Faculty Engineering and Technology
Department _Department of Chemical Technology and Ecology_

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

(code, name)

Semey – 2024

1 DEVELOPED

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2 DISCUSSED

At the meeting of the department __of Chemical Technology and Ecology _____
Protocol № _8__ "_11__" __03__ 2024 .

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1. Introduction

The program of the entrance exam to the doctoral program in GEP D089 – Chemistry 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 8D089 - "Chemistry":

have an idea:

- on 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, is able to analyze socially significant problems and processes;
- legal and ethical norms regulating human-to-human relations, society, and the environment in relation to professional activity;
- 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 activity
- 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 compounds, biologically active substances

to be able to:

- 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;
- to think creatively and creatively approach new problems and situations

to have skills:

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

- oratory, correct and logical presentation of their thoughts in oral and written form

be competent:

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

2. The name of the discipline and its main sections

I block – theoretical

Theoretical aspects of inorganic chemistry

The basic laws and concepts of chemistry (the law of conservation of mass and energy, the law of constancy of composition and multiple ratios, the law of equivalents). Mole is the amount of substance. Avogadro's law and its consequences.

Modern ideas about the structure of the atom. The wave function and the Schrodinger equation. Quantum numbers, radial and angular distribution of electron density. Atomic orbitals (s-, p-, d- and f-AO), their energies and boundary surfaces. The distribution of electrons by AO. The principle of minimum energy. The Pauli principle. Atomic terms, Hund's rule.

The modern formulation of the periodic law, the structure of the periodic system. Patterns of changes in the fundamental characteristics of atoms: atomic and ionic radii, ionization potential, electron affinity energy and electronegativity. The boundaries of the periodic table. Prospects for the discovery of new elements. The frequency of changes in the properties of simple substances and basic chemical compounds — oxides, hydroxides, hydrides, halides, sulfides, carbides, nitrides and borides.

Chemical bonding and the structure of molecules. The main provisions of the valence bond method (MVS). Hybridization of orbitals. Directivity, saturation and polarizability of the covalent bond. The effect of unshared electron pairs on the structure of molecules, the Gillespie model. The main provisions of the molecular orbital method (MMO). Two-center two-electron molecular orbitals. Energy diagrams of MO homonuclear and heteronuclear diatomic molecules. Ionization energy, magnetic and optical properties of molecules. Multicenter MO, hypervalent and electron-deficient molecules. Intermolecular interaction – orientation, induction and dispersion.

The first group of the periodic table. A subgroup of alkali metals. Sodium oxide and peroxide. Lithium oxide and peroxide. Getting and properties.

A subgroup of copper. Copper oxide and its hydrate. Compounds and properties of monovalent copper. Chemical properties of silver compounds.

The second group of the periodic table. Beryllium and magnesium. Alkaline earth metals. Calcium, strontium, barium and radium. Oxides and hydrates of oxides. Their properties. Quicklime and slaked lime.

A subgroup of zinc. Zinc oxide and hydroxide. Zinc compounds. Cadmium oxide and hydroxide. Properties of mercury. Mercury oxides.

The third group of the periodic table. Boron. Hydrogen compounds of boron. Aluminum. Production and properties of aluminum.

The fourth group of the periodic table. Carbon. Oxygen compounds of carbon. Carbon dioxide, production, properties. Carbonic acid and its salts (carbonates and bicarbonates). Carbon monoxide and its properties. Silicon. Silicon dioxide. Meta-, ortho-, and polysilicon acids and their salts.

The fifth group of the periodic table. Nitrogen. The structure of the molecule and the strength of chemical bonds. Nitric acid. Its oxidizing and reducing properties. Salts of nitric acid (nitrites). Nitric acid, its preparation. Oxidizing properties of nitric acid. The effect of nitric acid on nonmetals. Royal vodka.

The sixth group of the periodic table. Oxygen. The structure of the molecule and the oxidative capacity of oxygen. A subgroup of sulfur. Oxygen compounds of sulfur. Sulfurous acid and its salts (sulfites, bisulfites). Reducing properties of sulfurous acid. Sulfuric acid. Properties of sulfuric acid, its effect on metals. Salts of sulfuric acid. Oleum and pyroseric acid. Pyrosulfates. Sulfur peracids. Persulfates and their properties.

A subgroup of chromium. Chromium, molybdenum, tungsten. Chromium oxide and its hydrates. Chromium oxide salts and their hydrolysis. Chromium anhydride. Chromic acid and its salts. Dihromic acid and its salts (bichromates). Chromium isopolyacids. Oxidizing properties of hexavalent chromium. Mutual transitions of compounds of tri- and hexavalent chromium. Molybdenum and tungsten trioxides and their hydrates.

The seventh group of the periodic table. Chlorine. The solubility of chlorine in water. Chlorine water. Chlorine hydrolysis. Chlorine as an oxidizer. The interaction of chlorine with metals and non-metals. Bromine. Bromine water. Hydrolysis of bromine. Bromine as an oxidizer. Iodine, solubility in water, alcohol and potassium iodide solution. Iodine as an oxidizer. The reaction of iodine with starch. Fluorine. The chemical activity of fluorine. The effect of fluoride on water. Chlorine-oxygen compounds and their features. Chlorine oxides, preparation and properties. Hypochlorous acid and its properties. Intramolecular oxidation-reduction reactions. Hydrochloric acid and its salts (chlorates). Perchloric acid and its salts.

A subgroup of manganese. Manganese acid and its salts. Oxidation of permanganates in acidic, neutral and alkaline solutions. The oxidative equivalent. Rhenic acid and its salts (perrenates).

A subgroup of iron. Iron oxides and hydrates. Ferric acid and its salts (ferrates). Oxides of divalent and trivalent nickel and cobalt. Their chemical properties.

Modern problems of organic chemistry

Isomerism of organic compounds. Isomerism, homology, isology. Structural isomerism and its varieties. Spatial isomerism: concepts of configuration and conformation. Conformational analysis. Molecular models. Methods of depicting spatial structures (projection formulas of Fisher, Newman, etc.).

Reactivity of organic compounds. There are two groups of characteristics of the electronic structure: energy and those related to the distribution of electron density. Energy characteristics: total energy of molecule formation, potential surface of the molecule; binding energy, ionization potential, electron affinity, energy of boundary MO. Characteristics related to the distribution of electron density: the effective charge on an atom, the dipole moment of individual bonds and the molecule as a whole. Hybridization

and hybrid orbitals. Simple and multiple connections. Their description is based on the concepts of sp-, sp2 and sp3 hybridization. Reactivity of organic compounds. Classification of organic reactions: substitution, addition, cleavage, cycloprysodination, redox reactions and rearrangements.

The structure and properties of molecules. Inductive effect and field effect. Mesomeric effect. Mesomeric effect of the phenyl group, halogens. Hyperconjugation or superconjugation, as an intramolecular □, □ perturbation. Mesomerism in organic dyes and pigments. Static and dynamic electronic effects.

Acids and bases. Lewis acids and bases. Hard and soft acids and bases. The application of the principle of ZHMKO. The theoretical justification of the principle of LME. Brensted acids and bases. Comparison of acidity and basicity in different solvents. Common acidic and common basic catalysis with slow proton transfer. Common acidic and common basic catalysis with rapid proton transition.

The mechanism of organic reactions. Aliphatic nucleophilic substitution. The mechanisms of SN1 and SN2. Experimental evidence. Ion pairs. Stereochemistry of SN1 and SN2. 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 E1 and E2 mechanisms. Stereochemistry. The Zaitsev and Hoffman rules. Geometric orientation. The balance between elimination and substitution.

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 effect of substituents in the benzene ring on the rate and direction of electrophilic substitution. Consistent and uncoordinated orientation.

Joining by double C=C connections. Electrophilic connection. Free radical connection. The mechanism of reactions.

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.

Aliphatic electrophilic substitution. Reactions SE1 and SE2. The outgoing group. Stereochemistry of reactions. Nucleophilic assistance in electrophilic substitution.

Homolytic reactions. Methods of generating and evaluating the reactivity of free radicals. Mechanisms of radical substitution reactions. Stages of chain radical reactions.

Reactions of carbonyl compounds. Mechanisms of the most synthetically significant reactions of carbonyl compounds. Condensation reactions of carbonyl compounds

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.

The main postulates of statistical thermodynamics. Statistical mechanics and statistical thermodynamics. Micro- and macro-state of the system. Calculation of thermodynamic probability by the Boltzmann method. The distribution of molecules by energy. The statistical amount. The sum of states and its relation to thermodynamic functions. The translational sum of the states. The rotational sum of the states. The fluctuating 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. Entropy and thermodynamic probability of the system. Characteristic functions and thermodynamic potentials. 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. Colligative properties of solutions. Chemical interaction as the main condition for the stability of electrolyte solutions. The energy of the crystal lattice. The Born model and the Kapustinsky equations for calculating the energy of the crystal lattice. The Born-Haber thermodynamic cycle.

Solvation (hydration) of ions. The Born model and the Born-Haber thermodynamic cycle for calculating the solvation energy. The thermal effect of solvation. The Born-Bjerrum equation for calculating the solvation energy. The real and chemical energy of solvation. 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.

Dynamics of the development of the Debye-Hückel theory of strong electrolytes. Analysis of approximation equations I, II and III. 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 interaction of an ion with an 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. Dependence of mobilities, equivalent electrical conductivity and transfer numbers on concentration within the framework of the Debye-Hückel-Onzager 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 non-stationary molecular diffusion. The diffusion potential. The Nernst-Einstein equation. Electrical conductivity of melts and solid electrolytes.

Electrochemical potential. The causes of the electrode 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, 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 ion reactions, transfer numbers. Chemical processes during electrolysis. Quantitative laws of electrolysis. Practical applications of electrolysis.

Kinetics of chemical reactions. The dependence of the reaction rate on the concentration of reacting substances. Kinetic classification of chemical reactions. The order of the reaction. The effect of temperature on the reaction rate and activation energy.

The II and III blocks of the exam include solving problems and practical tasks on topics:

1) The method of valence bonds. Application of the valence bond method to explain the formation of a specific molecule and a molecular ion.
2) The structure of a solid and a liquid. The crystalline structure of the substance. Crystallohydrates. The concentration of solutions.
3) Kinetics of chemical reactions. The law of acting masses and kinetic equations.
4) Complex connections. Formation of complex compounds from the point of view of the theory of the crystal field. Formation and stability of complex compounds from the point of view of the valence bond method. Formation of low-spin and high-spin complexes.
5) General properties of metals. Physical and chemical properties of metals. The electronic structure of metals. The crystalline structure of metals. Production of high purity metals.
6) Chemistry of elements of the III group of the Periodic table. Properties of uranium and its compounds. Production and application of lanthanides.
7) Chemistry of the elements of group V of the Periodic Table. Properties of nitrogen and its compounds.
8) Chemistry of elements of the VI group of the Periodic table. Properties of sulfur and its compounds. Properties of chromium and its compounds.
9) Chemistry of elements of the VII group of the Periodic table. Properties of fluorine and its compounds. Properties of chlorine and its compounds. Properties of iodine and its compounds. Properties of manganese and its compounds.
10) Electrochemical processes. Electrolysis. The electrode potential. The Nernst equation.
11) Unsaturated hydrocarbons. Determination of hydrocarbon structure, chemical properties, preparation
12) Saturated hydrocarbons. Receiving. Chemical properties
13) Aromatic compounds. Receiving. Chemical properties.
13) Oxygen-containing compounds. Alcohols. Aldehydes, ketones. Carboxylic acids. Derivatives of carboxylic acids. Receiving. Chemical properties
14) Syntheses based on acetoacetic ether, malonic ether. Organomagnesium synthesis
15) Reduction of carbon and formation of a new carbon – carbon chain

16) Identification of organic compounds
17) Protective groups in organic synthesis
18) Orientation in the benzene ring
19) Ozonation of organic compounds
20) Substitution of functional groups in the molecule of an organic compound
21) Electrolyte solutions. Osmotic pressure of electrolyte solutions Electrical conductivity of solutions. Dynamics of the development of the theory of strong electrolytes Debye-Hückel and their application. The effect of ion solvation on the activity coefficient.
22) Basic thermodynamic properties of ions. The standard enthalpy of ion formation in solution. The standard Gibbs energy and the standard entropy of ion formation in solution. The Born, Haber, and Kapustinsky model for calculating the energy of a crystal lattice.
23) The second law of thermodynamics. About the possibility and direction of spontaneous processes. The relationship between entropy and thermodynamic probability. Boltzmann statistics.
24) The basic postulates of statistical thermodynamics. The statistical amount. The sum of states and its relation to thermodynamic functions.

IV block

Essays on physico-chemical methods of analysis

3. List of recommended literature

1. Шевельков А.В., Дроздов А.А., Тамм М.Е. Неорганическая химия. - М.: Лаборатория знаний, 2023. - 586 с.
2. Савинкина Е. В. Общая и неорганическая химия: в 2 т. Т. 2: Химия элементов. – М.: Лаборатория знаний, 2023. - 553 с.
3. Карпова Е.В., Ардашникова Е.И., Мазо Г.Н., Шевельков А.В. Неорганическая химия. Вопросы и задачи. - М.: Лаборатория знаний, 2023. – 174 с.
4. Ахметов Н.С. Общая и неорганическая химия: учебник. - Санкт-Петербур: «Лань», 2018. -744 с.
5. Шрайвер Д. Бейорганикалық химия: оқулық. – Алматы: Дәуір, 2013. – 688 б.
6. В.Л. Белобородов, С.Э. Зурабян, А.П. Лузин, Н.А.Тюкавкина. Органическая химия. М.:Дрофа,2008. Кн.1:Основной курс.-638 с.
7. В.Л. Белобородов, С.Э. Зурабян, А.П. Лузин, Н.А.Тюкавкина. Органическая химия. М.:Дрофа,2008. Кн.2:Основной курс.-592 с.
8. В.Ф. Травень. Органическая химия. М.: ИКЦ «Академкнига», 2008. Т.1. 727с.
9. В.Ф. Травень. Органическая химия. – М.: Академкнига, 2008. Т.2. 582с.
10. Реутов О.А., Курц А.Л., Бутин К.П. Органическая химия. Ч.2. М.: – Бином. Лаборатория знаний. – 2012.
11. Реутов О.А., Курц А.Л., Бутин К.П. Органическая химия. Ч.1. М.: – Бином. Лаборатория знаний. – 2012.
12. Реутов О.А., Курц А.Л., Бутин К.П. Органическая химия. Ч.3. М.: – Бином. Лаборатория знаний. – 2012.

13. Реутов О.А., Курц А.Л., Бутин К.П. Органическая химия. Ч.4. М.: – Бином. Лаборатория знаний. – 2013.
14. Основы физической химии. Теория и задачи. Учебное пособие для вузов. / Е.Е.Еремин и С.И.Каргов, др.-М.:Издательство «Экзамен», 2005.-480с.
15. Теории и проблемы физической химии: учебное пособие / А.К. Оспанова, Г.Х. Шабикова, Л.И. Сыздыкова. –Алматы: Қазақ университеті, 2021 – 192 стр.
16. Парамонов Ф. П., Несмеянова Р. М., Масакбаева С. Р. Современные проблемы физической химии: учебное пособие для магистрантов и студентов химико-технологических специальностей .- Павлодар : Кереку, 2014 - 102 с.
17. Еремин В.В., Лунин, В.В. Основы физической химии/.-М:Бином. Лаборатория знаний, 2013.-320 с.
18. Афанасьев Б. Н. Физическая химия: учебное пособие.-Санкт-Петербург: Лань, 2012.-464 с.
19. Зимон А.Д. Физическая химия / А.Д. Зимон. - М.: Красанд, 2015. – 318с.

Online resources

1. https://urss.ru/PDF/add_ru/190125-1.pdfКиселев Ю.М. Химия координационных соединений/ Учебник и задачник для бакалавриата и магистратуры. - М.: Издательство Юрайт, 2014. - 657 с. [Электрон. ресурс].
2. https://elar.urfu.ru/bitstream/10995/30864/1/978-5-7996-1384-6.pdf л. и. Балдина Л.И., Гусева А.Ф., Атманских И.Н., Кочетова Н.А. Неорганическая химия : химия d- и f-элементов : практикум : [учеб.-метод. пособие] . - Екатеринбург : изд-во урал. ун-та, 2015. - 68 с.