Entrance Examination in Chemistry

“Chemistry” Master's programme

Examination paper (example)

1. Basic concepts of the complex compound’s chemistry: the central atom and its coordination number; ligands, denticity, donor atom, internal and external coordination spheres. Isomerism of complex compounds. Crystal field theory (CFT) - basic concepts.

2. Alkanes. Methods of synthesis of alkanes. Isomerism and chemical properties of alkanes.

3. Thermochemistry. The thermal effect of a chemical reaction. Hess's Law. Dependence of the enthalpy of the reaction on temperature, Kirchhoff equation.

Chemistry examination paper consists of three theoretical questions and one task.
Examples of problems:

1. Calculate the change in entropy when 200 g of ice at 0°C are added to 200 g of water (90°C) in an insulated vessel. The heat of melting of ice is 6.0 $kJ \cdot mol^{-1}$, the heat capacity of liquid water is 75.3 $kJ \cdot K^{-1} \cdot mol^{-1}$.

2. The enthalpies of combustion of α-glucose, β-fructose and sucrose at 25°C are –2802, –2810 and –5644 kJ/mol, respectively. Calculate the heat of hydrolysis of sucrose.

3. The rate of the reaction proceeding at 35ºC in the presence of a catalyst turned out to be $8.4 \cdot 10^7$ times higher than the rate of the non-catalyzed reaction. Calculate the activation energy of the reaction in the absence of a catalyst if the activation energy for the catalyzed reaction is 42.5 kJ/mol.

4. Based on the values of the standard potentials $E°(Fe^{3+}/Fe^{2+})$ = 0.771 V and $E°([Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}])$ = 0.36 V, determine the ratio of stability constants of iron cyanide complexes at 25°C.

Program for entering “Chemistry” Master's programme

The program includes key issues of the main chemical disciplines studied not only at the chemical faculty of Moscow University, but also at all chemical faculties of classical universities of Russia: inorganic chemistry, analytical chemistry, physical chemistry, organic chemistry, high-molecular compounds, colloidal chemistry and chemical bases of life.

Inorganic chemistry

The structure of the Periodic table and its relation to the electronic structure of atoms, Moseley`s law. Periodicity of changes in the values of radii, ionization energy, electron affinity, electronegativity of atoms in the group and in the period. Periodicity of changes in properties of simple substances and general classes of chemical compounds (oxides, hydroxides, halides). Vertical, horizontal and diagonal analogies in the Periodic table.

Main types of chemical bonds. Characteristics of chemical bonds in molecules: energy, length, valence angle, order (multiplicity) and polarity. The idea of hybridization of atomic orbitals. The geometry of polyatomic molecules: the Gillespie model on the example of particles H_2O, SF_4, ICl_4^-.

The main provisions of the method of molecular orbitals (MMO). Method MO LCAO. Two-center two-electron molecular orbitals. Energy diagrams of diatomic homonuclear molecules formed by elements of the 1st and 2nd periods. Correlations between the order of coupling, ionization energy and magnetic properties on the example of particles O_2^+, O_2, O_2^-, O_2^{2-}.

Basic concepts of the complex compound’s chemistry: the central atom and its coordination number; ligands, denticity, donor atom, internal and external coordination spheres. Isomerism of complex compounds. The concept of classification of complex compounds. Chelate effect.

Crystal field theory (CFT). Symmetry of d-orbitals. Changes in the energy of d-orbitals in the spherical, octahedral and tetrahedral ligand fields. The crystal field stabilization energy (CFSE). Influence of the central atom nature (charge, radius, electronic configuration), nature, number and location of ligands on the value of energy splitting. Spectrochemical series.

Coloring and magnetic properties of complexes. Jahn–Teller effect, tetragonal distortion of octahedral complexes. Square-planar complexes. Comparison of the structure $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ complex ions.

Elements of 1st group (Li, Na, K, Rb, Cs). Regularities in the change of electronic configurations, values of radii, ionization energy and electronegativity of atoms. Diagonal similarity of lithium — magnesium. Preparation and comparison the stability of compounds Li_2O_2 and Na_2O_2; Li_2O and Na_2O.

Elements of 2nd group (Be, Mg, Ca, Sr, Ba). Regularities in the change of electronic configurations, values of radii, ionization energy and electronegativity of atoms. Diagonal similarity beryllium — aluminum. Preparation of hydroxides $M(OH)_2$ and comparison of their acid-base properties in Be– Mg–Ca–Sr–Ba series.

Elements of 13th group (B, Al, Ga, In, Tl). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Chemical methods of separation of aluminum and beryllium compounds. Preparation, structure, properties of diborane B_2H_6.

Elements of 14th group (C, Si, Ge, Sn, Pb). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Oxygen compounds of the 14th group. Comparison of the structure and properties of CO_2 and SiO_2

Elements of 15th group (N, P, As, Sb, Bi). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Comparison of strength of single (E–E), double (E=E) and triple (E≡E) bonds. Preparation, comparison of structure and properties (acidic, oxidative activity and thermal stability) HNO_2 and HNO_3.

Elements of 16th group (O, S, Se, Te, Po). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. The distinctive properties of oxygen, the multiplicity of bonds and features of catenation (forming of homoelements chains) in O–S–Se–Te series. Preparation, comparison of structure and properties (acidic, oxidative activity and thermal stability) H_2SO_3 and H_2SO_4.

Elements of 17th group (F, Cl, Br, I). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Fluorine features. Intermolecular interactions and physical properties of simple substances. Structure and properties (thermodynamic stability, oxidative, acidic properties) chlorine acids in series Cl(I)—Cl(III)—Cl(V)—Cl(VII).

Elements of 4th group (Ti, Zr, Hf). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Comparison of structure and properties of compounds of the same type in series Ti(IV)—Ti(III)—Ti(II) (oxides, hydroxides, halides). Complex compounds of Ti.

Elements of 5th group (V, Nb, Ta). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Structure and chemical properties of cationic and anionic forms of vanadium (V) compounds in aqueous solution. Preparation and comparison of oxidation-reduction and acid - base properties of compounds V(II)–V(III)–V(IV)–V(V in aqueous solution.

Elements of 6th group (Cr, Mo, W). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Acid-base, redox properties of chromium compounds in the Cr(VI)–Cr(III)–Cr(II) series. Preparation, comparison of structure and properties (acidic properties, thermodynamic stability and oxidative activity) of EO_3 oxides (E = Cr, Mo, W).

Elements of 7th group (Mn, Tc, Re). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Acid-base, redox properties of manganese in series Mn(II)-Mn(III)-Mn(IV)-Mn(VI)-Mn(VII). Preparation, comparison of structure and properties (thermodynamic stability, acid-base, redox) of Mn(VII)–Tc(VII)–Re(VII) compounds.

3d-elements of 8th, 9th и 10th groups (Fe, Co, Ni). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Acid-base, redox properties of hydroxides $M(OH)_2$ and $M(OH)_3$ in a series of Fe-Co-Ni. Preparation and comparison of properties (thermodynamic stability, acid-base, redox) of compounds Fe(II), Fe(III) and Fe(VI).

Elements of 11th group (Cu, Ag, Au). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Thermodynamic stability, acid-base and redox properties of Cu and Ag oxides and hydroxides. Preparation, structure and disproportion of Cu(I) compounds.

Elements of 12th group (Zn, Cd, Hg). Regularities in changes of the electronic configuration, the size of atoms, ionization energy, electron affinity, electronegativity, characteristic oxidation states and coordination numbers of atoms. Acid-base, redox properties of

hydroxides $M(OH)_2$ in the series Zn–Cd–Hg. Preparation, structure and disproportionation of the Hg_2^{2+} compounds.

Analytical Chemistry

The main characteristics of chemical analysis methods. The concept of systematic and random errors of chemical analysis. Statistical processing of measurement results.

Representative sample. Size and methods of sampling. Sample preparation for analysis.

Ideal and real systems. Activity, equilibrium and total concentration. Thermodynamic and concentration equilibrium constants.

Acid-base balance. Modern ideas about acids and bases. The main provisions of the acid-base theories of Brensted-Lowry and Lewis.Influence of the nature of solvents on the strength of acids and bases. Leveling and differentiating effects of solvents. Buffer solutions and their properties.

Acid-base titration. Indicators. Determination of acids (individual and their mixtures) and bases (individual and their mixtures).

Complex compound. Equilibrium of complex formation and its quantitative characteristics. Analytically important properties of CC. Application of complexes in chemical analysis. Complexometric titration. Metallochromic indicators. Direct, back, displacement and indirect titration. Methods for increasing the selectivity of complexometric determination of elements.

Oxidation-reduction reactions. Redox electrode potential (standard, equilibrium, formal), factors affecting it. Equilibrium constants and the direction of redox reactions.

Redox-titration. Methods for determining the end point of titration. Indicators. Redox-titration methods: dichromatometry, iodometry, permanganatometry.

Heterogeneous equilibrium in the sediment-solution system. Solubility product, solubility, factors affecting solubility.

Formation, properties, conditions of crystal and amorphous precipitation. Contamination of precipitation and ways to eliminate it.

Gravimetric analysis: the essence, advantages and disadvantages of the method. Examples.

Methods of separation and concentration in chemical analysis. Solvent extraction.

Chromatographic methods of analysis. Classification of methods according to different principles. Basic chromatographic parameters. Qualitative and quantitative analysis.

Gas chromatography. Sorbents and carriers. Separation mechanism. Detectors. Application.

Liquid chromatography (LC). The types of LC. Benefits of HPLC. Normal - phase and reversed-phase variants of HPLC. Mobile and stationary phases, principles of their choice. Detectors. Application.

Electrochemical methods of analysis: General characteristics, classification. Direct potentiometry and potentiometric titration. Measuring potential. Classification of indicator electrodes. Practical application of ionometry.

Coulometry and coulometric titration. Theoretical bases. Practical application.

Voltammetry. Characteristics of the current-voltage curve. Modern types of voltammetry, advantages and limitations in comparison with classical polarography. Amperometric titration.

Spectroscopic methods of analysis. Classification of spectroscopic methods by the nature of particles interacting with radiation, the nature of the process, the range of electromagnetic radiation.

Atomic-emission and atomic-absorption methods of analysis. Sources of atomization and radiation of particles. Physical and chemical processes in atomizers. Spectral and physico-chemical noise, methods of their elimination. Analytical capabilities and applications of methods.

Molecular absorption spectroscopy (spectrophotometry). The basic law of light absorption. Preparation of colored compounds, spectrophotometric reactions. Quantitative analysis, analysis of multicomponent systems, study of reactions in solutions. Metrological characteristics and analytical capabilities of the method. Examples of practical application.

Molecular luminescence spectroscopy. Classification according to the sources, mechanism and duration of glow. Fluorescence and phosphorescence. Scheme Yablonsky. Basic regularity. Factors affecting luminescence intensity. The luminescence quenching. Physico-chemical and spectral interference. Analytical capabilities of the method, its metrological characteristics. Example of use.

Organic Chemistry

The main functional groups and classes of organic compounds. Types of isomerism of organic compounds. The concept of conformations on the example of alkanes. Geometric alkene isomerism. The concept of optical activity and chirality with one asymmetric carbon atom. The concept of enantiomers and racemates. R,S - nomenclature. Connections with two chiral centers. The concept of diastereomers.

Alkanes. Methods of synthesis of alkanes. Chemical properties of alkanes. The mechanism of a chain radical reaction. Cracking.

Alkenes. Methods of synthesis of alkenes. The hydrogenation of alkenes. Hydroboration. Alkene ozonolysis. Oxidation of alkenes to diols. Electrophilic joining alkaram. Reaction mechanism. Bromine joining the alkenes. Hydrogenation. Acid-catalyzed hydration of alkenes, hydroxymercuration. Free radical reactions: addition of hydrogen bromide by Kharasch. Allyl bromination.

Alkynes. Methods of synthesis of alkynes. C-H-acidity of alkynes. Hydration of alkynes. Acetylene-allene isomerization. The shift of the triple bond in terminal position. Dienes. Methods of obtaining dienes. 1,2 - and 1,4-addition to conjugated dienes. Diels-Alder Reaction.

Reactions of nucleophilic substitution at a saturated carbon atom in the alkyl halides. Mechanisms SN_1 and SN_2. The main regularities of nucleophilic substitution reactions. β-Elimination. Elimination mechanisms (E1, E2). The main regularities of these reactions.

Alcohols as weak O-H acid. Substitution of hydroxyl group in alcohols for halogen. Dehydration of alcohols. Oxidation of alcohols. Pincon-pinacolada regrouping. Ether. Synthesis method. Oxiranes. Methods of obtaining. Epoxy opening reactions under the action of electrophilic and nucleophilic agents.

Aldehydes and ketones. Addition of nucleophiles to the carbonyl group. Mechanism. Reduction of carbonyl compounds. Oxidation of carbonyl compounds. 1,3-Dithiane. Synthesis, CH-acidity. Keto-enol tautomerism ketones, diketones and ketoesters. Reactions occurring through the formation of the enol form. Halogenation of carbonyl compounds. Haloform reaction. Aldol-conjugated enone condensation in acidic and alkaline medium. Directional aldol condensation. Ester condensation. Syntheses using acetoacetic ester and malonic ester.

Carboxylic acid. Effect of substituents on acidity. Decarboxylation. The reaction of halogenation at the α-carbon atom. Derivatives of carboxylic acids. Halides, anhydrides, carboxylic acids, esters. Synthesis and properties. Synthesis of amides of carboxylic acids. Sextet rearrangements. Nitriles.

Structure of benzene. Aromaticity. Huckel Rule. Criteria of aromaticity (energy, structural, magnetic). Signs of aromaticity (reactivity). Properties of the aliphatic side chain in aromatic hydrocarbons. Halogenation of toluene and its homologues in the side chain. Oxidation of the side chain. Hydrogenation.

Electrophilic substitution in the aromatic series. Electrophilic agents and reaction mechanism of nitration, halogenation, sulfation, Friedel-Crafts alkylation and acylation of aromatics. Orientation of electrophilic substitution. Side processes in alkylation reactions. Formylation. Nucleophilic substitution in the aromatic series.

Synthesis of aliphatic nitro compounds. Synthesis of amines. Properties of amines. Basicity. Protecting the amino group. Interaction of primary, secondary and tertiary aliphatic and aromatic amines with nitric acid.

Diazo - and azo-compounds. Diazonium salts. Diazotoluene primary aromatic amines. Reactions of diazo compounds with the release of nitrogen. Azo coupling. Diazomethane.

Phenols and quinones. Methods of synthesis of phenols. Properties of phenols. Preparation of o - and p-benzoquinones.

Classification of alicycles. Types of strain in cycloalkanes and conformation. Methods of synthesis of compounds of cyclopropane and cyclobutane. Features of chemical properties of compounds with a three-membered cycle. Synthesis of compounds of cyclopentane and cyclohexane series.

Five-membered heterocycles with one heteroatom. Methods of synthesis of five-membered heterocycles. Paal-Knorr Method. Electrophilic substitution. The acidity of the pyrrole. Indole. Synthesis of indoles by the Fisher.

Six-membered heterocycles. Pyridine, aroma, basicity. The synthesis of pyridines. Chemical properties of pyridine. Basicity. Electrophilic substitution reactions. N-pyridine oxide, preparation and use in synthesis. Nucleophilic substitution in pyridines. Quinoline.

Amino acid. Configuration of natural L-amino acids. Amphoteric, isoelectric point. Chemical properties of COOH and NH2 groups. The most important methods of amino acid synthesis. Methods of peptide bond formation. Protective groups for amino and carboxyl groups, activation of carboxyl group, synthesis of peptides on a solid carrier. Proteins.

Physical Chemistry

The first law of thermodynamics and its formulations. Differential and integral form of the 1st law. Internal energy and enthalpy, calculation of their changes in various processes. Heat and work for different processes in gases.

Thermochemistry. The thermal effect of a chemical reaction. Hess's Law. Dependence of the thermal effect of the reaction on temperature, Kirchhoff equation.

The second law of thermodynamics and its formulations. Entropy and its properties. Calculation of entropy change for different processes.

Characteristic functions, their definition and properties. The fundamental equations of Gibbs. The characteristic function in the role of thermodynamic potentials, conditions of equilibrium, the extrema and the direction of spontaneous processes.

Determination of phase, number of components, number of degrees of freedom. The conditions of phase equilibrium. Phase equation (Gibbs–Duhem equation). The Gibbs phase rule. Chemical potential.

Phase transitions of the first kind. Clausius–Clapeyron Equation. The state diagram of a single-component system (in any example).

Determination of the ideal solution. Expression for the chemical potential of a component. Raoult's Law. Non-ideal solutions. Lewis activity method.

The condition of chemical equilibrium. Isotherm of chemical reaction. Equilibrium constant. The dependence of the equilibrium constant on temperature, the isobaric van 't Hoff equation.

Adsorption. Langmuir equation, its thermodynamic derivation and scope. Calculation of Langmuir equation parameters from experimental data.

The canonical sum of States and the properties. The molecular sum of States and its components. The connection with the canonical sum of States. Calculation of entropy, internal energy, enthalpy, Helmholtz energy, and Gibbs energy by state sums.

The rate of chemical reaction. Elementary and complex reactions. The basic postulate of chemical kinetics. Molecularity and order of reaction. Rate constant. Methods for determining the reaction order and the rate constant.

Dependence of the chemical reaction rate constant on temperature. Arrhenius equation. Activation energy and methods of its determination.

Theory of active collisions for bimolecular reaction, basic concepts and assumptions. The Trautz–Lewis Equation.

Activated complex theory (transition state theory). Assumptions used in the construction of the theory. Statistical derivation of the basic equation.

Basic concepts of catalysis. The main mechanisms of catalytic reactions. Activity, selectivity and stability of the catalyst. The turnover number.

Enzymatic catalysis. Enzymes as catalysts, their features. Derivation of the Michaelis–Menten equation and determination of kinetic parameters from experimental data. Inhibition of enzymatic reactions.

Electrolyte solution. Activity, activity coefficient. Debye−Hückel theory: basic propositions and assumptions, the concept of ionic atmosphere. The first and second approximations of the theory for the calculation of activity coefficients.

Conductivity of electrolyte solutions: specific, equivalent and molar conductivity, mobility of individual ions. Dependence of mobility on concentration. The Kohlrausch`s law.

Electrochemical potential. Equilibrium conditions at the electrode-solution boundary. Galvanic cell. The concept of EMF. The Nernst equation.

Thermodynamics of a galvanic cell. Application of the Gibbs − Helmholtz equation to electrochemical systems. Determination of changes in Gibbs energy, enthalpy and entropy of chemical reaction by EMF method.

Interface and colloid science

Disperse system. Surface tension. Surfactants, their effect on surface tension. Gibbs adsorption equation.

Wetting. Young's Equation. Thermodynamic conditions of non-wetting, wetting and spreading.

Micelle formation in aqueous and non-aqueous media. Thermodynamics of micelle formation.

Methods of production and factors of stabilization of disperse systems.

Rheological behavior of disperse systems. Nature of contacts in connective disperse systems.

Chemical bases of life

Structure and functions of nucleic acids. Structure and functions of proteins. Structure and functions of biological membranes.

Genetic code. DNA replication and transcription. Fundamentals of genetic bioengineering.

Enzymes as protein catalysts. Classification of enzymes. Basic equations of kinetics of enzymatic reactions.

Enzymatic catalysis in chemistry, examples of practical use of enzymes. Drugs based on enzymes and their inhibitors.

Polymer Science

Features of the structure and properties of high-molecular compounds that distinguish them from low-molecular analogues. Average molecular weight and curves of molecular weight distribution of polymers.

The structural features of polymer molecules: configurational and conformational isomerism. The phenomenon of flexibility of macromolecules: causes and mechanism. Models of quantitative description of flexibility.

Thermodynamic and hydrodynamic features of polymer solutions. Equation of state of polymer in solution. Determination of molecular weight and size of macromolecules.

Polyelectrolytes and their classification, features of dissociative and conformational behavior. Osmotic pressure of polyelectrolyte solutions. Polyampholytes.

Synthesis of polymers by chain and step mechanisms. Influence of synthesis conditions on reaction rate, molecular weight and stereoregularity of macromolecules formed. Copolymerization.

Chemical reactions of polymers. Polymeranalogous transformations, intra - and intermolecular reactions, reactions of destruction.

Mechanical properties of polymers. Thermomechanical analysis. Nature and mechanism of highly elastic and forced-elastic deformations. Fragility of glass-like polymers.

Structure of crystalline polymers. Thermodynamics and kinetics of crystallization, especially the deformation behavior of crystalline polymers.