HCl solution (with continuous stirring) to stop the reaction. Then titrate the excess alkali with NaOH solution. The volume of NaOH solution used for this titration is denoted as n , mL. Phenolphthalein (4 drops) is used as the indicator.

Repeat the procedure under identical conditions for reaction time of 2, 4, 6, 9, 12, 16, 20, 25, and 30 minutes at temperatures of 20, 25, and 30 °C.

Record all experimental and calculated data in Table 17:

Table 17. Experimental and calculated data

a	Time from reaction start, τ , s	Volume of NaOH used for titration, n , mL	Concentration of hydrolysed aspirin, x , $\text{mol} \times \text{L}^{-1}$	Concentration of non-hydrolysed aspirin, $(a - x)$, $\text{mol} \times \text{L}^{-1}$	$\lg(a-x)$	Reaction rate constant, k , s^{-1}	Average reaction rate constant, $\bar{k}$, s^{-1}

Calculate the mass fraction of acetylsalicylic acid in the sample using the following equation:

$$\omega = \frac{m(\text{asp}) \times 100 \%}{m_{\text{sample}}} \quad (1)$$

where:

$m(\text{asp})$ – the mass of acetylsalicylic acid determined from titration, g.

Calculate the mass fraction taking into account the law of equivalents and the dilution factor:

$$\omega = \frac{M \times V(\text{NaOH}) \times c(\text{NaOH}) \times 5}{m_{\text{sample}}} \quad (2)$$

where:

M – the molar mass of acetylsalicylic acid, $\text{g} \times \text{mol}^{-1}$;

$V(\text{NaOH})$ – the volume of NaOH solution used for titration, mL;

$c(\text{NaOH})$ – concentration of NaOH, $\text{mol} \times \text{L}^{-1}$;

m_{sample} – the mass of the sample, g;

5 – the dilution factor.

Calculation of reaction order

Determine the initial concentration of acetylsalicylic acid, $c_0(\text{asp})$ or a , expressed in $\text{mol} \cdot \text{L}^{-1}$. The volume of the added NaOH solution is taken into account according to the dilution law:

$$a = \frac{\omega \times m_{\text{sample}} \times 10}{7.5 \times M} \quad (3)$$

where:

ω – the mass fraction of acetylsalicylic acid in the sample, dimensionless;

m_{sample} – the mass of the drug sample, g;

M – the molar mass of acetylsalicylic acid, $\text{g} \times \text{mol}^{-1}$;

10 mL – the total volume of the solution after preparation;

7.5 mL – the total volume of the reaction mixture.

Next, calculate the concentration of non-hydrolysed aspirin ($a-x$), ($\text{mol} \times \text{L}^{-1}$) at time τ , where x is the concentration of hydrolysed acetylsalicylic acid at time τ , determined from titration data.

The concentration of hydrolysed aspirin at time τ is:

$$x = \frac{c(\text{NaOH}) \times \left(5 - \frac{1}{2} \times V(\text{NaOH}) + n\right) - 5 \times c(\text{HCl})}{7.5} \quad (4)$$

Calculate the rate constant for each time point using the first-order kinetic equation:

$$k = \frac{2.303}{\tau} \log \frac{a}{a-x} \quad (5)$$

Plot $\log(a - x)$ versus τ . A linear relationship confirms first-order kinetics.

The slope allows calculation of the reaction rate constant:

$$\tan \alpha = -\frac{k}{2.303}, \quad \text{therefore} \quad k = -2.303 \tan \alpha$$

Compare the value of the rate constant obtained graphically with that calculated from equation (5).

Determination of half-life

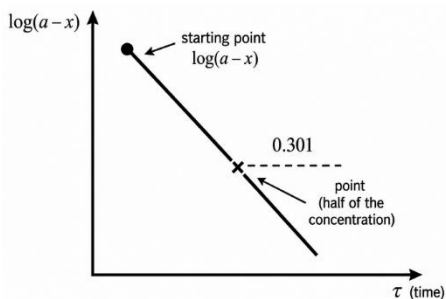


Fig. 8. Determination of half-life

From the graph, determine the half-life ($\tau_{1/2}$) of the reaction. Starting from the initial value $\log a$, subtract 0.301 (since $\log(a/2) = \log a - \log 2$ and $\log 2 = 0.301$). Draw a horizontal line to intersect the kinetic curve, then project onto the time axis.

The corresponding value represents $\tau_{1/2}$. Compare this with the calculated value:

$$\tau_{1/2} = \frac{0.6932}{\bar{k}}$$

Determination of activation energy

Plot $\log k$ versus $1/T$ for temperatures of 20 °C, 25 °C, and 30 °C.

Determine the activation energy from the slope of the resulting straight line.

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Kinetic study of the alkaline hydrolysis of acetylsalicylic acid”.
3. Problem-solving related to the topic: „Chemical kinetics and kinetic equations”.

Laboratory and practical work No. 14

Mechanism of chemical reactions

Determination of the rate constant for the catalytic decomposition of hydrogen peroxide in the presence of MnO_2

Significance of the topic

Homogeneous and heterogeneous catalysis are of great importance in modern chemical and pharmaceutical industries. The use of highly efficient catalysts in microbiological, chemical, pharmaceutical, and food industries, as well as in agriculture, enables the optimization of technological processes and an increase product yield.

Catalysis also plays an important role in living systems. Enzymes – biological catalysts of a protein nature – are present in all living cells. Nearly all biochemical reactions occurring in the organism and ensuring metabolism proceed with the participation of enzymes.

The practical application of knowledge about enzymatic reactions, contributes to solving problems related to food security, improving nutritional quality, and advancing technologies for food processing and storage.

Learning objectives

1. To acquire knowledge of:
 - a) complex reactions (parallel, consecutive, coupled, and reversible);
 - b) chain and photochemical reactions;
 - c) characteristics of heterogeneous reactions;
 - d) mechanisms of homogeneous catalysis.
2. To develop skills in applying theoretical knowledge to practical problem-solving.

Prerequisite knowledge

1. Photochemical reactions.
2. Mechanism of chain reactions.
3. Homogeneous and heterogeneous catalysis.

Homework assignment

1. Review of the prerequisite knowledge questions.
2. Preparation of the theoretical material related to the control questions on the topic: „Mechanism of chemical reactions”.
3. Study the problem-solving algorithms, independent solution of the assigned problems, and completion of the individual assignment.
4. Review of the experimental procedure for the laboratory work: „Determination of the rate constant for the catalytic decomposition of hydrogen peroxide in the presence of MnO_2 ”.

Control questions

1. Complex reactions: parallel, consecutive, coupled, and reversible.
2. Chain reactions. The elementary steps of chain reactions. Branched and unbranched chain reactions.
3. Photochemical reactions. Stark-Einstein law of photochemical equivalence. Quantum yield.
4. Characteristics of heterogeneous reactions. Rate of heterogeneous processes and factors affecting it. The kinetic region (reaction control) and diffusion region (mass transfer control) of heterogeneous processes. Examples of heterogeneous reactions of pharmaceutical relevance.
5. Homogeneous catalysis. Mechanism of catalyst action and activation energy of catalytic reactions. Acid-base catalysis.
6. Multiplet theory of catalysis (A. A. Balandin). Active ensemble theory (N. I. Kobozev).
7. Inhibition of chemical reactions. Mechanism of inhibitor action.

Self-assessment questions

1. Which reactions are called parallel reactions? Give examples. What equations are used to calculate their rate constants?
2. Which reactions are called consecutive reactions? Provide examples.
3. Which reactions are called coupled reactions? Give examples.
4. Which reactions are called reversible reactions? What equations are used to calculate the rate constants of first-order reversible reactions?

5. Write the equations describing the time dependence of the concentrations of substances A and B for a first-order reversible reaction when $n(B) \neq 0$.
6. List the characteristic features and specific properties of chain reactions.
7. What are free radicals and how can they be generated?
8. Provide an example of a chain reaction with an unbranched mechanism.
9. Provide an example of a reaction proceeding through a branched-chain mechanism.
10. What are photochemical reactions?
11. What is the principle of Stark-Einstein law of photochemical equivalence?
12. What is quantum yield? Why is $\gamma \leq 1$ for some reactions and $\gamma \gg 1$ for others?
13. How does the rate of a branched chain reaction depend on pressure at constant temperature? On what factors do the limits of self-ignition in branched chain reactions depend?
14. How do homogeneous reactions differ from heterogeneous reactions? Provide examples.
15. What are the characteristic features of heterogeneous reactions? Which stages may constitute a heterogeneous reaction?
16. By which criteria can it be determined whether chemical reaction or diffusion is the rate-limiting step in a heterogeneous process?
17. What is a catalyst and how does it differ from a reaction initiator?
18. How are catalytic reactions classified?
19. List the principal features of homogeneous and heterogeneous catalysis. Provide examples.
20. How does a catalyst affect the activation energy?
21. Which reactions are termed autocatalytic? Provide examples.
22. What is acid-base catalysis? Provide examples.
23. What are inhibitors? Provide examples of inhibited reactions.

24. What is the role of promoters and on what does the increase in catalyst activity depend?
25. What is the essence of Balandin's multiplet theory of catalysis?
26. What is the essence of Kobozev's active ensemble theory?

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (60 minutes).

Laboratory work

Determination of the rate constant for the catalytic decomposition of hydrogen peroxide in the presence of MnO₂

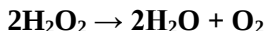
Laboratory objectives

To develop practical skills in:

- a) determining the kinetics of hydrogen peroxide decomposition in the presence of MnO₂ catalyst;
- b) determining the reaction order using the kinetic equations and the graphical method.

Theoretical background

Hydrogen peroxide in aqueous solution undergoes spontaneous decomposition according to the reaction:



The decomposition rate increases markedly in the presence of certain cations, anions, and solid substances. Consequently, this reaction serves as a classical example of both homogeneous catalysis (when catalysed by dissolved cations or anions) and heterogeneous catalysis (when catalysed by solid substances). In this laboratory work, the kinetics of the heterogeneous catalytic decomposition of hydrogen peroxide are investigated.

Experimental procedure

Apparatus and reagents

1. gas measuring apparatus;
2. hydrogen peroxide solution, mass fraction 1 %;
3. MnO_2 catalyst;
4. glass stirring rod;
5. water bath;
6. pipette.

The decomposition of hydrogen peroxide is accompanied by the evolution of oxygen gas (O_2). The volume of oxygen produced is directly proportional to the amount of hydrogen peroxide decomposed and can be measured using the apparatus shown schematically in Figure 9.

The apparatus consists of a reaction vessel (4) connected through a stopcock (3) to a gas burette (2), which is connected to a levelling vessel (1).

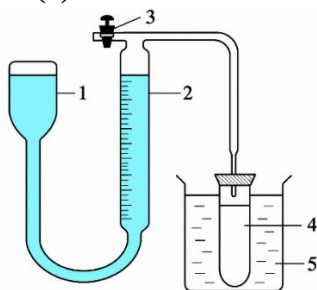


Fig. 9. Apparatus for measuring the volume of oxygen

Pour 15-18 mL of 1 % hydrogen peroxide solution into vessel 4, ensuring that the liquid level remains approximately 2 cm below the stopper.

Fill both the gas burette and the levelling vessel with water, adjusting the water level in the burette to the stopcock.

Add approximately 1 mg of MnO_2 to the reaction vessel and mix the contents thoroughly with a glass rod. Immediately close the vessel with the stopper while keeping the stopcock open. Allow the oxygen generated to displace the air from the apparatus for approximately 1 minute, then close the stopcock to connect the reaction vessel to the gas burette.

Raise the levelling vessel until the water level in the burette reaches the upper graduation mark, and start the stopwatch.

Record the burette reading after 10-30 s, then after 60 s, and continue taking measurements at regular time intervals while maintaining equal water levels in the burette and the levelling vessel before each reading. Perform a total of 12-16 readings.

Next, place reaction vessel 4 in an 80 °C water bath and heat it until the decomposition of hydrogen peroxide is complete, as indicated by a constant burette reading. Remove the vessel back to the initial experimental temperature and allow it to equilibrate for approximately 10 minutes.

Equalize the liquid levels in the burette and levelling vessel, then record the final burette reading. The starting point of the experiment is taken as the time corresponding to the third measurement under steady conditions.

Determine:

1. The elapsed time τ from the start of the experiment for each measurement;
2. The volume of oxygen released at time τ , V_{τ} ;
3. The total volume of oxygen released after completion of the reaction, V_{∞} .

Record the experimental data in Table 18:

Table 18. Experimental and calculated data

Catalyst						
Temperature						
Volume of H ₂ O ₂						
Stopwatch time, s	Time from start τ , s	Burette reading, mL	Volume of released O ₂ , V_{τ} , mL	log ($V_{\infty}-V_{\tau}$)	K	$K_{aver.}$

Calculate the reaction rate constant using the equation:

$$K = \frac{2,303}{\tau} \log \frac{V_{\infty}}{V_{\infty} - V_{\tau}}$$

Additionally, determine it graphically from the relationship:

$$\log(V_{\infty} - V_{\tau}) = f(\tau)$$

The value of V_{∞} is obtained as the difference between the burette readings at the start of the experiment and the final burette reading obtained after the complete decomposition of hydrogen peroxide. The value of V_{τ} is determined as the difference between the initial burette reading and the reading recorded at time τ .

Based on the results, determine the reaction order and the average value of the rate constant K .

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Determination of the rate constant for the catalytic decomposition of hydrogen peroxide in the presence of MnO_2 ”.
3. Problem-solving related to the topic: „Mechanism of chemical reactions”.

Laboratory and practical work No. 15

Mechanism of chemical reactions Determination of the rate constant for the oxidation of iodide ions by hydrogen peroxide

Learning objectives

To evaluate the acquisition of theoretical knowledge and the development of problem-solving skills in the topic: „Chemical kinetics and catalysis”.

Homework assignment

1. Review all control questions for laboratory and practical sessions No. 12-14.
2. Study of problem-solving algorithms, independent solution of the assigned problems, and completion the individual report.
3. Review of the experimental procedure for the laboratory work: „Determination of the rate constant for the oxidation of iodide ions by hydrogen peroxide”.

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of topic comprehension (15 minutes).
3. Performance of the laboratory work (60 minutes).

Laboratory work

Determination of the rate constant of the oxidation of iodide ions by hydrogen peroxide

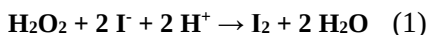
Laboratory objectives

To develop practical skills in:

- a) investigating the kinetics of the oxidation of iodide ions by hydrogen peroxide in an acidic medium;
- b) determining the reaction rate constant based on experimental data.

Theoretical background

Hydrogen peroxide reacts with iodide ions in an acidic medium according to the equation:



When the reaction is carried out at a constant concentration of iodide ions and in the presence of excess acid, the concentration of hydrogen ions also remains practically constant. Under these conditions, the reaction rate depends only on the concentration of hydrogen peroxide, and the kinetic rate equation can be written:

$$v = - \frac{d c (\text{H}_2\text{O}_2)}{d \tau} = K \times c (\text{H}_2\text{O}_2)$$

Thus, the reaction follows first-order kinetics, and the rate constant is calculated using the equation:

$$K = \frac{2.303}{\tau} \log \frac{n_0 (\text{H}_2\text{O}_2)}{n_0 (\text{H}_2\text{O}_2) - n_\tau (\text{H}_2\text{O}_2)}$$

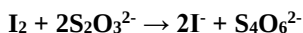
where:

$n_0 (\text{H}_2\text{O}_2)$ – the initial amount of hydrogen peroxide, mol;

$n_\tau (\text{H}_2\text{O}_2)$ – the amount of hydrogen peroxide, that has reacted by time τ , mol.

This relationship shows that, for the experimental determination of the rate constant of a first-order reaction, it is necessary to know the initial amount of H_2O_2 and the amount of H_2O_2 consumed at each time point. These values are determined by the substitution titration method.

According to reaction (1), the amount of molecular iodine formed is equivalent to the amount of hydrogen peroxide consumed. The iodine generated is determined by titration with a standard sodium thiosulfate solution according to the equation:



Accordingly:

$$n(1/2\text{I}_2) = n(1/2\text{H}_2\text{O}_2) = n(\text{Na}_2\text{S}_2\text{O}_3) = c(\text{Na}_2\text{S}_2\text{O}_3) \times V(\text{Na}_2\text{S}_2\text{O}_3)$$

Taking into account this relationship, as well as the equation

$$n(\text{H}_2\text{O}_2) = n(1/2\text{H}_2\text{O}_2) \times f_{\text{eq}}(\text{H}_2\text{O}_2)$$

the final expression for the rate constant of hydrogen peroxide consumption is:

$$K = \frac{2.303}{\tau} \log \frac{V(\text{Na}_2\text{S}_2\text{O}_3)}{V(\text{Na}_2\text{S}_2\text{O}_3) - V_\tau(\text{Na}_2\text{S}_2\text{O}_3)}$$

where:

$V(\text{Na}_2\text{S}_2\text{O}_3)$ – the total volume of the standard sodium thiosulfate solution used to titrate the iodine released after complete oxidation of H_2O_2 , mL;

$V_\tau(\text{Na}_2\text{S}_2\text{O}_3)$ - the volume of the same solution required to titrate the iodine formed at time τ , mL.

From the reaction between sodium thiosulfate and iodine, it follows that in the presence of $\text{Na}_2\text{S}_2\text{O}_3$ the oxidation of iodide ions by hydrogen peroxide proceeds at an approximately constant iodide ion concentration. This principle is used experimentally for two purposes: to determine the amount of hydrogen peroxide consumed at a given time and to maintain constant iodide ion concentration throughout the reaction.

Experimental procedure

Apparatus and reagents

1. burette, 25 mL;
2. conical flask, 200 mL;
3. standard $\text{Na}_2\text{S}_2\text{O}_3$ solution, molar concentration $0.05 \text{ mol} \times \text{L}^{-1}$;
4. KI solution, mass fraction 0.4 %;
5. H_2O_2 solution, molar concentration $0.025 \text{ mol} \times \text{L}^{-1}$;
6. H_2SO_4 solution, molar concentration $1.0 \text{ mol} \times \text{L}^{-1}$;
7. starch solution, mass fraction 0.5 %;
8. ammonium molybdate solution, molar concentration $0.05 \text{ mol} \times \text{L}^{-1}$;
9. graduated cylinders, 10 mL and 100 mL.

Into a 200 mL conical flask, add 100 mL of KI solution (mass fraction 0.4 %), followed by 5 mL of $1.0 \text{ mol} \times \text{L}^{-1}$ H_2SO_4 solution and a few drops of starch solution. Then add 1 mL of standard $0.05 \text{ mol} \times \text{L}^{-1}$ $\text{Na}_2\text{S}_2\text{O}_3$ solution from the burette.

Using a graduated cylinder, measure 10 mL of $0.025 \text{ mol} \times \text{L}^{-1} \text{H}_2\text{O}_2$ solution and rapidly add it to the prepared reaction mixture. The instant of addition is taken as the start time of the reaction.

While continuously stirring the solution, start the stopwatch and record the time at which the blue colouration appears. Then add another 1 mL portion of the standard $\text{Na}_2\text{S}_2\text{O}_3$ solution from the burette and record the time required for the blue colouration to reappear. Repeat this procedure 6-7 times.

After completing the measurements, add several drops of ammonium molybdate solution (catalyst) to the flask and titrate the iodine released with the standard $\text{Na}_2\text{S}_2\text{O}_3$ solution until the blue colouration disappears completely. Record the total volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution consumed for the titration of the released iodine.

Record the experimental and calculated data in Table 19.

Table 19. Experimental and calculated data

No.	Time from the start of the reaction, τ , s	$V_\tau(\text{Na}_2\text{S}_2\text{O}_3)$, mL	$V(\text{Na}_2\text{S}_2\text{O}_3)$, mL	K , s^{-1}

Based on the obtained results, prepare the laboratory report. In the conclusions, state whether the reaction follows first-order kinetics.

Independent study

1. Analysis of the experimental observations and processing of the obtained data.
2. Preparation of the laboratory report: „Determination of the rate constant of the oxidation of iodide ions by hydrogen peroxide”.
3. Problem-solving related to the topic: „Chemical kinetics and catalysis”.

Assessment No. 3

Learning objectives

Based on the above topics, to assess:

- a) the level of assimilation of theoretical knowledge;
- b) practical skills and competencies acquired during laboratory sessions;
- c) the ability to solve applied problems.

Written test on the topics

1. Thermodynamics of electrode processes.
2. Application of electrochemical methods of analysis.
3. Chemical kinetics.

Control questions

1. Electrode potential and electromotive force (EMF) of galvanic cells.
2. Electrodes and their classification.
3. The Nernst equation for electrode potential.
4. Reference electrodes:
 - a) standard hydrogen electrode;
 - b) calomel electrode;
 - c) silver/silver chloride electrode.
5. Measurement of EMF and electrode potentials.
6. Ion-selective electrodes. Glass electrode.
7. Potentiometric methods for pH measurement.
8. Potentiometric titration.
9. Potentiometric determination of ion activities and activity coefficients.
10. Potentiometric determination of equilibrium constants (K_p) and Gibbs free energy change (ΔG).
11. Importance of potentiometry in pharmaceutical practice.
12. Redox electrodes and redox galvanic cells.
13. Potentials and standard potentials of redox electrodes. EMF of redox galvanic cells. The Nernst-Peters equation.
14. Quinhydrone electrode and its application.
15. Concentration galvanic cells.

16. Diffusion and membrane potentials.
17. Electrolysis and electrode processes. Electrolyte decomposition potential.
18. Rate of chemical reactions. Dependence of reaction rate on various factors. Molecularity and reaction order. Zero-order reactions.
19. Unimolecular irreversible reactions. Derivation of the rate constant equation for a first-order reaction. Half-life.
20. Bimolecular reactions. Derivation of the rate constant equation for a second-order reaction.
21. First-order reactions. Methods for determining the reaction order.
22. Complex reactions: unimolecular reversible, parallel, coupled, and consecutive reactions.
23. Effect of temperature on the reaction rate. The Arrhenius equation. Methods for determining activation energy.
24. The collision theory. The number of active molecules. Activation energy.
25. Concept of the transition state theory.
26. Chain reactions. The steps of chain reactions. Non-branching and branching chain reactions.
27. Photochemical reactions. Einstein's law of photochemical equivalence. Quantum yield.
28. Characteristics of heterogeneous reactions. Kinetic equations and reaction order. Kinetic and diffusion-controlled regions of heterogeneous processes.
29. Homogeneous catalysis. Mechanism of catalyst action. Activation energy of catalytic reactions. Acid-base catalysis.
30. Heterogeneous catalysis. Theories of heterogeneous catalysis. Inhibitors and their mechanism of action.

Session overview

1. Review of the homework assignments, discussion of the control questions, and problem-solving.
2. Written assessment of the material based on control questions and problems analogous to those previously solved (60 minutes).
3. Analysis of errors made in the written test.

Appendices

Table 1. Thermodynamic constants

ΔH_{298}^0 - standard enthalpy of formation;

ΔG_{298}^0 - standard Gibbs free energy;

S_{298}^0 - standard entropy;

C_p^0 - heat capacity at constant pressure.

Compound	ΔH_{298}^0 , kJ $\times$ mol $^{-1}$	ΔG_{298}^0 , kJ $\times$ mol $^{-1}$	S_{298}^0 , J $\times$ mol $^{-1}\times$ K $^{-1}$	C_p^0 , 298, J $\times$ mol $^{-1}\times$ K $^{-1}$
Br ₂ (g)	30.92	3.14	245.35	35.99
HBr (g)	-36.23	-53.22	198.48	29.12
C(diamond)	1.897	2.866	2.38	6.07
C (graphite)	0	0	5.74	8.66
CO (g)	-110.5	-137.27	197.4	29.14
CO ₂ (g)	-393.51	-394.38	213.6	37.13
C ₂ H ₂ (g)	226.75	209.2	200.8	43.93
C ₂ H ₄ (g)	52.28	68.12	219.4	43.56
CH ₄ (g)	-74.85	-50.79	186.19	35.715
C ₂ H ₆ (g)	-84.67	-32.89	229.5	52.65
C ₆ H ₆ (l)	49.04	124.50	173.2	135.77
CH ₃ OH (l)	-238.7	166.31	126.7	81.6
C ₂ H ₅ OH (l)	-227.6	-174.77	160.7	111.46
CH ₃ COOH(l)	-484.9	-392.46	159.8	123.4
Cl ₂	0	0	223.0	33.93
HCl (g)	-92.3	-95.27	186.7	29.12
HCl (l)	-167.5	-131.2	55.2	-
Fe	0	0	27,15	25,23
FeO	-263.68	-244.35	58.79	51.1
FeCl ₂	-314.0	-302.08	119.66	-
H ₂	0	0	130.6	28.83
H ₂ O (g)	-241.84	-228.8	188.74	33.57
H ₂ O (l)	-285.84	-237.5	69.96	75.296
N ₂ (g)	0	0	191.5	29.12
NO ₂ (g)	33.85	51.84	240.46	37.90
N ₂ O ₄ (g)	9.66	98.29	304.3	38.70
NO (g)	90.37	86.69	210.62	29.86
NH ₃ (g)	-46.19	-16.64	192.5	35.65
NH ₄ Cl (s)	-315.39	-343.64	94.56	84.1
NH ₄ OH (l)	-366.69	-263.8	179.9	-
SO ₂ (g)	-296.9	300.37	248.1	39.79
SO ₃ (g)	-395.2	-370.37	256.23	50.7
H ₂ S (g)	-20.15	-33.02	205.64	33.97

H ₂ S (l)	39.33	-27.36	122.2	-
H ₂ SO ₄ (l)	-811.3	-742.0	156.9	137.57
CaO (s)	-635.1	-504.2	39.7	48.53
CaCO ₃ (s)	-1206.0	-1128.8	92.9	81.89
Fe ₂ O ₃ (s)	-821.32	-740.99	89.96	104.6
O ₂	0	0	205.03	29.37
CH ₃ OH (g)	-201.17	-162.38	239.76	44.13
CH ₃ Cl (g)	-86.31	-62.9	234.47	40.79
Al ₂ O ₃ (s)	-1675.0	-1576.4	50.94	79.0
Al ₂ (SO ₄) ₃ (s)	-3434.0	-3091.9	239.2	259.3

Table 2. Enthalpies of gases at various temperatures and standard pressure

T, K	Enthalpy, J×mol ⁻¹								
	H ₂	O ₂	N ₂	CO	CO ₂	H ₂ O	NH ₃	CH ₄	C ₂ H ₄
273	0	0	0	0	0	0	0	0	0
373	2900	2983	2870	2880	3920	3320	3620	3660	4300
473	5820	6010	5800	5840	8120	6760	7560	7940	9720
573	8750	9160	8800	8820	12560	10330	11800	12800	15500
673	11670	12360	11820	11930	17250	14020	16340	18200	25140
773	14650	15640	14980	15100	22200	17850	21170	24180	31200
873	17620	19000	18150	18300	27300	21740	26200	30540	45300
973	20630	22400	21350	21590	32600	25800	31580	37400	50100
1073	23700	25860	24820	24900	38000	29960	37100	44600	61000
1173	27670	29400	28000	28200	43700	34200		52300	72800
1273	29800	32900	31300	31700	49200	38500		60100	85500
1373	33000	36600	34700	35100	55100	43000		68500	99400
1473	36200	40200	37900	38600	61000	47500		77000	113600
1573	39300	43400	41600	42000	66800	52200		86000	129000
1673	42600	47606	45100	45600	72700	565800		94000	145000
1773	45800	51000	48600	49600	78600	61700		103800	162000

Table 3. Specific electrical conductivity of KCl solutions at different temperatures

KCl concentration, mol×L ⁻¹	κ, S×m ⁻¹ as a function of temperature T							
	273 K	278 K	283 K	288 K	291 K	293 K	298 K	303 K
0.01	0.0776	0.0896	0.1020	0.1447	0.1224	0.1278	0.1413	0.1552
0.02	0.1521	0.1752	0.1994	0.2243	0.2399	0.2501	0.2765	0.3036
0.1	0.715	0.822	0.933	1.048	1.120	1.167	1.288	1.412
1	6.541	7.414	8.319	9.252	9.83	10.207	11.180	—

Table 4. Limiting ionic mobilities of selected ions in aqueous electrolyte solutions at 291 K and 298 K

$\lambda_0 \times 10^4, \text{S} \times \text{m}^2 \times \text{mol}^{-1}$					
Cations	291 K	298 K	Anions	291 K	298 K
$\text{H}_3\text{O}^+(\text{H}^+)$	315	349.8	OH^-	171	198.3
Ag^+	53.5	61.9	F^-	47.3	55.4
Li^+	32.8	38.6	Cl^-	66	76.35
Na^+	42.8	50.1	Br^-	68	78.1
K^+	63.9	73.5	I^-	66.5	76.8
Rb^+	66.5	77.8	IO_3^-	33.9	41
Cs^+	67	77.2	NO_3^-	62.3	71.5
NH_4^+	63.9	73.5	MnO_4^-	53	61.3
$\frac{1}{2} \text{Cu}^{2+}$	45.3	56.6	ClO_4^-	58.8	67.3
$\frac{1}{2} \text{Mg}^{2+}$	44.9	53	CN^-	-	78
$\frac{1}{2} \text{Ca}^{2+}$	50.7	59.5	HS^-	57	65
$\frac{1}{2} \text{Ba}^{2+}$	54.6	63.6	HSO_3^-	-	50
$\frac{1}{2} \text{Zn}^{2+}$	45	54	HSO_4^-	-	52
$\frac{1}{2} \text{Pb}^{2+}$	60.5	70	HCOO^-	47	54.6
$\frac{1}{2} \text{Mn}^{2+}$	44.5	53.5	CH_3COO^-	34	40.9
$\frac{1}{2} \text{Fe}^{2+}$	44.5	53.5	$\text{C}_2\text{H}_5\text{COO}^-$	-	35.8
$\frac{1}{2} \text{Co}^{2+}$	45	54	$\text{C}_3\text{H}_7\text{COO}^-$	-	32.6
$\frac{1}{2} \text{Hg}^{2+}$	-	63.6	$\text{C}_6\text{H}_5\text{COO}^-$	-	32.3
$\frac{1}{2} \text{Cd}^{2+}$	45.1	54	$\frac{1}{2} \text{SO}_4^{2-}$	68.4	30
$\frac{1}{3} \text{Al}^{3+}$	61	68	$\frac{1}{2} \text{SO}_3^{2-}$	-	72
$\frac{1}{3} \text{Fe}^{3+}$	40	63	$\frac{1}{2} \text{S}^{2-}$	53.5	-
$\frac{1}{3} \text{Cr}^{3+}$	45	67	$\frac{1}{2} \text{CO}_3^{2-}$	60.5	69.3
$\frac{1}{3} \text{Ce}^{3+}$	-	69.6	$\frac{1}{2} \text{HPO}_4^{2-}$	-	57
			$\frac{1}{2} \text{C}_2\text{H}_4^{2-}$	72	85
			$\frac{1}{3} [\text{Fe}(\text{CN})_6]^{3-}$	-	99.1
			$\frac{1}{4} [\text{Fe}(\text{CN})_6]^{4-}$	-	111

Table 5. Standard potentials of redox systems at 298 K

Electrode	Reaction	$\varphi^{\circ}_{\text{ox/red}}, \text{ V}$
Pt/SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , OH ⁻	2SO ₃ ²⁻ + 3H ₂ O + 4e ↔ S ₂ O ₃ ²⁻ + 6OH ⁻	-0.58
Pt/Sn ⁴⁺ , Sn ²⁺	Sn ⁴⁺ + 2e ↔ Sn ²⁺	+0.15
Pt/Cu ²⁺ , Cu ⁺	Cu ²⁺ + e ↔ Cu ⁺	+0.159
Pt/[Fe(CN) ₆] ³⁻ , [Fe(CN) ₆] ⁴⁻	[Fe(CN) ₆] ³⁻ + e ↔ [Fe(CN) ₆] ⁴⁻	+0.364
Pt/H ₃ AsO ₄ , H ⁺ , HAsO ₂	H ₃ AsO ₄ + 2H ⁺ + 2e ↔ HAsO ₂ + 2H ₂ O	+0.56
Pt/MnO ₄ ⁻ , MnO ₂ , OH ⁻	MnO ₄ ⁻ + 2H ₂ O + 3e ↔ MnO ₂ + 4OH ⁻	+0.60
Pt/Fe ³⁺ , Fe ²⁺	Fe ³⁺ + e ↔ Fe ²⁺	+0.771
Pt/MnO ₂ , Mn ²⁺ , H ⁺	MnO ₂ + 4H ⁺ + 2e ↔ Mn ²⁺ + 2H ₂ O	+1.23
Pt/Cr ₂ O ₇ ²⁻ , H ⁺ , Cr ³⁺	Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ↔ 2Cr ³⁺ + 7H ₂ O	+1.33
Pt/PbO ₂ , H ⁺ , Pb ²⁺	PbO ₂ + 4H ⁺ + 2e ↔ Pb ²⁺ + 2H ₂ O	+1.455
Pt/MnO ₄ ⁻ , H ⁺ , Mn ²⁺	MnO ₄ ⁻ + 8H ⁺ + 5e ↔ Mn ²⁺ + 4H ₂ O	+1.51
Pt/H ₂ O ₂ , H ⁺	H ₂ O ₂ + 2H ⁺ + 2e ↔ 2H ₂ O	+1.77
Pt/Co ³⁺ , Co ²⁺	Co ³⁺ + e ↔ Co ²⁺	+1.95
Pt/S ₂ O ₈ ²⁻ , SO ₄ ²⁻	S ₂ O ₈ ²⁻ + 2e ↔ 2SO ₄ ²⁻	+2.01
Pt/ClO ₃ ⁻ , Cl ⁻ , H ⁺	ClO ₃ ⁻ + 6H ⁺ + 6e ↔ Cl ⁻ + 3H ₂ O	+1.45
Pt/PbO ₂ , PbSO ₄ , H ⁺	PbO ₂ + 4H ⁺ + SO ₄ ²⁻ + 2e ↔ PbSO ₄ + 2H ₂ O	+1.69
Pt/IO ₃ ⁻ , I ₂ , H ⁺	2IO ₃ ⁻ + 12H ⁺ + 10e ↔ I ₂ + 6H ₂ O	+1.19

Table 6. Standard potentials of selected electrodes at 298 K

Electrode	$\varphi^0, \text{ V}$	Electrode	$\varphi^0, \text{ V}$
Li ⁺ /Li	-3.14	Cd ²⁺ /Cd	-0.436
Cs ⁺ /Cs	-2.923	Ni ²⁺ /Ni	-0.228
Rb ⁺ /Rb	-2.294	Co ²⁺ /Co	-0.29
K ⁺ /K	-2.923	Sn ²⁺ /Sn	-0.140
Ba ²⁺ /Ba	-2.91	Pb ²⁺ /Pb	-0.126
Ca ²⁺ /Ca	-2.79	Fe ³⁺ /Fe	-0.058
Na ⁺ /Na	-2.713	2H ⁺ /H ₂	0.00
Mg ²⁺ /Mg	-2.37	Sb ³⁺ /Sb	+0.20
Al ³⁺ /Al	-1.66	Cu ²⁺ /Cu	+0.34
Mn ²⁺ /Mn	-1.17	Hg ₂ ²⁺ /2Hg	+0.792
Cr ²⁺ /Cr	-0.91	Hg ²⁺ /Hg	+0.850
Zn ²⁺ /Zn	-0.763	Ag ⁺ /Ag	+0.799
Cr ³⁺ /Cr	-0.74		
Fe ²⁺ /Fe	-0.473		

Table 7. Absolute mobilities of selected ions at 298 K

Cation	$v^{\circ}_{+}, m^2/V \times s$	Anion	$v^{\circ}_{-}, m^2/V \times s$
H ⁺	6.2	OH ⁻	20.50
K ⁺	7.62	Br ⁻	8.12
NH ₄ ⁺	7.60	I ⁻	7.96
Ag ⁺	6.42	Cl ⁻	7.91
Na ⁺	5.82	ClO ₄ ⁻	7.05
Li ⁺	3.88	SO ₄ ²⁻	8.27
Ba ²⁺	6.59	[Fe(CN) ₆] ⁴⁻	11.40
Ca ²⁺	6.16		
Mg ²⁺	5.60		

FURTHER READING

1. PETER ATKINS, JULIO DE PAULA. *Physical chemistry, Eighth Edition*; W.H. Freeman and Company, New York, 2006. ISBN: 0-7167-8759-8
2. PETER ATKINS, JULIO DE PAULA. *Physical chemistry for the life sciences*, W.H. Freeman and Company, New York, 2006. ISBN: 0-1992-8095-9
3. MILLER, F.M. *Chemistry, structure and dynamics*, McGraw-Hill, Inc., 1984. ISBN 0-07-041983-3
4. DAVID W. BALL. *Physical chemistry*. Cengage Learning, Copyright 2011. ISBN 0-534-26658-4

USMF „Nicolae Testemițanu”
 Centrul Editorial-Poligrafic *Medicina*
 Formatul hârtiei 60x84 ¹/₁₆ Tiraj: 50 ex.
 Coli de autor 4,6 ...Comanda nr. 268
 Chișinău, bd. Ștefan cel Mare și Sfânt, 165