APPROVED
at a meeting of the
Scientific Council
NJSC «Al-Farabi KazNU».
Minutes No.10 dated
May 13, 2023.

The program of the entrance exam for applicants to the PhD
for the group of educational programs
D089 – «Chemistry»

1. General provisions.

1. The program was drawn up in accordance with the Order of the Minister of Education and Science of the Republic of Kazakhstan dated October 31, 2018 No. 600 "On Approval of the Model Rules for Admission to Education in Educational Organizations Implementing Educational Programs of Higher and Postgraduate Education" (hereinafter referred to as the Model Rules).

2. The entrance exam for doctoral studies consists of writing an essay, passing a test for readiness for doctoral studies (hereinafter referred to as TRDS), an exam in the profile of a group of educational programs and an interview.

Block	Points
1. Essay	10
2. Test for readiness for doctoral studies	30
3. Exam according to the profile of the group of the educational program	40
4. Interview	20
Total admission score	100/75

3. The duration of the entrance exam is 4 hours, during which the applicant writes an essay, passes a test for readiness for doctoral studies, and answers an electronic examination. The interview is conducted on the basis of the university before the entrance exam.

2. Procedure for the entrance examination.

1. Applicants for doctoral studies in the group of educational programs D089 - «Chemistry» write a problematic / thematic essay. The volume of the essay is at least 250-300 words.

2. The electronic examination card consists of 3 questions.

Topics for exam preparation according to the profile of the group of the educational program.

1.1 Discipline **"Theories and Problems of Physical Chemistry"**

Topic 1. Chemical thermodynamics.
The first law of thermodynamics. Application of the first law of thermodynamics to processes in various systems. Applied aspects of Hess's law for real chemical processes. Thermochemistry. Approximate methods for calculating the heats of formation and combustion of inorganic and organic substances. Relation of heat capacity with thermodynamic functions. Kinds of heat capacity. Temperature dependence of heat capacity. Temperature dependence of the thermal effect of a chemical reaction.
Topic 2. The second law of thermodynamics.
Statistical substantiation of the second law of thermodynamics. Entropy. The second law of thermodynamics for reversible and irreversible processes. Change in entropy for different processes.
Topic 3. Chemical equilibrium.
Equation of isotherm of chemical reaction and equilibrium constant. Isotherm equation and the direction of a chemical reaction. Equilibrium constant and standard Gibbs energy of the reaction. Equilibrium constant and different ways of expressing the composition of the reaction mixture.
Topic 4. Effect of temperature and pressure on the equilibrium constant.
Effect of pressure on the equilibrium of a chemical reaction. Balance shift principle. Dependence of the equilibrium constant on temperature. Analysis of the isobar and isochore equations of a reaction. Determination of equilibrium constants of chemical reactions at any temperature using absolute entropies.
Topic 5. Basics of statistical thermodynamics.
Basic postulates of statistical thermodynamics. Micro and macrostate of the system. Calculation of thermodynamic probability by the Boltzmann method. Energy distribution of molecules. The partition function and its properties. Partition function and its relationship with thermodynamic functions. The translational, rotational partition function of the molecules. Vibrational sum partition function. Energy electronic state. Nuclear and electronic partition functions.
Topic 6. Theory of electrolyte solutions.
Chemical interaction is as the main condition for the stability of electrolyte solutions. The energy of the crystal lattice. Born and Kapustinsky's model for calculating the energy of the crystal lattice. Born-Haber thermodynamic cycle. Dependence of the energy of the crystal lattice on the ionic radius, charge, chemical nature of its constituent ions
Topic 7. Energy of solvation.
Solvation (hydration) of ions. The Born model and the Born-Haber thermodynamic cycle for calculating the energy of solvation. Thermal effect of solvation. Born-Bjerrum equation for calculating the enthalpy of solvation. The real and chemical energy of solvation. A.N. Frumkin's model. Dependence of the heat of solvation (hydration) of ions on its properties: ionic radius, charge, chemical nature.
Topic 8. Theory of strong electrolytes.
Thermodynamic description of ion-ion interaction in the works of Lewis and Randall. The development of the theory of strong electrolytes by Debye-Hückel.
Güntelberg, Huggenheim and Davies equations to calculate the activity mean ionic coefficient. Application of the Debye-Hückel theory to solutions of weak electrolytes.
Topic 9. Electrical conductivity of electrolyte solutions.
Specific and molar electrical conductivity. Concentration dependence of electrical conductivity of weak and strong electrolytes. The laws of Kohlrausch, Debye-Onsager. Electrophoretic and relaxation effects. Wien and Debye-Volkenhagen effects.

Topic 10. Theoretical and applied aspects of the theory of active collisions.
The main ways of activation of molecules, energy exchange in collisions. The theory of active collisions. Bimolecular reactions from the point of view of the theory of active collisions. Rate and rate constant of bimolecular reactions. Justification of the preexponential factor in the Arrhenius equation. Monomolecular reactions. Lindemann's theory.
Topic 11. Theoretical and applied aspects of the activated complex theory.
Potential energy surface. Transient State Theory. The main postulates of the activated complex theory. The main equation of the activated complex theory, derivation of Eyring, Evans and Polyany. Reaction rate and rate constant. Statistical and thermodynamic aspects of the activated complex theory.
Topic 12. Kinetic analysis of complex reactions.
Features of the kinetics of reversible, parallel and sequential reactions. Stationary and quasi-stationary reactions. Bodenstein's method of stationary concentrations.
Topic 13. Adsorption equilibria
Adsorption isotherm equations. Langmuir, Brunauer-Emmett-Teller adsorption isotherm equations. Gibbs adsorption equation. Surfactants and surface inactive substances. Hydrophilic-lipophilic balance of surfactant molecules.
Topic 14. Kinetics of electrochemical reactions.
Kinetic features of the course of an electrochemical reaction. Basic equation of electrochemical kinetics. Diffusion mode of the electrochemical reaction. Kinetic mode of the electrochemical reaction.
Topic 15. Theoretical foundations of polarization.
Polarization, types of polarization, reasons for polarization of electrodes. Concentration polarization, basic equations of concentration (stage of mass transfer) polarization. Electrochemical polarization, equations of cathodic and anodic polarization. Tafel's equations.

3. List of references.

Main:
1. Ira N. Levine. Physical Chemistry. Sixth Edition. *New York:* McGraw-Hill, 2009. 995 p.
2. Howard Devoe.Thermodynamics and Chemistry. Second Edition. Prentice-Hall, Inc., 2011. 531 p.
3. Denisov E.T., Sarkisov O.M., Likhtenshtein G.L. Kinetics. Fundamentals and new developments. Elsevier science B.V., Amsterdam, 2003. 547.
4. Robert G. Mortimer. Physical Chemistry.Third Edition. Elsevier Academic Press, Canada. 2008. 1385 p.
5. Дамаскин Б.Б., Петрий О.А., Цирлина Г.А. Электрохимия. – М.: Химия, КолосС, 2008. – 672 с.
6. Ягодовский В.Д. Статистическая термодинамика в физической химии. М.: БИНОМ, 2005. -496 с.
7. Байрамов В.М. Основы электрохимии. – М.: Academa, 2005. – 240 с.
8. Буданов В.В., Ломова Т.Н., Рыбкин В.В. Химическая кинетика. – М.:Лань, 2014. – 288 с.

Additional:
9. J. Bockris A.N.Reddy. Modern Electrochemistry. Volume 1. New York: Kluwer academic publishers, 2002. 769 p.
10. Peter Atkins, Julio de Paula. Physical Chemistry, Eighth Edition. Oxford University Press, 2006. 1050 p.
11. Бакеев М. Основы теории гидратации и растворения солей. - Алматы: Наука, 1990. -55 с.
12. Оспанова А.К.,Омарова Р.А. Основы статистической термодинамики. Алматы. 2011, 101с.
13. Основы физической химии. Под редакцией академика РАН проф. Лунина. М.: Издательство «Экзамен». – 2005. 480 с.
14. Васильев В.П. Термодинамическая свойства растворов электролитов.- М: Высшая школа.- 1982. - 320 с.

1.2 Discipline **" Modern problems of organic chemistry»**

Topic 1. Current state of the theory of organic structure
Subtopics Classification of reactions and reagents. Basicity, nucleophilicity, electrophilicity, acidity. The theory of hard and soft acids and bases.
Topic 2. Factors that determine the reactivity of subtopic molecules. Electrical properties of molecules and intermolecular forces. The theory of displacement of electron pairs. Electronic effects in organic compound molecules. Inductive and mesomeric effects in static and dynamic systems. Kinetic control of the organic reaction.
Topic 3. The mechanism of the reaction of radical substitution of the Subtopic. Alkyl radicals, structure and main methods of generation. Detection and establishment of the structure of free radicals.
Topic 4. Nucleophilic substitution in a saturated carbon atom.
the subtopics are Carbonium and carbenium ions. Factors affecting the stability of carbocations, explanation of the stabilizing effect of substituents. Mechanisms of SN1 and SN2. Experimental evidence. Factors affecting the mechanisms of nucleophilic substitution. Ion pairs in the processes of monomolecular nucleophilic substitution. Stereochemistry. Border area. One-electron shift theory. Other SN mechanisms.
Topic 5. Elimination reactions
Subtopics of the elimination reaction: E1, E1cB, E2. Stereochemistry of E2-elimination. Spatial orientation of the double bond in elimination products. Competition of substitution and elimination.
Topic 6. Electrophilic substitution of a saturated carbon atom.
Subtopics The mechanism of electrophilic substitution. Bimolecular and monomolecular reactions, stereochemistry. Nucleophilic assistance. Reactions of CH-acids.

Topic 7. Types of the mechanism of electrophilic aromatic substitution
subtopics Early and late transition state. The proton cleavage stage. Isomeric σ-complexes. Classification of substituents. Orientation as a reflection of the properties of the σ-complex.
Topic 8. Nucleophilic aromatic substitution.
Subtopics of Nucleophilic aromatic substitution. Anionic σ-complexes in SNAr reactions. Stabilizing groups and nucleophiles. Spirocyclic σ-complexes. Bipolar σ-complexes. Oxidation of σ-complexes. Interaction of σ-complexes with electrophiles. Bartoli's reaction. Kine-and tele-substitution. Vicarious nucleophilic substitution. Dimroth-type rearrangements.
Topic 9. Pericyclic reactions.
Subtopics General characteristics of pericyclic reactions. Theory of pericyclic reactions. Theory of electrocyclic reactions. Six-electron cycloaddition reactions.
Topic 10. Intramolecular rearrangements.
Subtopics. Classification of intramolecular rearrangements. Cyclic transition state. Theory of sigmatropic rearrangements. Other [1,j]-sigmatropic shifts. Nucleophilic rearrangements to the electron-deficient carbon atom. Wagner-Meerwein rearrangement and related processes. The speed of migration of different groups.
Electrophilic rearrangements. The mechanism of electrophilic rearrangements. Single-electron shift in electrophilic rearrangements. Thermal radical rearrangements. Photochemical rearrangements.
Topic 11. New ideas about the mechanism of tautomeric transformations.
Subtopics of Keto-enol tautomerism. Imine-enamine tautomerism. Tautomerism indiazoles.

3. List of references.

Main:
1.Смит В.А., Дильман А,Д. Основы современного органического синтеза./Учебник для высшей школы/. Бином, 2012
2. Реутов О.А., Курц А. Л., Бутин К.П. Органическая химия. Бином, 2012
3. Смит М**.** Органическая химия Марча. Реакции, механизмы, строение. / 4 т. Серия: Лучший зарубежный учебник/. 2020
4.Травень В.Ф. Органическая химия./ 3 т. : учеб. пособие для вузов/. 2013.

Additional:
1**.** Бутин К.П. Органическая химия. Часть 1,2,3 /Классический университетский учебник/. Бином, 2012
2. Травень В.Ф. Задачи по органической химии. / Учебник для высшей школы/ Бином, 2016

1.3 Discipline "Inorganic chemistry"

Topic "Method of valence bonds"
Subtopic "Application of the method of valence bonds to explain the formation of a specific molecule and molecular ion"
Topic "Molecular Orbital Method"
Subtopic "Application of the method of molecular orbitals to explain the formation of a specific molecule and molecular ion"
Subtopic "Construction of molecular orbital diagrams"
Topic "The structure of the atom. Periodic Law"
Subtopic "Model of the structure of the atom by Niels Bohr"
Topic "Complex compounds"
Subtopic "Formation of complex compounds from the point of view of crystal field theory"
Subtopic "Formation of complex compounds from the point of view of the method of valence bonds"

Subtopic "Formation of low-spin and high-spin complexes"
Subtopic "Coordination formulas of complex compounds"
Topic "Chemical bond and molecular structure"
Subtopic "Covalent bond"
Subtopic "Ionic bond"
Subtopic "Hydrogen bond"
Subtopic "Metallic bond"
Subtopic “Rules of Gillespie. Prediction of the geometric structure of molecules "
Topic "Structure of solid and liquid"
Subtopic "Intermolecular interaction"
Subtopic "Crystalline structure of matter"
Subtopic "Amorphous state of matter"
Subtopic "Liquids"
Subtopic "Crystalline hydrates"
Topic "General properties of metals"
Subtopic "Physical and chemical properties of metals"
Subtopic "Electronic structure of metals"
Subtopic "Crystalline structure of metals"
Subtopic "Obtaining metals of high purity"
Topic "Inorganic synthesis"
Subtopic "Gas-phase synthesis of inorganic substances"
Subtopic "Solid-phase synthesis of inorganic substances"
Topic "Chemistry of the elements of group V of the Periodic system"
Subtopic "Properties of nitrogen and its compounds"
Subtopic "Properties of phosphorus and its compounds"
Subtopic "Properties of antimony and its compounds"
Subtopic "Properties of bismuth and its compounds"
Topic "Chemistry of elements of the VI group of the Periodic system"
Subtopic "Properties of sulfur and its compounds"
Subtopic "Properties of selenium and its compounds"
Subtopic "Properties of chromium and its compounds"
Topic "Chemistry of elements of the VII group of the Periodic system"
Subtopic "Properties of manganese and its compounds"
Subtopic "Properties of rhenium and its compounds"

3. List of references.

Main:

1. Akhmetov N.S. Obshhaya i neorganicheskaya khimiya: uchebnik. Sankt-Peterburg, «Lan'», 2018. -744 s. (in Russian)

1.4 Discipline "Analytical chemistry»

Topic 1. Homogeneous equilibria in real solutions. Equilibrium constants. Thermodynamic derivation of the equilibrium constant. Kinetic derivation of the equilibrium constant.
Topic 2. Heterogeneous equilibria in real solutions. Equilibrium constants. Thermodynamic derivation of the equilibrium constant. Kinetic derivation of the equilibrium constant.
Topic 3. Distribution diagrams of various forms of monobasic and polybasic weak acids. Graphs of the dependence of the molar contents of various forms of acid on the pH of the solution. Construction and analysis of distribution diagrams (α – pH).

Topic 4. Equilibria in the processes of complex formation. Investigation of multi-stage complex formation by the Bjerum method. Complex formation function (Bjerum function). The complex formation curve.
Topic 5. Construction of a multi-stage complexation curve (ň-pL) for complexes of different composition. Analysis of complex formation curves.
Topic 6. Graphical dependence of the degree of complexation of cations on the concentration of the ligand (α-pL). Distribution diagrams. Plotting the distribution diagrams of various complexes and analyzing them.
Topic 7. Equilibria of redox processes in analytical chemistry. Distribution diagrams. The dependence of the molar contents of various forms of redox pairs of the system on the solution potential.
Topic 8. Equilibria in the "solid phase-saturated solution" system. Effect of the reaction of multi-stage complexation with the eponymous ion of the precipitate on its solubility. Derivation of the "S_{sed}.- pAn" dependence (on the example of silver halide).
Topic 9. Heterogeneous equilibrium. Regularities of the transfer of some poorly soluble electrolytes to others. Examples of their use in chemical analysis.
Topic 10. Analysis of real objects of complex composition for the content of various components: mixtures of metals, non-metals, salts, acids, etc. Selection of the analysis scheme, methods of separation and quantitative determination of the components of the mixture when they are jointly present in a given object.
Topic 11. Acid-base balance. Solving problems for determining the pH of highly diluted solutions: a) strong acids, bases; b) weak acids, bases.
Topic 12. Acid-base balance. Solving problems for determining the pH of dilute solutions: a) mixtures of strong and weak acids; b) mixtures of strong and weak bases.
Topic 13. Ionic equilibria in dilute salt solutions: solving problems for determining the pH of dilute salt solutions of different compositions (medium, acidic, amphoteric).
Topic 14. Ionic equilibria in solutions of buffer mixtures: solution of problems for determining the acidity and buffer capacity of solutions formed by weak acids of medium strength (h_{diss}.›5%).
Topic 15. Ionic equilibria in precipitation reactions. Solving problems for calculating the solubility of the sediment, taking into account the influence of various side processes: a) hydrolysis and protonation; b) multi-stage complexation and protonation.

3. List of references.

Main:

1. Матакова Р.Н., Наурызбаев М.К. Теоретические основы аналитической химии. Алматы: ҚазҰУ, 2006. – 120 с.
2. Золотов Ю.А. Основы аналитической химии в 2 кн. М.: Высшая школа, 2004. –361с.
3. Золотов Ю.А. и др. Основы аналитической химии. Задачи и вопросы. М.: ВШ, 2002. – 412с.
4. Дорохова Е.Н., Прохорова Г.В. Задачи и вопросы по аналитической химии.М.: Мир, 2001.- 267 с.
5. Золотов Ю.А. и др. Основы аналитической химии. Практическое руководство. М.: Высшая школа, 2018. – 462с.
6. Васильев В.П. и др. Аналитическая химия. Лабораторный практикум. М.: Дрофа, 2004. – 416с.

Additional:

1. Васильев В.П. и др. Аналитическая химия. Сборник вопросов и задач.М.: Дрофа, 2004. – 318 с.
2. Аналитическая химия. Проблемы и подходы./Подред.Р.Кельнер, Ж.-М.Мерме, М.Отто. Пер.с англ. В 2-х томах. Мир, 2004.
3. Кристиан Г. Аналитическая химия. Лучший зарубежный учебник. В 2 томах. М.: Бином, 2009. –504 с.
4. Янсон Э.Ю. Теоретические основы аналитической химии М.: ВШ, 1987. - 304с.
5. Скуг Д., Уэст Д. Основы аналитической химии в 2 ч. М.: ВШ, 1982.– 480с.