**PHYSICAL CHEMISTRY**

1. GENERAL DESCRIPTION OF THE DISCIPLINE

The work programme of the discipline is compiled according to the Federal State Higher Professional Education Standards

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| --- | --- | --- | --- |
| Code of the field of study | Field of study | Details of the order of the Ministry of Education and Science of the Russian Federation on approval and commissioning of the Federal State Higher Educational Standard | |
| Date | Number of order |
| 04.06.01 | Chemical Sciences / Organic Chemistry | 30 July 2014 with amendments dated 30 April 2015 | 869  amendments  464 |

**1. Objectives of the discipline**

The *Physical Chemistry* discipline contributes to mastering the basic professional competences and their components, and is aimed at in-depth studying the basic sections of physical chemistry, such as the fundamentals of chemical and statistical thermodynamics, chemical kinetics, transport phenomena, electrochemistry and electrochemical kinetics.

**1.2. Role of discipline in the structure of educational activities and the Principal Educational Programme**

The *Physical Chemistry* discipline refers to section B.1 of the variable part of the Principal Educational Programme of the postgraduate course and is aimed at preparing for passing the qualifying examinations for the PhD degree.

As a result of mastering the discipline, a postgraduate student should master the following competencies:

**Universal Competencies (UC):**

* the ability to critically analyse and evaluate current scientific achievements, generate new ideas for solving research and practical problems, including in interdisciplinary areas (UC-1);
* the ability to design and implement complex research including inter-disciplinary one based on a holistic and scientific view of the world using knowledge in the field of history and philosophy of science (UC-2).
* the readiness to engage in the work of Russian and international research teams to tackle academic problems (UC-3);

**General Professional Competencies (GPC):**

* the ability to individually carry out research activities in the relevant professional field using up-to-date research methods as well as information and communication technologies (GPC-1);
* readiness to arrange for the work of a research team in the field of chemistry and related sciences (GPC-2);
* readiness to carry out the teaching activities under the principal higher educational programmes (GPC);

**Professional Competencies (PC):**

* the ability to independently conduct research that meets the established requirements for the content of theses for the academic PhD degree in sciences in the area of focus (scientific specialty) 02.00.04 Physical Chemistry (PC-1);
* readiness to present the research results on the PhD topic in the form of publications in peer-reviewed scientific publications, reports at scientific conferences, review and edit scientific articles in the area of focus (scientific specialty) 02.00.04 Physical Chemistry (PС-2);
* the ability and readiness to carry out activities aimed at preparing and receiving scientific grants and entering into the physical chemistry research agreements (PС-3);
* the ability and readiness for pedagogical activity in the field of vocational training in higher educational institutions, additional vocational education, professional educational institutions in the field of physical chemistry (PС-4).
* the ability to develop educational programmes as well teaching and learning aids in the field of physical chemistry (PC-5).

1. **STUDY TIME STRUCTURE AND ALLOCATION**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Discipline | Term | Amount of time allocated for mastering the module disciplines | | | | | | |
| In-class learning, hours | | | | Self-guided work, hours | Discipline attestation (test, exam) | Total,  hour/credit |
| Total | Lectures | Practical exercises  занятия | Laboratory work |
| Physical chemistry | 4 | 4 | 4 |  |  | 104 | Exam, Term 6 | 108/3 |
| Mastering, total | | 4 | 4 |  |  | 104 |  | 108/3 |

|  |  |  |  |
| --- | --- | --- | --- |
| 1 | **Section 1. Fundamentals of Chemical Thermodynamics**  Theme 1. Basic concepts of thermodynamics. Reversible and irreversible processes. Equations of state. Heat and work of various kinds. The first law of thermodynamics. Internal energy. Enthalpy. The law of thermochemistry. Dependence of heat capacity on temperature and calculations of thermal effects of reactions.  Theme 2. The second law of thermodynamics. Entropy. Equation of the second law of thermodynamics for reversible and irreversible processes. The Carnot - Clausius theorem. Entropy as a function of state. Changes in entropy for various processes.  Theme 3. Fundamental Gibbs equations. Characteristic functions. Helmholtz energy, Gibbs energy. The Maxwell equation. The relation between the caloric and thermodynamic variables. The equilibrium conditions and the criteria for the spontaneous flow of processes expressed through the characteristic functions. Chemical potentials. | 12 |  |
| 2 | **Section 2. Chemical and adsorption equilibria**  Theme 1. The law of mass action. Different types of equilibrium constants and the bonds between them. The chemical variable. Chemical equilibrium in ideal and non-ideal systems. Thermodynamic derivation of the law of mass action. The role of activity coefficients. The change in the Gibbs energy and Helmholtz energy in a chemical reaction. Equilibrium constants calculations of chemical reactions using tables of standard values of thermodynamic functions. Calculations of the yield of products of chemical reactions of various types. Outputs of products in the joint flow of chemical reactions.  Theme 2. Dependence of the reaction equilibrium constant on temperature. Equations of the isobar and isochore of a chemical reaction and their thermodynamic yield. The use of different approximations for the specific heats of reagents in calculating chemical equilibria at different temperatures. Heterogeneous chemical equilibria and features of their thermodynamic description.  Theme 3. Phenomena of adsorption. Types of adsorption. Isotherms and isobars of adsorption. Henry equations. The constant of adsorption equilibrium. Langmuir equation. Adsorption from solutions. Gibbs adsorption. Polymolecular adsorption, its approximate description by the Brunauer-Emmett-Teller method (BET). Use of the BET equation to determine the surface of adsorbents. | 16 |  |
| 3 | **Section 3. Phase equilibrium. Solutions.**  Theme 1. The concept of phase, component, degree of freedom. Heterogeneous equilibria without chemical reactions. Conditions of phase equilibrium. The Gibbs phase rule. Phase transitions of the first kind. The Clapeyron-Clausius equation. Phase transitions of the second kind. The Ehrenfest equation, its derivation and application.  Theme 2. One-component systems and their state diagrams. Polymorphic phase transformations, enantiotropy and monotrophy. Two-component systems and their state diagrams. Peritectic transformation. Basic principles of physical and chemical analysis. Daltonides and bertholids. Three-component systems and their state diagrams.  Theme 3. Solutions of different classes. Different ways of expressing the composition of a solution. Ideal solutions. Thermodynamic classification of solutions. Mixing functions for ideal and non-ideal solutions. Extremely dilute solutions, strictly regular solutions and their properties. Partial molar quantities. The Gibbs-Duhem equation.  Theme 4. Colligative properties of solutions. Raoul's law. Ideal and non-ideal solutions and their properties. The activity method. Coefficients of activity and their definition. Standard states in determining chemical potentials of components. Symmetrical and asymmetrical reference frames. Solubility in ideal and extremely dilute solutions. Change in the solidification temperature of various solutions. Cryoscopic method. Osmotic phenomena. The Van't Hoff equation. Osmotic and membrane equilibria in solutions. The liquid-vapour equilibrium in two-component systems. The Gibbs - Konovalov laws. | 18 |  |
| 4 | **Section 4. Elements of statistical thermodynamics**  Theme 1. Micro and macro state of the system. Phase G- and р-spaces. Maxwell and functions. The Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein distribution laws. Statistical average of macroscopic quantities. Gibbs ensembles. The method of distribution functions for the canonical and microcanonical ensembles. Basic postulates of statistical thermodynamics.  Theme 2. The canonical Gibbs distribution function. Statistical expressions for the basic thermodynamic functions and their calculation in terms of sums according to the states. Statistical calculations of entropy. The molecular sum according to the states and the sum according to the states of the macroscopic system. The progressive sum according to the state. The rotational sum according to the states. The vibrational sum according to the states. Calculation of the equilibrium constants of chemical reactions in ideal gases by the method of statistical thermodynamics.  Theme 3. Point defects of crystal lattices. Vacancies. Interstitial particles. Equilibrium and non-equilibrium lattice defects. The sum according to the states and the thermodynamic properties of crystals with different kinds of point defects. Nonstoichiometric compounds and their thermodynamic properties. ‘Daltonids’ and ‘bertholids’ and their properties. | 14 |  |
| 5 | **Section 5. Elements of linear thermodynamics of non-equilibrium processes**  Theme 1. Description of irreversible processes in thermodynamics. Streams. Forces. Phenomenological laws for the rates of processes. Open and closed systems. Irreversible processes and the production of entropy. Dependence of the entropy production rate on the generalized flows and forces. Stationary state of the system and Prigozhin theorem.  Theme 2. Flows under the combined action of several forces. Onsager's reciprocity ratios and their applications in the linear thermodynamics of irreversible processes. Migration. Thermodiffusion. | 10 |  |
| 6 | **Section 6. Chemical kinetics**  Theme 1. Basic concepts of chemical kinetics. The reaction rate determination. Kinetic curves. Kinetic equations. The rate constant and the order of the reaction determination. Molecularity of elementary reactions. The kinetic law of mass action and the range of its applicability. Irreversible reactions of the first, second and third orders. Dependence of the rate constant on the temperature. The Arrhenius equation. Activation energy. Complicated reactions. Reversible reactions. Consecutive reactions. Kinetic curves of accumulation of particular products.  Theme 2. Chain reactions. Elementary processes of the origin, continuation, branching and chain termination. The length of the chain. Branched chain reactions. Kinetic features of branched chain reactions. The tongue of ignition. Photochemical reactions. The quantum yield. The Einstein law of photochemical equivalence. Determination of the kinetic constants of photochemical reactions.  Theme 3. The theory of active collisions. Calculation of the pre-exponential factor. The steric factor. Elementary acts of chemical reactions and the physical meaning of activation energy. The surface of the potential energy of interaction. The transition state method (of the activated complex). Statistical calculation of the rate constant. The main assumptions of the theory of the activated complex and the field of its applicability. Transmission coefficient. The thermodynamic aspect of the theory of the activated complex. Entropy of activation.  Theme 4. Catalysis. General principles of catalysis. Homogeneous catalysis. Acid-base catalysis. Classification of acid-base type reactions. Kinetics and the mechanism of specific acid catalysis reactions. Enzymatic catalysis. General information about the kinetics and mechanisms of enzymatic reactions. Heterogeneous catalysis. Determination of the heterogeneous catalytic reaction rate. Specific and atomic activity. Catalyst activity and selectivity. The role of adsorption in the kinetics of heterogeneous catalytic reactions. The activation energy of heterogeneous catalytic reactions. The theory of the Balandin multiplets. Principles of geometric and energy matching. The theory of Kobozev active ensembles. Oxidation-reduction reactions on oxide catalysts. Boreskov`s works. | 18 |  |
|  | **Section 7. Electrochemistry**  Theme 1. Solutions of electrolytes. The Arrhenius theory and its shortcomings. The energy of the crystal lattice and the energy of salvation. Ion-dipole interaction. Average activity and the average activity coefficient. The Debye-Gückel theory.  Theme 2. Non-equilibrium phenomena in solutions of electrolytes. Diffusion and migration flows. The Nernst-Einstein formula. The diffusion potential. Specific and equivalent conductivity. Transfer numbers and methods for their determination. The mobility of ions and the Kohlrausch law. Dependence of mobilities, equivalent electrical conductivity and transfer numbers on concentration according to the Debye-Guckel-Onsager theory.  Theme 3. The concept of electrochemical potential and the condition of electrochemical equilibrium at the interface of phases. Equilibrium electrochemical chains and their EMF. The Nernst formula and the Gibbs-Helmholtz equation. The concept of electrode potential. Classification of electrodes and electrochemical circuits. Surface, external and internal potentials; the potential difference between Galvani and Volta. The double electric layer. Electrocapillary phenomena; the basic equation of electrocapillarity. The capacity of the double layer. Basic model concepts of the structure of the ionic double layer.  Theme 4. Current density as a measure of the speed of the electrode process; polarisation of electrodes. Stages of the electrode process. Dependence of the current on the potential under conditions of slow steady-state diffusion to a flat electrode. Polarography; qualitative and quantitative polarographic analysis. Equation for the current in the theory of delayed discharge. Current exchange and overvoltage. Methods of protecting metals from corrosion. Chemical sources of current. | 20 |  |
|  | TOTAL | 108 | 3 |

**3.2 DISTRIBUTION OF THE DISCIPLINE EDUCATIONAL TIME VOLUME BY TOPIC AND WORK TYPE**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Code of section, topic | Discipline section, topic | Amount of study time allocated for mastering the discipline, credit/hour | | | | | |
| In-class learning | | | | Self-guided work | Section, total |
| total | including lectures | including seminar/ practical exercises | Including laboratory work |
| Р1 | Section 1. Fundamentals of the chemical thermodynamics. | 1 | 1 |  |  | 11 | 12 |
| Р2 | Section 2. Chemical and adsorption equilibria. |  |  |  |  | 16 | 16 |
| РЗ | Section 3. Phase equilibrium. Solutions. | 1 | 1 |  |  | 17 | 18 |
| Р4 | Section 4. Elements of the statistical thermodynamics. |  |  |  |  | 14 | 14 |
| Р5 | Section 5. Elements of the linear thermodynamics of non-equilibrium processes. |  |  |  |  | 10 | 10 |
| Р6 | Section 6. Chemical kinetics. | 1 | 1 |  |  | 17 | 18 |
| Р7 | Section 7. Electrochemistry. | 1 | 1 |  |  | 19 | 20 |
| Discipline, total | | 4 | 4 | 4 |  |  | 104 |

3.3 Self-guided work of the post-graduate students

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| --- | --- | --- | --- |
| Sections of the work programme for independent study | List of tasks for independent work (research papers, reports, translations, calculations, experiment planning etc.) | Work input | |
| Hours | Credits |
| Section 1. Fundamentals of the chemical thermodynamics. | Working with the recommended literature, reviewing abstract journals and electronic sources taking into account the content of the discipline (writing abstracts). | 11 |  |
| Section 2. Chemical and adsorption equilibria. | Reviewing abstract journals and electronic sources taking into account the discipline content (preparation of a report). | 16 |  |
| Section 3. Phase equilibrium. Solutions. | Working with the recommended literature, reviewing abstract journals and electronic sources taking into account the discipline content (writing abstracts). | 17 |  |
| Section 4. Elements of the statistical thermodynamics. | Working with the recommended literature, reviewing abstract journals and electronic sources taking into account the discipline content (writing abstracts). | 14 |  |
| Section 5. Elements of the linear thermodynamics of non-equilibrium processes. | Working with the recommended literature, reviewing abstract journals and electronic sources taking into account the discipline content (writing abstracts). | 10 |  |
| Section 6. Chemical kinetics. | Working with the recommended literature, reviewing abstract journals and electronic sources taking into account the discipline content (writing abstracts). | 17 |  |
| Section 7. Electrochemistry. | Working with the recommended literature, reviewing abstract journals and electronic sources taking into account the discipline content (writing abstracts). | 19 |  |
|  |  | 104 |  |

**4. DISCIPLINE LEARNING OUTCOME REQUIREMENTS**

An objective assessment of the level of compliance of the learning outcomes with the educational programme learning requirements is secured by a set of developed criteria (indicators) for assessing the knowledge acquisition, skills development and experience in performing the professional tasks.

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| --- | --- | --- | --- |
| Competence components | Features of the level of mastering competence components | | |
| threshold level | higher level | high level |
| Knowledge | A post-graduate student demonstrates the acquaintance knowledge, copy knowledge, i.e. recognises objects, phenomena and concepts, finds some differences in them, shows the knowledge of the sources of information, can independently carry out reproductive actions on knowledge by self-reproduction and application of the information. | A post-graduate student demonstrates the analytical knowledge, i.e. confidently reproduces and understands the acquired knowledge, assigns them to one or another classification group, independently arranges them, establishes interrelations between them and effectively applies them in familiar situations. | A post-graduate student can independently obtain new knowledge from the surrounding world and creatively use it to make decisions in new and unusual situations. |
| Skills | A post-graduate student is capable of correctly performing the prescribed actions following the instructions and/or an algorithm in a known situation, independently performing actions to address typical issues that require a choice from among the known methods, in predictably changing situations | A post-graduate student is capable of independently performing the actions (techniques, operations) to solve non-standard problems that require selection based on a combination of known methods, in an unpredictably changing situation | A post-graduate student is capable of independently performing the actions associated with solving research problems, demonstrates the creative use of skills (technologies) |
| Personal qualities | A post-graduate student has a low learning motivation, shows an indifferent, irresponsible attitude to studying and/or the assigned task. | A post-graduate student has a pronounced learning motivation and demonstrates a positive attitude towards learning and future activities, and is active. | A post-graduate student has a developed motivation for training and work, shows perseverance and enthusiasm, hard work, independence and creativity. |

**5. APPRAISAL TOOLS TO ENSURE THAT THE ACADEMIC PROGRESS CAN BE REGULARLY MONITORED AND INTERMEDIATE ATTESTATION CONDUCTED**

**The list of test questions (the verifiable competences UC-1, UC-2, PC-1 - PC-5)**

1. Thermodynamic basis for the creation of state diagrams.

2. Principles of the thermodynamic equilibrium displacement. Van der Waals equations.

3. Electrochemical methods for determining the thermodynamic characteristics.

4. Kinetics of solid-phase interactions.

A list of questions for the exam (verifiablecompetences UC-1, UC-2, UC-3, GPC-1, GPC-2, GPC-3, PC-1 - PC-5)

1. Thermodynamic systems and the thermodynamic method of their description.

2. Thermal equilibrium of the system. Thermodynamic variables. Temperature. Intensive and extensive values.

3. Heat capacities. Caloric and thermal values. Reversible and irreversible processes.

4. Heat and work of various kinds. Calculation of the work of expansion for various processes and various gases. The first law of thermodynamics. Internal energy.

5. Enthalpy. Hess’s law and its consequences. Standard states and standard heats of chemical reactions. Heats of combustion. Heats of formation.

6. Dependence of the reaction thermal effect on the temperature. The Kirchhoff formula. Dependence of heat capacity on the temperature and calculations of thermal effects of reactions.

7. The second law of thermodynamics and its various formulations. Entropy. Equation of the second law of thermodynamics for reversible and irreversible processes.

8. Entropy as a function of state. The change in entropy for various processes. The change in the entropy of an isolated system and the direction of the process.

9. Fundamental Gibbs equations. Characteristic functions. Helmholtz energy, Gibbs energy and their properties. The Maxwell equation. Using the Maxwell equation for deriving various thermodynamic relationships.

10. The relationship between the caloric and thermodynamic variables. Methods for calculating entropy, internal energy, enthalpy, Helmholtz energy and Gibbs energy. The equilibrium conditions and the criteria for the spontaneous flow of processes expressed through the characteristic functions.

11. Chemical potentials, their definition, calculation and properties.

12. The law of the mass action. Different types of equilibrium constants and the relation between them. Thermodynamic derivation of the law of mass action.

13. Dependence of the reaction equilibrium constant on the temperature.

14. Equations of the isobar and isochor of a chemical reaction and their thermodynamic yield.

15. Phenomena of adsorption. Types of adsorption. Isotherms and isobars of adsorption. Henry's equations. The adsorption equilibrium constant. The Langmuir equation, its thermodynamic yield.

16. Heterogeneous equilibria without chemical reactions. Conditions of phase equilibrium. The concept of phase, component and degree of freedom.

17. The Gibbs phase rule, its derivation.

18. Phase transitions of the first kind. The Clapeyron-Clausius equation and its application to various first-order phase transitions. Steam pressure curves.

19. Phase transitions of the second kind. The Ernfest equation, its derivation and application.

20. One-component systems and their state diagrams (examples). Analysis of the course of the diagram lines on the basis of the Clausius-Clapeyron equation. Polymorphic phase transformations, enantiotropy and monotropy (examples).

21. Two-component systems and their state diagrams. Peritectic transformation.

22. Basic principles of physical and chemical analysis. Daltonides and bertholids.

23. Three-component systems and their state diagrams.

24. Solutions of different classes. Different ways of expressing the composition of a solution. Ideal solutions.

25. Thermodynamic classification of solutions. Mixing functions for ideal and non-ideal solutions. Extremely dilute solutions, strictly regular solutions and their properties.

26. Partial molar values ​​and their determination from experimental data (for binary systems). The Gibbs-Duhem equation.

27. Pressure of saturated vapor of liquid solutions. Raoul's law. Ideal liquid solutions and their determination.

28. Non-ideal solutions and their properties. The activity method. Coefficients of activity and their determination by the partial pressures of the components.

29. Standard states in determining chemical potentials of the components. Symmetric and asymmetrical reference frames.

30. Solubility in ideal and extremely dilute solutions. Change in the solidification temperature of various solutions. The cryoscopic method.

31. Osmotic phenomena. The Van’t Hoff equation, its thermodynamic conclusion, and the range of applicability. Osmotic and membrane equilibria in solutions.

32. The liquid-vapour equilibrium in two-component systems. Equilibrium compositions of vapour and liquid. Different types of state diagrams.

33. Basic concepts of chemical kinetics. Determination of the reaction rate. Kinetic equations. Determination of the rate constant and the order of the reaction. Molecularity of elementary reactions.

34. Dependence of the rate constant on the temperature. The Arrhenius equation.

35. Irreversible reactions of the first, second and third orders. Determination of the rate constants from the experimental data. Methods for determining the reaction order and the kinetic equation form.

36. Complicated reactions. The principle of independence of elementary stages. Parallel reactions.

37. Sequential reactions on the example of two irreversible first-order reactions. Kinetic curves of accumulation of particular products and determination of rate constants from experimental data.

38. Chain reactions. Elementary processes of the origin, continuation, branching and chain termination. The length of the chain. Kinetics of chain reactions.

39. The method of transition state (of the activated complex). Properties of the activated complex. Statistical calculation of the rate constant. The main assumptions of the theory of the activated complex and the field of its applicability. The transmission coefficient.

40. The thermodynamic aspect of the theory of an activated complex. Entropy of activation. The relation between the experimental and the true activation energy.

41. The theory of collisions in chemical kinetics. Advantages and disadvantages of the collision theory.

42. Photochemical reactions. Elementary photochemical processes. Photochemically active particles. The quantum yield. The Einstein law of photochemical equivalence.

43. General principles of catalysis. The role of catalysis in chemistry. Homogeneous catalysis. Acid-base catalysis.

44. Basic concepts of the Arrhenius theory. Drawbacks of this theory.

45. The energy of the crystal lattice and the energy of salvation.

46. ​​The thermodynamic description of the ion-ion interaction. The concepts of the average activity and the average activity coefficient; their relation to the activity and the activity coefficient of individual ions.

47. The main assumptions of the Debye-Gückel theory; their physical meaning. The potential of the ionic atmosphere. Equations for the coefficient of activity in the first, second and third approximation of the Debye-Gückel theory.

48. Diffusion and migration flows. The Nernst-Einstein formula.

49. Specific and equivalent electrical conductivity.

50. Transfer numbers and methods for their determination.

51. The mobility of ions and the Kohlrausch law. Dependence of mobilities, equivalent electrical conductivity and transfer numbers on concentration in the framework of the Debye-Guckel-Onsager theory.

52. Dependence of the limiting mobilities on the ion radius and temperature.

53. The concept of the electrochemical potential and the condition of electrochemical equilibrium at the interface of phases.

54. Equilibrium electrochemical chains and their EMF. The Nernst formula and the Gibbs-Helmholtz equation.

55. Classification of electrodes and electrochemical circuits.

56. Determination of activity coefficients and transport numbers based on EMF measurement.

57. Current density as a measure of the speed of the electrode process; polarization of electrodes. Stages of the electrode process.

58. Equation for the current in the theory of delayed discharge. Current exchange and overvoltage.

**Electronic educational resources**

Zonal Scientific Library http://library.urfu.ru/

Catalogues of the library http://library.urfu.ru/about/department/catalog/rescatalog/

Electronic catalogue http://library.urfu.ru/resources/ec/

Resources http://library.urfu.ru/resources

Search http://library.urfu.ru/search;

**Databases, information, reference and search systems**

ScienceDirect Electronic Resources: http://www.sciencedirect.com

Electronic resources WebofScience: http: //apps.webofknowledge.com

Electronic resources ScienceDirect: http: // www. scifinder.com

Electronic Resources WebofScience: http://reaxys.org Scopus

Electronic Resources: http://www.scopus.com/