SCOPE OF THE QUALIFICATION EXAMINATION - CHEMICAL SCIENCES

Doctoral School of Exact and Natural Sciences

INORGANIC AND ANALYTICAL CHEMISTRY

1. Periodic table of elements. Division into blocks s, p, d and f. Electronic configurations of elements with the following exceptions: Cr, Cu, Mo, Pd, Ag, Pt, Au. Isoelectronic atoms, ions and molecules. Covalent and ionic radius - definitions, determination and variability in the periodic table. Influence of the size and charge of ions on the acid-base properties of their connections. The concepts of: ionization energy, electron affinity, electronegativity, standard potential and their variability in the periodic table. Relationship between electronegativity and the nature of bonds. Determining the spatial shape of simple covalent molecules and molecular ions (e.g. CO_2, NH_4^+, XeF_4), taking into account the position of non-bonding electron pairs (VSEPR).
2. **Properties of selected elements and their compounds. Hydrogen.** Conditions and possibilities of H2 reaction with other elements. Metal and non-metal hydrides - classification into ionic, covalent and metallic hydrides (examples for each group). Influence of hydrogen bonds on the properties of NH_3, H_2O and HF. Application of hydrogen combustion in oxygen in a fuel cell. **Alkali and alkaline earth metals** - reactivity, reactions with water and oxygen. Water hardness and its removal. The phenomenon of amphoterism on the example of $Zn(OH)_2$ and $Al(OH)_3$. **Carbon and silicon**. The structure of the most important allotropic forms of carbon (graphite, diamond, fullerene C60). CaC_2 carbide and its reaction with water. SiO_2 and its reaction with bases. The role of C-C and Si-O-Si bonds in the formation of carbon and silicon compounds. **Nitrogen**. Magnetic properties of the N_2 molecule. Formation of ammonia and nitric acid(V). Redox reactions of dissolution of metals in HNO_3. **Phosphorus.** Phosphorus allotropes and their structure. P_4O_{10} phosphorus oxide - structure and reactions with water. **Oxygen.** Magnetic properties of the O_2 molecule. Redox reactions involving hydrogen peroxide H_2O_2. **Sulfur.** Sulfur allotropes and their structure. The interaction of SO_2, H_2S with water. Preparation of H2SO4. **Halogens**. Physical properties and structure of elemental forms. Reactions of halogens and hydrohalides with water. **Elements of blocks d and f**. Examples of connections at different oxidation states: Cr^{3+}, CrO_4^{2-}, Mn^{2+}, MnO_2, MnO_4^-, Fe^{2+}, Fe^{3+}, Prussian blue, Co^{2+}, Co^{3+}. Equations of redox reactions involving transition metal ions. Dependence of the CrO_4^{2-} / $Cr_2O_7^{2-}$ equilibrium position on the pH of the solution. Typical and unusual oxidation states of lanthanides. Influence of lanthanide contraction on basic properties of lanthanide hydroxides.
3. **Coordination compounds.** Examples of complexes with typical coordination numbers: 2 (linear), 4 (tetrahedral and planar square) and 6 (octahedral). Ethylenediamine and EDTA as multidentate (chelating) ligands. Diagram of the splitting of central-ion d orbitals in the octahedral ligand field. The concept of high and low spin complexes. The dependence of the magnetic properties of the complexes on the ligand field strength.
4. **Universal basics of chemical analysis.** Significant figures. Definition of acid and base in Brønsted's theory. Conjugate acid-base pairs. Salt hydrolysis as an acid-base reaction. Definition of acid and base in Lewis theory. pH of solutions of weak and strong acids, bases, and salts of acids and bases of different relative strength. pH of the buffer solution. The concept of the solubility product and its relationship with the molar solubility of the substance. The influence of common ion, foreign ions, protonation and complexation on the solubility of sediments.
5. **Elements of qualitative analysis.** Burner flame colors generated by volatile elements. The colors of solutions of compounds of: alkali metals, alkaline earth metals, Cr (III), Cr (VI), Mn (II), Mn (VI), Mn (VII), Fe (II), Fe (III), Co (II), Ni (II), Cu (II), Zn (II), Ag (I), Au (I), Hg (II) and Hg (I). Water solubility of chlorides,

nitrates (V), sulphates (VI), sulphides and carbonates of these metals. The basis for the division of cations into analytical groups. Selected colored characteristic reactions: Fe(III) with SCN^-, Fe(III) with $Fe(CN)_6^{4-}$, Cu(II) with NH_3, Co(II) with SCN^-, Ni(II) with dimethylglyoxime. Comparison of Al(III) and Cr(III) reactions with NaOH. Distinction of Cl^-, Br^- and I^- on the basis of the reaction with $AgNO_3$.
6. **Elements of quantitative analysis. Weight analysis.** Methodology of typical determinations, e.g. sulfates in the form of $BaSO_4$ or calcium in the form of CaO. The essence of minimizing precipitate losses during washing. **Titration analysis.** Equivalence-point pH in the titrations of weak and strong acids and bases. Comparison-buffer definition. Typical pH indicators: phenolphthalein and methyl orange, and the optimal choice of indicator for a given titration. The principle of the acid-base titration of mixtures of carbonates, bicarbonates and hydroxides. Determination of calcium and magnesium with EDTA as an example of complexometric titration. **Elements of instrumental analysis.** Redox titration technique with a platinum electrode as the indicator electrode and a calomel electrode as the reference electrode. Calculation of the redox potential of a system at the equivalence point. Lambert-Beer law as the basis of absorption spectrophotometry. Molar absorption coefficient. Ilkovič equation as the basis for quantitative analysis using the polarographic method. Principle and application of the inversed voltammetric method. Potentiometry and ion selective electrodes. Atomic emission and absorption spectrometry.

ORGANIC CHEMISTRY AND BIOCHEMISTRY

1. **Hydrocarbons.** Division into classes. Hybridization of carbon atom. Structure of hydrocarbons: alkanes, cycloalkanes, alkenes, alkynes, aromatic compounds (aromatic character, Hückel's rule).
2. **Conformation:** alkanes (ethane, butane, slow rotation), cycloalkanes (ring stability). Isomerism: constitutional, geometric (cis / trans, Z / E), optical (absolute configuration R / S and its determination, Cahn-Ingold-Prelog rules; enantiomers, diastereoisomers, racemic mixture, relative configuration).
3. **Alkanes.** Synthesis and properties. Free radical substitution (SR mechanism, reaction orientation). Structure of a free radical. Stability of free radicals. Cycloalkanes: properties and reactions.
4. **Alkenes.** Synthesis and properties. Electrophilic addition of hydrogen halides and halogens (AdE mechanism, Markovnikov rule). Stability of carbocations. Free radical addition of hydrogen bromide (AdR mechanism). Hydrogenation and ozonolysis of alkenes.
5. **Alkynes.** Synthesis and properties. Alkynes (addition of hydrogen, halogen, hydrogen halide, water).
6. **Aromatic hydrocarbons (benzene).** Electrophilic substitution of aromatic compounds (SE mechanism). Nitration, sulfonation, halogenation, alkylation, acylation. Substituents effect (inductive and mesomeric effect). Alkyl derivatives of benzene, side chain substitution.
7. **Halogen derivatives.** Synthesis and properties. Haloalkanes: nucleophilic substitution, mechanisms and stereochemistry of SN1 and SN2 reactions. Elimination reactions, mechanisms E1 and E2. Reactivity of halogen derivatives: alkyl, allyl, vinyl and aromatic compounds.
8. **Alcohols.** Synthesis and properties. Classification. SN1 and SN2 substitution reactions. Elimination reactions (dehydration).
9. **Amines.** Synthesis and properties. Classification of amines. Alkylation of amines. Amine salts and quaternary ammonium salts. Aromatic amines – ring substitution. Reactions of amines with nitric (III) acid, reactions of diazonium salts.
10. **Aldehydes and ketones.** Synthesis and properties. Oxidation and reduction reactions. Nucleophilic addition (AdN) to a carbonyl group: addition of water, alcohols, hydrogen cyanide, bisulfite (bisulfate (IV)), ammonia derivatives, Grignard compounds. Cannizzaro reactions and aldol condensation (mechanisms).
11. **Carboxylic acids and their derivatives.** Synthesis and properties. Classification of carboxylic acids. Acidity of carboxylic acids - structure influence. Salts. Synthesis of acid chlorides and anhydrides, esters and amides, comparison of their reactivity. Esters: esterification and hydrolysis mechanism, Claisen condensation mechanism). Reduction of carboxylic acids and their derivatives.
12. **Heterocyclic compounds.** Heterocyclic five- and six-membered systems with one heteroatom. SE reactions of pyrrole, thiophene, furan. SE of pyridine.
13. **Multifunctional compounds.** Hydroxyketones, hydroxyaldehydes, halogen substituted carboxylic acids, amino acids, dicarbonyl compounds - synthesis and reactions. Keto-enol tautomerism.
14. **Identification of organic compounds by spectral methods.** The ability to interpret simple 1H-NMR, 13CNMR and infrared spectra (knowledge of the frequency of vibrations for basic functional groups) in order to identify compounds.
15. **Biochemistry.** Structure and function of biological membranes. Permeability and transport across membranes. The hierarchical structure of proteins (1st, 2nd, 3rd and 4th order structure). The relationship between the structure and function of proteins. Structure of enzymes, their classification,

function and mechanism of action. Basic concepts of metabolism (thermodynamics of biochemical reactions, coupled reactions, compounds with high phosphorylation potential, basic principles of the organization of metabolism). Photosynthesis and biological oxidation. Structure of DNA and RNA. The flow of genetic information. Concepts of replication, transcription and translation.

PHYSICAL AND THEORETICAL CHEMISTRY

1. **Kinetic theory of gases.** Ideal and real gases. Clapeyron equation and van der Waals equation. Critical temperature. Heat capacity of ideal gases.
2. **Thermodynamics** - basic concepts. Energy, work, heat. The concept of a state function. First law of thermodynamics. Internal energy (U) and enthalpy (H), their changes in various processes.
Thermochemistry. Thermal effects of a reaction under constant pressure and constant volume. Standard enthalpy changes in physical and chemical transformations. Hess's law and its applications. Kirchhoff's law.
Entropy (S). Second law of thermodynamics. The physical significance of entropy. The dependence of S on temperature. Thermodynamically reversible and irreversible processes. Third law of thermodynamics.
Helmholtz free energy (F) and Gibbs free energy (G). Thermodynamic criteria of reaction spontaneity based on changes of S, F, and G potentials. Chemical potential. Thermodynamic equilibrium conditions.
Chemical equilibrium state. Equilibrium constant of a chemical reaction (K) and the influence of various factors (e.g., temperature) on its value. Equilibrium constant and reaction quotient expressed in partial pressures, concentrations and mole fractions. Relationship between ΔGo and K. The effect of a changes in external conditions on chemical equilibria (Le Chatelier's principle).
Phase transitions in single and multicomponent systems. Phase diagrams of pure substances (water, CO_2). Triple point. Gibbs phase rule. Raoult's law. Phase diagrams of two-component systems (positive and negative azeotropes, eutectics).
3. Electrochemistry. Electrolyte solutions. Ion solvation. Ion activity in electrolyte solutions. Activity coefficient. Debye-Hückel limiting law. The concept of an electrode and its potential. Standard potential. Nernst equation. Type I and II electrodes and typical reference electrodes: standard hydrogen, calomel, silver chloride - reactions, description of the potential by Nernst equation. pH electrodes.
Galvanic cells, types of cells and associated reactions. Theoretical calculation and experimental determination of the electromotive force (SEM). Stockholm electrochemical convention. Relation between ΔG and SEM. Determination of thermodynamic quantities from SEM measurements.
Electrolysis and transport phenomena. Faraday's law. Electrolysis of aqueous solutions of various salts - electrode reactions. Overpotential (overvoltage) of an electrode process. Diffusion and Fick's laws. Concentration gradient and diffusion coefficient. Diffusion and kinetic currents.
Colloids - electrokinetic potential. Electrophoresis and electrophoretic mobility. Isoelectric point.
4. **Chemical kinetics.** Rate of chemical reaction - definition and influence of various factors. Reaction order (partial, total), methods of determination. Kinetic equations and changes of reagent concentrations over time for reactions of various orders. The half-life of a reaction. Activation energy and Arrhenius equation. Activated complex theory. The concept and role of a catalyst.
5. **Electric and magnetic properties of substances.** Permanent and induced dipole moments of a molecule. Electric permeability and relative permittivity. Diamagnetism, paramagnetism and ferromagnetism. Magnetic susceptibility. Curie's law.
6. **Crystallography.** Basic concepts: crystal features, spherical and stereographic projection, lattice, Bravais lattices. Point symmetry, symmetry operations and symmetry elements, coexistence of symmetry elements, Schoenflies and Hermann-Maugin point group notations. Complex symmetry elements. 3D lattices, geometric objects in 3D lattices (nodes, lines and planes). Miller indices. Space groups. Close-packing and densest packing. Reciprocal lattice - definition and properties, Ewald’s sphere construction. Basics of X-ray analysis of crystals’ structure.
7. **Quantum chemistry.** Statistical interpretation of the wave function. Energy levels (degeneration, distances between the adjacent levels), wave functions (variables, the number of nodes) and quantum numbers for the following quantum systems: one-dimensional potential box (particle in a box), one-dimensional harmonic oscillator, rigid rotator, hydrogen atom and hydrogen-like ions (here also the contours of the functions s, p, d). One-electron approximation. Orbitals and spinorbitals. Wave function for a multi-electron system.
Paulie's exclusion principle. Hartree-Fock method. Electronic configurations of atoms and multi-electron ions. Hund's rule. Atomic term symbols (the base term of a multi-electron atom). Born-Oppenheimer approximation. Molecular orbitals (MO) method. LCAO MO method. Mechanism of chemical bond formation in terms of the MO method. Molecular orbitals in diatomic homonuclear molecules (σg, σu,

πg, πu). Bonding, anti-bonding and non-bonding orbitals. Energy levels and electronic configurations in homonuclear diatomic molecules of elements from the second period and simple heteronuclear diatomic molecules. Potential energy diagrams for a diatomic molecule (vibrational and rotational levels). Molecular orbitals method for polyatomic molecules. Orbital hybridization. Hybridized orbitals of the following types: sp, sp^2, sp^3.

8. **Spectroscopy.** The nature and properties of electromagnetic radiation. Energy quantization of rotational, vibrational (including anharmonic vibrations), and electronic states in a molecule.
Boltzmann distribution and relative population of energy levels. Electromagnetic radiation frequency (and wavelength) range and the observed types of spectral transitions. Selection rules in rotational and vibrational absorption spectroscopy. Inelastic scattering: Stokes and anti-Stokes bands. Selection rules in vibrational Raman spectroscopy. Relative position of absorption and emission peaks in luminescence spectroscopy (fluorescence and phosphorescence). EPR spectroscopy. Hyperfine structure of EPR spectra. NMR spectroscopy: interaction of atomic nuclei of non-zero magnetic moment with an external magnetic field, nuclear shielding and chemical shifts. Interactions of magnetic nuclei (spin-spin coupling).

CHEMICAL TECHNOLOGY AND FUNDAMENTALS OF BIOTECHNOLOGY

1. **Fundamentals of chemical technology.** Unit operations and processes. Effectivity, yield, selectivity and Energy consumption as essential parameters of technological process evaluation. Material and Energy balances. Chemical and physical laws employed in material and energy balances preparation. The features of novel and green technologies. Waste Management in Chemical Technologies - environmental protection aspect.
2. **Technology rules:** sustainable utilization of sources, energy, instrumentation. Economic optimization of technological process. Designing of the technological process on a larger scale.