Ministry of Education and Science of Ukraine
V. N. Karazin Kharkiv National University

O. M. KORSUN
N. A. VODOLAZKAYA

MEDICAL CHEMISTRY

(in two modules)

MODULE NO. 1

ACID-BASE EQUILIBRIA AND COMPLEX FORMATION IN BIOLOGICAL LIQUIDS

Methodical recommendations to the practical lessons
for the first-year students of the School of Medicine

Kharkiv – 2021

УДК 54(075.8)
К 75

Reviewers:

M. M. Volobuyev – PhD in Chemistry, Professor of the Department of General and Inorganic Chemistry, National Technical University "Kharkiv Polytechnic Institute";

O. A. Kravchenko – PhD in Chemistry, Associate Professor of the Department of Applied Chemistry, V. N. Karazin Kharkiv National University.

Approved for publication by the decision of the Scientifically-Methodical
Council of V. N. Karazin Kharkiv National University
(Protocol No. 2 of November 18, 2021)

Korsun O. M.
К 75 Medical Chemistry (in two modules). Module No. 1: Acid-Base Equilibria and Complex Formation in Biological Liquids / O. M. Korsun, N. A. Vodolazkaya. – Kharkiv : V. N. Karazin Kharkiv National University, 2021. – 24 p.

Manual to the practical lessons on the Module No. 1 of Medical Chemistry course. Guidance designed for the first-year students of the School of Medicine (field of knowledge – 22 "Health Protection", speciality – 222 "Medicine").

УДК 54(075.8)

CONTENTS

TO THE STUDENT

Dear Student,

We are glad to greet You in Ukraine at V. N. Karazin Kharkiv National University.

To be successful in the Medicine and Healthcare Professions You should have a fundamental knowledge of the University's Chemistry. Understanding of Chemistry and other natural science disciplines allow You to appreciate its impact on society and personally on You as a highly intelligent individual.

The required discipline "Medical Chemistry" is a joint chemical course recommended by the Ministry of Health Protection and Ministry of Education and Science of Ukraine for the first-year students of the speciality 222 "Medicine" in the field of knowledge 22 "Health Protection".

The course "Medical Chemistry" that was designed to help You learn the fundamentals of Chemistry consists of the Modules No. 1 and No. 2. Both Modules include lectures, seminars and praxis. A lot of new formulas of compounds, equations of chemical reactions, laws and rules You will find within the course. Successful students should not only know them, but also should understand how to apply each one.

Well known that the best way of learning is the practical lessons. Praxis in Medical Chemistry will show You that the fundamental principles are applicable to all kinds of chemical and biochemical systems as well as living organisms.

We are wishing You successful learning and high-level grades!

Sincerely,
Authors

WORKING PROGRAM OF THE DISCIPLINE

1. Brief Description

Aim of discipline	to give fundamentals of General, Physical and Colloid Chemistry
Type of discipline	required
Year of the learning	first
Semesters	1-st and 2-nd
ECTS credits	3 (90 hours)
Lectures	12 hours
Practical lessons	40 hours
Self-work of the student	38 hours

2. Subject Plan

Module No. 1: "Acid-Base Equilibria and Complex Formation in Biological Liquids".

Theme 1. Biogenic *s*- & *p*-block elements: biological role, application in medicine.

Introduction to the structure of matter. Electronic structure of chemical elements. Periodic table. Valence electrons and oxidation numbers. Oxidation state of chemical element. Balancing redox equations. Biological role of redox reactions. *s*- and *p*-block chemical elements and their properties. Metals and nonmetals. Molecules and ions. Classification of biogenic elements. Macrominerals.

Theme 2. Biogenic *d*-block elements: biological role, application in medicine.

Electronic structure of *d*-elements. Typical chemical properties of transition metals. Biological activity and medical application of *d*-elements. Biocomplexes of Fe, Co, Cu, and Zn. Toxic properties of transition metals.

Theme 3. Chemical bonding.

Chemical bonding. Chemical bonds: covalent, ionic, metallic. Electronegativity. Types of coordination compounds. Chemical bonds in coordination compounds. Central ion and coordination sphere. Stability constants. Complex formation in biological systems.

Theme 4. Solutions. Electrolytic dissociation.

The dissolving process and solubility. Solvation and hydration. Expression of the solution concentration: mass and volume percents, molar fraction, molarity, molality. Electrolytic dissociation, electrolytes. Strong and weak electrolytes. The degree of dissociation and dissociation constant. Ostwald's dilution law.

Theme 5. Acid-base equilibrium in biological liquids.

General properties of acids and bases. Hydronium and hydroxide ions. Acid dissociation constant and base dissociation constant. The neutralization reactions. The law of equivalents. Acid-base indicators. The methods of the volumetric analysis. Acid-base titration, equivalence point. Titration curve and the equivalence point.

Theme 6. Dissociation of water, pH scale. Buffer solutions.

Ion product of water. pH scale and methods of pH determination. pH of biological liquids. Hydrolysis of salts. Buffer solutions. Mechanism of buffer action. Henderson–Hasselbalch equation.

Theme 7. Colligative properties of solutions.

Colligative properties of solutions: vapor pressure lowering (Raoult's law), elevation of boiling point and depression of freezing point of the solution, osmosis. Osmotic pressure, vant Hoff's equation. Biological role of osmosis. Cryoscopy, ebullioscopy, osmometry and their using in biomedical investigations.

Module No. 2: "Equilibrium in Biological Systems at the Phase Interface".

Theme 8. Chemical thermodynamics. Thermochemistry.

First law of thermodynamics. Exothermic and endothermic processes. Functions of state. Enthalpy and Hess's law. Thermodynamic equilibrium. Second law of thermodynamics. Entropy, Gibbs energy and Helmholtz energy. Endergonic and exergonic processes in the organism. Thermodynamics conjugation.

Theme 9. Kinetics of biochemical processes.

Main concepts of chemical kinetics: the rate of chemical reaction, reaction rate constant, homogeneous and heterogeneous systems. Mass action law. Molecularity and the reaction order. Kinetic equations for zero-, first-, and second- order reactions. Temperature dependence of the reaction rate. Mechanism of catalysis. Peculiarities of enzyme catalysis. Michaelis–Menten theory of enzyme catalysis.

Theme 10. Electrochemical phenomena in biological processes.

Electrochemistry. Voltage of electrochemical cell. Electrode potential. Nernst's equation. Diffuse membrane potential. Biopotentials. Diffusion and membrane potentials. The varieties of the electrodes: gas electrodes, 1-st type electrodes, 2-nd type electrodes, glass electrodes, ion-selective electrodes. Potentiometry. Potentiometric determination of the pH values of solutions. Potentiometric titration.

Theme 11. Colloidal solutions and colloid stability.

Physicochemical fundamentals of colloidal systems. Classifications of colloidal systems. Lyophobic systems. Preparation of lyophobic solutions and the structure of colloidal particles. Purification of colloidal systems. Hemodialysis. The colloid stability. Coagulation of lyophobic colloidal systems and coagulation threshold. Schultze–Hardy rule. Kinetic and aggregate stabilities. Phenomenon of protective action. Flocculation. Introduction to blood coagulation.

Theme 12. Electric double layer and electrokinetic phenomena. Adsorption. Chromatography.

Electric double layer and electrokinetic phenomena. The structure of the electric double layer. Electrokinetic potential. Surface phenomena. Adsorption. Gibbs's equation. The Langmuir adsorption theory. Medical applications of activated carbon. Chromatography. Macromolecules. Properties of polymers. Synthetic organic polymers. Proteins are polymers of amino acids. Protein structure. Nucleic acids.

3. Lectures

No.	Topic	Hours
	Module No. 1	
1	Atoms, molecules and ions. Periodic law and periodic table. Valence electrons and chemical properties of the atoms. Classification of biogenic elements. Chemical bond. Coordination compounds.	2
2	Solutions. Solubility. Effect of temperature and pressure on solubility. Acids and bases. Acidity of solutions, pH scale. Buffer solutions. Acid-base indicators.	2
3	Determination of the pH using indicators. Buffer solutions in an organism. Hydrolysis of salts. Colligative properties of solutions.	2
	Module No. 2	
4	Chemical thermodynamics. Chemical kinetics: fundamentals.	2
5	Electrochemistry: basic concepts. Concentration cells. Physicochemical fundamentals of colloidal systems.	2
6	The colloid stability. Coagulation. Electric double layer and electrokinetic phenomena. Adsorption. Chromatography. Macromolecules. Properties of polymers.	2
In total:		12

4. Practical Lessons

No.	Topic	Hours
	Module No. 1	
1	Safety rules in chemical laboratory. Seminar No. 1. Atoms, molecules and ions. Periodic law and periodic table. Valence electrons and oxidation numbers of the atoms.	2
2	Praxis No. 1. Qualitative reactions on some important ions in medicine. Test No. 1.	2
3	Seminar No. 2. Chemical bonding and complex formation in biological systems.	2
4	Praxis No. 2. Preparation of coordination compounds. Test No. 2.	2
5	Seminar No. 3. Solutions. Electrolytic dissociation. Acid-base indicators.	2
6	Praxis No. 3. Preparation of solution and acid-base titration. Test No. 3.	2
7	Seminar No. 4. Dissociation of water, pH scale. Buffer solutions. Hydrolysis of salts. Colligative properties of solutions.	2

8	Praxis No. 4. Determination of pH value of solutions by indicator method. Test No. 4.	2
9	Final Test.	2
10	Summing up of the Module. Grading.	2
11	Module No. 2	2
	Safety rules in chemical laboratory. Seminar No. 1. Chemical thermodynamics.	
12	Praxis No. 1. Determination of the integral heat of solution of a salt. Test No. 1.	2
13	Seminar No. 2. Chemical kinetics.	2
14	Praxis No. 2. Determination of the rate constant of the chemical reaction. Test No. 2.	2
15	Seminar No. 3. Electrochemistry: galvanic cells.	2
16	Praxis No. 3. Potentiometric titration. Test No. 3.	2
17	Seminar No. 4. Colloidal systems. Colloid stability.	2
18	Praxis No. 4. Preparation of hydrophobic colloidal systems and determination of a coagulation threshold. Test No. 4.	2
19	Final Test.	2
20	Summing up the Module. Grading.	2
In total:		40

5. Topics for the Self-Work

No.	Topic	Hours
1	Atomic orbitals. Electronic configurations of atoms. Three important atomic properties: the atomic and ionic radii, the ionization energy, and the electron affinity. Valence electrons and chemical properties of the atoms. Natural abundance of the elements. Classification of biogenic elements. The functions of biogenic elements.	6
2	Convertation of the solution content. Effect of temperature and pressure on solubility. Buffer solutions. Acid-base indicators.	6
3	pH of solutions in the organism and nature. Buffer solutions in an organism. Colligative properties of electrolyte solutions.	7
4	Calorimetry. The Hess's law. Energy content of foods and fuels. Calculation of the entropy changes. Catalysis. Enzyme catalysis. Enzyme kinetics: Michaelis–Menten equation, Lineweaver–Burk equation.	6

5	The types of electrodes. The hydrogen electrode. Standard reduction potential. The glass electrode. Applications of electrode potentials: potentiometric titration and determination of the pH values. Biological concentration cells. Purification of colloidal systems. Hemodialysis.	6
6	Introduction to blood coagulation. Ion exchange adsorption. Paneth-Fajans-Hahn adsorption rule. Medical applications of activated carbon. Practical application of adsorption. Chromatography. Macromolecules. Properties of polymers. Synthetic organic polymers. Proteins are polymers of amino acids. Protein structure. Nucleic acids.	7
In total:		38

6. Grading of the Modules

Type of the work	Points
Test	15 4 tests × 15 = 60
Praxis	15 4 praxis × 15 = 60
Final Test	80 1 Final Test × 80 = 80
In total	200

Grading for the Module No. 1 is according to the “Two-level Grade”.

Final Graded Credit according to the “Four-level Grade” is calculated as average points of two Modules (No. 1 and No. 2) and placed to the student’s Diploma Appendix.

7. Grading Level System

Points	Module No. 1 (Two-level Grade)	Final Graded Credit (Four-level Grade)
200 – 180	credit	excellent
179 – 150	credit	good
149 – 120	credit	satisfactorily
119 – 0	not credited	unsatisfactorily

HOW TO PREPARE PRAXIS REPORTS?

TYPICAL EXAMPLE FOR THE QUALITATIVE REACTIONS

Praxis report consists of sub-reports on the demonstration experiments. It should contain exhaustive information requested in the manual of exercise, *e.g.* the balanced equations of chemical reactions and prepared conclusions.

PRAXIS No. #
TITLE OF THE PRAXIS
Objective: objective of the praxis.
Experimental Section
#. Title of the Experiment

Report on the laboratory experiments must contain detailed information about execution sequence, all observing changes and, if necessary, equations of chemical reactions. For the last ones the standard designations are acceptable: "*aq*" – aqueous; "*g*" – gas, "*l*" – liquid; "*s*" – solid (precipitate), *etc.*

#. Dissolving of Calcium Carbonate in Acids

Pour by 2-3 mL of hydrochloric and sulfuric acids into two test tubes. To the both test tubes place several pieces of white marble (or chalk).

Describe observations and write down equations of chemical reactions.

Compare rates of dissolving and write down conclusion about dependence of the dissolving rate on the reaction products solubility.

Execution and Observations

<table>
<tr><th>Action</th><th>Test tube 1</th><th>Test tube 2</th></tr>
<tr><td rowspan="2">Execution</td><td>hydrochloric acid
(colorless solution)</td><td>sulfuric acid
(colorless solution)</td></tr>
<tr><td colspan="2">+ calcium carbonate (white solid)</td></tr>
<tr><td rowspan="4">Observations</td><td>1.1) relatively fast</td><td>1.2) relatively slow</td></tr>
<tr><td colspan="2">dissolving of white solid substance</td></tr>
<tr><td colspan="2">2) liberation of colorless gas</td></tr>
<tr><td>3.1) formation of transparent solution</td><td>3.2) formation of whitish-cloudy solution</td></tr>
</table>

Equations

Test tube 1: $CaCO_3(s) + 2HCl(aq) = CaCl_2(aq) + CO_2(g) + H_2O(l)$.

Test tube 2: $CaCO_3(s) + H_2SO_4(aq) = CaSO_4(s) + CO_2(g) + H_2O(l)$.

Rate of dissolving in the hydrochloric acid is observably greater rather than in sulfuric acid solution.

Conclusion: formation of the poorly soluble calcium sulfate ($CaSO_4$) in the test tube 2 inhibits further dissolving of the calcium carbonate ($CaCO_3$).

PRAXIS No. 1

QUALITATIVE REACTIONS ON SOME IMPORTANT IONS IN MEDICINE

Objective: investigation of the principal qualitative reactions on the carbonate, sulfate, nitrite, thiosulfate, permanganate, iron(III) and silver ions.

Theoretical Section

Carbonate is salt of carbonic acid (H_2CO_3) characterized by the presence of the carbonate ion (CO_3^{2-}). The name may also mean an ester of carbonic acid that is an organic compound containing the carbonate group. Metal carbonates generally decompose at heating, liberating carbon dioxide and leaving behind an oxide of the metal. In aqueous solution carbonate, bicarbonate, carbon dioxide and carbonic acid exist in dynamic equilibrium. In strongly basic conditions, the carbonate ion predominates, while in weakly basic conditions, the bicarbonate ion (HCO_3^-) is prevalent. In more acidic conditions, aqueous carbon dioxide ($CO_2(aq)$) is the main form.

Sulfate is a salt of sulfuric acid (H_2SO_4). Many examples of sulfates are known, and many of these are highly soluble in water. Exceptions include calcium sulfate, strontium sulfate, lead(II) sulfate and barium sulfate, which are poorly soluble. The barium derivative is useful in the gravimetric analysis of sulfate. In the test for the sulfate ion, when barium chloride is added, the formation of a white precipitate indicates the presence of the sulfate ion. Barium chloride gives white precipitate in the presence of carbonate anion, but the barium carbonate is soluble in acids while the barium sulfate is not.

Nitrite ion (NO_2^-) can be oxidized or reduced with the product somewhat dependent on the oxidizing or reducing agent and its strength. The oxidation state of nitrogen atom in a nitrite is +3. It means that it can be either oxidized to the oxidation state up to +5 or reduced to the oxidation state up to −3. The nitrite ion gives several reactions based on its redox properties. When it reacts with the I^- anion the nitrite ion is being reduced to nitrogen monoxide (NO).

In *thiosulfate* the prefix thio- indicates that given ion is the sulfate ion with one oxygen atom replaced by the sulfur ($S_2O_3^{2-}$). Thiosulfates are stable only in neutral or alkaline solutions, but not in acidic solutions due to fast decomposition to sulfur dioxide (SO_2) and elementary sulfur. Thiosulfate ion is reducing agent. For example, it can reduce molecular iodine or triiodide ion (I_3^-) in solution to iodide ion (I^-), and this reaction is accompanied by the solution discoloration. It should be noted that this is not a confirmatory test because many reducing agent can do the same.

Permanganate is general name for a chemical compounds containing the manganese in +7 oxidation state or MnO_4^- ion. The color of solution containing permanganate ion is violet or dark violet. Permanganate ion is a strong oxidizing agent because here the manganese is in the highest oxidation state. The exact chemical reaction of reducing of MnO_4^- is dependent upon the reducing agent utilized and the acidity of solution.

1. In an *acidic solution* the permanganate ion is usually reduced to the colorless manganese(II) ion:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- = Mn^{2+}(aq) + 4H_2O(l).$$

2. In a strongly *basic solution* the permanganate ion is reduced to the manganate ion (MnO_4^{2-}) in which the manganese is in +6 oxidation state:

$$MnO_4^-(aq) + e^- = MnO_4^{2-}(aq).$$

The color of solution containing MnO_4^{2-} is green.

3. In a *neutral solution* the permanganate ion is reduced to insoluble brown manganese dioxide (MnO_2) in which the manganese is in +4 oxidation state:

$$MnO_4^-(aq) + 2H_2O(l) + 3e^- = MnO_2(s) + 4OH^-(aq).$$

Aqueous solutions of *iron(III)* compounds easily undergo hydrolysis and as result the brown precipitate appears on vessel walls. Iron(III) ion corresponds to the iron(III) hydroxide ($Fe(OH)_3$, FeO(OH) in nature), which is not soluble in excess of aqueous ammonia ($NH_3 \cdot H_2O$) or alkali. Iron(III) cations also give deep blue precipitate after addition of potassium hexacyanoferrate(II) ($K_4[Fe(CN)_6]$).

Silver ion shows strong oxidizing properties due to its redox potential, but the simplest qualitative reactions of silver ions are based on the precipitation reactions. Silver halides, except silver fluoride (AgF), are insoluble in aqueous solutions and are used in gravimetric analytical methods.

Experimental Section

1. Carbonate Ion

1.1 Pour 1-2 mL of sodium carbonate solution to a test tube and add several drops of barium chloride.

1.2 After sedimentation remove the solution over resulting precipitate and add several drops of the concentrated solution of hydrochloric acid.

Describe observations and write down equations of chemical reactions.

2. Sulfate Ion

2.1 Pour 1-2 mL of sodium sulfate solution to a test tube and add several drops of barium chloride.

2.2 After sedimentation remove the solution over resulting precipitate and add several drops of the concentrated solution of hydrochloric acid.

Describe observations and write down equation of chemical reaction.

Compare all results obtained for carbonate and sulfate ions, and write down corresponding conclusions.

3. Nitrite Ion

3.1 Prepare solution of sodium nitrite by dissolving of 20-30 mg of solid salt in 2-3 mL of distilled water.

3.2 To the prepared solution add several drops of sulfuric acid, and then add dropwise potassium iodide solution.

Describe observations and write down equation of chemical reaction.

4. Thiosulfate Ion

4.1 Prepare solution of sodium thiosulfate by dissolving of 20-30 mg of solid salt in 2-3 mL of distilled water, and then divide prepared solution among two test tubes.

4.2 To the first test tube add several drops of the concentrated solution of sulfuric acid.

4.3 To the second test tube add dropwise iodine solution in alcohol.

Describe observations and write down equations of chemical reactions.

5. Permanganate Ion

Pour 1-2 mL of potassium permanganate solution into three test tubes.

5.1 To the first test tube add crystalline potassium sulfite.

5.2 To the second test tube firstly add 1 mL of the concentrated solution of potassium hydroxide, and than crystalline potassium sulfite.

5.3 To the third test tube firstly add several drops of sulfuric acid, and than crystalline potassium sulfite.

Describe observations and write down equations of chemical reactions.

Compare results obtained for the acidic, neutral and basic media, and write down corresponding conclusion.

6. Iron(III) Ion

Pour 1-2 mL of iron(III) chloride solution into two test tubes.

6.1 To the first test tube add single drop of potassium thiocyanate (KSCN) solution.

6.2 To the second test tube add dropwise potassium hexacyanoferrate(II) solution.

Describe observations and write down equations of chemical reactions.

Write down conclusion about sensitivity of soluble iron(III) salts to the used reagents.

7. Silver Ion

Pour 1-2 mL of silver nitrate solution into three test tubes.

7.1 To the first test tube add several drops of potassium chloride solution.

7.2 To the second test tube add several drops of potassium bromide solution.

7.3 To the third test tube add several drops of potassium iodide solution.

Describe observations and write down equations of chemical reactions.

Write down conclusion about the color dependence of precipitated silver halides on the anion.

PRAXIS No. 2

PREPARATION OF COORDINATION COMPOUNDS

Objective: preparation of the coordination compounds of copper(II), zinc, chromium(III), iron(III) and bismuth(III) ions.

Theoretical Section

Coordination (or *complex*) *compounds* are substances that contain at least one *complex particle* or *ion* in the structure. The complex particle (enclosed in square brackets) consist of the *central atom* (transition metal atom usually) that is covalently bonded to the molecules and ions around that are called *ligands*. The name originates from the Latin "*ligare*" that means "to bind". The complex ions are naturally associated with the *counter ions* according to the Coulomb law, and both are capable for independent existence in solutions. Historically the complex and counter ions are called the *inner* and *outer spheres*, respectively.

The typical examples of the coordination compounds are $[Co(NH_3)_6]Cl_3$, $K_4[Fe(CN)_6]$ and $[Ni(CO)_4]$. In first one the complex ion is $[Co(NH_3)_6]^{3+}$ (inner sphere), the central atom is Co^{III} (here Roman value is an oxidation number), the ligands are six NH_3 molecules, and the counter ions are three Cl^- anions (outer sphere). The second example is $K_4[Fe(CN)_6]$ where the complex ion $[Fe(CN)_6]^{4-}$ (inner sphere) is formed by the central atom Fe^{II} and six CN^- ions as ligands, and four K^+ ions are counter ions (outer sphere). The third compound is totally formed by the $[Ni(CO)_4]$ complex particle where the central atom is Ni^0 and four CO molecules are ligands.

In a complex particle or ion the ligand donates the lone electron pair and central atom accepts electron pair forming coordination bond by donor-acceptor mechanism. The number of coordination bonds which the ligand can form is an important property called *denticity*. The ligands having a single donor atom are called *monodentate* ligands. Such type ligands are capable to occupy single site in the coordination sphere of the central atom. The ligands having two or more activated donor atoms are the *bidentate* and *polydentate*, respectively. Such type ligands are occupying the two or more coordination sites, correspondingly. The typical examples of the monodentate and bidentate ligands are following: H_2O, NH_3, CN^-, OH^-, SCN^-, F^-, Cl^-, Br^-, I^- and $NH_2(CH_2)_2NH_2$ or $C_2O_4^{2-}$.

Any complex particle or ion is characterized by the *coordination number* that is how many donor atoms of ligands that are coordinated around the central atom. It shows the total number of σ-type covalent bonds the central atom forms with the coordinated ligands. The coordination number is determined by nature of the central atom and ligands and can vary from 2 up to 12. For the particular central atom the coordination number can be calculated as multiplication of the ligands number and its denticity.

Coordination compounds in solutions behave like the conditionally strong electrolytes and completely dissociate with formation of a hydrated complex and counter ions (inner and outer spheres). The complex ions typically behave like a polyatomic ions and the central atom with ligands remain bonded. For example, during the dissolving process of the solid $[Cu(NH_3)_4]Cl_2$ and $Na_3[Co(NO_2)_6]$ complexes:

$$\left[\mathrm{Cu}\left(\mathrm{NH_3}\right)_4\right]\mathrm{Cl_2}(s) \rightarrow \left[\mathrm{Cu}\left(\mathrm{NH_3}\right)_4\right]^{2+}(aq) + 2\mathrm{Cl}^-(aq),$$

$$\mathrm{Na_3}\left[\mathrm{Co}\left(\mathrm{NO_2}\right)_6\right](s) \rightarrow 3\mathrm{Na}^+(aq) + \left[\mathrm{Co}\left(\mathrm{NO_2}\right)_6\right]^{3-}(aq).$$

Thus, the dissociation of 1 mol of $[Cu(NH_3)_4]Cl_2$ yields 1 mol of $[Cu(NH_3)_4]^{2+}$ (complex ion or inner sphere) and 2 mol of Cl^- (counter ion or outer sphere); 1 mol of $Na_3[Co(NO_2)_6]$ yields 3 mol of Na^+ (counter ion or outer sphere) and 1 mol of $[Co(NO_2)_6]^{3-}$ (complex ion or inner sphere).

Experimental Section

1. Formation and Investigation of the Ammine Complex of Cu^{II}

1.1 Pour 2-3 mL of copper(II) sulfate solution into a test tube and add dropwise aqueous ammonia ($NH_3{\cdot}H_2O$) solution.

1.2 Add dropwise concentrated aqueous ammonia solution until complete dissolving of the precipitate.

Divide obtained solution among three test tubes and leave the first one as the control test tube.

1.3 To the second test tube add dropwise barium chloride solution.

1.4 To the third test tube add several granules of tin.

Describe observations and write down equations of chemical reactions.

Write down conclusion about an oxidation properties of the copper(II) in the structure of coordination compounds.

2. Formation of the Hydroxyl Complexes of Zn^{II} and Cr^{III}

Pour by 1-2 mL of zinc and chromium(III) chloride solutions into two test tubes.

2.1 To the both test tubes add dropwise sodium hydroxide solution until precipitates formation.

2.2 To the both test tubes add dropwise concentrated sodium hydroxide solution until complete dissolving of the precipitates.

Describe observations and write down equations of chemical reactions.

3. Formation and Stability of the Oxolate Complex of Fe^{III}

Pour 1-2 mL of iron(III) chloride solution into two test tubes and leave the first one as the control test tube.

3.1 To the second test tube add dropwise sodium hydroxide solution.

3.2 Add dropwise oxalic acid (HO(O)CC(O)OH or $H_2C_2O_4$) solution until complete dissolving of the precipitate.

3.3 To the both test tubes (including a control test tube) add single drop of potassium thiocyanate solution.

Describe observations and write down equations of chemical reactions.

Compare colors of obtained solutions and write down conclusion about stability of the chelate coordination compounds of iron(III).

4. Formation and Destruction of the Iodide Complex of Bi^{III}

4.1 Pour 1-2 mL of bismuth(III) nitrate solution into a test tube and add dropwise potassium iodide solution.

4.2 Add dropwise concentrated potassium iodide solution until complete dissolving of the precipitate.

4.3 Fill the test tube by distilled water.

Describe observations and write down equations of chemical reactions.

PRAXIS No. 3

PREPARATION OF SOLUTION AND ACID-BASE TITRATION

Objectives: preparation of the solution by dilution and determination of solution concentration by acid-base titration.

Theoretical Section

For many purposes the exact value of a solution molar concentration (or molarity) is not critical, in other cases the concentration of the solution and its method of preparation must be as accurate as possible. Determination of the composition of the solution is one of the most important tasks in the chemical practice. Quantitative analysis can be performed using the chemical or physico-chemical methods. One of the most common among them is *titrimetry*.

In a *titration procedure* the solution with accurately known concentration, called a *standard solution* or *titrant*, is added gradually to another solution with unknown concentration until the chemical reaction between the two regents is completed.

Titration is the most convenient technique used to carry out quantitative studies of acid-base reactions, for example, a typical reaction of neutralization between strong acid and base:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) = \mathrm{NaCl}(aq) + \mathrm{H_2O}(l).$$

In a general case the similar reactions may be written in the ionic form:

$$\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) = \mathrm{H_2O}(l).$$

When an acid is titrated with a standard solution of base the *equivalence point* is reached when all of the acid has been neutralized by the base. At this point the moles of base that have been added are equal or equivalent to the number of moles of acid that was in the sample:

$$n\left(\frac{1}{z_\mathrm{a}}\mathrm{acid}\right) = n\left(\frac{1}{z_\mathrm{b}}\mathrm{base}\right).$$

Since we do not know exactly when an equivalence point occurs, we have to approximate it by fixing the *end point* of titration as the state at which the acid-base indicator color is changed.

An *acid-base indicator* is a substance that changes color with the acidity (pH) or basicity (pOH) of solution. Usually it is a weak organic acid that has one color state when protonated (HInd) and another color state when deprotonated ($\mathrm{Ind^-}$). At low pH value of a solution the protonated form dominates, whereas at high pH value the excess of hydroxide ion causes deprotonation of the indicator and the change in color state of solution has place:

$$\mathrm{HInd}(aq)^{\mathrm{color}}_{\mathrm{state\ I}} + \mathrm{OH^-}(aq) = \mathrm{Ind^-}(aq)^{\mathrm{color}}_{\mathrm{state\ II}} + \mathrm{H_2O}(l).$$

In the titration of an acid with a base just after the equivalence point is reached there is suddenly an excess of hydroxide ion in solution. This excess of hydroxide ion deprotonates the indicator and a color change is observed pointing the end of titration and complete neutralization. At the end point the number of hydrogen ions from the acid is equal or equivalent to the number of hydroxide ions from the base. When the end point is reached the volume of the standard solution is determined. Indication of color change in solutions can be carried out visually or using instrumental techniques. In a case when the investigated substance and titrant are colored the special indicators are not used.

The concentration of solution in the *simplest case* of an acid-base titration can be determined using the next formula:

$$c(\text{acid}) \times V(\text{acid}) = c(\text{base}) \times V(\text{base}),$$

where c(acid) and c(base) are concentrations of solution and titrant, respectively, V(acid) and V(base) are volumes of the solution sample and titrant, respectively.

Experimental Section

1. Preparation of the Acetic Acid Solution by Dilution

1.1. Using molarity of the initial acetic acid (CH_3COOH or HAc) solution (c_1 = 1 mol L^{-1}), molarity and volume of the diluted solution (c_2 = 0.1 mol L^{-1} and V_2 = 100 mL) calculate the volume in mL of the concentrated solution (V_1).

1.2. Get the pipet and volumetric flask of required volumes (V_1 and V_2), and pipet pump. Fill the volumetric flask halfway with distilled water. Take the volume V_1 of concentrated solution using the pipet and pipet pump, and place it to the volumetric flask.

1.3. Stir solution in the volumetric flask, add distilled water up to the final mark (V_2), close the volumetric flask and stir solution again.

2. Determination of the Exact Molarity of Acetic Acid Solution

2.1. Get the new pipet (V(HAc) = 10 mL) and three flasks for the titration. Rinse the pipet with 2-3 mL of the previously prepared solution several times. Using the pipet and pipet pump place equal volumes of solution into the flasks, add to each of them ~50 mL of distilled water and 1-3 drops of phenolphthalein solution as indicator.

2.2. Fill a clean burette with the sodium hydroxide (titrant) solution with an exactly known molarity (c(NaOH) to the top of graduation scale (zero mark) and make sure that the burette tip is completely filled. Remove trace drops of titrant from the burette tip using a piece of filter paper. Place a pristine sheet of white paper on the surface under the tip.

2.3. Titrate solution in the flask slowly until appearance of the permanent light pink color. No drop of the titrant should be left on the burette tip. Record position of the titrant on the burette graduation scale and determine the volume of solution used for the titration (V(NaOH)).

2.4. Repeat the burette preparation (2.2) and titration (2.3) procedures two times for solutions in the second and third flasks. In the last two titrations it is recommended to add titrant from the burette rapidly up to ~1 mL less than the volume obtained within the first titration. Then carefully add the rest of the titrant by drops to determine the end point of titration accurately.

After performing of titrations make sure that all volumes of titrant are in agreement within ±0.3 mL. Fill the table of results below with V(NaOH) values.

2.5. Determine concentration of solutions (c(HAc)) and write down values to the table of results. Calculate the averaged molarity of solution (c_{av}(HAc)) and add given value to the table of results.

Solution #	V(NaOH), mL	c(HAc), mol L^{-1}	c_{av}(HAc), mol L^{-1}
1			
2			
3			

PRAXIS No. 4

DETERMINATION OF pH VALUE OF SOLUTIONS BY INDICATOR METHOD

Objective: determination of the pH value of solutions using the indicators and investigation of influence of the salts hydrolysis on the pH values.

Theoretical Section

Liquid water is a unique solvent. One of its special properties is the ability to act either as an acid or as a base (according to the Arrhenius theory). Water is the weak electrolyte and undergoes self-ionization in a very small extent:

$$\mathrm{H_2O}(l) \rightleftarrows \mathrm{H^+}(aq) + \mathrm{OH^-}(aq),$$

where $H^+(aq)$ and $OH^-(aq)$ are hydrated hydrogen cation ($H_3O^+(aq)$, $H_5O_2^+(aq)$, *etc.*) and hydroxide anion, respectively.

Water auto-ionization process is characterized by the equilibrium constant called ion product of water (K_w) that is completely applicable as for the pristine water as well as for the any aqueous solutions:

$$K_\mathrm{w} = a\left(\mathrm{H^+}\right) \times a\left(\mathrm{OH^-}\right) \simeq 10^{-14} \text{ (at 25 °C)}.$$

It is possible to rewrite K_w applying the decimal logarithmic function (log) and then introducing the index function of $\mathrm{p}X = -\log a(X)$ to receive the coupling of the practical important acidity (pH) and basicity (pOH) indexes:

$$\log K_\mathrm{w} = \log a\left(\mathrm{H^+}\right) + \log a\left(\mathrm{OH^-}\right) = -14,$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} = 14.$$

For the fast estimation the pH and pOH values can be approximated using equilibrium molar concentrations of H^+ and OH^-:

$$\mathrm{pH} \approx -\log c\left(\mathrm{H^+}\right) \text{ and } \mathrm{pOH} \approx -\log c\left(\mathrm{OH^-}\right).$$

The pH and pOH values are more useful than the corresponding molarities because the last ones are often have very small value and therefore troublesome to work with them. In the same time the pH index is traditionally more using on practice than pOH.

A special reference point at the pH or pOH scales corresponds to the self-ionization equilibrium in the pure water that is called the neutral medium:

$$c\left(\mathrm{H^+}\right) = c\left(\mathrm{OH^-}\right) \approx \sqrt{K_\mathrm{w}},$$

$$\mathrm{pH} = \mathrm{pOH} = 7.$$

Using the H^+ or OH^- equilibrium concentrations as well as the pH or pOH indexes the medium type of aqueous solution can be classified as acidic, neutral or basic according to the next table data (at 25 °C).

Medium	$c(H^+)$, mol L^{-1}	pH	$c(OH^-)$, mol L^{-1}	pOH
acidic	$> 10^{-7}$	< 7	$< 10^{-7}$	> 7
neutral	$\approx 10^{-7}$	$= 7$	$\approx 10^{-7}$	$= 7$
basic	$< 10^{-7}$	> 7	$> 10^{-7}$	< 7

Experimental Section

1. Colors of the Methyl Orange Indicator in Solutions

1.1 Pour 1-2 mL of hydrochloric acid solution, distilled water and sodium hydroxide solution into three test tubes, respectively.

2.1 Add 1 or 2 drops of the methyl orange indicator solution into each test tube.

Describe the color change of solutions and write down the corresponding equations of electrolytic dissociation in solutions.

2. Colors of the Universal Indicator in Buffer Solutions

2.1 Pour 1-2 mL of buffer solutions (at least three) with exactly known pH values into test tubes.

2.2 Add 1 or 2 drops of the universal indicator solution.

2.3 Estimate the pH value of solutions within ±0.5 unit using the color scale of universal indicator.

Fill the table of results below with known and estimated pH values.

Compare the known and estimated pH values and write down conclusion about agreement or disagreement between the two data sets.

Buffer solution #	Known pH	Estimated pH
1		
2		
3		

3. Influence of the Salts Hydrolysis on the pH Value of Solutions

3.1 Pour 1-2 mL of sodium chloride, bicarbonate and carbonate solutions, and also zinc and ammonium chloride solutions with the same molarity into five test tubes.

3.2 Estimate the pH value of solutions within ±0.5 unit using the universal indicator paper and corresponding color scale.

Fill the table of results below with pH values and classify medium type in solutions.

Write down equations of salts hydrolysis in molecular and ionic forms.

Salt	pH	Medium
$NaCl$		
$NaHCO_3$		
Na_2CO_3		
$ZnCl_2$		
NH_4Cl		

SELF-PREPARATION FOR THE FINAL TEST

TYPICAL PROBLEMS

Problem A

Ethylene glycol ($(CH_2OH)_2$) is used for preparation of antifreeze mixtures. It gives protection against freezing up to −25 °C. How many moles of solute are needed per 1000 g of water ($K_f = 1.86$ K kg mol^{-1}) to ensure such protection?

Problem B

Phenol (C_6H_5OH) may be considered as a weak monoprotic acid ($K_a = 1.0 \cdot 10^{-10}$). Write down equilibrium of the acid dissociation and Ostwald's dilution law. Estimate dissociation degree of the acid in 0.02 mol L^{-1} solution.

Problem C

Mn^{2+} ion interacts with leucine ($H_2NCH(CH_2(i\text{-}C_3H_7))COOH$ or L) amino acid forming the complex with 1:1 stoichiometry. Write down equilibrium of the complex formation and expression for the corresponding stability constant (β_1).

Problem D

Determine oxidation numbers for the sulfur atoms in the SO_3 molecule and $S_2O_3^{2-}$ ion.

Problem E

Write down equations of hydrolysis of sodium acetate (CH_3COONa) in (*a*) molecular and (*b*) ionic forms. Classify given solution as acidic or basic.

Problem F

Calculate volume (L) of 0.15 mol L^{-1} barium hydroxide ($Ba(OH)_2$) solution needed to neutralize 20 mL of 0.10 mol L^{-1} nitric acid (HNO_3) solution.

Problem G

Formula of the coordination compound is $[Cr(H_2O)_6]Cl_3$. Determine and write down central ion, ligands, coordination number, inner and outer spheres.

Problem H

Restore complete electronic configuration of an atom, determine atomic number and identify the chemical element if a partial configuration of the atom is $...s^1 4d^{10}$.

Problem I

Estimate the pH and pOH values for the solutions with lithium hydroxide (LiOH) molar concentration of (*a*) $4.5 \cdot 10^{-3}$ mol L^{-1} and (*b*) 0.053 mol L^{-1}. Assume the base is completely dissociated.

Problem J

A sample of 1.49 g of potassium chloride (KCl) is dissolved in water. The final volume of solution is 200 mL. Calculate molar concentration of the solution.

Problem K

Draw structural formula of sulfur dioxide (SO_2) molecule. Determine and write down the number of lone electron pairs in the molecule.

Problem L

Write down electronic configuration of Cr^{3+} ion.

Problem M

Calculate freezing point of 0.2 mol kg^{-1} aqueous (K_f = 1.86 K kg mol^{-1}) solution of calcium chloride ($CaCl_2$). Assume complete dissociation of the solute.

Problem N

Write down equations of electrolytic dissociation of the salts: (*a*) ammonium chloride (NH_4Cl); (*b*) potassium sulfite (K_2SO_3).

Problem O

Balance chemical equation: $H_2 + C \rightarrow CH_4$. Draw structural formula of methane (CH_4) molecule and write down the number of shared electron pairs.

Problem P

Write down electronic configuration of Fe atom.

Problem Q

Classify the following solutions as acidic, basic or neutral: (*a*) pH = 14; (*b*) $c(OH^-) = 10^{-2}$ mol L^{-1}. Explain the choice.

Problem R

Write down definition of the terms “solution” and “solvent”.

Problem S

Use electronegativities of the elements to classify the bond type in sodium chloride (NaCl) as ionic, polar covalent or nonpolar covalent. Electronegativities of the elements are 0.9 (sodium) and 3.0 (chlorine).

Problem T

The electronic configuration of an atom is $1s^22s^22p^63s^23p^2$. Determine chemical element. Write down the number of valence *s*- and *p*-electrons of the atom. Is this element metal or nonmetal?

Problem U

For each of the following atoms determine the number of electrons (e^-), protons (p^+) and neutrons (n^0) in the nucleus.

atom	e^-	p^+	n^0	atom	e^-	p^+	n^0
^3He				^{25}Mg			

REFERENCES

1. Chang, Raymond; Overby, Jason. Chemistry. – 13-th ed. New York: McGraw-Hill, 2019.

2. Burdge, Julia R. Chemistry. – 5-th ed. New York: McGraw-Hill, 2019.

3. Atkins, Peter; de Paola, Julio; Keeler, James. Atkins' Physical Chemistry. – 11-th ed. Oxford University Press, 2018.

4. Eltsov, Sergey V.; Vodolazkaya, Natalya A. Practical Medical Chemistry: Manual. – 2-nd ed. Kharkiv: V. N. Karazin Kharkiv National University, 2018.

5. Brown, Theodore L.; *et al*. Chemistry: the Central Science. – 14-th ed. Glenview: Pearson, 2018.

6. Silberberg, Martin S. Chemistry: the Molecular Nature of Matter and Change. – 6-th ed. New York: McGraw-Hill, 2012.

7. Laird, Brian B. University Chemistry. New York: McGraw-Hill, 2009.