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XXV INTERNATIONAL CONFERENCE ON CHEMICAL THERMODYNAMICS IN RUSSIA (RCCT 2026)

Book of Abstracts of the XXV International Conference
on Chemical Thermodynamics in Russia (RCCT-2026)

June 29 – July 3, 2026

Ekaterinburg
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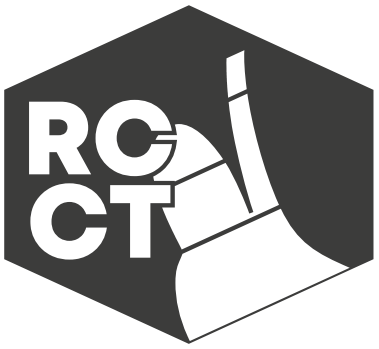

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RCCT ("Russian Conference on Chemical Thermodynamics", or "International Conference on Chemical Thermodynamics in Russia") is one of the most significant scientific events in Russia. This Book of Abstracts includes contributions from the leading scientists, affiliated with Russian and foreign academic institutions, to the field of chemical thermodynamics. The topics include, but are not limited to, fundamental issues of chemical thermodynamics, thermodynamic properties of solids, solutions and fluids, thermodynamic modeling and databases, and thermodynamic aspects of synthesizing, analyzing and predicting the properties of novel materials.

This book holds significant relevance to students, researchers and general public who are interested in the state of the art and cutting edge of modern chemical thermodynamics.

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PLENARY LECTURES

ПЛЕНАРНЫЕ ДОКЛАДЫ

CHEMICAL THERMODYNAMIC STUDY OF ENERGY MATERIALS

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Energy materials serve as the carriers for energy conversion, storage, and utilization. In these energy-related processes, chemical thermodynamics plays an irreplaceable role in providing guiding principles for the efficient conversion and clean utilization of energy materials. Consequently, the study of the thermodynamic properties of energy materials is of great significance for the design and synthesis of advanced energy materials. In this lecture, I will discuss the recent research progress of our group in the chemical thermodynamic study of energy materials. First, I will present our work on constructing adiabatic calorimeters for thermodynamic property measurement. We designed and developed a refrigerator-cooled adiabatic calorimeter for measuring the heat capacity of condensed matters within the temperature range of 4 to 100 K. The optimized repeatability and accuracy were determined to be within 0.8% and 1.5%, respectively. Additionally, we developed an adiabatic calorimeter for thermal safety assessment and used it to study the thermal decomposition reaction of di-tert-butyl peroxide. Second, I will elaborate on the thermodynamic property studies of various energy materials, including phase change materials (PCMs), magnetic materials, and CO_2 adsorption materials. These studies demonstrate that heat capacity calorimetry is a powerful tool for investigating the thermodynamic properties of energy materials. Finally, I will introduce the concept of "Spatiotemporal Phase Change Materials" we proposed recently, in which the thermodynamic properties of PCMs can be regulated to achieve controllable utilization of latent heat. Based on this concept, we designed and synthesized a series of erythritol-based composite phase change materials, which show promising potential in the field of long-term thermal energy storage and controllable utilization. In summary, this lecture outlines the research work of our group in calorimetry techniques, thermodynamic property analysis and regulation of energy materials, highlighting the critical role of chemical thermodynamics in the research and practical application of energy materials.

THERMODYNAMIC TUNING AND DATABASE ON NEW ENERGY MATERIALS

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New energy materials have attracted many researchers' attention. Hydrogen is regarded as one of the most promising alternatives to the energy crisis due to its high heating value, wide availability, and environmental compatibility. The primary technical components of the hydrogen energy system cover the production, supply, storage, conversion, and employment of hydrogen, among which the storage and conversion of hydrogen are consistently the keys to the effective utilization of hydrogen energy. Studies of economic, highly efficient, and safe hydrogen storage materials are of great importance in fuel cell-based vehicles. On the other hand, the application of phase change materials (PCMs) for solar thermal-energy storage has received considerable attention in recent years due to their high storage density.

In recent years, our research effort has been focused in developing hydrogen storage and PCMs based on micro/nano-technology, Li ion battery, fuel cells, hydrogen sensors, etc. The promising nanomaterials for hydrogen storage materials such as MH_x: M= Mg, La, Ni, etc., alanate, borohydride, and MOFs were conducted in our lab. Several composite PCMs with good performance have been synthesized through in-situ assembly, and their applications in thermal regulation of gypsum boards are presented.

The data-driven research paradigm-integrated high-throughput calculations, database, and machine learning is appealing to accelerate new material development. Recently, we will introduce our results on establishing a Materials Genome Initiative database and the property prediction based on machine learning for hydrogen-storage materials. Finally, we will summarize the thermodynamic regulation and database construction for hydrogen/heat energy storage and some other recent results in my group.

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THERMODYNAMIC INVESTIGATION OF NEW ORGANIC AND POLYMERIC MATERIALS

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Knowledge of the thermodynamic properties of chemical compounds and materials allows us to determine the best options for the processes involving them. The introduction of new materials in various fields of science and technology requires the study of the physico-chemical properties of compounds to optimize their production processes and rational use. Precision calorimetry is a powerful tool for studying the fundamental physico-chemical characteristics (heat capacity, enthalpy, entropy, thermodynamic potentials) of substances and materials. The most important aspect of this study is the determination of the thermodynamic characteristics of phase transitions.

In this work, the phase transitions of macromolecular nanoobjects (organosilicon and liquid crystal dendrimers of various natures, polypeptides, active pharmaceutical substances, bistable transition metal complexes with complex organic ligands, and organic derivatives of fullerene C60 and C70 were studied over a wide temperature range (6-650 K). Using low-temperature adiabatic calorimetry, the temperature dependences of their heat capacities were studied, the thermodynamic characteristics of phase transitions were determined, including the values of configuration and zero (residual) entropy; their physico-chemical interpretation was carried out taking into account the composition and structure of compounds. For the first time, using precision calorimetry methods, structural effects in dendrimers were revealed: a low–temperature anomaly caused by subtle vibrations of fragments of the inner sphere and the surface layer of macromolecules (G1–G4), as well as a high-temperature relaxation transition ("nanoscale effect") for G5-G6 dendrimers; a hypothesis of the occurrence of transformations was proposed and discussed; their thermodynamic properties were determined and analyzed. characteristics for several representatives of a number of dendrimers. Along with the peculiarities of the molecular structure, the identified effects open up new possibilities for using dendrimers for medical purposes, namely for targeted drug delivery to affected cells of the body. Polymorphic transitions have been identified for pharmaceutical substances in the crystalline state; their thermodynamic characteristics (temperature, enthalpy, entropy) have been determined and analyzed. In the case of some substances, thermodynamically metastable (supercooled) states were obtained.

A complex of standard thermodynamic functions has been defined for all the studied objects, which is necessary for modeling various processes involving promising materials and constructing phase diagrams. The revealed «structure – property» relationships are of interest for predicting the properties of compounds and functional materials based on them that have not yet been studied.

This work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (FSWR-2026-0013).

MULTICOMPONENT EQUIATOMIC SOLID SOLUTIONS

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Multicomponent solid solutions are of interest from scientific and practical point of view. Thus, this review describes several methods of synthesis of such solid solutions, their disordered atomic structure and novel functional properties.

Development and preparation of materials with prescribed properties is one of the tasks of chemistry. Traditional method of solving such a task for metallic materials consist of selection of base chemical element and post doping of this element by others elements in low amounts. Nevertheless about 20 years ago the development of materials made of five or more elements with nearly equivalent amount is began.

As a result, almost simultaneously by few independent groups of researches a new type of materials were developed and named as high-entropy materials. High-entropy materials are groups of constrictive and functional materials based on multicomponent equiatomic solid solutions [1].

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BEYOND POINT-LIKE CHARGE MODEL: A SELF-CONSISTENT THEORY FOR ELECTROLYTE CONDUCTIVITY

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In this plenary talk, we will discuss the Self-Consistent Debye-Hückel-Onsager (SCDHO) theory [1], a major theoretical advancement in understanding electrolyte conductivity. This theory incorporates the non-local charge distribution of solvated ions, going beyond the point-charge approximation used in classical theories for almost a century. We model ions with Slater-type charge form factors to regularize the Coulomb potential at short distances. This captures the fact that an ion's charge is distributed over a finite volume due to its electronic structure and solvation shell. Our theoretical framework is based on a solid foundation in statistical mechanics, combining classical density functional theory (cDFT) with the Ornstein-Zernike formalism. This approach provides analytical expressions for three key factors contributing to ionic conductivity: the mean-field effect, the correlation (aka relaxation) effect arising from the distortion of the ionic atmosphere, and the electrophoretic effect resulting from hydrodynamic drag. Importantly, we find that the electrophoretic effect predominates at high concentrations, while the correlation effect becomes negligible. This result clarifies long-standing questions about the relative significance of these effects and provides a more accurate understanding of ionic conductivity. The predictive power of the SCDHO theory has been demonstrated through extensive validation against experimental data. We have successfully reproduced molar conductivities for a wide range of electrolytes, including 1:1, 2:1, and 3:1 salts, over a concentration range from dilute to highly concentrated solutions. The model accurately captures the temperature dependence using only known solvent properties, without the need for additional fitting parameters. It also extends seamlessly to non-aqueous solvents, such as methanol, ethanol, and dimethyl sulfoxide.

A particularly interesting outcome is the determination of ion-specific charge smearing lengths. These parameters can be transferred across different electrolyte systems and have a clear chemical meaning. For halides, the smearing length increases as we move from fluoride to iodide, reflecting trends in electronic polarizability and the solvation shell structure. The framework we have developed is general and can be applied to multi-electrolyte solutions. Furthermore, by reducing the empirical component by calculating smearing lengths from first principles, we can transform the SCDHO theory into a fully predictive tool. This work provides a robust and physically grounded framework for predicting electrolyte conductivity over a wide range of conditions, with significant implications for areas such as electrochemistry, energy storage, and biophysics.

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QUANTIFICATION OF DISPERSION INTERACTIONS BY USING THERMOCHEMICAL METHODS

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Dispersion is the superordinate concept for attractive forces, which act between separated molecules or molecular fragments even in the absence of charges or permanent electric moments. These interactions are generally responsible for the thermodynamic stability and the structuring of the solid and the liquid state. Dispersion forces between molecules are much weaker than the covalent bonds within molecules. Due to this reason, it is not easy to give a quantitative interpretation of dispersion, because the size of the attraction varies considerably with the size of interacting molecules and their shape.

In this lecture we show our understanding of dispersion forces in large molecular systems and quantify them using experimental thermodynamic methods. Experimental methods: combustion calorimetry, differential scanning calorimetry, solution calorimetry, as well as with thermogravimetry and vapour pressure determination using Quartz Crystal Microbalance method, Knudsen method, transpiration technique, and static method). Theoretical methods: high level ab initio methods as well as correlation approaches between energetic properties and the structure of the molecules.

In the focus of this study are aromatic hydrocarbons, where attractive forces between $\pi-\pi$ orbitals of benzene rings could stabilize energetics of the molecule. Moreover, dispersion forces are analyzed in homologous series of the molecular and ionic compounds. The combination of experimental methods for determination of the interaction in the condensed phase with theoretical methods allows for quantification of dispersion interactions in the condensed phase and in gas-phase.

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SCIENTIFIC LEGACY OF NATALIA SMIRNOVA: PHYSICAL CHEMISTRY FROM THE PERSPECTIVE OF MOLECULAR THERMODYNAMICS

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Conferences of this series started 65 years ago, but we owe to Natalia Smirnova the rebirth of these conferences (under the present name and logo) in 2002, after an almost 10-year break.

Corresponding member of RAS Natalia Alexandrovna Smirnova (1933-2023) is widely known for her outstanding contribution to Physical Chemistry. Professor and Chair of Physical Chemistry at St. Petersburg State University, the recipient of numerous scientific and State awards, she served on the editorial boards of several reputable journals and chaired Section of Physical and Colloid Chemistry of the Mendeleev Russian Chemical Society.

Her early scientific career started under the leadership of Prof. Storonkin, within the walls of the world-famous St.Petersburg Thermodynamic school that traces back to Konovalov and Vrevsky in the early 1900s. Later, her pioneering works combined experiment, theory and computer simulation in the studies of phase equilibria and interfacial phenomena, liquid crystals and self-assembly in complex fluids [1-4].

The novelty of her approach lied in extensive use of Statistical Thermodynamics for solving problems of Physical Chemistry, and in a while she herself became an internationally recognized leader of St.Petersburg school of Molecular Thermodynamics. More than 10 years prior to the appearance of the celebrated SAFT theories, she formulated the same idea in different mathematical language for the description of nonuiniform fluids [1]. Her excellent textbook [5] translated in many languages is part of curricula of many generations of undergrads and PhD students studying Chemistry. More than 20 PhD and 4 DrSci degrees have been performed under her supervision. Colleagues and former students keep in memory her bright personality and outstanding mentorship.

Some of the original Smirnova's ideas are applied and developed further in a number of contributions at this conference.

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HEXAALUMINATES WITH MAGNETOPLUMBITE STRUCTURE FOR ADVANCED THERMAL BARRIER COATINGS: THERMODYNAMIC AND THERMOPHYSICAL PROPERTIES

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To protect parts of power plant and aircraft engine turbines that are explored at high temperatures and high-temperature corrosion, thermal barrier coatings (TBC) are used, which have a number of requirements for thermal conductivity, thermal expansion, corrosion resistance at high temperatures and long-term stability [1]. An increase in turbine efficiency can be achieved by using advanced ceramic coatings with higher performance. In particular, hexaaluminates with a magnetoplumbite structure are among the most promising candidates for TBC [2].

Based on experimental measurements of heat capacity, enthalpy of formation, thermal expansion, and thermal conductivity were made the conclusions about the prospects of using magnetoplumbite structure hexaaluminates $LaAl_{11}O_{18}$, $REMgAl_{11}O_{19}$ (RE=La-Gd), $LaM(II)Al_{11}O_{19}$ (M(II)=Mn,Zn,Co,Cu), as well as solid solutions $(NdSmGd)_{1/3}MgAl_{11}O_{19}$, $(LaPrNdSm\ Gd)_{1/5}MgAl_{11}O_{19}$, $La(MgMnCu)_{1/3}Al_{11}O_{19}$, $La(MgMnZnCoCu)_{1/5}Al_{11}O_{19}$ as components of TBC materials.

The stability of the studied hexaaluminates in the high temperature range was analyzed based on the temperature dependence of the Gibbs energy of possible decomposition reactions into simpler oxides. The assessment of corrosion resistance to the effects of oxides of the CMAS group was carried out by DSC and XRD, as well as by model calculation. Thermal expansion was determined by dilatometry and X-ray diffraction. Thermal conductivity in the high temperature range was calculated from thermal diffusivity data determined by the laser flash.

As a result of the performed studies, the most promising mixed oxides were identified. For hexaaluminates with the magnetoplumbite structure the influence of the number of components of solid solutions on the enthalpy and entropy components of the Gibbs energy of formation is assessed.

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The study was supported by Russian Science Foundation project 23-13-00051, https://rscf.ru/en/project/23-13-00051/

SCIENTIFIC SCHOOL OF ACADEMICIAN Y.D. TRETYAKOV IN THERMODYNAMICS AND MATERIALS SCIENCE

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Scientific School of academician Y.D.Tretyakov has manifested itself as a platform of alloying fundamental and practices – oriented research directions in inorganic, physical, solid state chemistry and materials sciences and it still plays a unique role in modern Russian science and education. In the contest of innovative development of perspective inorganic materials with advanced properties, the school is based on the legacy of academician Y.D.Tretyakov in thermodynamics, kinetics and the real structure concept of functional, nano- and biomaterials.

In the talk, several remarkable research directions of academician Y.D.Tretyakov and its scientific school in the frame of materials micro-revolutions will be presented:

– phase diagrams, calorimetry, thermodynamic research and defect chemistry of advanced ferrite systems for the development of magnetic materials, also, a formal kinetic approach for solid state reactions will be discussed as a powerful tool suggested by Y.D.Tretyakov,

– phase diagrams, microstructure, defects and melt processing of rare-earth barium cuprates for manufacturing high-temperature superconducting materials, also, a topochemical memory concept will be discussed in the contest of the real structure of solids,

– phase diagrams, microstructure, whisker crystal growth of various manganites, including those with colossal magnetoresistance,

– biomaterials research for the sake of their medical implementation,

– size and shape effects of silver nanoparticles for the Surface Enhanced Raman Spectroscopy analysis of ecotoxicants and biolological objects, nanomaterials for teranostics,

– educational issues for the development of materials science and its chemical aspects in Russian Federation exemplified on the experience of the faculty of materials science of Lomonosov Moscow State University founded and headed by academician Y.D.Tretyakov.

IMPORTANCE OF DEFECT CHEMISTRY FOR UNDERSTANDING THE THERMODYNAMIC PROPERTIES OF OXIDES WITH AND WITHOUT OXYGEN EXCHANGE

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Only thermodynamic analysis can unambiguously determine the compounds' stability and compatibility under particular conditions. However, such analysis requires the knowledge of temperature-depended Gibbs free energies, which can be derived from the enthalpy of formation and heat capacity data. Drop calorimetry is currently the most widely used techniques for the heat capacity measurements above room temperature. This technique is suitable nonstoichiometric oxides that exhibit oxygen exchange since the sample has enough time to reach equilibrium with environment at the measurement temperature.

For such oxides, the enthalpy increments should be recalculated so as to correspond to constant oxygen content by subtracting the enthalpy of oxygen exchange, which in turn is estimated using the defect structure model. The as obtained enthalpy increments of the constant-composition oxides are then fitted with the integrated $C_p(T)$ functions. The latter depends strongly on the composition of an oxide with respect to metals since they can undergo spin transition and charge disproportionation as it occur in cobalt-contained both cubic [1] and double perovskites [2].

For the oxides that do not exhibit the spin state transition above room temperature, $C_p(T)$ can be taken as equal to the sum of Einstein term, modified by taking into account the anharmonicity of atomic vibrations, and charge disproportionation contribution. The noticeable value of the latter highlights the seldom mentioned importance of defect chemistry for discussing the thermal properties of oxides, especially those containing cations that can change their oxidation state, even in the absence of oxygen exchange.

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2. R.E. Yagovitin et al. Thermodynamics of Formation and Disordering of $YBaCo_2O_{6-\delta}$ Double Perovskite as a base for Novel Dense Ceramic Membrane Materials. Membranes 2023, 13, 10. https://doi.org/10.3390/membranes13010010

CONFORMATIONAL EQUILIBRIA AT THE CRYSTAL-SUPERCRITICAL FLUID INTERFACE

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Supercritical fluids technologies(SCF) are increasingly being used for the synthesis and targeted modification of materials and composites. In pharmaceuticals, such materials are widely applied to enhance the bioavailability of drug formulations, control their release, and obtain multi-component crystals, among other applications. One promising SCF technology for pharmaceuticals is the formation of micronized particles for use in inhalers. The main advantages of SCF technologies for producing inhalation suspensions include the following: (a) the ability to obtain micronized forms of the target substance with control over the particle size of the resulting crystals across a wide range of state parameters; (b) a high degree of purity of the target product obtained using both rapid expansion of supercritical solution (RESS) methods and those based on the antisolvent effect (SAS), and (c) control over the polymorphism of the obtained target product by varying the thermodynamic parameters of the supercritical fluid during crystallization, which allows producing samples with the desired polymorphic purity.

Polymorphism screening is typically a completely empirical procedure. This report presents a new methodology for screening conformational polymorphism, based on a correlation discovered in the authors' previous works between the distribution of conformers of a drug compound dissolved in a supercritical solvent and the polymorph that forms under the studied state parameters. A methodology was developed for predicting polymorph formation, based on a combination of experimental (IR and NMR spectroscopy) and computational (quantum chemical calculations, molecular dynamics simulation, density functional theory) approaches. In order to understand the origin of correlation between of conformer population at fluid state and polymorfism MD simulation of three curcumin polymorphs at vacuum interfaces. More specifically, we employ layer-resolved molecular dynamics simulations to investigate the temperature evolution of the free surfaces of the three curcumin polymorphs along their low-index crystallographic faces. Across all systems, substantial structural rearrangements emerge well below the bulk melting temperature, consistent with the onset of thermally activated interfacial softening. However, both the onset temperature and the magnitude of the response are strongly anisotropic. By combining normalized layer displacement δR_[klm], positional fluctuations, joint position-tilt distributions, intermolecular packing descriptors (θ1,θ2), hydrogen-bond distance distributions, and conformational analysis, we resolve the coupled structural changes underlying this behavior.

This work was supported financially by the Russian Science Foundation (project 22-13-00257-P).

QUASI-EQUILIBRIUM OXYGEN RELEASE METHOD FOR STUDYING MATERIALS WITH MIXED IONIC - ELECTRONIC CONDUCTIVITY

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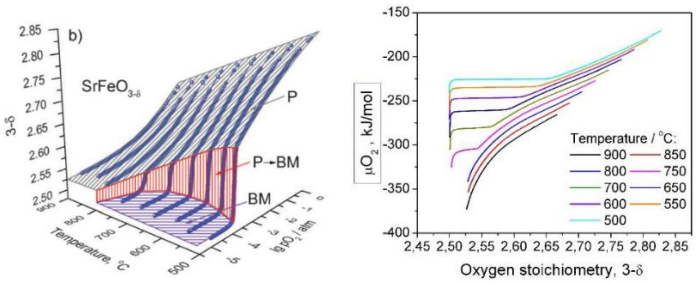
Nonstoichiometric oxides with mixed oxygen ionic and electron conductivity (MIEC), which typically possess a perovskite-like structure, have attracted sustained interest over the past several decades because they are promising materials for oxygen-permeable membranes and cathodes of solid oxide fuel cells (SOFCs) [1, 2]. The oxygen non-stoichiometry of MIEC oxides determines both the fundamental functional properties of membrane and electrode materials and the operating efficiency of catalytic membrane reactors and SOFCs. At the Institute of Solid State Chemistry and Mechanochemistry, a new method of quasi-equilibrium oxygen release (QEOR) has been developed, which makes it possible to obtain equilibrium dependences of oxygen nonstoichiometry on the partial pressure of oxygen (pO_2) and temperature (see figure) and to calculate thermodynamic parameters ($\Delta\mu(3-\delta)$, $\Delta H(3-\delta)$, $\Delta S(3-\delta)$) of oxygen exchange [3].



Equilibrium isotherms 3-δ - lg pO_2 and calculated from them chemical potential of oxygen in $SrFeO_{3-\delta}$ vs oxygen nonstoichiometry

Since changes in oxygen stoichiometry in MIEC oxides are accompanied by changes in the charge carrier concentration, the obtained data can be used to estimate the dependence of the density of states near the Fermi level on δ. The nature of the $\Delta H(3-\delta)$ and $\Delta S(3-\delta)$ dependences can be used to determine the conductivity type (metal-like or semiconductor). In addition, using the QEOR method, the dependence of the oxygen exchange reaction rate constant on the MIEC oxide surface on its chemical potential can be established in the form of the Brønsted-Evans-Polanyi relationship. Thus, thermodynamic parameters determine the important functional properties of MIEC materials and the operational efficiency of devices based on them.

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ON THE 75TH ANNIVERSARY OF THE DEPARTMENT OF CHEMICAL THERMODYNAMICS AND KINETICS OF SAINT PETERSBURG STATE UNIVERSITY

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The Department of Chemical Thermodynamics and Kinetics of Leningrad (now Saint Petersburg) State University was founded in 1951 by Professor Alexei Vasilyevich Storonkin (1916 – 1994). By this time, A.V. Storonkin was already a well-known scientist, the author of the monograph "On the conditions of thermodynamic equilibrium of multicomponent systems" (1948). The original name of the department ("Department of Theory of Solutions") reflected the continuity of the scientific school of St. Petersburg University, the origins of which were determined by the unprecedented contribution to world science of D.I. Mendeleev, D.P. Konovalov and M.S. Vrevsky.

The 1950s and subsequent years were a further development of the thermodynamic school, whose influence went far beyond the borders of St. Petersburg University. By 1978, the range of both scientific and pedagogical tasks had expanded even further, and the department received its current name. As noted in the paper [1], a thermodynamic school was created, "which can only be compared with the Dutch Van der Waltz school." The first graduates, as well as the first employees of the department (M.P. Susarev, A.G. Morachevsky, N.P. Markuzin, A.I. Rusanov, N.A. Smirnova and others) not only contributed to the development of A.V. Storonkin's ideas, but also became recognized as outstanding scientists with a worldwide reputation. For example, the scientific works of Academician A.I. Rusanov (an employee of the Department in 1955-1987, before being elected head of the Department of Colloidal Chemistry at St. Petersburg State University in 1987) are the basis of the modern thermodynamic theory of surface phenomena. With the name of academician M.M. Schultz (associate professor of the department in the early 1950s and professor in 1997 – 2006) is associated not only with work in the field of chemistry of the glassy state, but also with fundamental thermodynamic results, for example, in the field of stability theory. Corresponding member of the Russian Academy of Sciences N.A. Smirnova, a student of A.V. Storonkin and a graduate of the department is a well-known specialist in the field of statistical thermodynamics. Other graduates of later years still head the chemical departments of the largest universities in our country (A.I. Viktorov, M.V. Charykova, K.N. Semenov, A.M. Toikka and others). The report also provides other information about the contribution of the department and its staff (including professors V.T. Zharov and V.K. Filippov) to national and world science and education, their role in the development of chemical thermodynamics and related branches of physical chemistry.

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THERMODYNAMIC MODELLING: FROM THERMODYNAMIC DATABASE TO INDUSTRIAL PROCESS SIMULATION

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Since second half of the 20th century industrial-strength numerical methods of mathematic optimization emerged. Access to these methods led to computer-aided minimization of Gibbs energy, which gave birth to computational thermodynamics, the large part of which were gathered under the umbrella of the scientific field and society named Calculations of Phase Diagrams and Thermochemistry (Calphad).

The Calphad method is based on the basic idea of finding Gibbs energies as parametric regression models which are optimized using experimental and theoretical data with particular emphasis on a comprehensive critical evaluation of the data. This allows obtaining thermodynamic functions which are then used for carrying calculations of practical application use. In other words, thermodynamic modeling creates a bridge between experimental fundamental research and the application of its principles and data to practical problems.

However, in practice, the reactions occurring in real industrial processes are extremely complex. Therefore, the particular skill of materials scientists lies in their ability to decompose complex chemical processes into simpler reactions accessible to traditional thermodynamic analysis. Today, the active integration of computing resources and information technology into production processes makes these issues particularly relevant.

This report is devoted to main features of constructing thermodynamic models in the field of science and technology and differences between models developed by scientists and models in demand in practical calculations.

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THERMODYNAMICS OF COMPOSITIONALLY COMPLEX ("HIGH-ENTROPY") OXIDES

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In the current scientific literature, the "high-entropy oxide" (HEO) term is often applied rather loosely to oxides containing five or more metal cations within one sublattice, typically in equimolar proportions. In theory, if an assumption of random mixing holds true, such an oxide phase possesses a configurational entropy $\Delta S_{conf} \geq R\ln(5)$ per formula unit. This additional contribution to the total entropy of a HEO may boost its thermodynamic stability and is believed to play a significant, if not dominant, role in stabilizing some HEOs, especially those that are metastable at low temperatures. Consequently, HEO phases may comprise cations in atypical for them crystal structures – for instance, Zn and Cu in the rock-salt structure of (Co,Cu,Mg,Ni,Zn)O – possessing interesting properties that are not merely averages of the properties of simple oxide constituents. This possibility is what makes HEOs increasingly attractive research objects.

However, the great expectations for the enhanced stability and exceptional performance of high-entropy materials are not always met. Even in the field of high-entropy alloys, which have been investigated for nearly twice as long as HEOs, relatively few truly single-phase solid solutions have been identified, and their properties are often determined by the average of the properties of the constituting elements. Likewise, not always do the functional properties of HEOs exceed those of the "low-entropy" oxides. Therefore, while it is not known a priori what exact combination of elements will make up a HEO with outstanding characteristics, it is clear that arbitrary element selection is insufficient. The same applies to stability: one cannot expect to obtain a more stable material simply by adding more cations to an oxide sublattice. As of now, the stability issues of all HEOs, those with unique and mediocre properties alike, remain severely underinvestigated. Moreover, while valuable for rapid screening of the broad composition space in search of new HEOs, the statistical, empirical and purely computational approaches cannot yet be used for the deep analysis of stability and chemical compatibility of particular materials.

It is clear that enthalpy and all kinds of entropy (configurational, vibrational, electronic and magnetic) do contribute to formation and stability thermodynamics of compounds. The extent of these contributions remains to be ascertained with experimental thermodynamic methods. The results of such studies will be discussed in this talk.

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PECULIARITIES OF PHASE EQUILIBRIA IN OXIDE SYSTEMS BASED ON RARE EARTH, ALKALINE EARTH AND 3d (Fe, Co) METALS

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The results of a systematic study of phase equilibria in the oxide systems ½ Ln_2O_3 – MO – TO_x (Ln – rare earth elements; M – Ca, Sr, Ba; T = Fe, Co) at 1100°C in air are presented in the form of phase diagrams. It is shown that for M = Ca, Sr, the general appearance of the phase diagrams of systems containing iron and cobalt is similar, while for M = Ba, they differ significantly. The similarity of the diagrams of the first group implies the formation of solid solutions with the perovskite structure $(Ln_{1-x}M_x)TO_{3-\delta}$ and related representatives of the Ruddlesden-Popper type $(Ln_{1-x}M_x)_{n+1}T_nO_{3n+1-\delta}$ homologous series for practically all systems. The similarity of the diagrams, however, does not mean they are completely identical. As a rule, the homogeneity ranges of solid solutions in Sr-containing systems are much wider than in similar Ca-containing systems, and the set of Ruddlesden-Popper phases is larger in Fe-containing systems than in similar Co-containing systems.

A characteristic feature of Ba-containing systems, which distinguishes them from Ca- and Sr-containing analogues, is the formation of layered structures due to the increasing difference in the sizes of rare earth element and barium ions.

However, in Co-containing systems, the formation of a double perovskite phase $LnBaCo_2O_{6-\delta}$ is observed in air, whereas in similar Fe-containing analogous the formation of a triple-layered $LnBa_2Fe_3O_{8+w}$ (Ln = Dy, Ho, Y) or even a more complex quintuple perovskite structure $Ln_{2-\varepsilon}Ba_{3+\varepsilon}Fe_5O_{13+w}$ (Ln =Sm, Eu) is revealed. Fe-based double perovskites $LnBaFe_2O_{5+w}$ can also be obtained, but under much more severe reducing conditions ($Po_2 \approx 10^{-15}$ atm). It should be noted that the above-mentioned single-phase triple-layered 123-type ferrites exhibit significant nonstoichiometry in the metallic sublattices in air conditions, for example, $Y_{1.05}Ba_{1.92}Fe_{3.03}O_{8+w}$ or $Dy_{1.05}Ba_{1.95}Fe_3O_{8+w}$.

Another specific feature of phase relations in Ba-containing systems is the possibility of partial replacement of iron by a rare earth element in barium ferrite with the formation of cubic perovskite solid solutions $BaFe_{1-y}Ln_yO_{3-\delta}$ even for relatively large Pr. A similar substitution was also found in barium cobaltite $BaCo_{1-y}Ln_yO_{3-\delta}$, but for smaller rare earth elements (Ln = Sm, Y).

This work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (project № FEUZ-2026-0011)

FEATURES OF GIBBS EQUATION ($\Delta G = \Delta H - T\Delta S$) APPLICATION TO THERMODYNAMICS OF SOLVATION, VAPORIZATION, AND COMPLEX FORMATION IN SOLUTION AND GAS PHASES

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Gibbs equation is probably the most utilized in chemical thermodynamics. For a long time, researchers wondered whether there is a connection between the Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes in various processes, apart from the Gibbs equation. In this work, based on a large amount of experimental data (more than 5000 measurements), we analyzed the ΔG *vs.* ΔH relationship for the four types of processes: solvation, vaporization, electron donor acceptor and hydrogen bonding in solutions and in the gas phase [1, 2]. The following conclusions were made:

1. Classification of the solute-solvent systems, considering hydrogen bonding tendency, enabled the generalization of the ΔG *vs.* ΔH relationship in solvation/vaporization thermodynamics. A common linear relationship with a slope of 0.66 was observed for the solvation in non-hydrogen-bonded systems, while the deviations associated with solute-solvent complexation and solvophobic effect contributed to intercept only.
2. The linear ΔG *vs.* ΔH relationships for the solution- and gas-phase complexation with the same slope were derived from the above considerations for the solvation/vaporization processes and validated against numerous measurements, proving its predictive capability.

Summarizing, ΔG *vs.* ΔH relationship for the processes considered in this work obeyed the common expression:

$$\Delta G = \Delta H - T\Delta S_{\text{comp}} - T\Delta S_{\text{noncomp}} = 0{,}660 \cdot \Delta H - T\Delta S_{\text{noncomp}}$$

where ΔS_{comp} and $\Delta S_{\text{noncomp}}$ are the compensated and noncompensated (i.e., enthalpy-independent) contributions to the process entropy, with $T\Delta S_{\text{comp}}$ being $0.34\Delta H$. The above expression remained unchanged, regardless the type of intermolecular interactions (pairwise/collective) or the structure of interacting molecules.

Furthermore, the above equation could be applied for the description and prediction of the thermodynamic parameters of cyclodextrines complexation, even though it implies multiple interactions, such as electrostatic repulsion/attraction, hydrogen bonding, hydrophobic effects, charge transfer, and conformational changes.

Given that manifold experimental data were summarized, covering the diverse processes, objects, and interaction types, we conclude that the regularities observed should be considered as the general feature in the studies of intermolecular interactions.

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FUNDAMENTAL ISSUES AND NEW CHALLENGES IN CHEMICAL THERMODYNAMICS

ФУНДАМЕНТАЛЬНЫЕ ПРОБЛЕМЫ И НОВЫЕ ЗАДАЧИ ХИМИЧЕСКОЙ ТЕРМОДИНАМИКИ

MULTIREACTION APPROACH TO QUANTUM THERMOCHEMISTRY

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Gas-phase enthalpies of formation, $\Delta_f H_0^o(X)$, are often predicted using *ab initio* calculations. One selects a balanced chemical reaction involving *n* species, including the target molecule *X*. For all species besides *X*, (*n*–1) enthalpies of formation are taken from the literature. The reaction enthalpy is then obtained from calculation and the desired quantity is obtained by simple arithmetic. The best accuracy is obtained when the selected reaction successfully cancels the systematic errors in the *ab initio* method.

In practice, there are often difficulties. A clever reaction (e.g., one that conserves Benson groups [1]) may require data that do not exist. Data that do exist may have large uncertainties. Different choices of reaction yield different results. It may be difficult to estimate the uncertainty associated with the thermochemical prediction.

We propose [2] to solve these problems by using more than one reaction in combination with an estimator for the unreliability of each prediction. The unreliability of a reaction may be estimated as proportional to its enthalpy change. The unreliability of a value of $\Delta_f H_0^o(X)$ may be estimated as the reaction unreliability plus the uncertainty in the literature data plus a constant representing the unreliability in the *ab initio* method. The values of $\Delta_f H_0^o(X)$ obtained from many reactions may be combined using weighted statistics, where the weight of a prediction is the reciprocal of its unreliability. This yields a best estimate for the desired quantity, along with a quantitative estimate of its uncertainty.

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THERMODYNAMIC FOUNDATIONS OF BIOSYNTHETIC FUEL TECHNOLOGIES: OVERCOMING CHALLENGES IN BIOMASS HYDROGENATION AND HYDRODEOXYGENATION

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As fossil resources deplete, chemical thermodynamics becomes a critical engine for designing efficient biosynthetic fuel processes. This study presents a hybrid thermodynamic framework (combining high-precision experiments with quantum chemistry) to bypass kinetic bottlenecks and guide catalyst design for the hydrogenation and hydrodeoxygenation (HDO) of biomass.

Three key systems were investigated to validate this approach:

1. Lignin Models (Eugenol): Thermochemical properties (enthalpies of formation, vaporization, and phase transitions) for an 18-reaction HDO network were determined via transpiration, calorimetry, and G4 calculations. We demonstrate that while no thermodynamic barriers exist, product distribution is governed by support acidity. Ru/HNT catalysts showed a shift from 79% selectivity for methoxy-propylphenol to 42% for propylcyclohexane upon acid-etching, aligning with our predictions.
2. Terpenoid Conversion (Carvone): Gibbs energies and entropies were quantified for 15 pathways. The results explain observed chemoselectivity (exo > endo > C=O) and provide a quantitative basis for selective production of dihydrocarvone or carvacrol.
3. Hydrogen Storage (Limonene & LOHC): Thermodynamic assessment of direct and transfer hydrogenation confirms high equilibrium constants and near-complete conversions, proving these systems viable for hydrogen-carrier technologies.

The developed "centerpiece" approach offers a rapid, low-cost toolkit for screening renewable molecules and scaling industrial processes. These results support green chemistry priorities, providing a rigorous thermodynamic route to sustainable aviation and diesel fuels.

Keywords: chemical thermodynamics, biosynthetic fuels, hydrodeoxygenation, LOHC, quantum chemistry, catalyst optimization.

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NEW VOLUMETRIC CHARACTERISTIC FOR SOLUTION THERMODYNAMICS

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We introduce new solution volumetric characteristics (components' intrinsic molar volumes) which are real volumes assigned to solution components. Under real component volume we mean the part of space which is naturally inherent to it and include both component's molecules as well as parts of intermolecular voids being closer to that component's molecules that to other molecules. New characteristics differs fundamentally from known partial volumes which are just solution volume derivatives by components amount and do not reflect real volumes.

A theoretical meaning of new characteristics is that they are connected by rigid equations with observed parameters such as excess volume, components' partial volumes etc. It is important, that real volumes of molecules are determined by their arrangement. The new characteristics can hence relate solution molecular structure with its thermodynamic parameters.

Intrinsic volumes we have proposed to use are unable to measure in real experiments. It is possible however to obtain them in molecular-dynamic model. Having coordinates of all atoms given one is able to calculate real volume of each molecule with aid of Voronoi tessellation and establish components intrinsic volumes behavior in dependence of concentration. As a result, we can give a structural interpretation of observed macroscopic solution properties: we explain the presence of extrema on partial molar volumes of alcohols in solution [1]; we also explain the nature of negative excess volume in aqueous solutions of nonelectrolytes on the molecular level.

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HEAT CAPACITY AND VISCOSITY OF GLASSES AND MELTS IN THE SYSTEM Al_2O_3-CaO-MgO-SiO_2-TiO_2

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Experimental measurements of heat capacity and modelling of heat capacity and viscosity of melts and glasses in the Al_2O_3-CaO-MgO-SiO_2-TiO_2 system have been presented for selected unary, binary, ternary and quaternary subsystems. Adiabatic and differential scanning calorimetry have been used to measure heat capacity of synthesized glasses at low, intermediate and high temperatures. A unified model for both heat capacity and viscosity of melts and glasses in the Al_2O_3-CaO-MgO-SiO_2-TiO_2 system has been developed on the basis of the configurational entropy theory [1], extensive experimental database for viscosity [2] and collected from literature and measured heat capacity data. First, heat capacity of glasses has been modelled at temperatures above 300 K using a simple polynomial expression. Second, viscosity of melts and glasses has been described over a wide temperature range via the configurational heat capacity and Adam-Gibbs theory. Compositional dependences of the heat capacity and viscosity parameters have been described by both linear and quadratic rules of mixing depending on availability and/or agreement with experimental data. Using the developed model both heat capacity and viscosity of melts and glasses can now be predicted over the wide temperature and compositional ranges in the Al_2O_3-CaO-MgO-SiO_2-TiO_2 system including supercooled melts and glasses.

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THERMODYNAMIC ANALYSIS OF MODERN APPROACHES TO UNDERSTANDING THE NATURE OF DEEP EUTECTIC SOLVENTS

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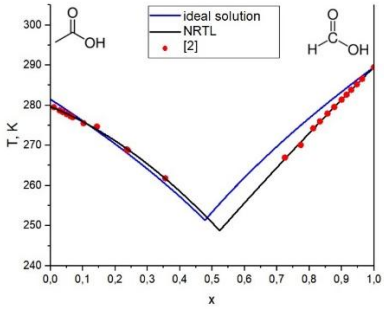
Although the deep eutectic solvents are already being studied for more than twenty years, the determination of which mixtures should be referred as deep eutectic ones remains as contestable as, in some cases, arbitrary. Up to now, there are several approaches proposed to distinguish deep eutectic solvents from other mixtures. For example, the presence of relatively strong hydrogen bonds in the mixture is believed to be marker for a "deep eutectic"; however, some researchers. e.g. [1], highlight that such an approach seems to be controversial as well.

In this work, the comparative analysis of melting diagrams, phase equilibria and physico-chemical properties for a number of binary mixtures, both deep eutectic and common ones, was carried out, e.g. see Fig. Based on the literature data, the modeling of thermodynamic properties was performed using several well-known approaches and equations (regular solution, Wilson equation, NRTL, UNIQUAC).



Melting diagram of the systems formic acid – acetic acid

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The work was carried out with the financial support of the Russian Science Foundation, project 25-23-00021.

MODELLING THE EFFECTS OF COUNTERION CONDENSATION AND CHAIN STRUCTURE IN AQUEOUS POLYELECTROLYTE SOLUTION WITH ADDED SALT

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The demand for tailoring polyelectrolyte materials to specific applications has spurred growing interest in understanding how the structural features of polyelectrolytes govern the behavior of their solutions. The variational-filed theoretical framework [1,2] has recently been formulated for solutions that contain polyelectrolyte chains, counterions and salt additives, taking into account structural features of chains and free ions. For strongly charged chains, the effect of counterion condensation plays an important role [3], diminishing significantly the effective charge of the chain. This effect is modulated by the presence of salt in solution.

In this work, we applied the theoretical framework that reflects the structural details of a macromolecule and the effect of counterion condensation to describe structural and thermodynamic properties of polyelectrolyte solutions in presence of salt.

We consider different distributions of charged monomeric units along the backbone of polyelectrolyte chain, different hard-sphere diameters of the units and counterions, as well as the effects of chain elasticity and distribution of electrical charge inside the ions. The condensation of counterions on the chain is described applying the scheme proposed in ref. [4]. Calculated results are compared with computer simulation and experimental data on the osmotic coefficients for polyelectrolytes of different chemistry. We show that structural details of polyelectrolyte have a substantial effect on the structure of polyelectrolyte solution and that the model in its present form may provide reasonable description of the structure factors and osmotic pressure.

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RELATIONSHIPS BETWEEN ENTHALPY AND VOLUME CHANGES ON MELTING OF ORGANIC NON-ELECTROLYTES

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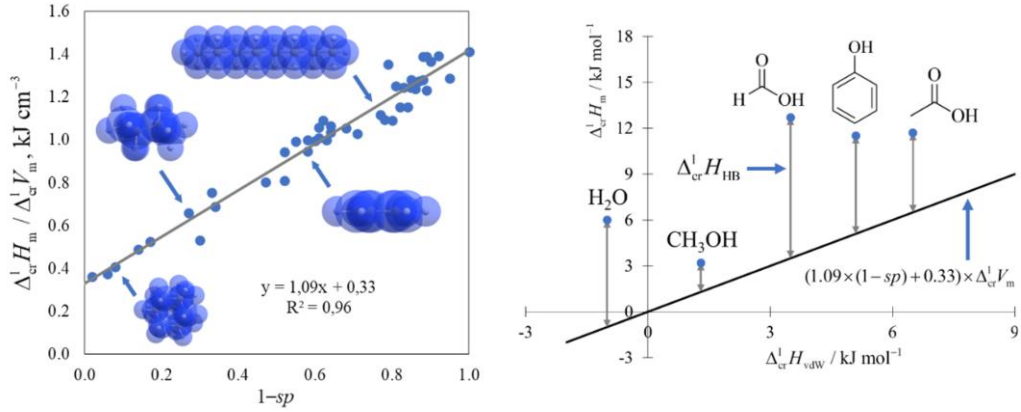
The search for the connection between thermochemical and structural parameters of matter has been a relevant direction of investigations in the field of thermodynamics of organic compounds for many decades. In this work, the relationship between the thermodynamic characteristics of melting and the molecular shape was analyzed. For non-associated compounds, a linear correlation was found (see Figure (left)) between the ratio of the fusion enthalpy to molar volume change during melting and the sphericity parameter (*sp*), defined as the ratio of the molecule's thickness to its length [1]:

$$\Delta H_m/\Delta V_m = 1.09 \cdot (1 - sp) + 0.33$$

This equation was used to investigate the influence of hydrogen bonding on the relationship between the thermochemical and volumetric characteristics of melting, and to identify the contributions of van der Waals interactions and hydrogen bonding to the fusion enthalpy of the associated compounds [2] (see Figure (right)). Correlations between enthalpy and volume changes accompanying phase transitions in liquid and plastic crystals were also found.



Left – correlation between the $\Delta H_m/\Delta V_m$ ratio and *sp* for non-associated organic compounds. Right – contributions of van der Waals forces (black line) and hydrogen bonding (grey arrows) to the fusion enthalpies of associated compounds.

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PROBLEMS OF THERMODYNAMIC ANALYSIS OF EUTECTIC SYSTEMS

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Thermodynamic analysis of phase diagrams of eutectic systems is a classical physico-chemical task that is not problematic. Indeed, the vast experimental material accumulated to date, mainly on inorganic binary and multicomponent eutectic systems, is already textbook: the corresponding diagrams are indispensable illustrations in textbooks on physico-chemical analysis. In recent years, the word “eutectic” has been most often found in the context of the concept of so-called deep eutectic solvents (DES), whose components are mainly organic compounds. Thermodynamic analysis of the phase diagrams and properties of these systems revealed a number of problems that were not so significant in the case of "ordinary" inorganic eutectic.

Although the works devoted to DES occupy a significant place in the modern scientific literature, the analysis of publications shows that the meaning of the term DES is becoming more vague and uncertain and does not fully correspond to the traditional statements of physico-chemical analysis, but is associated with the characteristics of intermolecular interactions (donors and acceptors of hydrogen bonds), which cannot be considered a unique feature of DES. One of the obvious gaps in publications is, for example, the frequent lack of data on solid phases necessary to present diagrams of eutectic systems.

In our opinion, the wide temperature range in the case of real DES does not allow direct application of traditional thermodynamic approaches, in particular, the Schroeder – Van Laar equation, including its modifications. The presentation examines these and other issues of common fundamental interest. In particular, what interactions in solid phases lead to the melting of a heterogeneous mixture of eutectic composition, including those formed by crystals of pure components (simple eutectic), at temperatures significantly different from the melting temperature of pure substances. Related to this are such problems as: a) what factors determine the "depth", that is, the relatively low melting point of eutectic, b) how the atomic-molecular structure of DES components and their interaction determines their macroscopic thermodynamic properties calculated at the atomic level. It is also advisable to take into account the difference between "organic" eutectics and "inorganic", which manifests itself not only in the structures of solid solutions (when they are formed as molecular crystals), but also in the formation of other forms, in particular, co-crystals. In this regard, the report also provides some results of our research and possible approaches to analyzing DES state diagrams based on data from molecular dynamics and quantum chemistry.

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LIGAND-MEDIATED REGULATION OF SERUM ALBUMIN FIBRIL FORMATION

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Amyloid fibrils are protein aggregates that form from monomers through a complicated mechanism which is still not fully understood. While many proteins exhibit a lag phase of fibril formation due to a slow nucleation stage, serum albumins near their denaturation temperature and acidic or neutral pH levels aggregate rapidly without a lag phase. Despite many examples of the inhibition of albumin fibrillization having been described in literature, kinetics and mechanism of inhibition have not been thoroughly studied.

In our work, we investigated the fibril formation of bovine and human serum albumins at 65 °C or higher temperatures and pH 7 in the presence of a series of organic ligands, predominantly clinical drugs. Kinetic curves of fibril formation were obtained using a Thioflavin T spectrofluorimetric assay. Additionally, albumin denaturation curves in the presence of the studied compounds were obtained using differential scanning calorimetry (DSC).

It was shown that albumin fibril formation obeys reversible first-order kinetics, and is not sensitive to seeding with preformed fibrils. The addition of substances exhibiting high albumin affinity significantly suppresses fibril growth and decreases the final yield. Using DSC data, the fraction of unfolded protein form α at the incubation temperature was determined for each ligand, concentration, and temperature. The initial aggregation rate appears to be proportional to α, and the final fibril yield is governed by the equilibrium between the protein monomer and fibrillar aggregates, which shifts towards the monomer by binding ligands. The results indicate that albumin fibrils are formed only from its unfolded form which slowly transforms into some specific, aggregation-prone conformation that quickly aggregates into fibrils. Strong native protein binders act as the best inhibitors of fibril formation, which appears to be a general rule for many different globular proteins.

COMPENSATION RELATIONSHIP IN THERMODYNAMICS OF GAS-PHASE MOLECULAR COMPLEXATION

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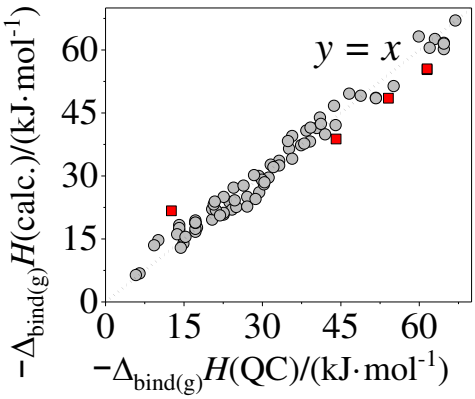
The phenomenon of compensation between changes in enthalpy and entropy in various physicochemical processes has been a subject of interest for scientists for over 90 years. In previous works, linear relationships were obtained between the changes in Gibbs energies and enthalpies for solvation and solution-phase complexation processes, which share the same slope [1].

The common slope in these dependences allows deriving a similar equation for complexation in the gas phase:

$$\Delta_{bind(g)}G\,/\,(\mathrm{kJ\cdot mol^{-1}}) = 0{,}660 \cdot \Delta_{bind(g)}H\,/\,(\mathrm{kJ\cdot mol^{-1}}) + 17{,}0 + 2{,}5\cdot n$$

In the present work, a comparison was made between the enthalpy values calculated using the obtained relationship from experimental Gibbs energy values and the values computed by quantum-chemical methods for 67 donor-acceptor pairs (graphical representation of this comparison is given in fig. below) [2].



The relationship obtained in present work allows creating an approach for determining binding enthalpies in the gas phase from a single value of the equilibrium constant at 298.15 K. Furthermore, the obtained results mean that, in each case, the compensation relationships have a common origin, which is beyond experimental artifacts, group additivity in homologous series, or solvent reorganization effects.

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STUDY OF THE CHEMICAL POTENTIAL CONCENTRATION DEPENDENCE FOR BINARY MIXTURES IN MOLECULAR DYNAMICS MODELS

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Modern molecular dynamics (MD) makes it possible to calculate thermodynamic quantities, including the chemical potential. This thermodynamic parameter determines the conditions of phase equilibrium in multicomponent systems.

In this work, MD models were produced for a number of binary liquid mixtures, including non-polar substances (benzene-toluene, hexane-cyclohexane, etc.) and aqueous solutions of several non-electrolytes. For each mixture, a series of models at various concentrations, including pure component models, were obtained. Subsequently, the chemical potential values of the components were calculated for these models using several approaches.

All approaches are based on the fluctuation theory. In the first method, the integral of the radial distribution function $g(r)$ is calculated, and its value at infinity is predicted. The resulting values G_{ij} allow for the calculation of the components' chemical potential according to Kirkwood-Buff theory. An additional method involves obtaining values from the structure factor $S(q)$ by extrapolating it to the limit $q \to 0$, with further calculations also carried out based on Kirkwood-Buff theory.

A geometric approach based on Voronoi volume statistics was also tested. In this approach, the Voronoi tessellation is calculated for the centers of molecules system for every single component. The Voronoi volume represents the volume per molecule in the mixture, and its average value is the inverse concentration. The variance of the distribution is directly related to concentration fluctuations and allows for their estimation within the MD model. The chemical potential calculation in this approach is carried out using fluctuation theory.

This work demonstrates the feasibility of calculating the chemical potential as a function of concentration for liquid mixtures and provides a comparison of several calculation methods, both classical and novel.

DEFINITION OF METASTABLE REGIONS BELOW THE LIQUIDUS TEMPERATURE T_L AND SOLIDUS TEMPERATURE T_S ON A EUTECTIC PHASE DIAGRAM

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Metastable phase equilibrium obeys the same thermodynamic rules that apply in the case of stable equilibrium. In particular, the temperatures and chemical potentials of all phases of the system at equilibrium must be equal. Metastable phase diagrams do not contain any unusual features, except for regions near the boundaries of metastability where the nucleation barrier ceases to exist. The displacement of the liquidus and solidus lines can be influenced by the cooling rate of the melt, its thermal history, the curvature of the phase interface, pressure, and so on.

At the same time, the definitions of "non-equilibrium" crystallization and "metastable diagram" do not mention the presence of pre-crystallization undercoolings in alloys (similar to those in pure substances) relative to the liquidus and solidus temperatures, which cause spontaneous, self-initiated crystallization.

By definition, equilibrium crystallization begins at the liquidus temperature T_L and ends at the solidus temperature T_S. Spontaneous crystallization, however, does not begin at the liquidus T_L or solidus T_S temperatures. It begins at temperatures T_{min} significantly below T_L and T_S. That is, for this type of crystallization, undercoolings $\Delta T_L^- = T_L - T_{min}$ and $\Delta T_S^- = T_S - T_{min}$ are necessary.

Plotting the T_{min} points on the diagram for all alloys allows for the construction of a non-equilibrium phase diagram with metastability boundaries across the entire concentration range.

Thus, for alloys, a wide variety of crystallization types are observed with undercoolings ΔT_L^- and ΔT_S^-, both relative to the liquidus line and relative to the solidus line, respectively.

IMPACT OF ORGANIC CATIONS ON THE THERMAL STABILITY OF ALBUMIN

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Maintaining protein structural stability is essential for their biological functions. Proteins fold into native conformations via noncovalent interactions, which are highly sensitive to the changes in temperature, pH, ionic strength, or the presence of cosolvents. These changes often lead to protein unfolding and loss of function, however, in some cases, the conformational stability increases.

The well-known Hofmeister series ranks inorganic ions by how they affect the solubility and stability of proteins: from stabilizing and salting-out kosmotropes to denaturing and salting-in chaotropes. At the same time, the effects of organic cations on protein stability are poorly studied, despite the widespread interest to the behavior of proteins in the presence of ionic liquids (ILs). Most common ILs contain alkylimidazolium or alkylammonium cations. Unlike metal ions, they can engage in many different types of interactions with proteins such as salt bridges, hydrogen bonding, hydrophobic and π-π stacking interactions, which makes it difficult to predict their effect on protein denaturation and aggregation.

In this work, the thermal stability of bovine serum albumin (BSA) in the presence of various organic thiocyanates was studied. The thermograms of BSA denaturation in the presence of different concentrations of thiocyanates were obtained using capillary DSC, and the temperatures of phase transition were determined. The cations were ranked by their destabilizing effect according to these temperatures. Guanidinium thiocyanate has shown the strongest destabilizing effect, while ethylenediammonium thiocyanate has led to the smallest decrease in denaturation temperature.

In addition, we performed molecular dynamics simulations of native and unfolded BSA in aqueous solutions of organic thiocyanates, which provided the information on the composition of BSA solvation shells. The difference in Kirkwood-Buff integrals of the solvent components can be interpreted as the preferential binding of one of the components. An increase in the preferential binding of organic salt upon BSA denaturation was shown to correlate with its denaturing effect.

The work was supported by RSF project №24-13-00062.

THERMODYNAMIC PROPERTIES AND PROCESSES IN SOLIDS

ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА И ПРОЦЕССЫ В ТВЕРДОФАЗНЫХ СИСТЕМАХ

STRUCTURE-PROPERTY RELATIONSHIP IN SUBSTITUTED BENZENES: MULTIFIDELITY METHODS TO QUANTIFY AND UNDERSTAND INTERACTIONS AMONG SUBSTITUENTS ON THE BENZENE RING

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Derivatives of benzene bearing electron-withdrawing or electron attracting substituents occupy a prominent position in synthetic organic chemistry, food chemistry, pharmaceutical science, energetic materials research, and, ultimately, in chemical thermodynamics [1]. A classical challenge in physical organic chemistry is the quantitative assessment of steric versus electronic interactions between neighboring groups in aromatic systems or the effect of the introduction of one or more groups into the aromatic ring as both can significantly alter its properties [2]. Whereas electron-donating groups make the benzene ring more reactive towards electrophilic aromatic substitution, while electron-withdrawing groups make it less reactive [3], being the extent of reactivity be assessed by determining their thermodynamic parameters.

A comprehensive study of the thermodynamic properties of methyl-, mono- and dinitro-substituted benzoic acids was carried out using various methods: thermogravimetry (under both isothermal and non-isothermal conditions), differential scanning calorimetry, combustion calorimetry, and transpiration method. In addition, complementary quantum chemical (high-fidelity) and empirical (low-fidelity) methods were employed to cross-validate the results obtained. This multifidelity approach is essential for the benchmarking of thermodynamic properties.

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LOW-TEMPERATURE THERMODYNAMIC PROPERTIES OF SINGLE CRYSTALS OF DOUBLE ALKALI METAL MOLYBDATES

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The development of cryogenic scintillating bolometers is a promising approach for the search for neutrinoless double beta (0ν2β) decay. In this context, significant efforts are currently focused on identifying and characterizing new scintillating materials. The performance of bolometers as thermal radiation detectors is governed by their sensitivity to temperature variations induced by particle interactions. Therefore, the heat capacity of the absorber material (i.e., the scintillating crystal) represents a key parameter in the design of bolometric detectors. In addition, heat capacity data over a wide temperature range provide valuable insight into the phase stability of the studied compounds as well as their thermodynamic functions. Adiabatic calorimetry remains the most accurate method for heat capacity measurements. In this work, we report, for the first time, a systematic investigation of the low-temperature thermodynamic properties of single crystals $LiCsMo_3O_{10}$, $NaCsMo_3O_{10}$, $LiRbMo_3O_{10}$, $LiCsMoO_4$, $LiRbMoO_4$, $LiKMoO_4$, $LiNa_5Mo_9O_{30}$, and $Cs_3Na(MoO_4)_2$.

The investigated molybdate single crystals were grown using spontaneous crystallization from the melt and the low-thermal-gradient Czochralski technique. Prior to calorimetric measurements, all samples were thoroughly characterized: the phase and elemental compositions were confirmed, and trace impurity levels were determined, with the total impurity content not exceeding 0.02 wt%. High-precision heat capacity data for single-crystal samples were obtained using adiabatic calorimetry over the temperature range of ~6 to ~320 K with a BKT-20 calorimeter. The heat capacity curve of $LiCsMoO_4$ exhibits two anomalies with maxima at T_{c1} = 171.5 K and T_{c2} = 208.9 K, associated with first-order phase transitions. No anomalies in heat capacity behavior were observed for the other studied compounds. Based on the measured heat capacity data, thermodynamic functions were calculated over the temperature range 0–320 K. The results indicate that the $LiNa_5Mo_9O_{30}$ single crystal is the most promising candidate for use as a scintillating material in cryogenic bolometers developed for neutrinoless double beta decay experiments. It offers several advantages over the widely used lithium molybdate Li_2MoO_4, including its non-hygroscopic nature, higher molybdenum content, and a higher Debye temperature at 0 K (337.0 K for $LiNa_5Mo_9O_{30}$ versus 316.15 K for Li_2MoO_4).

The study was supported by a grant from the Russian Science Foundation No. 24-19-00405, https://rscf.ru/en/project/ 24-19-00405/

THERMODYNAMICS OF DRUG POLYMORPHISM: PROBLEMS AND SOLUTIONS

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Bioavailability and biological activity of medical drugs relate to their crystal packing and polymorphic state. Respectively, the search for all possible polymorphs is needed both for drugs available on the market or drug candidates. The problem with this search is that the methods currently used for polymorph screening are based on the kinetic restrictions for crystallization process derived from the Ostwald rule of stages. For metastable crystal forms, these methods often demonstrate poor reproducibility, which brings on the term “disappearing polymorphs”. The present report proposes the use of solid-state processes to reach a reproducible polymorph screening.

Metastable polymorphs can be efficiently prepared using the solid-state exchange/repulsion of guest (solvent) in inclusion compounds (solvates) [1-3]. This process being slow enough brings about mostly thermodynamic control for the formation of the resulting product, which enables milder conditions for the phase transition without collapse to a more stable form [1]. Solid-state processes are much easier to stop on a thermodynamically higher level than crystallization from liquids. Solid-state approach to the polymorph screening makes it more predictable giving crystal forms that were known previously only in mixtures or new polymorphs. This is applicable also for solvates that cannot be prepared by crystallization from solutions. The efficiency of the developed method has been shown for such drugs as indomethacin [1], phenylbutazone [2] and olanzapine [3]. The positive results are achieved without high-throughput screening with quite a few experiments. The preparation of metastable polymorphs by solid-state processes without crystallization from melts or liquid solutions helps to avoid such phenomenon as the oxidation of drug with air oxygen, which may produce toxic or cancerogenic impurities [2,3]. The solid-state processes with thermodynamic control require minimal amounts of solvents and the tested drugs, thus fitting to the concept of green chemistry.

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CALORIMETRIC STUDY OF HYDROGEN REACTION WITH LAVES PHASE C14

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The initial compounds $ZrMn_2$, $ZrMn_{2.7}$, $Ti_{0.9}Zr_{0.1}Mn_{1.4}V_{0.7}$ and $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.8}$ were synthesized as described in [1]. Thermodynamic studies of the IMC-hydrogen systems were carried out on a DAK-12 calorimeter of the Tiana-Calve type in the temperature range 333 – 518 K and hydrogen pressure up to 5 MPa (see Table).

Temperature dependence of reaction enthalpy for the AB_2-H_2 system

Compounds	*T*, K	Range H/IMC (desorption)	$\Delta H_{des.}$, kJ/molH_2
$ZrMn_2$	373	0.1 – 1.9	40.16±1.02
	518	0.4 – 1.6	36.97±0.63
$ZrMn_{2.7}$	353	0.1 – 1.1	35.43±0.42
		1.1 – 1.9	32.15±0.65
$Ti_{0.9}Zr_{0.1}Mn_{1.4}V_{0.7}$	333	0.9 – 1.5	28.40±0.40
		1.5 – 2.1	30.13±0.30
	373	0.3 – 0.9	24.70±0.36
		1.0 – 2.0	30.22±0.43
$Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.8}$	373	0.1 – 0.85	30.05±0.45
		1.1 – 1.8	36.77±0.91
	418	0.1 – 0.6	28.86±1.41
		0.6 – 1.6	36.30±1.30

Enthalpy values of the hydrogen reaction with the IMC change with the temperature of the process under the study and the concentration of hydrogen in the IMC. For ZrMn2-H_2 the enthalpy values change only reaction temperature, but it does not depend on the hydrogen content in the IMC. In $ZrMn_{2.7}$-H_2 there are two sections where the enthalpy values are constant. For $Ti_{0.9}Zr_{0.1}Mn_{1.4}V_{0.7}$-$H_{2b}$and $Ti_{0.9}Zr_{0.1}Mn_{1.5}V_{0.8}$-$H_2$ systems the enthalpy values change with reaction temperature and hydrogen concentration moreover an increase in hydrogen concentration is accompanied by an increase in the reaction enthalpy.

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EXPERIMENTAL INVESTIGATION OF HOMOGENEITY REGIONS AND THERMODYNAMIC PROPERTIES OF G PHASE IN QUATERNARY Ni-{Mn, M}-Si SYSTEMS (M = Fe, Ti, Cr, Nb)

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G-phase (*cF116, Fm*-3*m*) is forming after prolonged operation in heat-resistant steels and is known to have a deteriorative effect on the strength characteristics of steels. Direct study of the chemical composition of the G-phase and equilibrium phase fraction at different temperatures is a rather rigorous experimental task due to the small particle size and low fraction of this phase in steels.

The aim of the current work was to establish the homogeneity range and phase equilibria during crystallization of the G-phase in the Ni-Mn-Si system. The study also aimed to determine the maximum solubilities of Fe, Ti, Cr, Nb in the G-phase originating from Ni-Mn-Si system. Thermodynamic properties, such as the standard enthalpy of formation and heat capacity, were experimentally investigated. Samples were obtained by arc-melting and analyzed in as-cast and annealed states using the SEM/EPMA, XRD, DSC, adiabatic calorimetry and drop-solution calorimetry.

This study demonstrates that the G phase in the Ni-Mn-Si system forms via congruent melting, and for the first time, phase equilibria during crystallization in the nickel-rich region were experimentally investigated. It was also demonstrated that, although Ti and Nb can completely replace Mn, Fe and Cr exhibit limited solubility in the G phase formed in the Ni-Mn-Si system.

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SOLID-PHASE SYNTHESIS OF TERBIUM AND DYSPROSIUM DOUBLE TITANATES AND THEIR THERMODYNAMIC PROPERTIES

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Solid solutions of double titanates of terbium-lutetium and dysprosium-lutetium with the general formula $(Ln_{1-x}Lu_x)_2Ti_2O_7$(Ln=Tb,Dy) in the ratios of Tb:Lu and Dy:Lu as 25:75, 50:50 and 75:25 at.% were obtained by solid-phase synthesis. The synthesis was carried out in a SH-FU-4MS furnace in a protective argon atmosphere in several stages: at temperatures from 800 to 1300°C for 8 hours, at 1400°C for 10 hours, at 1500°C for 12 hours, and the final stage at 1550°C for 24 hours with the total annealing time of up to 104 hours for terbium-lutetium titanates and up to 128 hours for dysprosium-lutetium titanates.

The exposure of diffraction patterns was made by a SmartLabRigaku X-ray diffractometer. X-ray structural analysis was performed using SmartLab software (Rigaku) and the full-profile analysis method by PDF-2024. The values of statistical parameters of fitting have been obtained in the range of R_p from 4.1 to 5.7% and R_{wp} from 5.5 to 8.3%, which is a satisfactory indicator and confirms the crystal structure of the samples corresponding to the type of pyrochlore of cubic syngony with the space group Fd-3m with a lattice parameter *a* from 10.02 to 10.12 Å.

The heat capacity measurements and thermodynamic functions calculations have been carried out for the samples of double titanates of terbium and dysprosium. Using the experimentally obtained data for double titanates of terbium and dysprosium based on lutetium and processed by methods of mathematical statistics, the smoothed temperature dependences of the heat capacity and tabulated values of thermodynamic functions of double titanates of terbium and dysprosium have been have been obtained (Table).

For the lanthanide titanates studied the excess components have been obtained over the entire temperature range. All of them contribute significantly to the heat capacity, at the same time some of them have a complex structure consisting of more than one maximum due to the presence of energy contributions from various excited levels.

Thermodynamic functions of terbium-lutetium and dysprosium-lutetium titanates

Function	Tb_{25}:Lu_{75}	Tb_{50}:Lu_{50}	Tb_{75}:Lu_{25}	Dy_{25}:Lu_{75}	Dy_{50}:Lu_{50}	Dy_{75}:Lu_{25}
$C_{p(298)}$	219.5±1.4	218.6±1.0	217.4±1.1	214.0±1.1	218.1±1.6	219.8±1.4
$S_{(298)}$	262.1±2.6	268.0±3.1	273.2±2.2	260.5±3.1	266.4±3.3	270.1±2.9
$H_T-H_{0(298)}$	37.21±0.3	37.68±0.2	37.86±0.2	37.03±0.2	38.00±0.3	38.55±0.3

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REFINEMENT OF THE AgI-Ag_2WO_4 PHASE DIAGRAM

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Silver-conducting solid electrolytes are promising materials for all-solid state batteries with a wide working temperature range, high stability, high safety, and low risk of leakage and corrosion, in contrast to batteries based on liquid organic electrolytes.

The system AgI-Ag_2WO_4 is known since early 1970s. There are two different versions of the phase diagram of the AgI – Ag_2WO_4 system [1, 2]. According to [1], it contains three chemical compounds: $Ag_5IW_2O_8$ (AgI/Ag_2WO_4=1:2), $Ag_4I_2WO_4$ (2:1) and $Ag_6I_4WO_4$ (4:1), while according to [2], there are only two – $Ag_5IW_2O_8$ and $Ag_6I_4WO_4$. All phases are ionic conductors, and the $Ag_6I_4WO_4$ compound exhibits superionic conductivity at ambient temperatures. Later, the composition of the superionic phase was represented by the formula $Ag_{26}I_{18}W_4O_{16}$ (4.5:1) [3]. Our repeated attempts to synthesize $Ag_6I_4WO_4$ and $Ag_{26}I_{18}W_4O_{16}$ compounds using the ampoule method (400°C, furnace cooling to 25°C) from AgI and Ag_2WO_4 each time resulted in non-single-phase products with a small amount of AgI impurity, which contradicts both versions of the phase diagram. Therefore, the goal of this study was to re-examine the phase equilibria in the AgI – Ag_2WO_4 system, refine its phase diagram, and establish the composition of the superionic phase.

Mixtures of the reagents AgI and Ag_2WO_4 in various molar ratios were prepared, sealed in ampoules and annealed according to the selected scheme. The phase composition of the products was analyzed using XRD and DSC. Single-phase products with the $Ag_{26}I_{18}W_4O_{16}$ structure, exhibiting superionic conductivity at room temperature, were obtained in a wide composition range from 3:1 to 3.9:1 (or 20.4…25.0 mol.% Ag_2WO_4); it corresponds to the general formula $Ag_{2+x}I_xWO_4$, where $x = 3 \div 3.9$. This region does not cover any of the superionic phase compositions described in the literature ($Ag_6I_4WO_4$ and $Ag_{26}I_{18}W_4O_{16}$) and is shifted toward a higher Ag_2WO_4 content. It is well known that solid electrolytes based on AgI, stabilized by oxoanions of the XO_4^{2-} type (where X is a transition metal) are prone to metastable states. A test performed by measuring the temperature dependence of conductivity in the thermal cycling mode confirmed the metastability of $Ag_{2+x}I_xWO_4$ except for 3.0:1. Based on the results obtained, it can be concluded that disagreements between the authors [1-3] are due to the fact that the metastable nature of phase equilibria was not taken into account. Changes and clarifications were made to the phase diagram of the AgI – Ag_2WO_4 system, and optimal conditions for the synthesis of single-phase products were selected.

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INFLUENCE OF TEMPERATURE AND OXYGEN PRESSURE ON THE STABILITY OF BARIUM-SUBSTITUTED NEODYMIUM MANGANITES

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The practical value of the $Nd_{1-x}Ba_xMnO_{3\pm\delta}$ manganites (x = 0.0; 0.15; 0.25) is related to the perspective of their use in electrochemical and catalytic applications. Another factor that draws attention to these materials is the manifestation of competing charge, spin, orbital, and lattice interactions. An important role in changing these properties is played by the electronic state of manganese, a change in the oxygen nonstoichiometry of compounds under the influence of external parameters – temperature, oxygen pressure of the gas atmosphere. The purpose of the work is to determine the boundaries of the thermal stability of neodymium manganites, the evolution of phase equilibria at variable temperature and oxygen pressure with changes in the concentration of barium. The stability of these complex oxides was studied by two methods: dynamic and static. Upon linear heating (dynamic method, $P(O_2) = 0.21$ atm.), the $NdMnO_3$ and $Nd_{0.85}Ba_{0.15}MnO_3$ manganites undergo a phase transformation of the Jahn-Teller nature from an orbitally ordered *O'* - phase to an orbitally disordered *O* - phase. The temperature of this transition decreases upon substitution with barium. In the substituted Ba manganite at a concentration of x = 0.25, the transition $O' \rightarrow O$ is provided by the substitution level and fixed at room temperature. Partial substitution of neodymium for barium expands the range of thermal stability of the crystal structure of the high-temperature *O* - phase of manganites. The largest range is found in manganite $Nd_{0.75}Ba_{0.25}MnO_3$. The evolution of phase equilibrium states in neodymium manganite samples has been established with a decrease in the partial pressure of oxygen in a gaseous atmosphere to $P(O_2) = 10^{-22.5}$ atm. The dissociation of the $NdMnO_3$ sample occurs in one stage and ends with the formation of Nd_2O_3 and MnO oxides. A two-stage sequence has been established for barium-substituted samples. It includes an intermediate stage of the formation of complex neodymium oxides. According to the data of the static method of investigation of heterogeneous equilibria in manganites, thermodynamic characteristics of reactions of dissociation of oxides and their formation from elements were obtained.

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EXPERIMENTAL STUDY OF THE THERMODYNAMICS OF SOLID-STATE REACTIONS

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This report presents the most significant results obtained at the Laboratory of Electrochemistry, Thermodynamics, and Mineral Physics at the IEM RAS, using the high-temperature galvanic cell (EMF-method) and a vacuum-block calorimeter. The EMF-method can be illustrated by the example of studies of silver selenide [1]. The reaction of naumannite formation from the elements is realized in an electrochemical cell: (–)Pt | Ag | SE or LE | Ag_2Se, Se | Pt(+), in a wide temperature range determined by the solid (SE – AgI, $RbAg_4I_5$, AgCl) or liquid electrolyte (LE – molten salts or glycerol solution) used. Thermodynamic properties of phases and phase relations in binary and ternary silver-containing systems have been determined over a wide range of temperatures and atmospheric pressure [2-5]. Experiments at hydrostatic argon pressure up to 0.7 GPa were carried out in high-pressure gas vessels developed by the IEM RAS [6, 7]. Another important variation of the EMF-method is the use of oxygen-conducting solid electrolytes [8], which is widely used to study the thermodynamic properties of oxide systems. At the Laboratory, this method has been applied to the study of natural objects: oxygen fugacity above the bulk sample was determined for some chondrites [9], and the $pO_2(T)$ dependence was obtained in high-temperature fumaroles on Kudryavy Volcano (Iturup Island, Kuril Islands) [10]. Standard enthalpies of formation of Sb_2Se_3 and other chalcogenides, pnictides and intermetallics were determined on a unique vacuum-block calorimeter of our own design [11].

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ENCAPSULATION OF THE ANESTHETIC SEVOFLURANE BY TERT-BUTYLCALIX[4]ARENE DERIVATIVE

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The development of receptors capable of encapsulating volatile anesthetics to form inclusion compounds (solvates) is a pressing challenge for capturing waste inhalation gases and for use in local (topical) anesthesia. A widely used inhalation anesthetic is sevoflurane. For local non-injection anesthesia, a solvate (inclusion compound) with sevoflurane, which is stable at room temperature and releases the anesthetic at body temperature, may be convenient.

In this work, the process of encapsulation of sevoflurane from the gas phase by a solid derivative of tert-butylcalix[4]arene, which does not possess significant cytotoxicity, was studied. Using previously described methods for preparing polymorphs of calixarenes and inclusion compounds [1,2], the ability of different polymorphic forms and the amorphous form of the receptor to include effectively sevoflurane from the vapor phase, also in the presence of saturated water vapor, was studied, as well as the ability of inclusion compounds prepared in different ways to desorb the included guest at different temperatures. The temperature dependence of the sevoflurane release from the inclusion compound and the kinetic parameters of this process upon heating were determined. The prepared inclusion compound of sevoflurane with calixarene was shown to release upon slight heating an optimal concentration of sevoflurane for local anesthesia.

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HEAT CAPACITY OF $Ca_2Ga_{2-x}Fe_xGeO_7$ (x = 0; 0.05)

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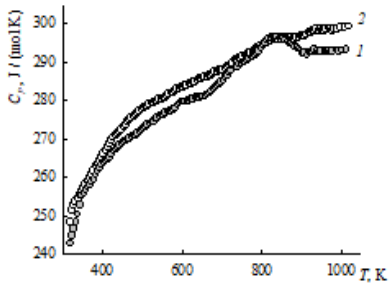
The compound of Ca- gallogermanate ($Ca_2Ga_2GeO_7$) with the spatial group $P42_1m$ belongs to the melilite family and is promising as a basis for the production of electroluminescent displays, detectors, lasers, imaging devices and sensors.

Gallogermanates $Ca_2Ga_{2-x}Fe_xGeO_7$ (x = 0; 0.05) were synthesized using a high-temperature solid-phase reaction. Stoichiometric mixtures of pre-calcined initial oxides (CaO, Fe_2O_3, GeO_2 and Ga_2O_3) were crushed in an agate mortar and pressed into tablets and fired in air at temperatures of 1073 K (20 h) and 1573 K (60 h). The phase composition of the obtained compounds was controlled via X-ray phase analysis using a D8 ADVANCE diffractometer from Bruker, a VANTEC-1 linear detector. The heat capacity in the range of 320 - 1050 K was determined by differential scanning calorimetry using the thermoanalytical system STA 449 C Jupiter (Netzsch, Germany).



Temperature dependences of the molar heat capacity of $Ca_2Ga_{2-x}Fe_xGeO_7$ (x= 0 (*1*); 0.05 (*2*))

The Ca-gallogermanate synthesized by us had the following unit cell parameters: a = 7.89268(9) Å, c = 5.20861(7), V = 324.4675(84)Å^3. The obtained values are in satisfactory agreement with the data in the literature [1]. Replacing a part of the gallium with iron leads to a slight change in the lattice parameters: a = 7.90744(19) Å, c = 5.21016(15) Å, V = 325.7785(181) Å^3. From fig. it is seen that on the dependence $C_P = f(T)$ for $Ca_2Ga_2GeO_7$, there is an extremum at 815 K, which disappears when part of the gallium is replaced by iron. This fact can be explained by the existence of incommensurate–normal phase transition in melilite at high temperatures [1].

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PHASE RELATIONSHIPS IN THE QUASI-TERNARY SYSTEM OF ORTHOPHOSPHATES OF La, Gd, AND Y AT T = 230 °C AND $P \approx 10$ atm

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Rare earth element (REE) orthophosphates (*REE*PO_4, where *REE* La → Lu, Y, and Sc) are a broad class of inorganic compounds that crystallize in various structural types: rhabdophane, churchite, monazite, xenotime, and anhydrite. Particular attention to REE orthophosphates and materials based on them is due to their unique physicochemical properties, such as high melting points (≈1800-2300 °C), low thermal conductivity, resistance to aggressive and aqueous environments, resistance to radiation damage, and the ability to widely substitute REEs for other REEs, actinides, and other elements.

Of considerable interest are multicomponent systems of rare-earth element orthophosphates, which can exist as either continuous solid solutions or phases with limited solubility of the components in the solid state. Such multicomponent systems hold promise for the production of structural and thermal insulation materials, as matrices for the immobilization of radioactive and toxic waste, luminescent materials, and so on. However, multicomponent systems remain a poorly understood area of rare-earth element orthophosphate chemistry, due to the diversity of chemical compositions and structural types they form depending on their composition and synthesis conditions. The least studied areas include the formation of rare-earth element orthophosphate nanoparticles, including those of variable composition, under “soft chemistry” conditions, structural evolution, and phase stability boundaries.

To date, studies of phase equilibria in complex systems based on REE orthophosphates have been conducted only for stable phases with monazite and xenotime structures at $T \geq 1000$ °C (at temperatures above the melting point of non-autonomous phases [1]), since below this temperature, the mass transfer rate of the components is low enough to approach the equilibrium state and avoid metastable or kinetically "inhibited" labile states.

In connection with the above, the aim of the study is to determine the phase state of particles in a $LaPO_4$-$GdPO_4$-YPO_4 system obtained under hydrothermal conditions at T = 230 °C and $P \approx 10$ atm, as well as to study the mechanism of structural transformations under conditions of limited mass transfer.

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PHASE EQUILIBRIA AND CHEMICAL PROCESSES IN SYSTEMS $ZnO-SiO_2-NiO$ AND $ZnO-SiO_2-MnO$

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This paper examines chemical interactions and phase equilibria in the ternary systems $ZnO-SiO_2-NiO$ and $ZnO-SiO_2-MnO$. This information is necessary for selecting optimal conditions for the synthesis of functional materials based on willemite Zn_2SiO_4 (green phosphor Zn_2SiO_4:Mn, cool blue pigment $Zn_{2-2x}Ni_{2-2x}SiO_4$) and olivine Ni_2SiO_4. Solid-phase reactions between three reactants begin at the interfaces of only two at a time. In the $ZnO-SiO_2-NiO$ and $ZnO-SiO_2-MnO$ systems synthesized in air, the first pair of oxides to react are metal oxides, forming solid solutions of $Ni_{1-x}Zn_xO$ (rock salt structure) and $Zn_{1-x}Mn_xMn_2O_4$ (spinel structure), respectively. With further increase in annealing time, the proportion of the dopant ion in the solid solutions increases. Upon heating to 900 °C, zinc and silicon oxides begin to react in both systems, forming willemite Zn_2SiO_4, which gradually becomes enriched with dopant metal ions to form the solid solution $Zn_{2-2x}M_{2-2x}SiO_4$ (M = Ni or Mn).

At higher temperatures, the reaction of $Ni_{1-x}Zn_xO$ and SiO_2 in the $ZnO-SiO_2-NiO$ system results in the formation of a phase with the olivine structure $Ni_{2-2x}Zn_{2-2x}SiO_4$. Phase equilibria in the system are determined by the quasi-binary equilibrium of the boundary compositions of the $Zn_{1.8}Ni_{0.2}SiO_4$ and $Ni_{1.5}Zn_{0.5}SiO_4$ solid solutions and the conodes connecting these compositions with the $Ni_{0.83}Zn_{0.17}O$ solid solution, as well as the conode connecting the boundary composition of the $Ni_{1.6}Zn_{0.4}O$ solid solution with Zn_2SiO_4.

In the $ZnO-SiO_2-MnO$ system, no phases with an olivine structure were detected. In the temperature range of 800-1250 °C, the sequential appearance of intermediate phases $ZnMnO_3$, $ZnMn_2O_4$, and $MnSiO_3$ was detected. Phase equilibria were established for temperatures of 800 °C and 1250 °C. It is shown that the phase relationships in the $MnOx–ZnO–SiO_2$ system are determined by changes in the charge states of manganese ions with increasing temperature, leading to phase transformations of manganese oxide $MnO \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$. Triangulation of the $Mn_2O_3–ZnO–SiO_2$ system at 800°C is determined by the conode $ZnMn_2O_4–Zn_2SiO_4$ and decomposes the system into elementary triangles $ZnO–Zn_2SiO_4–ZnMn_2O_4$, $Zn_2SiO_4–ZnMn_2O_4–SiO_2$, and $ZnMn_2O_4–SiO_2–Mn_2O_3$. The triangulation of the ternary system $MnO–ZnO–SiO_2$ is determined by the elementary triangle $Zn_{1.6}Mn_{0.4}SiO_4–ZnO–MnSiO_3$.

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THERMOLYSIS OF COMPOSITES BASED ON POLYANTIMONIC ACID CONTAINING Nb^{5+} IONS

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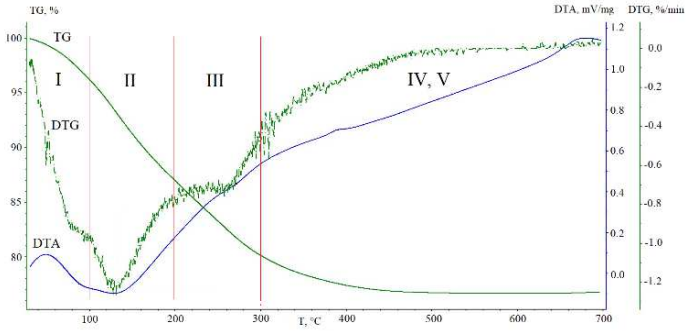
Particles of solid acids are introduced into the membranes of hydrogen-air fuel cells to increase their moisture capacity. Promising components include pyrochlore-type structure polyantimonic acid (PAA), amorphous niobium acid (NA), and composites based on them.

The purpose of this work was to determine the stages of thermolysis of PAA-based samples, containing Nb^{5+} ions.

The samples were synthesized using the co-precipitation method. Starting reagents: $SbCl_3$ (pre-oxidized to Sb^{5+}), $NbCl_5$. Samples were characterized by X-ray powder diffraction on DRON-3M and Rigaku Ultima IV diffractometers. The proton-conducting properties were studied using an Elins-Z1000J impedance meter in the frequency range from 1 Hz to 2 MHz, at a temperature of 25°C and a relative humidity of 58%. The thermal properties of the samples were studied in air using a Netzsch STA 449F5 Jupiter simultaneous thermal analysis system.

According to the data of X-ray phase analysis, the maximum concentration solid solution of substitution has the composition $H_2Sb_{1.6}Nb_{0.4}O_6 \cdot nH_2O$, $n \geq 1$, within the framework of the pyrochlore-type structure; the conductivity value is $5.0 \cdot 10^{-3}$ S/m. The highest conductivity values among the considered acids are exhibited by $H_2Sb_{1.4}Nb_{0.6}O_6 \cdot nH_2O$, $n \geq 1$, a composites based on PAA; the conductivity value is $11.5 \cdot 10^{-3}$ S/m. In contrast to PAA compositions, x=0, x=0.4, the DTG curve of the x=0.6 sample can be divided into stages I and II (Fig.).



Thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA) for the $H_2Sb_{1.4}Nb_{0.6}O_6 \cdot nH_2O$

In the composition x=0.6, proton-containing groups are removed in 3 stages: stage I: 0.85 H_2O (up to 100 °C); stage II: 2.00 H_2O (up to 200 °C); stage III: 1.50 H_2O (up to 300 °C); stage IV-V: 0.50 H_2O (up to 450 °C). A possible reason for the higher conductivity value is the non-equivalence of proton-containing groups.

MANUFACTURING OF ZrO_2 BASED TETRAGONAL AND CUBIC SOLID SOLUTIONS WITH LANTHANIDE OXIDES: THE EFFECT OF XEROGELS AND PRECURSOR POWDERS PROPERTIES

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High-symmetric (tetragonal and cubic) ZrO_2 modifications are considered as perspective materials for modern industry, such applications as solid electrolytes in electrochemical devices and dentistry materials could be mentioned. The most appropriate approach to obtain desirable high symmetric zirconia phases is ZrO_2 stabilization by the addition of some bivalent and trivalent metal oxides resulting in solid solutions formation. Sol-gel synthesis is widely used here due to the possibility to control the phase composition and the dispersity of the precursor powders obtained. The goal of the present work was the application of the above approach for the manufacturing of ZrO_2 stabilized by lanthanides, i.e., the synthesis of ZrO_2 tetragonal and cubic solid solutions with La, Ce, Pr, Nd, Sm, Gd, Tb, Ho, Er, and Yb oxides. The paper reports the study of the thermal effects in xerogels, the dispersity of products at all stages of powder manufacturing, and the phase composition of the obtained precursor powders.

The reagents used for lanthanides stabilized zirconia (LnSZ) synthesis are listed below: aqueous ammonia solution, $ZrO(NO_3)_2 \cdot 6H_2O$ and lanthanide hydrates $A(NO_3)_3 \cdot 6H_2O$, where A – La, Ce, Pr, Sm, Gd, Tb; $B(NO_3)_3 \cdot 5H_2O$, where B – Ho, Er, Yb. Systems $92ZrO_2$-$8Ln_2O_3$ (mol.%, Ln = Pr, Nd, Sm, Gd, Ho, Er, Yb), $91ZrO_2$-$9CeO_2$, $90ZrO_2$-$10La_2O_3$, and $88ZrO_2$-$12Tb_2O_3$; $97ZrO_2$-$3Nd_2O_3$, $97ZrO_2$-$3Sm_2O_3$, $96ZrO_2$-$4Ln_2O_3$ (Ln = Ce, Gd, Tb, Ho, Er, Yb), $95ZrO_2$-$5La_2O_3$ and $95ZrO_2$-$5Pr_2O_3$ were chosen for the investigation and corresponding 0.1M aqueous salts solutions were prepared. Then, the salts solution was added by drops at a rate of ~ 1–2 ml/min into the 1M ammonia aqueous solution; the pH level of about 9–10 was kept constant. Co-precipitation in an ice bath (0–5 °C) at permanent mixing by a multiblade mechanical agitator resulted in the hydroxide mixture formation. The obtained gel was aged for two days, then filtered using the Buchner funnel with the ashless paper filter (Grade 589/3 blue ribbon filter with an average pore size of ~ 2 μm) to remove the mother solution and then washed. The freshly formed metal hydroxides gel was dehydrated via freeze drying. The received amorphous powders were annealed at 450, 600 and 800 °C for 2 hours. Samples investigation was performed by thermal analysis, the X-ray diffraction analysis and particle size distribution analysis. It was found that experimental values of exothermic effects in xerogels agree well with crystallization enthalpy value for the cubic zirconia crystallization being ~ -9 kJ/mol and for the tetragonal zirconia crystallization being ~ -15 kJ/mol. It was shown that the increase in the calcination temperature up to 800 °C increases powders dispersity with mean particle size reduction up to ~ 20–40%.

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THERMODYNAMIC PROPERTIES OF REE STANNATES

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Compounds with the pyrochlore structure are considered potential thermal barrier materials due to their unique characteristics: high melting points, absence of phase transformations over a wide temperature range, and low thermal conductivity. Stannates of rare earth elements (REE) $REE_2Sn_2O_7$ form a complete series of pyrochlores from La to Lu [1]. A distinctive feature of the pyrochlore structure is the presence of oxygen vacancies. These vacancies are believed to play a key role in reducing thermal conductivity, which is crucial for thermal barrier materials [2,3].

The work defines temperature-time regimes for obtaining stannates by various methods and shows that high temperatures are required for the formation of ceramic samples. Porous ceramic samples of $Ln_2Sn_2O_7$ stannates with crystallite sizes of ≈100–400 nm were obtained. All obtained stannates were indexed under the assumption of a cubic syngony with parameters characteristic of compounds of the pyrochlore structural type. The chemical composition of the obtained stannates and the absence of impurities were confirmed using X-ray fluorescence spectroscopy.

Heat capacity measurements were performed in the temperature range of 5-350 K using a BKT-3 adiabatic vacuum calorimeter and at high temperatures (330-1300 K) using a Netzsch STA 449F1 Jupiter® differential scanning calorimetry (DSC). The temperature curves for the heat capacity of the studied stannates show no visible anomalies, indicating the absence of phase transitions in the temperature range under study. Based on smoothed values of the rare-earth stannate heat capacity in the range of 0–1300 K, the temperature dependences of standard thermodynamic functions—entropy $S^0(T)$, enthalpy increment $H^0(T)–H^0(0)$, and reduced Gibbs free energy $\Phi^0(T)$—were calculated.

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SYNTHESIS AND THERMODYNAMIC STUDY OF COMPOUNDS BASED ON BISMUTH, LUTETIUM AND INDIUM OXIDES

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Compounds on the basis of bismuth, lutetium and indium oxide are promising materials for environmentally friendly energy conversation technologies and engineering utilized photocatalytic activity, magnetic properties et al. Solid oxide fuel cells (SOFC) might become one of the most actively developing endeavors near term. Electrolytes based on yttria stabilized zirconia and gadolinia doped ceria have been widely used, however possess disadvantages: high operation temperature, certain demands on condition. That is why new high efficient oxide ion conductors are required. δ-Bi_2O_3 demonstrates high ion conductivity, but can exist within narrow band (1000-1100K). The inclusion lanthanide ions in cubic Bi_2O_3-structure may result to high conductivity with stability at intermediate temperatures. Lu^{3+} is the smallest amid lanthanide ions; therefore Lu could be a better dopant [1-2].

$Bi_{1.5}Lu_{0.5}O_3$ and $Bi_{1.5}Lu_{0.4}In_{0.1}O_3$ were obtained by solid state reaction method. Pure Bi_2O_3, Lu_2O_3 and In_2O_3 were applied as precursors. Planetary mill Fritsch Pulverisette 6 with corundum grinding jar and balls, a manual hydraulic press, a furnace SNOL 4/1300 were used to received $Bi_{1.5}Lu_{0.5}O_3$ and $Bi_{1.5}Lu_{0.4}In_{0.1}O_3$. Stoichiometric amounts of precursors were grinded for 10 cycles (160-200 rpm), total time is 7 h. A mixture was pressed into 5 pallets (13×2 mm). The pallets were placed in the furnace at 750° for $Bi_{1.5}Lu_{0.5}O_3$ and 700°C for $Bi_{1.5}Lu_{0.4}In_{0.1}O_3$ during 50h. Samples were characterized by X-ray diffraction method (Tongda TD-3700, 5–70 2θ, CuKα).

The dissolution enthalpies of Bi_2O_3, $Bi_{1.5}Lu_{0.5}O_3$ and $Bi_{1.5}Lu_{0.4}In_{0.1}O_3$ were measured by solution calorimetry at 298.15K in 2M HCl. Based on measured experimental and literature data the standard formation enthalpy, lattice enthalpy and stabilization energy were calculated.

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THE POSSIBILITY OF THE EXISTENCE OF MESOPHASES FOR SECOND-GENERATION ANTICOAGULANT RODENTICIDES

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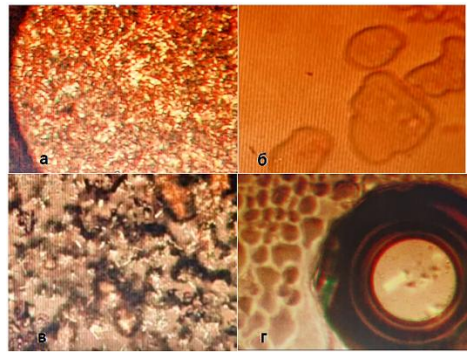
Second-generation anticoagulant rodenticides have been known since the late 1970s. Since the synthesis and scaling of the production process, melting point ranges reaching several tens of degrees have been established. Recently, we obtained various new modifications of difenacoum and brodifacoum. These modifications were subjected to comprehensive study, and the existence of significant melting point ranges was fully confirmed. We did not immediately recognize this fact, but after obtaining data on the crystalline structure of some modifications, we performed more precise measurements using visual polythermal microscopy, which confirmed the assumption that difenacoum and brodifacoum possess liquid crystalline states.

At the initial stage of melting, areas with textures reminiscent of the schlieren textures of smectics (Fig. 1 a-c) and clearly visible spherical areas similar to droplets of cholesteric (Fig. 1 g) are formed, which glow when the polarizers are crossed in the field of view of the microscope.



Textures obtained at x100 magnification in crossed polarizers a) difenacoum at 232 ºC, b) difenacoum at 230 ºC, c) difenacoum at 232 ºC, d) brodifacoum at 218 ºC

Textures for thermotropic liquid crystals are formed and visually recorded in a similar manner. Based on the crystal structures in which "rigid" and conformationally labile aromatic fragments are formed, various types of textures emerge, revealing the orientational order of molecules or molecular clusters during the transition from the crystalline to the isotropic phase.

ON THE MECHANISM OF MATERIAL CONSOLIDATION DURING SPARK PLASMA SINTERING

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Spark plasma sintering (SPS) is a modern method of electrostimulated consolidation of substances and materials under high pressure and temperature. The SPS has been described for a wide range of objects [1]. The presented work provides consolidated samples of graphene nanoflakes (GNFs), hetero-substituted with N, P, and Si atoms GNFs, as well as their surface oxidized analogues. To identify the mechanism and influence of the SPS processing parameters, the contributions of temperature (as the input heat Q) and pressure (as the performed work A) were estimated tale into account that both parameters affect the change in internal energy ΔU, according to the first law of thermodynamics:

$$\Delta U = A + Q$$

The mechanical work A used to shrink the samples can be calculated as the product of the applied force F, expressed in newtons, and the displacement d (sample shrinkage), expressed in meters:

$$A = F \cdot d$$

The force F was calculated as the multiplication of the pressure P and the area S of the sintered sample:

$$F = P \cdot S$$

The shrinkage of the samples over time strongly depended on the nature of the sintered sample. The greatest shrinkage and, consequently, the greatest mechanical work were characterized for P-doped GNFs. Surface oxidized GNFs were more compacted than GNFs.

The work of electric current Q was calculated using the equation:

$$Q = \Sigma i_n \cdot U_n \cdot (\tau_{n+1} - \tau_n),$$

where i – the current expressed in amperes, U is the voltage expressed in volts, and τ is the exposure time expressed in seconds.

The work of the current exceeded the mechanical work by several orders, which implies that it plays a significantly greater role in the consolidation of samples. The work Q strongly depends on the nature of the sample: non-conductive materials, as well as the presence of non-conductive impurities, lead to local overheating and breakdown [2]. This is why the greatest morphological changes occurred with the oxidized MGF sample, as the surface oxygen-containing groups are non-conductive.

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P,T-DIAGRAMS FOR DOUBLE MANGANITES $RBaMn_2O_6$, R = Sm, Nd, Pr, La

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Rare-earth element R radius determines the physical properties for both disordered $RMnO_3$ and ordered (double) rare-earth manganites $RBaMn_2O_6$; this dependence reflects the size effect. An external pressure is another instrument to tune (to decrease) the lattice parameters. We have studied structure and properties (electrical resistivity, magnetization, heat capacity) for double manganites $RBaMn_2O_6$, R= Nd, Pr, La at temperature interval 100 – 300 K and external pressure range 0 – 5 GPa.

We investigated the structure of ceramic samples using powder diffraction with synchrotron (Elettra and VEPP-3) and neutron (IBR-2) radiation; the properties were studied using high-pressure chambers in Vereshchagin Institute of High Pressure Physics, RAS. The pressure influence on the metal-insulator (MI) transition and Néel temperature were obtained, the compressibility and thermal expansion coefficients were obtained for both conducting and the insulating phases. The Table summarizes the pressure dependences of Néel temperature (T_N) and the temperature of Metal-Insulator transition (T_{MI}).

Pressure dependences of Néel temperature (T_N) and the temperature of Metal-Insulator transition for $RBaMn_2O_6$, R= Nd, Pr, La

R-atom	**Nd**	**Pr**	**La**
T_N	↑	↑	Const
T_{MI}	↓	↓	Const

In the raw Nd – Pr – La radius of R-atom increases; and T_{MI} decreases in this sequence. We observe the same effect because of high pressure. Néel temperature (A-type order) decreases for Nd- and Pr- based compounds while pressure dependence demonstrates an opposite effect. Surprisingly, there is no influence of pressure on T_N and T_{MI} for La-based compound. Mixed magnetic (ferromagnetic and antiferromagnetic) and conducting (conducting and insulating) state may be responsible for such a behavior.

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ADDITIVE MANUFACTURING AND THERMODYNAMICS

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Additive manufacturing technologies are used in various industries, including space, aviation, housing construction, instrument making, and other areas where there is a need for complex-geometry products made from existing and new materials. Functional products are created by layer-by-layer material growth, including direct metal deposition (DMD), surface laser sintering (SLM), and cold spray deposition (Cold Spray) from various materials.

When creating products using additive manufacturing methods, it is necessary to understand the physical, physicochemical, and other processes inherent to materials in various states (solid, liquid, etc.). To model these processes, laws and relationships used in thermodynamics are applied. Integrated modeling of materials based on the CALPHAD method (calculation of phase diagrams, modeling of material crystallization, heat treatment processes, diffusion, etc.) is widely used for additively manufactured products.

Micromodeling of additive manufacturing processes is also used, which involves calculating the distribution of powder particles of the used fraction across the powder bed and melting this layer with a laser at a specified power and pass rate to determine the temperature distribution.

Macromodeling, which calculates residual stresses and warpage of a product of a given shape based on the viscoplastic behavior of the material under specified layer-by-layer growth conditions, is also used. Thanks to comprehensive modeling of additive manufacturing processes occurring during the growth of products, it has become possible to produce products with complex geometries and internal cavities (for example, engine components with a cooling system), as well as to create unique composite and multilayer materials with a unique set of properties.

This paper presents the results of thermodynamic calculations in comparison with experimental data and presents optimization parameters for various materials obtained by additive manufacturing methods. The modeling of nonequilibrium crystallization of materials during double remelting of layers is presented.

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LOW-TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF A $Gd_2(MoO_4)_3$ SINGLE CRYSTAL

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Rare-earth molybdates, including $Gd_2(MoO_4)_3$, are of considerable practical interest due to their nonlinear optical and ferroelectric properties, which underpin their applications in photonics and optoelectronic devices. Reliable thermodynamic data, in particular high-precision heat capacity over a wide temperature range, are essential for an adequate description of their physical behavior. Available literature data are limited to temperatures below 4.2 K and the 60–305 K interval and have been obtained for polycrystalline samples, thus precluding a consistent thermodynamic description of single-crystalline $Gd_2(MoO_4)_3$ over an extended temperature range.

Gadolinium molybdate single crystal and titanium calorimeter container

In this work, a large optically homogeneous single crystal of gadolinium molybdate ($Gd_2(MoO_4)_3$) was grown using the low-thermal-gradient Czochralski method and comprehensively characterized in terms of its phase, elemental, and impurity composition. For calorimetric measurements, a cylindrical sample was prepared from the crystal, precisely matching the dimensions of the inner cavity of the calorimeter container. High-precision heat capacity data in the temperature range 6–330 K were obtained by adiabatic calorimetry using a BKT-20 calorimeter [1]. Based on the experimental data, thermodynamic functions (entropy, enthalpy and reduced Gibbs energy) were calculated for the entire studied temperature range. Low-temperature heat capacity data below 4.2 K from the literature were consistently incorporated to ensure correct extrapolation to 0 K. The results obtained in our study were compared with literature data.

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HEAT CAPACITY MEASUREMENTS OF $RbAg_4I_5$ AND Rb_2AgI_3

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Solid-state superionic conductors with general formula MAg_4I_5 (Me = K, Rb, NH_4) are known as solid electrolytes with very high (~10^{-1} $Ohm^{-1}\times cm^{-1}$) silver-ion conductivity at room temperature and below. Discovered in 1960s, $RbAg_4I_5$ is still the most interesting among them as it has the highest silver ion conductivity of 0.33 $Ohm^{-1}\cdot cm^{-1}$ at 25 °C. Moreover, it was experimentally confirmed unambiguously that high values of conductivity remain in the wide temperature range due to the low activation energy of conduction (0.10 eV), being 0.11 $Ohm^{-1}\times cm^{-1}$ at -50 °C [1]. However, accumulated over decades experimental information contradicts the available literature data. It was stated [2] that $RbAg_4I_5$ is thermodynamically unstable below 27 °C and tends to decompose to low-conductive phases according to the reaction

$$RbAg_4I_5 \rightleftarrows Rb_2AgI_3 + AgI$$

In order to solve this contradiction and theoretically confirm experimentally observed rather high stability of $RbAg_4I_5$ one need to obtain full thermodynamical characterization of the system RbI – AgI. In addition to $RbAg_4I_5$, it contains another compound Rb_2AgI_3. The goal of this work was to determine temperature dependencies of heat capacity from -196 to 230 °C ($RbAg_4I_5$) and 290 °C (Rb_2AgI_3), using differential scanning calorimetry (DSC) experimental techniques. The temperature dependences of the molar heat capacity at constant pressure $C_p(T)$ for the compounds $RbAg_4I_5$ and Rb_2AgI_3 were measured by the comparison method [3] using high-purity silver as a heat capacity standard. The obtained results relate to reference thermodynamic data and can be used in thermodynamic calculations.

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3 GOST R 56754-2015 (ISO 11357-4:2005) "Plastics. Differential scanning calorimetry (DSC). Part 4. Determination of specific heat capacity".

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THERMAL STABILITY OF $PrMnO_3$ AND $PrMn_2O_5$ PEROVSKITES IN REDUCING ATMOSPHERE

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The perovskite-like double oxides $PrMnO_3$ and $PrMn_2O_5$ and materials based on them have sufficiently high values of electrical conductivity and catalytic activity and can be used as materials for catalytic reactions. The specifics of the operation of these materials are constrained by the lack of necessary data to select synthesis modes that preserve their chemical and phase composition, and as a result, their properties. Obtaining such data requires thermodynamic analysis of oxides to determine the conditions of their chemical stability over a wide range of temperatures and oxygen pressures.

The thermal properties of the samples were studied using a dynamic method on a synchronous thermal analysis device STA 449 F3 using an attachment for regulating the partial pressure of oxygen in gaseous atmospheres. The experiment was carried out when heated from room temperature to 1000°C. Based on experimental data, the range of thermal stability of the crystal structure of the orbitally disordered *O*-phase of $PrMnO_3$ oxide was determined at an oxygen pressure in a gaseous medium $P(O_2) = 0.21$ atm. Analysis of changes in the oxygen content in $PrMnO_3$ and $PrMn_2O_5$ oxides when heated in a reducing atmosphere $P(O_2) = 10^{-23.5}$ atm allowed us to establish the sequence of changes in their phase composition and calculate the content of ions of various manganese. The temperature dependences of the equilibrium oxygen pressure for the reduction reactions of $PrMnO_3$ and $PrMn_2O_5$ oxides were obtained using the static method of studying heterogeneous equilibria in the Pr-Mn-O system:

$$PrMnO_3 = 1/2\ Pr_2O_3 + MnO + 1/4O_2,$$
$$PrMn_2O_5 = PrMnO_3 + 1/3\ MnO + 1/3O_2.$$

The thermal stability of oxides is determined by the reactions of oxygen exchange with a gaseous medium. Based on experimental data thermodynamic characteristics of the reactions of oxide dissociation and their formation from elements have been obtained.

This work was carried out according to the state assignment of the Vatolin Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences (IMET UB RAS) using equipment of the Collaborative usage centre "Ural-M."

STUDY OF THE KINETICS OF PHASE TRANSFORMATION OF γ-Al_2O_3 NANOPARTICLES INTO CORUNDUM

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Aluminum oxide is widely used as insulating and abrasive coatings, as well as a catalyst in oil refining processes. Al_2O_3-based ceramics are used to manufacture dental implants and hip replacements. The addition of Al_2O_3 nanoparticles to polymer matrices improves their mechanical and thermal properties. Aluminum oxide has many modifications, of which the most stable is the α-Al_2O_3 (corundum) phase. This material is chemically and thermally stable, possessing high strength and permittivity. In this study, the kinetics of nanocrystalline corundum formation under high-temperature annealing conditions was investigated.

The annealing precursor was obtained using the sol-gel method. A sample of $Al(NO_3)_3$ along with 2-3 drops of acetic acid was added to a 0.5 M solution of stearic acid in dimethylformamide at 70 °C with continuous stirring. The resulting mixture was then homogenized isothermally until the precursors were completely dissolved, yielding a clear solution. Gradually raising the temperature above 100 °C caused the melt to change color to bright red and boil, releasing nitrogen oxide (IV). After the solvent evaporated, a pale-yellow aluminum stearate gel was obtained. In the first series of samples, aluminum stearate was annealed for 2 hours at temperatures of 900 °C, 1000 °C, and 1100 °C. In the second and third samples, the annealing time was varied from 2 to 12 hours (in 2-hour increments) at 900 °C and 1000 °C, respectively.

As a result, three series of Al_2O_3 samples were obtained, the phase composition of which was studied using X-ray diffraction. The formation of the corundum phase exclusively was observed during annealing for 2 hours at 1100 °C (the first series of samples). With a decrease in the annealing temperature, the appearance of the α-Al_2O_3 phase was observed with a longer holding time (the second and third series of samples). The average crystallite size for the separately obtained γ-Al_2O_3 phase was 4±1 nm, and for corundum, 44±4 nm.

A NEW APPROACH TO OBTAINING A METASTABLE POLYMORPH OF IMATINIB MESYLATE

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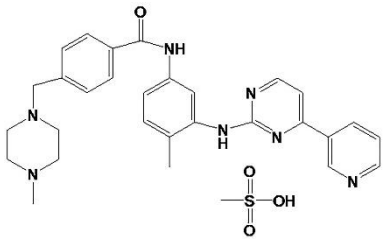
Discovery of all possible polymorphs of pharmaceutically active components is a necessary issue in pharmaceuticals because different polymorphs have a varying bioavailability. Of particular interest are metastable polymorphs, which exhibit enhanced dissolution kinetics in physiological fluids. However, reproducible preparation of metastable forms is a non-trivial task, typically requiring the development of complex, multi-step procedures or high-throughput screening.



Imatinib mesylate

In this study, we used for screening polymorphs of the pharmaceutically active component the approaches previously proven successful in working with phenylbutazone [1] and olanzapine [2]. We developed a method for the reproducible preparation of a metastable polymorph of imatinib mesylate (see the structure in the Figure above), whose melting point is lower than that of the stable commercial form by 70 K. Preparation of metastable forms of imatinib mesylate is complicated by its tendency to be oxidized by air oxygen in liquid solutions and upon heating, as well as by its ability to absorb water from the air. The developed method eliminates the possibility of undesirable reactions, ensuring reproducible results through thermodynamic control of the used solid-state processes, which are implemented by equilibrating solid samples with solvent vapors and desolvation.

1. M.N. Gabdulkhaev, A.V. Simdyanova, D.N. Bolmatenkov, A.T. Gubaidullin, T.A. Mukhametzyanov, M.A. Ziganshin, V.V. Gorbatchuk // CrystEngComm, 2025, 27, 2490. https://doi.org/10.1039/d5ce00094g

2. M.N. Gabdulkhaev, N.F. Idiyatullina, Kh.R. Khayarov, A.O. Surov, M.A. Ziganshin, V.V. Gorbatchuk // Crystal Growth & Design, 2026, 26, 734. https://doi.org/10.1021/acs.cgd.5c01154

This study was financially supported by the Russian Science Foundation, project no. 25-73-20073.

LOW-TEMPERATURE THERMODYNAMIC PROPERTIES OF SINGLE-CRYSTAL $Na_6Mo_{11}O_{36}$

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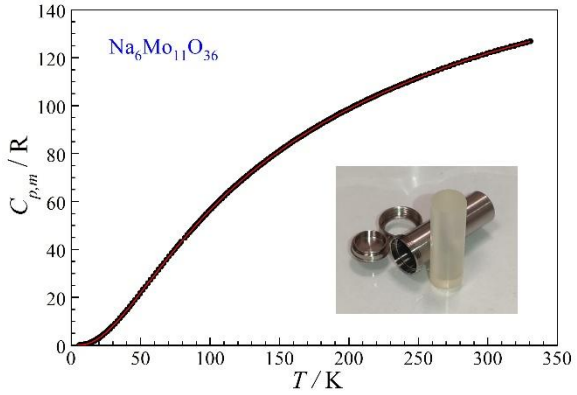
Single-crystal $Na_6Mo_{11}O_{36}$ is a promising material for cryogenic scintillating bolometers used in the search for neutrinoless double beta decay. Data on heat capacity are essential to determine the energy resolution of a cryogenic bolometer.

$Na_6Mo_{11}O_{36}$ single crystal was grown from the melt by the low-gradient Czochralski method [1]. The obtained single crystal was thoroughly characterized; its phase and elemental compositions were determined. The total impurity content is 0.015 wt%.

Heat capacity data for the $Na_6Mo_{11}O_{36}$ single-crystal sample were obtained in the range of 5.9 K to 330 K using a BKT-20 adiabatic calorimeter. The description of the experimental setup and the results of test heat capacity measurements for benzoic acid and copper were reported previously [2]. The measurement results are shown in the Figure. This data was obtained for the first time.



Experimental heat capacity of the $Na_6Mo_{11}O_{36}$ single crystal

The heat capacity data were used to calculate the characteristic Debye temperature at 0 K ($\Theta_D(0)$= 341 ± 5 K) and the thermodynamic functions in the range of 0–330 K. The results obtained suggest that the $Na_6Mo_{11}O_{36}$ single crystal is a promising candidate for use in cryogenic scintillating bolometer technology.

1. Grigorieva V.D., et. al. // Cryst. Growth Des. 2025, V. 25. P. 986.
2. Bespyatov M.A. // J. Chem. Eng. Data 2025. V. 70. P. 3630.

The study was supported by the grant from the Russian Science Foundation No. 24-19-00405, https://rscf.ru/en/project/ 24-19-00405/

SINGLE-CRYSTAL $NaCsMo_3O_{10}$: GROWTH, PHASE STABILITY, THERMODYNAMIC PROPERTIES

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At present, considerable efforts are devoted to the search for molybdenum-containing scintillation crystals with optimized properties for application in neutrinoless double beta decay experiments. In this study, a large-sized, optically homogeneous, and defect-free single crystal of sodium–cesium molybdate ($NaCsMo_3O_{10}$) was grown by the low thermal gradient Czochralski technique.

$NaCsMo_3O_{10}$ single crystal grown in the [001] direction

The as-grown single crystal was comprehensively characterized, including determination of its phase purity and elemental composition. Thermogravimetric analysis (TGA) combined with simultaneous differential scanning calorimetry (DSC) was performed over the temperature range of 300–900 K.

The DTA curve of $NaCsMo_3O_{10}$ exhibits a pronounced endothermic peak in the 800–820 K range, with a maximum at $T_{max} \approx 816$ K, corresponding to the melting process. No additional phase transitions were detected within this temperature interval. The onset of melting was determined to be $T_{onset} = 809 \pm 1$ K.

The heat capacity of the single crystal over the entire range of existence of the solid phase (from 0 K to melting) was measured using adiabatic and scanning calorimetry methods. Based on these data, the thermodynamic properties (entropy, enthalpy, and reduced Gibbs energy) were calculated.

The study was supported by the grant from the Russian Science Foundation No. 24-19-00405, https://rscf.ru/en/project/ 24-19-00405/

INVESTIGATION OF THE HEAT CAPACITY OF $Y_{3-x}Eu_xSc_2Ga_3O_{12}$ (0 < x < 3) SOLID SOLUTIONS

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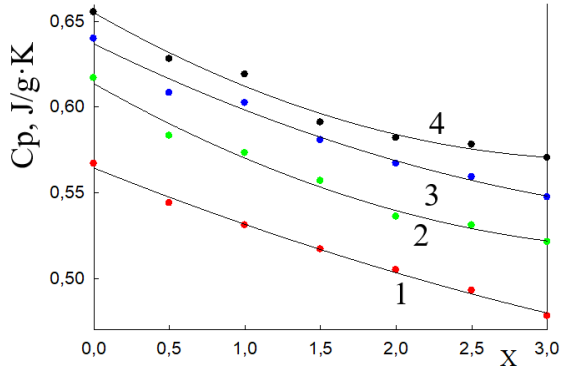
Yttrium-scandium-gallium garnet is a promising material for high-efficiency phosphors. Similar ionic radii, identical charge, and close electronegativity of Eu^{3+} and Y^{3+} ions facilitate lattice doping, enabling Y^{3+} substitution and solid solution formation. Substituting Y^{3+} with Eu^{3+} has the potential to enhance the luminescent properties of this material. However, the thermodynamic and thermophysical properties of the $Y_{3-x}Eu_xSc_2Ga_3O_{12}$ system have not been systematically studied.

Solid solutions of the $Y_{3-x}Eu_xSc_2Ga_3O_{12}$ system ($0<x<3$) were synthesized by a high-temperature solid-state reaction at 1793 K using B_2O_3 as a flux. The phase purity of the obtained samples was verified by XRD using a Bruker D8 diffractometer with a VANTEC -1 linear detector and CuKα radiation. The synthesized garnets belong to the cubic space group $Ia\bar{3}d$.

The temperature dependence of the heat capacity for all obtained substances was determined by differential scanning calorimetry (DSC) using a STA 449 S Jupiter instrument. The experiments were conducted in platinum crucibles with lids, with a heating rate of 20 K/min, from 323 K to 1023 K in an air atmosphere. The obtained results are presented in the figure.



Dependence of the specific heat capacity on the composition of $Y_{3-x}Eu_xSc_2Ga_3O_{12}$: 1 – T = 323 K, 2 – T = 523 K, 3 – T = 723 K, 4 – T = 923 K

Substitution of Y^{3+} ions with Eu^{3+} ions leads to a nonlinear decrease in heat capacity in the $Y_{3-x}Eu_xSc_2Ga_3O_{12}$ system throughout the studied temperature range.

*The work was carried out within the framework of the state assignment of the Ministry of Science and Higher Education of the Russian Federation for science of the Siberian Federal University, project FSRZ-*2026-0011.

EFFECT OF INDIUM SUBSTITUTION ON THE STRUCTURE OF $SrFeO_{3-\delta}$ AND ITS TRANSPORT PROPERTIES

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Materials based on $SrFeO_{3-\delta}$ are promising candidates for cathodes in solid oxide fuel cells and oxygen-permeable membranes. However, undoped $SrFeO_{3-\delta}$ exhibits a high thermal expansion coefficient and is prone to phase transformations in a reducing atmosphere, which limits its practical application. The introduction of dopants into the B-sublattice enables control over structural stability, oxygen nonstoichiometry, and transport properties. This approach is realized in the present work by substituting $Fe^{3+/4+}$ with In^{3+} and studying its effect on these characteristics.

Samples with the formula $SrFe_{1-x}In_xO_{3-\delta}$ (x = 0.00–0.35) were synthesized using a sol-gel method with citric acid, followed by annealing at 1100 °C and sintering at 1190 °C. The phase composition of the samples was studied by X-ray diffraction with Rietveld refinement. The homogeneity range is within $0.0 \le x \le 0.30$. The samples with an indium content of $x = 0.05$–0.30 crystallize in a cubic perovskite cell (space group *Pm*-3*m*), whereas the base $SrFeO_{3-\delta}$ composition possesses an orthorhombic structure (space group *Cmmm*). Cubic symmetry can exist for the undoped composition, however, this modification is unstable under standard conditions. Thus, the introduction of indium stabilized the cubic structure of $SrFeO_{3-\delta}$ system. The unit cell parameter increases monotonically with increasing indium content in the samples, which is attributed both to the size effect from substituting $Fe^{3+/4+}$ ions with larger In^{3+} ions and to the accompanying decrease in the average oxidation state of iron.

Oxygen nonstoichiometry was determined using iodometric titration. Doping with In^{3+} leads to an increase in the concentration of oxygen vacancies at room temperature. Thermogravimetric measurements revealed that the release of oxygen from the crystal lattice begins at 300 °C, with samples containing high indium content exhibiting a lower oxygen loss upon heating. Thermal expansion was measured using high-temperature dilatometry. The temperature dependences of relative elongation are nonlinear.

Electrical conductivity measurements were carried out using the four-probe DC method in a controlled atmosphere (pO_2 = 0.5–10^{-20} atm) in the temperature range 750–950 °C. The samples are characterized by mixed ionic-electronic conductivity throughout the entire temperature range studied. The maximum ionic conductivity value is observed for the composition $x = 0.05$. Upon further increase in indium content, the ionic conductivity decreases, which may be attributed to ordering of the crystal structure and partial blocking of the migration pathways for O^{2-} ions.

This work was carried out in accordance with the state assignment for the Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, topic No. 124061300025-8.

THERMODYNAMIC PROPERTIES OF TERNARY CESIUM LEAD HALIDES

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Ternary halides $CsPbX_3$, $CsPb_2X_5$, and Cs_4PbX_6 (X = Cl, Br) are promising semiconductor materials due to their potential applications in optoelectronics and photovoltaics. Stability of these compounds under real operating conditions, both in relation to decomposition into constituent components and in relation to the effects of oxygen, carbon dioxide and water vapor present in the air, is a current issue. The main aim of this work was to determine standard enthalpies of formation from binary halides and isobaric heat capacities of these substances.

$CsPbX_3$ and Cs_4PbX_6 samples were synthesized via melt crystallization and solid-state sintering, respectively. Cesium and lead halides (CsX and PbX_2; X = Cl, Br) were used as the precursors. The stoichiometric mixtures of the starting materials were carefully ground in an agate mortar and placed in evacuated and hermetically sealed glass ampules. The ampules with Cs_4PbX_6 were heated in a furnace at 300 °C for 24 h and then cooled to room temperature at a rate of 2 °C/h. This procedure was repeated 3 times with intermediate regrinding of the reacting mixture. The ampules with $CsPbX_3$ were heated in a furnace at 630 °C for 12 h and then cooled to room temperature at the same rate. $CsPb_2X_5$ were prepared by dissolving $(CH_3COO)_2Pb{\cdot}3H_2O$ in hot HX (X = Cl, Br) solution and subsequent adding of CsX powder. The precipitates were separated from cooled solutions on a glass filter, washed with ethanol, and dried at 70 °C for 1 h.

The standard enthalpies of formation from binary halides were determined using solution calorimetry. The obtained values for all studied samples are negative, of the order of -20 $kJ{\cdot}mol^{-1}$. This fact indicates the thermodynamic stability of these substances at T = 25 °C.

Temperature dependencies of the isobaric heat capacity were measured using adiabatic calorimetry (from 77 K to 350 K) and differential scanning calorimetry (from 350 K to temperatures near the melting points). Based on the analysis of captured data, a number of phase transitions in $CsPbX_3$ samples were obtained, their enthalpies and entropies were estimated. Additionally, temperature dependencies of the enthalpy increments from 373 K to temperatures near the melting points were determined for all synthesized samples using drop calorimetry.

THERMODYNAMIC AND ELECTROPHYSICAL CHARACTERISTICS OF THE Nd_2O_3–MgO–NiO–Mn_2O_3 SYSTEM

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Modification and combination of alloying elements in $NdMnO_3$-based compounds allow for the production of materials with valuable physical and chemical properties.

In the Nd_2O_3-MgO-NiO-Mn_2O_3 system, the compound $NdMg_2NiMnO_6$ was synthesized using a high-temperature ceramic method at 400–1200 °C.

The temperature dependence of the heat capacity of $NdMg_2NiMnO_6$ in the range 298.15–673 K was studied using the IT-C-400 calorimeter, the principle of operation of which is described in detail in [1].

The temperature dependence of the heat capacity of $NdMg_2NiMnO_6$ shows λ-shaped peaks at 348 and 473 K, which are probably related to phase transitions. Using these peaks, the following equations for C^0_p~$f(T)$, [J/(mol·K)], have been calculated:

$C^0_p = -(75\pm3) + (1024\pm41)\cdot10^{-3}T$, (298-348 K)
$C^0_p = (1004\pm40) - (2077\pm84)\cdot10^{-3}T$, (348-398 K)
$C^0_p = (2109\pm85) - (2286\pm92)\cdot10^{-3}T - (1618\pm65)\cdot10^{5}T^{-2}$, (398-473 K)
$C^0_p = (1187\pm48) - (1867\pm75)\cdot10^{-3}T$, (473-548 K)
$C^0_p = (541\pm22) + (33\pm1{,}32)\cdot10^{-3}T - (1185\pm48)\cdot10^{5}T^{-2}$. (548-673 K)

$S^0(298{,}15)$ of the $NdMg_2NiMnO_6$ compound is estimated by the method of ion entropy increments of Kumok. Using the experimental dependence of C^0_p~f(T) and the calculated $S^0(298{,}15)$, $C^0_p(T)$, $S^0(T)$, $H^0(T)$-$H^0(298{,}15)$, $\Phi^{xx}(T)$ are determined.

Using the LCR-781 setup in the 293-483 K (1, 5, and 10 kHz) range, it was found that the dielectric constant of $NdMg_2NiMnO_6$ increases sharply with increasing temperature ($\varepsilon \approx 1.16\times10^7$ at 483 K), while the resistance decreases ($1.53\times10^6 \rightarrow 1.38\times10^4$ Ohm), confirming the semiconductor nature of the conductivity.

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CALORIMETRIC AND ELECTROPHYSICAL STUDIES OF LANTHANUM–POTASSIUM CUPRATE–VANADATE–MANGANITE

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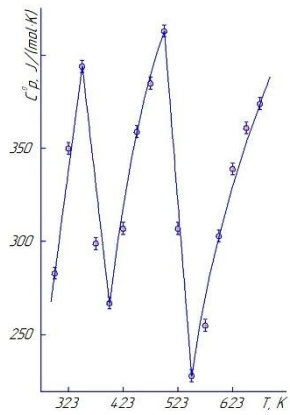
Perovskite manganites are of interest due to their enormous magnetoresistance, giant magnetostriction, and their potential for creating new functional materials.

The calorimetric study of $LaK_2CuVMnO_{7.5}$ was conducted in the range of 298.15-673 K using the IT-C-400 calorimeter.

The C^0_p~$f(T)$ curve shows λ-shaped peaks at 323 and 473 K (see Figure), which are characteristic of second-order phase transitions.



Temperature dependence of heat capacity $LaK_2CuVMnO_{7.5}$

Taking into account the temperatures of phase transitions, the equations describing the dependence C^0_p~$f(T)$ are derived. Based on the experimental dependence of the heat capacity and the calculated value of $S^0(298{,}15)$, the thermodynamic functions $C^0_p(T)$, $S^0(T)$, $H^0(T)$-$H^0(298{,}15)$ and $\Phi^{xx}(T)$ are calculated.

The electrophysical characteristics of $LaK_2CuVMnO_{7,5}$ were studied using the LCR 781 setup in the range of 293-483 K at frequencies of 1, 5, and 10 kHz. At a frequency of 1 kHz, there is a sharp increase in capacitance and dielectric constant with increasing temperature ($\varepsilon \approx 7\times10^8$ at 483 K), accompanied by a decrease in resistance from $\sim4\times10^5$ to $<7.6\times10^2$ Ohm.

This research is funded by the Committee of Industry of the Ministry of Industry and Construction of the Republic of Kazakhstan under program-targeted funding for scientific research for 2024-2026, BR23991563: «Creation of Innovative Resourch-Saving Technologies for Mining and Integrated Processing of Mineral and Technogenic Raw Materials.

THE 3rd-GENERATION CALPHAD MODEL FOR SOLID AND LIQUID Ge AND THE BINARY Ge-Si SYSTEM

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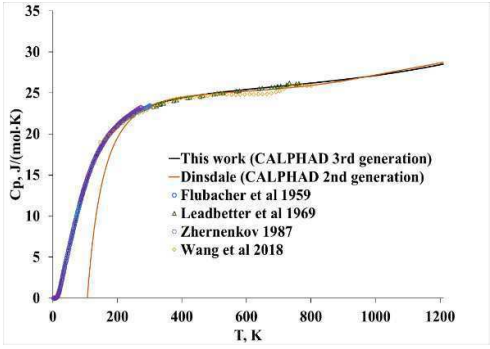
Germanium and silicon-germanium alloys serve as key materials in several advanced in technologies such as microelectronics, photonics and optoelectronic as well as solar cell elements especially in space technology. In response to improvements in experimental measurement and analysis methods and computational capabilities, it has become important to make new databases on the thermodynamic properties of pure germanium, silicon, and their alloys.

Third-generation CALPHAD models offer a superior alternative to the previously widespread polynomial expressions in existing databases. Based on modern thermodynamic data, these models provide an accurate description of thermodynamic function from absolute zero (0 K) up to temperatures above the melting point.

Critical review of available data for solid and liquid phases of Ge and Ge-Si were performed.

The stable crystalline modification with the diamond cubic structure type was described with two characteristic temperatures and two polynomial terms. The results of heat capacity modelling are shown in the figure below.



Experimental data and and calculation results of heat capacity of pure crystalline germanium in the temperature range 0-T_{fus}

A two-state model has been proposed to definition the liquid phase of Ge with two characteristic Einstein temperatures.

Combining thermodynamic models, including a liquid phase model with two characteristic temperatures developed for pure silicon and germanium, allows to describe the interaction in a binary system and obtain a more accurate prediction of the properties of the binary system in a supercooled liquid state.

The authors gratefully acknowledge the financial support of the Program "Chemical Thermodynamics and Theoretical Material Science" (№ 121031300039-1), Lomonosov MSU.

ACTIVITY COEFFICIENTS OF NEODYMIUM IN Fe-Nd ALLOY

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For the production of Fe–Nd–B permanent magnets, it is possible to use a Fe–Nd alloy, which can be obtained in various ways. This raises the question of studying the thermodynamic properties of such an alloy.

Using the emf method, the equilibrium potentials of the Fe–Nd alloy were measured in an equimolar mixture of sodium and potassium chlorides containing 3.3% by weight of neodymium chloride relative to the In–Nd alloy. Based on these measurements, the activity coefficients of neodymium in the alloy were determined. The activity of neodymium in the alloy with indium is known [1] and is expressed by the equation:

$\lg a_{\mathrm{Nd\,(In)}} = 4.271 - 12218 / T$.

Measurements were performed in the temperature range of 1003–1093 K. The neodymium concentration in the alloy with indium was 5.48% by weight, which corresponds to the two-phase region ($InNd_3$+Liq) [2].

Fe–Nd and In–Nd alloys are two-phase systems: a saturated solution of neodymium in equilibrium with an intermetallic compound, in the case of indium – $InNd_3$ [2], and in the case of iron – $Fe_{17}Nd_2$, $Fe_{17}Nd_5$ [3]. The activity of neodymium in the Fe–Nd alloy is determined by its activity in a saturated solution. The calculations were based on the assumption that neodymium in the alloys is reversible relative to Nd3+ ions in the salt phase [4]. Taking this assumption into account, a mathematical transformation was performed to calculate the activity of neodymium in the Fe–Nd alloy, taking into account the activity of neodymium in the In–Nd alloy and the measured potential difference between these alloys.

Based on the data obtained, an equation was developed for the functional dependence of neodymium activity in iron on temperature:

$\lg a_{\mathrm{Nd\,(Fe)}} = 104.18 - 0.243 / T + 1 \cdot 10^{-4} \cdot T^2$.

The resulting equation matches the E_{eq} (emf) temperature dependence for the peritectic reaction. Liq + $Fe_{17}Nd_2 \leftrightarrow Fe_{17}Nd_5$ [5].

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SILVER CONVERSION DURING PYROMETALLURGICAL PROCESSING OF MINERAL MATERIALS

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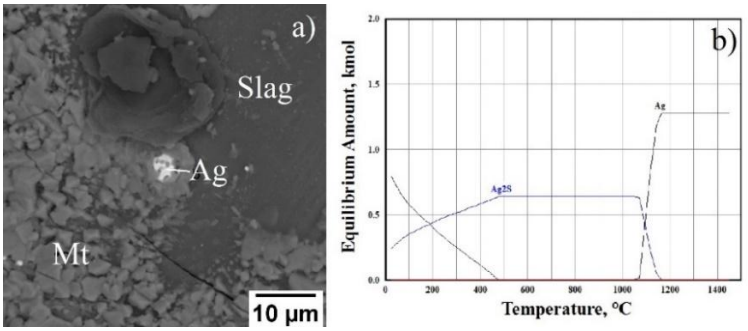
During pyrometallurgical processing of copper ores and concentrates, some silver is lost with slags [1]. To develop technologies for reducing losses, it is necessary to study the sequence of transformations of silver compounds during the heating and melting of mineral materials. The behavior of silver during the heating and melting of argillite, electrolytic sludge and technogenic sulfides was studied using thermodynamic modeling with the HSC Chemistry package, as well as experimentally. The melting products were analyzed using a scanning electron microscope. It has been shown that silver in its initial state is present predominantly in the form of Ag_2S. Based on the results of thermodynamic modeling, it was established that in the temperature range of 600-1050 °C, silver transforms into a metallic state in all of the listed mineral materials (see Fig). This is even lower than its melting point (~962 °C). The calculations are confirmed by experimental data. After heating all of the aforementioned materials to 1350-1450 °C, silver was found to be in metallic form (see figure). The heating rate was 10 °C/min. The sizes of Ag particles vary in the range from 1 to 30 μm.



Silver in mudstone when heated to 1450 °C: a) the Ag drop on the slag surface after melting; b) the equilibrium composition for silver compounds

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The study was carried out in accordance with the state assignment for the Ural State Mining University No. 075-03-2026-421 dated January 16, 2026.

PHASE EQUILIBRIA, STRUCTURE, AND PROPERTIES OF COMPLEX OXIDES IN THE $Eu_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ SYSTEM AT 1373 K IN AIR

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The aim of this work is a systematic study of phase equilibria, determination of the homogeneity ranges, and investigation of the structural features of complex oxides in the quasi-quaternary system $EuCoO_3 – SrCoO_{3-\delta} – SrFeO_{3-\delta} – EuFeO_3$.

A series of samples with the composition $Eu_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ with $0.1 \le x \le 0.9$ and $0.1 \le y \le 0.9$ was synthesized by a glycerol-nitrate technique, followed by final annealing at 1373 K in air and subsequent quenching to room temperature. The phase composition and crystal structure were studied by X-ray diffraction and the Rietveld full-profile analysis.

An isobaric-isothermal section of the phase diagram of the quasi-quaternary system $EuCoO_3 – SrCoO_{3-\delta} – SrFeO_{3-\delta} – EuFeO_3$ at 1373 K in air has been constructed. It was found that depending on the strontium (x) and iron (y) content the solid solutions $Eu_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ crystallize in one of three perovskite structures: cubic (sp. gr. *Pm*–3*m*), tetragonal (sp. gr. *I*4/*mmm*), or orthorhombic (sp. gr. *Pbnm*). The cubic phase is stable for compositions enriched in strontium and iron ($x = 0.9$ and $0.1 \le y \le 0.9$; $x = 0.8$ and $0.2 \le y \le 0.9$; $x = 0.7$ and $0.5 \le y \le 0.9$). The tetragonal superstructure $2a_p \times 2a_p \times 4a_p$, characterized by an ordered arrangement of Eu and Sr cations in the A-sublattice, observed for $x = 0.8$ and $y = 0.1$; for $x = 0.7$ and $0.1 \le y \le 0.4$; for $x = 0.6$ and $0.1 \le y \le 0.3$, while the orthorhombic structure is characteristic of europium-rich oxides with $x = 0.1$ and $0.1 \le y \le 0.9$. The unit cell parameters exhibit a linear dependence on composition upon substitution of europium by strontium in the A-site and of cobalt by iron in the B-site obeying Vegard's rule.

Thermogravimetric analysis of the oxides $Eu_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ ($0.6 \le x \le 0.9$ and $y = 0.3$; $x = 0.8$ and $0.3 \le y \le 0.8$) showed that all of them are oxygen-deficient. The oxygen content, determined by iodometric titration and reduction in a hydrogen stream, decreases with increasing temperature and increasing strontium and cobalt contents in the samples. Charge compensation upon substitution of Eu^{3+} by Sr^{2+} occurs through the formation of oxygen vacancies and an increase in the average oxidation state of 3*d*-metals.

The nonlinear temperature dependence of relative thermal expansion of $Eu_{1-x}Sr_xCo_{0.7}Fe_{0.3}O_{3-\delta}$ ceramic samples ($x = 0.6$, 0.7) in the range of 300–1373 K in air is caused by thermal and chemical factors. The latter is associated with the release of oxygen from the lattice at $T > 600$ K and a change in the oxidation state of 3*d*-metals. The increase in LTEC with increasing strontium content correlates with the increase in the oxygen nonstoichiometry.

This work was supported financially by the Ministry of Science and Higher Education of the Russian Federation (grant No. FEUZ-2026-0011).

A CALORIMETRIC STUDY OF SELECTED ACTIVE PHARMACEUTICAL INGREDIENTS

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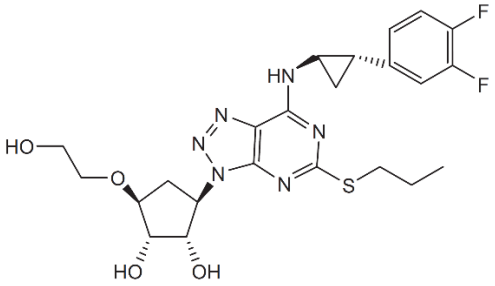
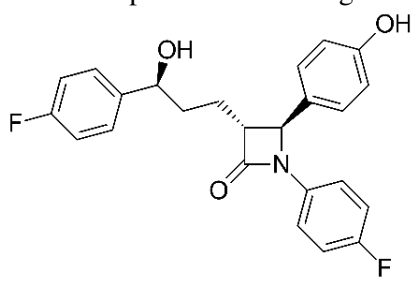
Thermal analysis and calorimetry present versatile characterization tools for the successful development of pharmaceutical products. These methods can provide valuable information required to determine the purity, the melting point and the heat of fusion of a substance. Alternatively, thermal analysis and calorimetry allow prediction of the physical stability of an active ingredient. It is also important to be aware of the different polymorphic modifications of active pharmaceutical ingredients in order to be able to optimize the production and storage conditions so that only the desired form is present.

In this work, the isobaric heat capacities of selected active pharmaceutical ingredients (see Figure) were determined over a wide temperature range using a precise adiabatic calorimetry and differential scanning calorimetry. Reliable heat capacity data for active pharmaceutical ingredients are essential for calculation of temperature dependence of their basic thermodynamic properties (enthalpy, entropy, the Gibbs energy).

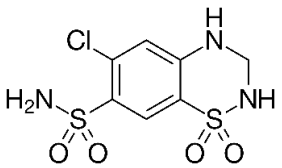
Chemical formulas of the studied active pharmaceutical ingredients



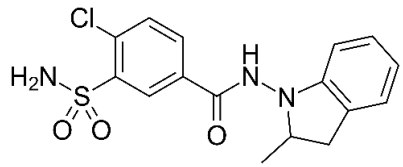
Ticagrelor (CAS RN: 274693-27-5)



Ezetimibe (CAS RN: 163222-33-1)



Hydrochlorothiazide (CAS RN: 58-93-5)



Indapamide (CAS RN: 26807-65-8)

The authors are grateful to the JSC AKRIKHIN for the provided samples of active pharmaceutical ingredients. This work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (FSWR-2026-0013).

A CALORIMETRIC STUDY OF PYRIDINE-FUNCTIONALIZED VINYLBENZYL CHLORIDE AND DIVINYLBENZENE COPOLYMER

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The unique combination of porous polymer materials properties determines their high potential for application in the analysis of gas mixtures, complex mixtures of non-polar and highly polar compounds, impurities in aqueous solutions, the concentration of trace impurities from air and water, etc. A significant expansion of the polymer materials specificity can be realized by introducing various functional groups into their composition. There are numerous works demonstrating the efficiency of the functionalization of vinylbenzyl chloride and divinylbenzene copolymer for use in various applications, however, important information on a comprehensive study of their thermodynamic properties is lacking.

In the present work, the temperature dependence of heat capacity of the pyridine-functionalized vinylbenzyl chloride and divinylbenzene copolymer were determined in the temperature range from 6 to 350 K by precision adiabatic vacuum calorimetry (BCT–3, Termis, Russian Federation). The thermophysical characteristics of the copolymer were determined in the range 290-570 K by differential scanning calorimetry (DSC 204 F1 Phoenix, Netzsch–Gerätebau, Germany). Based on the obtained experimental data the standard thermodynamic functions, namely, the heat capacity $C_p^\circ(T)$, the enthalpy $[H^\circ(T)-H^\circ(0)]$, the entropy $[S^\circ(T)-S^\circ(0)]$, and the Gibbs energy $[G^\circ(T)-H^\circ(0)]$ were determined in the range from $T \to 0$ to 350 K. The standard thermodynamic characteristics of the pyridine-functionalized copolymer were compared with those for the previously studied [1] initial divinylbenzene and vinylbenzyl chloride copolymer.

1. Abarbanel N.V., Zarubin D.M., Smirnova N.N., Markin A.V., et al. Thermodynamic properties of vinylbenzyl chloride and divinylbenzene copolymer // J. Therm. Anal. Calorim. 2026. In press.

The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation within the framework of scientific project No. FSWR-2025-0005.

HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF SINGLE CRYSTAL $LiRbMo_3O_{10}$ FROM 0 K TO THE MELTING POINT

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The search for new scintillation materials and the study of their properties are currently actively developing. Inorganic single crystal scintillators find application in areas such as medical imaging, nuclear safety, high-energy physics, and others. Double alkali metal molybdates are promising scintillation materials. In the presented work, we investigated for the first time the thermodynamic properties of single crystal $LiRbMo_3O_{10}$.

A $LiRbMo_3O_{10}$ single crystal (see Figure) was produced via the low-gradient Czochralski technique in air using a weight-controlled growth setup. The obtained crystal was then cut into samples of various sizes for further study.

$LiRbMo_3O_{10}$ single crystal grown in the [001] direction.

The phase and elemental composition of the grown single crystal were confirmed by X-ray phase analysis, mass spectrometry, and atomic emission spectroscopy. The total impurity content in the sample does not exceed $1 \cdot 10^{-2}$ wt%.

Heat capacity data for the $LiRbMo_3O_{10}$ single crystal in the interval from 5 K to the onset melting temperature (T_{onset}= 785±1 K) were obtained using a BKT-20 adiabatic calorimeter and a Netzsch 204 F1 Phoenix differential scanning calorimeter. Analysis of the experimental data revealed a boson peak in the heat capacity behavior below 10 K. Based on the obtained heat capacity data, thermodynamic functions (entropy, enthalpy, and reduced Gibbs energy) were calculated in the range of 0–785 K, and the characteristic Debye temperature was determined.

The study was supported by a grant from the Russian Science Foundation No. 24-19-00405, https://rscf.ru/en/project/ 24-19-00405/

DSC INVESTIGATION OF THE HEAT CAPACITY OF K_2SO_4 – $ZnSO_4$ SULPHATE GLASSES

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Sulphate glasses belong to a special group of glasses obtained from molten salts and, as a result, do not contain classical glass formers. For a long time, the study of sulphate glasses was primarily of scientific interest and was associated with attempts to explain the nature and mechanism of vitrification in salt systems. Therefore, the main focus of the study was on the structure. Significantly less attention was paid to the properties of the glasses.

The aim of this work is to investigate the specific heat capacity of $(100\text{-}x)K_2SO_4$–$xZnSO_4$ glasses (x = 40, 50, 60, 70, 80 mol%). The glasses were synthesized from anhydrous K_2SO_4 and $ZnSO_4$ at 750–900 K under an Ar flow in glassy carbon crucibles. Samples were obtained by "pressing" the melt between massive cold copper plates. Measurement of the specific heat capacity by the comparison method was carried out using a DSC214 Polyma differential scanning calorimeter with a CC200F3 cooling system (Netzsch, Germany). Glass samples weighing 30–40 mg with plane-parallel polished surfaces were heated in closed aluminum crucibles at a rate of 10 K/min under a nitrogen atmosphere. A 37.7 mg sapphire disk was used as a comparison sample. Measurements were performed in the temperature range from 193 to 723 K. For each of the studied glasses, the temperature dependence of the specific heat capacity C_p was obtained in the temperature range from 223 to 473 K. The C_p values for six temperature points are presented in the table.

Values of C_p for $(100\text{-}x)K_2SO_4$–$xZnSO_4$ glasses

x (mol.%)	C_p, J/(g·K)					
	223 K	273 K	323 K	373 K	423 K	473 K
80	0.58	0.64	0.69	0.75	0.77	0.63
70	0.57	0.64	0.70	0.75	0.79	0.80
60	0.56	0.62	0.67	0.73	0.78	0.80
50	0.63	0.71	0.78	0.83	0.87	0.89
40	0.65	0.71	0.77	0.82	0.85	0.88

THERMODYNAMIC ANALYSIS OF THE CATALYTIC ACTIVITY OF ALUMINUM OXIDE (Al_2O_3) AND PYRITE (FeS_2)

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In this work, the kinetics of anthracene hydrogenation in the presence of a mixture of pyrite and aluminum oxide in a 1:1 ratio at a hydrogen pressure of 3 MPa and temperatures of 648 K, 673 K, 698 K. were studied by equilibrium kinetic analysis. It was found that an increase in the temperature of the hydrogenation reaction leads to an increase in the degree of conversion of anthracene, equilibrium constants, and a decrease in Gibbs energies. Chromatographic analysis of anthracene hydrogenation products showed the presence of 9,10-dihydroanthracene (DHA), 1,2,3,4-tetrahydroanthracene (THA), methylnaphthalene (MN), naphthalene (H) and other unidentified compounds.

The use of equilibrium kinetic analysis makes it possible to establish the relationship between direct and reverse reactions for a better understanding of the catalytic properties of a mixture of aluminum oxide and pyrite during the hydrogenation of anthracene, as well as to establish the dependence of the reaction rate on time and temperature. Anthracene hydrogenation was carried out in a CJF-0.05 reactor with a capacity of 0.05 liters, equipped with a stirrer, temperature and pressure sensors. Anthracene hydrogenation was carried out at temperatures of 648 K, 673 K, 698 K, with an initial hydrogen pressure of 3 MPa and a heating rate of 10 °C/min in the presence of a mixture (1:1) of pyrite and aluminum oxide. It was found that the process of anthracene hydrogenation in the presence of a mixture of FeS_2 and Al_2O_3 is limited from the kinetic to the diffusion region as the temperature increases, which is confirmed by the activation energies of the forward (39.4 kJ/mol) and reverse reactions (13.04 kJ/mol). An increase in the rate constants of the direct hydrogenation reaction of anthracene with increasing temperature is probably due to an increase in the number of effective collisions of reagent molecules at the active centers of the catalyst, which reduces the likelihood of a dehydrogenation reaction.

Thus, there is reason to believe that the mixture of pyrite and aluminum oxide used in the reaction acts catalytically in both directions of the reaction, which, on the one hand, ensures its implementation in the selected temperature range and, on the other hand, explains its moderate total rate. In addition, it was found that the Gibbs energy decreases with increasing temperature, which makes the process of direct reaction (hydrogenation) more thermodynamically advantageous.Values of enthalpy (ΔH = 67.5 kJ/mol) and entropy (ΔS = 61.2 J/(mol·K)) The reactions calculated using the Gibbs-Helmholtz equation indicate the endothermic nature of the process. A positive value of entropy also implies an increase in disorder in the system, which may be due to a partial loss of aromaticity of anthracene during hydrogenation.

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THERMOPHYSICAL AND ELECTROPHYSICAL PROPERTIES OF ELECTRODE COKE

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The purpose of this work is to study the thermophysical and electrophysical characteristics of electrode coke obtained by mixing Shubarkol Komir pitch and Karmet pitch in a ratio of 1:2 at a temperature of 1000 °C and a coking time of 6 hours. For the first time, a comprehensive analysis of the temperature dependence of the specific heat capacity was performed for electrode coke, a phase transition was revealed at 373 K, the parameters of semiconductor conductivity (band gap ~0.67 and ~0.55 eV) were determined, and the values of permittivity reaching 109 were recorded. It should be emphasized that the phase transition at 373 K on the curve of the dependence of heat capacity on temperature can be attributed with some reservation to the temperature of the transition from semiconductor to metallic conductivity on the curve of the dependence of electrical resistance on temperature, which also indicates the nature of this phase transition.

The temperature dependence of the heat capacity of a sample of electrode coke obtained from the pakes of the Shubarkol Komir and Karmet coke chemical plants was measured using an IT-S-40 serial calorimeter. The study of electrophysical properties (permittivity and electrical resistance) was carried out by measuring the electrical capacity of samples on a serial device LCR-800. The temperature dependence of the heat capacity of the electrode coke sample was studied according to the procedure described above. At each temperature (after 25 K), five parallel experiments were performed and their results were averaged by determining the standard deviation (δ) for the specific heat.

It can be seen from the experimental data that the material (electrode coke obtained from a mixture of Shubarkol and Karmet pitches in a ratio of 1:2) demonstrates temperature-dependent conductivity. In the range of 293-373 K, the resistance decreases with increasing temperature (semiconductor behavior), increases at 373-393 K (metallic), and decreases again at 393-483 K, indicating a return to the semiconductor type of conductivity. The type II phase transition at 373 K (100 °C), confirmed both calorimetrically (peak heat capacity) and electrophysically (change of type of conductivity from semi-conductor to metallic and vice versa), may indicate a profound restructuring of the electronic structure of the material. Gigantic dielectric constant (ε ~ 108-109 at $T > 393$ K), characteristic of materials with strong interface polarization. This property opens up prospects for the use of coke not only as an electrode, but also in microelectronics, sensors and energy-intensive devices.

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THE EFFECT OF pH ON THE FORMATION OF NANOCRYSTALLINE PHASES IN THE Bi_2O_3-P_2O_5 SYSTEM

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"Soft chemistry" has gained considerable popularity due to the wide variety of techniques and strategies for obtaining compounds and materials with unique properties. This, in turn, dictates the importance of studying the effects of various parameters on the specifics of chemical reactions at relatively low temperatures. Special attention is paid to the role of acid-base equilibria on the processes of phase formation in aqueous-salt media.

In this regard, the work is devoted to studying the effect of the pH value of an aqueous-salt medium on the formation of compounds in the Bi_2O_3–P_2O_5–H_2O (NaOH, HNO_3) oxide system.

The synthesis of samples by treatment of aqueous-salt suspensions with pH values of 2.0, 8.0 and 5.0 was carried out by two methods: precipitation at T = 25 °C, and hydrothermal treatment at T = 200 °C for 20 hours.

It was shown that in an acidic medium (pH 2) at a temperature of 25 °C, hexagonal $BiPO_4$ is formed, and at pH values of 8 and 12, X-ray amorphous substances are formed at the deposition stage. After hydrothermal treatment of these suspensions at 200 °C, hexagonal bismuth phosphate is transformed into a monoclinic modification in an acidic medium, and nanoscale particles of $Bi_3O(OH)(PO_4)$ compounds are formed from amorphous precursors in slightly alkaline and alkaline media (with a crystallite size of about 62 nm) and Bi_2O_3 (with a crystallite size of about 70 nm).

By thermodynamic analysis, the dependences of the equilibrium molar solubility of these crystalline compounds on the pH value of the aqueous-salt suspension were obtained, taking into account the formation of mononuclear aquahydroxoplexes. Based on thermodynamic analysis, it was shown that the $BiPO_4$ compound is characterized by the highest stability in the pH range from 0 to 5.8 at temperatures of 25 and 200 °C. The pH range from 5.8 to 9.8 is characterized by the stability of the compound $Bi_3O(OH)(PO_4)_2$ at 25 °C, and a further increase in the pH value leads to the formation of Bi_2O_3, BiOOH or $Bi(OH)_3$.

The data obtained as a result of thermodynamic analysis are in satisfactory agreement with experimental data on the stability limits of compounds $BiPO_4$, $Bi_3O(OH)(PO_4)_2$ and Bi_2O_3 under the conditions considered.

The work was carried out with the financial support of the Russian Science Foundation, project 24-13-00445.

SYNTHESIS, FORMATION ENTHALPIES AND LATTICE ENTHALPIES OF BISMUTH NIOBATES DOPED WITH YTTERBIUM

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Bismuth oxides doped by elements of V, VI, VII group and rare-earth metals are promising materials for application in oxygen ceramic generators and as fuel cell electrolytes [1]. This is because one of the bismuth oxide forms (δ-Bi_2O_3) has high ionic conductivity. However, the problem is that this form is stable in a narrow temperature range (730-830° C). In order to expand the stability interval, bismuth oxide is doped by other elements. One of the promising compounds in this class is bismuth niobates doped by rare-earth elements. It is necessary to perform wide physical-chemical, in particularly, thermodynamic investigations for effectively application of these compounds.

The purpose of our paper is solid state synthesis and thermodynamic investigation of compounds $Bi_3Nb_xYb_{1-x}O_y$ (x = 0.1; 0.2) by solution calorimetry.

Compounds $Bi_3Nb_{0.2}Yb_{0.8}O_{6.2}$ and $Bi_3Nb_{0.1}Yb_{0.9}O_{6.1}$ were obtained by solid state synthesis. High purity precursors Bi_2O_3, Nb_2O_5 and Yb_2O_3 were used for preparation. Planetary mill Fritsch Pulverisette 6 with corundum grinding glass and balls, hydraulic press (PGR-400), a furnace SNOL 4/1300 were used to prepare $Bi_3Nb_{0.2}Yb_{0.8}O_{6.2}$ and $Bi_3Nb_{0.1}Yb_{0.9}O_{6.1}$. Stoichiometric amounts of precursors were grinded for 10 cycles (160-200 rpm), total time was 10 h. A mixture was pressed and heating in furnace at 700° C during 72 h. Samples were characterized by X-ray diffraction method (Tongda TD-3700, 5–70 2θ, Cu Kα). X-ray diffraction shown that samples were single phase with fluorite structure, space group Fm3m.

Solution calorimetry was used to determine formation enthalpies, lattice enthalpies and stabilization energies of $Bi_3Nb_{0.2}Yb_{0.8}O_{6.2}$ and $Bi_3Nb_{0.1}Yb_{0.9}O_{6.1}$. 4 M HCl was used as solvent. It was shown that compounds were stable in respect to decomposition on simple oxides.

1. Liu X. et al. A neutron total scattering study of defect structure $Bi_3Nb_{0.5}Y_{0.5}O_{6.5}$ // Solid State Ion. 2011. Vol 192. P. 176–180.

The research was supported by the Ministry of Science and Higher Education of the Russian Federation.

THERMODYNAMIC PROPERTIES OF COMPOSITIONALLY COMPLEX (HIGH-ENTROPY) OXIDES WITH PEROVSKITE AND ROCK-SALT STRUCTURES

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Compositionally complex oxides (also called "high-entropy oxides" or HEOs) have become a popular subject of scientific investigation over the past decade. These oxides usually have five or more cations mixed in equimolar proportions within one sublattice. The random cation distribution results in high configurational entropy, which compensates for the enthalpy of mixing and allegedly stabilizes the structure. Furthermore, this new material design approach provides vast possibilities for fine-tuning the chemical composition and, therefore, the properties.

However, up until very recently [1,2], experimental investigations into thermodynamics of HEOs have been quite limited, and so the understanding of their stability and stabilization issues had mostly been based on indirect or speculative evidence.

This work focuses on the synthesis and thermodynamic properties of selected compositionally complex A-site mixed rare-earth perovskite cobaltites and rock-salt oxides. All the studied cobaltites were synthesized via the standard glycerol-nitrate technique, while the rock-salt oxides were prepared via the solid-state reaction method. The crystal structure and elemental composition of the samples were characterized using X-ray diffraction (XRD) and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), respectively. In this study, several thermochemical techniques were employed, including high-temperature oxide melt solution calorimetry (to determine enthalpies of formation), adiabatic and drop calorimetry (to measure heat capacity and enthalpy increments), as well as differential scanning calorimetry and thermogravimetry (to measure heat capacity and investigate thermal stability).

Based on experimental and literature data, the standard enthalpies of formation and the temperature dependencies of heat capacity were determined for all studied oxides. For $Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2}O$, the first oxide designated in the literature as a HEO, the temperature dependence of the Gibbs energy was obtained over a wide temperature range. This study provides an experimental basis for discussing the factors affecting the thermodynamic stability of "high-entropy" cobaltites and highlights the contributions of both configurational and non-configurational entropy to the stabilization of $Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2}O$.

1. Sereda V. V., Tsvetkov D. S., Sereda A. V. et al. Thermodynamics of compositionally complex ("high-entropy") oxides – A-site mixed $(5R_{0.2})CoO_{3-\delta}$ (R = rare-earth element) perovskite-type cobaltites // Acta Materialia. – 2026. – Vol. 306, № 121943

2. Sereda V. V., Tsvetkov D. S., Sereda A. V. et al. Experimental thermodynamic study of the "high-entropy" oxide $(MgCoNiCuZn)_{0.2}O$: entropic stabilization confirmed, but is it all that matters? // J. Mater. Chem. A. – 2026. – Vol. 14, № 9, P. 5419-5441

CRYSTAL STRUCTURE AND THERMODYNAMIC STABILITY OF PHASES IN THE $(La,Pr,Nd)_2(Ni,Cu)O_4$

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The Ruddlesden-Popper $Ln_2NiO_{4+\delta}$ (Ln=La, Nd, Pr) complex oxides are considered by researchers as promising materials for electrochemical devices, particularly, as cathodes for intermediate-temperature (600-800 °C) solid oxide fuel cells (IT-SOFCs). Insufficient thermodynamic stability at T<900 °C in air is their main disadvantage. Stability can be improved by partial replacing of praseodymium with lanthanum/neodymium and nickel with copper. The purpose of this work is to synthesize and to study the stability of $La_{2-x}(Pr,Nd)_xNi_{1-y}Cu_yO_{4+\delta}$ at 700 °C in air.

The $La_{2-x}(Pr,Nd)_xNi_{1-y}Cu_yO_{4+\delta}$ (x = 0,5; 1,0; 1,5; y = 0,4; 0,6; 0,8) complex oxides were synthesized via a citrate-nitrate process. The phase purity of the samples was confirmed by XRD analysis. The XRD results showed that $La_{2-x}(Pr,Nd)_xNi_{1-y}Cu_yO_{4+\delta}$ (x=0,5–1,0; y=0,4–0,6) and $La_{0.5}Pr_{1.5}Ni_{0.6}Cu_{0.4}O_{4+\delta}$ complex oxides were single-phase after annealing at 900 °C with the K_2NiF_4-type tetragonal structure. The $La_{1.5}Pr_{0.5}Ni_{0.2}Cu_{0.8}O_{4+\delta}$ and $La_{1.5}Nd_{0.5}Ni_{0.2}Cu_{0.8}O_{4+\delta}$ samples contained little amounts (< 0.6%) of PrO_x and Nd_2O_3. Impurities were found in the remaining samples, the content of which increased with increasing concentrations of praseodymium/neodymium and copper. For single-phase samples, a parameter decreases as the dopant concentration increases. The c parameter increases with copper doping and decreases with increasing concentration of praseodymium/neodymium. Structural stability with the addition of dopants can be described using the tolerance factor of the Paul Poix (t) for phases with the K_2NiF_4 type structure [1, 2]. Limiting value of t=0.85 could define single phase domains of the studied solutions satisfactorily. To study the thermodynamic stability in the intermediate-temperature range (600-800 °C), single-phase oxides obtained at 900 °C were kept at 700 °C in air for 30 days. The XRD results showed that all solid solutions$La_{2-x}Nd_xNi_{1-y}Cu_yO_{4+\delta}$ were stable after annealing at 700 °C in air. In the $La_{2-x}Pr_xNi_{1-y}Cu_yO_{4+\delta}$ system, compositions with x = 0.5 and y = 0.6; 0.8 were stable at 700 °C. Other studied solid solutions of $La_{2-x}Pr_xNi_{1-y}Cu_yO_{4+\delta}$ contained significant amounts (> 5%) of $La_{1-x}Pr_xNi_{1-y}Cu_yO_{3-\delta}$ and PrO_x impurity phases.

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THERMOCHEMICAL PROPERTIES OF SOME METHANESULFONATES OF TRANSITION METALS

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This work continues the systematic investigation of the thermodynamic properties of methanesulfonic acid's salts. It is devoted to the study of the thermochemical properties of $Mn(CH_3SO_3)\cdot 2H_2O$, $Co(CH_3SO_3)\cdot 4H_2O$ and $Ni(CH_3SO_3)\cdot 4H_2O$. Methanesulfonates of 3d-metals can be used in their electrodeposition and extraction of manganese, cobalt and nickel from spent lithium-ion batteries and alloys containing these elements. Data on their enthalpies formation are necessary for correct modeling of phase equilibria.

Manganese methanesulfonate was obtained via reaction of $MnCO_3\cdot Mn(OH)_2$ and CH_3SO_3H in an aqueous solution. Tetrahydrates of nickel and cobalt methanesulfonates $Co(CH_3SO_3)\cdot 4H_2O$ and $Ni(CH_3SO_3)\cdot 4H_2O$ were synthesized according to the substitution reaction of barium methanesulfonate in an aqueous solution. The obtained samples were identified by X-ray, ICP-OES and TG analysis.

The thermochemical properties of methanesulfonates were investigated by method of solution calorimetry. The enthalpies of solution of $Mn(CH_3SO_3)\cdot 2H_2O$, $Co(CH_3SO_3)\cdot 4H_2O$ and $Ni(CH_3SO_3)\cdot 4H_2O$ were measured in water at 298.15 K in calorimeter Parr 6755 (Parr Instrument Company). The temperature rise in each run was measured by resistance thermometer (Parr 6772). The thermometric sensitivity was $2\cdot 10^{-4}$ K. The enthalpies of formation of methanesulfonates at 298.15 K were calculated on the basis of the experimental data and $Mn^{2+}(aq)$, $Co^{2+}(aq)$, $Ni^{2+}(aq)$ and $SO_3CH_3^-(aq)$ enthalpies of formation. The results are presented in Table. The enthalpy of formation of methanesulfonate ion in solid state was estimated according to the Mostafa's scheme on the basis of the obtained data for all studied methanesulfonates.

Thermochemical properties of methanesulfonates at 298.15 K

Sample	$\Delta_{sol}H^o_{298.15}$, kJ · mol^{-1}	$\Delta_fH^o_{298.15}$, kJ · mol^{-1}
$Mn(CH_3SO_3)\cdot 2H_2O$	−24.1 ± 0.5	−2138 ± 9
$Co(CH_3SO_3)\cdot 4H_2O$	−6.3 ± 0.4	−2564 ± 9
$Ni(CH_3SO_3)\cdot 4H_2O$	−15.6 ± 0.3	−2552 ± 9

This work was performed as part of State task (topic nos.121031300039-1 and 121031300090-2) and was done on the equipment (a Parr 6755 calorimeter and a NETZSCH TG 209 F1Libra thermal analysis) with funds from the Moscow University Development Program.

HEAT CAPACITIES AND FORMATION FUNCTIONS OF SOME 1,5-DIAZABICYCLO[3.1.0]HEXANES

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The compounds studied in this work belong to the class of diaziridine derivatives. Compounds of this class play an important role in various fields of science and technology.

The heat capacity of three diaziridine derivatives 6-phenyl-, 6-(4-methoxyphenyl)- and 6-(4-ethoxyphenyl)-1,5-diazabicyclo[3.1.0]hexanes (PDABH, MeOPDABH and EtOPDABH, respectively) was determined by low-temperature adiabatic calorimetry.

The studied compounds were synthesized and purified. The structure of the obtained compounds was monitored by spectroscopic methods. The purity of the sample of each compound was assessed by elemental analysis and by gravimetric analysis of combustion products.

The heat capacity of PDABH and MeOPDABH was determined in the temperature range of 6–350 K, where the calorimetric cell was cooled with liquid helium and nitrogen. The heat capacity of EtOPDABH was determined in the range of 80–350 K; its heat capacity in the temperature range of 5–80 K was estimated empirically by the Kelly method. Extrapolation to 0 K was performed using the Debye cube law. The data obtained in the temperature range of 5–350 K were smoothed by power polynomials of the $C_{p,m}(T) = \sum A_i\,(T)^i$, where A_i are the polynomial coefficients and i is the polynomial degree. By integrating these polynomials, the main thermodynamic functions, S^0_m, $\Delta^T_0 H^0_m$, $\Delta^T_0 G^0_m$, and the entropy of formation at 298.15 K, $\Delta_f S^0_m$, were found.

Using the obtained experimental data and literature data on the enthalpies of formation, $\Delta_f H^\circ_m$, the Gibbs free energy of formation was calculated, $\Delta_f G^0_m$ (Table).

Thermodynamic functions at 298.15 K of the studied compounds

	PDABH	MeOPDABH	EtOPDABH
$C_{p,m}$(cr)/ J K^{-1} mol^{-1}	201.18 ± 0.40	241.97 ± 0.48	270.37± 0.81
$\Delta_f S^0_m(cr)$/ J K^{-1} mol^{-1}	-1017.8 ± 1.4	-819.1±1.3	-1118.4 ± 3.1
$\Delta_f G^0_m(cr)$/ kJ mol^{-1}	373.1 ± 4.1	490.6±1.8	376.4 ± 2.8
$\Delta_f H^\circ_m$(cr)/ kJ mol^{-1}	246.4 ± 1.8 [1]	69.6 ± 4.1 [2]	43.0 ± 2.6

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EFFECT OF WATER AND HIGH PRESSURE ON VALYL-ALANINE AND ALANINE-VALYL DIPEPTIDES CYCLIZATION IN SOLID STATE

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Cyclic dipeptides (2,5-diketopiperazines) are currently of great interest to researchers in the field of medicine, as they have good cellular permeability and diverse biological activity. In addition, their ability to self-assemble into nanostructures with piezoelectric and luminescent properties makes it possible to use them in energy storage systems and OLEDs. Such properties make cyclic dipeptides promising compounds for research, which makes it an important task to develop new and improve existing methods for their synthesis. Widely used methods for obtaining 2,5-diketopiperazines, such as synthesis in solutions or under the influence of microwave radiation, and separation from living organisms, are still quite laborious. In the case of biological methods, in addition, synthesis of a limited number of compounds is possible. In contrast to the methods listed, solid-state cyclization of linear dipeptides upon heating leads to the production of cyclic dipeptides with high yield and low cost. However, the dependence of the thermal properties of linear dipeptides on their structure and heat capacity remains poorly understood, and the autocatalytic mechanism of cyclization has not yet been confirmed experimentally.

In this work, the cyclization reactions of L-alanyl-L-valine and L-valine-L-alanine dipeptides in the solid state under heating in closed and open systems were studied for the first time. The effect of high pressure on the onset point in the presence and absence of water vapor was established. Using non-isothermal kinetics approaches, the kinetic parameters of these reactions were calculated, and kinetic models describing these reactions were determined.

The structures of the products of solid-state reactions have been proven by physical and physico-chemical methods: FTIR, NMR, CD spectroscopy, HPLC-MS, PXRD.

STRUCTURAL PHASE TRANSITIONS AND THERMODYNAMIC STABILITY OF THE RUDDLESDEN-POPPER NICKELATE $La_3PrNi_3O_{10-\delta}$

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The Ruddlesden-Popper (R-P) nickelates $Ln_{n+1}Ni_nO_{3n+1}$ (Ln = La, Pr, Nd) belong to the class of materials promising for application as cathode materials for intermediate temperature solid oxide fuel cells. The alternation of n perovskite ($LaNiO_3$) and rock salt (LaO) layers along the c-axis is the unique feature of R-P oxides crystal structure. The increase of n in the series $Ln_{n+1}Ni_nO_{3n+1}$ enhances the thermal stability, electronic transport and electrochemical performance. Presently, there is no consensus concerning the crystal structure of higher-order (n = 3) nickelates. The results of numerous room temperature structure studies disagree with each other. The same applies to the details of the structural phase transitions observed in these oxides upon temperature change.

In the present work the detailed investigation of the crystal structure of $La_3PrNi_3O_{10-\delta}$ R-P nickelate was performed by combination of instrumental techniques, analysis of the available literature data and considering the group-subgroup relations.

Variation of $La_3PrNi_3O_{10-\delta}$ crystal structure with temperature was studied by in situ high-temperature X-ray diffraction (HT-XRD) with XRD 7000 diffractometer (Shimadzu, Japan) at 25–1000 °C in air. The crystal structure refinement was carried out by Rietveld method using the Rietica 4.0 software. The isobaric heat capacity (C_p) was measured by differential scanning calorimetry (DSC) with MHTC 96 (Setaram, France) calorimeter in the temperature range 25–900 °C in air. The resulting C_p temperature dependence possesses complex shape with three anomalies indicating the second order phase transitions and supporting the results of in situ HT-XRD. Accordingly, the HT-XRD patterns were analyzed based on group-subgroup relations using the software SUBGROUPGRAPH and WYCKSPLIT of Bilbao Crystallographic Server. During the analysis the structural data (atomic coordinates and Wyckoff positions) for related oxides available in the literature were used as an independent source of crystallographic information. As a result, the following sequence of the second order phase transitions in the temperature range from 1000 to 25 °C in air was proposed:

*I*4/*mmm* (No. 139) > *Fmmm* (No. 69) > *C*2/*m* (No. 12) > $P2_1/a$ (No. 14).

The thermodynamic stability limits of $La_3PrNi_3O_{10-\delta}$ depending on temperature and oxygen partial were determined by thermogravimetric analysis (TGA) and coulometric titration technique. TGA was performed using STA409PC (Netzsch GmbH, Germany) thermobalance in the temperature range 25–1200 °C in air. Coulometric titration was carried out in the original home-built setup in the ranges of temperature and oxygen partial pressure 800–950 °C and 10^{-5}–1 atm, respectively. The products of phase decomposition reactions were identified by equilibrating the $La_3PrNi_3O_{10-\delta}$ under required conditions followed by quenching with subsequent XRD analysis.

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THERMODYNAMIC PROPERTIES OF THE CeO_2-B_2O_3 SYSTEM

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The various CeO_2 based systems is of practical interest because their high ion conductivity and potential using for SOFC. On other hand B2O3 containing system uses as glasses for special purposes. Prediction of the behavior at high temperatures of such systems require the information of quantitative composition of vapor as well as thermodynamic properties (such as activities, activity coefficients and partial thermodynamic functions) for all components. In this study CeO_2-B_2O_3 system was studied by Knudsen effusion mass spectrometry (KEMS) as well as thermodynamics of the gaseous cerium oxyacid salt $CeBO_2$. Investigation was done using MS 1301 mass spectrometer at the ionization energy equaled to 30 eV. Vaporization of the samples under consideration was carried out from molybdenum and tungsten effusion cells heated by the electron bombardment. Temperature was measured by optical pyrometer EOP-66 with the accuracy ±10. Samples were obtained by heating mixtures of CeO_2 and orthoboric acid.

The $B_2O_3^+$, CeO^+ and CeO_2^+ ions were detected in mass spectra above the system under study in the temperature range 1500-2100 K. The mass spectrum analyses and appearance energies of ions in mass spectrum shown that the vapor over the systems consist of B_2O_3, CeO, CeO_2 and O molecules. The partial pressures of these vapor species were obtained using the ion current comparison method with silver as inner standard. Additionally gaseous molecule $CeBO_2$ was detected in the vapor. For this species standard formation enthalpy was derived.

In the studied system ceria is stabilized by second component and decomposition to Ce_2O_3 in the condensed phase wasn't observe. The thermodynamic activities of CeO_2 and B_2O_3 at the temperature 1600 K were found by the differential mass spectrometric method using ceria and B_2O_3 as the standard of the determination of the component activities. The CeO_2-B_2O_3 system demonstrate strong negative deviation from ideal case for boron oxide and weak negative deviation for ceria.

THERMODYNAMIC PROPERTIES AND PROCESSES IN SOLUTIONS AND FLUIDS

ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА И ПРОЦЕССЫ В РАСТВОРАХ И ФЛЮИДНЫХ СИСТЕМАХ

A SEMI-EMPIRICAL MOLECULAR APPROACH TO THE THERMODYNAMIC MODELING OF AQUEOUS SOLUTIONS OF NON-POLAR GASES AT INFINITE DILUTION

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The properties of non-polar substances in aqueous solutions – such as the Henry's law constant (k_H) and hydration parameters ($\Delta_{hyd}H^\infty$, $\Delta_{hyd}V^\infty$, $\Delta_{hyd}C_p^\infty$) – play a key role in thermodynamic calculations of natural and industrial processes involving sparingly soluble gases. Their accurate description is essential for predicting solubility over a wide range of temperatures and pressures, including the supercritical region.

Semi-empirical equations of state for infinitely dilute solutions are commonly used to describe standard properties of dissolved gases. In recent decades, equations of state based on empirical correlations (e.g., SOCW, POCW) have been extensively developed. However, these approaches require complex parameterization and often lack a clear physical foundation. Therefore, the development of molecular models based on physically justified approximations of intermolecular interactions in solution, and capable of ensuring correct limiting behavior, remains an important task.

In a recent study [1], an equation of state was proposed based on the approximation that the interaction energy between water and the dissolved gas can be represented by a square-well potential. This approach makes it possible to describe the Gibbs energy of hydration ($\Delta_{hyd}G^\infty$) explicitly within a unified formalism, without the need to integrate the dependencies of $\Delta_{hyd}V^\infty$ and $\Delta_{hyd}C_p^\infty$, as is done in traditional models.

The model requires only four fitting parameters, which makes the model simpler than its existing counterparts. Despite its simplicity and the small number of adjustable parameters, the model demonstrated high accuracy both in correlating experimental data and in extrapolation [1].

In the present work, a further development of this model is proposed, including an updated expression for the coordination number based on theoretical results reported by Hu et al. [2].

The model was tested on a series of noble gases, light hydrocarbons, and a number of weakly polar gases. The modeling results demonstrate that the model is suitable for describing the Henry's law constant (k_H) and several properties of gases at infinite dilution within experimental error.

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ANION EFFECTS ON THE DYNAMICS OF DEEP EUTECTIC SOLVENTS BASED ON TRIS SALTS AND ETHYLENE GLYCOL

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Deep eutectic solvents (DESs) are a class of materials combining properties of fluids and electrolytes which exhibit unique characteristics, such as high dissolving ability, a wide electrochemical window, low volatility, and a high boiling point. Additionally, their constituents (in the case of type III DESs, a hydrogen bond donor and a hydrogen bond acceptor) are often inexpensive and environmentally benign, making DESs an attractive choice for "green chemistry".

Even though the first DESs were discovered over 20 years ago, our knowledge of how the nature of their components influences their properties is still limited. For example, substitution of the anion in the electrolyte component of DESs remains largely unexplored in the literature. This is mainly due to the difficulty or high cost of ion-exchange processes required to replace the anion in choline chloride and tetraalkylammonium salts, which are typical hydrogen bond acceptors in most studied DESs. In contrast, protic ionic substances, formed by proton transfer from a Brønsted acid to a Brønsted base, do not exhibit this drawback.

In the present work, we investigated the influence of the anion on the dynamics of Tris (tris(hydroxymethyl)aminomethane) protic salts in ethylene glycol (EG) using dielectric relaxation spectroscopy. We show that, within the covered frequency range of $0.05 \leq \nu / \mathrm{GHz} \leq 89$, the obtained spectra can be described as a superposition of relaxation processes arising from Tris-associated species and EG dipoles. For the latter, processes exhibiting nearly unperturbed dynamics were found, as well as contributions considerably slowed down by the solute. The extracted effective solvation numbers of the Tris salts strongly correlate with the strength of anion–solvent interactions, decreasing in the order chloride > nitrate > perchlorate. A Tris cation slows down the dynamics of ~16 EG molecules at infinite dilution. One of them is essentially "frozen" and rotates together with the cation as a single entity. Analysis of the effective dipole moments indicates that, up to concentrations of about 1.5 M, the solutions are dominated by contact ion pairs, before gradually transitioning to the behavior of a "solvent-lubricated" molten salt.

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CRITICAL TEMPERATURES, PRESSURES, THERMAL DIFFUSIVITIES, AND HEAT CAPACITIES OF ALKYL LACTATES

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Lactic acid esters are a significant class of organic compounds widely used in various industrial sectors. Lactates have a number of attractive properties: low vapor pressure, nontoxicity, high solvency ability, biodegradability; they are noncorrosive, noncarcinogenic, nonozone-depleting, and easily recyclable. Therefore, they are currently considered as a promising alternative to traditional solvents and plasticizers [1,2]. The development of new technological processes using lactic acid esters requires reliable thermophysical data.

This report presents the results of measuring the critical temperatures, critical pressures, thermal diffusivities, and heat capacities of methyl (CASRN 547-64-8), ethyl (CASRN 97-64-3), propyl (CASRN 616-09-1), butyl (CARN 138-22-7), and pentyl (CASRN 6382-06-5) lactates. Alkyl lactates under study decompose at near-critical temperatures; because of this, the pulse-heating method applicable to measuring the critical properties of thermally unstable compounds has been used [3]. Heat capacity in the liquid phase has been measured using a differential scanning calorimeter DSC 204 F1 Phoenix (Netzsch, Germany) at atmospheric pressure in the temperature range from 298 to 473 K. The thermal diffusivity a has been measured by the laser flash method using a LFA 457 (Netzsch, Germany). The experiments have been performed for liquid compounds at atmospheric pressure at temperatures over a wide temperature range. The relative combined expanded uncertainties with 0.95 level of confidence are: $U_r(T_c) = 0.015$, $U_r(p_c) = 0.04$, $U_r(C_p) = 0.03$ и $U_r(a) = 0.05$.

The thermal conductivity λ was calculated from the experimental data on the thermal diffusivity and heat capacity and literature data for density.

The functional self-similarity method was applied to predict the critical parameters of higher-molecular-weight alkyl lactates using the experimental data obtained [4].

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EXPERIMENTAL INDICATION OF TRANSITION BETWEEN NADES AND MINAC

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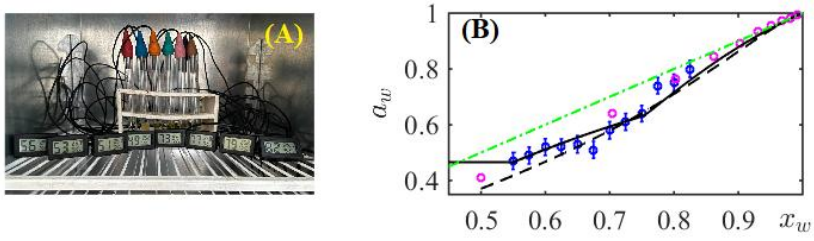
For the preparation of some types of natural deep eutectic solvents (NADES), a small amount of water must be added to the mixture to reduce the viscosity for practical applications. In such cases, an important feature of these aqueous systems is the possibility of a gradual transition from a deep eutectic solvent to a so-called Mixture of Natural Compounds (MINAC), i.e., a regular aqueous solution based on natural components. This transition is controlled by maintaining specific molar ratios of all components, in particular the molar fraction of water, at which noticeable deviations from the behavior of ordinary solutions are observed.

In this work, the fructose–citric acid–water system with a molar ratio of the main components of 1:1 is studied. The aim of the study is to investigate the dependence of the water activity, which is argued [1] an important indicator of molecular interactions in such mixtures, on the molar fraction of water plot. The figure below depicts the experimental setup developed for this purpose and results obtained.

By the comparison with model calculation curves, the range of responses to the water molar fraction, which either preserve the DES character of the system or exhibit transition between NADES and MINAC are revealed.



(A) The created experimental setup for determining water activity. (B) The data obtained (blue circles with error bars) in comparison with literature data [2] (magenta circles) and models: Norrish–Ross (solid black line) and PC-SAFT.

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ALL-ATOM MOLECULAR DYNAMICS MODELLING OF SURFACTANTS IN SOLUTIONS

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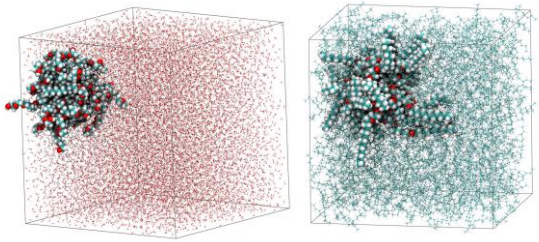
The results of all-atom molecular dynamics simulations of ionic and nonionic surfactants in polar and non-polar solvents are presented. Bulk systems that include direct or inverse micelles (see Figure) as well as surfactant monolayers at the water-hydrocarbon interface are simulated. Structural, transport, thermodynamic, and kinetic properties of the surfactant solutions are studied by analysing the molecular dynamics data.

The diffusion coefficients of direct and inverse micelles have been calculated using the Einstein formula [1]. The viscosities of micellar solutions have been estimated on the basis of the Stokes-Einstein relation [2]. The interfacial tension at the water-decane interface in the presence of different surfactants has been calculated on the basis of diagonal components of the pressure tensor [3]. The distribution of inverse micelles by their aggregation numbers is studied. The dependence of the obtained results on the simulation cell size is taken into account. MDynaMix and GROMACS software packages have been used to perform molecular dynamics simulations within CHARMM36 and CGenFF force fields. The simulation times range from several tens of nanoseconds to microseconds.



Direct and inverse micelles of $C_{12}E_4$ in water at T=298 K
and in heptane at T=223 K, correspondingly

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STABILITY OF GOLD(III) COMPLEXES WITH VARIOUS N,O-DONOR LIGANDS INCLUDING HYDRAZONES, MACROCYCLES AND BIOMOLECULES

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Among metals suitable for medicinal use and likely to enter the organism, gold attracts significant interest. This is due to the many promising antitumor agents synthesized from gold(III) complexes, which are isostructural and isoelectronic to the established anticancer drug cisplatin. The antibacterial potential of gold(III)-based organometallic compounds is also under active investigation (see, e.g., paper [1]), and gold coatings are already utilized in surgical instruments. It is important to note, however, that gold(III) complexes typically function as prodrugs rather than active pharmaceutical agents; they require prior activation to exert a biological effect [2]. This activation may involve ligand substitution in the gold coordination sphere (e.g., *via* hydrolysis) or redox processes (oxidation/reduction).

As we demonstrated [3], the dissociation of a metal complex in the presence of a protein can lead to the formation of a metal-protein associate. Therefore, to completely describe behavior of gold(III) complexes in biological fluid, equilibria involving metal ions (or their simple complexes, such as tetrachloroaurate(III), since Au^{3+} itself cannot persist in aqueous solution) with biologically active ligands, proteins and DNA must be taken into account.

In this report, we are going to provide the values for stability constants of gold(III) complexes determined by us for such classes of N,O-donor ligands as pyridoxal or pyridoxal 5'-phosphate-derived hydrazones [4], 18-crown-6 ester and its aza-substituted derivatives, blood serum proteins including albumins [5] and γ-globulins [6], and DNA [7]. The information about the structure of the complexes formed derived from multispectroscopic approach as well as quantum chemical calculations is also to be discussed.

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FREE ENERGY OF A SOLVENT MOLECULE: CONVENTIONAL IDEAL GAS APPROXIMATION *VS.* EXPERIMENTAL THERMODYNAMIC DATA

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Solvents modify reaction thermodynamics and kinetics through specific coordination, demanding the correct treatment of the role of the medium in molecular modeling. Computationally cheap implicit solvation models are commonly used to capture bulk electrostatic effects; however, the additional incorporation of solvent molecules into computational models is often essential for obtaining reliable results. The latter technique is specifically justified for processes in which solvent molecules are released into the bulk or become bound, behaving as active participants, such as in intermediates or transition states with high polarity differences. In this study, we compare Sackur-Tetrode (ST)-based conventional models, which treat the solute and solvent on equal terms, with Gibbs free energies derived from experimental thermochemical data for various solvents and assess the performance of the latter on a series of solvent–ligand exchange reactions.

Empirical free energy values for solvents were derived *via* a Hess cycle comprising experimental liquid-phase enthalpy, entropy (from low-temperature adiabatic vacuum calorimetry), and zero-point energy (from IR/Raman spectroscopy). Conventional ideal gas values were calculated using the DFT method at the PBE0/def2-TZVP level of theory, with symmetric and asymmetric reference states represented with 1 M and solvent self-concentration in the ST equation, respectively. While conventional approaches usually provide free energy contributions lying within 1 kcal·mol^{-1} from the experimental ones, in some cases they deviate by ~2 kcal·mol^{-1}; meanwhile, combining free volume correction with an asymmetric reference state yielded the best MAE in entropy values (1 kcal·mol^{-1}).

To validate the accuracy of experimental solvent Gibbs free energies, a dataset comprising complexation reactions with thermochemical data obtained via isothermal titration calorimetry (ITC) was compiled. For solvents where experimental and calculated values differ by >2 kcal·mol^{-1}, the experimental free energy contributions provide 1−2 kcal·mol^{-1} more accurate results for solvent−ligand exchange reactions, demonstrating that experimentally derived energy components can be combined with computed ones to yield improved results. None of the conventional approximations is universal, as they exhibit divergent trends for different solvents.

To conclude, Gibbs free energies for solvent molecules provide a compelling alternative to those calculated with ideal gas approximations, resulting in better agreement with experimental thermodynamic parameters.

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NUCLEOPHILICITY INDICES AS DESCRIPTORS FOR BOTH THERMODYNAMIC FEASIBILITY AND REACTIVITY OF C-ELECTROPHILES OXIDATIVE ADDITION TO Pt(II) SPECIES

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Oxidative addition (OA) is a crucial step in numerous C-C coupling reactions catalyzed by transition metals [1]. The efficiency of this process depends on the nucleophilicity of the metal donating electron pairs, as well as on the nature of the substrate and the reaction conditions. An appreciation and prediction of nucleophilic reactivity are of paramount importance for controlling the course of chemical reactions, understanding their mechanisms, and creating new approaches to the synthesis of organic compounds.

Recently, we developed a model cross-electrophile coupling reaction between methyl iodide and vinyl iodide to form propylene in a Pt(II)–NaI–acetone system [2; 3]. The key intermediate in the reaction is a methyl-vinyl derivative of Pt(IV), generated by the sequential oxidative addition of these electrophiles to Pt(II) iodo complexes. However, the sequence in which methyl iodide and vinyl iodide molecules bind to $[PtI_4]^{2-}$ remains unclear. A step toward resolving this issue could be comparing the reactivity of the $[Pt(CH_3)I_3]^{2-}$ and $[Pt(CH_2CH_3)I_3]^{2-}$ complexes in OA reactions with vinyl iodide and methyl iodide, respectively.

The results of DFT-modeling the energy profiles of OA reactions, along with correlations between the free Gibbs energies/barriers of the reactions and the calculated values of the condensed-to-atom (Pt) nucleophilicity indices will be presented and discussed.

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This work was supported by the Ministry of Science and Higher Education of the Russian Federation through State Assignment "Design of C-C and C-X coupling reactions catalyzed by simple transition metal complexes using acetylene and organic halides", Grant № FRES-2026-0010.

SOLVATION PROPERTIES OF PROTIC IONIC LIQUIDS WITH DIFFERENT NANOHETEROGENEOUS STRUCTURE

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Ionic liquids (ILs) are promising solvents for the separation and extraction of hydrocarbons, gas purification, desulfurization, and as a medium for organic reactions. Many ILs with a hydrocarbon substituent in the cation have a nanoheterogeneous structure consisting of polar and apolar domains in their bulk phase. The domain structure can be altered by changing the structure of the cation and/or anion. Nanosegregation in the liquid phase strongly affects the solvation properties of ILs and consequently their potential for use in various processes.

In this work, the activity coefficients at infinite dilution (γ^{∞}) of different organic solutes in thiocyanate- and hydrosulfate-based protic ILs were determined by gas chromatographic headspace analysis. The influence of the liquid phase structure probed by small-angle X-ray scattering and molecular dynamics simulations on the solvation properties of protic ILs was analyzed. The possible use of the studied ILs for various industrial separation problems is discussed.

The research was funded by the Russian Science Foundation, project 24-13-00062.

THERMODYNAMIC FEASIBILITY OF REDUCING ORGANOPLATINUM(IV) SPECIES BY IODIDE IONS AS A KEY STEP FOR CROSS-ELECTROPHILE COUPLING

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Exploiting the vast synthetic potential of reductive cross-electrophile coupling, i.e., the direct coupling of two C-electrophiles, remains challenging due to issues with controlling chemoselectivity caused by the identical chemical nature of both substrates [1]. A model Pt(II)–NaI–acetone catalytic system for reductive cross-electrophilic coupling was recently designed [2], providing a useful tool for exploring the causes of selectivity. In this system, the key intermediates of C-C coupling, bis-organic $Pt^{IV}(R_1)(R_2)$ complexes, are generated in a sequence of steps: oxidative addition (OA) of R_1-I to PtI_2 forming $Pt^{IV}(R_1)$ species – reduction of the latter by I^- to give $Pt^{II}(R_1)$ and I_3^- – OA of R_2-I generating $Pt^{IV}(R_1)(R_2)$. The reduction step here is facilitated by the solvent-specific binding of the released iodine with acetone and NaI into a poorly soluble polymeric complex tris(μ_2-acetone-κ^2O:O)-sodium polyiodide [3]. Reductive elimination of two organic ligands yields the C-C coupling product, R_1-R_2, and regenerates the catalyst. Thus, the reduction of organic Pt^{IV} derivatives by iodine ions to the corresponding Pt^{II} organometallic compounds, being one of the key steps in the overall catalytic process, could have an impact on the chemoselectivity.

To elucidate the possible contribution of the reduction step to the selectivity of C-C coupling, we estimated the Gibbs free energy and enthalpy of this transformation for a series of organic derivatives of Pt^{IV} using density functional theory (DFT) calculations. The results of DFT-modeling the energy profiles of the reactions, as well as correlations between the free Gibbs energies of the reactions and the calculated values of Pt^{IV} electrophilicity indices, will be presented and discussed.

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This work was supported by the Ministry of Science and Higher Education of the Russian Federation through State Assignment "Design of C-C and C-X coupling reactions catalyzed by simple transition metal complexes using acetylene and organic halides", Grant No. FRES-2026-0010.

THERMODYNAMIC PROPERTIES OF SUBSURFACE MONOLAYERS AND STRUCTURAL ASSIGNMENTS OF BULKY AGGREGATES BASED ON DICATIONICS

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Dicationic onium salts (DOS) with long alkyl substituents ("tails") perform excellently as surface tension reducers for the air/water and oil/water interfaces emerging as effective agents for surfactant-enhanced petrol recovery [1] from both nature basins and industrial reservoirs. Many other possible applications were supposed on a basis of unique properties of DOS as ionic liquids, ionic plastic crystals, and non-volatile electrolytes. For a task-oriented usage, detailed knowledge of thermodynamics in the fields looks needed. Small libraries of DOS encompassing majority of typical heads, spacers and counter-ions were constructed [2], their thermal, surface-reducing, and other properties were studied and compared with available literature data. Molecular structures of all library items were thoroughly inspected, and all usual experimental procedures for structure elucidation were maintained. Molecular geometry and electronic structure of virtual dications were evaluated with *ab initio* calculations, some representative examples were interpreted in a frame of Bader quantum theory of atoms in molecules QTAIM, reduced density gradient RDG and independent gradient model IGM approaches. Dicationic imidazolium halides DIH with short spacers dissociate into free ions (behave as strong electrolytes) in diluted water solutions. With a concentration rising, DIH molecules combine into supermolecular aggregates in bulky volume, and, in parallel, migrate to solution/air interface, slowly and far from diffusion control. Surface tension and dilatational rheology measurements made simultaneously and independently by DuNouy ring and hanging drop dynamical methods identified highly resilient layers of DIH on the interface, with extremely large dilatational moduli. Concentration dependences of storage and loss moduli in combination with tension dependences reveal lucid signs of an organized adsorbed layers at a first stage and further disordering. Highly negative Gibbs energies ΔG of interface layers formation support this notion. Specific for DIH models of supramolecular organization in volume and at the interfaces have been proposed, their differences from generally accepted Gemini style micellization analyzed from structural and thermodynamic point of view.

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The study has been funded in part by the Ministry of Science and Higher Education of the Russian Federation, FRES-0001-2023.

EFFECT OF THE SATURATION DEGREE OF A NANOCRYSTALLINE CELLULOSE AEROGEL WITH MEFENAMIC ACID ON THE PROBABILITY OF ITS REACTION WITH SUPERCRITICAL CARBON DIOXIDE WITHIN THE AEROGEL PORES

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In this work, we investigated the phenomenon of reaction blocking between mefenamic acid (MA) and carbon dioxide (CO_2) confined within the pores of a nanocrystalline cellulose (NCC) aerogel. The present work continues a series of our studies devoted to the conformational equilibria of MA and its chemical reactivity toward supercritical carbon dioxide ($scCO_2$), both in bulk solution and under conditions of aerogel confinement. In our recent work [1], we have found that the chemical reaction between MA and CO_2 can proceed via two distinct pathways: in bulk solution — nucleophilic attack by CO_2 on the MA carbonyl oxygen, and under the confined geometry of NCC aerogel pores — attack by CO_2 on the MA amino-group. In present work we checked if blocking the chemical reaction within the aerogel pores can be achieved by increasing the degree of pore saturation with the MA instead using the inhibitors. For this we increased the aerogel saturation degree with dopant by its impregnation at higher temperatures. It allowed us increasing the MA concentration retained in aerogel by one order of magnitude as compared to that achieved in [1]. A combination of low-temperature nitrogen sorption and IR spectroscopy revealed that with increasing aerogel saturation, the probability of forming an amorphous MA phase inside the aerogel pores increases, while the amount of retained CO_2 markedly decreases. In turn, the formation of the amorphous MA phase within the pores accompanied with arising the intermolecular hydrogen bonds between MA molecules – specifically those involving the amino-group. It is precisely this feature that acts as the key factor blocking the reaction proceeding through the amino-group attack. Moreover, we showed that the conformational equilibrium of MA released from MA-doped NCC aerogel differs from that observed in bulk MA/$scCO_2$ saturated solution. This divergence arises primarily from the combined effects of confinement within the pores of NCC aerogel and its ability to form hydrogen bonds with MA molecules retained inside them.

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This work was supported by the Russian Science Foundation (22-13-00257-P). The IR spectroscopy experiment was performed using the molecular fluid spectroscopy facility (http://www.ckp-rf.ru/usu/503933/) of G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences (Russia).

THERMAL EFFECTS OF CAESIUM ACETATE SOLVATES DISSOLUTION AND THE RELATIONSHIP OF STRUCTURE AND PROPERTIES

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Submitted work is part of a major study of water-electrolyte systems containing alkali metal acetates. It is devoted to obtaining enthalpy characteristics of the dissolution processes of caesium acetate solvates by calorimetry. Recently, the development of chemistry of highly concentrated aqueous solutions has received a new impetus – this is due both to the search for environmentally friendly electrolytes in new generation batteries (water-in-salt WIS systems) and to the intensive study and application of inorganic ionic liquids (ionic liquids IL) [1,2]. Salts of alkaline or alkaline earth metals with a non-toxic counterion and high solubility in water are ideally suited as objects for creating such systems. One of them is caesium acetate. However, CsOAc has an extremely high hygroscopicity, which makes it difficult to work with it and prepare mixtures based on it. At the same time, CsOAc forms solvates with acetic acid of various compositions, which are less hygroscopic and easy to obtain.

We suppose that systems based on caesium acetate solvates can be considered promising for creating highly concentrated mixtures with the properties of WIS or IL. Because the availability of additional acetate ions in such systems promotes the binding of free water molecules, which will make it possible to achieve the WIS state at lower salt concentrations.

The physicochemical properties of the known caesium acetate solvates are practically not represented in the literature. As a result of this work, the thermal effects of the process of dissolution of solid caesium acetate and its solvates CsOAc·HOAc, 3CsOAc·5HOAc in water were obtained: the enthalpy of dissolution, the energy of crystalline lattices, and the enthalpy of ions hydration. Using quantum calculations, enthalpy characteristics of the intermediate processes of gaseous ions formation were obtained, which made it possible to estimate the hydration energy of the hydroxonium ion. The resulting thermal effects correlate with the structural features of the solid solvates.

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The work was performed using the equipment of the St. Petersburg State University Science Park (Thermogravimetric and Calorimetric Research and X-ray Diffraction Centre).

WATER ACTIVITY MODELS FOR CHARACTERIZING TRANSITIONS BETWEEN DEEP EUTECTIC SOLVENTS AND REGULAR SOLUTIONS

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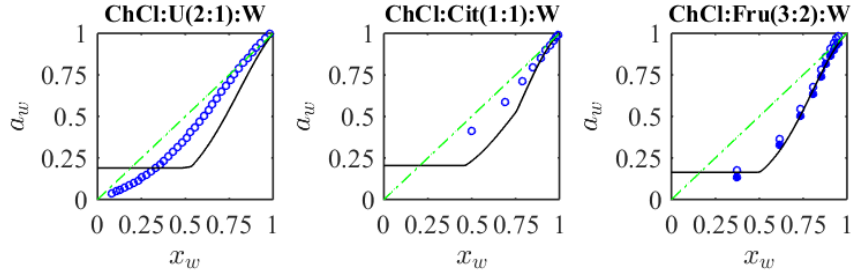
Many applications of deep eutectic solvents (DES) require their dilution with water to reduce viscosity and improve practical efficiency. However, this raises the question of what fraction of water still allows such a ternary mixture to be considered a DES rather than merely a strongly non-ideal solution, and how these two thermodynamic entities can be distinguished.

In contrast to sophisticated experimental methods such as NMR, as well as numerical analyses based on quantum-chemical estimates, it has recently been argued [1] that studying the water activity of such ternary systems can serve as a demonstrative indicator when experimental data are compared with the predictions of relatively simple thermodynamic models. In the present work, the applicability of the Ross method, complemented by the Caurie and Norrish models for the corresponding binary subsystems, can serve as a criterion for assessing the extent to which donor–acceptor interactions between DES components are compromised by the addition of excessive water.

The validity of the proposed approach is tested with a wide range of systems for which corresponding experimental data are available; see some examples in the figure below. The results are compared with microstructure-characterizing chemical indicators, and practical rules for testing DES-candidate mixtures are proposed.



Examples of systems exhibiting strong, range-limited, and absent properties of deep eutectic solvents indicated by the deviation of experimental data on the water activity (markers) from a theoretical model for a ternary regular mixture (black curve).

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PHYSICAL PROPERTIES OF Al-Ni-Co-Cu-Zr AND Al-Ni-Co-Fe-Cr HIGH-ENTROPY ALLOYS IN SOLID AND LIQUID STATES

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High-entropy alloys (HEAs) have been actively studied in recent years due to their high mechanical properties and corrosion resistance. A distinctive feature of these alloys is the formation of a solid solution as a result of the relatively high entropy of mixing of the components. HEA are promising materials for various industries. Despite this, the physical properties of HEA, especially at high temperatures and in liquid state, are practically unexplored to date. In this work, density, electrical resistivity, viscosity and magnetic susceptibility of Al-Ni-Co-Cu-Zr and Al-Ni-Co-Fe-Cr HEAs with different component ratios are investigated for the first time.

Al-Ni-Co-Cu-Zr and Al-Ni-Co-Fe-Cr alloys were obtained from pure initial components in an induction furnace at a maximum temperature of 1800 K in a protective helium atmosphere. Density of the alloys was measured on an automated set-up using the gamma-absorption method. Electrical resistivity was studied using contact-less method in a rotating magnetic field, magnetic susceptibility was studied using the Faraday method, and viscosity of the melts was studied using the damped torsional vibrations method. All experiments were carried out in a protective helium atmosphere at temperatures ranging from 300 up to 1800-1900 K.

It is shown that the investigated compositions are characterized by a practically linear decrease in density during heating and in liquid state their density can be described by linear functions. The temperature dependence of viscosity of melts can be described by the Arrhenius equation at high temperatures. In AlNiCoCuZr alloys, an anomalous decrease in electrical resistivity and a corresponding increase in magnetic susceptibility were found in the temperature range of 800–1000 K. The results of high-temperature diffraction experiments show that these anomalies are associated with structural changes in the composition of the alloys.

The obtained results can be used to optimize the preparation modes of Al-Ni-Co-Cu-Zr and Al-Ni-Co-Fe-Cr HEAs for quenching and to obtain finished products based on them.

LONG-TERM RELAXATION PROCESSES IN Ga-REM MELTS

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Gallium-based alloys are attracting researchers' attention in recent years and are considered as promising liquid metal coolants and materials in micro- and nanoelectronics. At the same time, data on their physical properties remain limited, which restricts their broader application. Moreover, such systems have been shown to exhibit long-term changes in their properties at high temperatures [1]. In this work, the physical properties (density and viscosity) of gallium melts containing rare-earth metals (REMs) were investigated, and their behaviour during long-term isothermal exposure at high temperatures was studied.

Binary Ga-REM alloys (REM: Nd, Sm, Gd, Tb, Ho) with the second component present at up to 5 at. % were obtained in a resistance furnace at 1400 K under a protective helium atmosphere. Density of the alloys was measured using the gamma-absorption method on an automated setup, kinematic viscosity was investigated using the damped torsional vibrations method (Shvidkovskiy method). Experiments were carried out under protective helium atmosphere.

It has been established that Ga-REM melts are characterized by long-term relaxation processes, which leads to a discrepancy between density and viscosity values obtained during heating and subsequent cooling. It has been shown that melts above the liquidus temperature are heterogeneous systems, containing two-scale inhomogeneities associated with the first intermetallic compounds of gallium with rare earth metals. The transition of melts to the equilibrium state (relaxation processes) takes tens of minutes and is associated with the dissolution of two-scale inhomogeneities. Relaxation processes can generally be described by a decay equation, which demonstrates the universal mechanism of inhomogeneity dissolution in such melts.

Results obtained in this study can be used to optimise the processes of preparing Ga-REM alloys for practical applications and may provide a basis for further research on the melts of these systems.

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SALTING-OUT IN AQUEOUS SOLUTIONS OF AMINO ACID IONIC LIQUIDS WITH DIFFERENT ADDITIVES

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Amino acid ionic liquids (AAILs) attract special attention among the structurally modified ionic liquids (ILs) due to their low toxicity and likely biocompatibility. Biocompatible chiral AAILs show a high efficiency of extraction of biomolecules and a high potential in the chiral ligand-exchange separation. Aqueous biphasic systems (ABSs) containing AAILs have been considered as eco-friendly and bio-friendly extraction media [1]. In context of the counter-ion effects, we have analyzed our data on phase behavior of ABSs containing AAILs together with available literature.

In last decades, polymerized ionic liquids (PILs) have attracted growing interest. PILs are water-soluble polyelectrolytes that contain ILs ions as their monomer units. An addition of salting-out agents results in the formation of ABSs. For specific applications such as extraction of biomolecules, an appropriate choice of ion pairs comprising new PILs is required. Thus, ABS with poly(1-butyl-3-vinilimidazolium bromide) and K_3PO_4 has a low extraction efficiency towards L-tryptophanate anions in comparison with non-polymerized ILs. A relationship between reduced extraction efficiency and competitive phosphate binding was supported by MD simulations [2]. To enhance the extraction efficiency, we studied other amino acid PILs based on poly(diallyldimethylammonium) cation as components of ABSs. The counter-ion effect on phase behavior is similar to the one in ABSs with non-polymerized AAILs. As found, an affinity of the IL/PIL-rich phase towards the model solute (deprotonated in basic media L-tryptophan or vanillin) is pronounced for ABSs with amino acid ILs/PILs as compared to halides.

In this work, we have also considered the counter-ion effects on the micellar aggregation of 1-dodecyl-3-methylimidazolium AAILs in aqueous-salt solutions. Sodium chloride, choline chloride and choline chloride+L-proline were chosen as additives. Surface properties, critical micellar concentrations and micellar size distributions are studied and discussed in terms of salting-out as well as chaotropy/cosmotropy of the ions.

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This work was supported by Russian Science Foundation (projects 20-13-00038, 25-43-01003). The experimental measurements were partially performed at the Research Park of St. Petersburg State University ("Center for Magnetic Resonance", "Center for Thermogravimetric and Calorimetric Research", "Center for Diagnostics of Functional Materials for Medicine, Pharmacology, and Nanoelectronics").

RELATIONSHIPS BETWEEN THE STRUCTURE, NANOSTRUCTURE, AND PROPERTIES OF IONIC LIQUIDS

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Many ionic liquids (ILs) exhibit a distinct nanoheterogeneous structure, composed of interpenetrating polar and apolar domains. Nanoheterogeneity is particularly prominent in ILs with longer alkyl chain lengths, which form large apolar domains. Domain segregation can be identified using experimental scattering techniques or from molecular dynamics simulations. However, there is no straightforward way to quantify nanoheterogeneity. The scattering peak position only provides an average length scale for both polar and apolar domains. When analyzing instantaneous configurations from computer simulations, the percolating sponge-like geometry of the domains makes it difficult to isolate apolar or polar atom clusters and measure their size.

In this work, the chord length distribution method was applied for the first time to the analysis of domain structure in different ILs. We define an apolar domain as all the points of space inside the simulation cell that are closer to the polar than to any apolar heavy atom in the liquid. In a polar domain, all the points lie closer to a polar atom. Hence, these domains consist of Voronoi cells around apolar or polar atoms. Random lines are then generated and the lengths of the line segments cut by the boundaries of the polar and apolar domains are determined. The distribution of these segment lengths characterizes the sizes and shapes of the clusters of apolar and polar atoms.

Molecular dynamics simulations of ILs were conducted at 298 K in the NPT ensemble using the OPLS force field in large cells containing 4000 ion pairs. The simulation results were validated by comparing the predicted and experimental SAXS curves. The instantaneous configurations were analyzed using a program written by the author.

The results of analysis revealed a number of interesting relationships between the structure of the cation and the nanostructure of the IL. Alkylammonium ILs with the same number of alkyl groups (mono-, di- or tri-) but with different alkyl chain size show very similar distributions of chord lengths in the polar domain. The size of clusters in the apolar domain grows up with increasing number of carbons in the alkyl group. At the same time, cations with different numbers of the same substituents (e.g. mono-, di- and tributylammonium) have almost the same structure of apolar domains and strikingly different polar domains. While polar atoms tend to aggregate in monoalkylammonium salts, their distribution is much closer to uniform in di- and especially trialkylammonium ILs. Similarly, imidazolium ILs with two identical alkyl substituents and those with one such substituent form apolar clusters of the same size. The nature of the IL anion also affects domain segregation. Large anions can impede apolar aggregation.

The nanostructure of ILs strongly influences their properties. This is shown by the example of solvation properties using experimental free energies of solvation and calculated free energies of cavity formation, which depend on the cluster size distribution.

The work was supported by RSF project №24-13-00062.

CALORIMETRIC STUDY OF THE OXOTRANSFER PROCESS INVOLVING TRIPHENYLPHOSPHINE AND A MOLYBDENUM-CONTAINING ANALOGUE OF THE ENZYME ACTIVE SITE

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The key process that forms the basis of molybdenum enzymes' operation is oxotransfer, i.e. the transfer of an oxygen atom between the enzyme's active site and the substrate. Molybdenum complexes with dithiolene ligands are commonly used as convenient models of the active site in molybdenum-containing enzymes. Research on these model active sites typically aims to obtain kinetic and electrochemical characteristics of the system. Nevertheless, thermodynamic data are essential for identifying the driving force behind the oxotransfer process [1].

In this study, the molybdenum complex with maleonitriledithiolate ligand (mnt^{2-}) of the composition $(Bu_4N)_2[MoO_2(mnt)_2]$ was used as a model of the enzyme active center, and triphenylphosphine PPh_3 was used as the substrate. The calorimetric study was performed using Calvet-type microcalorimeter (KYV) [2] to obtain data on the change in enthalpy during the dissolution processes of the solid sample $(Bu_4N)_2[MoO_2(mnt)_2]$ (a) in pure acetonitrile and (b) in acetonitrile containing a portion of PPh_3. Subsequently, the total changes in enthalpy upon interaction of the components in the liquid phase were calculated.

By varying the ratio of the complex to the substrate, the values of the total thermal effects during the oxotransfer process in this system were obtained. The increase in the phosphine quantity in the system leads to a significant increase in total the thermal effect. These data indicate a catalytic character of the process, which correlates with the nature of the synthetic model.

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The work was performed using the equipment of the St. Petersburg State University Science Park (CMR, CAMR and XRD Centre) and was carried out as part of an initiative project supported by St. Petersburg State University, grant 149039462. VDK acknowledges funding from FUNDECT/CNPq (grant 83/053.361/2024) The authors express special gratitude to Dr. Kondratiev Yu.V., who designed the KYV calorimeter.

A COLORIMETRIC METHOD FOR CHARACTERIZING FAST EXTRACTION PROCESSES IN NADES

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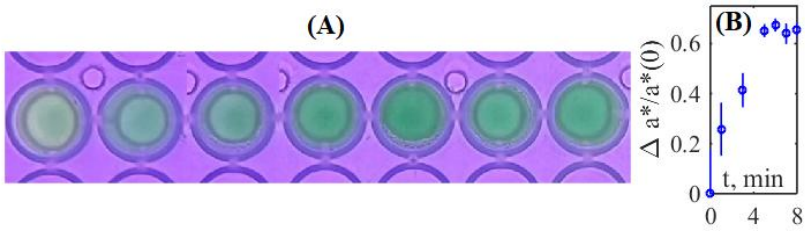
In the modern biotechnology industry, natural deep eutectic solvents (NADES) attract significant attention as they provide a route toward the transition to "green" extractants. At the same time, the molecular and thermodynamic background of their efficiency is hampered by the lack of kinetic data explaining the relevant intermolecular interactions. The situation is complicated by the high viscosity of NADES, which necessitates significant water dilution, filtration, and centrifugation of the samples to make them suitable for conventional spectrophotometry. As a result, this approach provides only overall yield data rather than enabling real-time monitoring.

In this work, we propose an alternative method based on a colorimetric approach that processes a time series of samples during short extraction periods. As a case study, the extraction of phycocyanin from *Arthrospira platensis* biomass in a NADES system composed of glycerol and glucose is examined, see the figure below. The key feature of the method is the monitoring of color trajectories in the device-independent CIE Lab* color space under specially developed illumination, filtered in accordance with the specific molecular absorption bands of the compounds involved.

The figure below illustrates that the developed colorimetric approach effectively overcomes the analytical challenges posed by the high density and viscosity of eutectic solutions based on sugars and polyhydric alcohols.

Based on the kinetic parameters obtained during the extraction process for this and several other NADES, the implications of the identified interplay between the thermodynamic properties of NADES and their biochemical interactions with plant tissue components will be discussed.



(A) Example of a solution's recorded color change during ten minutes from the beginning of extraction in NADES. (B) Kinetic extraction curve calculated coloimetrcally from these images.

HIGH-ENTROPY Li-Na-K FLUORIDE-CHLORIDE MELTS FOR MOLTEN SALT REACTORS

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This report presents a theoretical study that evaluates thermodynamic and thermophysical properties of high-entropy molten salt mixtures composed of lithium, sodium, and potassium fluorides and chlorides. These liquid mixtures of six alkali halide components have enhanced thermodynamic stability as a result of the high configurational entropy as expected [1]. The equimolar solution, $Li_{1/6}Na_{1/6}K_{1/6}F_{1/4}Cl_{1/4}$, maximizes configurational entropy with the value of $\frac{1}{2}R\ln 24 \approx 1.59R = 13.21$ J/mol·K approaches the high-entropy threshold of $R\ln 5$ (13.38 J/mol·K). Such entropy value significantly exceeds that of FLiNaK (6.9 J/mol·K). So they can be promising coolants for molten salt reactors (MSRs) due to improved thermodynamic stability [2]. Two eutectic compositions with reduced lithium content, derived from the phase diagram (melting points 606 °C and 630 °C), are also analyzed [3]. For example, composition on the phase diagram (point B) in which the proportion is LiF (10%) LiCl (10%) NaF (20%) NaCl (20%) KF(20%) KCl (20%) has high entropy as well: $\frac{\Delta S_{\text{conf}}}{R} = \frac{11}{10}\ln 2 + \frac{1}{2}\ln 5 \approx 1.57$.

Density, heat capacity, thermal conductivity, and viscosity are calculated from liquidus to 1000 °C using empirical superposition-extrapolation method, thermodynamic perturbation theory (TPT), as well as molecular dynamics with machine learning interatomic potentials (MLIP).

The diversity of high-entropy coolants offers significant flexibility for tailoring compositions to specific MSR needs, such as fast-spectrum actinide burning or thermal-spectrum efficiency. Through such efforts, high-entropy molten salts could enable MSRs to achieve a closed nuclear fuel cycle, reduce long-lived radioactive waste, and deliver sustainable, carbon-free energy, advancing the goals of Generation IV nuclear technology.

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EXPERIMENTAL STUDY OF THE DEPENDENCE OF THERMODYNAMIC PROPERTIES OF THE (PROPANOL-1 + N-OCTANE) SYSTEM IN LIQUID, GASEOUS, AND SUPERCRITICAL STATES

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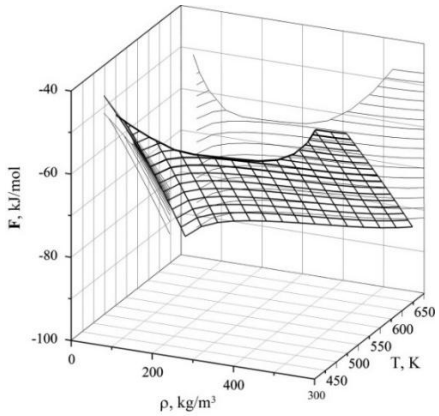
Experimental data on the *p, ρ,T,x* - dependences of 1-propanol + n-octane mixtures at various compositions (0.2, 0.5, and 0.8 mole fractions of n-octane) in the temperature range of 373.15–623.15 K, density range of 1–680 kg/m³, and pressures up to 56 MPa, obtained using a constant-volume piezometer [1], are described by a virial-type thermal equation of state by expanding the compressibility factor $Z = p/RT\rho_m$ into series in terms of reduced density and temperature:

$$Z = p/RT\rho_m = 1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} a_{ij}\,\omega^i/\tau^j, \text{and } p = RT\rho_m\left[1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} a_{ij}\,\omega^i/\tau^j\right]$$

Here, ρ_m is the molar density (mol/m³); $\omega = \rho/\rho_\kappa$, $\tau = T/T_\kappa$ are the reduced density and reduced temperature, respectively; ρ_c, T_c are the critical density and critical temperature; R = 8.314 J/(mol·K) is the universal (molar) gas constant. The mean relative deviation of the pressure values calculated using the equation from the experimental data is 0.8%.

Furthermore, based on this equation and thermodynamic relations [2], the principal thermodynamic properties of the investigated mixtures were calculated in the liquid, gaseous, and supercritical states. The figure illustrates the dependence of the Helmholtz energy F on density and temperature T for the composition x = 0.5.



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THERMODYNAMIC MODELING AND CALCULATION OF PHASE EQUILIBRIA IN TERNARY WATER-SALT SYSTEMS CONTAINING K^+, NH_4^+, SO_4^{2-} AND/OR NO_3^- IONS

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Complex fertilizers containing nitrogen, potassium, and sulfur are currently attracting increasing interest. Phase composition of such fertilizer is as important as chemical one, affecting how resulted product is hygroscopic, stable to detonation and effective in simultaneous release of macronutrients.

Phase equilibria in reciprocal K^+, NH_4^+|| SO_4^{2-}, NO_3^- - H_2O system are complicated due to existence of double salts and solid solutions. Slightest changes in type of granulator and conditions will result in a loss of predictive force of empiric results of phase-equilibria study. Thermodynamic modeling allows to calculate phase composition at any component ratios and conditions within its predictive range. Thus, the goal of the work is to obtain all solubility products and develop thermodynamic models of liquid and solid solutions in 298 – 373 K temperature range at least up in the ternary subsystems of the reciprocal K^+, NH_4^+|| SO_4^{2-}, NO_3^- - H_2O.

PSC model [1] was chosen for a liquid phase. Its parameters, along as solubility products of two double salts and $(NH_4)_2SO_4$, NH_4NO_3 are available for $(NH_4)_2SO_4$–NH_4NO_3–H_2O [1]. Solid solutions are absent in this system. PSC model parameters proposed in literature for K_2SO_4–H_2O [2] have too complex temperature dependence and give an ill extrapolation of luiquid phase properties to supersaturated solutions, which result in artifacts at high ionic strength in ternary systems. Therefore, these parameters were re-evaluated. New PSC parameters for KNO_3–H_2O were obtained. Ternary parameters for luiquid phase model were added to K_2SO_4–KNO_3–H_2O, solubility is adequate predicted.

The $(NH_4)_2SO_4$–K_2SO_4–H_2O and KNO_3–NH_4NO_3–H_2O systems require a solid phase model. Redlich-Kister model was chosen for sulfate and nitrate solid solutions. For sulfate solid solution, there is an isomorphous substitution for one structure, for nitrate solid solutions, there are three separate solid solutions. Phase equilibria were calculated without introducing new ternary parameters for luiquid phase model. Predicted liquidus and tie lines between solutions agree with experimental ones.

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Work was financed on base of "Chemical thermodynamics and theoretical material study" 121031300039-1.

STUDY OF THE PICOLINIC ACID INHIBITING EFFECT MECHANISM ON THE ASCORBIC ACID OXIDATION

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Synchrotron radiation allows for detail study of complex phenomena including biological and biomedical. X-ray crystallography of solid drugs in widely used in drug design and pharmacy, defining the kinds of intermolecular interaction. SAXS experiments help to understand processes in solution, such as complex formation. Molecular modelling helps in further understanding of such process's mechanisms.

Ascorbic acid (vitamin C) is one of the most important biologically active compounds, playing a key role in metabolic processes. Due to its reducing properties, it is widely used in medicine. However, the main drawback of ascorbic acid (AA) is its high chemical instability in aqueous solutions. When exposed to atmospheric oxygen, AA is easily oxidized. This process leads to the loss of biological activity of the drug.

It was shown by our colleagues that picolinic acid inhibits oxidation of AA in solution. It is intriguing that nicotinic acid despite its close structure has no such effect. The drastic difference was also in their influence on bioactivity of AA. A detailed elucidation of this process using is challenging. Traditional methods do not provide insight into the causes of stabilization. This study employed an integrated approach combining experimental data with computer modeling methods: molecular dynamics and quantum mechanics.

Molecular dynamics simulations allowed us to study solution at various pH values and identify the most stable complexes possibly responsible for the inhibitory effect. Quantum chemical calculations provided a detailed analysis of the process's energetics.

Modeling showed that picolinic acid forms a stable complex with ascorbic acid via two hydrogen bonds. The picolinic acid molecule simultaneously binds to two hydroxyl groups of ascorbic acid: the carboxyl group ($–COO^-$) interacts with one hydroxyl group (OH), and the nitrogen atom of the pyridine ring (N^+H) interacts with the other (O^-). This "double" bond firmly holds the molecules together, protecting ascorbic acid from oxygen and preventing its oxidation. For nicotinic acid, where N atom is shifted by 1 position in ring, such complementary complexes can not be formed.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for SRF "SKIF" Boreskov Institute of Catalysis (FWUR-2024-0040).

MONTE CARLO STUDY OF THERMODYNAMIC AND STRUCTURAL PROPERTIES OF A LENNARD-JONES FLUID AT DIFFERENT TEMPERATURES

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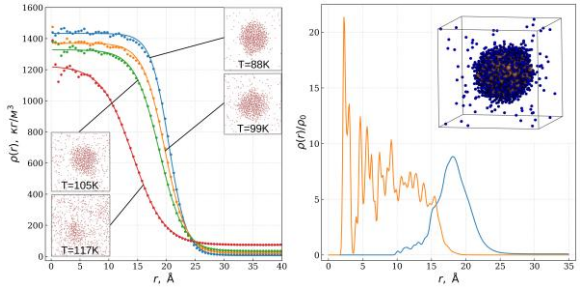
We present the results of computer simulation of one-component and two-component Lennard-Jones fluids in the canonical statistical ensemble using the Monte Carlo method [1-2]. The purpose of the study is to analyze the influence of temperature, size and composition of the considered systems on their structural and thermodynamic properties. A one-component system consisting of argon molecules has been simulated in the temperature range from 80 to 120 K. The formation of droplets surrounded by the vapor phase has been observed during the simulations (see Figure). The dependence of the density profile on the temperature at a fixed concentration of argon in the simulation cell has been studied. The obtained results are consistent with the data presented by other authors [3]. Our calculations show that the density of the vapor phase increases and the density of the liquid phase decreases with the increase of temperature. A two-component system consisting of argon and neon molecules has been also studied. Analysis of structural properties of the system has revealed the formation of a liquid film consisting of neon molecules on a solid core consisting of argon molecules at the temperatures below 60 K (see Figure). The influence of argon and neon concentrations, as well as temperature, on the density profiles, energy and heat capacity of the considered systems has been studied.



Density profiles and snapshots of one-component (argon) and two-component (argon and neon) Lennard-Jones fluids

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EVALUATION OF IONIC LIQUIDS FOR THIOPHENE/HYDROCARBON SEPARATION

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Organosulfur compounds act as catalyst poisons for many industrial and automotive catalysts. Moreover, together with their combustion products, they are hazardous pollutants. Current environmental standards limit the sulfur content in fuels to ultra-low levels. Extractive desulfurization with polar solvents is a promising method for thorough and selective removal of organosulfur compounds, including thiophene and its derivatives, from fuels. Ionic liquids (ILs) are often considered as potential thiophene extractants. The efficiency of the extractive process is assessed based on the parameters of solvent selectivity and capacity, which can be determined from the activity coefficients at infinite dilution of the substances being separated.

We have compiled a database of experimental values of the activity coefficients of thiophenes and hydrocarbons in ILs taken from literature. We have analyzed the influence of the structure of the IL cation and anion on these values. Based on these data, we have constructed predictive models for limiting activity coefficients, separation selectivities and capacities in various ILs. Furthermore, we have tested the models against our own experimental data for certain protic ILs that have been underrepresented in the training set.

The work was carried out with support from the grant provided in 2025 by the Science and Technology Foundation of the Republic of Tatarstan for conducting fundamental and exploratory research in scientific and educational institutions, enterprises, and organizations of the real sector of the economy of the Republic of Tatarstan.

THERMAL STABILITY OF HYDROGEN SULFATE PROTIC IONIC LIQUIDS

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Ionic liquids are promising solvents for many industrially significant processes, including the separation of aromatic and aliphatic hydrocarbons, extractive desulfurization of petroleum products, and biomass processing. In addition, ionic liquids containing the hydrogen sulfate anion are considered superacidic catalysts for a number of reactions such as alkylation of aromatic compounds. Unlike most traditional solvents and catalysts, ionic liquids are thought to be environmentally benign. Processes in which ionic liquids may potentially be applied are often associated with the use of high temperatures. In this regard, the studies of the thermal stability of ionic liquids become a critical issue.

In this work, the thermal stability of a series of hydrogen sulfate protic ionic liquids with cations based on mono-, di-, and trialkylammonium was investigated. The thermal stability was studied using thermogravimetric analysis (TGA) in dynamic mode and FT-IR spectroscopy. Particular attention was paid to long-term thermal stability, which more accurately reflects the real operational properties of ionic liquids. Differential scanning calorimetry (DSC) was used to determine the melting temperature. Based on the obtained data, the operating temperature ranges in which the studied ionic liquids can be used as solvents were determined. The upper operating limit was defined as the temperature at which signs of chemical degradation were observed in the IR spectrum.

The research was funded by the Russian Science Foundation, project 24-13-00062.

THERMODYNAMIC PARAMETERS OF PROTOLYTIC EQUILIBRIA FOR SOME AMINO ACIDS AND DIPEPTIDES IN AQUEOUS SOLUTIONS

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This work presents results of investigations of acid-base interaction processes in aqueous solutions of homoserine, cysteine, taurine, asparagine, glutamine, valyl-valine, valyl-leucine, valyl-glycine, leucyl-glycine, leucyl-leucine, α-alanyl-leucine, isoleucine, α-alanyl-isoleucine, methionine, norvaline, glycyl-norvaline, glycyl-methionine, glycyl-histidine, α-alanyl-histidine, α-alanyl-methionine, α-alanyl-serine, α-alanyl-glycine, β-alanyl-glycine, glycyl-β-alanine, glycyl-α-alanine, glycyl-valine, glycyl-leucine, glycyl-serine, glycyl-threonine, glutamic, glycyl-glutamic and glycyl-aspartic acids.

Thermodynamic parameters ($\log K$, ΔG, ΔH, ΔS) of protolytic equilibria have been determined at 298.15 K and at ionic strength values from 0.1 to 1.5 M (KNO_3). Stepwise dissociation constants of these compounds were determined potentiometrically. The heat effects of the relevant equilibria were measured calorimetrically. The influence of "background" electrolyte concentration on the thermodynamic parameters for the protolytic equilibria investigated was under consideration. The data obtained were extrapolated to the zero ionic strength. The corresponding thermodynamic quantity values have been calculated for the standard solution ($\log K^\circ$, ΔG°, ΔH°, ΔS°). The results have been compared with the corresponding data on related compounds (amino acids, complexones, dipeptides and diamines) investigated in this laboratory earlier [1-5]. A plausible explanation of changes in these quantities has been suggested in view of the aminocarboxylate structure, its set of functional groups, distance between carries of positive and negative charges, solvation features of zwitter ions, presence of hydrophilic and hydrophobic fragments (CH_2COOH, CH_2CONH_2, CH_2CH_2COOH, $CH_2CH_2CONH_2$, CH_2OH, $CH_2C_3H_3N_2$, $CH(CH_3)OH$, CH_2CH_2OH, H, CH_3, CH_2SH, $CH(CH_3)_2$, $CH_2CH_2SCH_3$, $CH_2CH_2CH_3$, $CH_2CH(CH_3)_2$, $CH(CH_3)CH_2CH_3$).

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THERMODYNAMIC CHARACTERISTICS OF AMMONIUM ION SOLVATION IN N-METHYLPYRROLIDONE–WATER SOLUTIONS

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Based on the standard values of the heat capacity $\overline{C^{\circ}_{p,i}}$ of an ammonium ion, the values of the change in heat capacity during the solvation $\Delta_{\text{solv.}}C^{\circ}_{p,i}$ of an ammonium ion in a mixed solvent N-methylpyrrolidone (MP)-water at 298.15 K are determined. The magnitude of the ammonium ion is represented as the sum of four contributions: electrostatic $\Delta_{\text{el.}}C^{\circ}_{p,i}$, cavity formation $\Delta_{\text{cav.}}C^{\circ}_{p,i}$, structural changes in the solvent $\Delta_{\text{str.}}C^{\circ}_{p,i}$, and specific ion-solvent interactions $\Delta_{\text{sp.int.}}C^{\circ}_{p,i}$. The values of the contributions are calculated based on experimental data and model representations. The calculation results are presented in the table.

The change in heat capacity during solvation $\Delta_{\text{solv.}}C^{\circ}_{p,i}$ of an ammonium ion in a mixed solvent MP – water, MP and water at 298.15 K and contributions to this value caused by specific interactions, electrostatic interactions, cavity formation, and changes in the solvent structure

J/mol·K	X_{MP}						
	0,00	0,10	0,33	0,50	0,75	0,90	1,00
$\Delta_{\text{solv.}}C^{\circ}_{p,i}$	-62	-78	-80	-41	-17	7	12
$\Delta_{\text{sp.int.}}C^{\circ}_{p,i}$	30	4	2	-7	-5	-8	-9
$\Delta_{\text{el.}}C^{\circ}_{p,i}$	-218	-225	-236	-319	-310	-285	-295
$\Delta_{\text{cav.}}C^{\circ}_{p,i}$	41	82	97	92	109	116	134
$\Delta_{\text{str.}}C^{\circ}_{p,i}$	85	60	57	193	189	170	155

The dependences of the obtained values on the composition of the mixture are discussed in connection with the structure of the mixed solvent.

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HEAT CAPACITY OF THREE-COMPONENT SYSTEMS CONTAINING AMMONIUM IODIDE, N-METHYLPYRROLIDONE AND WATER

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In this work, the heat capacities C_p of solutions of ammonium iodide in a mixed solvent MP-water were measured with high accuracy over the entire range of compositions at 298.15 K. Heat capacity measurements were performed on the LKB 8700 calorimetric unit with an error of $2 \cdot 10^{-3}$ J/g·K. On the basis of the data obtained, the apparent molar heat capacities of Φ_c were calculated, extrapolating the concentration dependences of which to the state of infinite dilution the standard partial molar heat capacities of ammonium iodide in the mixed solvent MP-water at 298.15 K were determined. To separate the values $\overline{C^\circ_{p,2}}$ of ammonium iodide into ionic components, we used our data on the iodide ion in MP and MP-water mixtures [1] and the additivity condition of partial molar quantities. The values $\overline{C^\circ_{p,i}}$ are shown in the table.

Standard partial molar heat capacities $\overline{C^\circ_{p,i}}$ of ammonium ion in the mixed solvent MP-water at 298.15

	X_{MP}						
	0,00	0,10	0,33	0,50	0,75	0,90	1,00
$\overline{C^\circ_{p,i}}$, J/mol·K	4	-12	-14	25	49	73	78

Compared with alkali metal ions, where the values $\overline{C^\circ_{p,i}}$ increase monotonously, the dependence on the composition of the mixed solvent for the ammonium ion is extreme: at low concentrations of MP, a minimum is observed, and at high concentrations, a maximum. In the entire range of compositions of the MP-H_2O mixture, the values $\overline{C^\circ_{p,i}}$ of NH_4^+ are higher than those of alkali metal ions, and the inversion of values occurs with a lower content of MP. This indicates the complex nature of intermolecular interactions in the studied solutions, which is significantly influenced not only by the properties of the MP-water binary system, but also by the structural behavior of the ammonium ion.

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The research was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation within the framework of the scientific project of the laboratory "Laboratory of Ion Materials" (LIM), project no. FSSM-2024-0006.

EXPERIMENTAL STUDY OF THE DEPENDENCE OF THERMODYNAMIC PROPERTIES OF THE WATER + PROPANOL-1 BINARY SYSTEM ON ITS COMPONENT COMPOSITION OVER A WIDE RANGE OF STATE PARAMETERS

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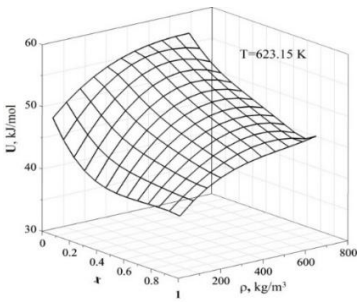
Measurements of the $(p,T\text{-}p,\rho,T)_x$ - dependences for 1-propanol aqueous solutions with compositions of 1-propanol (x = 0.1, 0.2, 0.3, 0.5, 0.8, 0.9 molar fractions), in two-phase, one-phase (liquid and vapor), and supercritical fluid states over temperatures ranging from 373.15 K to 673.15 K, densities between 1.5 kg/m³ and 850 kg/m³, and pressures up to 50 MPa have been carried out. The experimental values of $(p,T\text{-}p,\rho,T)_x$-dependencies are described by a thermal equation of state of virial form — an expansion of the compressibility factor $Z = p/(RT\rho m)$ into series of reduced density and temperature powers [1].

$$Z = p/RT\rho_m = 1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} a_{ij}\,\omega^i/\tau^j, \text{and } p = RT\rho_m\left[1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} a_{ij}\,\omega^i/\tau^j\right]$$

Herein: ρ_m is the molar density (mol/m3), $\omega=\rho/\rho_c$and $\tau=T/T_c$ are the expressions for reduced density and reduced temperature respectively, where ρc and Tc represent critical density and critical temperature; R=8.314 J/(mol·K) is a universal (molar) gas constant. The average relative deviation of calculated pressure values using this equation compared to experimental data amounts to 1.2%.

Based on Equation [1] and thermodynamic relations [2], variations of the main thermodynamic properties of the studied solutions were computed. A plot illustrating the dependence of internal energy changes (U) on solution composition (x) and density (ρ) at a temperature of 623.15 K is presented in the figure.



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A NEW METHOD FOR RECRYSTALLIZING FLUFENAMIC ACID FROM POLYMORPH I TO POLYMORPH III

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Preliminary studies conducted with representatives of several phenamates that contain an amino group, carboxyl, and aromatic fragments in their molecules, using quantum chemistry methods and in situ high-pressure IR spectroscopy, confirm the occurrence of a reaction with supercritical carbon dioxide. The presented work found that in a saturated solution of flufenamic acid in $scCO_2$ at a temperature of 140°C and a pressure of 500 bar, a chemical reaction occurs between these compounds. The reaction is facilitated by the attack of a carbon dioxide molecule on the carboxyl group of flufenamic acid. As a result, an amorphous reaction product is formed, which is thermally stable at least up to 140°C. Analysis of the product using ATR IR spectroscopy indicates the presence of a small amount of unreacted flufenamic acid in the reaction mixture, the dominant component of which is the reaction product. However, in the presence of crystallization centers, this compound decomposes under normal conditions within a relatively short period, depending on the morphology of these centers, releasing CO_2 and pure flufenamic acid in crystalline form. Through X-ray diffraction analysis of the crystalline phase obtained in this manner, it was established that during crystallization from the amorphous reaction mixture, a stable third polymorphic modification of flufenamic acid is formed, while the crystalline structure of the initial flufenamic acid is the first polymorph. Thus, a recrystallization method is proposed which, unlike standard physical recrystallization, is a chemically mediated process that allows for the production of a different polymorphic modification of the same substance.

The work was carried out with financial support from the Russian Science Foundation grant No. 22-13-00257-P.

MOLECULAR DYNAMICS SIMULATION OF ETORICOXIB UNDER CONFINED GEOMETRY CONDITIONS OF NANOCRYSTALLINE CELLULOSE-BASED AEROGEL IN A SUPERCRITICAL CARBON DIOXIDE MEDIUM

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Aerogels possess a number of unique physicochemical properties, such as low thermal conductivity, very low density, and high porosity, which make them highly attractive for use in various technologies. In pharmaceuticals, aerogels are promising delivery systems for active pharmaceutical ingredients, among which aerogels based on nanocrystalline cellulose have great potential for application. The use of carrier matrices such as aerogels makes it possible to increase the bioavailability of an active pharmaceutical ingredient through its amorphization in the pores. Furthermore, drug formulations based on aerogels allow for the controlled release rate of medicinal compounds.

This work studies the impregnation of nanocrystalline cellulose-based aerogel with etoricoxib, a nonsteroidal anti-inflammatory drug.

The report discusses molecular dynamics modeling of the impregnation of nanocrystalline cellulose-based aerogel with etoricoxib in a supercritical carbon dioxide medium. The modeling was performed at various temperatures and carbon dioxide densities equal to 1.1 times the critical density of CO_2. The metadynamics method was applied to calculate the free energy of conformers and the entire free energy landscape as a function of the dihedral angles of etoricoxib. This method enables accurate calculation of the free energy of conformational transitions between states separated by high energy barriers. The results of the performed calculations are discussed in the report.

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STUDY OF THE CRYSTALLIZATION PROCESS OF THE ANTIVIRAL DRUG TECOVIRIMAT USING THE MOLECULAR DYNAMICS METHOD

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The active ingredients of drugs are often solid phases. However, the polymorphism inherent in molecular crystals necessitates strict control over the polymorphic composition of active substances during drug production, as different solid forms can vary significantly in their physicochemical properties. Precipitation from solution is a widely employed method for producing solid pharmaceutical forms, where the formation of specific polymorphs primarily depends on the properties of the chosen solvent. Currently, identifying the crystallization conditions for particular polymorphs remains purely empirical. It is generally accepted that the precipitation process involves the formation of molecule clusters that gradually grow into crystal nuclei. The structure of these clusters is believed to dictate the architecture of the resulting solid form.

Molecular dynamics (MD) simulation, is well-suited for investigating processes occurring in solution. MD provides a comprehensive set of atomic coordinates, enabling the extraction of detailed information regarding molecular orientation, cluster size and morphology, and intermolecular interactions—both within solute clusters and with the surrounding solvent. Furthermore, these simulations allow for the calculation of various thermodynamic properties. Such data are essential for analyzing of a specific solvent influence on cluster architecture and, consequently, the structure of the resulting solid phase.

The antiviral drug Tecovirimat, having six known solid forms, was selected as the object of this study [1]. Using MD simulations, we constructed models of Tecovirimat solutions in various solvents and at different concentrations. The conformations of individual Tecovirimat molecules were investigated as well as mutual molecular orientation. Furthermore, the structure and stability of the resulting molecular associates in solution were examined. Finally, a comparative analysis was performed between the MD simulation data and experimental X-ray diffraction data for Tecovirimat. The correspondence between the structure of clusters and the precipitated solid form was shown.

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STRUCTURE AND THERMODYNAMICS OF WATER-DIOXANE MIXTURES BASED ON MOLECULAR DYNAMICS SIMULATION

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Thermodynamic data are often used to insight into molecular processes. It is usual to fit such parameters as molecular interaction energy or molecular complexes' structure to reproduce observed macroscopic values of enthalpy, heat capacity etc. Structural experiments like X-ray diffraction, SAXS or WAXS measurements can support or deny the chosen model. Currently, computer simulation tools such as molecular dynamics (MD) help one to combine structural and thermodynamic approaches together. In MD model all atomic coordinates in the system are known in every moment, so the model can be directly compared with structural data and explain the experimental observations. Because details of molecular interactions are also known for MD model, one can directly extract the thermodynamics data.

In the work we show the advantage of MD simulation for understanding experimental findings on the example of water-dioxane mixture study. Atomic pair correlation functions were compared with experimental SAXS data on the whole range of concentrations. Structure factors were calculated. Analysis of partial g(r) and S(q) for individual components gives better explanation of experimental data, where only total scattering on the all system atoms can be measured. Analysis showed that mixture is highly heterogeneous in the middle concentration range, with spanning clusters of water molecules formed. The fact explains the very slow changes of thermodynamics parameters, such as partial enthalpies, in these concentrations.

Analysis of hydrogen bonds support also showed slow change in the middle concentrations with high number of water-water bonds, what support the suggested structure. Additional analysis of intrinsic volumes also supported the picture and explained features of solution volumetric parameters, namely a minimum on the water partial volume.

The work underlined the fruitfulness of MD simulation in understanding structural and thermodynamics data and refining the structural model.

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DIAGRAMS WITH DISTINGUISHABLE DEFORMATION OF RESIDUE CURVES OF ZEOTROPIC THREE-COMPONENT SYSTEMS

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The identification of possible structures of vapor-liquid equilibrium diagrams is fundamental importance for evaluating the possibility of using distillation separation of liquid mixtures. Based on a qualitative analysis, L.A. Serafimov developed a classification of three-component systems, including diagrams with distinguishable deformation of residue curves. These are diagrams in which the course of K = 1 lines (K is the distribution coefficient of the component between the vapor and liquid phases) are different, but the course of the residue curve is qualitatively the same [1]. Systems belonging to class 3.0.0–1 [2], were considered as ideal solutions, at the same time the lines of K limit values were assumed to be straight, and for this class of systems there were no diagrams with distinguishable deformation of residue curves [1].

In the basic organic synthesis industry, as is known, a vast majority of mixtures are non–ideal solutions, which can be either azeotropic or zeotropic systems. In this regard, this work is devoted to the analysis of the course of K = 1 lines in non–ideal systems of class 3.0.0–1. Based on the construction of the K surfaces traces on the prism faces, corresponding to the binary constituents of the three–component system, we identified diagrams with distinguishable deformation of residue curves, characterized, in particular, by the presence of one-sided K = 1 lines. Applying the method of mathematical modeling of vapor-liquid equilibrium, the implementation of one of synthesized diagrams corresponding to the benzene – 1,2-dichloroethane – 1,1,2-trichloroethane system, which is part of the chlorine–balanced production of vinyl chloride, was confirmed.

It should be noted that identified K = 1 lines diagrams play an important role in the analysis of the evolution of the vapor-liquid equilibrium diagram structures of three-component systems, especially in the implementation of ternary biazeotropy.

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CALCULATION AND EXPERIMENTAL STUDY OF PHASE EQUILIBRIA IN BINARY AQUEOUS SYSTEMS CONTAINING MONOVALENT CATIONS AND METHANESULFONATE

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Methanesulfonic acid and its salts are of interest for green hydrometallurgical processing routes. Phase diagrams are the key instrument for element separation in such processes. Thermodynamic modeling allows to calculate phase composition in complex multi-component systems. At the same time, the literature data for thermodynamic properties of phases in even binary systems containing alkali metal and ammonium methanesulfonates remain fragmentary, which hampers the development of a consistent thermodynamic model.

In the present work, the binary systems H_2O–CH_3SO_3Me (Me = Li, K, NH_4) are considered. Only for the H_2O–$CH_3SO_3NH_4$ system, solubility data are available in the literature [1]. For the H_2O–CH_3SO_3Me (Me = Li, K) systems, solvent activity data at 298.2 K have been reported [2]. These data require extension to the high-concentration region and to other temperatures. The aim of this work is to obtain a new set of experimental data on vapor–liquid and solid–liquid equilibria in these binary systems and to provide their thermodynamic description.

Solubility in the H_2O–CH_3SO_3Me (Me = Li, K) systems was determined by the isothermal solubility method in the temperature range 253.2–323.2 K ($u(T)=0.2$ *K*). Methanesulfonate concentrations in saturated solutions were determined by evaporation of a sample of the saturated solution followed by weighing of the dry residue ($u_r(w)=0.5\%$). For these systems, data on the freezing-point depression of ice were obtained by DSC ($u_r(w)=0.5\%$, $u(T)=0.8$ *K*), using NETZSCH DSC 204 F1. Water activity of non-saturated liquid solutions was obtained at 298.2 K, 310.7 K and 323.2 K ($u(T)=0.2$ *K*, $u(aw)=0.003$) using the hygrometer Novacina LabMaster-aw neo.

Parameters of the Pitzer–Simonson–Clegg (PSC) model were determined for the liquid phase. Solubility products and their temperature dependence were evaluated for all salts. Phase diagram sections were calculated for the H_2O–CH_3SO_3Me (Me = Li, K, NH_4) systems.

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The work was carried out using equipment purchased with funds from the Lomonosov MSU Development Program (Novacina LabMaster-aw neo, NETZSCH DSC 204 F1). Work was financed on base of "Chemical thermodynamics and theoretical material study " 121031300039-1.

CHANGE IN THE STRUCTURAL CHARACTERISTICS OF AEROGEL MATRICES BASED ON SiO_2 AND NCC UPON IMPREGNATION WITH MEFENAMIC ACID

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Composites creation based on aerogels of various natures with active pharmaceutical ingredients (APIs) opens up broad prospects for controlled drug delivery. In this work a comparative analysis of the structural changes in the three-dimensional framework of aerogels based on nanocrystalline cellulose (NCC) and silica (SiO_2) upon impregnation with mefenamic acid (MA) at different temperatures was carried out. The drying and impregnation processes were carried out in a supercritical carbon dioxide medium.

Analysis of nitrogen sorption isotherms for the pristine aerogels showed that both types of matrices possess a developed mesoporous structure. The presence of nanoscale slit-like pores in the NCC aerogel samples is specifically noted. For such matrices, impregnation at 80°C proceeds without changing the three-dimensional structure. At the same time, impregnation at 140°C leads to a restructuring of the cellulose matrix, expressed in an increase in the number of pores of about 3 nm after the release of MA. This is associated with an increase in the concentration of MA, the formation of a bulk phase inside the pores, and as a consequence the emergence of disjoining pressure. For SiO_2 aerogels, similar studies were conducted in the same temperature ranges. A comparison of the behavior of the matrix framework depending on their nature is presented in the report.

Varying the nature of the matrix and the temperature regime of impregnation can make it possible to regulate the structural characteristics of the final composites, which is a key factor for optimizing the release profiles of poorly soluble APIs. These effects are discussed with more detail in the report.

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SOLVATION THERMODYNAMICS OF ORGANIC SOLUTES IN LACTATE ESTERS

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Lactic acid esters are low-toxic, biodegradable, nonflammable substances, the synthesis of which is relatively simple. They are used in the food industry, pharmaceuticals, perfumes, as solvents for nitrocellulose and paints. However, despite widespread use in various fields, their solvation properties, for example, the solubility of different compounds in these solvents, remain practically unexplored.

In the work, the activity coefficients at infinite dilution (γ^{∞}) of various organic compounds in lactic acid esters, ethyl lactate and butyl lactate, were determined by gas chromatographic headspace analysis at 298 K. The obtained values were used to calculate the Gibbs energies of solution and solvation of substances, as well as the capacity ($k = 1/\gamma^{\infty}$) and selectivity ($S_{12} = \gamma_1^{\infty}/\gamma_2^{\infty}$) parameters for various hydrocarbon separation problems. These parameters expand information about the solvation properties of lactic acid esters and make it possible to estimate their use as solvents for various processes.

The research was funded by the Russian Science Foundation, project 25-73-00291, https://rscf.ru/project/25-73-00291

EXPERIMENTAL INVESTIGATION AND THERMODYNAMIC ANALYSIS OF VOLUMETRIC PROPERTIES OF THE THYMOL–L-MENTHOL SYSTEM

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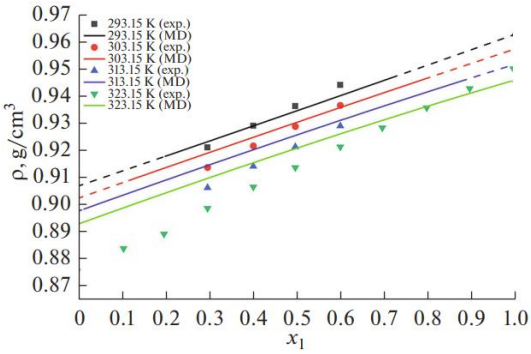
The thymol–L-menthol system has recently drawn increasing scientific attention as it belongs to a rather newly developed class of non-ionic deep eutectic solvents (DES), which is called Type V DES. As for the thymol-L-menthol mixture, there are some contradictory information on the thermodynamic properties and topology of the phase diagram for this mixture, e.g. [1,2], which indicates the necessity of further experimental study for more comprehensive observation.

In this work, density of thymol–L-menthol (see Fig.) and thymol/L-menthol-CCl_4 mixtures was studied in the temperature range 293.15 K – 323.15 K. The experimental results were compared with the molecular dynamics (MD) calculations. The molar excess volume was calculated for the studied mixtures to discuss deviation from ideal solution behavior. The ideal associated solution model was tested to be applied for evaluating association contribution to the non-ideality of the systems.



Experimental and calculated (MD) density for the thymol-L-menthol mixtures at 293.15 K, 303.15 K 313.15 K and 323.15 K

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PHASE EQUILIBRIA AND THERMODYNAMIC PROPERTIES OF SOLID AND LIQUID SOLUTIONS IN THE SYSTEM $(NH_4)_2SO_4$-K_2SO_4-H_2O

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Potassium and ammonium have close radii, resulting in mutual substitution in their salts [1]. Such solid solutions with sulfate ion contain potassium, sulfur and nitrogen and can be regarded as perspective fertilizer. It is essential to know a phase diagram to obtain a product with a known substitution rate and have a tool to a rapid check of a product quality.

However, phase equilibria with distribution rate between liquid and solid solution were studied only at 298.2 K [1] and are limited only to known liquid solution composition at other temperatures [1]. Thus, the primal goal of the present work was to obtain a phase diagram isothermal cross-section at an elevated temperature (313.2 K) and thermodynamic properties of both types of solutions (for further thermodynamic modeling).

Water activity of non-saturated liquid solutions were obtained at 298.2 K and 313.2 K ($u(T)$=0.2 K, $u(a_w)$=0.003) by a resistive hygrometer Novacina LabMaster-aw neo, expanding temperature and compositional range of results of El Guendouzi et al [2]. Isothermal cross-section at 313.2 K was obtained using isothermal solubility method ($u(T)$=0.2 K). Solid and liquid solution compositions were determined using gravimetric method (total water content in liquid solution, sulfate ion in both types of solutions, $u_r(w)$=0.5%), flame photometry (potassium content, $u_r(w)$=5%) and by ion-selective potentiometric method (ammonium content, $u_r(w)$=5%).

XRD patterns of solid solutions were obtained using TongDa TD-3700, unit cell parameters were refined. For an easier characterization of a solid solution, a dependence of temperature and enthalpy of a low-temperature phase transition of ammonium sulfate solid solution from substitution ratio was studied as well. Temperature and enthalpy of the transition were determined using NETZSCH DSC 204 F1.

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THE INFLUENCE OF POLYMER STRUCTURE ON THERMOCHEMICAL PARAMETERS OF FORMATION MICELLES AND GELS

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It is known that a significant part of the developed drugs are poorly soluble in aqueous systems, which affects their biological activity and stability. Polymers that are capable of self-organization in aqueous solutions with the formation of supramolecular aggregates (micelles) with medicinal preparations are used as systems to compensate for these disadvantages. At the same time, the thermodynamic parameters of micelles and gels influence the effectiveness of drug delivery.

In this work, a series of block copolymers (P123, F127, L64, F108) were selected as model compounds for studying the process of micelle and gels formation by calorimetry of dissolution and rheology. The enthalpies of dissolution of block copolymer solutions (P123, F127) in water with their different contents were determined by titration calorimetry of dissolution at T=298.15 and P=101.3 kPa. Methods for estimating the enthalpy of micelle formation and the critical concentration of micelle formation (CCM) for block copolymer solutions under standard conditions are proposed. The features of aggregate formation for polymer solutions are shown, and the differences between block copolymers P 123 and F 127 are discussed.

The role of the concentration of polymers (P123, F127) in the solution on the thermochemical parameters, as well as on the sizes of the aggregates formed in the solution, was established using the dynamic light scattering (DLS) method.

The role of the inclusion of the drug curcumin on the thermochemical and structural parameters of micelles is shown. The role of drug interactions with micelles in block copolymer solutions was discussed.

On the other hand, with increasing concentration of block copolymers in aqueous solutions, they are capable of forming gels. The role of polymer structure on the temperature and thermochemical parameters of gel formation was studied using the rheology method. The influence of hydrophobic-hydrophilic fragments in polymers on the studied parameters is shown. The possibility of controlling the thermal parameters of gelation due to inclusions has been revealed. A comparison of the studied parameters for micelles and gels for block copolymer solutions was carried out.

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DENSITY INVESTIGATION OF AlNiCoFeCr ALLOYS IN SOLID AND LIQUID STATES

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High-entropy alloys (HEAs) containing aluminum and transition metals have been actively studied in recent years due to their high functional properties (primarily, mechanical characteristics and corrosion resistance). Information on the physical properties of such alloys is a sought-after area in thermophysics and physics of condensed matter. In this work, the volumetric characteristics (density, molar volume) of HEAs with AlNiCoFeCr compositions have been studied.

AlNiCoFeCr alloys with different component ratios were prepared from pure initial metals (Al – 99.999 %, Ni – 99.5 %, Co – 99.5 %, Fe – 99.8 %, Cr – 99.9 %) in an induction furnace at a temperature of 1800 K under a protective helium atmosphere. The melting was carried out for half an hour in Al_2O_3 crucibles.

Density of the samples was studied using the absolute version of gamma-absorption method. The samples were investigated in Al_2O_3 crucibles under a protective helium atmosphere. The experiments were conducted in the heating and subsequent cooling mode at a rate of 5 K/min in solid state and 2 K/min in liquid state. Based on the experimental density data, molar volumes of the melts at high temperatures were calculated.

From the experimental results, it was established that density of the alloys in solid state decreases over the entire investigated temperature range. Melting of the alloys is associated with a stepwise decrease in density, and in the liquid state, temperature dependecies of density can be described by a linear functions.

The results obtained from the conducted experiments can be used for further research on high-entropy AlNiCoFeCr alloys, as well as for optimizing the production process of new functional high-entropy materials.

DETERMINATION OF THE COMPLEXATION CONSTANTS OF COPPER AND ZINC WITH EDTA AT 298.15 AND 288.15 K

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Ethylenediaminetetraacetic acid (EDTA) is a versatile and widely used complexing agent due to its ability to form stable chelate complexes with various metal ions. Studying the thermodynamics of complexation of ions such as copper, and zinc with EDTA is particularly relevant in the context of the development of modern chelated micronutrient fertilizers. With a set of experimental data on the true stability constants of complexes, calculations with high predictive power are possible. By parameterizing thermodynamic models with a small number of components and then combining them according to the pyramid principle, a thermodynamic model of a complex multicomponent system is constructed.

Despite numerous studies in the field of complexation, the thermodynamic parameters of complex formation of metal ions such as copper, and zinc with EDTA remain poorly understood at temperatures different from room temperature.

Experimental studies of complex formation were carried out using potentiometric titration at temperatures of 288.15 K and 298.15 K by using a TitroMatic 1S autotitrator and an ESK-10604 combined glass electrode. A metal-to-ligand concentration ratio of 1:1 or 1:2 was considered at different concentration levels. To accurately determine the content of metal ions in solutions, complexometric titration was carried out using standard methods with indicators.

To determine the protonation constants of the EDTA acid residue at a given temperature and ionic strength, a series of titrations of EDTA solution were carried out in the absence of metal cations.

The obtained potentiometric curves were processed using the AUTOEQUIL software package.

The obtained experimental data expand the database for modeling multicomponent systems containing chelated complexes. The established patterns of temperature influence on the stability of the complexes allow us to predict the behavior of chelated forms of micronutrients under real-world conditions.

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APPLICATION OF TEMPERATURE DEPENDENCIES OF SATURATED VAPOR PRESSURE FOR THE ANALYSIS OF PHASE DIAGRAM EVOLUTION OF A SOLVENT MIXTURE

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The choice of methods for liquid mixtures separation is determined by their phase equilibrium diagram structure and its evolution upon variation of external parameters. An important role in the analysis of vapor–liquid equilibrium diagram evolution is played by the mutual course of temperature dependencies of saturated vapor pressure ($P = f(T)$ dependencies) of components and azeotropes as well as information about the presence/absence of Bancroft points of different kinds on these dependencies. The latter makes it possible to identify the presence of different azeotropes in the systems and to determine the concentration ranges of their existence [1].

The work is devoted to the analysis of vapor–liquid equilibrium diagram evolution of the methyl ethyl ketone (MEK) – isopropyl alcohol (IPA) – n-heptane (H) system on the basis of the $P = f(T)$ dependencies of components and azeotropes.

The $P = f(T)$ dependencies of the components and azeotropes of the MEK–IPA–H system were obtained and analyzed in this work. The characteristics of Bancroft points of different kinds were identified, which made it possible to conclude that the system satisfies the condition for the mandatory presence of a ternary azeotrope. In a computational experiment, we established its type (unstable node), which is consistent with the data [2]. On the basis of $P = f(T)$ dependencies the full concentration range of its existence was determined and an analysis of the phase diagram evolution over a wide pressure range was carried out, confirmed by means of mathematical modeling.

It was found that increasing or decreasing the pressure relatively to the atmospheric value reduces the number of separation regions and, consequently, simplifies the distillation flowsheet. The MEK–H azeotrope, according to the $P = f(T)$ dependencies existing over a wide range of external parameters, imposes restrictions on the complete separation of the mixture at any pressure. This necessitates special separation methods based on the principle of redistribution of concentration fields. The results of the carried out analysis are the basis for the further development of separation flowsheets of MEK–IPA–H industrial mixture.

It should be noted that either a ternary azeotrope of the unstable node type or two ternary azeotropes of the saddle and unstable node types may be implemented in systems with a set of Bancroft points and an order of their achievement similar to the MEK–IPA–H system, maintaining the same sequence of formation and disappearance of binary azeotropes [3].

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THERMODYNAMIC MODELLING OF LIQUID CRYSTALLINE PHENYLBENZOATE-SOLVENT SYSTEMS

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Liquid crystals (LCs) have found a wide application in various fields of modern technology, primarily in display technologies. The development of new materials requires data on the nature of intermolecular interactions between components in systems containing LCs.

Binary systems based on nematic and smectic–nematic phenylbenzoates R_1-C_6H_4-COO-C_6H_4-R_2 (R = n-alkyl-, alkoxy-) and the nematic compound C_4H_9OCOO-C_6H_4-COO-C_6H_4-OC_2H_5 (H-23) with nonmesogens were studied by thermal analysis methods (DTA, visual polythermal analysis, and the solubility method).

T–x diagrams of H-23 systems with butyl acetate and 1-propanol were obtained. Polytherms of LC solubility in solvents of different classes were investigated; the enthalpy, entropy, and Gibbs energy of LC dissolution ($\Delta_{dissol}H$, $\Delta_{dissol}S$, $\Delta_{dissol}G$) were calculated according to the scheme [1]. In almost all systems, the calculated enthalpies of dissolution exceed the melting enthalpy of LC (for H-23 – 25.1 kJ/mol). The largest positive deviations from ideality were observed in LC systems with n-alkanes. For H-23 systems, $\Delta_{dissol}H$ increases with increasing alkyl chain length: with n-alkanes - from 43.8 (n-hexane) to 64.4 kJ/mol (n-octane), and with alcohols - from 41.9 (ethanol) to 57.6 kJ/mol (1-propanol). Phase demixing is observed in H-23 systems with alcohols and alkanes, which is confirmed by differences in Hildebrand solubility parameters and the Teas triangle diagram [1].

Activity coefficients of LC components were calculated using the Hildebrand and Hansen solubility parameters [2] (for LCs calculated by the group contribution method) and the UNIFAC equation.

The best agreement between calculated and experimental solubility polytherms was obtained using the UNIFAC equation (Dortmund modification).

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SIMPLIFIED PROCEDURE FOR ANALYZING VAPOR-LIQUID EQUILIBRIUM DIAGRAMS OF MULTICOMPONENT SYSTEMS

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The study of VLE diagrams of multicomponent systems is a rather difficult task. Well-known methods involve the graphical construction of a boundary or complete phase space, the construction and analysis of adjacency and reachability matrices. In some cases, this procedure can be simplified; in particular, when azeotropes relative to the constituents of the same component number are nodal points [1-2].

The initial information is data on the boiling points (BP) of all singular points. Let's illustrate specifics mentioned and stages of VLE diagram analysis using the example of a methanol (M) + ethanol (E) + ethyl acetate (EA) + toluene (T) + hexane (N) system. BP, type and Poincare index (PI) are given in the tables.

Boiling points and types of singular points ($N^{(un)st}$ – (un)stable node, S – saddle)

Sing. point	**M**	**E**	**EA**	**T**	**H**	**M+H**
BP, °C	64.53	78.31	77.20	110.68	68.73	50.98
Type (PI)	S (0)	N^{st} (+1)	S (0)	N^{st} (+1)	S (0)	N^{un} (+1)
Sing. point	**M+T**	**E+H**	**EA+H**	**E+EA**	**M+EA**	**E+T**
BP, °C	63.60	58.37	65.37	72.02	62.52	76.96
Type (PI)	S (0)	S (0)	S (0)	S (0)	S (0)	S (-1)

There are 4 edges adjacent to the vertex of each singular point, comparing the boiling points, it is possible to determine the type of points at the vertex (table). There will always be one unstable node in systems of type considered; it is azeotrope M+H. By solving the following equation [2], the number of binary saddles with a nonzero Poincare index can be determined:

$$2N_5^+ + N_4^+ - C_4^- + N_3^+ + C_3^+ + N_2^+ - C_2^- + N_1^+ = 2$$

The terms $N_5^+, N_4^+, C_4^-, N_3^+, C_3^+$ are equal to zero due to the absence of such points, $N_2^+ = 1$, $N_1^+ = 2$, so $C_2^- = 1$. The system contains one binary azeotrope of the saddle type with index -1 that can be formed only by points of pure components of the stable node type, i.e. azeotrope E+T. The latter will generate an internal separatric hypersurface of the third dimension (SH_3). The remaining singular points are saddles with zero index. Such binary azeotropes will generate separatric manifolds, but of a smaller dimension, which will form a boundary surface of SH_3. SH_3 separates diagram into two distillation regions. Thus, the complete structure of the composition pentatope is determined only based on qualitative analysis.

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QUANTUM CHEMICAL MODEL OF DYE EXTRACTION USING DEEP EUTECTIC SOLVENTS

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Deep eutectic solvents (DES) are a highly promising and environmentally friendly alternative to existing extraction methods; however, there is currently a significant deficit of fundamental thermodynamic data and theoretically grounded models capable of predicting extraction efficiency without the need for expensive and time-consuming experiments.

This work aims to perform quantum chemical modeling of the Sudan dyes extraction process using DES based on menthol/thymol and and carboxylic acids (C6-C10) to analyze the efficiency and accuracy of the chosen models in comparison with existing experimental data [1].

Molecular geometries were optimized using the ORCA 6.0.1 package at the B3LYP level of theory. Two distinct modeling variants were implemented. The first variant involved the evaluation of three competing complexation processes in the solution: the self-association of DES components (terpene-acid interaction) and the formation of complexes between the dye and individual DES components (dye-terpene and dye-acid), with their respective Gibbs free energies calculated. The second variant utilized the openCOSMO-RS package to calculate solvation free energies.

Both complex formation energies and solvation energies demonstrate high agreement with experimental extraction trends. For Sudan I, the calculated ΔG_{solv}values increased from -68,86 kcal/mol (C_6) to -66,61 kcal/mol (C_{10}), following the experimental drop in extraction efficiency. Analysis of the calculated Gibbs free energies of complex formation enabled a detailed evaluation of extraction feasibility and helped identify the specific DES component responsible for dye recovery.

The extraction process was successfully modeled using two complementary approaches, providing insights into both the molecular complexation mechanism and bulk phase behavior. The results confirm that evaluating Gibbs free energies of complex formation is a reliable method for determining the role of each DES component in the extraction process. This modeling framework allows for the efficient prediction of solvent performance and can be used to tailor DES compositions for specific analytical requirements in the future.

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THERMODYNAMICS OF HETEROGENEOUS SYSTEMS, SURFACES, INTERPHASE AND MEMBRANE PROCESSES, AND NANOSCALE SYSTEMS

ТЕРМОДИНАМИКА ГЕТЕРОГЕННЫХ СИСТЕМ, ПОВЕРХНОСТНЫХ ЯВЛЕНИЙ, МЕЖФАЗНЫХ И МЕМБРАННЫХ ПРОЦЕССОВ, СВОЙСТВА НАНОСИСТЕМ

STRUCTURE-PROPERTY RELATIONSHIPS AS A PRIMARY TOOL FOR ASSESSING THE CVD PRECURSOR PROPERTIES

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Chemical vapor deposition (CVD) has an undeniable priority when geometrically complex objects should to be covered conformally. The efficiency of the CVD processes can be significantly increased by incorporating quantitative data on sublimation/vaporization (*p-T* dependences) and the thermal behavior in the condensed phase (thermal stability, phase transitions) of the initial metal-containing compound (precursor). Clearly, these temperature-dependent parameters are largely determined by the structure of the compound. Therefore, identifying any structure-property relationships, whether qualitative or quantitative, can significantly facilitate the effective design of a precursor possessing the desired set of properties. This is especially important in cases where experimental data is unavailable. One of the few effective CVD precursors, (hexafluoroacetylacetonato)(cyclooctadiene-1,5)silver, $[Ag(cod)(hfac)]_2$, will be discussed as an example of compound with thermal properties which data are hardly-to-access on [1]. Another output of structure-property relationships is the validation of obtained and/or already existing thermodynamic data on solid-gas, liquid-gas, and solid-liquid phase transitions. This diagnostic benefit will be addressed by applying our original approach to a set of copper(II) β-diketonates [2,3]. Both metal compounds are used in CVD of Ag- or Cu-containing agents (nanoparticles/clusters/films) as a component of complex antibacterial biocompatible materials on the surfaces of cancer implants [4].

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DIFFERENT STATES OF WATER IN α-, β-, AND γ-CYCLODEXTRIN HYDRATES

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α -, β - and γ-cyclodextrins (CDs) are unique macromolecules that have a hydrophobic inner cavity and a hydrophilic outer surface. They are so-called molecular containers that are able to hold the molecules of the "guest" substance in their inner cavity forming inclusion complexes with a variety of organic and inorganic molecules or fragments of molecules. Cyclodextrins in the complex protect the "guest" molecule from damage by various reactive molecules and this contributes to their wide application in the pharmaceutical industry to increase the solubility of substrates and create long-acting drugs; in the food industry to stabilize low-stable molecules and protect the "guest" molecules from oxidation, steric rearrangements, hydrolysis, racemization and enzymatic degradation. The solid phase of cyclodextrins is almost always a hydrate, and therefore the formation of inclusion complexes is a process of complete or partial replacement of water molecules in CDs hydrates with guest molecules. Thus, quantitative thermodynamic characteristics of dehydration processes ($\Delta_{deh}H°$, $\Delta_{deh}S°$, $\Delta_{deh}G°$), which are practically absent in the literature by now, are very relevant for obtaining a variety of CDs inclusion complexes.

A new approach to the study of dehydration processes is proposed, which is mainly performed in closed volume by a static method with a membrane-gauge manometers [1], which previously showed its promise in the study of supramolecular compounds [2]. The p_{H2O}–T-x (molar fraction of water in CD hydrate) dependences obtained under equilibrium conditions provide information about the available phase transitions and the composition of the phases involved in them. The thermodynamic characteristics of the dehydration processes calculated from the experimental data will be used to quantify the binding energies of water molecules with the CD-framework.

As a result of this work, general patterns and specific differences in the chemical bonds of water with the frameworks of α-, β- and γ-cyclodextrins were revealed, which is valuable information for the targeted synthesis of new materials.

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DYNAMIC SURFACE ELASTICITY OF DISPERSIONS OF OVALBUMIN FIBRILS

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Proteins and fibrils obtained from them have recently been frequently used as stabilizers of foams and emulsions. They reduce the surface and interfacial tension by forming viscoelastic layers around oil droplets in water and air bubbles in foam thereby preventing coalescence. At the same time, the relatively high concentrations of native proteins are often required for effective stabilization of foams and emulsions. The use of fibrils makes it possible to reduce the total protein concentration in the system and thus reduce the cost of the products obtained. The determination of surface properties in particular the surface tension and surface viscoelasticity provides information on the structure of adsorption layers and helps to develop effective stabilizers of foams and emulsions.

In this work, the methods of surface rheology are applied to the adsorption layers of worm-like ovalbumin (OVA) fibrils on the surface of water in order to determine the mechanism of their formation and their structure. The morphology of the fibril layers as well as the shape and size of the fibrils were determined by atomic force microscopy. It has been shown that short worm-like OVA fibrils form a continuous loose adsorption layer on the water surface consisting of clusters of fibrils of different sizes and individual fibrils and is characterized by significantly lower values of the surface elasticity and surface pressure as compared with native protein layers. The admixtures of polypeptides formed as a result of the hydrolysis of OVA during the synthesis of fibrils cannot be completely removed by single purification of the dispersion by centrifugation. In addition, the centrifugation and the subsequent re-dispersion of the ovalbumin fibrils lead to the destruction of large OVA fibrils with high persistence and contour length. After the twice purification, a significant induction period appears on the kinetic dependences of the surface properties after which the properties change slower than in the case of native protein solutions due to an increase in the average size of kinetic units in the system. Thus ovalbumin belongs to a group of relatively rare proteins for which the native molecules can be better stabilizers of liquid-phase systems than fibrils. At the same time, it can be assumed that flexible and relatively short OVA fibrils will effectively interact with oppositely charged polyelectrolytes leading to the formation of complexes with high surface activity.

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OSMOLYTE-MODULATED DIFFERENTIAL CAPACITANCE AND DISJOINING PRESSURE IN NANOCONFINED ELECTROLYTES

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Electrolytes confined in nanoporous structures are heterogeneous systems in which interfacial phenomena govern electrical properties. The electric double layer (EDL) formed at the electrode–solution interface plays a central role, while nanoconfinement enhances surface interactions through EDL overlap, causing significant deviations from bulk electrolyte behavior [1].

We theoretically investigate the effect of zwitterionic osmolytes on thermodynamic properties of electrolytes confined in charged slit nanopores with conducting walls. The analysis employs a modified Poisson–Boltzmann framework accounting for finite particle size, dipolar solvent and osmolyte molecules, and field-dependent dielectric permittivity, with equilibrium states obtained via grand potential minimization [2].

Increasing osmolyte concentration restructures the EDL and increases differential capacitance due to preferential accumulation and orientation of dipolar molecules near charged surfaces, enhancing local dielectric response and interfacial charge storage. Osmolytes also increase the disjoining pressure between pore walls through reduced ionic screening and an additional osmotic contribution arising from their accumulation in nanopores, strengthening electrostatic repulsion between interfaces.

These results show that zwitterionic osmolytes enable control of interfacial processes in nanoconfined systems. The simultaneous enhancement of differential capacitance and disjoining pressure suggests improved energy storage performance and mechanical stability of nanoporous electrodes without increasing electrolyte concentration, highlighting the key role of dipolar additives in tuning EDL properties and interfacial interactions in heterogeneous nanosystems.

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MODELING OF ADSORPTION LAYERS ON NANOPARTICLES IN AQUEOUS SOLUTIONS OF NONIONIC SURFACTANTS

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Adsorption on solid nanoparticles is at the heart of many advanced technologies, including drug delivery, nanoreactor engineering and separation of chemicals. Of key importance is knowledge of structure of the adsorbed layers because it provides the insight in the molecular mechanisms that control adsorption and desorption in dependence on the characteristics of the nanoparticles and external conditions.

The major limitation of the well-known theoretical approaches proposed for adsorption systems [1,2] is that they do not take into account correlations between interacting functional groups of molecules, even though such correlations definitely play an important role in many cases, e.g., in aqueous and other hydrogen bonding fluids.

In this work, we apply the multilayer quasilattice model (MQuM) [3,4] to describe the details of local structure for adsorption layers on solid hydrophilic or hydrophobic particles submerged in aqueous mixtures that contain amphiphilic chainlike molecules. Within MQuM, the correlations between interacting functional groups are described within the Guggenheim quasichemical approximation; spatially nonuniform fluid around a spherical particle is represented by concentric spherical layers that accommodate segments of chainlike molecules in different orientations. Apart from mimicking adsorption in model systems, we also apply MQuM to a number of real aqueous solutions using the model interaction parameters estimated from vapor-liquid equilibrium data. We discuss the model predictions for the structure of solution around hydrophilic and lipophilic solid particles of varying curvature. We conclude by summarizing the advantages and limitations of MQuM.

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THERMODYNAMIC STUDY OF MIXED LIGAND COBALT B-DIKETONATE COMPLEXES AND THEIR IMPLICATIONS FOR Co-OXIDE THIN FILM DEPOSITION

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Co-oxide thin films exhibit semiconducting properties, rendering them relevant for applications in optics and electronics as well as for secondary electron emission composite materials. To obtain these films using chemical vapor deposition (MOCVD), active development of volatile precursors is underway. Cobalt(II) β-diketonate complexes could be promising precursors provided that mononuclear derivatives are stabilized by additional neutral ligands to precise control the vapor mass-transport during deposition process. However, the library of such complexes is limited, and even for known precursors like $Co(tmeda)(hfac)_2$ and $Co(tmeda)(acac)_2$ (tmeda = N,N,N',N'-tetramethylethylenediamine, hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionato, acac = pentane-2,4-dionato) there is a lack of quantitative data on thermochemical properties.

Here, the library of mixed ligand cobalt β-diketonate complexes $Co(tmeda)(L)_2$ for MOCVD application has been supplemented by three new fluorinated derivatives (L = pfpac (5,5,6,6,6-pentafluorohexane-2,4-dionato), hfbac (5,5,6,6,7,7,7-heptafluoroheptane-2,4-dionato), ofhac (3H,3H-octafluorohexane-2,4-dionato)). The structural features and thermochemical properties of these complexes and their closed analogues $Co(tmeda)(hfac)_2$ and $Co(tmeda)(acac)_2$ have been studied. The structures of $Co(tmeda)(hfbac)_2$, $Co(tmeda)(ofhac)_2$ and one new phase of $Co(tmeda)(hfac)_2$ have been revealed. The information on the condensed phase transitions for $Co(tmeda)(L)_2$ has been obtained. A characteristic feature of the complex with L = pfpac is its retarded crystallization and glass-forming ability.

The temperature dependence of saturated vapor pressure for $Co(tmeda)(hfac)_2$ was determined allowing us to develop MOCVD process of Co oxide films with controlled mass transport of precursor at the evaporator temperature range 333-353 K. This provides the optimal conditions for growth hexagonal CoO or Co_3O_4 films. The Co oxide films exhibit a minimal impurity level on C, F elements and no traces of N that makes them appropriated for different applications. The $Co(tmeda)(acac)_2$ has been tested to obtain Co_3O_4 films without F impurities. The influence of the oxygen flow rate and deposition temperatures parameters on the composition, morphology and thickness of Co oxide films deposited from these precursors has been determined.

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THERMODYNAMICS OF SUBLIMATION OF INDOLINE BASED SPIROPYRANS WITH DIFFERENT POSITIONS OF THE METHOXY GROUP

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Spiropyrans are organic photochromic compounds used to create multifunctional materials such as optical filters, photoswitches, biosensors, and other hybrid materials. In this work thermodynamics parameters were studied at heterogeneous equilibrium for 1,3,3-trimethyl-6'-methoxy-spiro[indoline-2,2'-2H-chromene] (SP-22), 1,3,3-trimethyl-8'-methoxy-spiro[indoline-2,2'-2H-chromene] (SP-23), and 1,3,3-trimethyl-5'-methoxy-spiro[indoline-2,2'-2H-chromene] (SP-24).

The Knudsen effusion mass spectrometry was employed to obtain saturated vapor pressure and sublimation enthalpy. Since difference of structure of the compounds is the position of the methoxy group, the mass spectra of all spiropyrans are identical and has following main peaks: 159, 292, 307. The peak at *m*/*z* 307 corresponds to the molecular ion (M^+), 292 to $(M\text{-}CH_3)^+$, and the ion at *m*/*z* 159 results from the cleavage of the molecule at the spiro-atom. The vapor is monomolecular since dimers and trimers were not discovered in the mass spectrum.

Above the solids the saturated vapor pressures were determined by the Knudsen effusion method, which, in combination with mass spectrometric data, allow us to recommend the following equations for the temperature dependence of pressure for each of the compounds:

SP-22: $\ln(p, \text{Pa}) = (-15.95\pm0.19)\cdot 1000/T+(41.42\pm0.52)$, ΔT = 328-373 K
SP-23: $\ln(p, \text{Pa}) = (-14.59\pm0.19)\cdot 1000/T+(38.25\pm0.57)$, ΔT = 322-348 K
SP-24: $\ln(p, \text{Pa}) = (-14.13\pm0.09)\cdot 1000/T+(36.83\pm0.26)$, ΔT = 330-372 K

The sublimation enthalpy was found using the second-law method of thermodynamics for the experimental temperature and recalculated to 298.15 K according to [1].

The thermodynamic data of sublimation

	ΔT, K	T_{hm}, K	$\Delta_{sub}H°(T_{hm})$, kJ·mol^{-1}	$\Delta_{sub}H°(298.15)$, kJ·mol^{-1}
SP-22	328-373	350	132.4±2.2	136.2±3.5
SP-23	322-348	335	121.3±2.1	124.1±2.9
SP-24	330-372	351	117.5±1.5	121.2±3.0

The first sample, in which the methoxy group is in the 6'- position, has the highest sublimation enthalpy. It correlates with the highest melting enthalpy and the lowest pressure among samples studied. The properties of SP-23 and SP-24 are similar.

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THERMODYNAMIC MODELING OF NICKEL-BASED SELF-FLUXING MATERIALS

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Using the TERRA and ThermoCalc software, thermodynamic modeling of self-fluxing powder materials based on nickel was carried out in the temperature range of 300-6000 K in an atmosphere of various plasma-forming gases: argon, nitrogen, air and mixtures "92 vol. % air + 8 vol. % propane" at a total pressure of $P = 10^5$ Pa. The initial composition of the simulated systems corresponded to the composition of nickel-based powder self-fluxing materials (wt. %): Ni – 79.3, C – 0.5, Cr – 15, Si – 3.2, B – 2 (PG-SR2), Ni – 74.3, C – 1, Cr – 17, Si – 4.1, B – 3.6 (PG-SR4). When preparing the initial data for modeling, the average technological parameters of the plasma spraying unit were taken into account: plasma gas consumption - 1 l/s, powder consumption – 1 g/s, 5 g/s and 10 g/s. The modeling took into account the possibility of the existence of elements, ions, compounds (oxides, carbides, silicides, and others) in condensed and gaseous states.

The temperature dependences of the components of the condensed and gaseous phases are calculated. It is revealed that the distribution of the components of the condensed and gaseous phases changes significantly with variations in the initial content of the powder material in the working fluid and the composition of the plasma-forming gas.

The temperature dependences of integral thermodynamic characteristics - enthalpy (I) and entropy (S) – for the PG-CP2 (PG-CP4) + gas (gas – Ar, N_2, air, air + propane) systems are constructed. It is shown that an increase in the consumption of powder material leads to an increase in enthalpy and a decrease in entropy for both systems. These trends become more pronounced at high temperatures ($T > 3000$ K), when active evaporation of the main components of the system occurs and a sharp increase in the partial pressures of the components of the gas phase is observed. A comparison of the temperature dependences of the condensed and gas phases and the thermodynamic characteristics shows that there is a correlation between them: kinks in the graphs are observed at the same temperatures. This can be explained by the phase transformations that occur in the condensed and gaseous phases, in particular, melting and evaporation.

The work was carried out according to the state assignment of the IMET UB RAS.

SURFACE TENSION OF VAPOUR PHASE NUCLEI IN OXYGEN–NITROGEN SOLUTIONS

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The decomposition of a homogeneous liquid phase, superheated beyond the phase equilibrium temperature, occurs as a result of the formation and the subsequent growth of critical bubbles. At high superheatings, the characteristic sizes of such bubbles are several nanometers. The properties of bubbles depend on their size.

We have investigated the kinetics of spontaneous nucleation in oxygen-nitrogen solutions in experiments measuring the expectation time for boiling-up [1]. Liquid volumes of 70–80 mm^3 were superheated in glass cells. Entry into the metastable region was accomplished by sharply reducing the pressure at fixed values of temperature and solution composition. Experiments were conducted on isobars of p = 0.5 and 1.0 MPa in the temperature range T = 106 – 138 K over the entire range of nitrogen concentrations x. From classical nucleation theory at a rate of $J = 10^7$ $m^{-3}s^{-1}$, using experimental data on the temperatures of attainable superheating, the surface tension σ at the critical bubble – solution boundary was determined.

The values of σ are compared with data on the surface tension of the solution at a flat interface σ_∞ [2]. The differential capillary rise method was used to determine σ_∞. Measurements were performed on an assembly of three glass capillaries. The surface tension of critical bubbles of pure liquids is 4–5% less than σ_∞ (x = 0). The ratio between σ and σ_∞ changes with changes in the solution composition. In the concentration range of 0.1–0.9, $\sigma > \sigma_\infty$. Near the equimolar composition, the discrepancy reaches 3-5%. It is assumed that it is associated with the curvature of the interface.

A similar relationship between σ and σ_∞ is given by the van der Waals capillarity theory [3]. However, according to this theory, the value of σ exceeds that of σ_∞ over a narrower concentration range and by a smaller amount. At T = 132 K, the maximum value of $(\sigma - \sigma_\infty)/\sigma_\infty$ is 0.3% for bubbles with a radius of 45 nm and a concentration of x = 0.73. The report also discusses some factors that can lead to changes in the surface tension of critical bubbles.

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SUBLIMATION THERMODYNAMICS OF SOME PHENYL-SUBSTITUTED PORPHYRINS

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Porphyrins belong to a broad class of tetrapyrrole macrocyclic compounds with unique properties, such as the ability to form complexes with most chemical elements, high chemical stability, etc. Materials based on porphyrins are used to create active layers for sensors, photo- and electrocatalysts, solar cells, etc.

Thermodynamic parameters of porphyrin evaporation, such as saturated vapor pressure and sublimation enthalpy, are of interest due to the possibility of forming thin films of functional materials by vapor deposition methods.

In this work, the thermodynamic parameters of sublimation of 5,15-diphenylporphyrin (**H_2DPhP**) and 5,10,15,20-tetrakis(4-methylphenyl)porphyrin (**H_2T(4-MePh)P**) were determined by the Knudsen effusion mass spectrometry method. Sublimation of porphyrins was carried out in the temperature ranges of 443-527 K for **H_2DPhP** and 542-620 K for **H_2T(4-MePh)P**. The mass spectra of both compounds contain two main peaks corresponding to the M^+ and M^{++} (M is the monomer molecule).

The saturated vapor pressures of porphyrins were determined using the Knudsen effusion method in combination with mass spectrometric measurements of ion currents. The obtained data are described using the following linear equations:

$$\ln(p/\text{Pa}) = -(20.24\pm0.19)\ 10^3/T + (35.80\pm0.39),\ \textbf{H}_2\textbf{DPhP},\ 443\text{-}527\ \text{K};$$

$$\ln(p/\text{Pa}) = -(27.50\pm0.22)\ 10^3/T + (41.85\pm0.37),\ \textbf{H}_2\textbf{T(4-MePh)P},\ 542\text{-}620\ \text{K}.$$

The sublimation enthalpy at the harmonic mean temperature (T_{hm}) of measurements was found from the slope of the temperature dependence of vapor pressure and recalculated to 298.15 K in according to [1].

The values determined in this work and in [2] are listed in Table and show an increase in enthalpy with increasing complexity of molecular structure of the considered structural analogs.

Sublimation enthalpy, $\Delta_{sub}H°(T)$ / kJ·mol^{-1}

Compound	ΔT / K	T_{hm} / K	$\Delta_{sub}H°(T_{hm})$	$\Delta_{sub}H°$(298.15 K)
H_2DPhP	443-527	487	168 ± 2	183 ± 8
H_2TPhP [2]	490-615	557	195 ± 2	220 ± 12
H_2T(4-MePh)P	542-620	583	227 ± 2	263 ± 17

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EFFECT OF THE MONOLAYER FORMATION ON THE pK_a OF CARBOXYLIC ACIDS AT THE AIR/WATER INTERFACE WITHIN QUANTUM CHEMICAL APPROACH

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Acid-base properties of a substance are crucial in biology, organic synthesis, etc. The ionization degree of a compound affects its solubility in various media, which is especially important for studying its behavior at different interfaces. Computational methods have also been added to experimental ones for estimation of the acidity index (pKa) with the development of modern computers and computational algorithms.

The purpose of this work was to identify the dependence of the dissociation constant of monolayers for saturated carboxylic acids $C_nH_{2n+1}COOH$ (n=6-16) and their perfluorinated counterparts at the air/water interface on their chain length using a quantum chemical approach developed and successfully tested earlier when describing the film formation of more than ten classes of nonionic surfactants. The proposed model includes the calculation of the Gibbs energies of acid formation and dimerization in neutral and ionized forms, as well as the corresponding monomers, in the aqueous and gaseous phases. The approach does not require the construction of any thermodynamic cycles. The calculations were performed using semi-empirical quantum chemical methods PM3 and PM6 within the frameworks of the conductor-like screening model COSMO.

It is shown that the minimum Gibbs energy of clusterization corresponds to associates with the degree of dissociation α=0.5. A relationship has been derived between the values of surface and bulk pK_a. It follows that, unlike the bulk pK_a, the value of the surface pK_a depends on the surfactant chain length, which is due to the difference in the solvation energy of the hydrocarbon tails of the corresponding neutral and dissociated monomer. Thus, the calculated data showed that the elongation of the carboxylic acid chain by one CH_2 fragment leads to an increase in the surface pK_a by 0.43 units, and by 0.50 per CF_2 for perfluorinated ones. The obtained results are in good agreement with the available experimental data. [1, 2].

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FEATURES OF VAPORIZATION AND THERMODYNAMIC PROPERTIES OF SOME LOW-VOLATILE AMINO ACIDS

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The work presents the results of a study of low-volatile proteinogenic amino acids L-histidine, L-aspartic acid, L-asparagine, L-glutamine, L-glutamic acid, L-lysine, and L-arginine using Knudsen effusion mass spectrometry. There are no sublimation thermodynamics data for these compounds. Commercial samples (Aladdin, Macklin; mole fraction 0.99) were loaded into a Knudsen cell (Mo; an evaporation-to-effusion area ratio of ~400) coupled with a MI1201 single-focusing magnetic mass spectrometer.

The main task of the study was to select experimental conditions (temperature range, heating duration) for congruent sublimation. The thermal stability of the substances was monitored using IR spectroscopy and visual observation. Most of the studied amino acids were found to decompose at any conditions. Only L-histidine (L-His) and L-aspartic acid (L-Asp) could be sublimed congruently in the limited temperature and time ranges. Due to these limitations, the saturated vapor pressure could not be determined by classical Knudsen effusion method. Therefore, the pressure was obtained by a mass spectrometric method of ion current comparison; L-methionine [1] was used as a standard. The vapor pressures for L-histidine and L-aspartic acid were fitted by equations presented in Table.

Saturated vapor pressure equations ln(p, Pa), temperature range ΔT, K, enthalpy of sublimation $\Delta_{sub}H°$, kJ·mol^{-1} at 298.15 K

Subst.	$\ln p = -a/T+b$		ΔT	$\Delta_{sub}H°$(298.15 K)	
	a	b		2nd law	3rd law
L-His	21983 ± 485	42.411 ± 1.029	448-480	184.7 ± 4.4	183.5 ± 4.2
L-Asp	22350 ± 600	43.757 ± 1.351	420-450	186.8 ± 5.2	183.2 ± 3.6

Sublimation enthalpy was obtained by the methods of the second and third laws of thermodynamics; see Table. The data obtained by the independent approaches agree within the uncertainties. The third law values were used in further derivation of the formation enthalpies for the gaseous amino acids: −283.2 ± 5.0 kJ·mol^{-1} (L-His), and −791.1±4.6 kJ·mol^{-1} (L-Asp); they agree reasonably with the corresponding values from [2]: −289.4 ± 4.0 kJ·mol^{-1} (L-His) and −796.8 ± 4.0 kJ·mol^{-1} (L-Asp), obtained by isodesmic reaction approach.

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THERMODYNAMICS OF THE ADSORPTION OF VOLATILE ORGANIC COMPOUNDS BY CYCLODEXTRIN-CONTAINING PHASES ACCORDING TO INVERSE GAS CHROMATOGRAPHY DATA

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The ability of cyclodextrins to form inclusion complexes with molecules of various natures determines their widespread use in sorption and separation technologies. A pressing issue is the study of the thermodynamic aspects of sorption and complexation by cyclodextrins to understand the mechanisms of enantioselective recognition.

This paper summarizes the results of studies on the sorption of organic compounds of various classes by systems based on β-cyclodextrin and its derivatives dissolved in various initial matrices. Polymeric, liquid-crystalline, and ionic liquid matrices were used. Using inverse gas chromatography, the thermodynamic characteristics of sorption and complexation were determined, and Infinite dilution activity coefficient were calculated. The selectivity of the studied cyclodextrin-containing phases with respect to structural and optical isomers of organic compounds under gas chromatographic conditions is examined. The patterns of influence of orientational, solvophobic and associative effects on the formation of "guest – host" complexes in the studied systems were revealed.

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STUDY OF THE CHEMICAL POTENTIAL OF WATER IN SMECTITE CLAYS

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The chemical potential of water in montmorillonite pores is studied using molecular dynamics simulations. Thermodynamic integration (TI) was employed as this method enables precise calculation of free energy differences between alchemical states and is well-established for studying hydration thermodynamics in layered materials. While Grand Canonical Monte Carlo (GCMC) simulations are commonly used to determine water adsorption isotherms and equilibrium water uptake in clays, TI offers the advantage of directly yielding the chemical potential at fixed hydration states, which is essential for systematic comparison of temperature effects and cation types[1].

Montmorillonite is described with the ClayFF force field, which is flexible and non-polarizable. Its structure consists of an octahedral layer sandwiched between two tetrahedral layers. Models with Ca^{2+} and Na^{+} interlayer cations are considered.

Water is modeled using the TIP4P force field, in which the charge of the oxygen atom is displaced by 0.14 Å along the bisector of the hydrogen-bond angle. Coulomb interactions are treated with the particle-particle particle-mesh method. The model imposes rigid bonds and angles.

The system is brought to the target conditions and equilibrated for 1 ns. Subsequently, thermodynamic integration is performed. The interaction between one water molecule and the rest of the system is gradually decoupled. First, the Coulomb term is linearly ramped down with the coupling parameter over 12 steps. Then, the van der Waals term is switched off. Each trajectory at a given value of the coupling parameter is run for 500 ps, which exceeds the time required for the studied molecule to diffuse between the montmorillonite layers. The chemical potential is computed using 32 distinct values of the coupling parameter.

The temperature dependence of the chemical potential is investigated. A comparison between the Na^{+} and Ca^{2+} forms reveals distinct temperature dependent behaviors, which are interpreted in terms of differences in interlayer structure and cation hydration.

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INTERPOLYMER REACTIONS AND PHASE BEHAVIOR IN THE LIGNOSULFONATE–CHITOSAN SYSTEM WITH THE FORMATION OF POLYELECTROLYTE COMPLEXES

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Polyelectrolyte complexes (PECs) formed via the interaction of natural polycations and polyanions are of interest both from a fundamental standpoint and because of the possibility of creating new functional materials on their basis. One of the promising systems is the lignosulfonate (LS) – chitosan (CS) pair, in which intermolecular binding is governed by a combination of electrostatic interactions, hydrogen bonding, and cooperative effects, leading to the formation of water-soluble associates and water-insoluble PECs. The aim of this work was to study interpolymer reactions and phase behavior in the LS – CS system using aspartic acid as the medium for chitosan dissolution.

Potentiometric titration of chitosan solutions (0.025 – 0.100 wt%) with lignosulfonate solutions (0.025 – 0.100 wt%) was carried out, and the onset of turbidity was monitored as the beginning of macrophase separation. The resulting precipitate was characterized by FTIR spectroscopy, SEM, and thermal analysis (TGA).

It was found that in all systems the addition of LS causes a gradual increase in pH without a pronounced jump, indicating the progressive nature of the interpolymer interaction. The onset of phase separation was observed at $[\sim(NH_3^+)]/[\sim SO_3^-]$ ratios ranging, depending on the composition, from 0.015 to 0.566. The position of the cloud point depends on the initial concentration of CS and reflects changes in the conditions governing the transition from soluble interpolymer associates to a water-insoluble PEC. In all cases, macrophase separation begins in the region of excess cationic groups of chitosan.

The FTIR spectra of the insoluble PECs indicate the involvement of hydroxyl, amino, carboxyl, and sulfonate groups (3400, 1600, 1380, and 1080 cm^{-1}) in complex formation. According to SEM data, the PEC is characterized by a pronounced plate-like, layered morphology, indicating the formation of ordered aggregates during coagulation of the complex from solution.

The thermal behavior of the PEC differs from that of the initial chitosan: the complex exhibits different ratios of the low-temperature and main mass-loss stages, confirming the formation of a new interpolymer structure rather than simple mechanical mixing of the components.

The results obtained are of interest for the further thermodynamic description of complexation processes and for the targeted design of biopolymer materials based on natural polyelectrolytes.

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THERMODYNAMICS OF PHASE TRANSITIONS OF METAL β-DIKETONATES AS A BASIS FOR CONTROLLING THEIR MASS TRANSFER IN MOCVD PROCESSES

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Volatile metal β-diketonates are widely used as MOCVD precursors in the production of various functional materials. Successful implementation of gas-phase processes requires reliable data on the saturated vapor pressure, enthalpies and entropies of sublimation or vaporization of these compounds, but the data available in the literature, as a rule, have a significant scatter [1, 2]. In this regard, we have developed a methodology for checking the reliability of thermodynamic data using the example of *tris*-β-diketonates of various metals [1-3], the essence of which is to establish the relationship between the composition and the corresponding properties in a series of isoligand chelates. The condition for its successful application is the availability of reliably determined standardized thermodynamic data for a series of complexes of one metal (the base series) and at least one compound of the tested series.

The next vector of development of the technique is the transition to β-diketonate complexes of metals of a different valence. In this work, we focused on copper(II) compounds, since, on the one hand, this is the most extensive series of complexes with existing literature thermodynamic data (more than 20 compounds), and on the other hand, they are synthetically and economically available, which makes them convenient objects of study. In addition, the extension of the method to heteroligand metal β-diketonate complexes is of particular interest. We selected magnesium *bis*-β-diketonates with tetramethylethylenediamine as the test series [4].

As a result of a systematic study, a standardized array of thermodynamic characteristics of copper(II) and magnesium(II) complexes was obtained, with the help of which we extended the technique to β-diketonate complexes of metals(II), and also demonstrated the possibility of its application to heteroligand compounds.

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THERMODYNAMIC PROPERTIES OF TELLURIUM ALLOYS WITH d-ELEMENTS – NICKEL, IRON, MOLYBDENUM, CHROMIUM

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Design and operation of a molten salt reactor (MSR) directly depend on the selection of structural materials working in contact with the fuel salt. The operation of such a reactor is complicated by high corrosive activity of fluoride fuel salts. In addition to the aggressiveness of fluoride melts, tellurium, being a typical product of uranium and plutonium fission in MSRs, causes intergranular fracture of metals along grain boundaries, which leads to deterioration of mechanical properties and intensification of corrosion processes. To understand the causes of such interaction, it is necessary to study the thermodynamic characteristics of compounds, which tellurium forms with typical d-block metals, i.e. nickel, iron, chromium and molybdenum. The aim of this work was obtaining the thermodynamic characteristics of binary compounds formed in tellurium–nickel, tellurium–iron, tellurium–chromium, and tellurium–molybdenum systems, as well as comparing their formation energies.

The research methodology was based on measuring the potentials of tellurium–metal alloys relative to pure metals. Measurements were carried out using two methods – polarization and chronopotentiometry – at temperatures of 500, 600, and 700 °C in the melt based on the eutectic mixture of sodium, potassium and cesium chlorides.

The experiments revealed that the interaction of iron, chromium, nickel and molybdenum with metallic tellurium exhibited significant deviations from ideality and substantial energy effects. In terms of the Free Gibbs energy change of interaction with tellurium, the studied transition metals can be arranged in the following order: chromium, iron, nickel, molybdenum. Thus, tellurium–chromium system showed the maximum deviation from ideality, while tellurium–molybdenum binary system exhibited relatively weak interaction. Formation of the alloys between tellurium and chromium, iron, and molybdenum can occur even without direct contact: the driving force of such interaction is the transport phenomenon caused by disproportionation reactions. Disproportionation is characteristic of tellurides or compounds of tellurium in intermediate oxidation states.

Thus, the obtained thermodynamic characteristics allow predicting the corrosion behavior of structural materials under molten salt reactor operating conditions and justify the selection of the most resistant alloys.

DYNAMIC SURFACE ELASTICITY OF THE LAYERS OF PLANT PROTEIN AGGREGATES AT THE LIQUID SURFACE

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It is frequently discussed that the animal proteins can be replaced by cheaper and more ecologically friendly proteins of plant origin in many applications. This replacement is not always simple because the functional properties of plant proteins are usually worse than those of their animal counterparts; in particular, they are usually characterized by low solubility in water and lower surface activity. At the same time, although the surface properties of protein solutions are the most important for many applications, for example, for the stabilization of foams and emulsions, their intensive investigation have been started only recently. Special attention in these studies is paid to the dilational dynamic surface elasticity because just this quantity determines the stability of liquid disperse systems. In this work we analyzed the dynamic surface properties, especially the dynamic surface elasticity, of solutions of a number of plant proteins and compare them with the data for aqueous dispersions of their aggregates, mainly amyloid fibers. It proved that the kinetic dependencies of the dilational dynamic surface elasticity of the solutions of some proteins can have a local maximum, which is followed by a local minimum. The analysis of the protein primary structure allowed to discover in this case rather long intrinsically disordered fragments of the protein chains and thereby to find correlations between the protein structure and the properties of the protein aqueous solutions. The kinetic dependencies of the dynamic surface elasticity of the dispersions of plant protein fibrils proved to be always monotonic. At the same time, the modulus of the dynamic surface elasticity of the fibril dispersions proved to be significantly higher than that of the most native protein solutions. This result indicates that the plant protein nanofibrils can be successfully applied for the stabilization of foams and emulsions instead of native proteins with a lower surface activity.

This study was financially supported by Russian Science Foundation, grant № 24-13-00261.

POLYMORPHISM OF 4,7-DIPHENYL-2,1,3-BENZOTHIADIAZOLE DERIVATIVE CRYSTALS

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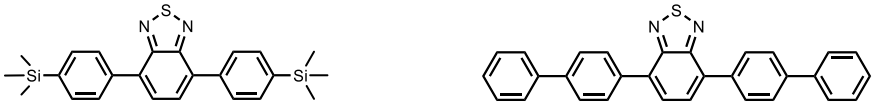
4,7-Diphenyl-2,1,3-benzothiadiazole (P-BTD) and its derivatives (R-P-BTD) are thermo- and chemically stable luminophores featuring a large Stokes shift and efficient emission in both solutions and crystals. Consequently, they are in demand for a wide range of applications in photonics and electronics [1]. Crystalline materials based on these compounds, both in bulk and thin-film form, are of particular interest. However, according to recent studies, conformational crystal polymorphism is frequently observed in the R-P-BTD family of compounds [1,2], which is of great interest for elucidating structure–property relationships. This work discusses the results of a study on the polymorphism of crystals of R-P-BTD-type compounds bearing trimethylsilyl (TMS-P-BTD) [2] and phenyl (P-P-BTD) terminal substituents (see Figure).

TMS-P-BTD **P-P-BTD**



Chemical structural formulas of the compounds studied

Using single-crystal X-ray diffraction, three polymorphic forms were identified for **TMS-P-BTD**: I – monoclinic (sp. gr. $P2_1/c$, $Z/Z' = 32/8$), II – orthorhombic *Pnaa* (sp. gr. Pnaa, $Z/Z' = 12/1.5$) and III – triclinic (sp. gr. P-1, $Z/Z' = 8/4$) [2]. For **P-P-BTD**, two polymorphic forms were established: α – triclinic (sp. gr. P-1, $Z/Z' = 2/1$; a=10.1065(2), b=10.5274(2), c=10.7378(2) Å; α=91.106(1)°, β=98.363(1)°, γ=103.839(1)°) and β – monoclinic (sp. gr. C2/c, $Z/Z' = 16/2$; a=23.0533(2), b=27.5264(10) c=18.9876(12) Å; β=127.159(1)°). The thermodynamic and kinetic aspects of phase transitions in the studied polymorphic systems are discussed.

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This work was supported by Russian Science Foundation (project № 22-13-00255-П), https://rscf.ru/en/project/22-13-00255/

THERMODYNAMIC CHARACTERISTICS OF THE INTERACTION OF FLUORAPATITE WITH LACTIC ACID

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Polylactide is one of the most widely used bioresorbable polymers in orthopedics and dentistry, serving as a matrix for implants and drug delivery systems. During its biodegradation, lactic acid is locally released, leading to a decrease in pH in the near-surface layer and initiating the dissolution of the mineral component of bone tissue [1]. Fluorapatite ($Ca_{10}(PO_4)_6F_2$, FAP) is a key inorganic constituent of tooth enamel and a promising material for implant coatings due to its high chemical stability. However, the thermodynamic aspects of its interaction with lactic acid under physiological conditions remain insufficiently understood [2].

Based on experimental data on the partial dissolution of fluorapatite in lactic acid solutions as a function of pH, and on the complete inhibition of dissolution at pH = 3.8, a thermodynamic model for the interaction between these compounds was developed. The model is based on the stoichiometric equation:

$$Ca_{10}(PO_4)_6F_2 + 6HL \rightarrow 6CaHPO_4 + CaF_2 + 3Ca^{2+} + 6L^-,$$

where HL denotes lactic acid and L^- denotes the lactate ion.

The developed thermodynamic model was experimentally validated and enables prediction of FAP behavior in acidic and neutral environments arising during polylactide biodegradation and carbohydrate metabolism. It was established that the key factors limiting FAP dissolution are the formation of a passivating CaF_2 layer and the protonation of fluoride ions with the formation of HF. Further research in the field of kinetics, consideration of multicomponent media, and experimental validation of the model will enable the transition to the design of biomaterials with tailored properties.

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MOLECULAR MODELING OF INTERFACIAL TENSION AND CONTACT ANGLES AT RESERVOIR CONDITIONS

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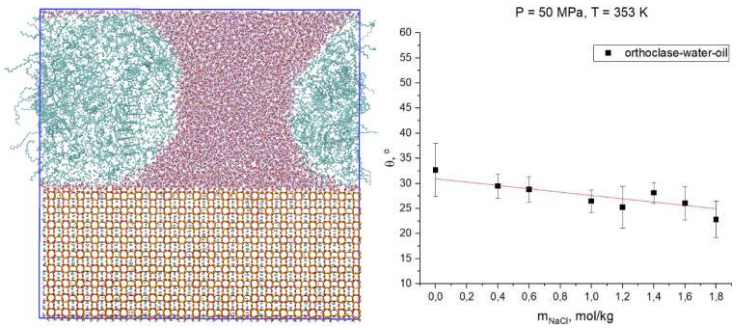
This work presents an experimentally informed molecular simulation study of wettability at feldspar–fluid–fluid interfaces under reservoir conditions. Contact angles at the three-phase contact line are evaluated as a function of temperature, pressure and brine salinity for feldspar–oil–brine, feldspar–oil–methane, and feldspar–brine–methane contact lines. Both K^+ and Na^+ feldspar (orthoclase and albite) are considered. Solid–fluid interaction parameters are quantitatively validated against available ambient-condition contact-angle measurements for water–decane–feldspar systems, and the validated models are transferred to reservoir conditions.

Crude oil is represented as a real-component mixture of alkanes and arenes based on chromatographic and distillation experimental data, with special attention to methane present at reservoir conditions [1]. Contact angles are computed using a robust, adjustable protocol [2].

The resulting dataset enables sensitivity analysis of feldspar wettability to reservoir conditions and composition. The simulation results are parameterized with multivariate linear regression, providing a compact predictive correlation for contact angle as a function of temperature, pressure, gas content, and brine salinity for feldspar-containing rock formations.



(left) Snapshots of molecular configurations at orthoclase – oil – water contact line
(right) dependence of the contact angle on brine salinity at fixed *T* and *p*

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DESCRIPTION OF EQUILIBRIUM LIQUID INTERFACES IN NONIONIC FLUIDS BY MULTILAYER QUASICHEMICAL APPROACH

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Planar and curved liquid interfaces occur in many different systems such as micellar solutions, mixtures of oil with water, microemulsions and other partially miscible liquids. The interfacial properties of such systems play crucial role in many fields, including oil-recovery, drug delivery, micellar catalysis, etc. Engineering applications of these spatially nonuniform systems need understanding of thermodynamic behavior that requires knowledge of the structural details of the interfacial boundaries. Most theoretical approaches proposed for such systems are limited to weakly interacting functional groups of molecules, as they do not take into account the correlations between interacting species [1, 2]. For nonuniform fluids that contain chainlike and associating species, most powerful instruments to predict structural details are computer simulations and iSAFT [3]; however, their application is rather involved computationally.

In this work, the description of local structure for liquid interfaces is performed with the aid of the multilayer quasichemical model (MQuM) [4, 5]. The model takes into account specific interactions between functional groups and connectivity of chainlike molecules. Correlations between interacting groups are described within the Guggenheim quasichemical approximation. The local structure of the interface is presented by the concentration profiles of the molecular segments, the profiles of orientations of the functional groups and chemical bonds of molecular chains in three directions. Within the model, we calculate the profiles of normal and tangential pressure and the interfacial tension for amphiphile-oil-water, alcohol-water, alkane-water and other organic-water systems. We also demonstrate the effect of chain branching on the structure and thermodynamic properties of fluid interfaces.

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CALORIMETRIC SCREENING OF INTERFACIAL INTERACTIONS IN GLASS POLYMER COMPOSITES

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Polymer nanocomposites consist of two phases: a polymeric matrix phase and an inorganic filler phase. The creation of multicomponent filled polymer composites is aimed at forming new materials with the combined properties of a polymer matrix and a disperse filler.

Recent decades have seen a considerable growth of interest in filled composites owing to the development of nanotechnologies and the use of nanodispersed fillers. With an increase in the degree of dispersion of the filler, the fraction of the polymer at the interface tends to increase and the interfacial effects become more pronounced. A considerable number of studies have indicated that the energetics of interfacial interactions plays the decisive role in the description of properties of composite polymer materials and phenomena occurring at the interface. Thus, structuring of the polymer at the interfacial layer, formation of adsorption layers, densification or loosening of the polymer matrix, and the effect of polymer reinforcement in the presence of fillers are usually attributed to the manifestation of interfacial interactions.

The experimental investigation of interfacial phenomena in the condensed multiphase superfine system is a complicated problem. One of the approaches to solving this problem includes measurement of increments for basic thermodynamic functions of the system during introduction of the filler into it and formation of corresponding structures linked to the interfacial layer.

The enthalpy of mixing of composites based on a glassy polymer matrix filled with particles was estimated by calorimetric method. The alternating sign pattern of the enthalpy of mixing was established. This parameter assumed negative values in the case of composites with a high content of the polymer and positive values at a high content of the filler. It was suggested that the alternating sign pattern of the concentration dependence of the enthalpy of mixing is related to superposition of the effects of adhesion interfacial interaction on the filler surface and the effect of additional vitrification of the polymeric matrix in the filled composite. To account for these two processes, the equation for the dependence of the enthalpy of mixing of the polymer with the filler on the composite composition was proposed. Application of this equation to a range of glassy polymers in combination with nanodispersed fillers demonstrated that the model good corresponds to experiment.

Calorimetric screening using the proposed model allows us to solve the following problems in the of glass polymer composites: the influence of the polymer nature, the efficiency of filler surface modification, particle aggregation, and the influence of particle shape and size on interfacial interaction.

STUDY OF ELECTROLYTE PARTITIONING BETWEEN PHASES OF DIFFERING POLARITY: EXPERIMENTAL AND COMPUTATIONAL APPROACHES

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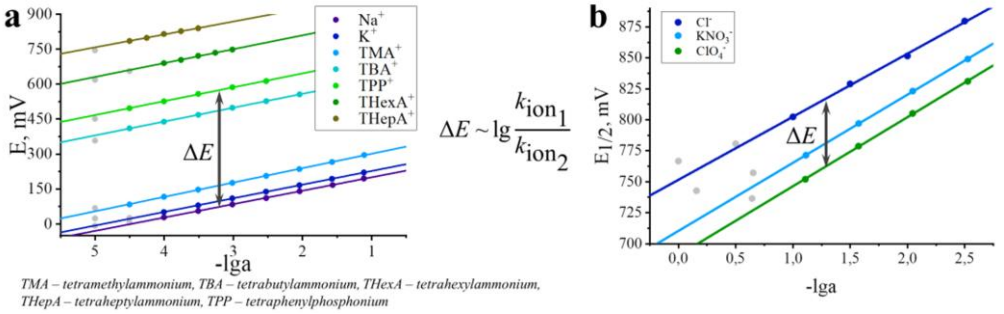
Partition coefficients may be of interest when considering equilibrium in multiphase systems. Lipophilicity of ions governs partitioning of electrolytes and ion exchange. There are several methods which can be applied to measure corresponding equilibrium constants. The shake-flask method [1] and calculation from solubility data [2] are applicable to both ionic and non-ionic substances, while ion exchange constants can also be determined voltammetrically [3] and potentiometrically [1]. However, consistency between different methods is not always observed [1,2], and each technique is suitable for a specific range of partition coefficient values.

In our study we estimated partition coefficients of ions between an aqueous phase and plasticized poly(vinyl chloride), a typical matrix for ion-selective sensors. Both hydrophilic inorganic and lipophilic organic ions were of interest. The shake-flask method and potentiometry (Fig. a) were employed as techniques typically used for such systems. To our knowledge, voltammetry was applied for the first time to a system with a polymeric matrix to obtain the ratios of partition coefficients (Fig. b).



Experimental data used to obtain ratio of partition coefficients:
a) potentiometric, b) voltammetric

Molecular dynamics offers access to properties difficult to obtain experimentally. For partition coefficients far from unity, free energy calculation methods are required. We used umbrella sampling with the Weighted Histogram Analysis Method to obtain partition coefficients of electrolytes between water and nonpolar organic solvents.

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The work was financially supported by Russian Science Foundation (project № 25-23-01071).

PHYSICO-CHEMICAL PATTERNS OF PRECONCENTRATION OF Sm(III), La(III), Er(III) BY A COPOLYMER OF POLYVINYL ALCOHOL, FORMALDEHYDE AND UREA

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Various sorption models are used to study surface phenomena in the preconcentration of rare earth metals. In this work, sorption theories are applied to the preconcentration of Sm(III), La(III), Er(III) with a copolymer of polyvinyl alcohol, formaldehyde and urea (PVF-U).

The PVF-U sorbent quantitatively extracts (recovery rate > 98%) REM from aqueous solutions at pH 4-7. The sorption capacity of the sorbent is relative to La(III), Sm(III), Er(III) is 0.086, 0.078, and 0.057 mmol/g, respectively.

The experimentally obtained sorption isotherms were analyzed by the sorption models of Langmuir, Freundlich, Dubinin-Radzhdankevich, Temkin (see the table).

Parameters of La(III), Sm(III), Er(III) sorption isotherms with PVF-U sorbent

Sorption theory	Characteristics	La(III)	Sm(III)	Er(III)
Langmuir	a_{max}, mmol/g	0.085	0.074	0.057
	K_L, l/mmol	3.0	2.0	3.4
	R_L	0.15–0.94	0.23–0.94	0.19–0.95
	r	0.952	0.951	0.944
Freundlich	a_{max}, mmol/g	0.061	0.058	0.048
	1/n	0.44	0.62	0.48
	n	2.3	1.6	2.1
	r	0.995	0.954	0.989
Dubinin-Radzhdankevich	a_{max}, mmol/g	0.047	0.027	0.059
	K_D, mmol^2/ kJ^2	0.0042	0.0061	0.0043
	E, kJ/mol	10.9	9.1	10.8
	r	0.982	0.971	0.972
Temkin	A_T, l/g	63	35	69
	B, J/mol	0.016	0.017	0.011
	r	0.912	0.962	0.900

The REM sorption corresponds to the Langmuir model, which indicates the sorption of metals on an energetically homogeneous surface. The values of the separation coefficient (R_L) according to the Langmuir model and 1/n according to the Freundlich model are in the range 0-1, which indicates a high adsorption capacity of the sorbent in relation to recoverable REM ions. The calculated free energy of adsorption (E) according to the Dubinin-Radostkevich model indicates the chemical mechanism of sorption, and the energy according to the Temkin model (B) indicates the exothermic process.

INFLUENCE OF TEMPERATURE AND MACROMOLECULES ON PHASE TRANSITIONS IN TWO-DIMENSIONAL LIPID FILMS

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Interactions between macromolecules and lipids influence on the processes occurring on the surface of living cells and the functional properties of cell membranes. For investigations of these interactions, a lipid monolayer on the surface of a liquid is used usually as a model system instead of a lipid bilayer of the cell membrane.
In this work, the interactions of polyelectrolytes and proteins (beta-lactoglobulin (BLG) and lysozyme) with a lipid monolayer were investigated by the methods of surface rheology, microscopy and spectroscopy under conditions close to physiological. In this case monolayer contains a mixture of zwitterionic and anionic lipids, which is the basis of cell membranes. The presence of polyelectrolyte with positively charged functional groups under the lipid monolayer leads to a change in the phase state of molecules in the surface layer due to electrostatic interactions. Both an increase in temperature and the presence of an oppositely charged polyelectrolyte in the sublayer leads to a disorder in the structure of the lipid monolayer and prevents the transition of the monolayer from a liquid-expanded to a liquid-condensed state. The effect of macromolecules on the surface layer increases with increasing concentration of negatively charged lipid in the monolayer. It was previously shown that positively charged BLG macromolecules at pH 2 have a significant effect on the properties of a negatively charged lipid monolayer due to both electrostatic and hydrophobic interactions [1]. At a pH of 7.4, BLG has a negative charge, and lysozyme has a positive charge, which significantly increases effect of lysozyme on the structure of the negatively charged lipid monolayer. Lysozyme strongly reduced the dynamic surface elasticity of the lipid monolayer, while BLG had practically no effect. Probably, the presence of both electrostatic and hydrophobic interactions between lysozyme macromolecules and the lipid monolayer contributes to the bactericidal activity of this protein against gram-negative bacteria.

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This research was funded by the Russian Science Foundation, grant № 24-13-00261.

CONSTRUCTION OF EXCESS GIBBS ENERGY DIAGRAMS FOR FOUR-COMPONENT SYSTEMS USING THE MARCHING CUBES ALGORITHM

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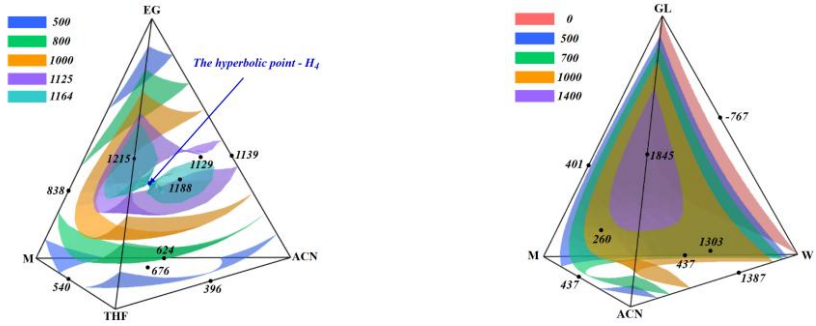
Using the «marching cubes» algorithm, the visualization of datasets representing composition – excess Gibbs energy for four-component systems methanol (M) – tetrahydrofuran (THF) – acetonitrile (ACN) – ethylene glycol (EG) and methanol (M) – acetonitrile (ACN) – water (W) – glycerol (GL) was performed at a pressure of 101.32 kPa. Calculations were carry out using the Non Random Two Liquid (NRTL) model, which allows describing the concentration dependencies of G^E in binary systems with different deviations from ideal behavior, as well as structures of G^E diagrams with several inner singular points [1].

In figure, the arrangement of iso-manifolds of excess Gibbs energy (G^E) is shown in concentration tetrahedrons of four-component systems. For the G^E structures of the ternary diagrams, the conditions of topological verification are satisfied for the complete systems: $2E_3 + E_2 + E_1 = 2H_3 + H_2 + 2$, where E – elliptic point; H – hyperbolic point; 1, 2, 3 – the number of components in singular point. Furthermore, the condition holds for the boundary contour: $E_2^{max} + H_2^{max} + E_1^{max} = E_2^{min} + H_2^{min} + E_1^{min}$, where the numbers of binary singular points with maximum (max) and minimum (min) values of G^E on the binary systems are equal [1,2].

The application of the marching cubes algorithm allows determining the compositions of G^E for four-component singular points, which significantly simplifies the analysis of G^E diagrams when studying solution structure and extractive agents selectivity for separating ternary mixtures with multiple azeotropes.



The iso-manifolds of the excess Gibbs energy (J/mol) of M-THF-ACN-EG and M-ACN-W-GL mixtures at a pressure of 101,32 kPa

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THERMODYNAMIC STUDY OF VOLATILE Ru(II) AND Co(I) CYCLOPENTADIENYL DERIVATIVES

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To improve the electrical parameters of integrated circuits, modifications to the circuit architecture are essential, including reductions in the size of metal lines. In this case replacing traditional Cu with other conductive materials such as Ru and Co is required. Atomic layer deposition (ALD) is the method of choice for producing such films due to the most precise possibilities of thickness control and conformality.

To be applied to ALD, the metal precursors must be highly volatile, thermally stable, and highly reactive towards to surface groups of the substrate and gas-co-reagent. Liquid precursors as $Ru(^{Et}Cp)_2$ and $Co(CO)_2Cp$ (Cp is cyclopentadienyl, ^{Et}Cp is ethylcyclopentadienyl), are effective for obtaining metal layers. Data on their thermal properties are limited. For $Ru(^{Et}Cp)_2$, the available volatility data were measured indirectly while the gas phase composition was not controlled [1]. For $Co(CO)_2Cp$ there are only data on vapor pressure in a single point [2]. To supply and verify these data, the current work was devoted to the comprehensive thermodynamic of $Ru(^{Et}Cp)_2$ and $Co(CO)_2Cp$ ALD precursors.

According to DSC, both compounds are thermally stable in the condensed phase over wide temperature ranges up to 393 K and 473 K for $Co(CO)_2Cp$ and $Ru(^{Et}Cp)_2$, respectively. The thermodynamic characteristics of melting were first determined to be: *m.p.* = 256.4±0.5 K, $\Delta_{melt}H_{m.p.}$ = 12.7±0.6 kJ/mol for $Co(CO)_2Cp$ and *m.p.* = 274.2±0.5 K, $\Delta_{melt}H_{m.p.}$ = 22.9±0.5 kJ/mol for $Ru(^{Et}Cp)_2$. The saturated vapor pressures over the liquid precursors have been measured by the static method with a membrane-gauge manometer within wide temperature intervals: 293–399 K for $Co(CO)_2Cp$ and 369–462 K for $Ru(^{Et}Cp)_2$. Also, the thermodynamic parameters of precursor's evaporation were determined: $\Delta_{vap}H_{346}$ = 44.4±0.3 kJ/mol, $\Delta_{vap}S_{346}$ = 98.4±0.9 J/mol·K for $Co(CO)_2Cp$ and $\Delta_{vap}H_{420}$ = 59.3±0.9 kJ/mol, $\Delta_{vap}S_{420}$ = 103.5±2.3 J/mol·K for $Ru(^{Et}Cp)_2$. Unsaturated vapor pressure measurements confirmed the monomolecular nature of the vapor composition. Thus, the obtained data provide a suitable basis for selecting evaporation temperature parameters in ALD processes.

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CAPILLARY-INDUCED SELF-COACERVATION IN ZWITTERIONIC POLYMER SOLUTIONS: A MEAN-FIELD THEORY

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We investigate the phase behavior of zwitterionic polymer solutions confined within attractive slit-like nanopores. Extending a previous mean-field model for bulk self-coacervation [1], we incorporate chain connectivity, excluded volume, electrostatic dipole-dipole correlations, and adsorbing pore walls. Using a thermomechanical approach based on Noether's theorem [2], we compute disjoining pressure, which characterize the underlying phase behavior.

The results show that strong electrostatic correlations, combined with preferential wall adsorption, can induce capillary-driven liquid-liquid phase separation within the pore — a "capillary-induced self-coacervation". This leads to the formation of a dense coacervate film bridging the opposing walls, which subsequently ruptures upon increasing pore width, producing highly non-monotonic disjoining pressure curves.

A key finding is the crossover between two distinct film formation mechanisms depending on the strength of polymer-wall attraction. In the weak adsorption regime, bridging by single chains dominates, with the critical pore width scaling as $H_c \sim N^{1/2}$, reflecting the chain size. In the strong adsorption regime, the system enters a cohesion-dominated regime, where the critical pore width saturates to an N-independent plateau, indicating that film formation is driven by a confinement-induced shift of the local binodal that stabilizes a cohesive coacervate phase even when the bulk is supercritical.

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PHASE EQUILIBRIA OF THE SYSTEM $NH_4^+, K^+ \parallel SO_4^{2-}, NO_3^- – H_2O$

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Nitrates and sulfates of potassium and ammonium are widely used in the chemical industry and agriculture, including the production of fertilizers. Phase diagrams of water – salt systems allows us to reduce the time and material costs in a search for optimal fertilizer composition. Phase composition of a fertilizer affects storage conditions, detonation stability and macronutrient uptake ratios in a soil.

Although data on solubility in all limiting ternary systems ($NH_4NO_3 – (NH_4)_2SO_4 – H_2O$, $K_2SO_4 – KNO_3 – H_2O$, $KNO_3 – NH_4NO_3 – H_2O$, $K_2SO_4 – (NH_4)_2SO_4 – H_2O$) are avialable in the literature [1], information about solubility in the reciprocal system $NH_4^+, K^+ \parallel SO_4^{2-}, NO_3^- – H_2O$ at 298.2 K is limited.

Experimental data on solubility of the $NH_4^+, K^+ \parallel SO_4^{2-}, NO_3^- – H_2O$ system were obtained by isothermal solubility method at 298.2 K. The saturated solution was analyzed using classical gravimetry (sulfate ion and water content), flame photometry (potassium content), and potentiometry (ammonium content). Saturated solution compositions form liquidus surface. To verify the obtained results on solubility, the Allan method was used for samples with single solid phase in equilibria with a solution.

Solid phases were separated from a saturated solution, their phase composition was determined by X-ray phase analysis (XRD) using a TongDa TD-3700 diffractometer (China). Phase transition studies in these solid mixtures were carried out on a DSC 204 F1 Phoenix® calorimeter (Germany, NETZSCH) in the temperature range of –80 – 140°C.

Existence of solid solutions requires additional experiment on solidus. Solidus data were obtained by slow evaporation of water from a mixture of a known composition until reaching a dry precipitate at 298.2 K. The resulting solid phase mixtures were analyzed by XRD and DSC.

As a result, a fragment of the liquidus and solidus projection of the $NH_4^+, K^+ \parallel SO_4^{2-}, NO_3^- – H_2O$ system was constructed in Jenneke coordinates at 298.15 K. The stability region of solid solutions based on ammonium nitrate, ammonium sulfate, and the double salts 3AN·AS and 2AN·AS was discovered.

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Work was financed on base of "Chemical thermodynamics and theoretical material study" 121031300039-1. The work was carried out using equipment purchased with funds from the Lomonosov MSU Development Program (NETZSCH DSC 204 F1).

DYNAMIC WETTING OF NITROCELLULOSE–BUTYL ACETATE–DIBUTYL PHTHALATE SOLUTIONS ON GLASS

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One of the challenges in the production of multilayer metal-ceramic packages based on high-temperature ceramics for integrated circuits is the formation of a vacuum-tight monolithic structure of the ceramic package containing metallized traces. Monolithicity and vacuum tightness are achieved by using a paste to bond several layers of the ceramic wafer and subsequent firing. The paste must have good adhesion properties to the unfired ceramic material. Therefore, in this study, we analyzed the surface wetting process with solutions used as lamination pastes for multilayer metal-ceramic integrated circuit packages. The pastes studied were three-component solutions consisting of nitrocellulose as a binder, butyl acetate as a solvent, and dibutyl phthalate as a plasticizer.

An equation was proposed that describes the dynamic contact line during the spreading of a solution droplet on the surface of a glass substrate as a function of time (Fig. 1):

$$r(t) = r_\infty - p_1 \cdot \exp(-\alpha_1 \cdot t^{1/2}) - p_2 \cdot \exp(-\alpha_2 \cdot t^{1/2}) \quad (1)$$

The proposed empirical equation is the sum of two exponential functions, each dependent on the square root of time, which may correspond to a diffusion process (Fig. 2). The relationship between droplet height and radius during spreading is shown, which for these solutions can be described by a logarithmic function. An experimental relationship between the dynamic contact angle and capillary number is presented.

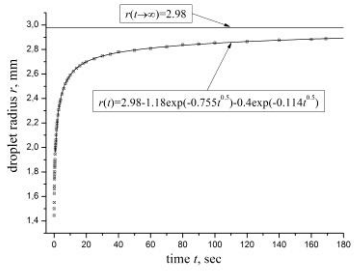

Figure 1. Time dependence of the droplet radius vs. time. Horizontal line corresponds to the equilibrium radius at t→∞. Solis line corresponds to Eq. (1).

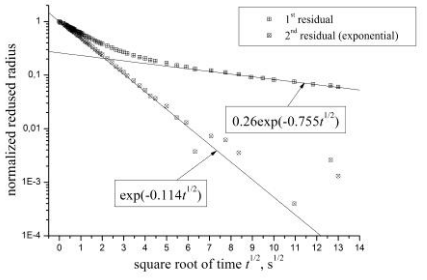

Figure 2. The procedure of decomposition of the original time dependence $r(t)$ on two exponential components according to Eq. (1).

STUDY OF THE THERMODYNAMICS OF SORPTION OF VOLATILE ORGANIC COMPOUNDS IN "IONIC LIQUID-MACROCYCLE" SYSTEMS BY INVERSE GAS CHROMATOGRAPHY

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In gas chromatography, ionic liquids (ILs) are successfully used as stationary phases in capillary columns, mainly due to a number of properties such as high thermal stability, high melting temperatures, vapor pressure from low to negligible even at high temperatures, viscosity from moderate to high, as well as tunable selectivity. Recently, many papers have been published related to the combination of cyclodextrin and ILs. It has been recognized as a universal tool in analytical methods, for example, in separation studies, since the functional group of the ionic liquid is able to improve the efficiency of cyclodextrin extraction.

The aim of the work was to study the thermodynamics of sorption from the gas phase of organic compounds of different classes by fixed phases based on the ionic liquid 1-butyl-3-methylimidazolium bromide with macrocyclic addition, as well as to establish the possibility of the formation of "sorbate-macrocycle" complexes. *heptacys*(2,6-di-*O*-methyl)-β-cyclodextrin and β-cyclodextrin were used as macrocyclic additives.

The temperature dependences of the retention of different classes of waste by stationary phases were constructed and studied. It is shown that the introduction of a macrocyclic component into an ionic liquid can lead to a decrease or increase in retention, depending on both the nature of the organic matter and the structure of the macrocycle. Based on the experimental data obtained, the thermodynamic characteristics of sorption (changes in internal energy and entropy), as well as the activity coefficient at infinite dilution, were calculated. The Hansen solubility parameters were determined to evaluate the interactions of organic compounds in mixed "ionic liquid-macrocycle" systems. It was found that the contribution of various types of intermolecular interactions, estimated using Hansen solubility parameters, correlates with the enthalpy and energy characteristics of the sorption process.

It is proved that "ILs-macrocycle" systems exhibit structural and enantioselectivity under gas chromatography conditions.

THERMODYNAMIC AND KINETIC PARAMETERS OF URANIUM RECOVERY FROM SULFURIC ACID SOLUTIONS USING ORGANOPHOSPHORUS EXTRACTION MIXTURES

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Currently, the processing of radioactive waste (RW) is an important and widely discussed topic. The decline of waste volumes will reduce the potential radioactive contamination of environment and allow the return of uranium to the nuclear fuel cycle. One effective method for processing uranium-containing waste is uranium leaching with sulfuric acid, followed by liquid extraction. However, several factors complicate this approach: the heterogeneity and complex composition of the waste and, consequently, of the pregnant leach solutions (PLS), as well as the temperature and duration of the process. The efficiency of the extraction stage directly depends on these factors. Thus, the aim of this work was to study the behavior of uranium under varying temperature and phases contact time during extraction using di-(2-ethylhexyl)phosphoric acid (D2EHPA) diluted in an inert diluent Shellsol D60 from pregnant solutions after sulfuric acid leaching of uranium from RW.

The study was conducted using both model and real pregnant solutions of uranium leaching. The real PLS were characterized by high concentrations of components, g L^{-1}: 0.53 – U; 3.4 – Fe; 2.9 – Mg; 2.8 – Ca; up to 9.2 – F^-; 50 – H_2SO_4. The model solutions (MS) contained, g L^{-1}: 0.5 – U and 50 – H_2SO_4. The extraction process was carried out at an organic and aqueous phases ratio of 1:5.

The effect of temperature on uranium extraction efficiency was investigated in the range of 20 to 80 °C. The experimental results revealed that an increase in process temperature led to a decrease in uranium recovery from both the MS (from 85.77 to 60.02 %) and the real PLS (from 61.93 to 1.91%). The change in Gibbs free energy in the former case increased from -8.3 to -5.9 kJ mol^{-1}, while in the latter this value increased from -5.1 to 6.8 kJ mol^{-1}, indicating a decrease in the reactivity of the system.

Based on the results of the previous experiment, extraction kinetics were studied at 20 °C over a range of 1 to 60 minutes. From the kinetic curves of uranium extraction from the MS, it was established that equilibrium in the "MS – D2EHPA" system was reached within the first 3 minutes and kept constant throughout the remaining time, with uranium recovery reaching 88.66% and ΔG equal to -8.9 kJ mol^{-1}. Subsequent experiments with real PLS yielded, as expected, different results: uranium recovery reached 77.6 % during the first 3 minutes, but decreased to 31.21 % over the remaining time due to the competitive extraction of impurity elements and the displacement of uranium from organic phase. The ΔG value over the considered time interval varied from -6.9 to -2.0 kJ mol^{-1}.

The work was supported by the Russian Science Foundation, project No. 25-29-01057 (https://rscf.ru/en/project/25-29-01057/).

THERMODYNAMIC EQUILIBRIUM GROWTH OF CO-N_2 CRYSTALS IN CONDITIONS OF THE INTERSTELLAR MEDIUM

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The densest and coldest parts of the interstellar medium, called dense molecular clouds or dense cores, have temperatures as low as 10 K and pressures of 10^{-13}–10^{-11} Pa. These clouds consist mostly of gaseous H_2 and microscopic dust particles. Such Most of molecules (except H_2) in these clouds condense on dust grains forming icy mantles. regions are cradles of young stars, which form after the gravitational collapse of dense cores. The two main components of icy mantles in these regions are H_2O and CO. The former forms amorphous icy structure on dust surfaces, while the latter forms in the gas phase and then partially condenses. It is believed that rapid CO condensation upon a temperature decrease leads to the formation of a separate CO-rich ice layer above the H_2O-rich layer. Recent findings have shown that CO molecules are sufficiently mobile to form equilibrium crystals on the surface of H_2O ice even at temperatures close to 10 K. The thin-film mode of CO crystal growth is the equilibrium Stranski–Krastanov mode, where a CO adsorbate layer wets the surface of H_2O ice and then segregated CO crystallizes, forming the α-CO phase [1].

Molecular nitrogen, though not detected but likely present in molecular clouds, exhibits gas–grain interaction behaviour similar to that of CO, and the CO–N_2 binary system forms a continuous series of solid solutions. Thus, N_2 should be involved in the equilibrium between the adsorbate layer, CO segregates, and the α-CO phase, as we assume in this study.

The recent launch of the James Webb Space Telescope has allowed the investigation of dangling OH (dOH) features of H_2O ice, which have been detected but not yet studied in detail. These features correspond to free OH groups that are not hydrogen-bonded, carrying information about the composition of apolar molecules in the bulk of H_2O ice and on its surface. In this study, we grew a series of H_2O ices at 10 K and then separately deposited on it a CO–N_2 mixture with specified CO:N_2 molecular ratios (1:0, 1:0.5, 1:1, 1:2, 1:4) at 20 K; the latter temperature is required to reach equilibrium within timescale of laboratory experiment. We recorded the infrared spectra of the resulting layered ices. We traced the CO:N_2 ratio in CO-rich crystals through the dependence of the CO band position on N_2 content, which was preliminary obtained, and determined this ratio on the H_2O ice surface via the dOH features of dOH–CO and dOH–N_2 clusters. The results allowed us to determine how N_2 distributes between adsorbate and CO crystals in conditions of thermodynamic equilibrium. This study may help to determine N_2 abundances in interstellar ices through the analysis of interstellar dOH features.

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MOLECULAR SIMULATION AND THERMOMECHANICAL PREDICTION OF BRINE-VAPOR TENSION AT RESERVOIR CONDITIONS

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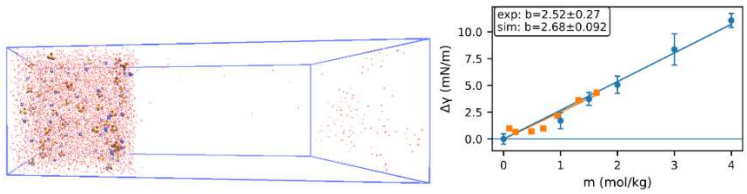
Accurate prediction of interfacial tension (IFT) between reservoir fluids across broad ranges of temperature, pressure, salinity, and gas composition is essential for planning upstream processes, in particular for CO_2 mineralization. However, reservoir-condition IFT data is scarce and often inconsistent, especially for concentrated multicomponent brines (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-) and vapors (CH_4, CO_2, H_2S). High-pressure measurements for H_2S-rich vapors are very laborious and expensive due to safety concerns. This work reports experimentally informed molecular simulation studies of brine—vapor interface at ambient and reservoir conditions. The effects of brine and vapor composition, pressure and temperature are systematically examined. Good agreement with experiments is achieved for most of the system of interest, and systematic correction are proposed for sulfates and carbonates. Experimental data and simulations are applied in parameterization of a thermomechanical model [1], in which surface tension is obtained from the mismatch of normal and tangential stresses derived from the grand thermodynamic potential of an inhomogeneous Coulomb fluid. The theory is fitted to diverse systems using a minimal number of physically interpretable parameters related to the structural characteristics of the interfacial layer obtained in molecular modeling. The final outcome is a compact predictive model (with uncertainty bounds reflecting experimental scatter) suitable for reservoir-scale workflow integration.



(a) Snapshot of the aqueous $MgSO_4$ solution–air interface at m = 0.64 mol kg^{-1}, (b) dependence of the interfacial tension on brine salinity for $MgCl_2$

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THERMODYNAMIC MODELING OF HIGH-TEMPERATURE OXIDATION OF $Al_xCoCr_yNiNb_z$ HIGH-ENTROPY ALLOYS

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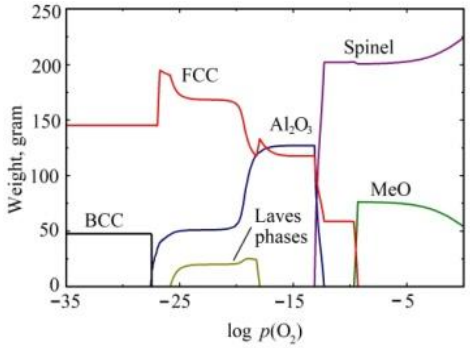
High-entropy alloys (HEAs) consist of five or more elements in near-equiatomic ratios to achieve maximum configurational entropy of mixing. This concept allows designing a wide variety of compositions and can assist in obtaining materials with unique characteristics. It is known that $Al_xCoCr_yNiNb_z$ type HEAs exhibit an optimal combination of strength and ductility and can be used to produce critical components for shipbuilding or aerospace industries [1]. For aerospace applications, the parts are constantly exposed to elevated temperatures. Therefore, niobium-containing HEAs are of particular interest for research into high-temperature oxidation resistance.

Thermodynamic modeling of the high-temperature oxidation process of alloys can optimize and significantly contribute to research in this field. This modeling is performed using the Calphad methodology, for which we applied the FactSage software package (version 7.3). We used data from the SGTE (2011) database to model the metallic phases, and the FToxid database, supplemented by FactPS data, to model the oxide phases. An example of the results of this calculation is shown in the figure below.



Results of thermodynamic modeling of high-temperature oxidation of $AlCoCrNiNb_{0.2}$ HEA at 1100 °C

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AGGREGATION BEHAVIOR OF AQUEOUS SOLUTIONS OF ALKYLIMIDAZOLIUM AMINO ACID IONIC LIQUIDS: EFFECTS OF "NATURAL" ADDITIVES

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The demand for greener chemistry that implies sustainability via renewable, biodegradable and eco-friendly chemicals is rapidly growing. Of particular interest are formulations of aggregates in bio-derived solvents because such systems may provide reaction media with enhanced reaction rates, solubilization capacity, and a potential for the aggregate-mediated separation of the products. Micellar solutions and microemulsions, among others, have been widely used in micellar catalysis, nanoreactor engineering, controllable drug release and micelle-mediated separation. Recently, a number of bio-derived solvents have emerged, including natural deep eutectic solvents (NADES) and renewable solvents derived from biomass. The surface-active ionic liquids, particularly, the amino acid ionic liquids (AAILs), are of a high potential as bio-based surfactants [1]. It is well known that the aggregation behavior of surfactants in mixed solvents depends substantially on the specific chemistry of the constituent substances.

In this work, we study aggregation behavior of 1-dodecyl-3-methylimidazolium AAILs in aqueous-salt solutions. Sodium chloride, choline chloride and choline chloride+L-proline (components of NADES) were chosen as modulators of micellar aggregation. The aggregation characteristics, including critical micelle concentration (CMC), surface tension and aggregate size are determined using tensiometry, photon correlation spectroscopy, and conductometry techniques. Structural characteristics of the aggregates are also examined by molecular dynamics simulation. Our study combines experiment and computer simulation with development and application of a molecular thermodynamic aggregation model that takes into account both the coulombic and the specific interactions in the aggregating fluid.

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This work was supported by Russian Science Foundation (project 25-43-01003). The experimental measurements were partially performed at the Research Park of St. Petersburg State University ("Center for Magnetic Resonance", "Center for Thermogravimetric and Calorimetric Research", "Center for Diagnostics of Functional Materials for Medicine, Pharmacology, and Nanoelectronics").

APPLICATION OF ADSORPTION THEORIES TO DESCRIBE CEFOPERAZONE PRECONCENTRATION USING AMINATED SILICA

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The use of theoretical sorption models makes it possible to describe the equality in the system and calculate the physico-chemical characteristics to optimize the conditions and understand the mechanisms of interaction. In this work, the application of sorption theories to the preconcentration of cefoperazone (Cefoper) with silica modified with polydimethyldialammonium (PDDA), polyhexamethylene guanidine (PGMG) and polyethylenimine (PEI) was studied.

Cefoper is quantitatively (98%) extracted from aqueous solutions with sorbents SiO_2-PDDA, SiO_2-PGMG at pH 3-6. The experimentally determined sorption capacity of SiO_2-PDDA, SiO_2-PGMG, and SiO_2-PEI according to Cefoper is 0.118, 0.087, and 0.104 mmol/g, respectively. The experimental sorption isotherms are satisfactorily described by the Langmuir model (see the table). The adsorption equilibrium constant KL decreases with the transition from SiO_2-PDDA and SiO_2-PGMG to SiO_2-PEI, which is associated with the greater strength of the interaction of Cefoper with PGMG and PDDA, and this is confirmed by experimental data. The values of the coefficients RL of the Langmuir model and n of the Freundlich model indicate active sorption. The energy of interaction between Cefoper and sorbent polyamines decreases as the surface is filled. The free energy according to the Dubinin-Radostkevich model $E < 8$ kJ/mol indicates the physical mechanism of sorption, the energy according to the Temkin (B) model indicates the exothermic nature of the process.

Parameters of theoretical models of Cefoperazone sorption

The sorption model	Parameter	SiO_2- PDDA	SiO_2- PGMG	SiO_2- PEI
Langmuir	a_{max}, mmol/g	0.134	0.104	0.192
	K_L, l/mmol	11.0	9.28	1.91
	R_L	0.1-0.9	0.1-0.9	0.3-1.0
	R^2	0.993	0.994	0.757
Freundlich	K_F, mmol/g	0.258	0.162	0.211
	1/n	0.662	0.617	0.888
	R^2	0.933	0.963	0.943
Dubinin-Radostkevich	a_{max}, mmol/g	0.129	0.098	0.121
	K, mol^2/kJ^2	0.017	0.017	0.032
	E, kJ/mol	5.36	5.44	3.92
	R^2	0.984	0.987	0.995
Temkina	A_T, l/mg	209	165	54
	B, kJ/mol	23.5	18.4	27.7
	R^2	0.922	0.937	0.934

NEW APPROACHES, METHODS AND GOALS IN THERMODYNAMIC MODELING. THERMODYNAMIC DATABASES

НОВЫЕ ПОДХОДЫ, МЕТОДЫ И ЗАДАЧИ В ОБЛАСТИ ТЕРМОДИНАМИЧЕСКОГО МОДЕЛИРОВАНИЯ. БАЗЫ И БАНКИ ДАННЫХ

NATIONAL THERMODYNAMIC DATABASE FOR MODELING OF PHASE EQUILIBRIA OF OXIDE SYSTEMS AT HIGH TEMPERATURES

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Progress in high temperature technologies such as microelectronics, the nuclear, space, aviation and optical industries as well as metallurgy requires of development of advanced materials which have to be stable under operation during long high-temperature impacts up to the temperature 3000 K. During increasing the temperature, as a rule, the complex changes of physicochemical properties of materials may be observed as the result of processes available in the condensed and gaseous phases. At present the thermodynamic data bases for modeling of phase diagrams of multicomponent systems at high temperatures are widely used abroad in the frame of CalPhad (Calculation of Phase Diagram) approach. However the similar thermodynamic data bases are absent in Russia. Development and approbation of new additional thermodynamic semi-empirical and statistical thermodynamic approaches for calculation of thermodynamic properties and phase equilibria in multicomponent oxide systems containing hafnium, zirconium and rare earth oxides were illustrated and recommended for the application in the National thermodynamic data base. The availability of such National data base will allowed to predict and to prevent the ecological accidents at high temperatures with the participation of inorganic materials as well as to develop and to apply in industry ultra high-temperature materials for ensuring of national interests in the variety of the high-temperature adaption areas [1, 2].

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NEW APPROACH TO THE THERMODYNAMIC ANALYSIS OF POLYMORPHIC SYSTEMS

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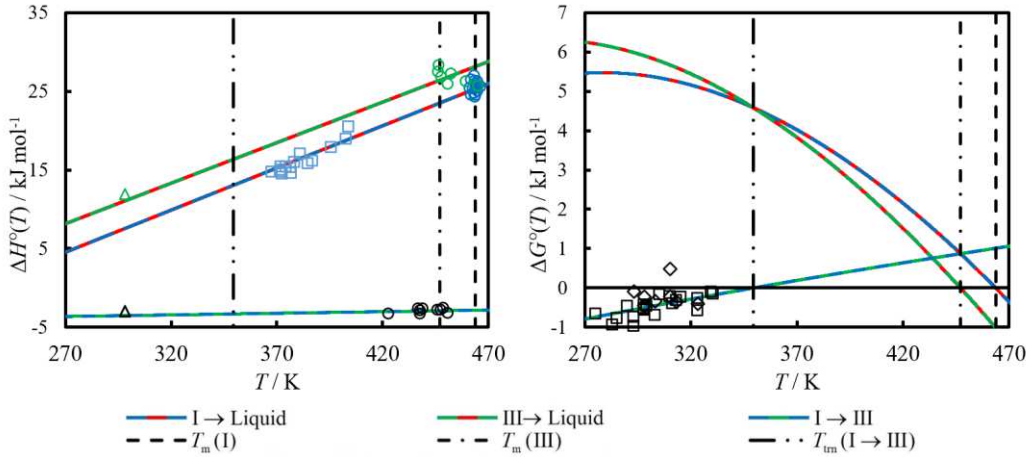
The polymorphic state of compound defines its practically important properties, such as stability, bioavailability, solubility, dissolution rate. Characterization of the thermodynamic relationships between two crystal polymorphs is usually based on experimental melting or solubility data [1]. Due to experimental features and neglecting the heat capacity correction results of these methods may differ significantly.

In this work, we proposed an algorithm for simultaneous treatment of the fusion, solubility and related data to get self-consistent phase diagram for polymorphic compounds. The method combines melting temperatures, enthalpies of fusion, crystallization, dissolution, and solid-solid transitions, equilibrium solubilities, dissolution rates, vapor pressures, and the heat capacity data to achieve their mutual agreement and access ***G*-*T*** and ***H*-*T*** diagrams over a wide temperature range.



Thermodynamic characteristics of phase transitions between crystalline I, crystalline III and liquid carbamazepine. Symbols represent different types of the experimental data used to calculate the diagram.

The proposed approach was tested using our and literature experimental data on several polymorphic systems (see figure). Its ability to distinguish between the reliable and erroneous data make it valuable instrument in the thermodynamic analysis of polymorphism, fusion, and crystallization.

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MODELING OF PHASE EQUILIBRIA IN THE SrO-La_2O_3-Fe SYSTEM

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The Sr-La-Fe-O system is a promising base for multicomponent oxide materials that are essential for various applications, e.g., cathodes and electrolytes in solid oxide fuel cells, oxygen separation membranes, catalysts for high-temperature processes, and oxygen sensors [1, 2]. However, the development of new materials based on the Sr-La-Fe-O system is hindered by a lack of reliable information on the phase equilibria. This is the primary rationale for the present study, which deals with the calculation of the phase diagram of the SrO-La_2O_3-Fe and SrO-La_2O_3-Fe_2O_3 systems and comparison of the results obtained with the information available in the literature [2, 3].

Modeling of the phase equilibria in the Sr-La-Fe-O system was carried out using the NUCLEA database and GEMINI2 calculation software [4]. In the system under study, eight isothermal sections of the phase diagram were calculated, revealing how phase relations change with temperature and component contents. The equilibria were shown to involve only pure components and binary compounds. No ternary phases containing Sr, La, and Fe were observed. Two eutectic points were identified, establishing the maximum application temperature for materials in the SrO-La_2O_3-Fe system. The reasons for the discrepancies with the literature data [2, 3] were analyzed.

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DEVELOPMENT OF NUMERICAL METHODS FOR PHASE EQUILIBRIA CALCULATION INVOLVING MODELS WITH INTERNAL DEGREES OF FREEDOM

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Multicomponent systems often include non-stoichiometric phases that require complex thermodynamic models based on sublattices, ions, associates etc. In this case phase models often have internal degrees of freedom, i.e. number of independent components is less than the number of species. And computation of Gibbs energy of phase requires its minimization. It may require specialized approaches, especially in the case of the convex hull method. And the aim of this work is to suggest such methods for further usage during further development in the Laboratory of Chemical Thermodynamics of Lomonosov MSU.

Each phase can be characterized by molar fractions of independent components ($\vec{x}$) and species ($\vec{y}$). The $\vec{x}$ vector can be unambiguously calculated from $\vec{x}$ as $\vec{x} = f(\vec{y})$ where *f* is a model-specific function. But if internal degrees of freedom are present and f is not bijective then computation of $G(\vec{x})$ will require the solution of the next nonlinear minimization problem:

$$G(\vec{x}) = \min_{\vec{y}} G(\vec{y}) ; \vec{x} = f(\vec{y})$$

In the case of convex hull method that is used for robust search of an initial approximation two approaches were suggested:

1) Solve the *G* minimization problem at each point of the grid used by the convex hull method during the Gibbs energy discretization. It makes the method not derivative free.
2) Monte Carlo approach with generation of large amounts of $\vec{y}$ pseudorandom or quasi-random vectors with their further projection to $\vec{x}$ coordinates. The procedure is continued until the $G(\vec{x})$ with the desired discretization step is stabilized. It may be computationally extensive but doesn't require derivatives.

Both methods allow to reduce the number of dimensions in the convex hull method; it is important because it may slow down at grids with more than 4 components.

In the case of phase equilibria computation based on an explicit minimization of *G*, e.g. by means of Lagrange multipliers method, the minimization procedure can either directly integrate $\vec{y}$ into the problem or assume optimization of $\vec{y}$ vectors inside thermodynamic models of phases. Both variants require the analytical $\partial G/\partial y_i$ and $\partial^2 G/\partial y_i \partial y_j$ derivatives, especially for sublattice models. Their addition to the developed software complex allowed us to increase numerical stability.

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THE 'CENTERPIECE' APPROACH: A HIGH-THROUGHPUT THERMODYNAMIC TOOL FOR LOHC AND BIOSYNTHETIC FUEL TECHNOLOGIES

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Conventional group-additivity (GA) methods often fail for complex cyclic and polycyclic molecules because ring strain and substitution effects are difficult to parametrize. To address this, we present the "centerpiece" approach — a refined GA variation that utilizes a well-characterized experimental "core" molecule to mimic the target structure, followed by the addition or removal of precisely calibrated fragments.

The reliability of this method is demonstrated across several key LOHC and biofuel families:

- Aromatic & Naphthenic Carriers: Dicyclohexylmethane and perhydro-dibenzyltoluene (errors $\leq$ 1–2 kJ·mol^{-1}).
- N-Heterocycles: 6,7-benzindole and its perhydrogenated (8H- and H_{12}-) forms, including methyl-substituted decahydroquinolines.
- Oxygenated Biomass Derivatives: Methoxy- and ethoxy-derivatives of bicyclohexane, decalin, indane, and benzofuran.

In all cases, the calculated enthalpies of formation (gas/liquid), vaporization, and sublimation align with both experimental data and high-level G4 quantum-chemical results within combined uncertainties. The approach effectively resolves literature contradictions and provides the precise hydrogenation/dehydrogenation enthalpies required for LOHC screening.

The "centerpiece" method is a "pen-and-paper" fast-prediction tool that requires only reliable data for the core molecule. Its integration with quantum chemistry creates a robust hybrid toolbox for the rapid, low-cost design of next-generation hydrogen storage and sustainable fuel technologies.

Keywords: chemical thermodynamics, group additivity, centerpiece approach, LOHC, enthalpy of formation, hydrogen storage, renewable fuels.

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THERMODYNAMIC PREDICTION OF THE COMPOSITION OF POLYCHLORINATED BIPHENYL NITRATION PRODUCTS AS A FUNCTION OF THE NITRATING MIXTURE EXCESS

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Polychlorinated biphenyls (PCBs) are persistent organic pollutants. The development of effective approaches for their neutralization through a sequence of chemical modification and thermolysis methods is a relevant task. The aim of this study is to perform thermodynamic modeling of electrophilic substitution reactions in a series of PCBs, using the nitration processes of tri- and tetrachlorobiphenyls as an example.

The nitration process was modeled by the HSC software package (0.001 mol PCB, 0.005–0.11 mol HNO_3:H_2SO_4 (1:1), T = 100–200°C). It was found that with a small excess of the nitrating mixture (0.005 mol), the conversion of the initial PCBs is incomplete, with the residual concentration of the parent congener being higher for trichlorobiphenyl than for tetrachlorobiphenyl. Increasing the amount of nitrating mixture to 0.11 mol leads to the complete absence of the initial PCBs in the products, which are represented exclusively by deep nitration products – penta-, hexa-, and heptanitro derivatives.

However, experimental data indicate that as the number of chlorine atoms in the biphenyl structure increases, the proportion of deep nitration products decreases. For 2,4,5-trichlorobiphenyl, a mixture of di- (78%) and trinitro derivatives (22%) was obtained, while for 2,5,3',4'-tetrachlorobiphenyl, a mixture of mono- (15%) and dinitro derivatives (85%) was obtained, contradicting the thermodynamic calculations. This discrepancy is explained by kinetic limitations: thermodynamically permitted reactions may proceed at a slow rate. It is likely that increasing the reaction time would bring the experimental results closer to the thermodynamic equilibrium, and for tetrachlorobiphenyl, the proportion of deeper nitration products would increase, becoming comparable to that for trichlorobiphenyl.

Thus, the modeling confirms the principal feasibility of exhaustive PCB nitration with an excess of the nitrating mixture, taking into account the kinetic factors of the chemical process. The obtained thermochemical data can be used to predict the behavior of other PCB congeners in electrophilic substitution reactions.

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TENSOR NETWORK APPROACH FOR MODELING THERMODYNAMIC PROPERTIES OF ADSORPTION SYSTEMS WITH MANY-BODY INTERACTIONS

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Thermodynamic properties of adsorption monolayers are determined by the nature of intermolecular interactions. Most theoretical studies are restricted to pairwise intermolecular potentials. The reason is the computational complexity of models with many-body interactions.

On the other side, quantum chemical calculations show the substantial contribution of many-body interactions in some cases [1]. These interactions can even lead to qualitative changes in the system behavior [2].

We have developed a unified tensor (UT) algorithm for lattice gas models of adsorption layers. This algorithm efficiently incorporates many-body interactions up to the third nearest neighbor in adsorption monolayers. In contrast to classical methods (Monte Carlo, transfer matrix), where accounting for such interactions is challenging, the tensor network approach affects only the tensor network construction stage. This opens up possibilities for the thermodynamic analysis of complex quasi-2D systems.

The UT algorithm was applied to the model metal-organic layer of 1,3,5-tris(4-pyridyl)benzene (TPyB) and copper on the Au(111) surface. This system is of interest for the fabrication of metal-organic nanostructures. The interaction energies were calculated using density functional theory. It was shown that these energies cannot be reduced to combinations of pairwise interactions.

Adsorption isotherm calculations revealed both quantitative and qualitative differences in the phase behavior of the system when many-body interactions were taken into account. The stability regions of ordered phases shift along the chemical potential (or gas phase pressure) axis. Qualitatively, several types of changes occur. Low-density phases disappear, while the thermal stability of dense ordered structures, such as the "superflower" phase, can be significantly reduced. Many-body interactions lead to disordered configurations with increased layer density. It is driven by the filling of the surface with copper atoms.

The proposed approach demonstrates high efficiency in studying complex adsorption systems with many-body interactions. The developed algorithm can be used to predict the thermodynamic properties of new molecular and metal-organic monolayers, which are promising for catalysis, nanoelectronics, and sensing.

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MODELING OF THE OXIDE MELT STRUCTURE: GLASS TRANSITION VS CRYSTALLIZATION

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Due to the increasing demand for the quantitative description and investigation of various processes in oxide systems, the creation of models of multicomponent melts, glasses, and their crystallization products is an extremely relevant task. Although glasses possess an unusual combination of properties that are in many ways closer to liquids than to true solids, on a human timescale they also demonstrate hardness, elasticity, and even fracture like solids. Given that crystalline materials preserve their internal structure and external configuration even for an infinitely long time and do not undergo plastic deformation at low temperatures under the influence of gravity, they are considered as real solids.

The present work is based on a thermodynamic description of the melt phase, which allows us to determine the conditions of the melting and differentiation processes, as well as to develop various methodologies for use in materials science and geological research. Using the quasicrystalline approximation based on the assumption that melts are composed of ideal associated solutions, the thermodynamic characteristics of crystalline silicates can be applied to describe the melt structure in terms of the distribution of Q^n units. It is known that silicate melts contain disordered polymerized anions which form the structural units of glasses and crystalline silicates. These consist of silicon–oxygen tetrahedra Q^n, which differ in the number of non-bridging and bridging oxygen atoms (n), with a central silicon atom and four oxygen atoms

The thermodynamic modeling method, which has proven highly effective for modeling melts at different temperatures, is used for the calculation of glass structure in this work. Since the melt and glass crystallization model is still under development, we used DFT analysis calculations. The structure of oxide melts, glasses, and crystals lends itself well to analysis using Raman spectroscopy. Since calculations of structure or chemical composition must be validated experimentally, this study demonstrates the potential of computational methods in comparison with experimental results. A qualitative comparison between theory and practice glass formation and crystallization of silicate melts containing equal amounts of lithium and potassium, with a total content of 33, 40, and 50 mol % was carried out using the methods of spectroscopy and X-ray diffraction.

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SOFTWARE DESIGN FOR THERMODYNAMIC MODELING AND PROPERTY CALCULATION

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In the contemporary landscape of computational materials science, the complexity of multicomponent systems necessitates a rigorous architectural distinction between thermodynamic models and the numerical algorithms employed to solve them. Inspired by the C++ Standard Template Library (STL), where the separation of algorithms and data structures serves as a cornerstone of efficiency and flexibility, this report proposes a similar approach for thermodynamic databases and corresponding software.

The crucial part of this methodology is usage of the TDB (Thermodynamic Database) text format. While the TDB format is traditionally used as a static repository for Gibbs free energy parameter, we also demonstrate that the TDB format can serve as a universal, high-level abstraction layer. For example, it has object-oriented features, which are inherently useful for definition of parameters of phases utilizing diverse thermodynamic models in a structured, hierarchical manner.

TDB format provides means for seamlessly merging of multiple sub-databases while maintaining strict human-readability. Being just plain text files, it enables seamless integration with version control systems, essential for tracking of the evolution and highlighting differences of thermodynamic assessments.

This report introduces specific software features of our developed suit, focusing on the parsing and internal representation of TDB files as dynamic data structures. We discuss how these technical choices directly translate into a superior User Experience (UX). Treating the TDB file not just as a flat data source but as a modular codebase enables advanced search capabilities, support for language extensions for setting additional settings of computational environment, and a streamlined workflow for the assessment and refinement of thermodynamic data.

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DEVELOPMENT OF A THERMODYNAMIC DATABASE FOR CORROSION MODELING IN MOLTEN SALT REACTORS

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During molten salt reactor (MSR) operation, fuel salt composition changes continuously because of burn-up, fissile make-up, accumulation of soluble fission products, removal of gaseous and volatile fission products to the gas-off system, deposition of insoluble phases on in-circuit components, and ingress of corrosion products from container materials to the molten salt mixture. These changes modify the physicochemical state of the fuel salt and cause tight coupling between neutronic, thermochemical, corrosion, and thermal-hydraulic phenomena in the reactor circuit. Therefore, proven MSR calculations require a unified thermodynamic and thermophysical database [1-4].

At the National Research Centre "Kurchatov Institute", an extensible database of thermodynamic and thermophysical properties for applicable molten salt mixtures is being developed within the MULTIMSR calculation complex, which can be used by the thermal-hydraulic, neutronic, and corrosion modules of the package [1] and follows current international approaches to special thermochemical and thermophysical databases for multiphysics analysis of MSR.

For molten 0,73LiF-0,27BeF_2-AnF_3 and 0,66LiF-0,34BeF_2 salt mixtures, considered as the fuel salt and intermediate coolant for test and full-scale MSRs, recommended values of liquidus temperature, heat of fusion, density, volumetric thermal expansion coefficient, heat capacity, thermal conductivity, and viscosity have been determined in the temperature range from the liquidus to 750-800 °C. Thermodynamic constants required for modeling mainly chromium corrosion, have also been evaluated and justified. The database accounts for changes in thermophysical properties throughout the reactor campaign due to fuel burn-up, as well as accumulation of soluble fission and corrosion products.

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CHEMICAL DATABASES AS A PROMISING TOOL FOR OBTAINING THE VAPORIZATION CHARACTERISTICS OF ORGANIC COMPOUNDS

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Understanding the thermodynamic properties of vaporization for organic compounds is necessary for industrial applications such as separation, synthesis and for developing theoretical models of intermolecular forces and solubility. Despite there being over 20 million known organic compounds, thermodynamic data exists for only about 0.1% of them. This fact is due to the substantial time and resources required for experimental measurement of saturated vapor pressures and vaporization enthalpy.

Chemical databases like Reaxys and SciFinder hold a large number of boiling point data (usually collected during substance identification in synthesis studies); these values often contain significant errors due to equipment limitations or sample impurity. Consequently, thermodynamics specialists have rarely used this data.

This study presents a methodology to process such existing data to model the temperature dependence of saturated vapor pressure in a wide range. Testing on five reference compounds showed that the method determines vapor pressure with up to 20% error and vaporization enthalpy with up to 2.0 kJ/mol error, which is comparable with the precision of many experimental techniques [1].

The procedure was successfully applied to over 100 compounds, yielding vapor pressure and enthalpy dependencies. For several substances, this data is novel; for others, it corroborates existing literature or helps resolve discrepancies through critical analysis [2]. Given the sheer volume of data in chemical databases, this approach can be scaled to analyze thousands of substances lacking high-precision studies and serves as a tool for validating uncertain literature values.

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THERMODYNAMIC MODELING OF MULTICOMPONENT LITHIUM INDUSTRIAL BRINES

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The sedimentary cover of the Siberian Platform contains chloride brines with a high content of lithium and other valuable components (Rb, Cs, Br). Such brines are thermodynamically nonequilibrium systems with a complex composition. They are characterized by high mineralization and density, which makes them similar in properties to melts. The study of salt crystallization processes under changes in temperature and pressure is an important practical task.

Crystallization in the temperature range of 0... -22 °C and a pressure of 1 bar was simulated using the Selector software package based on minimizing Gibbs energy [1]. Cambrian brines from the Siberian Platform (Nepsky Dome). Brines are acidic - pH (3.8), the content of the main components (in g/l): Ca 153.9; Mg 13.2; Na 2.9; K 15.7; Li 0.2; Cl 334.0. The model contains about 500 probable components (components of the aqueous phase, minerals, gases).

As a result of the modeling, it was found that the beginning of stable ice formation (freezing of brines) occurs at a temperature of -12 °C. At a temperature of -10 °C, chlorides begin to crystallize, their composition and quantity are shown in the table.

Properties of brine and mineral phases during brine crystallization, in g per 1 kg of brine

T, °C	pH	TDS (g/kg)	$KMgCl_3(H_2O)_6$	KCl	$NaCl(H_2O)_2$	NaCl	$CaCl_2(H_2O)_6$	$MgCl_2(H_2O)_6$
-10	3.6	524.9	15.91	1.01	0.16	0.07	0.03	0.01
-12	3.6	548.4	37.07	1.89	0.38	0.17	0.07	0.02
-14	3.7	663.9	66.47	2.49	0.84	0.38	0.14	0.03
-16	3.8	779.0	83.81	2.24	1.27	0.56	0.18	0.03
-22	4.2	1116.2	105.08	0.90	2.39	1.04	0.23	0.03

The first generalized model of strong Cambrian brines has been obtained, which can be used to study phase transitions in the Ca-Mg-Na-K-Li-Cl-H_2O system as the basis for the well production cycle of this type of raw material.

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THE FORMATION ENTHALPIES OF INTERMETALLIC COMPOUNDS IN SYSTEMS (Ni,Pd,Pt)–(Al,In,Sn) BY pySIPFENN SOFTWARE TOOL

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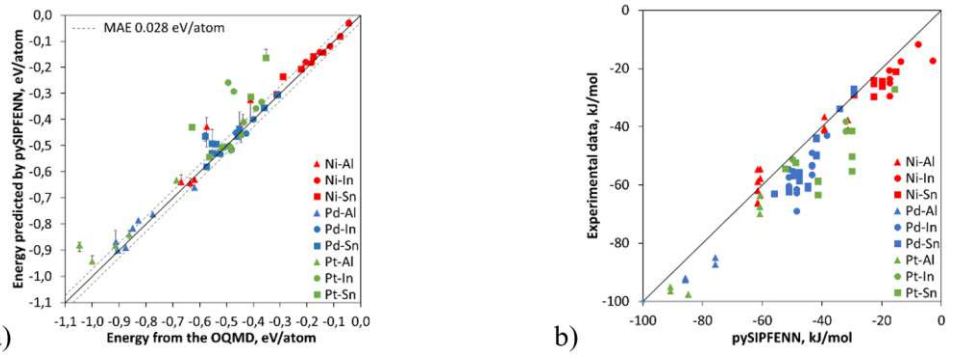
First-principles calculations based on density functional theory (DFT) serve as an important source of input data for calculations using the CALPHAD method. They not only complement experimental results for stable phases but also provide data on metastable and virtual phases required for such calculations.

DFT calculations are resource-intensive and complex, so deep neural network (DNN) models have been increasingly used in recent years to determine formation energies. An example of a DNN-based tool is pySIPFENN [1].

The performance of pySIPFENN was assessed for the calculation of formation enthalpies of the compounds formed by transition metals from 10th group with *p*-metals from groups 13 and 14. Published structural data in the CIF format were used as initial data. In Figure 1(a), the calculation results are compared with OQMD data [2], while Figure 1(b) presents a comparison with available experimental values. In most cases, the pySIPFENN results agree with DFT calculations within the mean absolute error (MAE) of 0.028 eV/atom declared by the pySIPFENN developers. For two isostructural compounds, Pd_8Al_{21} and Pt_8Al_{21}, unsatisfactory results were obtained. A comparison with experimental data reveals that pySIPFENN predictions exhibit a systematic shift of approximately 0.073 eV/atom (~7 kJ/mol) and a root-mean-square deviation of 0.092 eV/atom (~9 kJ/mol). This accuracy is sufficient to use pySIPFENN for estimating formation enthalpies of phases or end-members.



Comparison of pySIPFENN forecast results with (a) OQMD and (b) experimental data

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CHEMICAL SEPARATION OF AMERICIUM AND CURIUM IN MOLTEN SALTS. THERMODYNAMIC MODELING

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Americium and curium are completely artificial elements. They are formed in reactors during the irradiation of nuclear fuel. They are highly radioactive, making their separation during spent nuclear fuel reprocessing a very complex problem, as they destroy almost everything—water, ion-exchange resins, and so on. Molten salts exhibit significant radiation resistance. Currently, the molten LiCl-KCl eutectic is most often used as a medium for reprocessing spent nuclear fuel.

In the molten LiCl-KCl eutectic, the most stable form of americium is $AmCl_2$, while curium is always trivalent - $CmCl_3$. Available literary data on their equilibrium potentials are collected in [1]. The potentials are so close (-2.87 ± 0.05 V vs. Cl_2/Cl-) that it is impossible to determine which is more positive and which more negative. The use of active cathodes shifts the deposition potentials of these metals by almost the same amount. Therefore, the feasibility of their electrochemical separation is questionable.

At the same time, the properties of di- and trivalent ions (Am^{2+} and Cm^{3+}) differ significantly. For example, if quartz wool is immersed in a melt of $(LiCl\text{-}KCl)_{eut.}$ + $AmCl_2$ + $CmCl_3$, americium will precipitate as a silicate, while curium will remain in the melt:

$AmCl_2 + 0.5SiO_2 = 0.333AmSiO_3 + 0.667AmCl_3 + 0.167Si$, ΔG = -86 kJ

$CmCl_3 + 1.25SiO_2 = 0.5Cm_2SiO_5 + 0.75SiCl_4(g)$, ΔG = +229 kJ

Instead of SiO_2, other oxides, TiO_2, SnO_2, can also be used:

$SnO_2 + 0.5AmCl_2 + 0.5Zn = 0.5AmSnO_3 + 0.5SnO + 0.5ZnCl_2$, ΔG = - 33.8 kJ

Another approach involves selectively precipitating curium with lithium nitride or oxide, while americium remains in the melt as $AmCl_2$ + $AmCl_3$. Other trivalent ions, U^{3+} and Pu^{3+}, are also precipitated along with curium.

$CmCl_3 + Li_3N = CmN\downarrow + 3LiCl(l)$, ΔG = -430 kJ

$CmCl_3 + 1.5Li_2O = 0.5Cm_2O_3\downarrow + 3LiCl(l)$, ΔG = -234 kJ (500 °C)

Thus, the work proposes a thermodynamic justification for several methods of separating americium and curium in LiCl-KCl melt using the difference in the chemical properties of Am^{2+} and Cm^{3+} ions.

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VERIFICATION OF THE ENTHALPIES OF FORMATION OF ORGANIC COMPOUNDS: A REFINEMENT STRATEGY BASED ON QUANTUM CHEMICAL CALCULATIONS

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Prediction and verification of thermochemical properties are central to assessing the feasibility, selectivity, and efficiency of chemical processes. In industrial practice, the majority of transformations occur in the liquid phase, making standard enthalpies of formation and entropies in the condensed state key parameters for reliable thermodynamic modeling. However, for complex and multifunctional organic compounds, the availability of consistent and experimentally validated data remains limited, which significantly constrains accurate process design.

Traditional estimation methods, such as group additivity approaches and structure–property correlations, often fail to provide sufficient accuracy for condensed systems and require extensive calibration against reliable datasets. At the same time, quantum chemical thermochemistry offers significant predictive capabilities, but widely used approaches – atomization methods and well balanced reaction schemes – suffer from systematic errors, dependence on reference compounds, and methodological ambiguity in reaction selection.

To address these challenges, a hybrid GAQCC (Group Additivity with Quantum Chemical Calibration) approach is proposed for the calculation and verification of gas-phase standard enthalpies of formation. The method is based on decomposition of molecular energy into two contributions: an additive term associated with transferable structural fragments and a non-additive term reflecting specific intramolecular effects, including conjugation, steric strain, and electronic interactions.

In contrast to conventional group contribution methods, the additive parameters are not purely empirical but are calibrated using high-level quantum chemical calculations (G3MP2) in combination with critically evaluated experimental thermochemical data. The quantum chemical calculations are primarily used to determine the non-additive contribution, which is significantly smaller than the total molecular energy and therefore less sensitive to residual methodological errors.

The proposed approach eliminates the need for constructing balanced reaction schemes, reduces systematic uncertainties, and ensures internal consistency of the results. As a consequence, GAQCC provides a robust and reproducible framework for validation, refinement, and extension of thermochemical databases, enabling more reliable thermodynamic analysis and design of chemical processes.

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METHOD FOR DETERMINING INFORMATIVE PARAMETERS IN NEURAL NETWORK MODELING OF CHEMICAL KINETICS

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The problem of approximating the temporal evolution of a hydrogen–oxygen mixture using a neural network is considered. A fully connected network with 5 layers and LeakyReLU activation was used, trained with Adam (lr = 0.01, 100 epochs) on MSE. Both the input and output of the neural network are vectors comprising the time step Δt, the system temperature, and the molar concentrations of 11 chemical species, with relevant parameter ranges: $T \in [250, 5000]$ K, $p \in [10^4, 2 \times 10^7]$ Pa, and $\Delta t \in [10^{-10}, 10^{-5}]$ s.

Analysis of the test trajectories revealed significant heterogeneity in the error. For the groups with minimal and maximal errors, the spectrum of the Jacobian of the original system was studied. It was found that the key difference is associated with the minimal eigenvalues: for well-approximated trajectories, $\lambda_{\min}$ is on the order of 10^4, while for poorly approximated ones, $\lambda_{\min}$ ranges from 10^{-2} to 10^1. Small $\lambda_{\min}$ values are caused by slow reactions (small k), low concentrations, and quasi-steady-state balancing of forward and reverse reactions. Therefore, the model error is determined by the regimes of the predicted profiles.

Based on this identified relationship, a modification of the loss function is proposed. In addition to the standard MSE term, an additional term is introduced that accounts for the discrepancy between predicted and true values of the logarithms of reaction rate constants, computed using the Arrhenius formula from the predicted temperature.

Comparison of different training variants shows: baseline model: MSE = 1.374×10^{-3}, STD = 2.183×10^{-2}; using all rate constants: MSE = 6.554×10^{-2}, STD = 8.211×10^{-2}; using the selected subset of constants associated with the formation of the slow modes of the system: MSE = 6.482×10^{-4}, STD = 9.308×10^{-3}.

It is shown that the inclusion of a physically informed term in the loss function is effective only with a targeted selection of reactions. Using all constants leads to a deterioration of model quality, whereas considering the reactions that determine slow modes results in more than a twofold reduction in error compared to the baseline approach.

Thus, spectral analysis of the Jacobian can serve as a tool for identifying informative kinetic parameters in neural network modeling of chemical kinetics.

The work was carried out within the framework on the topics FNEF-2024-0001 and FNEF-2024-0002.

EVALUATION OF THERMODYNAMIC PROPERTIES OF PALLADIUM AND NEODYMIUM INTERMETALLIC COMPOUNDS

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A pyrochemical process for reprocessing spent nuclear fuel (SNF) is currently being developed in the Russian Federation. One of the objectives is to create thermodynamic models for each stage of SNF reprocessing. Spent nuclear fuel has a complex composition, and reliable thermodynamic data are not available in the literature for all compounds, even the most important ones.

The aim of this study is to evaluate thermodynamic data on NdPd, $NdPd_3$, and Nd_3Pd_4 intermetallic compounds, which are formed during the electrolytic reduction of spent nuclear fuel. Accounting for these intermetallic compounds is important for the proper distribution of rare earth and noble metal flows.

The enthalpies of formation of NdPd and $NdPd_3$ are available in [1]. The enthalpy of formation of Nd_3Pd_4 was estimated as $\Delta H_f(Nd_3Pd_4) = 1.036 \cdot \Delta H_f(NdPd)$ based on the general trend of similar palladium alloys [2]. The entropy and heat capacity were estimated using the Neumann–Kopp rule. The heat capacity was approximated by the generally accepted equation:

$$C_p(T) = A + 10^{-3}BT + 10^5 CT^{-2}$$

The obtained data on the enthalpy of formation and entropy, as well as the coefficients of the heat capacity equation are given in the table.

Thermodynamic properties of Nd and Pd intermetallic compounds

Intermetallic compound	ΔH^0, kJ/g-atom	ΔH^0, kJ/mol	ΔS^0, J/(mol·K)	Coefficients of the equation		
				A	*B*	*C*
NdPd	-77.2 [1]	-154.4	108.91	38.942	32.709	4.479
$NdPd_3$	-73.3 [1]	-293.2	184.56	87.5	44.263	4.479
Nd_3Pd_4	-80.0	-560	364.55	141.106	103.905	14.437

The data obtained are used in thermodynamic modeling of processes for the pyrochemical technology being developed for spent nuclear fuel reprocessing.

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THERMODYNAMIC ASPECTS OF SYNTHESIZING, ANALYZING AND PREDICTING THE PROPERTIES OF NOVEL MATERIALS

ТЕРМОДИНАМИЧЕСКИЕ АСПЕКТЫ СОЗДАНИЯ НОВЫХ МАТЕРИАЛОВ, АНАЛИЗА И ПРОГНОЗИРОВАНИЯ ИХ СВОЙСТВ

THERMODYNAMIC ASPECTS OF PIEZOPHOTOCATALYSIS AND DESIGN OF PIEZOPHOTOCATALYTIC MATERIALS

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In the report it will be discussed a new rapidly developing area that has shown its effectiveness in increasing the photocatalytic activity of oxide materials – using the piezoelectric properties of oxides and achieving a synergy of light and mechanical effects to enhance catalytic activity.

An overview of both the history of the development of the research area and the results of recent years for various classes of materials will be presented.

The approach to increasing photocatalytic activity is based on the introduction of an external field to reduce carrier recombination and accelerate their separation and migration [1,2]. In this case, the use of photoactive ferroelectric semiconductors opens the way for synergetic catalysis – piezophotocatalysis.

The report focuses on thermodynamic criteria for the possibility of photo– and piezophoto-catalytic processes of oxidation of organic pollutants in water and the production of hydrogen from water and aqueous solutions of organic substances including plant biomass derivatives.

Thermodynamic criteria use data on the band structure of a semiconductor oxide and data on the reduction potentials of semi-reactions involving ions and radicals participated in the photocatalytic process as a whole.

The main attention will be devoted to the prospects of perovskite-like materials, most of which contain bismuth cations, for piezophotocatalysis. As an example will be considered the Aurivillius phase of Bi_3NbTiO_9 and the results of testing their piezophotocatalytic activity under simultaneous exposure of light and ultrasound. It is shown how an internal piezoelectric field, suppressing the rapid recombination of charge carriers, activates additional pathways for the formation of superoxide anion radicals that are inaccessible under photocatalytic conditions, resulting in a pronounced synergistic effect when exposed to light and ultrasound simultaneously.

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INVESTIGATION OF THE THERMODYNAMIC STABILITY OF ULTRASTABLE GLASSES BY SOLUTION CALORIMETRY AND DSC

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An ultrastable glass is a nonequilibrium amorphous state of matter corresponding to a deep minimum on the potential energy landscape [1] and therefore exhibiting anomalously high thermodynamic stability. Quantitative assessment of this stability still relies mainly on an indirect parameter, the fictive temperature (T_f), determined by differential scanning calorimetry (DSC) [2].

In the present work, a direct approach to determining the relative thermodynamic stability of glasses at 298.15 K is proposed and experimentally implemented.

1,3,5-Tris(α-naphthyl)benzene and N,N′-diphenyl-N,N′-bis(3-methylphenyl)benzidine were selected as model compounds. The glasses were prepared by slow physical vapor deposition onto substrates held at controlled temperature and by rapid quenching of the melt.

The relative thermodynamic stability was evaluated as the difference in Gibbs free energy between the glassy states at $T_0 = 298.15$ K using the Gibbs equation. The experimental ΔH values were obtained from solution calorimetry in benzene. In addition, these results were compared with estimates based on the Kirchhoff relation. The entropy difference, ΔS, was evaluated analogously using the fictive temperature.

$$\Delta_{g,II}^{g,I}H = \Delta_{g,I}^{l}H - \Delta_{g,II}^{l}H = \Delta^{soln}_{g,I}H - \Delta^{soln}_{g,II}H = \int_{T_f(I)}^{T_0} \Delta_g^l C_{p,m} dT - \int_{T_f(II)}^{T_0} \Delta_g^l C_{p,m} dT$$

Here, ΔH is the enthalpy change, $\Delta C_{p,m}$ is the change in isobaric heat capacity, $T_0 = 298.15$ K, and (T_f) is the fictive temperature. The subscript (l) refers to the liquid, (g, II) to the vapor-deposited glass, (g, I) to the melt-quenched glass, and (soln) to the infinitely dilute solution.

A method is proposed that, for the first time, enables a quantitative comparison of the thermodynamic stability of glasses prepared by different methods at a fixed temperature. The crystallization behavior of the glasses was also studied and correlated with their structural and thermodynamic parameters.

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THERMODYNAMICS OF GUEST INCLUSION BY POLYMORPHS OF NATIVE CYCLODEXTRINS

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Cyclodextrins (CDs) are applied to encapsulate drugs, food additives, dyes, essential oils and many other target guests used in various applications. Typically, such encapsulation is performed in solid mixtures, slurries or paste-like systems where there is not enough water to fully dissolve cyclodextrin and guest. Such systems require a different approach than the classical CDs' complexation in aqueous solutions.

The key feature of guest inclusion in solid state is phase transition from solid CD to solid inclusion compound. This process involves a complex interplay between the size exclusion effect for guest inclusion, the cooperative activation of this process by a third component such as water (or organic solvent) additive, and the competition between the guest and water for the space inside CD cavity. As an additional factor, the newly discovered polymorphism of natural CDs can be used [1]. All these processes can be analyzed using classical thermodynamics.

To make a fair comparison of solid state and solution processes, they were analyzed using a thermodynamic activity scale [2]. This approach allowed us to estimate the quantitative contribution of the hydrophobic effect and other important factors affecting the stability of complexes, such as the shape of guest molecules, H-bonding, and repulsion of «high-energy» water molecules.

Fast scanning calorimetry (FSC) is state-of-the-art method which allowed to find the melting points and enthalpies for the natural CDs [1]. The obtaining of such data is possible due to extremely high heating rates up to 2,400,000 K/min, enabling a study of processes that are 'hidden' for the conventional methods of thermal analysis. Such data are essential for understanding structure-property relationships; for calculations on the energy of the crystal lattice for CD polymorphs, which has a crucial effect on inclusion properties; for evaluation of the temperature limits during modification of drug complexes by fast heating and cooling. Such data also give the innovative possibility to determine thermodynamic parameters of CDs liquid state which is essential for the understanding and the molecular modeling of guest inclusion by CDs.

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FORMATION THERMODYNAMICS FOR IPRONIAZID MULTICOMPONENT CRYSTALS WITH DIHYDROXYBENZOIC ACIDS

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The rational design of pharmaceutical multicomponent crystals has emerged as a key strategy for tailoring the physicochemical properties of drug substances without compromising their therapeutic efficacy. While structural characterization provides essential insights into molecular recognition patterns, a fundamental understanding of formation thermodynamics (Gibbs energy, enthalpy, and entropy) is crucial for predicting stability and guiding the selection of optimal solid forms for pharmaceutical development. This work focuses on the quantitative thermodynamic characterization of five iproniazid multicomponent crystals with 2,3-, 2,5-, 2,6-, 3,4-, and 3,5-dihydroxybenzoic acids.

The Gibbs energy of formation (ΔG_f) for the studied multicomponent crystals was determined using a solubility-based method in acetonitrile within the temperature range of 20 to 40 °C, which directly probes the equilibrium between the solid phase and the solution. The negative values of ΔG_f confirm that the formation of all investigated systems is a spontaneous process, ensuring their thermodynamic stability relative to the pure components. The temperature dependence of the solubility products allowed for the calculation of the enthalpies and entropies of formation. The results reveal that the process of multicomponent crystal formation between iproniazid and dihydroxybenzoic acids is primarily enthalpy-driven, indicating the dominant role of strong intermolecular interactions, such as hydrogen bonding, in the stabilization of the crystal lattice.

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THERMODYNAMIC AND ELECTRONIC FACTORS GOVERNING STABILITY OF CYCLOTRIPHOSPHAZENES

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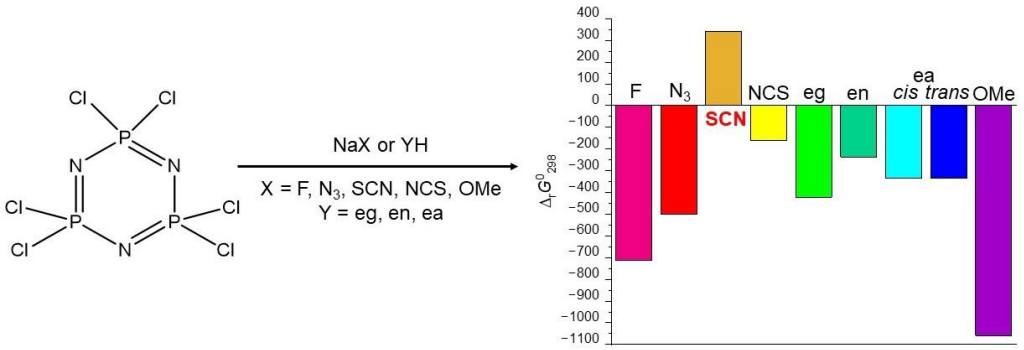
Cyclotriphosphazenes ($N_3P_3X_6$) represent a versatile class of phosphorus–nitrogen heterocycles whose remarkable chemical stability and tunable electronic properties make them promising building blocks for advanced functional materials[1, 2]. However, the fundamental origin of their stability and the role of substituents in controlling their thermodynamic and electronic behavior remain insufficiently understood.

DFT calculations were performed to show that ring formation is strongly exergonic, whereas substitution reactions are enthalpy-controlled and substituent-dependent. Notably, SCN derivatives are thermodynamically unfavorable, while NCS analogues remain stable (see figure).



Thermodynamics of Cyclotriphosphazenes Substitution;
eg is ethylene glycol; en is ethylenediamine; ea is 2-aminoethanol

Despite substituent variation, the P_3N_3 framework remains structurally invariant, with constant P–N bond lengths and polarized closed-shell interactions (QTAIM). In contrast, P–X bonding varies significantly, reflecting substituent-dependent polarity.

Overall, the obtained results establish a thermodynamic framework for understanding and predicting the behavior of cyclotriphosphazenes. The combination of calculated reaction energetics and electronic structure descriptors enables rational assessment of substituent effects on both stability and reactivity. In particular, the revealed polarization-driven stabilization of the P_3N_3 ring provides a unifying explanation for its exceptional robustness and substituent tolerance. These findings demonstrate that targeted modification of substituents can be employed as an effective strategy for tuning thermodynamic properties and guiding the design of phosphazene-based functional materials with predictable performance.

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INFLUENCE OF MOLECULAR SYMMETRY ON THE ENERGY OF VAPORIZATION OF ETHYLENE GLYCOL ETHERS AND C_1–C_{10} ALCOHOLS

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Ethers of ethylene glycol and C_1-C_{10} alcohols of various structures have found wide application in modern high-tech industries: they are employed in absorption processes for the purification of natural gases from acidic impurities; they are used as components of hydraulic and brake fluids; and they serve as effective co-solvents and transdermal conductors in pharmaceuticals and cosmetology.

Such a wide range of applications for representatives of this series of compounds is due to their high thermodynamic stability and low volatility, as well as the possibility of varying other physicochemical properties through targeted modeling of the chemical structure when creating symmetrical or asymmetrical ethers.

The determining parameter for considering the applicability of ethylene glycol ethers in a particular area is the enthalpy of evaporation, on the basis of which it is possible to evaluate intermolecular interactions in organic liquids or thermodynamic compatibility with materials for various purposes.

The diversity of ethylene glycol ethers (both symmetrical and asymmetrical in nature) imposes experimental limitations on the determination of the enthalpy of vaporization values by direct or indirect methods (mass transfer, ebulliometry, etc.) due to the labor-intensive nature of the synthesis and isolation of compounds.

As alternative approaches in world practice, empirical correlation dependencies of the enthalpy of evaporation on chromatographic retention parameters or physical/structural quantities (boiling temperatures, enthalpies of solution, number of homologous elements, etc.) are used, as well as high-level quantum-chemical calculations based on gas-phase enthalpies of formation.

This paper validates available literature data on the enthalpies of vaporization of ethylene glycol ethers and C_1-C_{10} alcohols of varying structure and symmetry. Correlations between the enthalpies of vaporization and the above-mentioned arguments (in the form of structural or thermophysical parameters) are demonstrated for a wide range of ethers. The obtained values are compared with those obtained through quantum-chemical calculations. An array of enthalpy of vaporization values is proposed and substantiated for a number of the ethers considered.

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STANDARD REFERENCE MATERIALS OF THE MELTING POINT OF PURE ORGANIC SUBSTANCES IN THE RANGE FROM +40 TO +250 °C

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VNIIM has completed development and type approval of the sets of certified reference materials (CRMs) for phase transition temperatures in the range of +40 to +250 °C: 1st GSO 12820/12822-2025 and 2nd GSO 13150/13152-2025. The sets comprising several types of melting point CRMs based on high-purity organic substances: benzophenone, benzoic acid, caffeine (1st set) and acetanilide, biphenyl, benzoguanamine (2nd set).

Development of the new set of CRMs was necessary due to solve several issues with the current tools and procedures used for of melting point measurement of organic materials. Current state revealed the absence of a unified approach to determine the metrological characteristics of measuring instruments, including procedures for their verification and calibration. This issue appears from different interpretation of the melting temperature definition as a thermodynamic property of a substance when using different measurement methods. Significant discrepancies in experimental data obtained by various techniques (particularly at different heating rates) were also noted, along with difficulties in interpreting both the obtained data and the observed discrepancies.

These factors adversely affect measurement uniformity in this field. Consequently, a novel approach was implemented in the development of the CRMs, anticipated to reduce the effects of these shortcomings.

The certified value of the developed CRMs was determined through direct measurements using the State Working Standard of Temperature (Grade 2) in the range of +40 °C to +250 °C (3.1.ZZB.0453.2024), in accordance with Part 2 of the State Verification Scheme for Temperature Measuring Instruments. The standard setup consists of two precision thermometric systems: one implementing the melting process in a custom-designed cell under constant heat flux, and the other using a dry-block thermostat with direct contact between the temperature sensor and the substance.

In the author's opinion a generalized method- and instrument-independent definition of melting point should be used, described as the temperature at which thermodynamic equilibrium between the solid and liquid phases of a substance can be achieved, provided that the liquid phase retains its initial composition and the amount of solid-phase crystals tends to zero.

The certified property of the CRMs is a melting point. It was determined as the temperature corresponding to the local minimum of the first derivative (or the point where the second derivative changes sign) within the two-phase region (melting plateau) when the liquid fraction is getting closer to 1.

The experiments were conducted under near-equilibrium conditions, with a heating rate in the range (0.2 – 1.0) °C/min, and temperature measurements were performed using a temperature sensor in direct contact with the substance (traceable to ITS-90).

ENERGY THEORY OF SCROLLING: A TOOL FOR LAYERED COMPOUND MORPHOLOGY FORECAST

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Recently, increased attention has been paid to the scrolling of crystalline layers of varying chemical compositions, which occurs due to internal or external factors, as well as a combination of both. Unlike the more widely known nanotubes, the scrolled nature of the layer allows for extensive morphological modification: scrolling at various angles, scrolling with a variable radius of curvature, and response to changing external conditions. Partial loss of translational symmetry by the layer are also of fundamental interest in connection with the applicability, in this case, of the classical definition of the thermodynamic phase of matter.

Despite the wide diversity of compositions and structures, the class of nanoscrolls is currently presented in the literature more as a collection of disparate studies than as a unified whole. In this regard, the first part of the report formulates the fundamental equations of the energy theory of scrolling and attempts to apply them (at a qualitative level) to various currently known cases of scrolls formation from graphene, C_3N_4, MXenes, chalcogenides, oxides, layered double hydroxides, and other compounds. The second part focuses on the objects fundamental to this theory – phyllosilicates [1,2]. The following cases are considered:

– Correlation of the energy effect of scrolling and Calvet calorimetry data for $Mg_3Si_2O_5(OH)_4$ with the chrysotile structure;
– Isovalent and heterovalent substitution in the structure of phyllosilicates as a method for controlling morphology;
– Comparison of the energetic and thermodynamic factors of the formation of the distribution of substituting cations over a layer of variable curvature;
– Prediction of the scrolling potential and dimensional characteristics of nanoscrolls of 2:1 layered silicates (with talc and montmorillonite structures).

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SYNTHESIS OF AlBiZnSnGa ALLOYS AND STUDY OF THEIR PROPERTIES

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Alloys consisting of elements with a low melting point play an essential role in the development of next-generation low-temperature fusion technologies in microelectronics. This group of alloys, for the most part, are lead-free solders. Currently, publications have appeared on the production of wind turbines from low-melting elements [1]. In such alloys, a major role is played not by hardness or wear resistance, but by resistance to fatigue loads, plasticity, and adhesion to other metallic materials.

In the present work, the synthesis of the AlBiZnSnGa alloy is carried out, where the gallium content was 2 at.%, and the remaining components were taken in an equiatomic ratio (24.5 at.% each). When studying the microstructure of this sample, pronounced needle-like phases are found in the alloy structure. The microhardness of the alloy averages 34.747 kg/mm². According to the XRD results, the main component of the alloy is Bi (33.4 wt.%). The content of tin and zinc is approximately the same: 20.9 and 20.1 wt.%, respectively. The aluminum content is 8.4 wt.%, gallium – 0.8 wt.%. In addition to pure metals, the intermetallic compound AlSn (3.0%) and the oxides Sn_3O_4 (4.0%), SnO_2 (4.4%) and ZnO (5.0%) are formed.

Simultaneous thermal analysis (STA) was performed in an argon medium in the temperature range of 20–700°C, with a heating and subsequent cooling rate of 10 K/min, in Al_2O_3 crucibles. On the DSC heating curve, the beginning of melting of the sample is characterized by an endothermic peak at 123°C. At a temperature of 140°C, the melting of more refractory compounds begins. The crystallization of the alloy begins at a temperature of 129°C. Several endothermic and exothermic peaks are observed on the heating and crystallization curves, the presence of which may be due to the formation of phases and the occurrence of eutectic, peritectic or monotectic reactions. The change in the mass of the sample during the study was 0.15%. The results of the analysis allow us to conclude that the melting point of the resulting alloy is significantly lower than that of all the initial components, except gallium.

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STABILITY FIELD OF ENTHALPICALLY STABILIZED COMPOUNDS OF VARIABLE COMPOSITION WITH PYROCHLORE STRUCTURE IN THE Bi_2O_3–Fe_2O_3–WO_3–(H_2O) SYSTEM

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When using the hydrothermal synthesis method, the stabilization of the crystalline phase occurs at low temperatures (100 – 200 °C), which means that it is primarily due to the enthalpic contribution to the change in Gibbs energy ($\Delta G = \Delta H - T\Delta S$), while the influence of the entropic term is minimized.

Compounds of variable composition with pyrochlore structure in the Bi_2O_3–Fe_2O_3–WO_3 system, obtained under hydrothermal conditions (T = 90 – 200 °C, $P \leq 7$ MPa), are enthalpically stabilized phases [1], since they are unstable at temperatures above ~725 °C [2]. The study of these compounds is of particular interest because their properties may reveal features that are not typical of compounds in which the entropy factor plays a significant role in the change in Gibbs free energy.

In this work, the concentration limits of the stability field of $(Bi_zVac_{2-z})(Fe_{2-y}W_y)O_6O`_\delta$ compounds (where Vac is a cation vacancy) with pyrochlore structure (T = 200 °C and P ~ 7 MPa: $0.60 \leq z \leq 1.35$; $1.32 \leq y \leq 1.96$; δ ~ 1) were determined and it was shown that they are several times higher than those for pyrochlore phases obtained in most other oxide systems using the solid-phase synthesis method.

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MODELING OF ELECTRIC DOUBLE LAYER ON A METAL-ELECTROLYTE INTERFACE IN THE FRAMEWORK OF SELF-CONSISTENT FIELD THEORY

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Modeling the electrical double layer at a metal electrode–electrolyte interface remains a fundamental challenge due to the coupled electrostatic, steric, and chemical interactions operating across different length scales. We present a self-consistent field theory incorporating key physical components neglected in classical models: short-range specific interactions, ion hydration, dielectric saturation of the solvent, and excluded volume effects. By solving a modified Poisson–Boltzmann equation derived from the grand thermodynamic potential, with parameters informed by quantum chemistry calculations, we accurately reproduce the differential capacitance of aqueous electrolytes at silver electrodes. The approach was first validated on the Ag(100) face for systems without specific adsorption (KPF_6, $NaClO_4$) [1], then extended to account for specific adsorption and partial charge transfer in the Ag(100)/NaF system [2]. A Morse potential for adsorption energy and explicit charge transfer yielded fitted parameters in good agreement with quantum chemical and ab initio molecular dynamics estimates. We further apply the model to Ag(111) and Ag(110) faces in NaF electrolyte, obtaining face-dependent adsorption energies, potential range parameters, and partial charge transfer coefficients that reveal how ion–surface and water–surface interactions vary with surface structure. These results explain the experimentally observed ordering of fluoride adsorption strength across the three low-index silver faces and establish a pathway for incorporating electrode crystallography into continuum EDL modelling, with direct applications in supercapacitors and electrochemical energy storage.

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MIXED ADSORPTION LAYERS OF CHITOSAN AND COLLAGEN

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Collagen and chitosan are promising materials because of their unique biological and manufacturing properties. Chitosan can affect the self-assembly process of collagen through electrostatic interactions. Chemical crosslinking provides new opportunities for obtaining biodegradable materials with well-defined microarchitecture and mechanical properties. In this work we apply this approach based on the simultaneous use of chitosan, collagen type I, and glutaraldehyde (GA) as a cross-linker for obtaining thin layers at the air–water interface with controlled morphology. The properties of the layers were studied using the oscillation ring method, ellipsometry, and atomic force microscopy (AFM). The properties of the composite films strongly depend on the ratio between components, pH, and the presence of the cross-linker. At pH 2, both chitosan and collagen possess a positive charge and almost do not interact. The dynamic surface elasticity, dynamic surface tension, and the adsorbed amount for the mixed systems change from the values typical for one component to those typical for the other, regardless of the presence or absence of GA. However, AFM images demonstrate various types of morphology and a significant impact of GA on the layer structure. When chitosan dominates, one can see numerous islands consisting of short rods. They can transform into a coral-like structure with a clearly noticeable center of growth under the influence of GA. When the main component is collagen, numerous dots are observed. At a ratio of 1:1, the surface layer consists of aggregates of complex shape, which turn into a structure resembling roof tiles when GA is added.

At pH 6, both chitosan and collagen separately demonstrate relatively weak surface activity. However, the complexes of collagen and chitosan show a significant surface activity. At a ratio of 1:1, the dynamic surface tension reaches about 57 mN/m at equilibrium, as compared to 71 and 70 mN/m for pure chitosan and collagen, respectively. The dynamic surface elasticity of the mixtures is in between the values for pure components and ranges from 20 to 30 mN/m, depending on the component ratio. GA addition at a concentration of 0.2 mg/ml results in a significant increase in the dynamic surface elasticity, up to 200 mN/m, and thge film thickness, up to 30 nm. On the basis of AFM data, we can expect the formation of a continuous structure where both components are connected into a single network. Probably the elementary building blocks of this network are the collagen microfibrils, which were observed for collagen–chitosan mixtures without GA. It can be suggested that the addition of the cross-linker allows the formation of a chitosan shell on the surface of the fibrils, connects them, and thus improves the mechanical properties of the adsorption layer.

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THE ESTIMATION OF Ni-BASED SUPERALLOYS THERMODYNAMIC CHARACTERISTICS

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This paper presents the results of a thermodynamic calculation of the structural and phase characteristics of VZhM1 (generation III), VZhM4 (generation IV) and VZhM8 (generation V) alloys. The lattice parameters of the γ and γ' phases, the γ' solvus temperature, the interfacial energy at the γ/γ' phase boundary and the antiphase boundary energy were determined.

Negative misfit ($a\gamma > a\gamma'$) contributes to an increase in creep resistance. It is shown that the VZhM8 alloy exhibits the highest negative misfit (−0.27% at 20 °C and −0.41% at 1200 °C), while the VZhM1 alloy has a positive misfit (0.07% at 20 °C and 0.14% at 1200 °C), which is due to the absence of ruthenium in its composition. The γ'-solvus temperature is a critical parameter for thermal stability. The highest γ'-solvus temperature (1322 °C) is observed in the VZhM8 alloy due to its high ruthenium content (6%) and optimal balance of W (4.2%) and Ta (6%). VZhM1 and VZhM4 have similar γ'-solvus temperatures (1299.3 and 1294.5 °C, respectively).

The interfacial energy at the γ/γ' boundary determines the morphology of γ' particles: low energy promotes uniform particle distribution, increasing the alloy's strength. The lowest interfacial energy at the γ/γ' boundary at 1200 °C was found in the VZhM4 alloy and is 32.8 mJ/m². In the VZhM1 and VZhM8 alloys, the interfacial energies are 37.1 and 37.7 mJ/m², respectively.

The antiphase boundary energy affects the microstructure's resistance to degradation. The highest energy value was observed in the VZhM1 alloy (238.9 mJ/m² at 1200 °C), while in the VZhM4 and VZhM8 alloys it was lower (200.3 and 203.6 mJ/m²), which is due to the ruthenium content.

An analysis of the dependence of the calculated values of the structural-phase characteristics on the alloy composition showed that rhenium, tantalum, and tungsten increase the γ'-solvus temperature, slowing down atomic diffusion and stabilizing the γ'-phase; chromium and cobalt reduce thermal stability by reducing the solubility of aluminum in the γ'-phase; Ruthenium, when present in the alloy at a content of up to 6-7%, increases the γ'-solvus temperature, but when present in excess, causes lattice distortions, worsening the properties.

TOWARDS UNDERSTANDING THE IMPACT OF SURFACE MATERIAL PROPERTIES ON CONFINED IL BEHAVIOR

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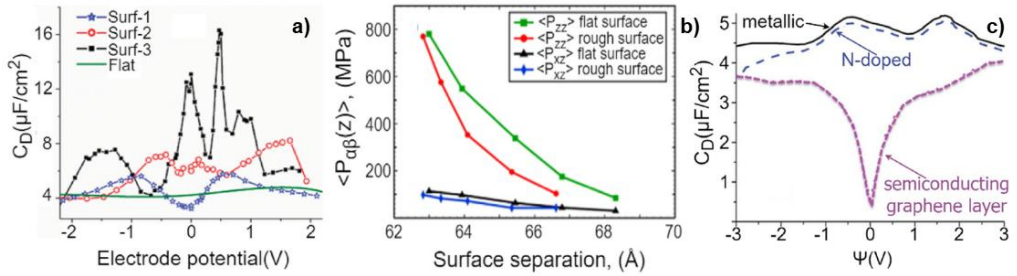
Recent advancements in ionic liquid (IL) research are driven by their application as electrolytes in various technological applications due to their specific and tunable properties. Special attention is attributed to IL behavior in the confinement because of phenomena such as overscreening and the superionic state. To understand the mechanisms governing confined IL behavior, current research mainly examines the role of IL properties, while the impact of confining material properties is not less important.

We have analyzed recent theoretical and simulation findings, which reveal the contribution of substrate material properties and suggest possible extensions required to improve our understanding in this field (see Figure). Particularly, we cover the impact of surface morphology and multiscale nanoporous geometry on the capacitance properties of confined IL and ion diffusion. Then we provide a literature background on mechanical properties and deformation for the system of confined IL between two surfaces. Additionally, we addressed the influence of confining material chemical composition on confined IL properties, covering ionophobicity, polarizability, and quantum capacitance issues [1]. Overall, this work emphasizes the critical role of surface material properties in confined IL research and identifies key gaps for future investigation.



a) Differential capacitance variation near electrodes with different structures, b) Stress tensor components for flat and rough confinement, c) the impact of the chemical composition of the confining surface on the differential capacitance profile

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MODELING STRUCTURE AND PROPERTIES OF DOPED MANGANITES

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The search for new compositions and design of complex oxide materials is an attractive scientific area with enormous opportunities and potential for technological applications. In this framework, crystalline solids contribute many branches, such as energy, superconductors, electronics, catalysis, medicine, and others. Nowadays, studies are greatly assisted by computational and data-driven approaches for accelerating new materials discovery and searching for composition–structure–property relations. Particular attention is paid to the strategies that aim to predict new stable and metastable crystalline materials. To achieve this goal, different heuristics comprising the density functional theory (DFT) calculations and high-throughput screenings of modern data collections were developed. Moreover, such combinations of methods provided reliable information on the processes in solids, such as ionic transport and deintercalation and synthesis condition effects.

REE manganites contribute significantly to the current demand for high-performance functional materials. Such phenomena as colossal magnetoresistance and magnetocaloric effects have also been discovered in them. To speed up the the design of optimal compositions, comprehensive studies of the production methods, phase compositions, structure, and properties of compounds known from the literature have been conducted. However, to date, very few compositions have been comprehensively studied, and for those that have been studied, experimental data are presented in various forms, creating difficulties in processing.

Fortunately, the possible space groups and unit sell parameters corresponding to the manganite structures have been determined, and experimental preparation of compounds using various methods is possible to verify the calculated data. Existing evolutionary algorithms are, in principle, capable of varying the chemical composition, creating new compounds/phases, and choosing the most promising candidates based on the energy landscape exploration. In practice, their computational cost is low enough to enable comprehensive modeling of the complex oxides.

In this work we developed and applied the hybrid DFT/data-driven approach for searching for new stable doped lanthanum manganite. Theoretical predictions of new stable complex oxides, their structural properties, and compositions were made and the theoretical predictions were tested experimentally. This model will allow the possibility of predicting the structure and properties to be extended to a wide range of perovskite-like materials.

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LIQUID CRYSTALS. PROPERTY ESTIMATION

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At present more than 100,000 compounds forming mesophases are synthesized [1]. However, for the majority of them (~98 %) only temperatures and enthalpies of phase transitions are known. To enlarge of industrial application areas, it is necessary to have a complete set of data on physical and thermodynamic properties of individual mesogens and mixtures [2]. For property evaluation, a scheme based on the minimum experimental information (molecular structure) is used. The normal boiling temperature is selected as the key property. Applicability of the group-contribution methods has been first tested on p-substituted "model substances", (i.e. compounds having a structure typical for calamitic mesogens, for which a set of physical properties had been well studied). Methods, that gave the minimum difference between the estimated and experimental data, have been tested on liquid crystalline substances. Scheme for the estimation of density, surface tension, thermodynamic properties in mesophase and in isotropic state, is proposed. Precision is enough for engineering calculations. Existing prediction methods for temperatures and enthalpies of phase transitions are analyzed. Different correlation dependencies have been tested on a large volume of experimental data from [3].

It is also demonstrated applicability of the group-contribution methods for mixture properties estimations. It is possible to calculate physical properties for mixtures and phase diagrams of binary and ternary systems containing liquid crystals basing on the activities of components (the UNIFAC-Dortmund method).

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DYNAMIC SURFACE PROPERTIES OF SILK FIBROIN FIBRILS

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Due to the formation of stable and durable interfacial films silk fibroin can be considered as an alternative to many traditional emulsifiers and surface modification agents in various branches of industry, from pharmacy to cosmetic industry [1]. Propensity of this protein to form different types of aggregates may expand the diversity of 2D fibroin-based materials. The influence of self-assembled structures of native silk fibroin, amyloid-like fibrils obtained by thermal treatment of native protein solution and their composites on dynamic surface properties was studied in this work. The difference in the behavior of silk fibroin in different forms at the air-water interface was determined using a combination of dilatation surface rheology, ellipsometry, and atomic force microscopy.

The high dynamic surface elasticity of native silk fibroin solutions (>220 mN/m) is due to the formation of a thick, dense, interconnected network at the interface. The properties of adsorbed and spread layers of silk fibroin fibrils differ significantly from those of the native protein and turns out to be similar to the amyloid fibrils of globular proteins. For fibril dispersions purified from unreacted molecules, the dynamic surface elasticity can reach only 140 mN/m due to the presence of a thin layer (7-15 nm) of intertwined aggregates on the surface, which do not form a continuous network.

In mixed systems, silk fibroin fibrils prevent the formation of supramolecular structures in the surface layer. Neither the adsorption of unreacted protein molecules in the unpurified fibril dispersion nor the addition of fibroin to a preformed fibril layer results in the formation of films with mechanical properties similar to native fibroin. Thus, the fibroin fibrils act as structural modifiers that suppress the interfacial self-organization of fibroin molecules, leading to thinner, less resilient but stable surface layers. Controlling the properties of the surface layer by combining different forms of fibroin at the interface may allow the creation of functional materials with desired properties.

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CRYSTALLIZATION BEHAVIOR OF Fe-Ni-B-Nb AND Fe-Ni-B-Si-Nb AMORPHOUS ALLOYS WITH DIFFERENT COMPONENT RATIOS

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Fe-Ni-B-Nb and Fe-Ni-B-Si-Nb alloys in a disordered condensed state (in the form of amorphous ribbons and bulk amorphous rods) have been actively studied in recent years due to their unique electrical and magnetic properties. Such alloys in an amorphous state are beginning to be used as promising materials in industry. In this work, the crystallization of amorphous Fe-Ni-B-Nb and Fe-Ni-B-Si-Nb alloys with different component contents is investigated for the first time.

Fe-Ni-B-Nb and Fe-Ni-B-Si-Nb alloys were obtained in the form of ribbons with a width of 2-3 mm and a thickness of up to 45 μm by spinning (planar flow casting) method in a protective argon atmosphere. Crystallization processes were studied using differential scanning calorimetry (DSC) at various heating rates and X-ray diffraction.

Based on the results of diffraction experiments with Fe-Ni-B-Nb and Fe-Ni-B-Si-Nb ribbons, it was established that all obtained samples are X-ray amorphous. It has been shown that the crystallization processes of amorphous Fe-Ni-B-Nb and Fe-Ni-B-Si-Nb alloys are multistage (1-3 crystallization stages depending on the alloy composition). Based on the DSC data, the activation energy of the various crystallization stages was calculated using the Kissinger method, and the kinetic parameters and Avrami index were determined using the Kolmogorov-Jones-Mehl-Avrami (KJMA) model in the variant for non-isothermal crystallization. It is shown that after the first stage of crystallization of amorphous Fe-Ni-B-Nb and Fe-Ni-B-Si-Nb alloys, the main phase is the metastable $(Fe,Ni)_{23}B_6$ phase with partial replacement of iron and nickel atoms by niobium atoms.

The obtained results can be used for further research into the physical and chemical properties of amorphous and partially crystallized Fe-Ni-B-Nb and Fe-Ni-B-Si-Nb alloys, as well as for their practical application in industry.

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THERMODYNAMICS OF LITHIUM INTERCALATION INTO GRAPHITE NANOFLAKES

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Carbon nanostructures are widely used as electrode materials for energy storage and accumulation devices. Graphene, a single layer of sp^2-hybridized carbon atoms, is one of the most promising carbon allotropes. Various approaches have been developed to improve the performance of graphene-based materials. In particular, the introduction of heteroatoms into their composition alters their electrochemical properties [2]. In the present study, N-, P-doped graphene nanoflakes (GNFs) were obtained.

Electrode charge-discharge processes, involving the transformation of chemical compounds into others, entail changes in thermodynamic functions: the free Gibbs energy ΔG, entropy ΔS, and enthalpy ΔH. Knowledge of these parameters allows for the prediction of electrochemical processes occurring in the system [3]. However, the thermodynamics of lithium intercalation into the GNFs structure have not been addressed in the literature.

In this study, we analyzed the thermodynamic functions of lithium intercalation into the -N, -P structures of GNF in a 1 M $LiPF_6$ solution in a 1:1 mixture of ethylene carbonate and diethylene carbonate, EC + DEC. The measurements were carried out in coin-cells using galvanostatic intermittent titration technique and OCV measurements in the temperature range of 20-50°C. The parameters were evaluated using known equations [3]:

$$\Delta G = -nFE_{OCV},$$
$$\Delta S = -nF\frac{\partial E_{OCV}}{\partial T}.$$

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PHYSICAL PROPERTIES OF Fe-Ni-B-Si-Nb ALLOYS IN CRYSTALLINE, LIQUID AND AMORPHOUS STATES

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Bulk metallic glasses (BMG) are the objects with unique magnetic, mechanical, and anticorrosive properties. They significantly exceed crystalline analogues and can be used in chemically aggressive environments and in difficult climatic conditions. For example, iron-based metallic glasses have excellent soft magnetic characteristics (the saturation induction reaches B_{max} = 1 T at a coercive force H_c = 1 A/m; for the same alloys in crystalline state B_{max} = 0.2 T at H_c > 100 A/m). In addition, these BMGs are characterized by ultra-high values of fracture resistance at the level of 4250-4450 MPa and plastic deformation of 0.6-1.3% (for crystalline analogs, these parameters are 4-5 times lower). However, the widespread use of BMG is limited by the instability of the amorphous state, which can crystallize under certain external influences.

In this paper we studied temperature dependences of physical properties (density, viscosity, electrical resistivity and magnetic susceptibility) of Fe-Ni-B-Si-Nb alloys, and investigated the influence of chemical composition and regimes of melts preparation for quenching on properties and stability of the alloys in amorphous state. Some parameters of electronic structure of the alloy were calculated from the experimental data: the effective magnetic moment per atom μ_{eff}, the paramagnetic Curie temperature θ and the density of electron states at Fermi level $N(E_F)$.

The combination of the obtained data on volumetric (density and viscosity) and electronic (electrical resistivity and magnetic susceptibility) characteristics, as well as the discovered temperature ranges in which anomalies in density and electrical resistivity curves for iron-based melts were observed, became the basis for the creation of several regimes for melts heat treatment before amorphization. It was established, in particular, that crystallization occurs in one or two stages depending on chemical composition of the sample. The decreasing of nickel content in the samples increases both the crystallization onset temperature and the peak temperature of the second stage. An increase in boron content has a similar effect, i.e. the most stable amorphous state was in the sample containing 20 at.% boron. However, this sample has the lowest Curie temperature.

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THERMODYNAMIC OPTIMIZATION OF THE UN-PuN-Fe SYSTEM

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Operational safety is the foremost criterion in the design of nuclear power plants (NPPs). Modern NPPs employ a defense-in-depth strategy aimed at preventing the release of radioactive material into the environment. An indispensable step in the safety assessment of any NPP is the simulation of accident scenarios, including severe accident sequences involving core meltdown, and the development of measures for managing and mitigating the consequences of hypothetical severe accidents. Knowledge of high-temperature material properties and phase equilibria among the constituent phases plays a central role in the modelling and prediction of severe accident scenarios in nuclear reactors.

The challenge of incorporating plutonium and minor actinides into the nuclear fuel cycle requires the advancement of fast neutron reactor technology. Alongside sodium-cooled fast reactor technology (BN-800, BN-1200M), lead-cooled fast reactor technology is currently under active development. The Russian BREST-OD-300 reactor project employs a lead coolant, with steel as the fuel cladding material. A novel materials engineering solution is the use of mixed uranium–plutonium nitride (MNUP) as the fuel. Compared with conventional oxide fuel, nitride fuel offers several advantages, including higher density and thermal conductivity. A drawback of nitride fuel is its thermochemical instability at elevated temperatures, which complicates the investigation of its high-temperature properties.

To address the scarcity of thermodynamic data on the high-temperature thermodynamic properties of UN and PuN, the high-temperature heat capacities of these nitrides were modelled on the basis of defect formation contributions and correlations with the properties of uranium and plutonium oxides and carbides. The properties of the nitrides in the liquid state were modelled by exploiting the relationship between heat capacities and coefficients of thermal expansion. The resulting data enabled the calculation of phase equilibria in the quasi-binary UN-PuN system, and its phase diagram was constructed for the first time. Using experimental melting data, the phase diagram of the UN-Fe system was calculated, and the model was subsequently extended to the PuN-Fe system. On the basis of the binary subsystem models, the phase diagram of the ternary UN-PuN-Fe system was calculated. The present work demonstrates that phase equilibria in the UN-PuN-Fe system play a key role in analyzing the thermochemical stability limits of nitride fuel pins with steel cladding.

DETERMINATION OF VAPOR PRESSURE AND ENTHALPY OF VAPORIZATION OF NEOPENTYL GLYCOL ESTERS OF FATTY CARBOXYLIC ACIDS

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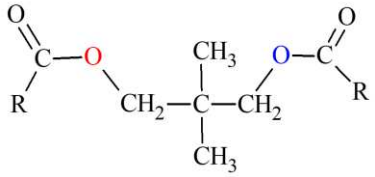
Esters based on fatty acids and neopentyl glycol (NPG) are used as base oils and can also serve as one of the components of synthetic lubricants.

In this work, a series of esters of neopentyl glycol and octanoic, 2-ethylhexanoic, decanoic, and dodecanoic acids was synthesized (see Figure).



Structure of Neopentyl Glycole Diesters

Esters of neopentyl glycol and fatty acids of the C_8-C_{12} series were obtained by esterification in a self-catalytic mode in the presence of a solvent *n*-decane. The purity of the samples was determined by gas chromatography. The purity of the samples was more than 98% by weight. The values of sorption enthalpies, vapor pressures, and evaporation enthalpies were determined for the obtained samples.

The value of the change in internal energy $\Delta_{sorp}\bar{U}$ (kJ/mol) and sorption enthalpy $\Delta_{sorp}H$ (kJ/mol) at an experimental temperature was determined from the dependencies:

$$\ln(k/T) = C - \frac{\Delta_{\text{sorp}}\bar{\text{U}}}{RT}\ ;\ \Delta_{\text{sorp}}H = \Delta_{\text{sorp}}\bar{\text{U}} - RT \text{ and } k = \frac{t_R - t_M}{t_M},$$

where t_R– adjusted retention time of the esters, min; t_M - retention time of nonsorbing substance (*n*-hexane), min.

The vapor pressures of NPG esters were determined by the transpiration method. The obtained *p-T*-dependences were described by the equation of the form:

$$R \ln\left(\frac{P}{P_{aw}}\right) = A_f - \frac{B_f}{T} + \Delta^n_{\text{ж}}Cp^0 \ln\left(\frac{T}{T_{aw}}\right),$$

where P – is the vapor pressure at T; P_{aw} – is the vapor pressure at the average temperature of the study T_{aw}; A_f and B_f are empirical coefficients obtained by processing *p-T* data by the least squares method; $\Delta^n_{\text{ж}}Cp^0$ – the difference between the molar heat capacities of the gas and liquid phases [1].

$$\Delta_{\text{vap}}H^0_m(298{,}2) = -B_f + 298.2\ \Delta^n_{\text{ж}}Cp^0.$$

1. E. L. Krasnykh and S. V. Portnova. Journal of Structural Chemistry. 2017, 58, 4, 706

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GLYCOL ETHERS AS PROMISING BATTERY ELECTROLYTES

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In recent decades, lithium-ion batteries have increasingly been used for efficient electrical energy storage. Solutions based on lithium salts and organic ether solvents are volatile, flammable, and unstable during long-term use. To address the challenges associated with lithium-metal batteries, several researchers have considered the use of electrolyte solutions based on glycol diesters, also known as "glymes" [1].

Glymes possess physicochemical properties that address the key challenges associated with lithium-metal batteries: liquid state over a wide temperature range, high chemical and thermal stability, relatively low vapor pressure, and low toxicity. This is particularly true for polyglycol diesters.

A challenge has been the lack of experimental thermodynamic data for long-chain glymes. Only the first four compounds in the homologous series have been thoroughly studied. Therefore, filling in these missing data is a priority for this study. Various approaches were used, including a combination of empirical methods (correlations using Kovacs indices, correlations with enthalpies of solution, etc.) and high-precision quantum chemical calculations (G3MP2, B3LYP with CREST conformational analysis) to predict enthalpies of vaporization, heat capacities, and Gibbs energies.

Experimental enthalpies of vaporization for a homologous series of ethylene glycol ethers were collected and validated using empirical methods: correlations using enthalpies of solution, the number of -[O-CH_2-CH_2]- units in the glyme molecule, Kovacs indices, surface tensions, boiling points, and Hildebrandt solubility parameters. The enthalpies and entropies of formation in the gas phase of ethylene glycol ethers were obtained using high-precision quantum chemical calculations. Using the enthalpies and entropies of formation in the gas phase and the enthalpy of vaporization, the enthalpies and entropies of formation in the liquid phase were calculated.

This yielded reliable thermodynamic data that were used to calculate the lower flammability limit, flash point, adiabatic temperature rise, and decomposition temperature. These parameters help evaluate the decomposition reaction and the thermal stability of glymes. The results suggest that glymes offer high safety and are promising electrolytes for batteries.

1. Brouillette D., Perron G., Desnoyers J. E. Apparent Molar Volume, Heat Capacity, and Conductance of Lithium Bis(trifluoromethylsulfone)imide in Glymes and Other Aprotic Solvents // J. Solution Chem. 1998. Vol. 27, P. 151–182. https://doi.org/10.1023/A:1022609407560

Acknowledgments: This work was supported by the Ministry of Science and Higher Education of the Russian Federation (theme № FSSE-2025-0006) as part of the state task of the Samara State Technical University.

THERMODYNAMIC FUNCTIONS OF SOME ALKALINE EARTH METAL BOROSILICATES

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Alkaline earth metal borosilicates are used in modern technologies, particularly in the creation of low-temperature ceramic materials, liquid crystal matrices, sensors, and glass ceramics. The introduction of boron oxide in varying concentrations imparts multifunctionality to borosilicate glasses. Boron-containing compounds are also used in medical practice, the construction industry, and in magneto-optical components of devices.

This work is devoted to a comparative analysis of experimental and theoretical thermodynamic constants, the correlation of IR frequencies with the structure of oxides and composites based on them. The theoretical values of the studied systems were calculated by the ion increment method [1], and also obtained using the quantum-chemical software package Gaussian16 and methods of electron density functional theory and semi-empirical approximation [2].

By studying the bifurcation of the Na_2SiO_3 - B_2O_3 components, the composition of a new composite was determined: Na_2O - 41.2%, SiO_2 - 42%, B_2O_3 - 16.8%, the formula of which was assumed to be $Na_4Si_2O_6 \cdot B_2O_3$. This composite was synthesized using the solid-phase method at a temperature of 900 °C. The resulting glass was X-ray amorphous and transparent. The composition of the obtained substance was analyzed by IR spectroscopy. The thermodynamic data of the composite, according to the ion increment and quantum chemistry methods, are as follows:

Formula	Calculation method	$-\Delta_f H^0_{298}$, kJ/mol	$-\Delta_f G^0_{298}$, kJ/mol	S^0_{298}, J/mol·K	$C_p{}^0_{298}$, J/mol·K
$Na_4Si_2O_6 \cdot B_2O_3$	Ion increment	3985.55	4132.90	281.14	312.59
	PM3MM	3575.14	3758.03	613.49	276.55

The methods used show good agreement between the results obtained, with the exception of entropy, which, according to the semi-empirical method, indicates that the system under consideration is twice as disordered.

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2. Frisch M.J., Trucks G.W., Schlegel H.B., et al. Gaussian16, Revision A.03, Wallingford: CT, 2016.

THERMODYNAMIC INVESTIGATION OF THE $Ag_7B^{IV}Se_5I$ COMPOUNDS AND $Ag_{8-x}B^{IV}Se_{6-x}I_x$ (B^{IV}-Ge, Sn) SOLID SOLUTIONS BY THE EMF METHOD WITH SOLID ELECTROLYTE

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Compounds of the argyrodite family and related phases are of considerable interest as environmentally safe, multifunctional materials exhibiting thermoelectric, photovoltaic, and optical properties, as well as high ionic conductivity.

In this work, the thermodynamic properties of the $Ag_7B^{IV}Se_5I$ compound and solid solutions $Ag_{8-x}B^{IV}Se_{6-x}I_x$($B^{IV}$-Ge, Sn) were studied for the first time using the EMF method with a solid Ag^+ conducting electrolyte Ag_4RbI_5.

The compounds Ag_8GeSe_6, Ag_8SnSe_6, Ag_7GeSe_5I, and Ag_7SnSe_5I were synthesized by co-melting stoichiometric mixtures of high-purity elemental substances (Ag-rod, 99.997%; Ge-ingot, 99.999%; Sn-ingot, 99.999%; Se-granules, 99.999%; I_2-powder, 99.999%) in evacuated (10^{-2} Pa) sealed quartz ampoules. Considering the high saturated vapor pressures of iodine (T_b = 457 K) and selenium (T_b = 958 K) at the melting temperatures, the syntheses were performed in a two-zone inclined furnace.

The phase purity of all synthesized parent compounds was confirmed by X-ray diffraction (XRD) and differential thermal analysis (DTA), and the results were consistent with literature data. For the investigations, alloys of various compositions were prepared from the presynthesized and identified compounds.

EMF measurements were performed using concentration cells of the type

(-) Ag (solid) | Ag_4RbI_5 (solid) | (Ag – in alloy) (+)

Linear temperature-dependent EMF equations were obtained in the temperature range of 300–390 K based on the experimental data. For the EMF measurements, a high-impedance digital voltmeter Keithley 2100 6½, with an input resistance of 10^9 Ω, was used. Analysis of the EMF data for electrochemical cells of type (1) showed that, within the studied temperature range, the EMF isotherms are linear functions of temperature. Using the obtained equations for the temperature dependence of the EMF, the partial thermodynamic functions of silver in the alloys were calculated. Based on the solid-phase equilibria data in the Ag_2Se-AgI-$B^{IV}Se_2$ system, a fragment of the quaternary phase diagram of the Ag-B^{IV}-Se-I system was constructed. This diagram was used to formulate the equations of the potential-forming reactions corresponding to the synthesized alloys. Based on these reactions, the standard thermodynamic functions of formation and the standard entropies of the $Ag_7B^{IV}Se_5I$ compound and the solid solutions $Ag_{8-x}B^{IV}Se_{6-x}I_x$ (x = 0.2, 0.4, 0.6, 0.8) were calculated.

THERMODYNAMIC STUDY OF LAYERED MANGANESE-BISMUTH AND GERMANIUM-ANTIMONY TELLURIDES

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Tetradymite-type layered materials have attracted considerable attention because of their unique structural and electronic properties and their potential for thermoelectric applications, phase-change functionality, and topological insulator behavior. Among these materials, the A-B^V-Te systems (A = Mn, Ge, Sn, Pb; B^V = Sb, Bi) are of particular interest because they include a wide range of compounds with layered crystal structures and diverse functional properties A characteristic feature of these compounds is their layered crystal structure with covalently bonded sheets separated by weak van der Waals gaps. Understanding their thermodynamic behavior is therefore essential for clarifying phase stability, guiding controlled synthesis, and supporting the design of materials for advanced electronic and energy applications.

In the present work, the thermodynamic properties of manganese-bismuth tellurides and germanium-antimony tellurides were investigated by electromotive force measurements under standard conditions. The solid-phase equilibria in the MnTe-Bi_2Te_3-Te and GeTe-Sb_2Te_3-Te systems were studied to identify the relevant heterogeneous regions and to select suitable electrode compositions for reliable electrochemical measurements. It was found that all telluride phases in these systems are connected by tie-lines with MnTe in the manganese-containing system and with elemental tellurium in the germanium-containing system. Based on these results, concentration cells of the type (-) MnTe (GeTe) (solid) | glycerol-KCl | alloys (solid) (+) were assembled. EMF measurements were performed in the temperature range 300-450 K and exhibited linear temperature dependences. Assuming a linear relationship between EMF and temperature, the experimental data were analyzed using the least-squares method, and the relative partial molar functions of manganese or germanium in the alloys were subsequently determined. Taking into account the stability of the coexisting phase compositions in the investigated phase regions, the standard integral thermodynamic functions of the ternary compounds were then calculated using the virtual-cell reaction approach. The obtained thermodynamic data satisfy internal consistency criteria and are consistent with the established phase relations, confirming their compatibility with the Mn-Bi-Te and Ge-Sb-Te phase diagrams.

ANALYSIS OF THE DISTRIBUTION OF URANIUM RADIONUCLIDES IN THE CONDITIONS OF HEATING REACTOR GRAPHITE IN THE AIR ATMOSPHERE

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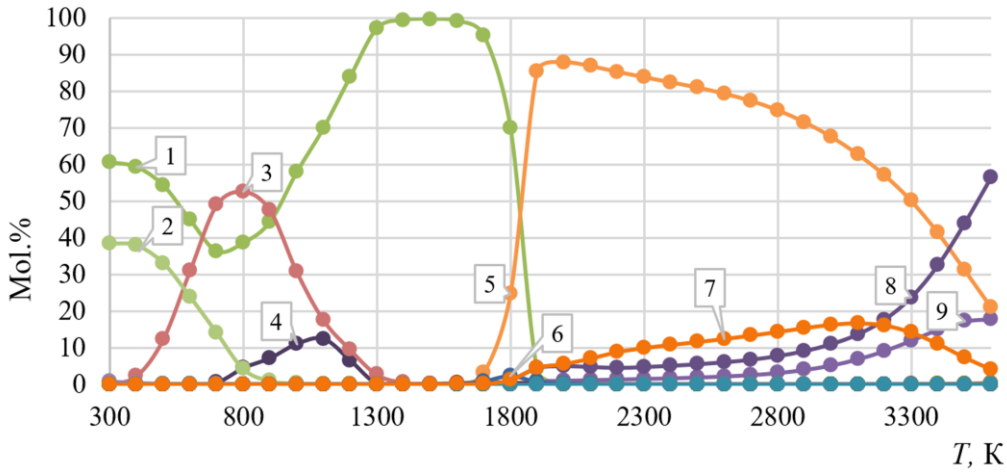
The largest amount of reactor graphite is found in RBMK power reactors, the mass of graphite masonry in one unit is about 1800 tons. The total amount of irradiated reactor graphite in Russia reaches 60 thousand tons. The available technologies for processing graphite nuclear waste are based on the principle of isolation from the environment, which in turn cannot provide a significant reduction in volume.

Currently, incineration is the most promising way to handle spent graphite materials. To study the temperature conditions of processing and physico-chemical processes occurring in the atmosphere (O_2 : N_2 = 1.0 : 3.3), it is necessary to conduct a thermodynamic analysis.

The calculation of thermodynamic modeling of the behavior of uranium radionuclide was carried out in the TERRA program. In the temperature range from 300 to 3600 degrees Kelvin (K) in increments of 100 K, at a pressure of 0.1 MPa. The paper presents the results of an analysis of the behavior of uranium radionuclides in the air atmosphere.



Distribution of uranium: 1 – $UO_{2(к.)}$; 2 – $UOCl_{2(к.)}$; 3 – $UOCl_{(к.)}$; 4 – UCl_4; 5 – UO_3; 6 – $CaUO_{4(к.)}$; 7 – UO_3^-; 8 – UO_2^+; 9 – UO_2

When the temperature rises from 400 to 2000 K, uranium compounds in the condensed phase are observed in the form of ($UO_{2(к.)}$, $UOCl_{2(к.)}$, $UOCl_{(к.)}$, $CaUO_{4(к.)}$). As the temperature increases from 1000 K to 3600 K, uranium compounds enter the ionized phase (UO_3^-, UO_2^+) and the gaseous phase (UO_2, UO_3, UCl_4).

THERMODYNAMIC PROPERTIES AND THERMAL EXPANSION OF "HEAVY" RARE-EARTH DITITANATES AT HIGH TEMPERATURES

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Rare-earth dititanates, $RE_2Ti_2O_7$, with a cubic structure are promising components in the design of catalysts, solid-state fuel cells, optical and laser materials, protective coatings and matrices for the disposal of radioactive waste.

Previously, the heat capacity of $RE_2Ti_2O_7$ was measured systematically in the low-temperature region, and the results obtained are in satisfactory agreement (e.g., [1, 2]), while the measurements in the high-temperature region were carried out fragmentarily. Data on the enthalpies of formation of rare-earth dititanates of the yttrium subgroup are presented in [3].

In this study, $RE_2Ti_2O_7$ titanates (RE=Tb-Lu) were synthesized by reverse precipitation followed by stepwise calcination to 1500°C. The samples were characterized by X-ray diffraction (phase composition and lattice parameters) and SEM with EDX spectroscopy (particle size, element composition).

The heat capacity of rare-earth dititanates was determined in the temperature range of 300–1850 K by differential scanning calorimetry using the ratio method. Based on the obtained values and literature data, Gibbs energies were calculated to assess the stability of rare-earth dititanates towards action of high temperature and of CMAS oxides.

Crystallographic parameters of RE dititanates were studied by X-ray diffraction at high temperatures and thermal expansion coefficients were calculated.

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3. K.B. Helean, S.V. Ushakov, C.E. Brown, et al. // J. Solid State Chem. 2004. V. 177. P. 1858–1866. https://doi.org/10.1016/j.jssc.2004.01.009

This work was performed under the State Assignment of Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF COMPLEX OXIDES WITH β-PYROCHLORE STRUCTURE

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Complex metal oxides are of great interest to researchers due to their ferroelectric, catalytic, optical, ionic or electronic conductivity, and other important properties. These properties make them promising materials for use as capacitors, superconductors, semiconductors, and in piezoelectric devices. The series of compounds based on the perovskite, fluorite, pyrochlore, corundum, rutile, and other stable mineral structures are distinguished among such complex oxides. The changeable elemental composition of compounds in a series while the overall crystal structure is maintained offers a way to tailor various useful properties of the compounds.

The studied β-pyrochlore oxides are of interest in the context of this task, as their structure is stable, their composition can be varied over a wide range, and accordingly, their photocatalytic activity-associated physical properties, such as the bandgap width, can be controlled.

The heat capacity of complex oxides with β-pyrochlore structure: $CsTeMoO_6$, $CsV_{0.625}Te_{1.375}O_6$, $RbTe_{1.5}W_{0.5}O_6$, $Rb_{0.95}Nb_{1.375}Mo_{0.625}O_{5.79}$, $CsMo_{0.25}W_{1.75}O_6$, $CsSn_{0.25}W_{1.75}O_6$ was investigated by adiabatic vacuum and differential scanning calorimetry in the temperature range of $T = (6 – 640)$ K. The standard thermodynamic functions: heat capacity, enthalpy $[H°(T)–H°(0)]$, absolute entropy $[S°(T)]$ and the Gibbs energy $[G°(T)–H°(0)]$ for the range from $T \rightarrow 0$ to 640 K were calculated based on the obtained experimental data. The low-temperature ($T < 50$ K) heat capacity dependence was analyzed on the basis of multifractal model and chain-layered structure topology of the studied compounds was established.

The thermodynamic properties of the studied complex oxides with β-pyroclore structure were compared and analyzed.

The research was carried out with financial support via State assignment in Research scientific laboratory of "Chemistry of natural products and their synthetic analogues", grant number FSWR-2024-0002.

EFFECT OF POLYPHOSPHORIC ACID AND ZINC PHOSPHATE ON THE THERMO-OXIDATIVE STABILITY OF GRAPHITE FOIL

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Graphite foil (GF) is a unique material with high chemical resistance to most aggressive substances uses as a gasket materials or heat spreader. Thus, it is widely used in the oil and gas, energy, aerospace, instrumentation manufacturing and other industries. A pure GFs have high oxidation rate in air at elevated temperatures, carbon losses being up to 15-20 mass%/h at 670°C. Different methods of GF modification are used to reduce oxygen influence and extend service life of graphite material. The aim of the work is to identify the composition of the additives and methods of their addition to the development of a modified material with high temperature resistance based on the natural flake graphite (NG).

GF is obtained by pressure treatment of thermally expanded graphite (TEG) produced by reduction-oxidation with fuming nitric acid and heat treatment of NG. Phosphorous insertion in the graphite matrix structure results in oxidation decrease. Modifying agents are considered to be phosphorus compounds: polyphosphoric acid (PPA) $H_{n+2}P_nO_{3n+1}$ (~115% H_3PO_4 basis) and monosubstituted zinc phosphate $Zn(H_2PO_4)_2 \cdot 2H_20$ (ZP). PPA was added into the oxidation solution with different concentration. PPA content increase was shown to reduce GF oxidation noticeably (0% - 15±2 mass%/h, 10 % - 2,3±0,2 mass%/h, 40% - 1,0±0,3 mass%/h).

Carbon loss reduction method with ZP-based precursor during NG hydrolysis oxidized with 5% PPA was also investigated. Oxidation was 3,0±0,2 mass%/h without the ZP and – 1,9±0,1 mass%/h with it. Energy-dispersive X-ray spectroscopy paired with SEM was used to examine residual phosphorous and zinc contents in GF samples (without ZP additive: P = 600 ppm; with it: P = 1800 ppm, Zn = 5000 ppm). Since oxidized graphite undergoes heat treatment it is obviously that these elements are impregnated into the graphite, where they help passivate active sites and lattice defects formed during heat treatment.

STUDY OF THE TEMPERATURE DEPENDENCES OF HEAT CAPACITY OF SOLID SOLUTIONS BASED ON HEXAGONAL STRONTIUM FERRITES SUBSTITUTED WITH GALLIUM

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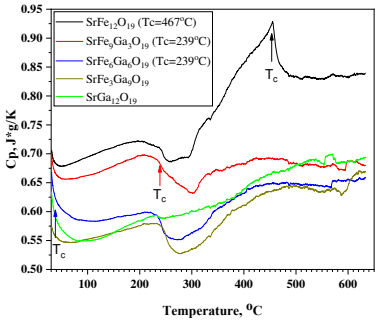
Synthesis of samples of the composition $SrFe_{12-x}Ga_xO_{19}$ was carried out using the solid-phase reaction method, with iron oxide (Fe_2O_3), gallium oxide (Ga_2O_3), and strontium carbonate ($SrCO_3$) as starting components. Sintering of the stoichiometric mixture was performed at a temperature of 1400 °C for 5 hours. X-ray phase analysis showed that the samples have a single crystalline phase belonging to the magnetoplumbite structure. Electron microscopy and EDS analysis confirmed the homogeneous distribution of elements throughout the sample volume.



Temperature dependences of heat capacity

Measurements of the temperature dependence of heat capacity (C_p) were carried out using a Netzsch differential scanning calorimeter, model STA 449 C. The heat capacity was calculated by comparison with a standard (single-crystal Al_2O_3). From Figure 1, it can be seen that for the $SrFe_{12}O_{19}$ sample, two thermal effects are observed. The exothermic effect is associated with the ferrimagnet–paramagnet transition (denoted as Tc). For the $SrFe_9Ga_3O_{19}$ and $SrFe_6Ga_6O_{19}$ samples, no thermal effect associated with the magnetic phase transition is observed; however, these samples are ferrimagnets and have Curie temperatures above room temperature (indicated by arrows in Figure). The nature of the second thermal effect (endothermic), observed for all samples except $SrGa_{12}O_{19}$, is unknown. It has been suggested that it is related to the redistribution of Fe^{3+} cations over crystallographic positions.

The study was carried out with financial support from the Ministry of Education and Science of the Chelyabinsk Region through a grant in the form of a subsidy № 184/3 dated December 25, 2024, for the establishment of a regional youth laboratory.

INVESTIGATION OF LUMINESCENT PROPERTIES OF NANOPARTICLES (La, Gd, Y)PO_4:Eu^{3+}

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It is known that the luminescent properties of phosphor nanoparticles depend on the crystal structure, morphology, and particle dimensions of the matrix into which the phosphor ion is incorporated [1]. In addition, the concentration of the alloying agent and the symmetry around the luminescent ion are strongly influenced. In this context, REE orthophosphates (*REE*PO_4) have garnered significant interest among researchers due to their electron configuration and several properties, including the capacity for isomorphic substitution of other REE, low toxicity, elevated refractive index, superior quantum yield of luminescence and high chemical and thermal resistance [2]. An important aspect of obtaining nanomaterials based on *REE*PO_4 is the potential to form various crystalline phases (matrices) with rhabdophane, monazite and xenotime structures using "soft chemical" methods. This allows for the purposeful synthesis of nanoparticles with different structures, compositions, shapes, and properties. Therefore, this research to investigate the relationship between the chemical composition of phosphors, the structural and morphological characteristics of nanoparticles composed of multicomponent REE orthophosphates with Eu^{3+} doping ions, and the luminescent properties of the material.

Nanoparticles with the structures of rhabdophane, monazite and xenotime based on the $LaPO_4$–$GdPO_4$–YPO_4–(H_2O) quasi-ternary system with the addition of Eu^{3+} ions, have been synthesized. The molar fraction of Eu^{3+}, which is a part of the (La, Gd, Y)PO_4 matrix, varied over a wide range, depending on the crystalline structure of the matrix. The samples were prepared by precipitation, followed by hydrothermal treatment (T = 230 ºC, P ≈ 10 МПа, pH ≈ 1). The synthesis time ranged from 2 hours to 5 days, depending on the luminoform composition.

Based on the findings of the research, emission bands that are characteristic of the Eu^{3+} ion were observed in all luminescence emission spectra. These emission bands correspond to intra-configuration *f-f* transitions from $^5D_0 \rightarrow {}^7F_J$ levels.

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CHARACTERIZATION OF DOMESTIC MATERIALS FOR 3D PRINTING BY THERMAL AND SPECTRAL ANALYSIS METHODS

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3D-printing with polymer filaments has become an integral part of modern electrical engineering, especially in the field of creating housings and insulation elements. Traditional thermoplastics, such as polyethylene terephthalate, ABS, or polyamide-6, have excellent dielectric properties, which allows manufacturing reliable enclosures for electronic devices, terminal blocks, and fastening elements of complex geometry.

Domestic manufacturers have established production of 3D-printing materials from a wide range of polymers. However, technical specifications generally do not provide information on physical-chemical parameters important for their application. Moreover, the physical-chemical constants inherent in the base polymer do not always correspond to the filament based on it. Therefore, it seemed important to evaluate the properties of the most common 3D-printing materials using thermal and spectral analysis methods, and to compare the results obtained with data known from the literature.

Studies were carried out using IR-Fourier spectroscopy with attenuated total reflectance, thermogravimetric analysis, and differential scanning calorimetry. Data on phase transitions, thermal stability, and spectral characteristics were obtained for a large number of materials of different brands with polymer bases presented in the table:

Polymer Base of Investigated 3D Printing Materials

Polymer Base Type	Material Brand	Manufacturer
Polylactide	REC PLA	LLC «REC»
Polymethyl methacrylate	PMMA CAST	LLC «REC»
Polyether ether ketone	PEEK	LLC «REC»
Polysulfone	PSU	LLC «REC»
Polycarbonate	PC AVIA	LLC «REC»
Polyurethane	TPU Soft	Bestfilament
Polystyrene	HIPS	Bestfilament
Poly(acrylonitrile-styrene-acrylate)	ASA	Bestfilament
Poly(Acrylonitrile-butadiene-styrene)	ABS	Bestfilament
Polyethylene terephthalate, glycol-modified	PETG "Avatar"	«FDplast»
Polyamide-6	PA-6	Ecc Market

FEATURES OF PRODUCING GELS BASED ON CYCLIC DIPEPTIDES

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Gels, belonging to the class of soft condensed matter, are popular research objects owing to their high potential for application in various technologies. Alongside physical gels, supramolecular gels are being actively studied; they demonstrate biocompatibility, biodegradability, and the possibility of fine-tuning their properties, representing an environmentally friendly alternative to conventional synthetic polymers.

Cyclic dipeptides, derivatives of 2,5-diketopiperazines, are promising low-molecular-weight gelators capable of self-assembly into supramolecular structures through hydrogen bonding and van der Waals interactions. Gel materials based on them possess unique physicochemical properties and can be used in biomedical applications as delivery systems for active pharmaceutical ingredients, as well as in optoelectronics and catalysis. Despite the growing number of studies devoted to the gelation of cyclic dipeptides, the literature still lacks any established regularities describing these processes, and the general methodology for preparing such gels remains undefined.

In the present work, a comprehensive investigation of the gelation of a series of cyclic dipeptides: *cyclo*-(Phe-Phe), *cyclo*-(Phe-Leu), *cyclo*-(Phe-Ala), *cyclo*-(Leu-Val), *cyclo*-(Leu-Ala), and *cyclo*-(Val-Ala), was carried out in systems with organic solvents of various classes, both in the presence and in the absence of water. A search for a correlation between the ability of cyclic dipeptides to gel and the physicochemical parameters of these compounds, as well as the medium used, was carried out.

SYNTHESIS AND CHARACTERIZATION OF ZnO/g-C_3N_4 COMPOSITES FOR PHOTOCATALYTIC APPLICATIONS

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Low-temperature formation of carbon nitride from supramolecular precursors provides a model system for studying kinetically controlled structure formation and defect organization. In this work, ZnO/g-C_3N_4 composite materials were synthesized via thermal treatment of mechanically mixed precursors (melamine–thiobarbiturate supramolecular complexes[1] and zinc hydroxide) in an inert atmosphere using a low-temperature synthesis approach for g-C_3N_4[2].

Differential scanning calorimetry (DSC) analysis was performed to determine the optimal synthesis temperature. The results showed that the optimal synthesis temperature for the composite is 316 °C, which is higher than that of pure g-C_3N_4 (305 °C), indicating modification of the condensation pathway and effective energy landscape of condensation due to ZnO incorporation. The supramolecular structuring of the precursor system enables a preorganized condensation pathway leading to reduced structural randomness and non-random defect distribution, allowing a reduction of the synthesis temperature by approximately 200 °C compared to conventional g-C_3N_4 synthesis. The formation of the composite structure was confirmed by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR), demonstrating the coexistence of both ZnO and g-C_3N_4 phases without formation of secondary phases.

Morphological analysis using scanning electron microscopy (SEM) revealed that at low ZnO content, ZnO particles are uniformly distributed on the layered g-C_3N_4 surface, forming a developed interface. With increasing ZnO content, particle agglomeration becomes dominant, leading to structural changes in the composite. Energy-dispersive X-ray spectroscopy (EDX) confirmed the presence of all key elements, including sulfur, indicating successful doping and preservation of the modified structure.

Optical properties were investigated using UV–Vis spectroscopy and Tauc plots. The obtained bandgap values lie between those of pure ZnO and g-C_3N_4.

Electron paramagnetic resonance (EPR) analysis revealed the presence of stable defect states. In addition to the characteristic signal of g-C_3N_4 ($g \approx 2.003$), an additional signal at $g \approx 2.01$ was detected, associated with sulfur-related defect centers stabilized at the ZnO/g-C_3N_4 interface.

It is shown that ZnO particles can serve as growth centers in g-C_3N_4 crystals, influencing defect formation and structural organization. The results indicate that the formation of ZnO/g-C_3N_4 composites is governed by supramolecular preorganization and kinetically controlled condensation, leading to structural inheritance and stabilization of sulfur-related defect centers at the heterointerface.

The work was supported by the Russian Science Foundation (project № 24-13-00355).

HYDROGELS BASED ON THE Fmoc-FF DIPEPTIDE WITH ACTIVE PHARMACEUTICAL INGREDIENTS

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Currently, the development of ways to increase the bioavailability of poorly water-soluble drugs is actively underway. It is known that an increase in the bioavailability of the drug is possible when it is encapsulated in a gel matrix, which can be both polymer and supramolecular gels. Supramolecular gels with a high water content, hydrogels, have a high potential for use.

Short-chain oligopeptides, in particular, Fmoc-substituted linear dipeptides that form gels due to intermolecular interactions, can act as a low-molecular-weight gelating agent. Such gels have high stability, mechanical strength, they are biocompatible and non-toxic. In combination with bioactive molecules, such materials can be used to treat life-threatening diseases such as cancer, in the development of non-invasive drug delivery systems, and can also promote the healing of soft and hard tissues.

In this work, we propose a method for obtaining hydrogels based on Fmoc-FF with encapsulated active pharmaceutical ingredients (API) belonging to the class of antibiotics and antitumor drugs. The strength of a pair of interactions between dipeptide molecules and API in the systems studied is evaluated. The structural and mechanical properties of the hydrogels were characterized using IR spectroscopy, rheology, and powder X-ray diffractometry. The effect of API on the kinetics of gelation was studied by NMR spectroscopy. The features of the structural organization of xerogels containing APIs have been demonstrated by atomic force microscopy.

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THERMODYNAMIC STUDY OF THE $BiS_{1-x}Se_xI$ AND $Bi_{19}S_{27(1-x)}Se_{27x}I$ SOLID SOLUTIONS

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Chalcohalides of the arsenic subgroup elements and the phases on their basis have recently attracted considerable attention from researchers due to their functional properties, including thermoelectric, optical, etc., as well as Rashba-type semiconducting characteristics. These properties enhance the potential of such materials for application in various devices in the fields of quantum computing and spintronics [1, 2].

In this work, the thermodynamic properties of the $BiS_{27(1-x)}Se_{27x}I$ and $BiS_{1-x}Se_xI$ solid solutions formed in the Bi_2S_3-Bi_2Se_3-BiI_3 system is investigated.

At the initial stage, experimental studies of solid-phase equilibria in the Bi_2S_3-Bi_2Se_3-BiI_3 system were carried out. To this end, the relevant binary and ternary compounds were synthesized in advance. The synthesis was conducted in a two-zone inclined furnace to accommodate the high vapor pressures of elemental iodine, sulfur, and selenium. To prepare alloys of various compositions in the studied system, the synthesized and identified starting compounds were melted at 850 K in evacuated quartz ampoules. The alloys were subsequently homogenized by stepwise annealing at 650 K for 300 hours and 370 K for 100 hours. Differential thermal analysis (multichannel device based on a TC-08 thermocouple recorder), powder X-ray diffraction technique (Bruker D2 PHASER), and electromotive force measurements (Keithley 2100 6½-digit multimeter) were employed to systematically characterize of all the alloys.

For thermodynamic investigations the following type concentration cells:

(−) Bi (solid) / liquid electrolyte, Bi^{3+} / (Bi in alloy) (solid) (+)

were composed and their EMF was measured over the temperature range 300-370 K. An ionic liquid (morpholine formate) containing $BiCl_3$ was employed as the electrolyte. Analysis of the experimental data revealed a linear dependence of EMF on temperature for all samples. The data were processed using the least-squares method, yielding linear E–T relationships. Based on these equations, the partial molar functions of bismuth in the alloys were calculated at 298 K. By integrating the Gibbs–Duhem equation, the standard thermodynamic functions of formation ($\Delta_f G°$, $\Delta_f H°$, $\Delta_f S°$) and standard entropies for the $BiS_{1-x}Se_xI$ and $Bi_{19}S_{27(1-x)}Se_{27x}I$ solid solutions were calculated.

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Cu_8SiS_6–Ag_8SiSe_6 SYSTEM: PHASE EQUILIBRIA AND HIGH ENTROPY ALLOYS

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Argyrodite-type compounds are complex copper and silver chalcogenides that are environmentally benign and exhibit a wide range of functional properties. Many of these phases attract interest due to high thermoelectric performance in the intermediate temperature range, as well as photoelectric and optical properties, which make them promising multifunctional energy materials. Argyrodite compounds undergo polymorphic phase transitions at relatively low temperatures (≤530 K). The low-temperature modifications crystallize in ordered structures with lower symmetry, whereas the high-temperature modifications adopt a cubic lattice. In high-temperature phases, Cu^+ and Ag^+ cations are statistically distributed over several crystallographic sites, resulting in high ionic mobility and increased configurational entropy. Simultaneous substitution in both the cation (A^I) and anion (X) sublattices increases structural disorder in the crystal lattice and enhances configurational entropy, leading to the formation of thermodynamically stable single-phase solid solutions based on argyrodite-type high-entropy alloys.

The aim of the present work is to investigate phase equilibria in the Cu_8SiS_6–Ag_8SiSe_6 system and to identify possible high-entropy phases. For this purpose, the Cu_8SiS_6 and Ag_8SiSe_6 compounds were first synthesized. The synthesis was carried out by co-melting high-purity elemental components in evacuated quartz ampoules using a two-zone heating regime. After synthesis and identification of the initial compounds, the Cu_8SiS_6–Ag_8SiSe_6 alloys were prepared by co-melting of parents compounds in various proportions. The obtained alloys were annealed at 800 K for 500 hours. The synthesized samples were investigated by differential thermal analysis (DTA) and X-ray diffraction (XRD). DTA measurements were performed using a NETZSCH 404 F1 Pegasus instrument, while XRD patterns were recorded on a Bruker D2 PHASER diffractometer ($CuK\alpha_1$ radiation). The obtained diffraction patterns were analyzed using the Topas V3.0 Software (Bruker), and the lattice parameters of alloys were calculated.

Based on the DTA and XRD results the phase diagram of the title system was plotted. It was established that the Cu_8SiS_6–Ag_8SiSe_6 system forms a continuous series of solid solutions based on the high-temperature cubic modifications of the initial compounds, whereas only limited solid-solution regions are observed for their low-temperature modifications. The formation of solid solutions leads to a decrease in the polymorphic transition temperatures of the initial compounds. As a result, all alloys in the Cu_8SiS_6–Ag_8SiSe_6 system within the 10–90 mol % Ag_8SiSe_6 composition range are single-phase and crystallize in a cubic structure (Sp. Gr. *F-43m*). Samples containing 34–66 mol % Ag_8SiSe_6 of this phase can be considered as high-entropy alloys.

THERMODYNAMIC MODELING OF PHASE EQUILIBRIA IN Mg-Ca-Li-BASED SYSTEMS

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Modern materials science is confronted with the challenge of developing novel structural materials that combine low density, high strength, significant ductility, and chemical resistance, which are in demand in the aerospace, transportation, and energy sectors. In this context, Light High-Entropy Alloys (LHEAs) are considered particularly promising. However, the LHEAs developed to date are predominantly aluminum-based and contain a large quantity of brittle intermetallic compounds, which limits their practical application.

The core scientific problem lies in the development of fundamentally new approaches for the design and synthesis of aluminum-free LHEAs, capable of minimizing the formation of phases that degrade mechanical properties and ensuring an optimal balance of hardness, strength, ductility, and corrosion resistance.

This study addresses the following interrelated tasks: performing thermodynamic modeling of phase equilibria in (Ca,Sr,Ba)MgLi systems to substantiate optimal compositions; optimizing melting techniques to minimize the loss of low-melting-point components; conducting a comprehensive investigation of the phase and chemical composition of the obtained samples using X-ray diffractometry, electron microscopy, and EDS analysis; determining mechanical properties and corrosion resistance; and formulating recommendations for the creation of new LHEAs for high-tech industries.

A key objective of the project is the thermodynamic modeling of phase equilibria in the selected systems using modern algorithms (CALPHAD). This approach enables the prediction of probable phases, their composition, and relative fractions at various temperatures and component concentrations.

This work utilizes the capabilities of the FactSage 8.0 software package, within which a proprietary user database is being developed to describe the investigated Mg-Ca-Li-based systems. Phase diagrams of the simulated systems have been constructed. Furthermore, the Scheil-Gulliver model is employed to simulate the solidification behavior of the melts in the studied systems.

This modeling serves as the foundation for the well-founded selection of experimental compositions and the optimization of synthesis conditions.

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PHASE DIAGRAM OF THE Fe–Si–Al–Ni SYSTEM

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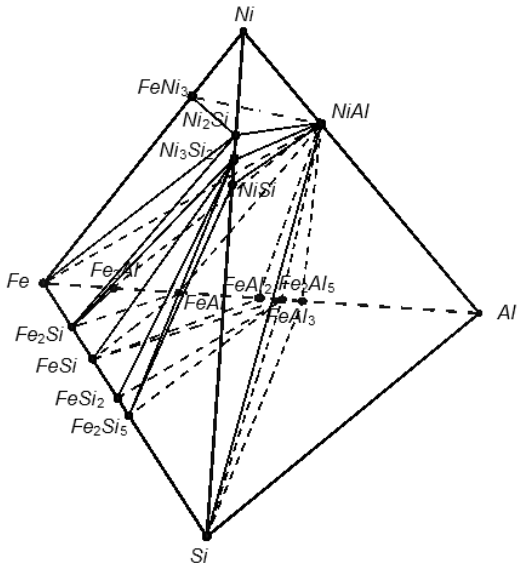
Using the thermodynamic–diagrammatic analysis method, the optimal compositions of complex ferro-silicon–aluminum–nickel alloys were determined, along with the construction of phase relationship diagrams for individual sections in the Fe–Si–Al–Ni system [1, 2].



Phase diagram of the Fe–Si–Al–Ni system

In the Fe–Si–Al–Ni system, it can be seen that in order to produce ferrosilicoaluminonickel with the highest nickel content, it is necessary to aim for the region of the Si–Fe_2Al_5–NiAl–Al tetrahedron, which has the largest volume (0.2978). The optimal alloy composition is: Fe = 9–10%; Al = 17.21%; Si = 65–68%; Ni = 0.5–4%.

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PHASE STABILITY OF $A_2B_2O_7$-TYPE ULTRAHIGH-ENTROPY COMPOUNDS

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The research is aimed at the synthesis and investigation of the structure, stability, and properties of novel oxide ultrahigh-entropy phases, whose compositions correspond to the formulas $A_2Zr_2O_7$, $A_2Hf_2O_7$, $A_2Ti_2O_7$, $A_2Ce_2O_7$, $A_2Pr_2O_7$, and $A_2Sn_2O_7$, where A represents a high-entropy sublattice composed of 12–13 rare-earth elements (excluding Ce, Pr, and Pm).

Experimental samples are synthesized using solid-state sintering at temperatures of 1500–1600 °C, as well as via a modified Pechini method. The composition and structure are characterized using SEM, EDS, and XRD. The results demonstrate various fluorite-type structures (fluorite, defect fluorite, pyrochlore). The coefficients of thermal expansion and thermal conductivity of the obtained materials are studied. Additionally, electrochemical properties are investigated due to their potential relevance for the use of these substances as catalysts in various chemical processes.

Special attention is given to the study of the phase stability of the synthesized materials over a wide temperature range using differential thermal analysis. The obtained results indicate that the studied phases exhibit high structural stability.

As part of the research, a thermodynamic description of the new high-entropy oxide phases is developed, based on the analysis of literature data and our own experimental results (primarily data on the temperature and concentration stability limits of solid solutions in the studied systems). Expressions correlating the Gibbs energy of such phases with their composition and temperature have been derived.

These studies employ modern thermodynamic modeling techniques implemented in contemporary specialized software (the FactSage 8.0 software package, in which a proprietary user database has been developed based on the results of this work).

The analysis of the obtained experimental data will allow the formulation of general trends governing the formation of high-entropy oxide phases, which should include criteria for the structural stability of such phases.

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CATALYTIC PROPERTIES OF Ni-Mo COATINGS IN ALKALINE ELECTROLYSIS OF WATER

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Most recent research has been focused on the search for new energy sources. In this regard, the development of hydrogen energy holds great promise. High-purity hydrogen can be produced by electrolysis of alkaline electrolyte solutions. Monopolar electrolyzers with high energy consumption are used for water electrolysis. To reduce the cell voltage, it is necessary to select an electrode material that simultaneously acts as a catalyst for the hydrogen evolution reaction (HER) and exhibits low cathodic overpotential. Nickel has a low overpotential for HER and is less expensive compared to precious metals. Adding molybdenum to nickel facilitates the HER: molybdenum improves charge transfer, while nickel ensures the structural integrity of the coating.

The study compares Ni-Mo coatings obtained by galvanostatic and pulsed electrolysis. At a constant quantity of electricity (300 C), deposits were obtained at 80 and 150 mA/cm^2. In pulsed electrolysis, deposits were obtained at a peak current density of 400 mA/cm^2, with pulse/pause alternation in different ratios: 3 ms/7 ms (6000 cycles), 5 ms/5 ms (3600 cycles), and 7 ms/3 ms (2571 cycles) on various substrates: AISI 304 steel, a nickel plate, and AISI 304 steel with a nickel coating. The electrolyte used for deposition contained $NiSO_4$, Na_2MoO_4, and $Na_3C_6H_5O_7$. Energy-dispersive X-ray diffraction (EDX) was used to determine the composition of the resulting coatings, including their nickel and molybdenum content. Increasing the growth pulse duration increased the molybdenum content in the deposit.

Catalytic properties were evaluated by analyzing the polarization curves of hydrogen reduction from a 1 mol/L NaOH solution, which were converted into coordinates of the Tafel equation. The coating with the smallest value of the constant $\boldsymbol{a}$ in the Tafel equation was recommended as the electrode material.

The HER is a heterogeneous chemical reaction, so high catalytic properties will be demonstrated by a coating with a larger active surface area. The catalytic surface area was estimated from the shift in the polarization of the hydrogen bonds on the smooth surface and on the coating at a current density of 200 mA/cm^2 (S_{act}), and from the cyclic voltammogram (CVA) analysis near the equilibrium potential (S_{ECSA}). The electrochemically active surface area (S_{ECSA}) was always greater than Sact due to the abundant hydrogen evolution, which resulted in the shielding of part of the electrode surface.

Under constant current, coatings obtained at 150 mA/cm^2 exhibit higher catalytic activity. In pulsed electrolysis on all substrates, the constant $\boldsymbol{a}$ is lower at a pulse/pause ratio of 3 ms/7 ms. Coatings obtained under galvanostatic conditions at 150 mA/cm^2, and those deposited by pulsed electrolysis onto a steel substrate at a pulse/pause ratio of 3 ms/7 ms, have a larger electrochemically active surface area.

OXIDATION BEHAVIOUR OF $MoSi_2$ POWDER AT 800–1100 °C

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Oxidation process of molybdenum disilicide $MoSi_2$ powders is very complex and strongly depends on synthesis technology. Stable results are obtained only at high temperatures (above 1300 °C) or long holdings (tens of hours), after the solid and homogeneous layer of SiO_2 is formed on the surface. But great phase and volume changes occur at initial stages of oxidation, complicated by volatility of forming MoO_3. Experimental information for this range shows significant scatter and needs clarification.

In this study, commercial $MoSi_2$ powder was annealed in a furnace in an air atmosphere for up to 6 hours at 800 and 900 °C and up to 4 hours at 1000 and 1100 °C.

SEM investigation of powder annealed for 2 hours at 1000 °C revealed a heterogeneous diffusional zone on the surface that had chemical composition significantly different from initial disilicide (Fig. 1; dark areas indicate decreased molybdenum content, about 3 wt. % according to electron probe microanalysis). X-ray diffraction of oxidized powder showed the presence of β-SiO_2 (cristobalite), $MoSi_2$, Mo_5Si_3 and MoO_3 with weak peaks of MoO_2 and SiO_2 in quartz and tridymite modifications.

The change of the mass of the powder at all temperatures passed through a maximum (see Figure 2). The reason of initial increase of mass was the reaction $MoSi_2 + (7/5)\,O_2 \rightarrow (1/5)\,Mo_5Si_3 + (7/5)\,SiO_2$, and that of subsequent decrease was $(1/5)\,Mo_5Si_3 + (21/10)\,O_2 \rightarrow (3/2)\,SiO_2 + MoO_3$, since MoO_3 is volatile and evaporates. At 900, 1000 and 1100 °C fast decrease of mass slowed down after formation of continuous layer of SiO_2 on the surface that prevented MoO_3 from leaving the particles.

Kinetics of the first two stages of oxidation (before formation of SiO_2 layer) can be described by a power law $\Delta m(t)/m_0 = (A_1 t)^1 - (A_2 t)^{3/2}$ where $A_1 = 0.043\exp(-6540/T)$ and $A_2 = 0.14\exp(-8140/T)$ s^{-1}.

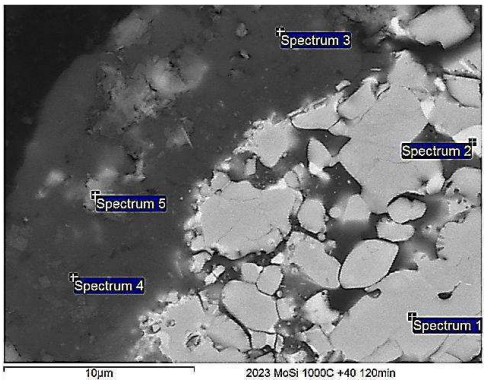

Figure 1. SEM microstructure of $MoSi_2$ powder oxidized for 2 hours at 1000 °C

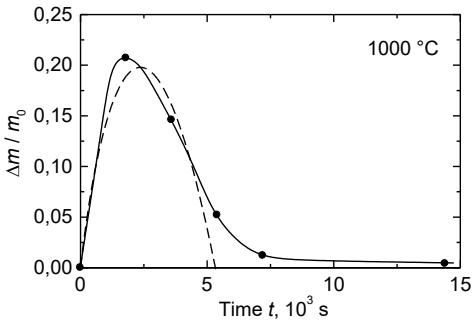

Figure 2. Relative change of mass of the powder at 1000 °C

EFFECT OF CATION COMPOSITION ON THE STABILITY AND PROPERTIES OF FLUORITE-TYPE HIGH-ENTROPY FLUORIDES

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The concept of high-entropy materials, originally developed for metallic alloys, has been actively extended to ceramic compounds over the past decade. A key role in the stabilization of such complex multicomponent systems is played by the configurational entropy of mixing, which makes it possible to obtain single-phase solid solutions even from components that do not exhibit mutual solubility under ordinary conditions. Despite advances in the synthesis of high-entropy oxides and carbides, research on high-entropy fluorides (HEFs) is still in its initial stages. From a thermodynamic perspective, it is critically important to understand how variations in the cationic composition affect the stability of the crystal lattice, the defectiveness of the structure, and, consequently, the macroscopic properties of the material. The aim of this work was to establish the fundamental "composition – structure – property" relationship for novel HEFs with a fluorite-type structure.

In this study, three compositions of high-entropy fluorides were synthesized using the co-precipitation method followed by annealing with NH_4F as a flux: HEF1 ($CaSrBaPbCeF_{11}$), HEF2 ($CaSrBaPbLaF_{11}$), and HEF3 ($CaSrPbCeLaF_{12}$). X-ray diffraction analysis showed that all samples crystallize into a single-phase cubic fluorite structure (space group Fm-3m), despite significant differences in the ionic radii of the elements.

It was found that the composition of the cation sublattice significantly affects the lattice parameters, with Pb^{2+} making the dominant contribution to the formation of the framework, as its lattice parameter is the closest to the obtained values. The most interesting and thermodynamically significant result is a sharp decrease in the band gap E_g of the synthesized materials compared to the dielectric binary fluoride constituents. Furthermore, the cationic composition directly determines the morphology and surface energy of the particles, which range from nanoporous to dense micron-sized structures.

Thus, the ability to purposefully tune the band gap and morphology by varying the cationic composition opens up broad prospects for the thermodynamic design of novel functional materials. The obtained HEFs may find applications as visible-light photocatalysts, sensitizers in solar cells, and active supports or coatings in heterogeneous catalysis, where controlled porosity plays a key role.

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SPECIAL SESSION
ON THE DEVELOPMENT OF MEASUREMENT METHODS AND EXPERIMENTAL SETUPS IN THERMAL ANALYSIS AND CALORIMETRY

СПЕЦИАЛЬНАЯ СЕССИЯ, ПОСВЯЩЕННАЯ РАЗВИТИЮ МЕТОДОВ И СОЗДАНИЮ ПРИБОРОВ ТЕРМИЧЕСКОГО АНАЛИЗА И КАЛОРИМЕТРИИ

DEVELOPMENT OF METROLOGICAL ASSURANCE IN THE FIELD OF THERMAL ANALYSIS AND CALORIMETRY

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As stated in a lately accepted definition, "Thermal analysis (TA) is the study of the relationship between a sample property and its temperature as the sample is heated or cooled in a controlled manner" [1]. Due to the diversity of the types of studied samples and their measurable properties, a broad range of experimental techniques is currently employed in TA, with new methods continuously developing alongside scientific and technological progress.

Obtaining reliable measurement results, that are suitable for reasonable interpretation, requires performance evaluation for both methods and instrumentation. From a metrological perspective, it requires a well-defined traceability chain, established procedures, and appropriate reference standards. However, such means of metrological assurance are not available for some TA and calorimetric techniques, particularly for recently developed or rapidly evolving methods.

The goal of this study is to evaluate the current state of metrological assurance in TA and calorimetry, highlighting known issues, perspectives for development and available alternative tools in modern knowledge-intensive fields of TA application.

An overview of TA and calorimetric techniques is presented, covering both classical methods, such as thermogravimetric analysis (TG), bomb calorimetry, and differential scanning calorimetry (DSC), and more recent or specialized approaches.

As expected, largest deficits in metrological assurance are observed for newer techniques (i.e. Chip Calorimetry). Metrological assurance for classical methods is mostly well established, although for some well-known techniques such as Thermomechanical Analysis (TMA) and Dynamic Mechanical Analysis (DMA) a shortage of suitable reference materials and standardized procedures is observed. Similar issues are reported for classical methods operating near the limits of measurement ranges (e.g., low-temperature DSC, microcalorimetry, high-temperature dilatometry) [2,3]. Some cases where reliability of measurement results is negatively affected by the lack of metrological assurance are presented in detail.

Based on the analysis, general recommendations are formulated for performance evaluation in thermal analysis and calorimetry. Where available, official means of metrological assurance are presented, provided by metrology institutes in Russia and internationally. In addition, non-certified reliable sources, such as IUPAC recommendations, are considered when relevant. Current limitations in metrological assurance are summarized and identified as priority areas requiring further development.

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EDUCATIONAL HEAT FLUX DIFFERENTIAL SCANNING CALORIMETER "KOLIBRI-1.1"

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One of the goals of the educational process is to help students acquiring practical skills in their chosen field. In this regard, the importance of various practical training sessions, demonstration and laboratory work, research activities, educational research projects, etc. cannot be overestimated. The level and feasibility of all these activities are largely determined by the state of the educational institution's resources, i.e., the availability and condition of existing instruments and equipment.

Considering thermal analysis as a broad area of expertise, it is regrettable to note that in most cases, student experiences in this field are limited to constructing cooling curves for alloys, which is typically included in laboratory practical training for general courses of physical chemistry. Some time is provided for teaching modern calorimetry and thermal analytical equipment in various specialized courses, but to a much extent this remains largely theoretical. Practical and (most importantly) independent training on modern instruments is usually limited and not widespread. This is largely due to their high cost and limited resources for spare parts and repairs, and recently, in some cases, the impossibility of such repairs due to geopolitical reasons. Therefore, a pressing task is the development and creation of training instruments that are as close as possible to full-featured professional instruments in their capabilities, characteristics, software, and operating features, while being significantly less expensive.

This report will present the results of the development of such an educational instrument – the Kolibri-1.1 heat flux differential scanning calorimeter. The device is designed for thermal analysis and measurements of thermodynamic characteristics (temperature and enthalpy of phase transitions, heat capacity) of solid, powdered, and liquid materials, as well as for constructing phase diagrams. The calorimeter is a benchtop laboratory instrument consisting of a heating furnace, a three-position calorimeter cell, a cooling system, an analog-to-digital converter combined with an amplifier and data acquisition system and is controlled by an external computer. The design of the three-position calorimeter cell allows for the simultaneous measurement of two samples relative to a single reference sample.

The operating temperature range is 25–200 °C, the heating rate range is 0.5–10 °C/min, the DSC sensor sensitivity is 110 μV/mW, the resolution is 0.01 mW, the noise level (RMS for 1 hour at 100 °C) is 0.045 mW, and an emergency protection system is available in case of overheating of the measuring unit.

A practical course on thermal analysis was implemented using the manufactured calorimeter prototypes; the laboratory work on melting diagrams was modernized as part of the general course in physical chemistry; and laboratory work on thermal analysis was conducted at the Sirius Educational Center as a part of the thermodynamics educational program.

FAST SCANNING CALORIMETRY AS A TOOL FOR THERMODYNAMIC MEASUREMENTS – ADVANTAGES AND LIMITATIONS

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Fast scanning calorimetry (FSC) is an advanced development of the widely used differential scanning calorimetry (DSC) technique. It allows rapid heating and cooling (up to 10^6 K/s and above) of nanogram-scale samples. Rapid heating and cooling enable the probing of processes and states on much shorter time scales than conventional DSC and provide significant advantages. These include the prevention of thermal degradation in thermally labile compounds, the suppression of reorganization during heating, the inhibition of crystallization during cooling, and many others.

The application of FSC has allowed, for the first time, the measurement of melting temperatures, enthalpies, and heat capacities in the supercooled liquid state for various compounds. These range from small organic molecules to biological polymers, including metastable polymorphs. Tremendous progress has been achieved in studying the properties of supercooled amorphous phases and the processes occurring within them, including their associated thermodynamic parameters. Other applications of FSC in thermodynamics include measuring vaporization and sublimation parameters, accessing the thermodynamics of folding intermediates, and evaluating the effects of confinement and surfaces on thermodynamic properties, among others.

However, like any instrument, FSC has its own limitations. These include the impossibility of direct sample mass measurement, the need to account for thermal gradients, the avoidance of unwanted vaporization, and size effects.

This presentation outlines the experience gained from applying FSC at Kazan Federal University, as well as recent developments reported in the literature.

The work was supported by RSCF project No. 25-73-20073.

THERMOELECTRIC MODULES FOR CRYOSCOPIC ANALYSIS: EMPLOYING PELTIER ELEMENTS AS BOTH HEAT FLUX SENSORS AND THERMAL ACTUATORS

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Thermoelectric modules are widely employed in modern instrumentation for diverse purposes, including thermal management via the Peltier effect when an electric current is passed through the modules, as well as heat flux sensing based on the Seebeck effect [1].

In turn, the use of low-cost “Peltier modules” enables the development of a device that combines both the Seebeck and Peltier effects, as demonstrated in this work through an instrument designed for extended or synchronous cryoscopic analysis. By connecting high-power thermoelectric modules via a reversible semiconductor H-bridge, the measurement zone can be both heated to +60 °C and cooled down to –30 °C.

The heat flux to and from these modules passes directly through differentially connected small-scale Peltier modules characterized by a high Seebeck coefficient, allowing the detection of thermal effects associated with phase transitions in liquid and solid samples, as well as dilution and dissolution effects, with a resolution on the order of milliwatts. Temperature control and monitoring are implemented using a microcontroller-based circuit equipped with digital semiconductor sensors. The study also presents examples of polythermal studies conducted on selected binary systems using this setup. Results of test measurements indicate that the proposed device is well suited for widespread use in standard laboratory conditions.

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ADVANTAGES OF FAST SCANNING CALORIMETRY IN STUDYING THE THERMODYNAMICS OF PHASE TRANSITIONS IN PHARMACEUTICALS

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The study of the thermodynamic properties of pharmaceutical compounds is one of the most essential tasks in modern pharmaceuticals. The thermodynamic parameters of phase transitions significantly influence key physicochemical characteristics of compounds, such as solubility, stability, and bioavailability. However, a great number of pharmaceutical drugs is thermally unstable, which complicates their investigation.

To address this issue, a wide range of direct and indirect experimental methods have been proposed so far, as, for example, differential scanning calorimetry, solubility measurements, and solution calorimetry. In the context of thermally unstable compounds, fast scanning calorimetry is particularly interesting [1,2,3]. Due to the small sample size required for measurements, fast scanning calorimetry enables the study of the thermodynamic properties of compounds at high (up to 10000 K s^{-1}) scanning rates. This allows for the investigation of previously inaccessible thermodynamic parameters of substances by suppressing kinetically controlled processes, including decomposition, crystallization, and polymorphic transitions, and improving sample volatility for vapor pressure measurements.

In this work, we conducted a comprehensive study of the thermodynamic parameters of phase transitions for several pharmaceutical and model compounds using fast scanning calorimetry in combination with differential scanning calorimetry, solution calorimetry, and computational methods. As a result, a consistent set of thermodynamic data was obtained: the vapor pressure over the liquid and crystalline phases, the heat capacities of the ideal gas, liquid, and crystalline phases, and the enthalpies of fusion, vaporization, and sublimation over a wide temperature range.

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RESEARCH AND DEVELOPMENT OF PHASE TRANSITION TEMPERATURE REFERENCE MATERIAL FOR MEASURING INSTRUMENTS IMPLEMENTING THERMAL ANALYSIS METHODS METROLOGICAL SUPPORT

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Thermal analysis (TA) is a group of methods in which the physical properties of a substance are measured as a function of temperature or time while the substance is subjected to a program of controlled temperature changes. The most common methods are differential thermal analysis (DTA) and differential scanning calorimetry (DSC) [1], the detailed classification of the main methods is given in [2]. In addition to the above methods, others are being developed [3]. In turn, achieving the required metrological characteristics of TA devices is impossible without providing them with reference material (RM).

More than 100 types of measuring instruments (MI) TA have been entered into the state register of MI. The temperature range (TR) of MI is from minus 150 °C to plus 2000 °C. Until recently (2022), the list of RM for metrological support of the above SI consisted of 6 types of RM, covering TR from plus 30 °C to plus 770 °C. At UNIIM - a branch of the FSUE "VNIIM named after D. I. Mendeleyev" continues research and development of phase transition temperature RM for metrological support of MI implementing TA methods. Currently, the list of RM comprises 23 types and covers TR from plus 30 °C to plus 1600 °C. Future developments include expanding of the TR (from minus 150 °C to plus 1800 °C), expanding the range of RM compatibility with various crucible types, and increasing the accuracy of approximation during calibration of MI TA.

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MEASUREMENT UNCERTAINTY IN ISOTHERMAL TITRATION CALORIMETRY

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Isothermal Titration Calorimetry (ITC) has a wide range of application in chemical and biochemical research. This method is based on the measurement of the heat effects of the studied process and allows to simultaneously determine several thermodynamic parameters in a single experiment. Several issues were previously reported in literature concerning metrological aspects of ITC [1], and more recent research [2] still emphasizes calibration and uncertainty evaluation in ITC as an ongoing problem.

In 2023 VNIIM calorimetry lab finished a project on improvement of the State Primary Standard of heat quantity in the field of solution and reaction calorimetry GET 133. A new calorimetric complex including a standard titration microcalorimeter (TMC) and a NanoITC SV microcalorimeter-comparator was developed that allowed to implement the ITC method and broaden the measurement capabilities of the GET 133 Primary Standard to the microcalorimetry range.

The goal of current work was to study and evaluate the uncertainty contributions based on the measurement model developed for the TMC considering its operating principle, which consists in determining the energy equivalent of the calorimeter ε in stationary mode and measuring the amount of heat Q released during the titration process. The contributions studied included instrumental sources from the characteristics of the measuring equipment and methodological sources from the experiment design, data analysis and interpretation.

The standard GUM approach [3] and the Monte Carlo method [4] were used to estimate combined standard and expanded uncertainties for determining the energy equivalent and measuring the amount of heat. As a result of microcalorimeter studies, the capability of realizing the unit of heat quantity in a range from 100 μJ to 5000 μJ with an expanded uncertainty from 1.2 % to 8.6 % was confirmed.

Our uncertainty estimates obtained using the “bottom-up” approach basing on the uncertainty components were compared with the “top-down” estimate based on the interlaboratory study results described in [1].

In perspective, the results of this study can be adapted to get more reliable uncertainty estimates for heat effects measured by commercial measuring instruments.

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