Research School of Physical and Chemical Sciences

Department "Chemistry and Ecology"

The program of the entrance exams to PhD-doctoral studies in the group of educational programs D089 Chemistry

Semey – 2026

1 DEVELOPED

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2 DISCUSSED

At the meeting of the department "Chemistry and Ecology"
Protocol № 7 "10" 02 2026.

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1. Introduction

The program of the entrance exam in the special discipline of doctoral studies is formed in the scope of the program of the previous stage of postgraduate education (master's degree).

The main requirements for the level of training of specialists in the group of educational programs D089 Chemistry

Applicants for doctoral studies are required to:

understand:

- the role of science and education in public life;
- about current trends in the development of scientific knowledge;
- on current methodological and philosophical problems of natural (social, humanitarian, economic) sciences;
- about the processes and patterns of chemical science;

to know:

- fundamentals of the humanities and socio-economic sciences, able to analyze socially significant problems and processes;
- legal and ethical standards governing human-to-human relations, society, and the environment as applied to professional activities;
- the theory and essence of economic processes, the direction of development of the modern economy;
- knows the basic teachings in the field of humanities and socio-economic sciences and, taking into account the requirements of the labor market and the employer, is able to use the methods of these sciences in various types of professional activities
- theoretical and practical foundations of inorganic chemistry, qualitative and quantitative analysis, chemistry of organic compounds, physical chemistry, chemical technology, physical research methods, quantum mechanics, computer chemistry;
- composition and structure of chemical compounds, reaction mechanisms, structure of matter, methods of synthesis of inorganic and organic substances, high molecular weight compounds, biologically active substances;

be able to:

- set goals and formulate tasks related to the implementation of professional functions in the field of chemistry;
- organize your work on a scientific basis;
- independently acquire new knowledge in the field of chemistry;
- to use modern scientific research methods for tasks arising in professional activity;
- to use the acquired knowledge for the original development and application of ideas in the context of scientific research;
- apply interactive learning methods;
- think creatively and be creative in solving new problems and situations;

have the skills:

- scientific research activities, solving standard scientific problems;
- the use of modern information technologies in the educational process;
- professional communication and intercultural communication;

- public speaking, the correct and logical formulation of their thoughts in oral and written form;

be competent in:

- in the field of scientific research methodology;
- in matters of modern educational technologies;
- in carrying out scientific projects and research in the professional field;
- in ways to ensure continuous updating of knowledge, expansion of professional skills and abilities.

The doctoral entrance exam is conducted in written or computer format in accordance with the Model Regulations for admission to studies in educational organization, implementing educational programs of technical and vocational education, approved by the Order of the Minister of Education and Science of the Republic of Kazakhstan of October 31, 2018 № 600.

2. The name of the discipline and its main sections

Theory and problems of physical chemistry.

Theoretical and practical foundations of the achievements of modern physical chemistry, necessary for the study of complex multicomponent systems. The possibilities of using mathematical signs and models to study thermodynamic and kinetic reactions and phase transformations.

Basic postulates of statistical thermodynamics. Statistical mechanics and statistical thermodynamics. Micro- and macro-state of the system. Calculation of thermodynamic probability by the Boltzmann method. Energy distribution of molecules. The statistical sum. The sum of states and its relation to thermodynamic functions. The translational sum of states. The rotational sum of states. An oscillating sum of states. Electronic and nuclear sums by states.

Basic concepts and definitions of thermodynamics of nonequilibrium processes. Open and closed systems. The emergence of entropy in open systems. Continuous systems. Material and energy balance. Application of the laws of nonequilibrium thermodynamics for chemical reactions.

The development of ideas about the mechanism of formation of solutions. Chemical interaction as the main condition for the stability of electrolyte solutions. The energy of the crystal lattice. The Born model and Kapustinsky equations for calculating the energy of a crystal lattice. The thermodynamic Born-Haber cycle.

Solvation (hydration) of ions. The Born model and the Born-Haber thermodynamic cycle for calculating the solvation energy. Thermal effect of solvation. The Born-Bjerrum equation for calculating the solvation energy. Real and chemical solvation energy. The dependence of the heat of solvation (hydration) of ions on its properties: ionic radius, charge, chemical nature.

Basic thermodynamic properties of ions. The standard enthalpy of ion formation in solution. The standard Gibbs energy of ion formation in solution. The standard entropy of ion formation in solution. Thermodynamics of ion solvation.

The results of the most important early works in the theory of strong electrolytes: the theory of Milner, Ghosh, and Bjerrum. Thermodynamic description of ion-ion interaction in the works of Lewis and Randall.

Dynamics of the development of the Debye-Hückel theory of strong electrolytes. Analysis of approximation equations I, II, and III. The Guntelberg, Guggenheim and Davis equations for calculating the average ion activity coefficient. Application of the Debye-Hückel theory to solutions of weak electrolytes.

The average ionic activity coefficients of electrolytes and the influence of various factors on their values. The energy of ion interaction with the ionic atmosphere, the radius of the ionic atmosphere.

Ionic association in electrolyte solutions. The effect of ionic association on equilibrium in electrolyte solutions. The effect of the ionic strength of the solution on the rate of ionic reactions. Electrochemical properties of polyelectrolytes. Equilibrium concentrations and activity. Chemical interaction as a measure of deviation from the main theoretical dependencies.

Theoretical interpretation of the electrical conductivity of electrolytes. The relationship of electrical conductivity with the properties of electrolytes and the nature of the solvent. The dependence of mobilities, equivalent electrical conductivity, and transfer numbers on concentration within the Debye-Hückel-Onsager theory. Hydrodynamic and kinetic theories of electrical conductivity. Electrical conductivity of non-aqueous solutions of electrolytes and some other systems. Diffusion in electrolyte solutions. Stationary and unsteady molecular diffusion. Diffusion potential. The Nernst-Einstein equation. Electrical conductivity of melts and solid electrolytes.

Electrochemical potential. The causes of the occurrence of an elskgrodny potential. Theories of electrode potential. Thermodynamic derivation of the Nernst equation. Factors influencing the value of the electrode potential. Equilibrium, compromise (stationary), mixed potential. Classification of electrodes: electrodes of the I, II, III kind, indicator electrodes, reference electrodes. Electrochemistry of membranes. Ion-selective electrodes. Potentiometry and its varieties. Thermodynamics of a galvanic cell, the Gibbs-Helmholtz equation. The use of EMF to determine physico-chemical quantities: activity coefficient, equilibrium constants of ionic reactions, transfer numbers.

Theoretical aspects of inorganic and coordination chemistry

The concept of inorganic and coordination compounds. Terminology of inorganic and coordination chemistry. Nomenclature of inorganic and coordination compounds. Theories of inorganic and coordination chemistry. Werner's coordination theory. Methods of inorganic and coordination chemistry.

Classification of inorganic and complex compounds.

Classification of complex compounds by the type of central atom, by the stability of complexes, by the type of coordinated ligands, by the specifics of the structure, by the nature of binding.

Ion-covalent and electrostatic representations. The ionic bond. A covalent bond. The size of the ions. Ionic and crystalline radii. The concept of an effective atomic number.

The energy of the crystal lattice. The theory of repulsion of valence shell electron pairs. The calculation algorithm according to the Gillespie theory. Advantages and disadvantages of electrostatic theories. Classical theory of chemical structure. The postulates of classical theory. The criterion for the existence of a molecule. The valence.

Quantum mechanical models. The method of valence circuits (valence bonds). Theory of the crystal field. "Crystal" fields. Energy stabilization by the crystal field. The theory of the ligand field.

Geometry of inorganic and coordination compounds. Isomerism of inorganic and coordination compounds. Types of isomerism of coordination compounds: hydrate, ionization (including coordination polymerization), structural, bond isomerism, geometric, optical, conformational. The influence of the type of isomerism of a coordination compound on its physico-chemical properties.

Stereochemistry of complex compounds. Jan-Teller effects. Geometry of coordination polyhedra and their shape. Factors influencing the structure of coordination polyhedra. Steric effects. The nature of the central atom and ligands. The structure of coordination compounds of intransitive elements. Alkaline and alkaline earth metals as complexing agents. Types of complexes formed and their stability. Coordination compounds of p-elements.

Stability of coordination compounds. Complex compounds in solutions. Direct and inverse problems of the theory of chemical equilibria in solution. Stability constants:mathematical modeling. Enthalpy and entropy contributions to stability constants. Patterns in the stability of coordination compounds. Features of complexation of rare earth elements (REE). Patterns of changes in the stability and structure of coordination compounds in the REE series, the role of "lanthanide" compression. Extrinsic cations and stability of solid complex compounds. The "mutual influence" model. Thermal stability of complex compounds.

Reactivity of coordination compounds. Description of the reactivity. General theoretical description of chemical interaction. Properties of potential surfaces. Symmetry and direction of reactions. The theory of mutual influence.

Acid-base transformations of coordination compounds. Acid-base properties of complex compounds. The concept of Lewis acids and bases. Theory of hard and soft acids and bases. Lewis acidity in reactions of xenon fluorides.

Redox reactions of coordination compounds. Classification of redox reactions. The external sphere mechanism. The Marcus-Hache theory. The Marcus cross ratio. The intra-sphere mechanism. Special redox reactions.

The influence of the environment on the rate of chemical reactions. Classification of solvents. Coordination properties of solvents. Solvent donor power. Formation of complexes in solutions. Description of redox reactions in a solvent. Interaction of ions with solvent. Electron transfer. "Recharge" reactions. Reactions with a change in the coordination sphere of the complex. Heterogeneous reactions. Reactions of oxidative fluorination.

Methodological features of the study of coordination compounds. Theoretical and experimental use of physical research methods. Methodological features of the study of

the chemical individuality of solid complexes and solution systems. Chemical and physical methods of central ion oxidation states.

Fundamentals of synthesis of coordination compounds. The strategy of synthesis of coordination compounds. Direct and indirect synthesis paths. Thermodynamically and kinetically controlled synthesis reactions. Examples of the synthesis of coordination compounds with monodentate, chelate, and macrocyclic ligands. Features of the synthesis of polynuclear compounds. Template synthesis of complex particles. Synthesis methods related to the freezing of complexation equilibria. Oxidation or reduction of a dominant complex in a system of complex particles.

Applied aspects of coordination chemistry. Coordination compounds in living organisms. Biometals, their brief description. The concept of biocoordination chemistry. Biocomplexes and bioclusters. Biocomplexes with anions of inorganic acids. Biocomplexes with amino acids and proteins. Biocomplexes with porphyrins. Metal toxicity: the role of complexation. The main aspects of the application of coordination compounds. Platinum complex compounds as anticancer drugs. Problems of developing dosage forms based on them. The use of volatile coordination compounds in the technology of obtaining materials from the gas phase (MOCVD).The main types of materials produced by CVD technology. Prospects for the use of heteronuclear compounds in the synthesis of multicomponent materials. Features of various methods of converting complex compounds into steam, choosing the optimal method in accordance with the nature of the complex. Complexes in electroplating, analytical chemistry, and other fields.

Modern problems of organic chemistry

The current state of the theory of organic structure. Classification of reactions and reagents. Basicity, nucleophilicity, electrophilicity, acidity.

Electronic effects in molecules of organic compounds. Factors determining the reactivity of molecules. Polarity, polarizability of molecules.

Hybridization and shape of polyatomic organic molecules. Pairing of atomic orbitals. Multistructural description of the electronic structure of molecules.

Intra- and intermolecular interactions. Electrical properties and intermolecular forces. Theory of electron pair displacement. Inductive effect and field effect. The mesomeric effect. Mesomeric effect of the phenyl group, halogens. Hyperconjugation or superconjugation, as an intramolecular disturbance. Mesomerism in organic dyes and pigments. Static and dynamic electronic effects.

Perturbation of molecular orbitals. The molecule-dimer equilibrium. The hydrogen bond. Donor-acceptor complexes. Theory of perturbations of molecular orbitals.

Molecular π -orbitals. Graphical construction of π -orbitals. π -systems: π -systems containing a heteroatom. Alternative hydrocarbons and their features. Cyclic π -systems. Molecular π -orbitals. Orbitals of fragments of molecules and their use. Flat methane

Free radicals. Alkyl radicals, structure and main methods of generation. Detection and establishment of the structure of free radicals. Major radical reactions, recombination, disproportionation. Oxidation and reduction of free radicals. The chain mechanism and its

key stages. Stable radicals of the triphenylmethane series. Biradicals and their role in photochemical reactions.

Carbations. Carbonium and carbenium ions. Carbations in the gas phase and in solutions. Factors affecting the stability of carbations. Nonclassical carbations.

Carbanions. Production of carbanions in solutions in super-cold media. Factors affecting the stability of carbanions

Lewis acids and bases. Hard and soft acids and bases. Application of the ZHMKO principle. The theoretical justification of the principle of ZHMKO.

Brensted acids and bases. Comparison of acidity and basicity in different solvents. Common acid and common basic catalysis with slow proton transfer. Common acidic and common basic catalysis with rapid proton transition.

Aliphatic nucleophilic substitution. Mechanisms of S_N1 and S_N2. Experimental evidence. Ion pairs. Stereochemistry of S_N1 and S_N2. The border area. Solvolysis of alkyl substrates. The effect of structure and solvent on the mechanism: substrate structure, leaving group, nucleophile. Ambident nucleophiles. The SN1 mechanism.

Elimination reactions. Characteristics of the E_1 and E_2 mechanisms. Stereochemistry. The Zaitsev and Hoffman rules. Geometric orientation. The balance between elimination and substitution.

Aliphatic electrophilic substitution. Reactions S_E1 and S_E2. The outgoing group. Stereochemistry of reactions. Nucleophilic assistance in electrophilic substitution.

Joining via double C=C connections. Electrophilic connection. Free radical affiliation. Nucleophilic attachment. Carbonyl group addition and related reactions. Simple addition, acid-base catalysis. Joining with substitution, joining with elimination. Aldol condensation. Hydrolysis of carboxylic acid esters.

Aromatic electrophilic substitution. The nature of the electrophile. Orientation, reactivity. π-, σ-complexes. Electrophilic substitution reactions: nitration, halogenation, sulfonation, nitrogen combination, Friedel-Crafts reactions. The nature of the active reagent in the nitration and halogenation of aromatic compounds. The results of kinetic and chemical studies of nitration and halogenation. The effect of substituents on the relative number of isomers formed.

Aromatic nucleophilic substitution. The $S_N2(ap)$ mechanism. The Meisenheimer complex. The effects of the outgoing group. Activating groups. Nucleophilicity is the mechanism of $S_N1(ap)$. Decomposition of salts. The arin mechanism.

Aromatic homolytic substitution. Reactions of alkylation, arylation and hydroxylation. Orientation in arylation reactions.

Chiral molecules. Types of chirality. Configuration and conformation. Absolute and relative configuration. Fischer projections. The Kahn-Ingold-Prelog system. Enantiomeric and diastereomeric conformations. Enantiotopic and diastereotopic ratios of atoms and groups. Conformation of acyclic molecules. Configurations and conformations of cyclic molecules. Stability of cyclic molecules. Conformational equilibrium.

Selected Chapters of Analytical Chemistry

Chemical equilibrium. The constant of chemical equilibrium. Types of equilibrium constants: thermodynamic, concentration, conditional, mixed constants. Their relationship and the factors influencing the significance of each of them.

Theories of acids and bases. The theory of Arrhenius, the theory of Lewis, the theory of Brensted, the theory of Usanovich. Advantages and disadvantages of theories. Comparison of classical and modern concepts of acids and bases.

Brensted's quantitative theory. The derivation of the Brensted equation. Constants of double protolytic equilibrium. The constant of intrinsic acidity, intrinsic basicity. Consequences of the Brensted equation. The dependence of the acid dissociation constant on its own acidity, on the value of the dielectric constant of the solvent, and the charging type of the acid (cationic acids and uncharged acids).

The effect of solvents on the strength of acids and bases. Classification of solvents by acid-base properties: protonic, aprotic solvents. Protogenic, protophilic, and amphirotic solvents. Leveling and differentiating effect of solvents on the strength of dissolved acids and bases.

The acidity of non-aqueous solutions. Determination of pH in non-aqueous and mixed solvents. pH scale in non-aqueous solvents . Standardization of pH in non-aqueous solvents. Comparison of pH in different solvents. A single scale of acidity. The Gammet method for determining acidity. The Gammet function is for uncharged and charged acids. Disadvantages of the Gammet method.

Solutions of strong acids. Calculation of pH for concentrated solutions of strong acids. Calculation of pH for medium acids, for highly dilute solutions of strong acids.

Solutions of medium strength acids. Solutions of medium strength acids. Calculation of pH for uncharged and charged acids of medium strength, for solutions of polybasic acids of medium strength.

Calculation of pH for solutions of ampholytes. Ampholiths, from a variety. Features of pH calculation in ampolite solutions.

Graphical description methods for acid-base systems. Graphical methods for describing equilibria: distribution diagrams (RD), concentration-logarithmic diagrams (KLD). Distribution diagrams for acid-base systems. Calculations and diagrams for monobasic and dibasic weak acids. Concentration - logarithmic diagrams of acid-base systems, their construction and visibility.

Methods of graphical analysis of redox systems.

Distribution diagrams for redox systems, the construction of distribution diagrams in a certain range of potential. Concentration-logarithmic diagrams for redox systems, characteristic point, construction of concentration-logarithmic diagrams. The E-pH diagram.

Equilibrium during complexation. The function is the formation of complex compounds. The degree of formation of complex compounds. Calculation of the molecular fraction of a complex particle. Curves of formation of complex compounds. Distribution diagrams for complex connections.

Deposition processes. Solubility of precipitation. Solubility, intrinsic solubility, product of solubility. The effect of ionic strength, total ion, pH on solubility. The effect of complexation and hydrolysis on the solubility of precipitation.

3. List of recommended literature

Core Literature

1. Стромберг, А.Г. Физическая химия: учебник / А.Г. Стромберг, Д.П. Семченко. – шестое издание, стереотипное. – Москва: Высшая школа, 2006. – 527 страниц.

2. Зимон, А.Д. Физическая химия: учебник / А.Д. Зимон. – Москва: Агар, 2003. – 316 страниц.

3. Эткинс, П. Физикалық химия: оқулық / П. Эткинс, Дж. Де Паула; қазақ тіліне аударғандар: Г.Х. Шабикова, А.С. Тусупбекова. – Алматы: Полиграфкомбинат, 2012. – Том 1: Тепе-теңдік термодинамика. – 594 бет.

4. Кругляков, П.М. Физическая и коллоидная химия: учебное пособие / П.М. Кругляков, Т.Н. Хаскова. – второе издание, исправленное. – Москва: Высшая школа, 2007. – 319 страниц.

5. Киселев, Ю.М. Химия координационных соединений: учебник и задачник для бакалавриата и магистратуры / Ю.М. Киселев. – Москва: Издательство Юрайт, 2014. – 657 страниц. – Электронный ресурс: https://biblio-online.ru.

6. Киселев, Ю.М. Химия координационных соединений: учебное пособие / Ю.М. Киселев, Н.А. Добрынина. – Москва: Академия, 2007. – 352 страницы.

7. Скопенко, В.В. Координационная химия / В.В. Скопенко, А.Ю. Цивадзе, Л.И. Савранский, А.Д. Гарновский. – Москва: ИКЦ Академкнига, 2007. – 488 страниц.

8. Соколов, М.Н. Координационная химия. Часть 1. Электронное строение, устойчивость, механизмы реакций, неводные растворители: учебное пособие / М.Н. Соколов, А.Л. Гущин, Д.Г. Самсоненко. – Новосибирск: Издательство Новосибирского государственного университета, 2011; 2013. – 161 страница; 194 страницы.

9. Гельфман, М.И. Неорганическая химия. Комплексные соединения: учебное пособие / М.И. Гельфман, В.П. Юстратов. – Кемерово: Кемеровский технологический институт пищевой промышленности, 2004. – 112 страниц.

10. Бруис, П.Ю. Органикалық химия негіздері. 1-бөлім: оқулық / П.Ю. Бруис. – Алматы: Полиграфкомбинат, 2013. – 420 бет.

11. Сейітжанов, Ә.Ф. Органикалық химия: оқулық / Ә.Ф. Сейітжанов. – Алматы: Print-S, 2005. – 446 бет.

12. Травень, В.Ф. Органическая химия. Том 1 / В.Ф. Травень. – Москва: Академкнига, 2008. – 727 страниц.

13. Травень, В.Ф. Органическая химия. Том 2 / В.Ф. Травень. – Москва: Академкнига, 2008. – 582 страницы.

14. Белобородов, В.Л. Органическая химия. Книга 1 / В.Л. Белобородов, С.Э. Зурабян, А.П. Лузин, Н.А. Тюкавкина. – Москва: Дрофа, 2008. – 638 страниц.

15. Реутов, О.В. Органическая химия: в четырех книгах / О.В. Реутов, А.Л. Курц, К.П. Бутин. – Москва: Лаборатория знаний, 2004.

16. Илиэл, Э. Основы стереохимии / Э. Илиэл. – Москва: Бином. Лаборатория знаний, 2005.

17. Илиэл, Э. Основы органической стереохимии / Э. Илиэл, С. Вайден, М. Дойл. – Москва: Бином. Лаборатория знаний, 2007. – 703 страницы.

18. Ли, Дж. Дж. Именные реакции. Механизмы органических реакций / Дж. Дж. Ли. – Москва: Бином. Лаборатория знаний, 2006. – 456 страниц.

19. Аналитическая химия и физико-химические методы анализа. В двух томах. Том 1: учебник / под редакцией А.А. Ищенко. – Москва: Академия, 2010. – 352 страницы.

20. Аналитическая химия и физико-химические методы анализа. В двух томах. Том 2: учебник / под редакцией А.А. Ищенко. – Москва: Академия, 2010. – 412 страниц.

21. Кристиан, Г. Аналитическая химия. В двух томах. Том 1: учебное издание / Г. Кристиан; перевод с английского В.А. Гармаша, Н.В. Колычевой, Г.В. Прохоровой. – Москва: БИНОМ. Лаборатория знаний, 2009. – 623 страницы.

22. Кристиан, Г. Аналитическая химия. В двух томах. Том 2: учебное издание / Г. Кристиан; перевод с английского В.А. Гармаша, Е.Э. Григорьевой, А.В. Ивановой и других. – Москва: БИНОМ. Лаборатория знаний, 2009. – 504 страницы.

23. Харитонов, Ю.Я. Аналитическая химия. Аналитика. В двух книгах. Книга 1. Общие теоретические основы. Качественный анализ: учебник / Ю.Я. Харитонов. – третье издание, стереотипное. – Москва: Высшая школа, 2005. – 615 страниц.

24. Харитонов, Ю.Я. Аналитическая химия. Аналитика. В двух книгах. Книга 2. Количественный анализ. Физико-химические методы анализа: учебник / Ю.Я. Харитонов. – третье издание, исправленное. – Москва: Высшая школа, 2005. – 559 страниц.

25. Аналитическая химия. В трех томах. Том 1. Методы идентификации и определения веществ: учебник / А.А. Белюстин и другие; под редакцией Л.Н. Москвина. – Москва: Академия, 2008. – 576 страниц.

26. Аналитическая химия. В трех томах. Том 2. Методы разделения веществ и гибридные методы анализа: учебник / И.Г. Зенкевич и другие; под редакцией Л.Н. Москвина. – Москва: Академия, 2008. – 304 страницы.

27. Аналитическая химия. В трех томах. Том 3. Химический анализ: учебник / И.Г. Зенкевич и другие; под редакцией Л.Н. Москвина. – Москва: Академия, 2010. – 368 страниц.

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Supplementary literature

1. Минаев, Ю. А. Физикалық химия: ерітінділердің термодинамикалық теориясы : термодинамическая теория растворов / Ю. А. Минаев, К. Ж. Симбинова. - Алматы : Рауан, 1991 - 2-бөлім. - 171 с.

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6. Нухұлы, А. Химиялық термодинамикадан қысқаша мағлұматтар : оқу құралы / А. Нухұлы. - Алматы : Ақыл кітабы, 1997. - 72 с

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9. Дамаскин, Б.Б. Электрохимия. / Б.Б. Дамаскин, О.А. Петрий. - М.: Высшая школа. – 1987. – 295с.

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