

# XX

## INTERNATIONAL CONFERENCE ON CHEMICAL THERMODYNAMICS IN RUSSIA

### SCHOOL-CONFERENCE ON CHEMICAL THERMODYNAMICS FOR YOUNG SCIENTISTS

# ABSTRACTS

**NIZHNI NOVGOROD  
22 — 26 JUNE, 2015**





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The XX International Conference on Chemical Thermodynamics in Russia (RCCT 2015) is organized to bring together scientists from all domains of Physical Chemistry in order to exchange their recent experience and achievements, to improve scientific cooperation. Traditionally the Conference is organized since 1961 in different Russian scientific centers (including former USSR member states during Soviet time): seven times in Moscow, three times in Saint Petersburg, twice in Tbilisi and once in such cities as Krasnoyarsk, Novosibirsk, Nizhni Novgorod, Ivanovo, Suzdal, Kazan, and Samara. Conference program includes plenary lectures, oral presentations, round tables and poster sessions.

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**Plenary lectures**



**ON THE SIZE DEPENDENCE OF THE SURFACE FREE ENERGY OF LIQUID, GAS AND CRYSTAL NUCLEI (BY DATA OF MOLECULAR DYNAMICS SIMULATION)**

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The problem of the size dependence of surface free energy is the central one in nucleation theory. One of the approaches to the solution of this problem is connected with the use of methods of computer simulation. According to Gibbs, the surface free energy of a new-phase nucleus, as a function of the tension surface curvature, may be calculated from data on the work of formation of a critical nucleus and conditions of its mechanical and real equilibrium with the phase of the environment. In its turn, the work of formation of a critical nucleus is accessible for both a direct determination in a molecular dynamics experiment and obtaining from homogeneous nucleation theory by data on the nucleation rate and other parameters of the nucleation process.

We used the molecular dynamics method to investigate the kinetics of spontaneous cavitation and crystallization of a Lennard-Jones fluid at reduced temperatures  $T^* = k_B T / \epsilon = 0.35-1.1$ . Here  $k_B$  is the Boltzman constant, and  $\epsilon$  is the potential parameter. Calculations were made in models containing from 2 048 to 1 000 000 particles by the methods of lifetime measurement, mean first-passage time, and the transition interface sampling. Along with the nucleation rate, which in computer experiments varied over 10 orders, we determined the diffusion coefficient of nuclei in the space of their dimensions, the Zeldovich nonequilibrium factor, the size and pressure in a critical nucleus. The work of formation of a critical nucleus was calculated from these data.

In investigating cavitation a striking discrepancy has been revealed between classical nucleation theory and simulation results, which in the nucleation rate reached 20 orders at  $T^* = 0.35$ . It has been found that such a discrepancy is connected with the fact that classical theory does not take into account "the size effect", i.e. dependence of the properties of a nucleus on its size. An equation that describes the size dependence of the surface free energy of cavitation pockets at temperatures  $T^* = 0.35-0.8$  has been obtained in the framework of an extended Tolman expansion. Using data of Ref. [1] on the kinetics of condensation of a Lennard-Jones gas, we determined the surface tension of critical-size droplets. It is shown that data obtained in changing the sign of the Tolman parameter from negative to positive are qualitatively and quantitatively described by the equation for vapor bubbles.

The baric dependence of the spontaneous crystallization rate of a Lennard-Jones fluid has been determined. Discrepancies in the nucleation rate between simulation results and classical nucleation theory do not exceed 2 orders. The data obtained were used to determine the size dependence of the surface free energy of critical crystals. It has been found that at reduced temperatures above 0.55 the difference in the values of the surface free energy at a flat and at a curved interface does not exceed 10 %. At  $T < 0.55$  the liquid and crystal phases cannot coexist at a flat interface even in metastable states, whereas at a curved interface such a coexistence is observed. At negative pressures nucleation in a supercooled liquid may also proceed at temperatures below the endpoint of the melting line.

[1] Wedekind, J.; Wölk, J.; Reguera, D.; Strey, R. J. Chem. Phys., 2007, 127, 154515.

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## MEASUREMENT AND MODELING OF THERMODYNAMIC PROPERTIES OF GAS HYDRATES IN RELATION WITH THEIR POTENTIAL USE IN NOVEL PROCESSES

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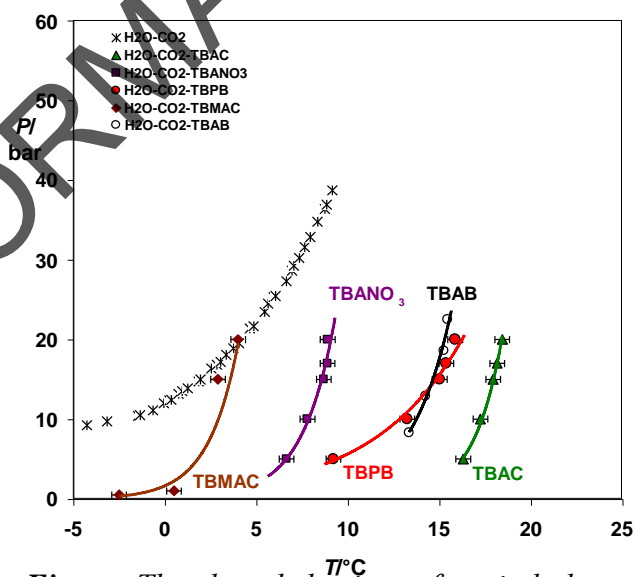
Gas hydrates are ice-like inclusion compounds, in which guest molecules, mostly light hydrocarbons, acid gases ( $H_2S$ ,  $CO_2$ ),  $N_2$ ,  $H_2$  etc., are entrapped into cavities made of hydrogen-bonded water molecules arranged in polyhedral patterns. These compounds have been extensively studied in relation with the oil and gas industry, where they are responsible for flow assurance and safety issues. Applications of gas hydrates in various processes, such as gas storage and transport, gas separation, water purification, or refrigeration engineering, have recently been proposed. Those potential developments, though really promising, have to be compared and validated against existing, mature technologies. This requires large amounts of experimental work to be done. Besides, the modeling of phase behaviour and related thermophysical properties of a variety of new hydrates is necessary for future process development purposes.

High-pressure differential scanning calorimetry has been used to determine the stability limits of a variety of hydrates (Figure is an example, new results will be provided) and to measure their enthalpies of dissociation and heat capacities.

Furthermore, reactor experiments were performed to determine the gas occupancy and selectivity of various hydrate structures in the presence of gas mixtures.

The thermodynamic modeling of semi-clathrate hydrates of several quaternary salts in the presence of gases has been performed using an extended van der Waals and Platteeuw approach for the hydrate phase and SAFT-VRE equation of state to represent the fluid phases in the presence of electrolytes.

The experimental and model results will be discussed in the view of assessing the following hydrate-based processes: sea water desalination for drinking water production ; methane and carbon dioxide purification for the valorization of biogas ; storage of hydrogen for the fuelling of vehicles and non mobile devices ; phase change materials for the storage and transport of thermal energy in heating and refrigeration applications. Some conclusions regarding the feasibility and economical viability of those technologies will be given.



**Figure:** The phase behaviour of semi-clathrate hydrates of tetrabutyl-ammonium chloride (TBAC), bromide (TBAB), nitrate (TBANO<sub>3</sub>), methyltributyl-ammonium chloride (TBMAC), and tetrabutyl-phosphonium bromide (TBPB) in the presence of  $CO_2$ .

## CONTINUOUS DRYING OF GASES BY IONIC LIQUIDS

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The drying of gases is a common process with a variety of applications:

- At the well, natural gas usually contains significant quantities of water vapor. Changes in temperature and pressure may condense this vapor. For domestic usage or other downstream gas processes, the level of water vapor has to be maintained below a certain value to prevent corrosion and hydrate formation in transportation pipelines. Usually, a dew point of about  $-5^{\circ}\text{C}$  is required.
- Pure  $\text{O}_2$  and  $\text{N}_2$  are produced by the separation of air by cryogenic distillation. In this process, the air is compressed and cooled. To prevent freezing, the air is dried to remove water (and  $\text{CO}_2$ ).
- In some cases, water vapor may lead to a deactivation of catalysts and has to be eliminated from feed gases, e.g. in the case of producing syngas for ammonia production.

There are several methods to dry gas. The most common of these are (1) refrigeration, in which the gas is cooled - e.g. by the Joule-Thomson effect - to the desired dew point and the condensed water is separated, (2) selective adsorption of water vapor on molecular sieves, and (3) selective absorption of water vapor by suitable liquid solvents. It is beyond the scope of this work to discuss the pros and cons of these processes. The focus of this work is on the selective absorption of water vapor in gas by liquids.

It is known for decades that gases can be dehydrated by solutions of solid salts like  $\text{KCl}$ ,  $\text{LiCl}$  and  $\text{LiBr}$  in water [1,2]. Particularly favorable is  $\text{LiBr}$ . Contrary to ionic liquids these salts melt at temperatures far above  $100^{\circ}\text{C}$  (e.g.  $\text{LiBr}$  at  $552^{\circ}\text{C}$ ), i.e. the liquid solvent is formed by the dissolution of a solid salt in water. The solubility of these salts and therefore the degree of dehydration is limited. For example, gas dehydration with a saturated solution of  $\text{LiBr}$  leads to an equilibrium (minimum) water vapor pressure of about 3 mbar (at  $30^{\circ}\text{C}$ ), which is equivalent to a dew point of about  $-7^{\circ}\text{C}$ . In industrial practice saturated solutions are not used, as the thermodynamic equilibrium is not reached (finite number of separation stages), and therefore the achievable dew point is higher.  $\text{LiBr}$  solutions have been applied for many decades in absorption chillers for air conditioning and for dehumidification of air (where glycols cannot be used as solvents). The application for drying of natural gas is not common (anymore) today.

Today, the standard method for natural gas dehydration by absorption is scrubbing with glycols. In most cases triethylene glycol (TEG) is used. The water-loaded glycols are regenerated by distillation. The regeneration temperature is limited to  $190^{\circ}\text{C}$  for TEG because decomposition starts at higher temperatures. This leads to a (minimal) residual water content of 2 wt-%, if the distillation is not done under vacuum. Without vacuum, the lowest dew point that can be achieved by gas scrubbing is about  $-10^{\circ}\text{C}$ . Although TEG is a high boiling liquid with normal boiling point and  $287^{\circ}\text{C}$ , losses by vaporization during absorption and most notably during regeneration at elevated temperatures cannot be avoided. Another source of glycol loss is foaming, which results from contamination of the glycol with hydrocarbons brought in with the gas. Foaming can only be controlled by the addition of foam inhibitors. According to literature [2] the loss at normal operating conditions is around 10 liters of glycole per million standard  $\text{m}^3$  of gas. Thus for a typical throughput of up to 10 million  $\text{m}^3$  per day of natural gas, this adds up to about 100 liters per day. Not much indeed, but more than nothing. Another problem is that



oxygen should not be present in the feed gas to prevent an oxidative decomposition of glycol and the formation of organic acids, which lead to corrosion. Thus, dehydration of air is not possible, just as the regeneration by stripping with air.

An ideal solvent for dehydration of a gas by absorption (scrubbing) of water vapor should have the following properties: low vapor pressure, high thermal stability, high affinity to water, low viscosity, and high oxidation and thermal stability. Ionic liquids like [EMIM][MeSO<sub>3</sub>] have most of these favorable properties, thus, making ILs promising alternatives to glycols.

As a contribution to the development of the processes discussed above, mixtures of water with the ionic liquid [EMIM][MeSO<sub>3</sub>] were investigated with regard to their suitability as drying agent in absorption columns.

The affinity to water can be described by the activity coefficient  $\gamma_{\text{H}_2\text{O}}$  in Raoult's law and should obviously be very small for an efficient absorbing process. In fact,  $\gamma_{\text{H}_2\text{O}}$  for [EMIM][MeSO<sub>3</sub>] is about 0.1, which is six times lower than  $\gamma_{\text{H}_2\text{O}}$  for TEG. Furthermore [EMIM][MeSO<sub>3</sub>] shows a high stability against oxidative decomposition. Therefore, in contrast to TEG, distillation (e.g. at 90 °C) or air stripping are appropriate and advantageous process steps to regenerate water loaded ionic liquid without significant loss of IL absorbent due to its very low vapor pressure.

Apart from choosing the suitable ionic liquid, design of continuous gas drying units requires the knowledge of crucial parameters such as the temperature-dependent activity coefficient and the mass transfer coefficient of water in ILs as well as loading/flooding point of the column. Thus, a continuous absorption unit was set up and used to determine such parameters for the representative system H<sub>2</sub>O-[EMIM][MeSO<sub>3</sub>]. The loading and flooding point was calculated using the correlation of Mersmann et al. [3] and validated experimentally. Furthermore, measurements of the gas and liquid side transfer coefficients were conducted and compared with correlations of Onda et al. [4]. Based on this data, a column design with the common HTU/NTU-model was developed to predict current and future drying tasks. Finally, a continuously operated absorption and desorption column was constructed and implemented. In this unit, long-term loop experiments for gas drying and regeneration of the ionic liquid were conducted. Here, the absorption and desorption temperature, water vapor content, flow rate of the IL and gas as well as the size and kind of packing (Raschig rings, spheres) were varied.

The experimental data show quite satisfactory and promising results with regard to the efficiency of gas drying using the ionic liquid [EMIM][MeSO<sub>3</sub>] in comparison to TEG.

[1] Schmidt, J. VEB Verlag für Grundstoffindustrie, Leipzig, 1970.

[2] Kohl, A. L.; Riessenfeld, F.C. Gulf Publishing, Houston, 1979.

[3] Mersmann, A.; Kind, M.; Stichmaier, J. Springer-Verlag Berlin Heidelberg, 1st Edition, 2011.

[4] Onda, K., Takeuchi, H.; Okumoto, Y. J. of Chem. Eng. of Japan, 1968, 2, 2, 56-62.

## ENERGY DEMAND FOR GLOBAL WELFARE AND ECOSYSTEM HEALTH

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During the last 60 years, the global primary energy consumption has grown by a factor of 4.5, whereas the global population has increased by a factor of 2.5. Hence, the average global requirements have almost doubled from 1 tonne of oil equivalent (1 toe = 42 GJ) per capita (pc) and year to 1.8 toe pc and year, mostly driven by the increasing energy demand of industrialized countries in North America and Europe.

The global primary energy consumption is 13 billion toe/a, and fossil fuels fill about 80% of the supply. The contribution of nuclear and hydro is 4% and 6%, respectively. The share of biomass is 8%, mainly traditional (not traded) biomass (7%) with the severe problem of negligible reforestation. Other renewables such as solar and wind do not play a role on a global basis (< 1%).

At present, a small part of the world's population has the lion's share of the energy consumption. The OECD-countries with a population of 1.2 billion people (18% of global population), have a share of 42% of the global energy consumption. In Asia (excl. China) and Africa, the annual demand per capita is only 0.7 toe compared to the OECD-value of 4.6 toe.

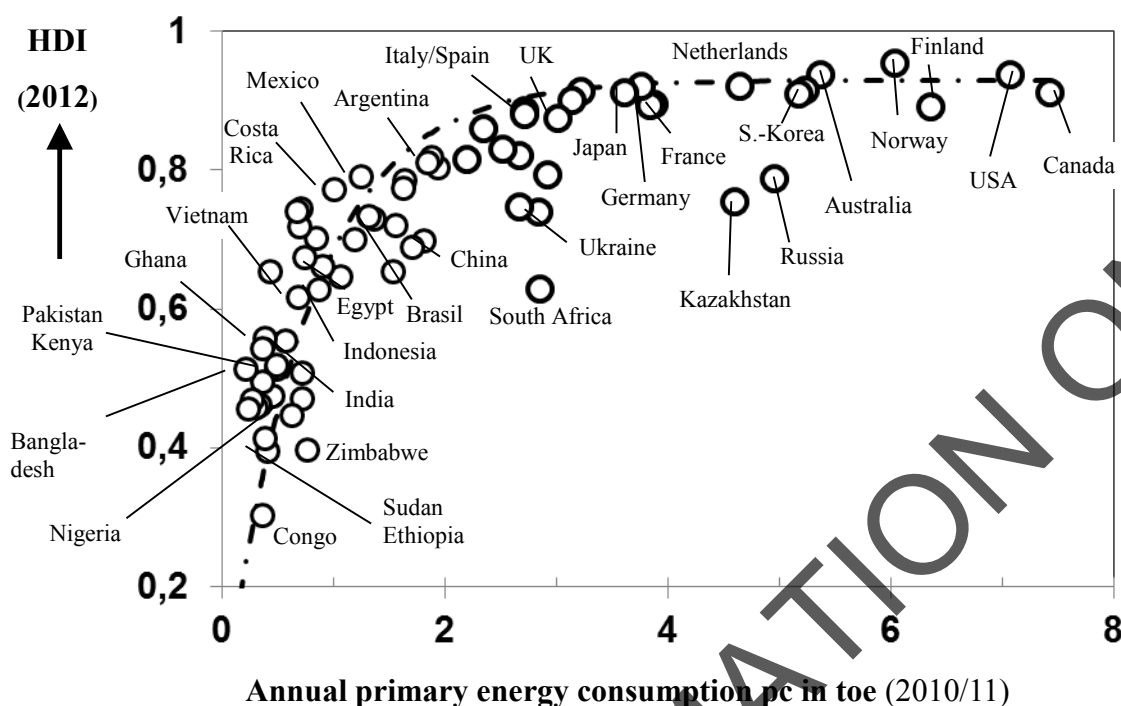
The current global energy consumption and mix, the continuous growth of the world population, and the still growing energy demand will inevitably lead to a conflict between stable societies and stable ecosystems [1, 2]. Thus, the question arises how the global energy demand can be reconciled with the necessity to preserve the integrity of the biosphere. To analyse the 21<sup>st</sup> century sustainability threats, three key questions have to be answered:

1. What is the energy demand per capita to ensure welfare of a society, i.e. how much energy is really needed to reach a *happy world population* on a global average basis?
2. What is on the other hand the maximum global energy consumption to ensure stable ecosystems, i.e. to ensure a *happy planet*?
3. Finally, how are we able to reconcile the world's future energy demand to ensure welfare for all people with the absolute necessity to preserve the integrity of the biosphere?

Social indicators of prosperity, welfare and happiness - e.g. measured by the Human Development Index - show that an annual energy consumption of 2 toe per capita (pc) should be enough to ensure a sufficient global average level of welfare (Figure 1). Hence, rich countries with currently up to 8 toe pc should reduce and poor should legitimately increase their energy demand until 2 toe pc are reached.

At today's global energy mix with 80% fossil fuels, even this optimistic scenario will inevitably lead to a conflict between welfare and stable ecosystems: The *ecological footprint* is a measure of human demand on the Earth's ecosystem, and is defined as the sum of the area of all cropland, grazing land, forest, build-up land, and fishing grounds required to produce food, fibre, timber etc., and of the carbon (CO<sub>2</sub>) footprint representing the biocapacity needed to absorb CO<sub>2</sub> emissions. Today, humanity's total ecological footprint equals 1.5 planet Earths [3]. In other words, humanity uses ecological services 1.5 times as fast as Earth is able to renew them. Without counteractions ("business as usual"), a value of about 3 global Earths will be reached in 2050. Today, North America and Europe have the largest footprints, 4 and about 2.5 planet Earths (if the whole world would act as the people these regions) compared to Latin America, Asia Pacific, and Africa with 1.5, 0.9, and 0.8, respectively.





**Figure:** Human Development Index (HDI) versus energy consumption per capita [4]. The HDI ranks countries by level of "human development" and combines with equal weighting factor normalized measures of life expectancy, education, and GNP per capita.

The world population will grow to 9 billion in 2050 compared to 7 billion today, and even an annual average energy consumption of 2 toe pc (scenario of "happy world population") would rise the ecological footprint at current energy mix from today 1.5 to 2 planet Earths.

The only solution to provide an average energy consumption of 2 toe pc ("happy population") without increasing the ecological footprint ("happy planet") is to reduce the single largest demand humanity put on the biosphere, which is the carbon (CO<sub>2</sub>) footprint with a share of 50% on the total footprint. Hence, only a complete shift from fossil fuels to renewables (except of the small amount probably still needed for chemicals and coke/steel) would half the ecological footprint; and that is exactly what is needed to achieve a value of one planet Earth. Fossil fuels like gas and oil may be limited on the long run, but the availability of fossil energy is not the problem of primary concern; the major problem lies in the CO<sub>2</sub> produced when they are burned. This can be clearly deduced from the comparison of the carbon inventory of fossil fuels reserves and of the atmosphere: The carbon inventory in the atmosphere, estimated with climate models for a global warming of 2 K above pre-industrial level, would be reached, if only 50% of the fossil fuel reserves are used (and much less, if we also take the resources into account).

How can the goal of 2 toe pc and year be reached without damaging the world's ecosystems? There is one clear conclusion: The non-solar renewables may be huge, but they are not huge enough. Even the technically feasible potential of wind, hydro, tide, wave, and geothermal energy would only cover 0.8 toe pc and year compared to the goal of 2 toe pc. To complete an energy plan that adds up, we must rely on one or more forms of solar power, or we use nuclear power (or both).

[1] Jess, A. Energy Policy, 2010, 38, 4663-4678.

[2] Kern, C.; et al. Chem. Ing. Techn. 2011, 83, 1777-1791.

[3] Global footprint network, Living planet report 2012, www.footprintnetwork.org.

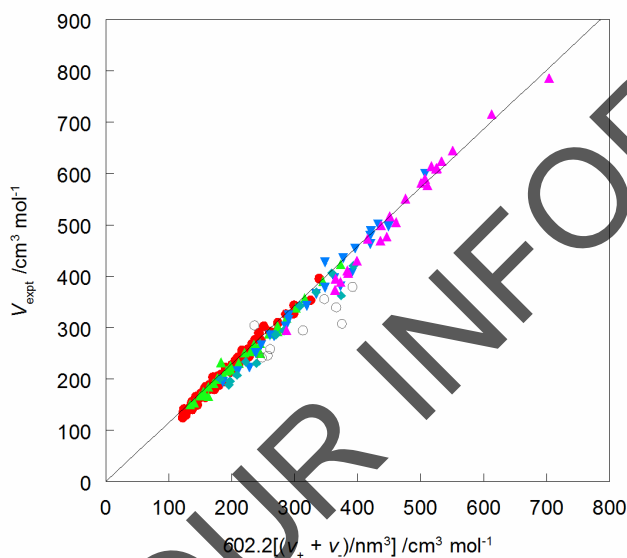
[4] United Nations Development Programme (UNDP), Human development report 2013.

## VOLUMETRIC PROPERTIES OF ROOM TEMPERATURE IONIC LIQUIDS

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RTILs are stoichiometric combinations of cations and anions that have melting points,  $T_m$ , generally in the range 0 to 100 °C, hence are liquid at ambient conditions or somewhat above. They have been proposed as “green” solvents because of their low vapor pressures and non-flammability, in spite of their being rather viscous and expensive. Their volumetric behavior depends on their measured densities. The isobaric expansibilities and isothermal compressibilities depend on the availability of densities as functions of the temperature and the pressure [1]. Several attempts have been made to predict the densities,  $\rho$ , hence the molar volumes,  $V$ , of room temperature ionic liquids (RTILs) from group contributions and the individual ionic volumes of the constituting cations,  $v_+$ , and anions,  $v_-$  [2-4]. A comprehensive table of the relevant ionic volumes has been prepared [5]. The molar volumes  $V$  of the RTILs are accordingly:  $V/\text{cm}^3 \text{ mol}^{-1} = 602.2[(v_+ + v_-)/\text{nm}^3]$ . However, the ionic volumes pertain to ions in crystals, hence this expression under-estimates the  $V$  of liquid RTILs, as shown in Figure.



**Figure:** The experimental molar volumes of RTILs at 25 °C plotted against their estimates from the ionic volumes. ●  $C_n\text{mim}^+$  salts, ▲  $C_n\text{Py}^+$  salts, ▼  $R_4\text{N}^+$  salts, ◆  $C_n\text{MePyrr}^+$  salts, and ■  $R_4\text{P}^+$  salts.

The difference is ascribed to the expansion of the crystal on melting, but there are only few relevant data on this for RTILs. Still, a large fraction of this discrepancy in the  $V$  calculated from the ionic volumes and the experimental data can be explained on this basis. The empirical expression  $V_{\text{est}}/\text{cm}^3 \text{ mol}^{-1} = 689.5[(v_+ + v_-)/\text{nm}^3]$  describes the data [5] for 160 RTILs of various kinds well. The resulting densities,  $\rho = M/V_{\text{est}}$  then have a standard error of 3.8%, better than other estimates. Used as a learning set, this permits the estimation of  $\rho$  for other RTILs.

The expansion on melting creates cavities in the liquid [6] that are related to the surface tension of the liquid [7]:  $\sigma_{\text{calc}}/\text{mN m}^{-1} = 4.9[(V - 602.2(v_+ + v_-)/\text{nm}^3)/\text{cm}^3 \text{ mol}^{-1}]^{-2/3}$ . Although the scatter of the plot of experimental vs. calculated surface tension is fairly large, the relationship is valid. On the other hand, the cavities are related also to the fluidity  $\Phi$  (the reciprocal of the viscosity) of the RTILs by the expression [8]:  $\Phi = B[(V - V_0)/V_0]$ , where  $(V - V_0)/V_0$  is the fraction of void volume and  $V_0$  is that molar volume “at which the molecules are so closely crowded as to prevent viscous flow while still retaining rotational freedom”. This volume differs from the molar volume at 25 °C by only 1%, denoting the absence of large cavities, contrary to what is expected from the surface tensions.



The thermal expansibilities of RTILs are substantially constant [3,4] and the ionic volumes at  $T$  are:  $(v_+ + v_-)(T) = (v_+ + v_-)^0 [1 + 0.67 \times 10^{-3} \{(T/K) - 298.15\}]$  to be used in the expression for the molar volume  $V_{\text{est}}$  above.

There are only few data for the isothermal compressibility,  $\kappa_T$ , of RTILs, practically limited to 1-alkyl-3-methylimidazolium salts. These range from 0.337 to 0.612  $\text{GPa}^{-1}$ . The surface tension data,  $\sigma$ , also have a span of a factor of 2, but the product  $\kappa_T \sigma$  is fairly constant,  $16.3 \pm 2.2 \text{ nm}$ , and is not inversely correlated with the cohesive energy of the RTILs, contrary to the case of the high temperature molten salts [9]. Since surface tension data are much more widely available, unknown isothermal compressibilities may be estimated from  $16.3/\sigma$  as a good approximation.

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**APPLICATIONS OF CONSTRAINED GIBBS ENERGIES IN PROCESS AND MATERIALS RESEARCH**

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Mastering of complex chemical and physical interactions is a lasting problem in process and material science. Physico-chemical relations are utilized for the purposes of developing structural and operational material properties and controlling the durability of materials under various conditions. In a similar manner, the process technology aims at achieving optimal functionality with a focus on both saving raw materials and energy and reducing the environmental impacts of the overall process.

The chemical and physical interactions occurring in reactive flows and material structures can be mathematically described using the thermodynamic free energy. The minimization of the free energy combines the basic laws of the thermodynamic theory and quantifies all changes generated by the physical and chemical driving forces in various materials. The spontaneously occurring chemical change is guided by the tendency of the reaction system to reach equilibrium (Gibbs free energy minimum). As thermodynamics also gives a mathematical form to the respective energetic changes, the approach provides its masters an access to an efficient and systematic methodology for managing both material properties and behavior of processes. Over the past few decades, the rapid development of computers has contributed to transforming the abstract thermodynamic theories to practical solutions. Fortuitously, solving thermodynamic problems does not usually require large computational capacity, as the numerical performance of personal workstations is quite sufficient in most cases.

Conventional thermodynamic calculation methods focus on phase changes and on products of chemical reactions as function of temperature and pressure. Therefore the methods in wide international use are specifically suited for calculating chemical equilibrium compositions and for drawing diagrams describing multicomponent phase equilibria. Both approaches are extensively used in chemical technology and material sciences.

Yet, in practical processes equilibrium is seldom reached, or the composition of the material being processed is affected also by other than purely chemical factors. Accordingly, a new approach is necessary for problems in which both the time dynamics of the chemical change and various physical preconditions must be taken into account. The novel Constrained Gibbs Free energy (CFE) technique provides a quantitative methodology for such chemical or biochemical processes which are affected by specific physical functions deciphered as thermodynamic work. Based on computational multiphase thermodynamics, CFE deals with the complexity of matter in systems involving changes in energy and in chemical or phase composition. The salient feature of the method is its ability to incorporate the contribution from generalized work to a multiphase free energy computation, which facilitates quantifiable solutions of intricate chemical problems in systems affected by either internal or external forces due e.g. to surface tension, charge and electric-magnetic factors. The same principle can also be applied to non-equilibrium processes, allowing for the inclusion of chemical reaction rates as affinity related constraints in the thermodynamic multiphase analysis.

The scope of CFE applicability ranges from functional behavior of nanosize particles to features of dynamic superequilibria in large scale industrial and environmental processes [1-3]. Thus the method gives an exceptionally large array of potential uses in the fields of materials and process chemistry as well as in the development of sustainable technology.

## XX International conference on chemical thermodynamics in Russia

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The presentation will cover a number of examples of recent applications of the multicomponent thermodynamic approach with particular focus on the methodology of constrained partial or local equilibria, including saving of raw materials and energy in industrial multiphase processes and applying constrained equilibria to paraequilibrium and interfacial systems in materials science.

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**THE CONCENTRATION TRANSITION FROM WATER-ELECTROLYTE TO  
ELECTROLYTE-WATER SOLVENT**

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Aqueous electrolyte solutions in a wide range of concentrations (including high concentrated and saturated solutions) have very different thermodynamic properties. State and role of water and ion organization in such systems are considered. A general model of structural, dielectric and thermodynamic changes in transition from dilute solutions to aqueous melts of crystalhydrates and salts is suggested. This structural transformation is caused by a decrease in electrostatic hydration effects and decrease of static dielectric permittivity on the boundary of the first concentration region. The real values of permittivity are determined by us from microwave dielectric measurements for more than 20 different solutions[1]. The existence and limit of the first area are connected with the stability of the initial water structure in solutions. The concentration boundary is determined more than 50 systems. The appearance of ion and water-ion cluster nanostructures in the second region is considered to be a common property of highly concentrated solutions of electrolytes[2-4]. It follows from our data of experimental physical methods, using X-ray small angles, electronic and dielectric spectra for different solutions (8 systems) and computer simulation results by molecular dynamic method[5,6] (for Li<sub>2</sub>SO<sub>4</sub>: and LiCl solutions).

Macroscopic properties of solutions also exhibit the specific features that can be due to the above structural transformation. We can see it in microwave dielectric dependences, as well as thermodynamic (activity of water, partial enthalpy and volumetric effects) and molecular-kinetic (specific conductivity, viscosity, etc) for many systems. The changes of homogeneous (the complex formation and aggregation) equilibria of double and multicomponent water-salt systems are interpreted in term of the concept developed [7,8]. The changes of temperature and pressure dependences of salt solubility and their relationship with hydration and solution structure are considered (about 200 systems), using thermodynamic model (that include partial enthalpy and partial molar volumetric effects of solubility) and assuming the division of these values into components corresponding to the contributions of ion-ion, water-ion and water-water interactions in the solid phase and solution. Polytherm specific features of binary phase diagrams in the two structural concentration regions are established. The difference of aqueous and nonaqueous systems (5 solvents) is caused by specific structure and solvation effects. The behavior and some singular points for the isotherm of solubility in ternary water-salt systems are explained using solution structure-kinetic and dielectric data (10 model systems). Therefore, the above-mentioned general approach can account for and sometimes predict various properties and chemical equilibria in aqueous electrolyte solutions.

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## DEVELOPMENT OF EXPERIMENTAL EQUIPMENT AND MODELS FOR THERMOPHYSICAL PROPERTIES

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Thermophysical properties, for e.g. critical properties, vapour pressures, liquid viscosities, infinite dilution activity coefficients, etc, are essential for the design, simulation and optimization of chemical processes and plants. The experimental measurement of some of these properties can be challenging, which results in experimental data for these properties either not being available or available for limited numbers of compounds. This requires the subsequent development of correlative and predictive models.

Over the last 30 years, the Thermodynamics Research Unit at the University of KwaZulu-Natal has built a reputation for the development of equipment for the measurement of thermophysical properties. In the last 15 years, we have also undertaken the development of various correlative and predictive models for thermophysical properties. We have a strong belief in the complementarity of experimental and computational studies and have endeavored to develop both aspects.

In this presentation, some of the experimental equipment developed in our laboratories for vapour pressure measurements, determination of infinite dilution activity coefficients, critical property measurement, pressure-temperature-volume measurements, heat capacity, etc, will be discussed.

With regard to the development of correlations and predictive models for thermophysical properties, a range of group contribution (GC), and quantitative structure property relationship (QSPR) models which have been developed will be presented and discussed. Models have been developed for vapour pressure, boiling points, critical properties, liquid viscosity, liquid thermal conductivity, thermal decomposition temperatures, electrical conductivity, sublimation and vaporization enthalpies, saturated liquid speeds of sound, standard molar chemical exergies, refractive indices, and freezing points. In addition for ionic liquids, models and correlations were developed for heat capacity, surface tension, infinite dilution activity coefficients, and critical temperature. The computational methods used have enabled large databases to be utilized for thermophysical property development, which affords greater applicability of models developed. Novel algorithms developed for the determination of model parameters will also be briefly discussed.

NOVEL THERMODYNAMIC POTENTIALS FOR SOLIDS  
AND HETEROGENEOUS SYSTEMS

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The necessity of introducing new thermodynamic potentials appears in the thermodynamics of solid or mixed systems subjected to complex external mechanical forces when ordinary free energy and Gibbs energy cannot serve as potentials, i.e. do not produce work. Indeed, using, for example, free energy as a thermodynamic potential requires invariability of the system boundaries, but this condition cannot be fulfilled for a loaded solid because of strain. Classical Gibbs energy is better in that respect and can serve as a thermodynamic potential, but only in the case when the external force is a uniform outer pressure (for a capillary system with phases of different pressures, Gibbs energy should be defined with respect to one chosen pressure to be under the control, which is typically outer pressure). The case of arbitrary loading requires a more general potential corresponding to a given constant loading.

The novel-for-chemical-thermodynamics  $J$ -potential is defined as [1, 2]

$$J \equiv \Omega - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA,$$

where  $\Omega$  is grand thermodynamic potential,  $\mathbf{P}$  is an external force (stress) per unit area of the system surface as a function of location on the surface ( $A$ ),  $\mathbf{u}$  is the local vector of the surface displacement, and  $A$  is the surface area; the integration is carried out over the whole surface of the system.

The quantity  $\Omega$  in is read as the grand thermodynamic potential generalized for solids with account of chemical potentials of both mobile and immobile (forming the solid lattice) species in the form [3]

$$\Omega \equiv F - \sum_i \mu_i N_i - \mu_j^\beta N_j = F - \sum_i \mu_i N_i - \mu_{j(mn)}^\alpha N_j,$$

where  $F$  is free energy,  $\mu$  is chemical potential,  $N$  is the number of molecules, the subscript  $i$  and  $j$  refer to mobile and immobile species, respectively, the superscript  $\alpha$  refers to a solid phase, and the superscript  $\beta$  refers to a real or imaginary fluid phase in contact and equilibrium with phase  $\alpha$ . The quantity  $\mu_j^\beta$  is the chemical potential of species  $j$  in solution, while  $\mu_{j(mn)}^\alpha$  is the normal-to-the-surface component of the chemical potential tensor of species  $j$  in the solid phase.

Omitting the last term defines hybrid potential  $\tilde{\Omega}$ , and, correspondingly, hybrid  $J$ -potential is defined as

$$\tilde{J} \equiv \tilde{\Omega} - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA$$

The equilibrium principle for  $J$ - and  $\tilde{J}$ -potentials is written as [1]

$$(\delta J)_{T,P,\mu_i,\mu_{j(mn)}} = 0, \quad (\delta \tilde{J})_{T,P,\mu_i} = 0$$

and can be used for finding equilibrium configurations in complex (say, capillary) systems. The fundamental equations of both the potentials are derived separately for bulk phases and interfaces. Some examples of the practical use of the novel potentials are given for the sake of illustration.

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## THERMODYNAMIC PROPERTIES AND THERMAL BEHAVIOR OF LITHIUM BATTERIES

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Lithium batteries are presently the most interesting electrochemical devices for energy storage applications in electrical vehicles, renewable energies (solar, wind) and portable consumer electronics. Their high energy and power density combined with excellent electrochemical cycling behavior is the base for numerous commercial applications. However, significantly improved thermal and safety properties as well as longer life time at high energy capacity levels are major concerns initiating worldwide scientific and engineering research.

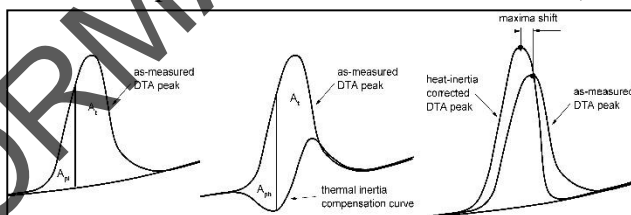
Thermodynamics and phase diagrams of advanced materials used for lithium battery design are directly linked to electrochemical performances, heat generation and safety behavior during electrochemical cell operation. However, such thermodynamic data are largely missing even for the most important cathode materials e.g.  $\text{Li}(\text{Ni},\text{Mn},\text{Co})\text{O}_2$  (NMC),  $\text{LiFePO}_4$  (LFP),  $\text{LiMn}_2\text{O}_4$  (LMO) and their derivatives. The situation is similar for anode materials based on  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO), tin alloys and conversion-type compounds (e.g. Cu-based), respectively. Therefore, the priority program SPP1473 (WeNDeLIB), funded by the German Research Foundation (DFG), aims at investigating thermodynamic properties and phase diagrams and link them to electrochemical and thermal cell behavior. *The presentation will give an overview on these activities and introduces selected examples to illustrate the work done.* The fundamental research includes heterogeneous phase equilibria, heat capacities, enthalpies, chemical potentials as well as entropy measurements on full electrochemical cells. CALPHAD-type thermodynamic models and descriptions of ternary and multicomponent systems are then used to calculate reversible open circuit voltages of electrochemical (half) cells. Also full coulometric titration curves are calculated and compared with experimental information. The thermodynamic datasets and additional thermophysical data can then be used for an advanced application-oriented electrochemical-thermal modeling. The ultimate aim is the simulation of thermal behavior, heat generation and physico-chemical conditions for thermal runaway of lithium batteries.

## YET UNSETTLED CONSEQUENCES OF SAMPLE HEAT INERTIA AND TEMPERATURE GRADIENTS IN DIFFERENTIAL THERMAL MEASUREMENTS

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Thermophysical measurements are historically outlined through the cases of differential thermal examinations (revealed from Rudberg 1820s to Russian Kurnakov 1940s) accentuating its impact to solid-state processes and application to both the fingerprinting, qualitative and quantitative studies. Particular interest is paid to the study of glasses showing its convenient applicability in the characterisation of temperatures (glass transformation, crystallization and determination of various glass-forming criteria, Hruby glass-forming coefficient), reaction dynamics (such as relaxation phenomena and data treatment for portraying reaction kinetics of nucleation, crystallization). The early and even current DTA peak analysis seems to habitually follow the straightforward patterns of spectral analysis (such as XRD) so that some specific aspects heat measurements are discussed such as the impact of the term of heat transfer sluggishness affecting the DTA peak background, creation of temperature gradients (particularly critical when using the extreme heating/cooling rates), impact of the size of sample and the extent of its surface, etc. The complexity of a DTA peak is analysed in more details including necessary corrections created by the effect of the sample thermal inertia and temperature gradients. Faulty applications to study reaction kinetics are discussed (especially critiquing the Kissinger evolution method).



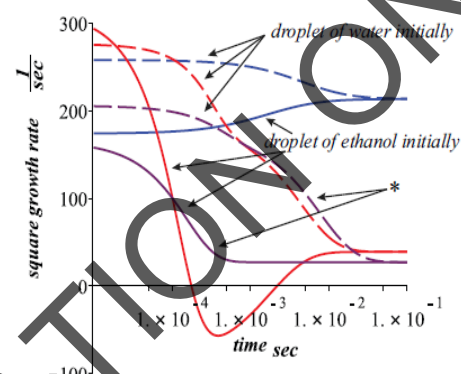
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## THERMODYNAMICS OF MULTICOMPONENT CONDENSATION ON SMALL FREE DROPLETS

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Equilibrium and non-equilibrium chemical thermodynamics is a tool for description of stationary and non-stationary characteristics of multicomponent droplets. It allows one to find the evaporation rates for a multicomponent droplet and relate them to the chemical composition, size and temperature of the droplet. The balance conditions for matter and enthalpy in the thermally isolated system (which includes the droplet and the vapor-gas shell around the droplet affected by the vapor component fluxes) lead to equations regulating the behavior of the droplet and vapor-gas environment. On a such thermodynamic basis, we report here a rigorous derivation of a new set of equations for the size, composition and temperature of a small multicomponent droplet at its evaporation or condensation in mixture of vapors and non-condensable gas-carrier. This set includes also equations for local nonsteady diffusion fluxes of vapor components and heat in the vapor-gas mixture with macroscopic flow caused by condensing or evaporating droplet. The set allows one to take accurately into account the non-stationary effects of diffusion [1], heat conduction [2, 3], transient processes in the droplet before reaching the stationary concentration and composition [2-4], cross-effects of mutual and thermal diffusion, the Stefan flow and motion of the boundary of the droplet [1, 2]. The solution in the droplet is considered to be non-ideal, and the effects of non-ideality on the partial volumes, evaporation and specific heats, saturation pressure of components are included [4]. Our analysis shows that a correct description of the thermal effects at condensational growth or evaporation of multicomponent droplets is only possible within the non-stationary approach to the heat and mass transfer in the vapor-gas environment. Under the condition that the concentrations of condensable vapors are much smaller than the concentration of passive gas, we simplified the set of equations to the case when the effects of non-stationary diffusion and thermal conductivity are considered, but the effects of thermal diffusion, the Stefan flow and the movement of the boundary of the droplet can be neglected. The numerical solutions of the simplified equations for the droplet size, composition and temperature have been found in the case of binary and ternary droplets (Figure). In the steady regime of growth or evaporation of a multicomponent droplet, the equations for the stationary values of temperature and component concentrations in the droplet have been derived and analyzed.



**Figure:** Growth rate of square radius of ethanol-water droplet (red and purple lines – non-isothermal and ideal solution; blue line – isothermal and ideal solution).

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## VAPOR PRESSURE MEASUREMENTS OF METAL BROMIDES BY THE KNUDSEN EFFUSION METHOD

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### Introduction

During incineration of electrical/electronic waste (E-waste), valuable metals can be vaporized and distributed into dust as metal bromides after reaction with bromine-containing flame retardants used in printed circuit boards and plastic parts. However, only limited vapor pressure data of metal bromides are currently available. Thus, in this study, the vapor pressures of copper bromide (CuBr) and zinc bromide (ZnBr<sub>2</sub>), bromides of industrially important base metals, were measured by the Knudsen effusion method. The vapor species were also identified using mass spectrometry.

### Experimental

The vapor pressures of CuBr and ZnBr<sub>2</sub> were measured by the Knudsen effusion method. Knudsen cells made of platinum were used for the vapor pressure measurements. The Knudsen cell has an orifice (diameter of 0.16 mm) on the lid. The powder sample was charged in the bottom of the cell. The cell was then introduced into a thermal gravimetric analyzer (TG, Thermo plus TG8120, Rigaku Corp., Japan). The interior of the analyzer was evacuated to less than  $5 \times 10^{-4}$  Pa and subsequently heated to the measurement temperature at a rate of 10 K/min. At the measurement temperature, the weight loss of the Knudsen cell during effusion of the sample vapors was measured. The details on how to derive the vapor pressure from the measurement results have been described in a previously published paper [1].

A mass spectrometer (JMS-QI050GC, JEOL Ltd., Japan) was used to identify the vapor species produced from the metal bromide solids. The metal bromide powder was inserted in a capillary tube (PYLEX®,  $\phi = 2$  mm, length = 14 mm), which was then set into a direct-insertion probe (DIP for JMS-QI050GC, JEOL Ltd.). The direct-insertion probe was then introduced into the ion-chamber in the mass spectrometer system, and the vapor species were directly analyzed under high-vacuum conditions (approximately  $10^{-4}$  Pa) while controlling the temperature.

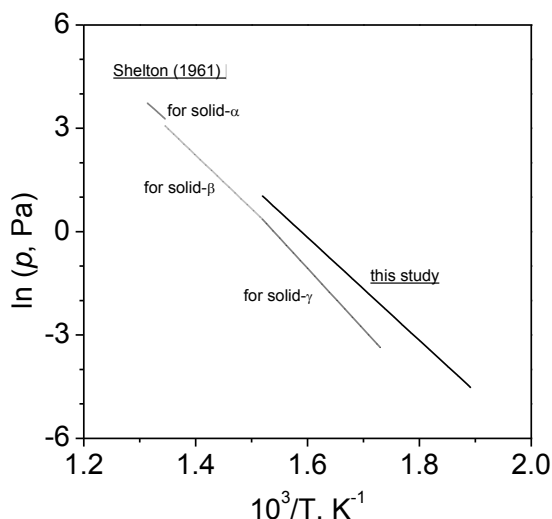
### Results

Figure 1 shows a comparison between the vapor pressures of CuBr and other previously reported values [2]. Compared with the reported values, in which the Knudsen method was also used, the vapor pressure values of CuBr measured in our study were 1.96–3.49 times higher than previously reported values.

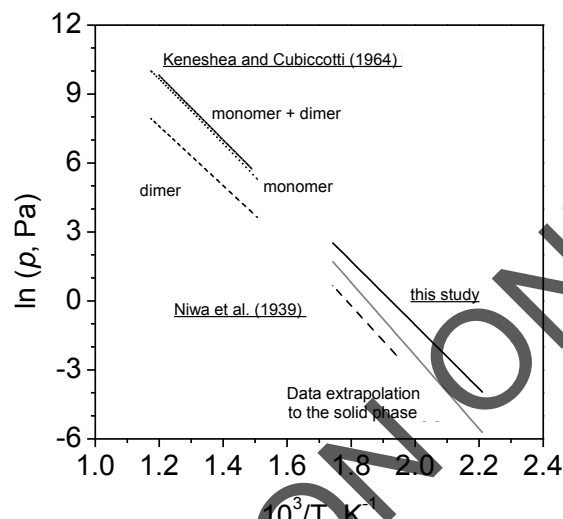
Figure 2 shows a comparison between the ZnBr<sub>2</sub> vapor pressures and previously reported values [3, 4]. For ZnBr<sub>2</sub>, only the 1939 study of Niwa et al. [3] reported vapor pressure data using the Knudsen method. However, it is believed that vapor pressure studies using the Knudsen method, particularly prior to about 1955, are unreliable because the chemical nature of the vaporizing systems were poorly defined [5]. The vapor pressure values of ZnBr<sub>2</sub> measured in our study were 6.54–8.45 times higher than the values reported by Niwa et al. [3]. Even if the reported vapor pressure values over liquid ZnBr<sub>2</sub> by Keneshea and Cubicciotti [4] were extrapolated to the solid phase using the literature values of the fusion enthalpy of ZnBr<sub>2</sub>, our measured ZnBr<sub>2</sub> vapor pressure values were still several times higher.

Tables 1 and 2 summarize the temperature dependence of the vapor pressures and sublimation enthalpies and entropies obtained in the current study for CuBr and ZnBr<sub>2</sub>, respectively.





**Figure 1:** Comparison of CuBr vapor pressures in this study with previously reported values of Shelton [2].



**Figure 2:** Comparison of ZnBr<sub>2</sub> vapor pressures from this study with previously reported values [3, 4].

**Table 1.** Temperature dependence of the vapor pressures and sublimation enthalpies and entropies obtained in the current study for CuBr

Run	$T$	$\ln(p/\text{Pa}) = -A/(T/\text{K}) + B$		$\Delta H_{\text{sub}}$	$\Delta S_{\text{sub}}$	$R^2$
	K	A	B	kJ/mol	J/mol·K	-
<b>CuBr (m.p. 761 K)</b>						
Run 1	532.0 – 658.2	$14741 \pm 320$	$23.47 \pm 0.54$	$122.6 \pm 2.7$	$195.2 \pm 4.5$	0.998
Run 2	530.1 – 656.8	$15322 \pm 501$	$24.28 \pm 0.85$	$127.4 \pm 4.2$	$201.9 \pm 7.1$	0.995
Run 3	528.8 – 655.2	$14746 \pm 293$	$23.42 \pm 0.50$	$122.6 \pm 2.4$	$194.7 \pm 4.1$	0.998
Average	528.8 – 658.2	$14936 \pm 371$	$23.73 \pm 0.63$	$124.2 \pm 3.1$	$197.3 \pm 5.2$	

**Table 2.** Temperature dependence of the vapor pressures and sublimation enthalpies and entropies obtained in the current study for ZnBr<sub>2</sub>

Run	$T$	$\ln(p/\text{Pa}) = -A/(T/\text{K}) + B$		$\Delta H_{\text{sub}}$	$\Delta S_{\text{sub}}$	$R^2$
	K	A	B	kJ/mol	J/mol·K	-
<b>ZnBr<sub>2</sub> (m.p. 675 K)</b>						
Run 1	452.8 – 568.0	$13657 \pm 362$	$26.35 \pm 0.71$	$113.5 \pm 3.0$	$219.1 \pm 5.9$	0.997
Run 2	453.6 – 572.3	$14544 \pm 280$	$27.83 \pm 0.55$	$120.9 \pm 2.3$	$231.4 \pm 4.6$	0.998
Run 3	452.5 – 570.3	$13617 \pm 186$	$26.21 \pm 0.37$	$113.2 \pm 1.5$	$217.9 \pm 3.0$	0.999
Run 4	453.1 – 574.0	$13650 \pm 162$	$26.32 \pm 0.32$	$113.5 \pm 1.3$	$218.9 \pm 2.7$	0.999
Average	452.5 – 574.0	$13867 \pm 247$	$26.68 \pm 0.49$	$115.3 \pm 2.1$	$221.8 \pm 4.1$	

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**THERMODYNAMIC MASS SPECTROMETRIC STUDIES  
OF MULTICOMPONENT SILICATE SYSTEMS**

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Review on advantages of high temperature mass spectrometric method to study thermodynamic properties and vaporization processes of multicomponent silicate systems up to the temperature 2500 K are presented. In the present study the experimental results as well as modeling of thermodynamic properties of multicomponent silicate systems obtained during last ten years are summarized. The systems under consideration are of great importance in various fields of high temperature materials chemistry and technologies such as glass, ceramics, coatings production, metallurgy, geochemistry, nuclear and space technologies and some others. Data on the vaporization processes and thermodynamic properties of the ternary silicate systems such as  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{Cs}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{MgO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{SrO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{BaO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{PbO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{CdO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ,  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ,  $\text{CaO}-\text{TiO}_2-\text{SiO}_2$ ,  $\text{BaO}-\text{TiO}_2-\text{SiO}_2$ ,  $\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{Bi}_2\text{O}_3-\text{GeO}_2-\text{SiO}_2$  and  $\text{Bi}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$  are discussed. Some industrial applications of experimental studies and the theoretical approaches for understanding the thermodynamic behavior of multicomponent silicate systems were also illustrated. It was shown that the content of vapor over multicomponent silicate systems was in agreement with the composition of the gaseous phase over the corresponding binary systems where associated, dissociated and polymerized products were found. The regularities of the vaporization of multicomponent silicate systems were discussed from the point of view of the acid-base concept. Results on determination of thermodynamic functions in the silicate systems mentioned were considered taking into account the main requirements for the confirmation of their reliability. Thermodynamic functions of these systems such as activities and chemical potentials of components as well as the Gibbs energies showed various signs of the deviations from the ideal behavior. For modeling of thermodynamic properties of these silicate melts studied the theory of the ideal associated solution and the general lattice theory of associated solutions were used. Using these approaches the different levels of deviation from the ideality in the silicate melts studied were clarified.

It should be noted that further development of high temperature mass spectrometry for the solution of the task "High temperature materials science and processing of silicate systems" has to include mainly consideration of the following important questions:

- to obtain new additional reliable experimental data on thermodynamic properties of silicate systems;
- to create data bases of thermodynamic properties of oxide systems and models for prediction:
  - a) the partial pressures of vapor species over oxide materials,
  - b) thermodynamic properties of oxide materials,
  - c) phase diagrams of the complex oxide systems;
- to predict thermodynamic properties of silicate materials using statistical thermodynamic approaches including the consideration of the correlation between the thermodynamic properties studied and the structure of these materials;
- to find the regularities of vaporization processes of silicate systems and materials at high temperatures.

*The present study was done according to the financial support of the Russian Foundation for Basic Research (Project No. 13-03-00718).*

THERMODYNAMIC STUDY ON DICATIONIC IONIC LIQUIDS AND SOLIDS.  
SHADOWS AND LIGHT IN THEIR THERMAL STABILITIES

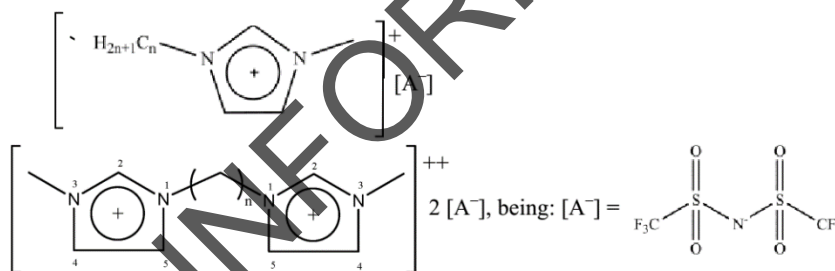
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One of the more rapidly growing areas of chemistry research involves room-temperature ionic liquids (RTILs) and low-melting ionic solids (LMICs). The wide range of possible cation and anion combinations allows for a large variety of tunable interactions and applications [1]. Although the number of ionic liquids described in the literature is growing rapidly, the relationship between their structure/makeup and their physicochemical properties and solvation properties is not well understood. Early studies seem to indicate that the anion may have a greater influence on their physical and chemical properties, but this could be reasonably explained by the fact that usually a series of liquid ionics is represented by anions with very different structure (i.e., fluoride, chloride, iodide, hexafluorophosphate, bis(trifluoromethylsulfonyl)-imide, NTf<sub>2</sub>), while cations (i.e., 1-alkyl-3-methylimidazolium) are closely related and structurally similar. Recently, Shirota and co-workers [2]



**Figure:** Chemical structures of the imidazolium-based ILs studied, where:  $A^- = NTf_2$ .

the dicationic ILs are substantially higher than that of the monocationic because of their higher densities and viscosities, as found by other authors in the past [3]. Recently, our group carried out a study focused on the vaporization of the prototypical ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide (BmImNTf<sub>2</sub>) using the Knudsen Effusion Mass Loss (KEMML) and the Knudsen Effusion Mass Spectrometry (KEMS) techniques [4]. The aim of the present study is to compare the vaporization characteristics of MILs and DILs having NTf<sub>2</sub> as common anion in both types of ILs.

According to our results, focused in particular on DILs with  $n=4, 8$  and carried out under equilibrium conditions, it is evident that volatility of both DILs is much lower than that of the corresponding MILs (with  $n=2, 4$ ). This result will be critically compared with the claimed higher thermal stability of the latter [2].

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**KIRCHHOFF'S LAW OF THERMOCHEMISTRY: NEW CENTURY – NEW CHALLENGE**

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Kirchhoff showed in 1858 that the variation of the heat of a chemical reaction is given by the difference in heat capacities between products and reactants:  $d\Delta H / dT = \Delta C_p$ . Integration of this equation permits the evaluation of the heat of reaction at one temperature from measurements at another temperature. The same equation is also applied for the temperature adjustment of the phase transitions liquid-gas, solid-gas, and solid-liquid. Thus, a heat effect at any temperature of request can be obtained by using the Kirchhoff's Law, provided that heat capacity values  $C_p$  are available. Last century, heat capacity measurements were traditionally performed by using the cryogenic adiabatic calorimetry. This technique is the most accurate but only a few labs are remaining active on this field. Instead, less accurate, but more simple and commercially available differential scanning calorimetry method developed since 1962 have allowed reliable measurements of heat capacity values for liquids and solids. Experimental measurements of the gas phase heat capacities is a challenging task and it is possible only for small volatile molecules by using, e.g. flow calorimetry. Fortunately, the recent developments of the quantum-chemical methods render the assessment of  $C_p(g)$  possible. Thus, it seems to be that all prerequisites for successful application of Kirchhoff's Law for practical and theoretical questions are fulfilled. However this optimism is deceivable. Indeed, appearance of neoteric non-volatile materials like ionic liquids, deep eutectic solvents, fullerenes, nanotubes, etc. require experimental studies of their properties at elevated temperatures significantly different from ambient conditions. Thermal stability of new materials is one of the important features for their practical application. The latter feature is directly connected to the measurable vapor pressure referred to the temperature range of application. Thus vapor pressure of new materials have to be checked experimentally in each case. In practice researchers are confronted with two main problems. At room temperature the low vapor pressures of materials are practically not measurable, whereas at high temperatures some of them may begin to decompose. To date, there are only a few experimental studies of vapour pressures and vaporization enthalpies of extremely low-volatile compounds, and rapid progress to address this paucity of data is hardly to be expected, due to the time-consuming nature of these experiments. Last decade we have deliberately developed in our lab a set of complementary techniques for reliable determination of volatility and vaporization/sublimation enthalpies of extremely low-volatile compounds. They are: quartz-crystal microbalance, static method, thermogravimetry and transpiration method. Using combination of all available techniques we are able to localise the optimal experimental conditions where measurements are performed still without possible thermal decomposition. As a rule, the average experimental temperatures  $T_{av}$  of our studies are of 100-250 K above the common reference 298 K. In order to adjust vaporization enthalpies from  $T_{av}$  to 298 K, the Kirchhoff's Law have to be applied. However, there are a number of issues which aggravate this application. First of all, according to the textbook the Kirchhoff Law can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. The second issue is that the  $C_p(g)$ -values for such materials are not measurable at all. In addition, the quantum-chemical methods suitable for calculations of  $C_p(g)$  of conventional molecules failed to predict reasonable value due to the large size and the complexity of the conformational composition.

We have been able to overcome these complications and we have developed few empirical, half-empirical or theoretical procedures to estimate  $\Delta C_p$ -values based either on the



experimental measurements or based on the volumetric properties. Using  $\Delta C_p$ -values estimated from these procedures, the experimental vaporization/sublimation enthalpies have been adjusted to the reference temperature.

For validation of the  $\Delta C_p$ -procedures we additionally used combination of the combustion, solution, and differential scanning calorimetry with the modern high-level *quantum-chemical* calculations according to the following equation:

$$\Delta_f^g H_m(1 \text{ or cr}) = \Delta_f H_m^\circ(g) - \Delta_f H_m^\circ(1 \text{ or cr}), \quad (1)$$

where  $\Delta_f H_m^\circ(1 \text{ or cr})$  is the molar enthalpy of formation in the liquid (or crystalline) state obtained by calorimetry, and  $\Delta_f H_m^\circ(g)$  the gaseous enthalpy of formation calculated by one of the suitable theoretical methods method (e.g. G3MP2, G4, CBS-QB3, etc.). It is important to mention that all values in the equation 1 are referenced to 298 K. The mutual consistency of the vaporization/sublimation enthalpies directly measured by the complementary experimental techniques with those derived indirectly from calorimetric and quantum-chemical methods will be shown. Thus, new procedures to assess  $\Delta C_p$ -values open a broad window for application of the Kirchhoff's Law of Thermochemistry to studies of extremely low-volatile neoteric materials.

**EQUILIBRIUM NETWORKS IN SOLUTIONS OF WORMLIKE AGGREGATES:  
UNIVERSAL BEHAVIOR VS SPECIFIC CHEMISTRY**

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Reversible spatial networks are formed in a plethora of systems of a totally different molecular nature. Particles of silica in sols, surfactant's wormlike micelles, microemulsion droplets, dipolar hard spheres, associative polymer chains, aggregating patchy (Janus) colloids, may all assemble to give reversible physical gels. Solutions that contain network-forming material exhibit rich viscoelastic behavior that is sensitive to concentration, temperature, acidity, salinity, etc. Network reversibility and controllable viscosity make such systems very useful for numerous applications, [1] e.g., for drag reduction, paints, self-healing coatings, controlled release of drugs, etc.

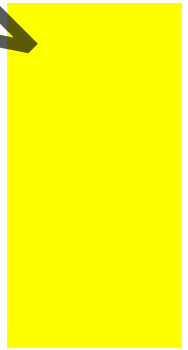
A surprising similarity has been established [2, 3] in the behavior of network-forming solutions of quite different microscopic origin. Universality of thermodynamic behavior and of kinetic properties are expected for solutions where sticky particles form aggregates that tend to grow in length but may also branch. This behavior is controlled by the interplay of the defects (the terminal and the branching portions of a wormlike aggregated chain).

The microscopic portrait of the system is reflected in the models of the branching portion of an aggregate and in the models of its terminal part. Specific microscopic models have been derived from the Wertheim theory of sticky spheres [4], from the mean-field theory of sticky polymer chains [5], and from molecular thermodynamic models of micellization [6 - 9]. We give brief overview of the microscopic models of branches and networks and show our own results. Special attention is given to the effect of specific ions on the growth and branching of wormlike micelles of ionic surfactants in presence of simple salts [8]. Particularly, we explain a surprisingly strong coion's specific effect [9] on the location of the viscosity peak in viscoelastic solutions of wormlike ionic micelles. For solutions of wormlike micelles, we summarize the advances of molecular thermodynamic theory and discuss potential applications of micellar systems with controllable viscoelasticity.

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**Section 1**  
**General problems of**  
**chemical thermodynamics**



FOR YOUR INFORMATION ONLY

# Section 1. General problems of chemical thermodynamics

## THERMODYNAMIC DESCRIPTION OF BIFURCATION

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A characteristic feature of nonequilibrium systems is the presence of fluctuations, instability, symmetry breaking, the appearance of coherence, correlation, "self-organization" and others. If there are effects that disturb equilibrium behavior of the system becomes ambiguous, from which it is possible not only one way of evolution. The unpredictability of the system situation appear in the bifurcation points. Bifurcation processes in chemical reactions can be determined based on the triangulation of multicomponent systems based by N.S. Kurnakov. In this report shows the triangulation system CaO-SiO<sub>2</sub>-H<sub>2</sub>O based on the new concept of "The Gibbs function normalized to the total number of electrons" ( $\Delta\bar{G}_{298}^0$ ) and the ways of determining the bifurcation. The physical meaning of "The Gibbs function normalized to the total number of electron" is determination of chemical bond as a collective effect of electron-nuclear interaction. It is calculated by dividing the value of the Gibbs energy of formation of the compound to the total number of electrons in this compound that determines the density of the energy of formation of the compound per electron and characterizes the accumulation density of the Gibbs energy at the molecular bonds. "The Gibbs function normalized to the total number of electrons" with the formation of bonds adequately responds to changes in the structure of the compound, gives an indication of the reactivity of the compound, on its stability, determine the value of the chemical potential and affinity to calculate the production and flow of entropy, thermodynamic force and flow thermodynamic "probability" interaction conversion components in a chemical reaction, to carry out triangulation and set multicomponent reaction mechanisms.

In multicomponent systems exist Radishehev conversion point, at this point, the system becomes unstable, and there are new solutions of evolution due to branching (bifurcation), this is the point of bifurcation. If there is a small shift of the initial components the system is able to abrupt transitions between stable states.

According to transition state theory, chemical reaction is associated with the formation of an intermediate complex between starting components. Further transition starting materials to the final product depends on the energy of the colliding molecules from their proper orientation in space, from structural changes. Chemical bonds are broken in the starting compounds and the formation of new chemical bonds to form reaction products, lead to an abrupt change in the properties.

It is shown that in exchange reactions symmetric bifurcation sequence was observed. Converting the original components will depend on the temperature of the process of entropy production, structural changes and the rate constants of reactions. The system in the processes of dehydration occurs asymmetric bifurcation. All of these processes are described by "The Gibbs function normalized to the total number of electrons".



## THERMODYNAMIC PARAMETERS OF MELT CRYSTALLIZATION UNDER UNIFORM COMPRESSING

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The equations of pressure dependence for a set of thermodynamic parameters were derived by analyzing of change in Gibbs energy during crystallization from the melt under high pressure of uniform compressing.

The phase transformation temperature  $T_L$  dependence on pressure may be written as

$$T_L^p = T_L^0 (\Delta H^0 + \alpha p^2 V) / \Delta H^0, \quad (1)$$

where the index “0” and the index “p” are related to the normal pressure and to the high pressure, respectively,  $\Delta H$  is the enthalpy of fusion,  $\alpha$  is the uniform compressing coefficient,  $\rho$  is the density, and  $V$  is the volume.

The expression for the enthalpy of fusion is

$$\Delta H^p = \Delta H^0 + \alpha p^2 V, \quad (2)$$

And the pre-crystallization overcooling  $\Delta T$  and the surface interfacial energy at the crystal-liquid interface  $\sigma_{SL}$ , respectively, will look like

$$\Delta T^p = \Delta T^0 + \alpha p^2 T_L^0 / (\rho L^0), \quad (3)$$

and

$$\sigma_{SL}^p = \sigma_{SL}^0 (1 - \alpha p). \quad (4)$$

In conclusion the expressions (1) - (4) were used to analyzing the work of nucleus formation  $A_k^p$  and the nuclei sizes  $l_k^p$  under external pressure:

$$A_k^p = \frac{32(\sigma_{SL}^0 - \alpha p)^3}{(\Delta q^0 + \alpha p^2)^2}, \quad (5)$$

$$l_k^p = \frac{4\sigma_{SL}^0(1 - \alpha p)}{\Delta q^0 + \alpha p^2}. \quad (6)$$

# Section 1. General problems of chemical thermodynamics

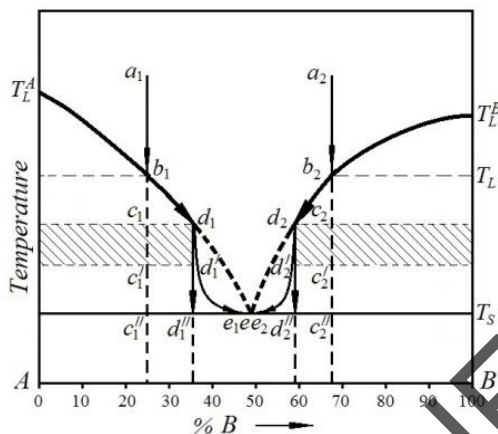
## ANALYSIS OF MELT CRYSTALLIZATION WAYS IN EUTECTIC SYSTEMS

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Melting and crystallization were studied at binary alloys of the eutectic type. As a result of the study the thermal effect bifurcation of the phase transformation was found. The main feature is that the fraction of thermal effect falls on the liquidus temperature  $T_L$  and another one falls on the solidus temperature  $T_S$ .

Taking into account that a character of melt crystallization at the liquidus temperature  $T_L$  is independent of crystallization behavior at the eutectic temperature  $T_E$ , the report considers the melt crystallization diagram ways by the example of a single pre-eutectic alloy and a post-eutectic one along the state diagram  $A-B$  (Figure).



**Figure:** Melt crystallization ways in pre- and post-eutectic regions, where  $T_L^A$  and  $T_L^B$  are melting temperatures of pure components A and B, respectively.

$a_1 \rightarrow b_1 \rightarrow d_1 \rightarrow d_1' \rightarrow e$  (or  $a_1 \rightarrow b_1 \rightarrow d_1 \rightarrow d_1' \rightarrow e_1 \rightarrow e$ ), and for a post-eutectic one —  $a_2 \rightarrow b_2 \rightarrow d_2 \rightarrow d_2' \rightarrow e$  (or  $a_2 \rightarrow b_2 \rightarrow d_2 \rightarrow d_2' \rightarrow e_2 \rightarrow e$ ).

When temperature decreases, for example, from point  $a_1$  to point  $b_1$ , precipitation of the crystalline substance A starts. If precipitating process of the substance A continuously runs till point  $c_1''$ , the crystallization way would pass through points  $a_1 b_1 e$ . The initial crystallization way will be  $a_1 b_1 d_1$ , and the crystallization will complete in the point  $d_1$ , if precipitation of the substance A completes in the point  $c_1$  at the first stage of crystallization. The way of the secondary crystallization near the eutectic temperature  $T_E = T_S$ , in theory, will be isothermal from point  $d_1''$  to point  $e$  (Figure 1). Actually, close to the temperature  $T_S$  the remains of substrate A may crystallized together with eutectic formation. In this case, the crystallization will pass through the way  $d_1' e_1 e$ . Similar regularity also occur in a post-eutectic melt which is cooled down from the figurative point  $a_2$ .

Finally, by merging ways for the initial and the secondary crystallization, the way for a pre-eutectic melt will be

VAPOR–LIQUID–LIQUID EQUILIBRIUM MEASUREMENTS AND  
MODELING OF METHANETHIOL OR ETHANETHIOL OR  
1-BUTANETHIOL IN METHANE + WATER TERNARY SYSTEMS AT 303,  
335, AND 365 K AND PRESSURE UP TO 9 MPA

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New vapor–liquid–liquid equilibrium (VLLE) data for methanethiol + methane + water, ethanethiol + methane + water, 1-propanethiol + methane + water, and 1-butanethiol + methane + water ternary systems have been measured at three temperatures (303, 335, and 365 K) and pressures up to 9 MPa. A “static-analytic” method was used for performing all the measurements. The total system pressure was maintained by CH<sub>4</sub>. The objective of this work is to provide experimental VLLE data with thermodynamic modeling for mixtures of mercaptans (thiols) with other natural gas contents at its crude form, for which no data are available in the open literature. Such data will help the industrial modeling of processes relevant to reduction of sulfur emissions. The Cubic-Plus-Association (CPA) equation of state was applied to describe the phase behavior of the investigated systems. It is shown that the CPA EoS satisfactorily describes the solubilities of mercaptans (thiols) in all phases. It is observed from the experimental data that the solubility of CH<sub>4</sub> in the aqueous and organic phases increases with an increase of the total system pressure and decreases with an increase of the temperature. However, the solubility of CH<sub>3</sub>SH in the aqueous and organic phases decreases slightly with an increase of the total system pressure and increases significantly with an increase of the temperature. The new VLLE data of ternary system were compared with predictions of the cubic-plus-association equation of state. The model tends to under predict the concentration of CH<sub>3</sub>SH in all phases, particularly the vapor phase. However, the model underestimates the water content of the vapor phase, especially at low pressures and at the highest investigated temperature, i.e., at 365 K. Only the ethanethiol + methane + water system showed significant cross-association effects. Furthermore, no cross association (solvation) was found to be significant in 1-propanethiol + methane + water and 1-butanethiol + methane + water ternary systems.

## Section 1. General problems of chemical thermodynamics

### CALORIMETRY OF THE IONIC EXCHANGE IN MULTICOMPONENT SYSTEMS

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Opportunity to take measurements at the time of course of reaction distinguishes a calorimetry from other methods of research therefore definition of an enthalpy of reaction by direct calorimetric measurement is more exact than indirect methods. Thermochemical definition allows to define most precisely and unambiguously power characteristics of processes of interaction of substances at formation of communications of various nature between a sorbent and sorbate. The aforesaid causes traditional use of a calorimetric method for studying of chemical balance in multicomponent systems.

For definition of thermal effects of sorption processes two types of calorimetric installations are used: the tight liquid multiampullary calorimeter working in the izoperibolic mode which is convenient for applying to sorption processes, of no more than 1.5 hours, and the differential heat-conducting calorimeter of MID-200 suitable for longer processes. The izoperibolic calorimeter is modernized by the digital automated scheme of measurement of temperature and thermal calibration of a calorimeter of variable temperature with computer management which thermometric sensitivity makes  $10^{-4}$  K, calorimetric –  $10^{-2}$  J, fluctuation of temperature in a calorimetric cell after establishment of thermal balance doesn't exceed  $\pm 5 \cdot 10^{-3}$  K.

Redistribution of substances between phases of solution and an ion exchanger results not only an ionic exchange, but can be followed by change of hydration of participants of reaction, not exchange interactions in a phase of an ion exchanger and interpartial interactions in solution; a complex formation both in an ion exchanger phase, and in equilibrium external solution, etc.

So for example, mixture of an ion exchanger in a metal form and water solution of amino acid is followed except sorption interaction by a number of the accompanying processes which thermal effect is excluded at a stage of planning of calorimetric experiment. In particular, the enthalpy of neutralization or protonation decides in separate experience by mixture of an ion exchanger on water solution, pH that is similar to the studied. As a result of  $\Delta H$  calculates taking into account only sorption interactions between amino acid and an ion exchanger:

$$\Delta H = \Delta H_{meas.} - (\sum_i \Delta_h H + \Delta_r H + \Delta_n H + \Delta_c H),$$

where  $\Delta H_{meas.}$  – the mixture enthalpy measured by a calorimetric method;  $\sum_i \Delta_h H$  – enthalpies of hydration, swelling or dilution of all participants of process;  $\Delta_r H$  – enthalpies of the conformational transformations proceeding in an ion exchanger phase after amino acid absorption;  $\Delta_n H$  – an enthalpy of neutralization or protonation;  $\Delta_c H$  – a complex formation enthalpy in external solution.

For definition of an enthalpy of interaction of monoionic forms of amino acids with the cation exchanger experiment was planned so that solution contained one type of ions.

Thermochemical researches allow to track influence of various structures of polymers and number of the sewing agent in it, the nature of sorbent, their concentration and other parameters on sorption by ion exchangers which need to be considered at their use.

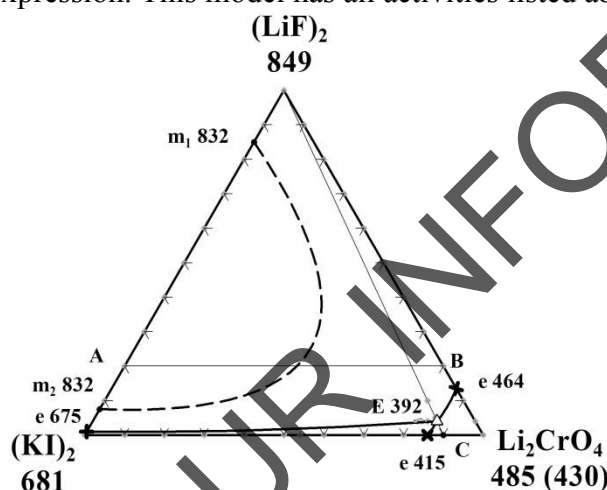
## COMPUTER 3D-MODELLING OF PHASE COMPLEX FOR TERNARY SYSTEM

A.B. Burchakov, E.M. Dvoryanova, I.M. Kondratyuk

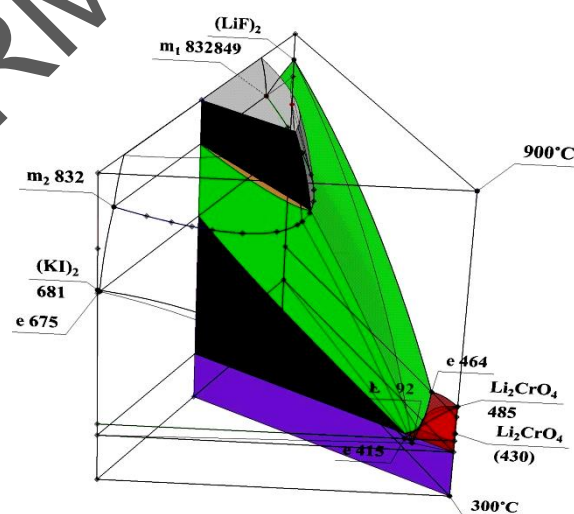
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Phase complex of ternary systems in form computer 3D-model in T-x-y coordinates has the goods on traditional methods presentation of multicomponent systems, because it describes phase transitions and equilibria to the full, it's informative method of record retention about system based experimental data. Based T-x-y-model we can construct required polythermal and isothermal sections, liquidus surface isotherms, calculate material phase balance of ternary system, make a forecast unstudied systems [1].

In this work we studied the ternary system LiF-KI-Li<sub>2</sub>CrO<sub>4</sub> in the first time (Fig.1). This system is stable triangle of quaternary reciprocal system Li,K||F,I,CrO<sub>4</sub>. The experimental investigation of phase transformations in system LiF-KI-Li<sub>2</sub>CrO<sub>4</sub> was performed by differential thermal analysis on a standard setup [2]. We used the projection thermographic method [3] for found nonvariant point. Ternary eutectic E 392 forms in this system. Liquid phase stratification field takes a lot of space in the concentrated triangle. For explored system we designed solid state 3D-model of phase complex (Fig. 2). Each phase equilibria volume is painted in its colour for visual expression. This model has all activities listed above.



**Figure 1:** Projection of the liquidus surface of the system LiF-KI-Li<sub>2</sub>CrO<sub>4</sub> to the concentrated triangle.



**Figure 2:** Solid state 3D-model of phase complex of the ternary system LiF-KI-Li<sub>2</sub>CrO<sub>4</sub> with polythermal section.

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This work was done within the framework of state task of Samara State Technical University, code of project is 1285.

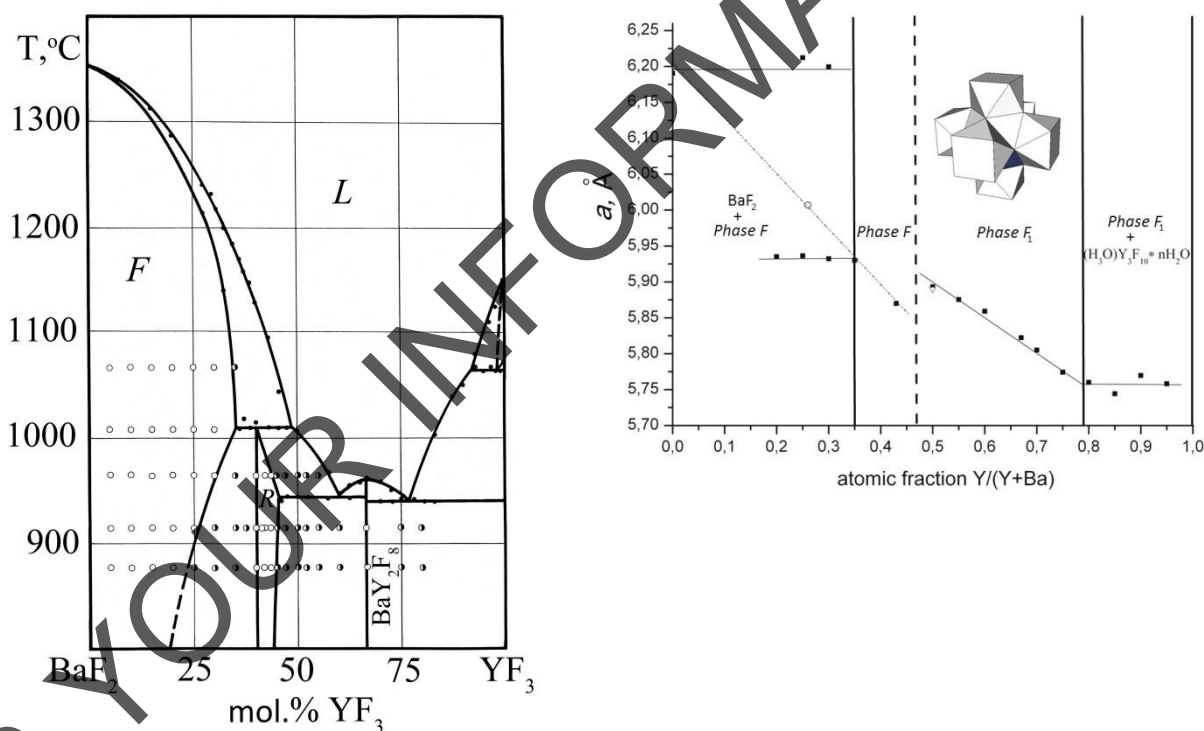
## Section 1. General problems of chemical thermodynamics

### LOW-TEMPERATURE SYNTHESIS – A ROAD FOR THE REALIZATION OF NON-EQUILIBRIUM STATES IN FLUORIDE SYSTEMS

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Systematic study of phase formation in the  $\text{NaF-RF}_3$ ,  $\text{MF}_2\text{-RF}_3$  ( $M = \text{Ca, Sr, Ba; R} = \text{rare-earth elements}$ ) systems at low temperature [1-4] revealed that the nanophases formed by co-precipitation from aqueous solutions were non-equilibrium phases with excessive free energy, disordered structure, high crystal lattice defect concentrations and wide homogeneity composition intervals. Some of low-temperature phases had structures similar to the ones of the equilibrium phases formed at higher temperature and underwent exothermal transformations to the equilibrium phases under heating. Formation of crystalline nanophases occurred according to Ostwald's step rule. Primary nanoparticles underwent agglomeration according to different mechanisms, including non-classic oriented growth mechanism [5]. Prepared nanopowders can be used as electrochemical, biomedical, lumiphore, solar power and light source materials, etc.



**Figure:** Equilibrium phase diagrams of the  $\text{BaF}_2\text{-YF}_3$  system (left) and the phase composition in this system after co-precipitation with using of HF as fluorinating agent (right) [2].

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## THERMODYNAMICS OF IRON CARBON MARTENSITE FROM MOLECULAR DYNAMICS

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On rapid cooling of a *fcc* phase in Fe-C alloys specific low-temperature transformation occurs, named martensitic transformation. This transformation is the basis of quench steel hardening, since it is martensite formation that provides an abrupt hardness and strength increase which often forms a practical purpose of quenching. Investigations of the martensite crystal lattice carried out first by G.V. Kurdjumov et al. [1] showed that martensite has a tetragonal lattice that is to be considered as a *bcc* lattice of  $\alpha$  iron slightly tensioned in one direction. Martensite lattice parameters  $a$  and  $c$  depend linearly on the carbon content.

C. Zener [2] and later A.G. Khachaturyan [3] developed a theoretical approach to describe the ordering of carbon atoms in martensite, which predicts the transition from state with cubic lattice to tetragonal one at temperatures:

$$T_{crit} = 0.36 \frac{c\lambda_0}{k}, \quad (1)$$

where  $c = n_C/N$  is content of carbon atoms ( $N$  and  $n_C$  are numbers of atoms of iron and carbon respectively),  $\lambda_0$  is the strain interaction parameter. It should be noted that the key parameter of the Zener – Khachaturyan theory is  $\lambda_0$ . However, different works [2-4] give a great discrepancy in estimates of this parameter ranging from  $-2.73$  to  $-10.77$  eV/atom due to different methods and calculation parameters used. To eliminate these difficulties we propose to use atomistic modeling for the calculation of the interaction parameter and martensite tetragonality. We used direct calculation of the  $\lambda_0$  parameter by molecular dynamics via LAMMPS package (<http://lammmps.sandia.gov>) in an isobaric-isothermal (*NPT*) ensemble with semiempirical interatomic potential [5] for Fe-C system. The following procedures were performed to obtain equilibrium configurations of martensite:

- initial configurations had tetrahedral lattice consisted of 16000 Fe atoms and number of carbon atoms was calculated respective to concentration value,
- then structure relaxation by MS was performed, and tetragonal distortion appeared,
- the next step was performing MD in the *NPT* ensemble; the time simulated being 500 ns.

On the last stage the system comes to equilibrium and diffusive redistribution of carbon atoms between octahedral sites takes place. Changing temperature we defined  $T_{crit}$  at given  $c$  and  $\lambda_0$  parameter can be calculated according to eq. (1). Our molecular dynamics calculations with Fe-C interatomic potential [4] show that  $\lambda_0$  equals  $-5.55$  eV/atom what consists with previous works.

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# Section 1. General problems of chemical thermodynamics

## THERMODYNAMICS OF MORPHOTROPY

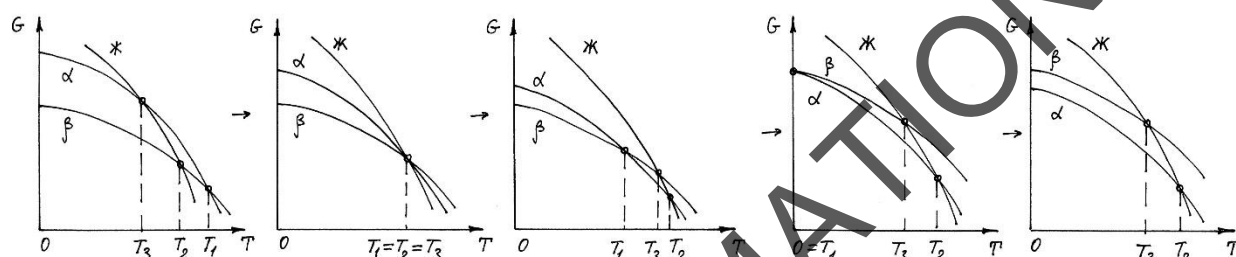
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Morphotropy is a change of crystal structure, which occurs when compound chemical composition changes. One may analyze thermodynamics of morphotropy for ideal morphotropic series (IMS) by describing thermodynamic properties of competing crystalline phases and melts with smooth functions of such parameters as ionic radii  $r$  [1]. This approach results in the following conclusions (Figure):



**Figure:** Correlations between isobaric-isothermal potential for melt and two crystalline phases ( $\alpha$  and  $\beta$ ); entropy of melting for  $\alpha$ -phase is lower than the one for  $\beta$ -phase,  $\Delta S_\alpha < \Delta S_\beta$

- More stable modification has the higher melting temperature than the less stable modification, and melting point inversion is a general cause of the morphotropic transition;
- In general, morphotropy is accompanied with polymorphism;
- Correlations between the melting points and polymorphic transition temperatures vs. ionic radii  $r$  within IMS are described by the smooth functions;
- Tangent lines for the polymorph transition temperature functions  $T(r)$  near absolute zero temperature are always vertical for IMS. It means that morphotropic transition cannot be “protracted” at lower temperature; instead, it should occur in a very “acute” manner (the latter conclusion, for example, has allowed a correct description of lower temperature polymorphism of rare earth oxides [2].)

Taking into account  $C \sim T^m$  exponential dependency for heat capacity at near absolute zero temperatures, one can get  $T = a(r-r_0)^n$ ,  $n = 1/(m+1)$  correlation, i.e., a particular case of Simon’s equation. If  $m = 3$  (Debye’s approximation), then  $n = 0.25$  (similar treatises can be carried out for  $(k + 1)$ -phase equilibria in  $k$ -component systems at near absolute zero temperatures as well).

Please see Table for the corresponding analysis of experimental data for rare earth compounds’ IMS).

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**Table.** Experimental data

Compound	$r_0, \text{\AA}$	$a, \text{K/\AA}$	$n$
$\text{Pb}_4\text{R}_3\text{F}_{17}$	1.230	1430	0.091
$\text{Ca}_8\text{R}_5\text{F}_{31}$	1.165	1800	0.136
$\text{Ca}_2\text{RF}_7$	1.171	2030	0.192
$\text{RF}_3$ ( $\beta\text{YF}_3$ )	1.226	3160	0.284
$\text{B-R}_2\text{O}_3$	0.977	3600	0.132

## THERMODYNAMICS OF COPPER(II) COMPLEXATION WITH NICOTINATE-ION IN AQUEOUS ETHANOL AND DIMETHYLSULFOXIDE

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Nicotinic acid (HL) is biologically active compound, which participate in coenzyme and non-coenzyme processes and has anti-inflammatory effect. Ethanol and dimethylsulfoxide are widely used as pharmaceutical solvents.

The general aim of our research is to find patterns of solvent influence on the complexation in solution.

We determined the stability constants and enthalpies of nicotinate-ion complexation with  $\text{Cu}^{2+}$  in water-ethanol and water-DMSO mixtures.

The stability constants of  $[\text{CuL}]^+$  were obtained by potentiometric titration of aqueous organic solution of  $\text{Cu}(\text{ClO}_4)_2$  and  $\text{HClO}_4$  by sodium nicotinate aqueous organic solution at  $25.0 \pm 0.10$  °C and ionic strength 0.25 ( $\text{NaClO}_4$ ) with glass sensoric electrode ( $\text{H}^+$ ) and silver-chloride reference electrode. The constants of nicotinic acid protolytic equilibria in mixed solvents were found in reference [1].

The heat effects of copper(II) complexation with nicotinate-ion in binaric solvents were determined by the calorimetric method on dilution calorimeter at  $25.00 \pm 0.01$  °C and ionic strength 0.25 ( $\text{NaClO}_4$ ). The enthalpies of reaction transfer from water to aqueous organic solvents were calculated.

The stability constant of copper(II) nicotinate complex increases when the organic component concentration rise. Gibbs energies of reaction transfer from water to binaric solvents were obtained from the equation:  $\Delta_r G_r = -RT(\ln K_S - \ln K_{\text{H}_2\text{O}})$ , where  $K_S$  – stability constant of  $[\text{CuL}]^+$  in mixed solvent,  $K_{\text{H}_2\text{O}}$  – stability constant of  $[\text{CuL}]^+$  in water.

The results discussion was carried in scopes of the solvation-thermodynamic approach, founded on the thermodynamic characteristics of the complexation reactants solvation. The Gibbs energies of nicotinic acid [2] and  $\text{Cu}^{2+}$  ion [3] transfer from water to aqueous ethanol and dimethylsulfoxide were determined earlier. The enthalpies of nicotinic acid and copper(II) ion transfer were found in reference [4, 5].

We concluded, that the complex stability increasing connects with solvation stabilization of  $[\text{CuL}]^+$  and solvation destabilization of  $\text{Cu}^{2+}$ . As a result of solvation-thermodynamic analysis, we established that the ions contribution to transfer Gibbs energy of reaction dominates above the ligand contribution.

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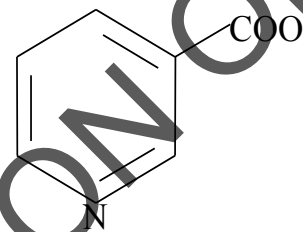
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**Figure:** Structure of nicotinate-ion.

## Section 1. General problems of chemical thermodynamics

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### MOLTRAN – A PROGRAM FOR THE THERMODYNAMIC CALCULATIONS CONSIDERING THE INTERNAL ROTATIONS IN NON-RIGID MOLECULES

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The thermodynamic properties evaluations for the small and medium-size rigid molecules in the ideal-gas state based on the quantum chemical calculations is a routine task today. However, the calculation of these properties for the large flexible or non-rigid molecules is not so simple because it requires the accurate consideration for the large-amplitude motions among which the internal rotations are the most common and important case. The most complicated cases of the internal rotations include several linked rotors or the rotors on another rotating rotor. Up to date, there is no exact theory describing this kind of motions. Although several approximate theories were proposed since the middle of XX century, they are not so simple for the use due to the complicated and ambiguous partitioning of the molecule onto the linked rotors. In the current work, we propose the new computer code MOLTRAN specially designed for the automated consideration of the internal rotation contributions for the thermodynamic calculations based on the data of quantum chemical calculation. The program provides an interface to the output files of many commonly-used quantum chemistry packages including Gaussian03/09, Gamess-US, PC GAMESS/Firefly, CFOUR, Priroda and others. The input data of MOLTRAN are the structure and vibrational frequencies of the molecule optimized with a quantum chemical method. The total energy and spin multiplicity of a molecule can be read in automatically or be user-supplied. At the first step of work, MOLTRAN determines the exact and approximate symmetry groups of a molecule in order to estimate the rotation symmetry number. Then partition functions of the molecule are calculated using the rigid rotor – harmonic oscillator (RRHO) approximations. A special feature of the new program is an original Automated Recognition of Internal Rotations (ARIR) algorithm. ARIR works on the basis of graph theory trying to perform all the possible rotations of two molecular fragments relatively to each another. The decision on the possibility of such a rotation is made on the basis of the prescribed limits for the interatomic distances. After the rotating tops are determined, the activation barrier for the internal rotations can be estimated by three ways: evaluated from the corresponding vibration frequency, calculated by the direct scanning of the PES with a semiempirical method implemented in the program, set from the user-supplied data, or calculated with the high-level theory by an external quantum chemical program using the automatically generated input files. Once the internal rotation energy profile is evaluated, the calculation of the thermodynamic properties is performed using the different levels of the Pitzer-Gwinn-Killpatrick theory. Additionally, the results obtained in the RRHO and free rotor approximations are calculated. All the calculated quantities (partition functions, internal energy, enthalpy, thermal capacities, entropy, and the Gibbs free energies) are printed out as a table for a set of temperature conditions. The user can also supply the desired pressure and temperature conditions as well as the multiplicity and the molecular symmetry data. Using the pressure variation, it is also possible to model the liquid phase conditions (providing the proper free volume) which is important for the improving the modern solution-state electronic structure calculations (SCRF) which do not contain usually the molecular motion contributions in their outputs, and the special options for calculations of the thermodynamic functions of transition states. The MOLTRAN program is now accessible at the website of our group <http://www.qchem.unn.ru/moltran>.

## LIFE ORIENTATION HYDRATE THEORY (LOH-THEORY): THERMODYNAMICS OF FORMATION OF AMINO ACIDS FROM NATURAL GAS AND NITER

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The Life Origination Hydrate Theory (LOH-Theory) is the instrument for understanding the physical and chemical mechanisms applied by Nature for the living matter origination and propagation [1, 2]. We affirm that living matter originated as a result of thermodynamically caused chemical transformations, which are inevitable under definite ambient conditions and are governed by physical and chemical laws universal for any celestial body. According to the LOH-Theory, living matter originated from the unique set of mineral substances: CH<sub>4</sub>, niter, phosphate, and H<sub>2</sub>S. The syntheses of living matter simplest elements (LMSEs), i.e., nitrogen bases, riboses, and nucleosides, and of simplest forms of the precellular living matter (DNAs) proceeded within the cavities of the CH<sub>4</sub>-hydrate honeycomb structure, localizations of which represented natural thermostated "incubators". DNAs were synthesized on the basis of the intrastuctural CH<sub>4</sub> and of nitrate- and phosphate-ions that diffused into the CH<sub>4</sub>-hydrate structure from the outside. The reaction process was initiated by Konoyalov's reaction between CH<sub>4</sub> and NO<sub>3</sub>-ions. The formation of cells and first symbiotic reactions between DNAs proceeded within the semi-liquid media (super-cytoplasm) produced after liquation of the hydrate structure as a result of the excessive H<sub>2</sub>O formation through polycondensation reactions and temperature increasing. The origin of living matter from mineral substances and the extended self-reproduction of living organisms have in their ground the same physicochemical phenomenon that consists in the formation/destruction of the so-called gas-hydrate structures. Earlier thermodynamic calculations [3] showed that formation of LMSEs, DNAs, and proto-cells from CH<sub>4</sub>, niter, and phosphate is thermodynamically possible on the basis of the internal energy of the source substances with no ambient energy; moreover significant energy amounts liberated.

In this work, we consider the chemical and thermodynamic possibilities of formation (on the basis of natural gas and niter) of the amino acids (AAs) that enter into living matter. It is known that living matter contains 20 AAs, including two S-containing ones. Meanwhile, the gas-hydrate deposits contain, along with CH<sub>4</sub>, admixtures of H<sub>2</sub>S, CH<sub>4</sub>S, and other S-containing substances. According to the LOH-Theory, the processes of living-matter origination proceeded within the honeycomb CH<sub>4</sub>-hydrate structure at about 273±20 K under the CH<sub>4</sub> pressure. These conditions differ from the standard ones; however, the estimation of the degree of deviation of the conditions from the standard ones is complicated and, therefore, our estimations of the possibility of formation of AAs were performed for standard conditions. They are made on the basis of available literature data on the standard thermodynamic functions of the source substances and AAs. For a majority of the reactions, for which the calculations are performed, the decreases in the Gibbs's free energy in the course of AAs formation are so great in magnitude that the possibility of their formation is beyond question. The S-containing AAs can be formed on the basis of CH<sub>4</sub>, KNO<sub>3</sub>, and H<sub>2</sub>S and other S-containing components of the natural gas; however just the reaction of CH<sub>4</sub> and KNO<sub>3</sub> with H<sub>2</sub>S that is the most abundant S-containing component of the natural gas goes with the highest decrease in the Gibbs's free energy.

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## Section 1. General problems of chemical thermodynamics

### SELECTION OF PARAMETERS OF THE POTENTIAL OF INTERMOLECULAR INTERACTION FOR SOLUTIONS OF SILICON FLUOROCHLORIDES IN SiCl<sub>4</sub>

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In the process of synthesis of SiCl<sub>4</sub> by reaction  $3\text{SiF}_4 + 4\text{AlCl}_3 = 3\text{SiCl}_4 + 4\text{AlF}_3$  the intermediate silicon fluorochlorides are formed. Partial condensation of SiCl<sub>4</sub> from the initial gas mixture is a possible technique for purification of the product from these impurity substances. Preliminary estimations of the distribution coefficients of impurity substances between the gas-solid phases or the gas-liquid phases of the purified substance are of great concern. There are several methods for calculation of these values at the present time. The methods, based on the use of the potential model for interaction of molecules in solution, are of special interest. In these methods the calculation of distribution coefficients  $K_{I,II}$  between phases I and II can be carried out by formula [1]  $\ln(K_{I,II}) = \Delta\mu_{II}^+ - \Delta\mu_{I}^+$ , where  $\Delta\mu_{I}^+$ ,  $\Delta\mu_{II}^+$  are the difference of dimensionless configurational chemical potentials of impurity and of the main component in phases I and II, respectively.

Lennard-Jones potential is a sufficiently suitable and widely used potential  $U(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right]$ , where  $r$  is the distance between molecules. Determination of parametric values  $\varepsilon$  and  $\sigma$  is a separate problem being solved by different methods. The literature describes the techniques for their determination based on viscosity, parameters of critical and triple point of substances, dependence of the pressure of saturated vapors on temperature, etc. These methods give noticeably different values which can lead to significantly different conclusions on the considered problems.

With the goal to select the optimum variant for determination of parametric values  $\varepsilon$  and  $\sigma$  as well as the method for calculation of coefficients of impurity distribution (fluorochlorides) in silicon tetrachloride, large arrays of calculated values of the stated quantities were processed using various theoretical models. Apart the known ideal models, the calculations were carried out according to the theory of conformal solutions (TCS) [2], to some variants of the free-volume theory [3], to the method of deformed cells (MDC) [4], to approximation of calculations by Monte-Carlo method (MC) [5].

The following conclusions are made. Due to the fact that the process is conducted at temperatures close to the melting point of the base, the mostly compatible results of different theories and available experimental data are obtained by the method of calculation of parameters  $\varepsilon$  and  $\sigma$  by thermodynamic characteristics of triple point of substances. The most reliable results are obtained using TCS (liquid-vapor) as well as MDC and MC (liquid-crystal).

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ISOBARIC THERMAL CAPACITY WITH ACCOUNT OF CONFIGURATION  
CONSTITUENT

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Achievements in theoretical calculations of thermal capacity, based on statistical thermodynamic expressions for simple substances, are well known. Polyatomic compounds with variable interaction energy of the constituent particles become increasingly important in practical problem.

The aim of the represented work is the development of the approach connected with the use of representation of differences in the energetic scale of interaction of different groups comprising the considered compounds.

Accounting for the configuration constituent of thermal capacity is the greatest challenge in the consistent technique. Usually, this part of energy is considered as a constant value (i.e., not contributing to thermal capacity) which background is used to describe the contribution of acoustic and optical vibrations of particles. The statistical sum is written as  $Z = \sum_n \exp(-E_n/kT)$

where  $n$  is the number of microscopic state of the system,  $k$  is the Boltzmann constant.  $E_n$  is determined by the number  $s$  of configuration of particles in crystal nodes and by the assembly of vibration rotational states of  $r$  assumed to be independent (relatively low temperatures are considered). Then  $Z = Z_s Z_r$ . Since  $C_p = (\partial E / \partial T)_p$  and  $E = kT^2 (\partial \ln Z / \partial T)_v$ , the contributions of these states to thermal capacity are of additive nature.

The representations of the theory of heterophase fluctuations are used to consider the configuration constituent. During fluctuation deviation by small value of  $\Delta T$  from the point of phase transition  $T_0$  there is a certain probability of appearance of structures corresponding to the new phase in individual areas of the stable phase. The number of minimum nucleus of the new phase, comprising  $m$  structural units, is denoted as  $N_m$ . Their number increases with the increase of temperature and the system changes over to the new phase. Close to the phase transition for Gibbs potential the linear decomposition for the corresponding phases  $i=1, 2$ :  $G_i = G_{i0} + a_i \Delta T$  is valid. Probability  $w$  of appearance of the required fluctuation is proportional to  $w \sim \exp(-R_{\min}/kT_0)$ .  $R_{\min}$  is the minimum work required for the given change in the local structure of substance.  $N_m$  value is exponentially increasing in the area of phase transition. The contribution to thermal capacity is determined by product of fluctuation work on possibility of its realization, i.e., the product of exponential  $\Delta T$  by constant parameter which gives the  $\lambda$ -type of thermal conductance. We obtain  $\Delta C_{\text{conf}} = \exp[A(T-B)] + \exp[a(T-b)]$  for ascending and descending branches of the phase transition. Basing upon the additive contribution of the oscillating components of the chemical bonds of molecules [1] we obtain the evaluation formula

for isobaric thermal capacity  $C_p = R \sum_{i,j} \frac{(\theta_i^{(j)}/2T)^2}{2 \text{sh}^2(\theta_i^{(j)}/2T)} + \Delta C_{\text{conf}}$ . Proximity of the calculated

approximation values of  $\theta_A$ , their generality for the considered functional groups proves the correctness of the model used in calculation of thermal capacity in complex coordination compounds.

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## Section 1. General problems of chemical thermodynamics

### DISPERSION OF SINGLE-WALLED CARBON NANOTUBES IN ETANOL-CHOLIC ACID MIXTURES: MOLECULAR DYNAMICS SIMULATION AND EXPERIMENT

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Single-walled carbon nanotubes (SWNTs) are promising materials due to their unique electronic, mechanical, and optical properties. Their physicochemical properties depend on the chirality of SWNTs and the degree of their agglomeration. The characteristics of conductivity, the band gap, and the optical properties depend significantly on chirality. The preparation of stable suspensions of individual nanotubes with a definite set of chiralities is thus an important challenge in physical chemistry.

In the present study, the nanotubes which are mixtures of different chirality in agglomerates were investigated. In order to get the dispersion of carbon nanotubes, ethanol used as the solvent and cholic acid used as the surfactant. The reason for application of this particular compound is a relatively high solubility of cholic acid in ethanol, and the high energy of its binding to the surface of the nanotube. On the other hand, the important peculiarity of cholic acid is relatively small size of its molecule. Suspension SWNTs in ethanol-cholic acid mixtures were prepared as described in [1].

The Raman-spectroscopy and molecular dynamics simulation provide reliable evidences that a molecular association in suspension of SWNTs in ethanol-cholic acid mixtures changes nonlinearly depends on concentration. At low concentrations, (<0.03 mol / kg) cholic acid molecules form contact pair with surface of CNT. While concentration of cholic acid increases, the self association of cholic acid molecules become more preferable compare to association with CNT.

The practical significance of this finding is connected with obtaining the optimal concentration of cholic acids in solvent for obtaining suspension with CNT. The concentration of CNT in suspension, obtained in our experiment increases symbatically with concentration of cholic acid up to reaching the maximum and further addition of cholic acid leads to decreasing of CNT concentration. For a theoretical assessment of the processes, the molecular dynamics simulation has been carried out for SWCNT chirality (11,10) derived from experimental studies in solution of cholic acid in ethanol at a ratio of 2:1, 3:1, 4:1, 6:1 and 8:1 cholic acid molecules per nanotube, which corresponds to the concentration of the solution of cholic acid 0.0146, 0.0221, 0.0296, 0.0409, 0.0548 mol / kg of ethanol accordingly.

The alcohol solutions of cholic acid have dispersing properties relative to SWNTs. The number of single isolated nanotubes in suspensions that are stable in time was maximum at a concentration of cholic acid in ethanol of 0.018 mol/kg (SWCNT chirality (11,10)).

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## NON-EQUILIBRIUM AFFINITIES IN MULTI-PHASE GIBBS ENERGY MINIMISATION

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It has been shown earlier that local and partial chemical equilibria, paraequilibrium systems as well as irreversible non-equilibrium processes constrained by extent of reactions can be calculated within the Gibbs energy minimizing programs by using complementary conservation balance equations for selected immaterial properties in addition to the conservation of molar amounts of the physical system components [1]. The solution of the calculation then is by a differential-algebraic procedure, which combines the necessary constraint (either static or dynamic) with the linearized  $\min(G)$  problem. The chemical potentials of the system components will be obtained as the Lagrange multipliers of the constrained minimization problem. As the complementary constraints are introduced via immaterial system components, the solution of the constrained systems will provide additional Lagrange multipliers, each of those representing another physically meaningful potential for the said system. For non-equilibrium conditions, the Gibbs'ian solution of the constrained multi-component system gives the non-zero affinity of the irreversible reactions.

The constraints derived from reaction kinetics (or e.g. from paraequilibrium conditions) are also introduced into the multicomponent  $\min(G)$  system by using additional virtual components, which incorporate the kinetic conditions to the computation by using the appropriate molar stoichiometry (or e.g. mass ratios). It follows that there will be an additional Lagrange multiplier solved for each of the virtual components in the system. Superposition of the multipliers then gives the affinity of each constrained stoichiometric reaction as a function of its advancement (extent of reaction), giving the non-equilibrium affinity in terms of the stoichiometric content of the virtual system components in each constrained reaction. When equilibrium is reached as the limiting case, the mass balance condition brings the thus determined affinity to zero. Thus, while applying the virtual component – virtual constituent combination to include irreversible kinetically constrained reactions in multicomponent systems the procedure remains consistent with the conventional definitions of affinity.

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## Section 1. General problems of chemical thermodynamics

### QSPR-METHOD OF PREDICTION OF VAPORIZATION ENTHALPY FOR HALOGENALKANES

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In works [1-2] we have proposed a method of prediction of vaporization enthalpy (298.15 K) for alkanes and some classes of oxygen-containing substances. In this work the method was extended and supplemented by halogenalkanes of different structure.

This method is based on the modified scheme of Randich using connectivity indices from 0 to 3 orders by the equation (1)

$${}^n\chi = \sum_1^n 1/\ln(\prod_0^3 \delta_i) \quad (1)$$

and their subsequent summation by the equation (2)

$${}^{0-3}\chi = {}^0\chi + \frac{{}^1\chi}{2} + \frac{{}^2\chi}{3} + \frac{{}^3\chi}{4} \quad (2).$$

Enthalpies of vaporization at 298K were calculated by equation (3)

$$\Delta H_{v,298K} = 1.6883 \cdot {}^{0-3}\chi + 2.0781 \quad (3)$$

The values of descriptors ( $\delta_i$ ) corresponding to the primary, secondary, tertiary and quaternary carbon atoms were taken from the work [1]. Their values are shown in the table.

Then, the resulting equation was used to calculate vaporization enthalpy for Cl-, Br- and F-containing alkanes of various structure and with different numbers of halogens in molecules. In order to calculate descriptors, in the work were used the test rows of corresponding mono- and  $\alpha$ - $\omega$  di-halogenalkanes, whose elements had a good agreement against each other. The resulting values of descriptors for atoms of Cl, Br and F also are shown in the table.

The correctness of the calculation has been checked on test rows of halogenalkanes. It was found out, that containing of two geminal or vicinal halogen atoms has led to reducing of a difference between experimental and calculated values of vaporization enthalpy on 3-5 kJ/mol, that most probably is coming from intermolecular interactions.

*Table. The values of descriptors*

Descriptor	Value	Descriptor	Value
—CH <sub>3</sub>	1.4773	Cl-	1.1661
—CH <sub>2</sub> —	1.6201	Br-	1.1333
—CH— 	2.3685	F-	1.3513
—C— 	7.5949		

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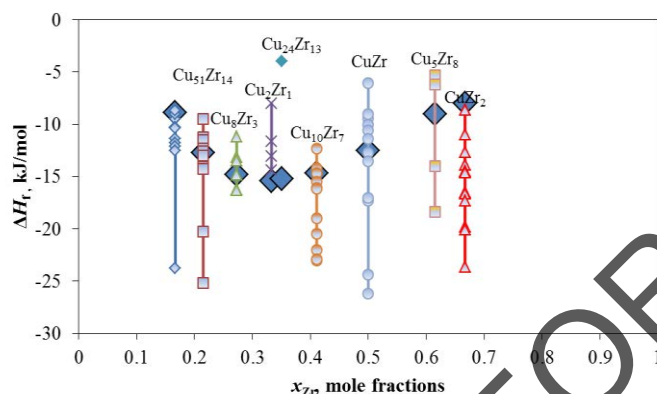
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## INVESTIGATION OF THERMODYNAMIC PROPERTIES OF INTERMETALLIC COMPOUNDS OF Cu-Zr SYSTEM

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The investigation of bulk amorphous alloys is one of the most intensively developing field of modern material science. The Cu-Zr-based alloys play special role among the other bulk metallic glasses. The binary Cu-Zr alloy has unique glass forming ability. In order to determine the key characteristics that control predisposition to amorphization of the melt and to establish their relation between the components with the peculiarities of the chemical interaction is necessary carry out a thorough of thermodynamic liquid and solid phases of Cu-Zr system. Available in the literature [1-10] enthalpy of formation ( $\Delta H_f$ ) intermetallics of Cu-Zr system are shown in Figure.



**Figure:** Enthalpy of formation ( $\Delta H_f$ ) intermetallics of Cu-Zr system;  $\blacklozenge$  - our data  $\Delta H_f$ .

There are serious disagreements between the results of different authors. Such a situation is typical enough in the study of the thermochemical properties of metallic alloys. *Ab initio* calculation methods on the current stage of development do not allow calculating these properties with sufficient accuracy. For this reason, semi-empirical methods for estimating the thermochemical properties have become very popular variety in particular the standard enthalpies of formation [11]. The enthalpy of formation 9 phases have been evaluated and refined using the approval

procedure based on the non-linear regression equations (1) (see Figure).

$$H_f(j) = [\Delta H^{\circ}_{298}]_j / n_j \text{ (kJ} \cdot \text{(mole} \cdot \text{atom)}^{-1}) \quad (1)$$

(or  $[\Delta H_f]_j / n_j = f(X(i)_j)$ ),

where  $[\Delta H^{\circ}_{298}]_j$  - standard enthalpy of formation of the  $j$ -th binary compound of the elements;  $n_j$  - the number of atoms in the formula unit  $j$ -th compound;  $(X(i)_j)$  - mole fraction of the  $i$ -th element in the  $j$ -th compound.

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## Section 1. General problems of chemical thermodynamics

### THERMAL STABILITY OF THE INTERFACE STATES OF d-METALS (Cu, Pd, Ti, Ni) AND Al WITH GRAPHENE

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We examined the results from MD modeling of the thermal evolution of isolated clusters and interface nanosystems for contact between clusters and island films of d metals and Al, taken for comparison, with mono- and bilayer graphene [1, 2]. We assessed both structural and dynamic characteristics (diffusion and electric transfer) along with thermodynamic effects, depending on temperature in the range of 300 to 4000 K. It was shown that compared to insulated clusters, the resistance of the structure at interfaces to the thermally activated development of diffusion and recoordination up to complete disordering as an analog of the melting of low-dimensional objects depended primarily on the type of contact sorption, and on the number of metal atoms on its faces and metal/graphene interfaces. Calculations for the cohesion energies of all contact surfaces— graphene/graphene and metal graphene—showed that this was associated with the rise in Me–C interaction forces due to the stabilizing influence of an additional graphene layer. In the case of Ni/G and Ti/G interfaces with the highest cohesion energy of contact between metal and graphene, metal atoms were held on the hexagonal surface of G in the range of 3800–4000 K with no signs of evaporation up to 3300 K for Ni/G2, and up to 3500 K for Ti/G2 (G2 with two graphene sublayers). The diffusion components in the X–Y ( $D_{xy}$ ) interface planes and the normal along axis Z ( $D_z$ ) for all considered Me/G systems depended differently on the heating temperature, reflecting the different natures of variations in the electron structure (adhesion energy and the types of sorption at interfaces). For interfaces with physical adsorption, variations in the diffusion activity differed in their smoothness with a notable rise for the Cu/G contact in the region of ~1000 K, and for Al/G/Al (with a double coating) in the region of ~1800 K, but with a different degree of nonmonotonicity. For the chemisorption interfaces formed during the hybridization of  $\pi_z$ – $d_z$  orbitals, however, slowgrowth at the initial stages of heating in the high-temperature region (~2000 K) changed with an abrupt increase in both diffusion components. Along with an increase in the lowfrequency contribution to the vibrational spectrum, one more distinction between the thermally activated dynamics of Ni and Ti atoms on bilayer graphene was an increase in diffusion mobility along the normal (component  $D_z$ ) and its unusually wavy temperature dependence, which was similar to the one observed for the normal component of the stress tensor. A monotonic rise in diffusion component  $D_z$  was characteristic of the interface with single-sheet graphene, while two maxima were observed for the temperature dependence of this component in the case of Me/G2. The anisotropy of the diffusion motion of metal atoms for all considered interface systems was more intense along the zigzag directions in planes X–Y adjoining the graphene sheets.

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## PRESENTATION OF EXCESS THERMODYNAMIC FUNCTIONS OF GLASS-FORMING SYSTEMS IN DATABASES

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«The fundamental theory is too complicated ... instead of it there is always an intermediate, phenomenological theory describing this or that phenomenon. The true role of the fundamental theory is not how to describe immediately, available theoretically nontreated experimental data, but in explaining the relatively small number of parameters of the phenomenological theory in terms of which a huge amount of experimental data was described.»

**J. Schwinger. Engineering Approach to the Theory of Elementary Particles**

Presentation of the phenomenological theory (model), the parameters of which can form the structure of storage in databank, and which through her mathematical apparatus upon request provides the necessary information on the thermodynamic properties of the substance in the form of a temperature and pressure function, begins with the fundamental theory in the report. Her role is played by using the *NPT*-ensemble statistical model of the fluid whose properties are completely determined by the volumetric pseudopotential interaction of particles. Analytical expressions for the set of thermodynamic properties in the fluid conditions including the critical state are obtained as a result of a number of mathematical transformations.

The results of model-statistical analysis of the elementary excitations of the vacancy type (Schottky with Bose-Einstein statistics and Frenkel with Fermi-Dirac statistics) were consolidated in the quasiparticle with intermediate statistics or parastatistics based on the concepts of quasi-crystalline liquid (P. Debye, Ya. Frenkel). Thus, the contribution of acoustic degrees of freedom in the thermal properties of liquid or melt are defined by the functions of parastatistics. For describing optical, quasilocal vibrational modes were used Einstein functions, taking into account the vibrational anharmonicity.

The defining expressions of statistical fluid made it possible to explain and decipher a relatively small number of parameters of the phenomenological model used in the report for describing not only the so-called thermal functions, but also functions relating to the thermic equation of state.

As an example, the properties of selenium, polyethylene and tungsten-tellurite glass with addition of lanthanum oxide were used.

Finally, the glassy state within the framework of the phenomenological model, retaining both the type of statistics and the values of the parameters of the liquid with lowering of temperature is followed from the supercooled liquid as a result of the "critical" change of the parameter of internal dimension from infinity at vitrification temperature  $T_g$  up to the final (fractal) values of  $d_0$  at 0 K.

# Section 1. General problems of chemical thermodynamics

## CONCENTRATION FIELDS FOR THE MATERIALS GENOME DECODING

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Science-funding agencies are working to halve the time it takes for newly discovered materials to reach the market. The vision and goals of their effort are presented in the white paper "Materials Genome Initiative for Global Competiveness" (June 24, 2011) [1-2]. "Materials Genome Project" was announced on the First International Conference LAPAMS'08 (Algeria, 23–26 June 2008 [3]. Phase diagrams (PD) application for computer-aided design (CAD) of heterogeneous materials was presented in Kyiv (Ukraine) in 2001 at the 6<sup>th</sup> International School-Conference "Phase Diagrams in Materials Science PDMS VI" [4-9].

**Calculation technique of one-dimensional tie-lines and crystallization paths** [8]. The main problem of heterogeneous materials CAD is to estimate the compositions of coexisting phases. In many cases, the necessary thermodynamic parameters are not available and therefore a mathematical description for the phase regions boundaries is used. In particular, the mathematical characteristics of the curvature of phase area boundaries can be employed. The division of surface isotherms into equal portions is suggested for the calculation of the conjugate compositions in the two-phase regions of the ternary phase diagrams.

**Hypersurfaces of T-x-y-z diagrams** [9]. Four-dimensional hypersurfaces of the T-x-y-z diagram have been depicted by a one-dimensional linear contour and equations have been elaborated for two types of the skewed hyperplanes: with one-dimensional and with two-dimensional originating simplexes.

**Quaternary isobaric PD three-dimensional sections construction** [6]. As the isothermal hyperplane intersects the unruled and ruled hypersurfaces with one- and two-dimensional originating simplexes within the T-x-y-z diagram, the corresponding isotherms (unruled surface, a ruled surface and a plane) have been realised. Algorithms and appropriate computer programs have been devised to depict on screen various projections of phase region sections.

**Isobaric quinary systems visualization** [5]. The three- and two-dimensional pentatop projections obtained from different pentatop positions are used for the graphical representation of a quinary system. Pentatop projections are compared with the degeneracy of multidimensional simplexes. The optimal three- and two-dimensional projections have been considered.

**Microstructures design algorithms** [7]. To demonstrate the CAD algorithms the quaternary A-B-C-D isobaric PD with incongruently melting compound  $R=A_mC$  has been chosen. It was shown, that 3-fold division of concentration area forms a genotype of multicomponent material.

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## ON THERMODYNAMIC PROPERTIES OF NANOCRYSTAL OF SIMPLE MATTER

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A model of nanocrystal in the form of a rectangular parallelepiped with a variable surface shape (RP-model) [1] is used to study of the dependencies of the thermodynamic properties versus of size and shape of the “free standing” nanocrystal of simple monoatomic matters.

It was assumed that the interatomic interaction in a nanocrystal of a simple single component compound is governed by the Mie–Lennard-Jones pair potential [2]:

$$\varphi(r) = \frac{D}{(b-a)} \left[ a \left( \frac{r_0}{r} \right)^b - b \left( \frac{r_0}{r} \right)^a \right]$$

Here,  $D$  is the depth of the potential well,  $r_0$  is the coordinate of the minimum of the potential well,  $b$  and  $a$  are parameters:  $b > a \geq 1$ .

There are analytic expressions for the size-shape dependencies for next thermodynamic properties: Debye temperature ( $\Theta$ ), for the first ( $\gamma = -[\partial \ln(\Theta)/\partial \ln(V)]_T$ ), second ( $q = [\partial \ln(\gamma)/\partial \ln(V)]_T$ ) and third ( $z = -[\partial \ln(q)/\partial \ln(V)]_T$ ) Grüneisen parameters, specific (per unit area) surface energy ( $\sigma$ ), surface pressures ( $P_{sf}$ ), melting temperature ( $T_m$ ), isothermal elastic modulus ( $B = -V(\partial P/\partial V)_T$ ), Poisson's ratio ( $\mu$ ), Young's modulus ( $Y$ ), shear modulus ( $G$ ), isobaric thermal expansion coefficient ( $\alpha_p = [\partial \ln(V)/\partial T]_P$ ) and heat capacity ( $c_v$  and  $c_p = c_v(1 + \gamma \alpha_p T)$ ). Here,  $V$  is the system volume,  $T$  is temperature, and  $P$  is pressure.

The concrete calculations are done for diamond (C-diamond), silicon (Si) and germanium (Ge). It is shown that at the isomorphous decrease of nanocrystal size (of the number of atoms  $N$ ) the values:  $\Theta$ ,  $q$ ,  $\sigma$ ,  $T_m$ ,  $B$ ,  $Y$  and  $G$  are decreasing, but functions:  $\mu$ ,  $\alpha_p$ ,  $c_v$ ,  $c_p$  and  $c_p - c_v$  are increasing along isotherm. The values  $\gamma$  and  $z$  are independent versus of nanocrystal size.

It is shown that the surface pressure ( $P_{sf}$ ) of nanocrystal is always lower than the pressure determined by the Laplace equation. Moreover, the surface pressure changes the sign and stretches the nanocrystal at high temperature. An expression for the temperature corresponding to the zero surface pressure was obtained, i.e., the temperature at which the equality  $P_{sf} = 0$  is satisfied. Than nanocrystal shape deviates from the most energetically stable shape (for RP-model it is cube), the more noticeably the changes of mentioned functions at the decrease of the nanocrystal size along of isotherm.

For functions of  $\alpha_p$  and  $c_v$  were show that:

- (i) at  $T = 0$  K, the surface contributions to the thermal expansion coefficient and to the specific heat disappear without a violation of the third law of thermodynamics;
- (ii) at  $T/\Theta = \infty$ , the surface contributions to the thermal expansion coefficient and to the isochoric specific heat disappear without violation of the law of classical statistical physics on uniform kinetic energy distribution over degrees of freedom (the Dulong–Petit law is a particular case);
- (iii) at  $T_{\max}(N) = 0.2145 \Theta(N)$ , the surface contributions to the thermal expansion coefficient and to the isochoric specific heat reach a maximum.

[1] Magomedov, M.N. *Nanotechnologies in Russia*, 2014, 9, 5-6, 293-304.

[2] Magomedov, M.N. *Technical Physics*, 2014, 59, 11, 1658-1668.

*This study was supported by the Presidium of the Russian Academy of Sciences (Project No. 13P) and the Russian Foundation for Basic Research (Project No. 12–08–96500-r-yug-a).*

## Section 1. General problems of chemical thermodynamics

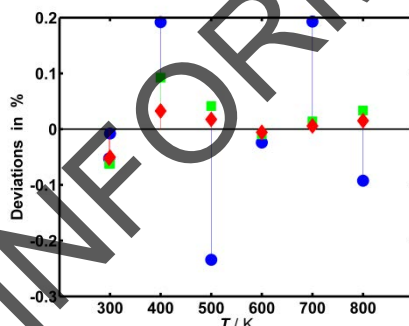
### ESTIMATION OF THERMODYNAMIC PROPERTIES OF CRYSTALLINE ZEOLITES

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Acquisition of information about thermodynamic properties of multicomponent phases of constant or variable composition is usually associated with complex and time-consuming experiments. Therefore, the correct evaluation of these data is an important problem for calculating the chemical and phase equilibria in multicomponent systems. The systems containing hydroaluminates and hydroaluminosilicates of alkali and alkali-earth metals with Fe, Ti and other additives are typical examples of such systems. The aim of the present research is applying a group contribution method for calculating thermodynamic properties of crystalline zeolites  $(R_2, R')O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$ , where R is an alkali metal and R' is a bivalent metal.

In our earlier research a general scheme has been developed for calculating thermodynamic properties of crystalline aluminosilicates. Its feature is using a single unified set of Plank-Einstein functions for description of different thermodynamic properties in the wide temperature range. This approach allows to approximate experimental and tabulated thermodynamic functions with high precision [1] (see for example Figure)



**Figure:** Errors of approximating the tabulated data [2] for analcime at different temperatures:

● –  $C_p$ ; ■ –  $H(T)-H(298.15)$ ; ◆ –  $S^0_T$ .

In present research a database on thermodynamic properties of zeolites has been created for calculating corresponding increments. All known heat capacity values,  $C_p(T)$  of zeolites have been approximated using Plank-Einstein functions taking into account the contribution of the standard entropy,  $S^0_{298}$  in order to provide more accurate behavior of heat capacity between 0 and 298 K when corresponding experimental  $C_p$ -values were absent. In calculations, the weighted contributions of  $S^0_{298}$  were high enough because these values are usually known more precisely than those of  $C_p$ . The uncertainties of all increments were calculated. It is necessary to evaluate the errors of estimated thermodynamic functions of zeolites.

[1] Voronin, G.F.; Kutsenok, I.B. J. Chem. Eng. Data, 2013, 58(7), 2083-2094.

[2] Robie, R. A.; Hemingway, B.S. US Geological Survey Bulletin 2131; US Government Printing Office: Washington, 1995.

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## THE DEVELOPMENT OF THERMOPHYSICAL DATABASE

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The efficiency of using compounds and materials in the solution of many pressing problems of our time is largely determined by the reliability, completeness and consistency of thermophysical data. A huge amount of available experimental data on thermophysical properties of substances and the rising flow of new data makes it necessary to create computer databases, transforming rapidly as new information becomes available.

The database of thermo-physical properties includes the three most important values for most of the tasks in science, technology, nuclear industry, construction and medicine - the coefficients of thermal expansion, heat capacity and thermal conductivity. Whatever the task may be standing in front of the user - the creation of parts, construction material or block the execution of research work - the database will help you choose the most profitable and best materials in existence.

There are some possibilities of this thermophysical database. Search can be either in elemental composition, and selecting a desired number atoms using the program integrated periodic system of chemical elements, or by thermal parameters, such as the coefficients of the linear and volumetric expansion, obtained from crystallographic data or dilatometer, the heat capacity as well as the coefficient conductivity. Data is stored in the form of temperature dependence, which allows to know the value of each parameter at a particular temperature or temperature range at a predetermined pitch, depending on the purpose. In addition, the database will contain references to the original literature from which the information was taken.

For a more visual representation of data written visualizer for three-dimensional shapes of thermal expansion of their sections, animation demonstrating the dynamics of changes in temperature gradient, as well as plots temperature dependence of the heat capacity and thermal conductivity. It allows quickly analyzing the change in thermal properties and choosing the optimal material.

A prediction function was developed to thermal expansion and heat capacity. Prediction of thermal expansion is performed by summing the contributions of structural units with known coefficients. Prediction of heat capacity based on theories of Debye and Einstein.

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## Section 1. General problems of chemical thermodynamics

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### THE CITATION OF RESEARCHERS AND SCIENTIFIC JOURNALS IN THE FIELD OF THE CHEMICAL THERMODYNAMICS

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In the given thesis, the data concerning modern scientometric (bibliometric) indicators of scientific journals in the field of chemical thermodynamics and fields of physical chemistry and chemical physics that are connected with chemical thermodynamics, have been presented and analyzed. These data have been borrowed from Web of Science (WoS) citation database. It has been noticed that the citation level (the quantitative characteristics of which, impact-factor is considered now) of many international scientific journals in the field of the physical chemistry and in the chemical physics that publish articles on the chemical thermodynamics, and which are published most authoritative scientific Publishing Houses Wiley and Elsevier (among their number, Journal of Physical Chemistry, Chemical Physics), at the whole, is extremely high. At the same time, this bibliometric parameter of many special journals on the chemical thermodynamics (for example, Journal of Chemical Thermodynamics, Journal of Thermal Analysis and Calorimetry) is essentially lower.

It has been ascertained that impact-factors (and, accordingly, citation) of Russian scientific journals on the above-mentioned profile are considerably lower than ones of corresponding foreign ("western") journals.

In this connection, it has been noted that, on the one hand, this fact should be connected with such an important circumstance that even English versions (not to mention the Russian-language ones) of our articles in Russian Journals (which are published, by Pleading Publisher or Springer, for example, Russian Journal of Physical Chemistry, Russian Journal of General Chemistry etc.) for a variety of reasons (including political) do not use with any considerable attention among researchers of leading scientifically Western countries and, accordingly, are not studied and not cited.

On the other hand, Russian researchers cited and, unfortunately, continue to cite the publications of "western" researchers essentially more often (in average, about in 60% cases) than on works of our countrymen. Western scientists, and, first of all, American ones, cited publications of our Russian colleagues only not more than in 5% cases [1]. In this connection, a series of steps directed to rise of citing of Russian scientific journals at all and in the field of chemistry and the chemical thermodynamics, specifically.

The information about general citation and h-indexes (Hirsch indexes) of a series of well-known Russian researchers who work in the field of the chemical thermodynamics and in related field of knowledge, according to data of Russian Index of Scientific Citation (RISC) and, also, according to basis international databases of citing, namely Web of Science (WoS) and Scopus, has been presented, too.

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ENERGIES OF REORGANIZATION OF RADICALS

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On the base of fundamental definitions of chemical physics, the design procedure of energies of chemical bonds and energies of reorganization of fragments of molecules into radicals after unimolecular radical reaction of molecules decomposition have been offered. Energies of reorganization for different compounds of composition  $C_aH_bO_cN_dHal_e$ , including polyradicals have been determined.

The equations (1) for bonds of dissociation energies and enthalpies of atomizations, and also replacement of one of average thermochemical energies of bonds on energy of dissociation of bonds in enthalpies of atomizations, it is possible to use the equations for definition of values of energies of reorganization of fragments of molecules in the radicals,  $\epsilon_R$ .

$$\Delta_{at}H = \Sigma\Delta_fH(at) - \Delta_fH^0 = \Sigma E_i; \quad D(R_1 - R_2) = E + \epsilon_{R1} + \epsilon_{R2}, \quad (1)$$

where  $\Delta_fH(at)$  – enthalpies of formation of the atoms making compound;  $E$  – average thermochemical energies of bonds;  $\epsilon_{R1}$  and  $\epsilon_{R2}$  – energies of reorganisation of fragments of molecules in radicals.

**Table.** Energies of reorganization (kJ/mol)

Radical	$\epsilon_R$	Radical	$\epsilon_R$	Radical	$\epsilon_R$
$C^{\bullet}H_3$	23.4(23.2[1])	$(C_2H_5)(CH_3)_2C^{\bullet}$	-2.6	$(NO_2)_3C^{\bullet}$	-16.8
$C^{\bullet\bullet}H_2$	54.5	$(CH_3)_3CC^{\bullet}H_2$	6.5	$(NO_2)_2C^{\bullet\bullet}$	34.5
$C^{\bullet\bullet\bullet}H$	41.8	cyclo- $C_6H_{11}^{\bullet}$	7.1(-10.6[1])	$NO_2C^{\bullet\bullet\bullet}$	24.2
$C_2H_5^{\bullet}$	5.1(-5.6[1])	n- $C_6H_{13}^{\bullet}$	2.6(-13.0[1])	$NO_2C^{\bullet}H_2$	23.5
n- $C_3H_7^{\bullet}$	6.8(-6.2[1])	$N^{\bullet}H_2$	59.3	$(NO_2)_2C^{\bullet}H$	1.2
i- $C_3H_7^{\bullet}$	0.0(-14.7[1])	$N^{\bullet\bullet}H$	27.4	$(NO_2)_3CC^{\bullet}(NO_2)_2$	-49.5
n- $C_4H_9^{\bullet}$	5.5(-13.0[1])	$NH_2N^{\bullet}H$	24.9	$HO^{\bullet}$	33.6
i- $C_4H_9^{\bullet}$	6.2(-9.8[1])	$CH_3N^{\bullet}H$	34.6	$HOO^{\bullet}$	-34.5
s- $C_4H_9^{\bullet}$	1.2(-14.6[1])	$(CH_3)_2N^{\bullet}$	-0.8	$CH_3O^{\bullet}$	-23.2
t- $C_4H_9^{\bullet}$	-2.8(-13.5[1])	$CH_3N^{\bullet}NO_2$	-36.8	$C_2H_5O^{\bullet}$	-24.1
n- $C_5H_{11}^{\bullet}$	3.4(-13.0[1])	$(NO_2)_2N^{\bullet}$	-30.8	$HOC^{\bullet}H_2$	-13.7
$(C_2H_5)_2C^{\bullet}H$	0.8	$NO_2$	0.0	$C^{\bullet}F_3$	52.7
$(n-C_3H_7)(CH_3)C^{\bullet}H$	4.9	$ONO_2$	0.0	$C^{\bullet}Cl_3$	-33.1

[1] Orlov, Y.D.; Lebedev, Yu.A.; Saifullin, I.S. Thermochemistry of organic free radicals. Moscow: Nauka, 2001, 304 p.

## Section 1. General problems of chemical thermodynamics

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### HEAT CAPACITY AT HIGH TEMPERATURES FROM THE LOW TEMPERATURE CALORIMETRY DATA

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To obtain the specific heat at high temperatures, we use the method proposed in [1]. The method is based on reconstructing the density of phonon states of  $g(\omega)$  from the low-temperature curve  $C_p(T)$  and allows calculating the heat capacity at constant volume  $C_v$  and temperatures up to the melting point based on the  $g(\omega)$  spectrum. The calculation of  $g(\omega)$  is performed in three steps. First, a zero approximation  $g_o(\omega)$  is chosen, which corresponds to the heat capacity  $C_o(T)$ . The function is chosen to correctly describe the behaviour of  $g(\omega)$  at  $\omega \rightarrow 0$  and at  $\omega$  approaching the cut off frequency of the spectrum  $\omega_{cut}$ . Then it is iteratively adjusted, where redistribution over the frequencies of vibrational modes of the zero approximation takes place. The iterative process of calculating  $g(\omega) = g_o(\omega) + \sum g_i(\omega)$  is performed by the sequential determination of the  $g_i(\omega)$  function parameters at different parts of the frequency spectrum. The  $g_i(\omega)$  function parameters are determined so that the sum of the corresponding calculated dependences of  $C_i(T)$  with account of  $C_o(T)$  provides a good description of the heat capacity  $C(T)$  in the entire temperature range with the accuracy corresponding to the error of its determination. The agreement of the experimental and calculated heat capacities is performed using the least squares method. To eliminate errors caused by the arbitrary choice of the initial iteration of the iterative process the calculation of  $g_i(\omega)$  is run several times (for example,  $N$  times), and the results are averaged. The averaging procedure significantly reduces the uncertainty in the determination of  $g(\omega)$  of the spectrum. It reduces the uncertainty in the  $1/N^{0.5}$  times. We give examples of calculations for a number of real-world objects. See also article [2].

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### SURFACE ENERGETIC HOMOGENEITY OF THERMALLY STABILIZED CRYSTAL BODIES RELATIVE TO CHEMISORPTION AND CATALYTIC PHENOMENA

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The surface energetic “homogeneity vs. heterogeneity” problem has been studied rather widely for about 90 years. Its solution is important for adequate understanding of different processes in the fields of solid-state physics, electronics, surface thermodynamics, catalysis, chemisorption and chemabsorption and for multiple practical applications. It is also important to achieve an adequate understanding of a general physical, thermodynamic, and chemical problem relevant to crystals of a definite composition: whether the individual features of crystal atoms or the characteristics of the crystals as generalities determine the reactivity of the atoms at thermally stabilized surfaces. Different techniques can provide insight into this problem, and all they should be taken into account; however, just the calorimetric chemisorption studies are most informative in this segment of the knowledge and, therewith, in our opinion, only correctly performed simultaneous calorimetric and kinetic studies of chemisorption are capable of closing this subject. The reviews dedicated to the progress in this field are rare and are as a rule imperfect and lenient as to the technical and procedural defects in the works under consideration. Owing to the smallness of the values under measurements, difficulties in the isolation of a process from the side ones, and instrumental refinements, the literature is filled with contradictory results, and, for the users, it is difficult and, at times, impossible to sift the grain from the chaff. This lecture resumes the many-decade works of the author aimed at solution of the “homogeneity vs. heterogeneity” problem and systematic analysis of available data obtained over the world. The conclusion on the surface homogeneity of thermally stabilized surfaces relates to the crystalline bodies with the crystal sizes of 3–5 nm and more, when the number of the volume atoms exceeds significantly the number of surface atoms in the crystals, and to the chemical (not physical) interactions of gases with the surfaces. It is stated on the basis of calorimetric data on chemisorption heats measured in the period of more than 5 decades by about 40 author groups for about 20 gas/metal-oxide and 45 gas/metal systems at films, powders, and supported chemisorbents and is confirmed by a number of works performed by other techniques, a number of systems being studied in several works with the same result. It is shown that combined measurements of the differential heat effects and differential rates of chemisorption confirm the surface homogeneity over a wide range of the surface coverages. Non-calorimetric experiments on the step-wise poisoning of catalysts in catalytic processes and on the measurements of the specific catalytic activity of the samples of the same composition but different degrees of sintering support the conclusion of the surface homogeneity of thermally stabilized surfaces of crystal bodies. For the following gas/metal systems, the surface homogeneity is stated on the basis of calorimetric measurements performed by different authors: H<sub>2</sub> at Fe, Fe/K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>, Ni, Pt (black), Pt/SiO<sub>2</sub>, Pt/W/SiO<sub>2</sub>, Pt, Pt (powder), Ce, Dy, Lu, Er, Tm, Yb, W; O<sub>2</sub> at Fe, Ni, Pt/W/SiO<sub>2</sub>, Nb, W, Mn, Co, Mo, Ta, Ti, Cu, Ag, W/SiO<sub>2</sub>, Au; N<sub>2</sub> at Ni, Fe/Al<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O, W; CO at Ni, Cu in ZnO/Cu<sub>4</sub>(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Dy, Ni, Ni/K, Ni/Cs, Pt, Pt/Rb, Pt/Cs; C<sub>2</sub>H<sub>2</sub> at Pt; H<sub>3</sub>C–C≡CH at Pt and for the following gas/metal-oxide systems: H<sub>2</sub> at Cr<sub>2</sub>O<sub>3</sub>, ZnO in ZnO/Cu<sub>4</sub>(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>; O<sub>2</sub> at Cr<sub>2</sub>O<sub>3</sub>, CuO; H<sub>2</sub>C=CHCOOH at V/Mo, V/Mo/Cu, V/Mo/P, V/Mo/Cs oxides; C<sub>2</sub>H<sub>4</sub> at Co/Mg/Mo, Ni/Mg/Mo, Cu/Al<sub>2</sub>O<sub>3</sub>, Ti, Ag oxides; C<sub>3</sub>H<sub>8</sub> at Co/Mg/Mo, Ni/Mg/Mo, Cu/Al<sub>2</sub>O<sub>3</sub>, Ti, Ag oxides; CO<sub>2</sub> at Cr<sub>2</sub>O<sub>3</sub>, CuCr<sub>2</sub>O<sub>4</sub>, ZnO in ZnO/Cu<sub>4</sub>(OH)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Thus, the reactivity of surface atoms is determined by the characteristics of the crystals as generalities but not by individual atomic features such as their positions on the crystal faces.

## Section 1. General problems of chemical thermodynamics

### NEW POTENTIAL BASED ON SHORT MOLECULAR SPHERICAL SHELL MODEL

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The study of thermodynamic properties of systems of polyatomic molecules by statistical physics and computer simulations (Monte Carlo and molecular dynamics) is based on specifying the pair interaction potential of molecules. An effective way to select the optimal potential is not available. The standard approach lies in determining the parameters of the potential with given shape as fitting on the properties of substances. Among the many functions at an early stage of searching we had been allocated the potential of spherical shells (PSS) [1, 2]. The authors dealing with the model of shells in the standard approach emphasized its visibility: at free rotation of a "rigid" molecule atoms "are smeared" on its shell. Unlike the standard approach we set a task to find that most general characteristic of the model object, which forms the potential curve (PC). This characteristic  $g_s$  has been found and named shell rigidity. Its values are calculated according to the minimum information about the structure of the molecule. Relations were obtained [3, 4] defining parameters: energy- and r-coordinates of three singular points (zero, minimum, inflection) of PC. The expressions were found connecting coordinates of inflection points of two levels of modeling – PC (molecular) and the critical isotherm (thermodynamic) [5]. They formed the basis for the prediction of the critical parameters of substances. Besides, the way of a choice in family of the potentials of  $M_i$  (n-m) of PC analogs found in family PSS( $g_s$ ) was offered [6]. These results gave the grounds to consider the model of shells as rather physically based model.

This work continues the study of the molecular model of spherical shells. Direct calculations proved validity of replacement of full adequate potential of spherical shells (eight contributions) by the truncated potential (two terms) answering to interaction of the near arcs - "dipoles", replacing shells [7]. It gives the chance to apply much simpler physically reasonable function in computer and other calculations, having kept thus the results and calculated ratios obtained earlier. The offered potential has the form:

$$U_{n-n} = \frac{A}{r(r-d)^9} - \frac{B}{r(r-d)^3}.$$

Here  $r$  is the distance between the centers of the shells,  $d$  - the diameter of the shell,  $A$ ,  $B$  are the uncertain coefficients. The resulting physically reasonable potential can be applied in several ways. First, the usual - as intermolecular function with the adjustable parameters on the properties of substances. Second, - as a new function with parameters for which we have already received calculated expressions in the model of shells. Third, the approach realized by us in the model of shells can be applied to new potential that allows to express coefficients of a new potential of arcs - "dipoles" through the parameters fixing its features and to connect them with parameters of the initial potential (12-6) describing interaction of a pair of free atoms.

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## STUDY OF ACID-BASE PROPERTIES OF WEAK ELECTROLYTES BY CONDUCTOMETRIC TITRATION

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Conductometric titration has the potential not only for analytical tasks, but also for studying protolytic equilibria, complementing and extending the possibility of direct conductometry, especially for weak electrolytes.

The main factor limiting the scope of the direct conductometry for low concentrations of weak acids ( $pK_a > 6$ ), is the presence of the carbon dioxide in solution and the influence of dissociation of water, which is usually not taken into account when processing conductometric data in commonly used mathematical models.

We have proposed to use the conductometric titration to determine the acidity constants of weak acids (bases) in aqueous and aqueous-organic solutions at concentrations of less than  $10^{-4}$  M and the technique for processing nonlinear conductometric titration data. The mathematical model is based only on the equations of the material and the charge balance with carbonic acid and dissociation of water with taken in account in framework of the Bronsted-Lowry theory. This does not include any transport properties of individual ions or solvent properties. At these concentrations, the values of molar conductivities were considered as limiting and additive.

The proposed method allows to determine the acidity constant ( $K_a$ ), the limiting ionic conductivity ( $\lambda_i$ ) for the test substance and carbonic acid, the average concentration of carbon dioxide.

On the first stage conductometric titration was performed according to the schemes: NaOH,  $\text{Na}_2\text{CO}_3 + \text{HCl}$ ;  $\text{Na}_2\text{CO}_3 + \text{HCl}$ ; NaOH + HCl; NaOH + HCl;  $\text{Na}_2\text{CO}_3 + \text{AcOH}$ ;  $\text{Et}_3\text{N} + \text{HCl}$ ;  $\text{Et}_3\text{N} + \text{AcOH}$ . Each conductogram contains at least 100 pairs of experimental values.

As a result of joint processing of these series we obtain the limiting conductivities for basic titrants and electrolytes, acidity constants ( $K_{\text{Et}_3\text{N}^+}$ ,  $K_{\text{AcOH}}$ ), and the acidity constants of carbonic acid ( $K_{c1}$ ,  $K_{c2}$ ) independently. Since the main requirement for application of the proposed technique is maintenance a constant  $\text{CO}_2$  content of the solution over the entire series, titration was carried out in a system isolated from the atmosphere. Titrants and solutions of studied acid prepared in water with a known concentration of  $\text{CO}_2$  (X).

Unknown values were found by the minimization of sum of squared relative deviations of the experimental values of conductivity and calculated from the equations of the type (1) using numerical methods.

$L(C_j) = 10^3 ([\text{H}^{(+)}]\lambda_{\text{H}^+} + [\text{OH}^{(-)}]\lambda_{\text{OH}^-} + (X + Y)(\beta_1\lambda_{\text{HCO}_3^-} + 2\beta_2\lambda_{\text{CO}_3^{(2-)}}) + \alpha C_j\lambda_A + 2Y\lambda_{\text{Na}^+})$  (1)  
where (for titration of  $\text{Na}_2\text{CO}_3$  by acetic acid), Y - the concentration of  $\text{Na}_2\text{CO}_3$ , C - concentration of acid,  $\alpha$  - the degree of dissociation of acid,  $\beta_1$  and  $\beta_2$  degree of dissociation of carbonic acid by the first and second stages.

On the second stage assuming obtained parameters as known, the acidity constants of phenol, aniline, glycine, tryptophan, benzoic acid, quinoline, nitrophenol were found in a similar manner. All obtained values were in good correspondence with literature data with exception of  $K_{c2}$  [1].

Thus, the method allows to determine the values of the acidity constants of several weak acidity ( $pK_a > 6$ ) acids in a single experiment, and the concentration of carbon dioxide and other known impurities in solution under study.

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# Section 1. General problems of chemical thermodynamics

## EVALUATION OF THE PROPORTIONALITY COEFFICIENT IN RUSANOV'S FORMULA FOR THE SURFACE TENSION OF NANOPARTICLES

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In our previous works [1, 2] thermodynamic stability conditions (derived from non-negativity of the second variation of the free energy) have been analyzed for two cases: (i) the nanoscale region when the surface tension depends on the particle size; (ii) the limiting case when the surface tension becomes equal to its macroscopic value. One has shown that the thermodynamic condition of mechanical stability of small objects relates to its effective surface tension  $\sigma$  with the isothermal compressibility of the corresponding bulk maternal phase  $\beta_1$ . For nanosized region, i.e. for  $R < R_{ch}^{(\sigma, \varepsilon)}$  ( $R_{ch}^{(\sigma, \varepsilon)}$  is a characteristic radius), the condition may be written as  $K \leq K_{ch} = 3/(12\nu - 2) \cdot \beta_1^{-1}$ . In this paper a method is proposed to calculate the proportionality coefficient  $K$  in Rusanov's linear formula  $\sigma = K_\sigma(T)R$  for the surface tension  $\sigma(R)$  of a small object using the size dependence of the specific total surface energy  $\varepsilon(R)$ , where  $R$  is the particle radius. Contrary to  $\sigma(R)$ , the  $\varepsilon(R)$  dependence can be easily enough found via computer simulation results. The coefficient  $K_\sigma(T)$  can be expressed via the coefficient  $K_\varepsilon(T) = \varepsilon(R) / R$ :

$$K_\sigma(T) = K_\varepsilon(T) + T \left( R_{ch}^{(\varepsilon)} \right)^{-1} \left( d\sigma_\infty / dT \right)^{bulk}.$$

When  $K_\sigma(T)$  is found, the characteristic particle radius  $R_{ch}^{(\sigma)}$  can be also evaluated. In turn, the coefficient  $K_\varepsilon(T)$  can be easily enough found using computer simulation results on the potential part of the cluster internal energy [3]. According to the results of our calculations presented in Table 1,  $R_{ch}^{(\sigma)} > R_{ch}^{(\varepsilon)}$  for all the systems under consideration at temperatures  $T < T_m$  ( $T_m$  is the particle melting temperature).

**Table.** Calculations of parameters of Rusanov's linear dependence for the surface tension and for the specific total surface energy ( $T = 586K$ )

Substance	$\left( \frac{d\sigma_\infty}{dT} \right)^{bulk}$ , $\mu J / (m^2 K)$	$R_{ch}^{(\varepsilon)}$ , $10^{-10} m$	$K_\varepsilon$ , $10^7 J / m^3$	$K_\sigma$ , $10^7 J / m^3$	$\sigma_\infty$ , $mJ / m^2$	$R_{ch}^{(\sigma)}$ , $10^{-10} m$
Au	-52.6	15.1	68.6	66.6	1388	20.8
Cu	-67.0	11.0	128.6	125.0	1789	14.3
Al	-53.4	18.5	57.4	55.7	1133	20.3

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The work was supported by the Ministry of education and science of the Russian Federation in frames of the State program in sphere of scientific activity and under support of the Russian Foundation for Basic Research (Grant No. 13-03-00119).

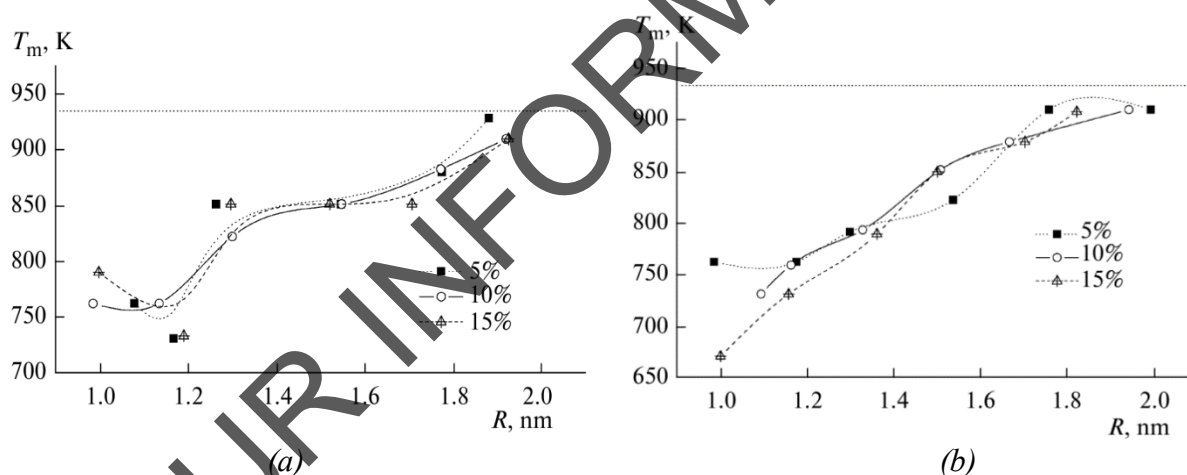
**ON THE INFLUENCE OF SURFACE AND BULK DEFECTS  
ON THE THERMODYNAMIC AND STRUCTURAL CHARACTERISTICS  
OF Al NANOPARTICLES DURING MELTING**

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Using computer simulation, we studied the influence of vacancies on the thermodynamic and structural characteristics of Al nanoclusters. We developed a computer program based on the Monte Carlo method (the Metropolis scheme) [1-3]. We made a comparative study of the melting and crystallization of Al nanoclusters containing 43–1055 atoms in the presence of bulk and surface vacancies. To simulate nanoparticle evolution as their temperature and diameter vary, we used the computational scheme applied previously [1-3].

The first kind phase transition was discovered using the jump (the knee) on the thermal curve, i.e., the dependence of the potential part of the specific (per one atom) internal energy of the nanoparticle–vapor system. Figure 1 shows the corresponding dimensional dependences. We note that, for small nanocluster sizes, precisely they determine the numerical value of the melting temperature to a larger extent, while, for large sizes, the defect (vacancy) concentration is a key factor.



**Figure:** Dimensional dependences of the melting temperature for Al nanoclusters in the case of fractions of surface (a) and volume (b) defects ranging from 5 to 15%.

As a result of simulation of the melting process by the Monte Carlo method using the Gupta potential for Al nanoclusters containing bulk (surface) defects (vacancies) we have calculated the thermal dependences of the potential part of the specific internal energy, the analysis of which made it possible to obtain the dimensional dependences for the melting temperatures. We have established the degree of influence of the vacancy concentration on the specific internal energy.

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*The work was supported by the Ministry of education and science of the Russian Federation in frames of the State program in sphere of scientific activity and under support of the Russian Foundation for Basic Research (Grant No. 13-03-00119).*



## Section 1. General problems of chemical thermodynamics

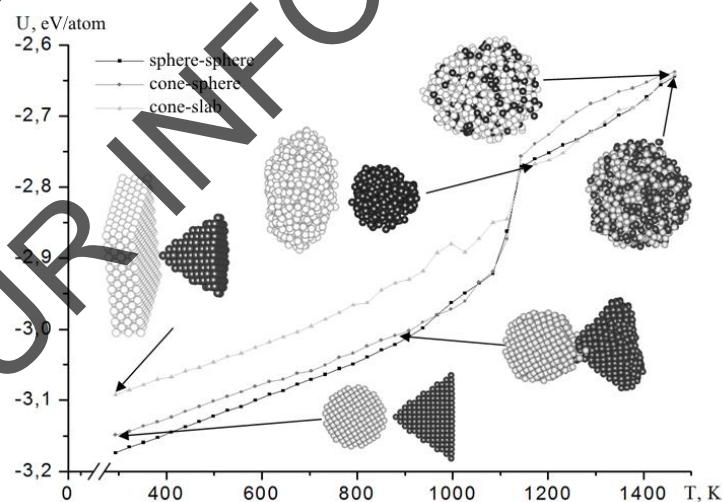
### INFLUENCE OF SHAPE AND LATTICE ORIENTATION OF NANOPARTICLES ON THE COALESCENCE PROCESS

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High interest to nanoclusters is associated with great prospects for their practical applications in various fields of science. Substance properties significantly change upon transition from macrostructures to nanosystems which depend on the nanoclusters sizes and a way of their organization. Therefore, there are many problems associated with miniaturization of system and control of its structure. Reduction of logical elements of integrated microchips leads to problems of creation of nanoclusters and nanowires. Processing and information transfer leads to a problem of creation of nanoclusters and films which possess magnetic properties. Creating devices with magnetic recording, nanodiodes, nanowires, single-electron transfer devices, which are rearranged by changing the size of the laser leads to a problem of receiving and organization of nanoclusters. On the basis of analyzing the simulation data it can be concluded that the sphere-sphere system is energetically favorable (see fig. 1). It has the smallest potential energy per atom. And highest energy system has cone-slab. At some systems, in particular, with lattices orientation (001), (110) and (011) of nanoparticles, energy falling, at distances when the coalescence occurs before melting process is observed. It is associated with occurrence of surface defects and as a result with destruction of a crystal lattice. In most cases, this process is accompanied by rotation one of the nanoparticles or overall system. In such cases, the formation of neck occurs much faster, thus considerably increasing the contact area and the dihedral angle nanoparticles [1, 2].



**Figure:** Dependence of potential part of specific internal energy for systems with various forms of nanoparticles is shown. Instant configurations of systems at points are presented. The distance between particles makes 0.3 nm.

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## NEW METHODS FOR DETERMINATION OF PHASE TRANSITION ENTHALPIES OF AROMATIC AND HETEROCYCLIC COMPOUNDS

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Determination of thermodynamic functions of phase transitions “liquid-gas” and “solid-gas” is one of the most important fields of chemical thermodynamics. Nowadays several well-known methods for determination of phase transitions enthalpies exist. Practically all of them are based on the study of transition of substances studied from a condensed phase to a gas at different temperatures. This way has some problems. The most fundamental of them are adjustment of obtained values to the reference temperature 298.15 K, accounting the thermodynamics of polymorphic transitions, low volatility and thermal stability of studied compounds.

In this work we develop experimental methods for determination of phase transition enthalpies using solution calorimetry technique directly at 298.15 K. These methods suggest the validity of the complementary thermochemical option for vaporization/sublimation data evaluation, which also permits the rapid gathering of reliable information for very low volatile chemicals.

These methods are based on the general relationship between enthalpy of solution of solute A in solvent S,  $\Delta_{\text{soln}}H^{A/S}$ , enthalpy of vaporization (liquid solute),  $\Delta_l^gH^A$ , or enthalpy of sublimation of A (solid solute),  $\Delta_{\text{cr}}^gH^A$ , and enthalpy of solvation of solute A in solvent S ( $\Delta_{\text{solv}}H^{A/S}$ ). All values refer to 298.15 K.

$$\Delta_{\text{soln}}H^{A/S} - \Delta_l^gH^A (\Delta_{\text{cr}}^gH^A) = \Delta_{\text{solv}}H^{A/S}.$$

This equation can be practically applied to assess vaporization/sublimation enthalpies of any solute A provided that the solvation and solution enthalpies are available.  $\Delta_{\text{soln}}H^{A/S}$  is directly measured at 298.15 K using the solution calorimetry or any other indirect techniques (gas chromatography, spectroscopy and etc.).  $\Delta_{\text{solv}}H^{A/S}$  is not directly available from the experiment, except for gases. In this work different approaches for estimation of enthalpies of solvation are discussed. New group-contribution method for calculation of solvation enthalpies is proposed. Some exceptions from additivity rules were analyzed and taken into account.

Obtained using solution calorimetry approach vaporization/sublimation enthalpies were compared with available literature values determined by conventional methods (more than 200 compounds). It was shown that they are in good agreement.

Also, enthalpies of solution of studied solutes were compared with their enthalpies of fusion at 298.15 K. Temperature effect on the enthalpies of fusion was discussed.

## Section 1. General problems of chemical thermodynamics

### AB INITIO MODELING OF THE INTERACTION OF H INTERSTITIALS WITH GRAIN BOUNDARIES IN BCC FE

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Hydrogen that is accumulated within the grain boundaries (GBs) can lead to a decrease of the critical strain required to fracture the material. The paper presents results of ab initio modeling hydrogen–grain boundary interaction in ferromagnetic bcc iron. Three symmetric tilt GBs,  $\Sigma 3(111)$ ,  $\Sigma 5(310)$  and  $\Sigma 5(210)$ , were chosen to study. The calculated tilt grain boundaries were constructed using the coincidence site lattice (CSL) model. Mechanical properties of GBs and effect of hydrogen on the properties can be described by quantitative characteristics:

$$\gamma_f = E_{gb} - 2E_{fs}, \quad (1)$$

$$\gamma_{gb} = \frac{1}{2S}(E_{gb} - E_{bulk}), \quad (2)$$

$$\Delta E = E_{Fe_nH}^{tot} - E_{Fe_n}^{tot} - \frac{1}{2}E_{H_2}, \quad (3)$$

$$\Delta E_B = E^f(GB) - E^f(FS), \quad (4)$$

$$E_{gbH}^{bin} = E_{gbH}^{tot} - E_{gb}^{tot} - E_{bulkH}^f, \quad (5)$$

where  $E_{gb}$  is the energy of GB,  $E_{fs}$  is energy of free surfaces (FS),  $E_{bulk}$  is the energy Fe bulk, and  $S$  is the area of GB,  $E^f(GB(FS))$ - the formation energy of H on the GB (FS),  $E_{bulkH}^f$  is formation energy of H into a perfect lattice.

**Table.** Energy characteristics of the grain boundary

	Our results			Other results			Exp.
	$\Sigma 5(310)$	$\Sigma 5(210)$	$\Sigma 3(111)$	$\Sigma 5(310)$	$\Sigma 5(210)$	$\Sigma 3(111)$	
(1) $\gamma_f$ , eV	-5.77	-5.24	-4.19	—	-5.41[1]	-3.32[2]	—
(2) $\gamma_{gb}$ , J/m <sup>2</sup>	1.44	1.83	1.46	1.48[3]	2[4]	1.52[3]	0.98[5]
(3) $\Delta E$ , eV	-0.1	-0.48	-0.1	-0.14[6]	—	-0.19[7]	—
(4) $\Delta E_B$ , eV	0.68	0.07	0.41	—	—	0.31[8]	—
(5) $E_{gbH}^{bin}$ , eV	0.43	0.81	0.39	0.4[9]	—	0.49[10]	0.5[11]

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4D COMPUTER MODEL OF THE Fe-Ni-Cu-S SYSTEM T-x-y-z DIAGRAM

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The 4D computer models of T-x-y-z diagrams are designed in some steps [1]: design of boundary T-x-y diagrams 3D computer models, prediction of the T-x-y-z diagram possible geometrical construction, design of its prototype and finally improvement of the prototype into the real system diagram model. For instance, after the systematic experimental study of ternary systems, forming the quaternary system Fe-Ni-Cu-S [2], and on the basis of its studies [3], it is possible to conclude that there are no quaternary compounds and, therefore, its geometrical construction may be predicted on the base of ternary systems by the phase reactions scheme (Table). Obviously that the surface  $k_{A1B}k_{A1C}k_{A1R1}$  and the hypersurface with the critical point  $\xi$  correspond to the metatectic reaction  $\delta\text{-Fe} \rightarrow \gamma\text{-Fe} + L$  ( $A \rightarrow L + A1$ ) with allotropy forms of iron  $\delta\text{-Fe} = A$ ,  $\gamma\text{-Fe} = A1$ , and the liquid immiscibility (Figure). According to this scheme it is assumed that the liquidus must include hypersurfaces of the iron high-temperature polymorphous modification  $\delta\text{-Fe} = A$ , the compound  $\text{Ni}_3\text{S}_2 = R3$ , and solid solutions  $\gamma\text{-Fe}(\text{Ni,Cu}) = A1(B,C)$ ,  $\text{FeS}(\text{NiS}) = R1(R2)$  and  $\text{Cu}_2\text{S}(\text{FeCu}_4\text{S}_3) = R4$ , which intersect over 8 surfaces. It is possible that the liquid participates in invariant reactions  $L(\pi) + \text{FeS}(\text{NiS}) \rightarrow \gamma\text{-Fe}(\text{Ni,Cu}) + \text{Ni}_3\text{S}_2 + R4$  and  $L(\varepsilon) \rightarrow \gamma\text{-Fe} + \text{Ni}(\text{Cu}) + \text{Ni}_3\text{S}_2 + \text{Cu}_2\text{S}(\text{FeCu}_4\text{S}_3)$  at temperatures not above 753°C and 585°C, correspondingly. Further the transformation of the phase reactions scheme (Table) into the uni- and invariant states scheme [1] will make it possible to design 4D "skeleton" of the T-x-y-z diagram prototype and to plan experiment for the construction of the corresponding real system T-x-y-z diagram.

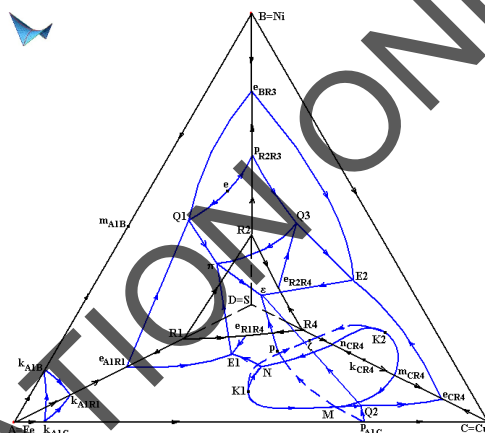


Figure: Prediction of the system Fe-Ni-Cu-S liquidus.

Table. Possible scheme of 4- and 5-phase reactions of the Fe-Ni-Cu-S system liquidus

Fe-Ni-S=A-B-D	Fe-Ni-Cu-S=A-B-C-D	Fe-Cu-S=A-C-D	Ni-Cu-S= B-C-D
		M(N), 1074°C: $L1 \rightarrow L2 + A1 + R4$	
		Q2, 1070°C: $L + A1 \rightarrow B(C) + R4$	
	E1, 914°C: $L \rightarrow A1 + R1(R2) + R4$		
Q1, 789°C: $L + R1(R2) \rightarrow A1 + R3$	$\pi, < 753^\circ\text{C}: L + R1(R2) \rightarrow A1 + R3 + R4$		Q3, 753°C: $L + R1(R2) \rightarrow R3 + R4$
$A1 + R1(R2) + R3 + R4$			
	$\varepsilon, < 585^\circ\text{C}: L \rightarrow A1 + B(C) + R3 + R4$		E2, 585°C: $L \rightarrow B(C) + R3 + R4$
$A1 + B(C) + R3 + R4$			

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# Section 1. General problems of chemical thermodynamics

## PARTICIPATION OF LAVES' PHASES IN EUTECTIC-PERITECTIC TRANSFORMATIONS IN Zr-Cr-{V, W, Mo} SYSTEMS

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3D models of T-x-y diagrams are designed first as virtual models (prototypes), which formally correspond to their geometrical construction only. Then the prototype is filling with experimental data and is converted into the model of real system. But if data do not have single-valued interpretation, then it is possible to construct all possible versions of phase diagram. For instance, liquidus of the system V-Zr-Cr=A-B-C with the compound  $V_2Zr=R$  and two R1, R2 (or three R1, R3, R2) polymorphous modifications of the compound  $ZrCr_2$  consists of surfaces of primary crystallization of Zr, solid solutions V(Cr) and R(R2) - the compound  $V_2Zr=R$  with the low-temperature modification R2 plus the high-temperature modification R1 (first variant in Figure 1). The second variant is the same liquidus but with two fragments of intermediate modification R3 (second variant). In this case its T-x-y diagram may be used also as the prototype for T-x-y diagrams of analogous systems with W and Mo.

How it was founded the eutectic-peritectic transformation from  $L \rightarrow A(C)+R(R2)$  to  $L+A(C) \rightarrow R(R2)$  has a place in the system with V, whereas systems with W or with Mo have two analogous transformations, but in phase regions  $L+A(C)+R1$  and  $L+R+R(R2)$  [1]. Since the special surface corresponds to the change of the reaction types in 3-phase regions [2], then temperatures of these transformations are not constant, as it is said in [1]. For instance, the type of reaction is changed in the phase region  $L+A(C)+R(R2)$  on the surface *abc* in both versions of T-x-y diagram with V (Figure 1). It is possible that the analogous surface exists in the systems with W and Mo. To control a change of the masses in the 3-phase region is convenient with the aid of the mass-balance diagrams (Figure 2). Thus, the liquid  $G(0.32, 0.20, 0.48)$  crystallization passes the 3-phase region in the temperature interval 1485-1467°C. Firstly quantity of solid solution R(R2) increases ( $\Delta m_{R(R2)} > 0$ ), quantity of liquid L and solid solution A(C) decreases ( $\Delta m_L < 0$ ), as in peritectic reaction. But at temperatures below 1476°C only a quantity of liquid decreases, as in eutectic reaction:  $\Delta m_{A(C)} > 0$ ,  $\Delta m_{R(R2)} > 0$ . At 1476°C the 3-phase reaction is transformed to 2-phase one  $L \rightarrow R(R2)$  at passive presence of third phase A(C):  $\Delta m_{A(C)} = 0$ .

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This work was partially supported by the Russian Foundation for Basic Research (Projects No. 14-08-00453, No. 14-08-31468, No. 15-43-04304).

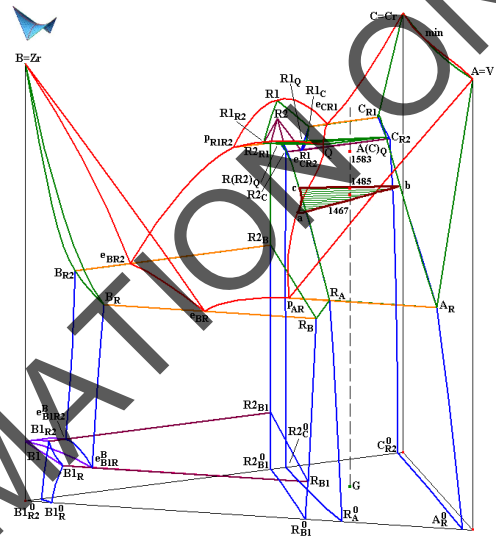


Figure 1: First variant of the system V-Zr-Cr T-x-y diagram.

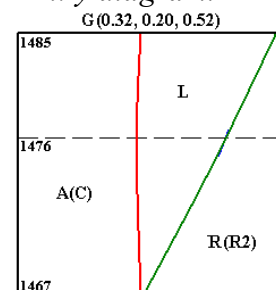


Figure 2: Mass-balance diagram for the melt G in the 3-phase region  $L+A(C)+R(R2)$ .

A NEW MODIFICATION OF THE MAXIMUM LIKELIHOOD METHOD  
FOR APPROXIMATION OF THERMODYNAMIC DATA SERIES

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Thermodynamic modelling of multicomponent systems includes an optimization of model parameters based on experimental data series. The least squares method that is usually used to solve this task requires an absence of systematic errors in input data that is hard to reach in the case of data series from different sources. An alternative approach suggested by E.B. Rudnyi [1, 2] is the representation of residuals  $\varepsilon_{ij}$  ( $i$  – index of data series,  $j$  – index of a point) as the sum of random error  $\varepsilon_{r,ij}$  and two kinds of systematic errors: «shift» error  $\varepsilon_{a,i}$  and «tilt» error  $\varepsilon_{b,i}$ :

$$\varepsilon_{ij} = F(\beta, x_{ij}) - y_{ij} = \varepsilon_{r,ij} + \varepsilon_{a,i} + \varepsilon_{b,i}(x_{ij} - x_i); x_i = N_i^{-1} \sum_j x_{ij},$$

where  $\beta$  is the vector of model parameters,  $F$  is the model function,  $N_i$  is the number of points in  $i$ -th data series,  $x_{ij}$  and  $y_{ij}$  are coordinates of experimental points. The optimization of  $\beta$  and  $\sigma^2_{r,i}=D[\varepsilon_{r,i}]$ ,  $\sigma^2_{a,i}=D[\varepsilon_{a,i}]$ ,  $\sigma^2_{b,i}=D[\varepsilon_{b,i}]$  values ( $D$  means dispersion) is based on the maximization of the likelihood function  $L$ :

$$L(\beta, \sigma^2) = -\ln \{ \det[D(\varepsilon)] \} - \varepsilon^T D(\varepsilon) \varepsilon; D(\varepsilon) = \text{cov}(\varepsilon, \varepsilon).$$

The algorithm of  $L$  maximization used in [1,2] consists of two steps repeated in iterative cycle:

1. Minimization of  $SS = \varepsilon^T D(\varepsilon) \varepsilon$  weighted sum of squares at fixed  $\sigma^2$  values
2. Maximization of  $L$  by solving  $(\partial L / \partial \sigma^2) = 0$  system of equations at fixed  $\beta$  values

In this work it has been shown that  $(\partial L / \partial \sigma^2) = 0$  equation system can have multiple solutions in some cases that correspond to local minima of  $L$  function and the result can depend on initial approximations for  $\sigma^2$  and used minimization algorithms. To increase the robustness two modifications of this algorithm have been proposed:

1. Independent estimation of  $\sigma^2_{r,i}$  for each series by means of ordinary non-weighted least squares method. Such technique allows to solve isolated independent  $(\partial L / \partial \sigma^2_{a,i}) = 0$  and  $(\partial L / \partial \sigma^2_{b,i}) = 0$  non-linear equations instead of the  $(\partial L / \partial \sigma^2) = 0$  equation system
2. Normalization of systematic «tilt» errors contribution, i.e. usage of  $2\varepsilon_{b,i}(x_{ij} - x_i) / (x_{\max} - x_{\min})$  (where  $x_{\max} = \max x_{ij}$ ,  $x_{\min} = \min x_{ij}$ ) instead of the  $\varepsilon_{b,i}(x_{ij} - x_i)$ . Such replacement prevents the dependence of  $\sigma^2_b$  values from the measurement units used for  $x$ .

The modified method has been implemented in the computer program and successfully tested on the test examples from [1], vaporization of KCl [1] and thermodynamic functions of calcium aluminates  $\text{Ca}_3\text{Al}_2\text{O}_6$ ,  $\text{CaAl}_2\text{O}_4$ ,  $\text{CaAl}_4\text{O}_7$ , and  $\text{CaAl}_{12}\text{O}_{19}$  [2]. To make the program more flexible and exclude its recompilation after adding the new model (as in [1]) input data series and thermodynamic models are described in either Lua or MATLAB programming language.

It has been shown that the modified version of the algorithm from is more robust and less dependent from the initial approximations for  $\sigma^2$  than the original version [1, 2]

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*This work was financially supported by the Russian Foundation for Basic Research (Project No. 13-03-00328-a).*



## Section 1. General problems of chemical thermodynamics

### ELABORATION OF COMPUTER MODELS OF T-X-Y DIAGRAMS ON THE BOUND OF SYSTEM LiF-KF-RbF-PuF<sub>3</sub>

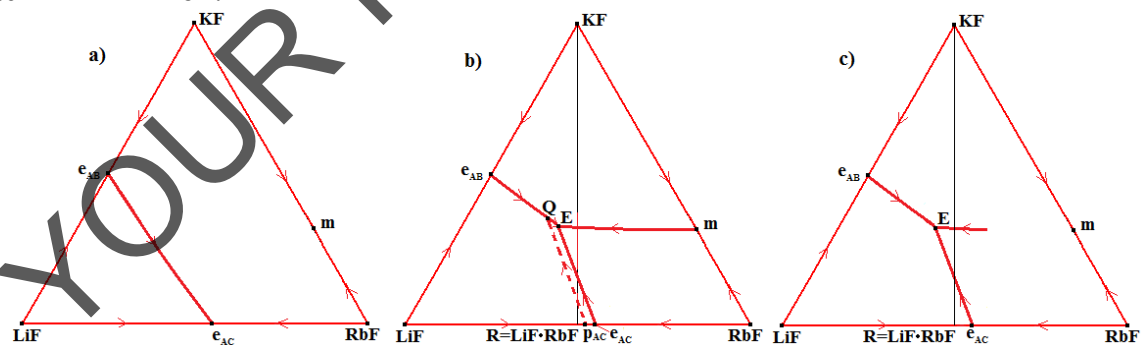
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The preference of developed computer models of phase diagrams of fluoride systems is not only their detailed 3D visualization, but also an opportunity to consider the variants of topological structure for systems having the different interpretations of geometric structure. The developed model of phase diagram is a base for complex investigation including the analysis of stages of phase transformations in any part of phase diagram and the identification of concentration fields with coincident sets of microconstituents of phases assemblage [1]. The computer models of phase diagrams of systems LiF-KF-PuF<sub>3</sub>, LiF-RbF-PuF<sub>3</sub> и KF-RbF-PuF<sub>3</sub> were constructed using data about the structure of liquidus surfaces and binary systems [2]. The same template is using for simulation of systems LiF-KF-PuF<sub>3</sub> and LiF-RbF-PuF<sub>3</sub> with similar topological structure and including two eutectic and one quasi-peritectic equilibria. The system LiF-KF-RbF does not have a clear description and three variants of phase diagram model were simulated. Its binary system LiF-RbF described as: 1) a simple eutectic system [3]; 2) eutectic system with the compound decomposes in the solid phase [4]; 3) system with a binary incongruently melting compound [5]. Other binary system LiF-KF is eutectic type and system KF-RbF contains the continuous range of solid solutions with minimum. In one case, it is assumed that the system LiF-KF-RbF has not a three-phase transformation [3] (Figure a). In another case, the formation of ternary eutectic and quasi-peritectic (not confirmed) points is discussed [5] (Figure b). The third variant of the structure of phase diagram with the formation of ternary eutectic point and the fold from system KF-RbF can be assumed (Figure c). The forecast of geometric structure of system LiF-KF-RbF-PuF<sub>3</sub> is based on the construction of bounding ternary systems and the schema of mono- and invariant equilibria, so it is necessary to consider all alternatives of phase diagram structure for system LiF-KF-RbF.



**Figure:** Topological variants of structure of liquidus surfaces for system LiF-KF-RbF

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## CALCULATION METHODS OF INVARIANT POINTS OF T-x-y-z DIAGRAMS AND THE GRAPHS CORRECTION OF MULTICOMPONENT SYSTEMS

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Determination of invariant points of T-x-y-z diagrams is possible as the selection of models of liquidus hypersurfaces and the using of tie-lines method. In the first case, the invariant points are calculated as the intersection of (hyper)surfaces or (hyper)planes. Depending on the method of linear approximation of hypersurfaces it may occurs the negative coordinate values and the ambiguity solutions. The calculation of quaternary eutectic point  $\epsilon$  as the intersection of three planes  $e_{IJ}E_{IJK}E_{IJL}$  [1] or four hyperplanes  $Ie_{IJ}E_{IJK}E_{IJL}$  [2] (Figure) gives the different variant for combination of equations systems, which gives the multiplicity of solution (the different sets of coordinates of point  $\epsilon$  can be obtained) [3]. The describing of liquidus hyperplanes as  $Ie_{IJ}E_{IJK}E_{IJL}$  [4] has a unique solution, at that the coordinates of ternary and quaternary eutectics are calculated. However, depending on the structure of T-x-y-z diagrams, it can be both positive and negative coordinates of calculated points. To solve this problem we propose to use a non-linear approximation of liquidus hypersurfaces. The setting of curvature increases the equations degree, but avoids the intersection outside of the concentration tetrahedron.

An alternative method of determining of coordinates of invariant points is the tie-lines method. Modernization of this method is proposed, based on the construction of three 2-dimensional non-planar vertical sections [5]. Two first sections (not belonging to the same plane) allow to determine the point on tie-line at the temperature of quaternary eutectics. The third vertical section is constructed through the obtained point and the nearby vertex of tetrahedron to the intersection with the horizontal hyperplane. This section will contain the point of quaternary eutectic.

The use of this method to the series of salt systems permits to establish the inaccuracies in experimentally constructed isopleths. The matrix transformations are used for the determination of points coordinates, which define the arrangement of the vertical sections.

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[1] Gasanaliev, A.; Gamataeva, B.; Rasulov, A.; et al. Russ. J. Inorg. Chem., 2009, 54, 1494-1501.

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This work was partially supported by the Russian Foundation for Basic Research (Projects No. 14-08-00453, No. 14-08-31468, No. 15-43-04304).

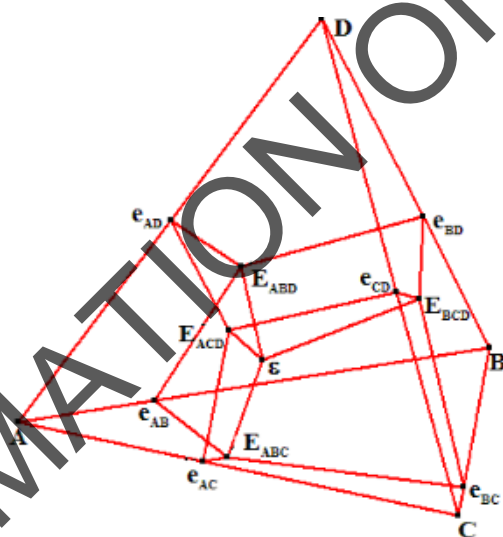


Figure: Liquidus hypersurfaces of T-x-y-z diagram of eutectic type.

## Section 1. General problems of chemical thermodynamics

### QSPR-METHOD OF PREDICTION OF VAPOUR PRESSURE AND HEAT CAPACITY “LIQUID-GAZ” FOR ACYCLIC OXIGEN COMPOUNDS

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In works [1, 2] has been proposed a method of prediction vaporization enthalpy (298.2 K) for alkanes and some classes of oxygen-containing substances. In this work, is shown a possibility of application reached total connective indexes for prediction of heat capacity of liquid-gas transition and vapor pressures of acyclic oxygen-containing substances on base of developed QSPR-method for  $\Delta_{\text{vap}}H^\circ(298.15)$ .

In order to calculate vapor pressures, was used equation (1)

$$R \cdot \ln(p) = A_0 - \frac{B_0}{T} + C_0 \cdot \ln\left(\frac{T}{298.15}\right), \quad (1)$$

$C_0$  – coefficient is numerically equal to heat capacity of liquid-gas transition;  $p$  – pressure (Pa);  $T$  – temperature (K). For the obtaining of a correlative dependence of  $\Delta_7^s C_p^\circ$  from total connective index ( ${}^{0-3}\chi$ ), were used existing experimental heat capacity data for liquid and gaseous phases of alkanes, ethers and esters. As a result, was obtained a linear equation (2), that can be applied for prediction of  $\Delta_7^s C_p^\circ$  (J/(mol\*K)).  $\Delta_7^s C_p^\circ = -2.395 \cdot {}^{0-3}\chi - 11.52$   $R^2=0.9966$  (2). The coefficients  $A_0$  and  $B_0$ , taken from experimental data were processed in the dependence from  ${}^{0-3}\chi$  with derivation of linear equations (3) and (4).

$$A_0 = 4.7955 \cdot {}^{0-3}\chi + 158.34 \quad R^2=0.9938, \quad (3)$$





$$B_0 = -24242 \cdot {}^{0-3}\chi - 4197.70 \quad R^2=0.9971. \quad (4)$$

The values  ${}^{0-3}\chi$  were calculated on the strength of equations (5) and (6)

$${}^{0-3}\chi = {}^0\chi + \frac{{}^1\chi}{2} + \frac{{}^2\chi}{3} + \frac{{}^3\chi}{4}, \quad (5)$$

$${}^n\chi = \sum_1^n 1 / \ln\left(\prod_0^3 \delta_i\right). \quad (6)$$

*Table. The values of descriptors*

Descriptor	Value	Descriptor	Value
—CH <sub>3</sub>	1.4773		1.1664
—CH <sub>2</sub> —	1.6201		1.1319
—CH— 	2.3685		1.1467
—C— 	7.5949	—OH	1.2115
—O—	1.6062		1.0425

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**Section 2**  
**Thermodynamics of individual  
chemical compounds**



## Section 2. Thermodynamics of individual chemical compounds

### EXPERIMENTAL DETERMINATION OF FUSION ENTHALPY OF EUTECTIC IN THE SYSTEM $\text{Nd}_2\text{S}_3 - \text{Nd}_2\text{O}_2\text{S}$

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The system  $\text{Nd}_2\text{S}_3 - \text{Nd}_2\text{O}_3$  refers to the infusible, which substantially complicates determination the liquidus line position. It is advisable to assess the fusion enthalpy of  $\text{Nd}_2\text{S}_3$  and  $\text{Nd}_2\text{O}_2\text{S}$  and to carry out thermodynamic calculations [1].

At the first time by differential scanning calorimetry (DSC) method the fusion enthalpy of eutectic, consist of phases  $\text{Nd}_2\text{S}_3$  and  $\text{Nd}_2\text{O}_2\text{S}$  was defined, this allowed to estimate the melting point of eutectic component.

DSC was conducted on STA 449 F3 Jupiter equipment. Fusion enthalpy calculated using the calibration dependence, it is built by fusion enthalpy of the fixed point. The accuracy of deducting enthalpy of fusion is 10–15%.

Compounds melt congruently:  $\text{Nd}_2\text{S}_3 - 2070 \text{ K}$ ,  $\text{Nd}_2\text{O}_2\text{S} - 2320 \text{ K}$ . System  $\text{Nd}_2\text{S}_3 - \text{Nd}_2\text{O}_2\text{S}$  is a eutectic type. The composition of the eutectic according to microstructural methods is 23 mol.%  $\text{Nd}_2\text{O}_3$ , this corresponds to ratio of phases  $0.655\text{Nd}_2\text{S}_3 + 0.345\text{Nd}_2\text{O}_2\text{S}$ , the melting point of eutectic crystals 1820 K.

Fusion enthalpy of eutectic crystals was defined of constructing a Tammans triangle according to DSC:  $\Delta H_{\text{fus}} = 158 \text{ J/g}$  (Table).

**Table.** DSC and thermogravimetry data for samples of the system  $\text{Nd}_2\text{S}_3 - \text{Nd}_2\text{O}_3$

Characteristics	Parameters							
Sample composition	6.6 mol.% $\text{Nd}_2\text{O}_3$	10 mol.% $\text{Nd}_2\text{O}_3$	15 mol.% $\text{Nd}_2\text{O}_3$	20 mol.% $\text{Nd}_2\text{O}_3$	23 mol.% $\text{Nd}_2\text{O}_3$	25 mol.% $\text{Nd}_2\text{O}_3$	33 mol.% $\text{Nd}_2\text{O}_3$	63 mol.% $\text{Nd}_2\text{O}_3$
Sample weight (mg)	101.4	101.2	100.1	102.6	99.8	100.9	101.5	101.1
Mass change at thermal processing $\Delta m$ (mg)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Received value	1817	1823	1820	1821	1820	1820	1821	1818
$T_{\text{melt eutectic}}$ (K)	$\pm 7$	$\pm 5$	$\pm 5$	$\pm 5$	$\pm 5$	$\pm 5$	$\pm 5$	$\pm 5$
Area of peak of eutectic melting S ( $\mu\text{V/mg}$ )	0.53	0.07	6.0	13.5	13.4	18.1	12.59	10.79
Fusion enthalpy of eutectic crystals $\Delta H$ (J/g)	6.21	0.7	61.4	146.8	158.1	159.2	147.7	126.73

The balanced equation of melting of the eutectic crystal is formulated:

$$158 \text{ J/g} (\Delta H_{\text{eut}}) = 0.655(\text{MM}) \Delta H_{\text{fus}} \text{Nd}_2\text{S}_3 (\text{J/g}) + 0.345 (\text{MM}) \Delta H_{\text{fus}} \text{Nd}_2\text{O}_2\text{S} (\text{J/g}).$$

Conditions for determination of  $\Delta H_{\text{fus}} \text{Nd}_2\text{S}_3$  by DSC-method were formulated. It will make possible the calculation of  $\Delta H_{\text{fus}} \text{Nd}_2\text{O}_2\text{S}$ .

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The investigation was carried out with financial support of Rendering Services of State Task No. 2014/228 (No. 996).

**THERMODYNAMICS OF HYPERBRANCHED POLY(PHENYLENE-PYRIDIL)  
POLYMERS IN THE RANGE FROM  $T \rightarrow 0$  TO 680 K**

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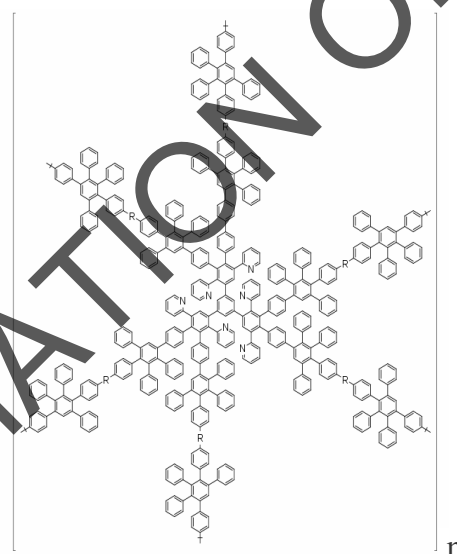
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Hyperbranched polymers have a row of unique properties: high solubility, low viscosity solutions and melts, high sorption capacity and thermal stability. In this work, three samples of hyperbranched polyphenylene pyridine polymers of different structure and composition obtained in the laboratory of Macromolecular Chemistry of Institute of Organoelement Compounds were investigated. The polymer samples were characterized by gel-permeation chromatography and NMR spectroscopy. The general scheme is shown in Figure 1, where R – oxygen atom (sample 1), C=O group (sample 2) or absence group (sample 3).

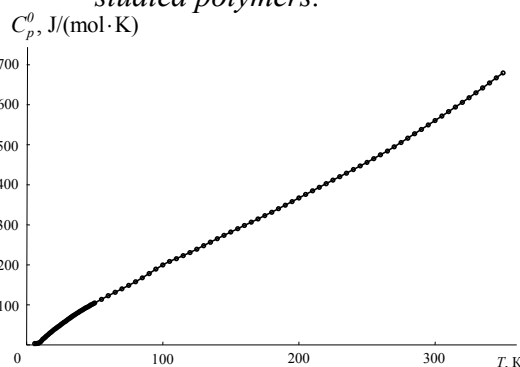
The thermal stability of the polymer samples was studied by thermal gravitational analysis. It was observed that the polymers are stable to ~680 K. The temperature dependence of the heat was studied by adiabatic vacuum and differential scanning calorimetry. In Figure 2 as an example curve  $C_p^0 = f(T)$  of one of the samples in the range (6–380) K is showed, for the other two samples curves are similar in form. In the range of (8–20) K, low-temperature relaxation transformation was found; the thermodynamic parameters of this transformation (temperature, an increase in the heat capacity on the conversion, zero and configuration entropies) were found. The changes of heat capacity of the studied samples are identical and similar, but temperatures of the physical transformation depend on the structure and composition of the samples.

In the temperature range above 480 K energy release was observed for all samples is probably due to the internal cross-linking of the studied copolymers. On cooling to 480 K and reheating heat capacity, curves for all studied polymers are not reproduced. In the interval from  $T \rightarrow 0$  to 380 K standard thermodynamic functions (enthalpy, entropy, and Gibbs energy of heating) were calculated. All obtained values are reference data and can be used in the calculation of the thermodynamic parameters of the synthesis of these polymers.

*This work was financially supported by the Ministry of Education and Science of the Russian Federation (task No. 2014/134) and by the Russian Foundation for Basic Research (Project No. 15-03-02112).*



**Figure 1:** The structure of the studied polymers.



**Figure 2:** Heat capacity of poly-(phenylene-pyridil) polymer over the range (6–380) K.

## Section 2. Thermodynamics of individual chemical compounds

### CALORIMETRIC STUDY OF THE COPOLYMER OF CARBON MONOXIDE–ETHYLENE–BUTENE-1 OVER THE RANGE FROM $T \rightarrow 0$ TO 500 K

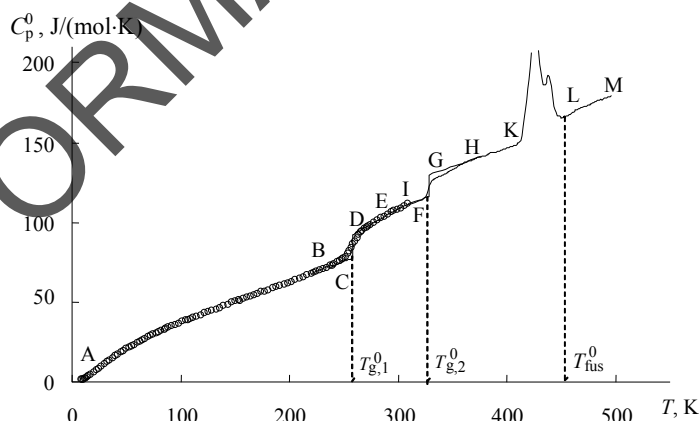
P.D. Aphonin<sup>1</sup>, N.N. Smirnova<sup>1</sup>, A.V. Markin<sup>1</sup>, L.Ya. Tsvetkova<sup>1</sup>, O.N. Golodkov<sup>2</sup>, G.P. Belov<sup>2</sup>

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Aliphatic polyketones are class of new functional materials, which obtained by the polymerization of olefins and carbon monoxide on a palladium catalyst. These polymers have a row of valuable properties: mechanical strength, chemical resistance, good barrier properties, that allows to use them in electrical engineering, medicine and instrumentation. One of representatives of such materials is copolymers of carbon monoxide with ethylene and different olefins. In this work, the sample of alternating terpolymer of carbon monoxide with ethene and butene-1 with the mole fraction of 14.6% butane fragments was investigated. The structure and composition of the copolymer were characterized by NMR techniques, IR spectroscopy and elemental analysis. It was concluded from X-ray analysis and obtained calorimetric data that the sample was partially crystalline. The thermal stability of the samples was investigated by thermogravimetric method. As the result, it was found that the temperature thermal degradation beginning is 520 K.

The temperature dependence of the heat capacity of copolymer was studied by adiabatic vacuum and differential scanning calorimetry in the range from 6 to 500 K, the thermodynamic parameters of the glassy state (glass transition temperature, the increase of the heat capacity at glass transition, zero and configuration entropies) and thermodynamic characteristics of melting (temperature, enthalpy and entropy of fusion) were determined, the standard thermodynamic functions (enthalpy, entropy and Gibbs energy) were calculated in studied temperature range. The energy of combustion of the copolymer sample was measured in combustion calorimeter B-08 with an error of  $\pm 0.02\%$ , the standard enthalpy of combustion and thermodynamic parameters of formation (enthalpy, entropy and Gibbs energy) were calculated at 298.15 K. The obtained data allowed to calculate thermodynamic parameters of copolymer synthesis (enthalpy, entropy, Gibbs energy of copolymerization) over the range from  $T \rightarrow 0$  to 500 K, on the basis of which it was concluded that the reaction is thermodynamically allowed over studied temperature range.



**Figure:** Heat capacity of copolymer: AB – partially crystalline state, HK – highly elastic, LM – liquid. BE, EH – intervals of devitrification, CD, FG – increases in the heat capacity at  $T_g^0$ , KL – the apparent heat capacity in the range of melting of the crystalline part of the sample.

This study was supported by the Ministry of Education and Science of the Russian Federation (task No. 2014/134).

**THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS  
OF REDOX-ISOMERIC *o*-SEMIQUINONIC COBALT COMPLEXES**

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Redox-isomerism phenomenon is of great interest during last three decades due to possible application in molecular devices. *o*-Semiquinonic complexes of cobalt exhibit a redox-isomerism, i.e. the ability to exist in two forms differing by valent and spin state of metal and ligands. It was shown that the conversion of redox isomers is accompanied by phase transition.

Phase transition of *o*-semiquinonic cobalt complexes with 2,2'-dipyridil (2,2'-bpy)Co(3,6-DBSQ)<sub>2</sub> (1) and 1,10-phenanthroline (1,10-phen)Co(3,6-DBSQ)<sub>2</sub> (2) was quantitatively characterized [1, 2]. Complexes 1 and 2 are isomorphous and form solid solutions one in another with any ratio. Each solid solution reveals phase transition which follows redox-isomeric transformation upon temperature change. Thermodynamic parameters of phase transitions depend on the composition of solid solution. The heat capacity of solid solution (1:1) was studied in the range (7–350) K in an adiabatic vacuum calorimeter and the other ones were investigated by differential scanning calorimetry.

Resulting diagrams “transition temperature – composition”, “enthalpy – composition” allow us to evaluate the reciprocal influence of isomorphous lattices belonging to different redox-isomeric complexes.

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## Section 2. Thermodynamics of individual chemical compounds

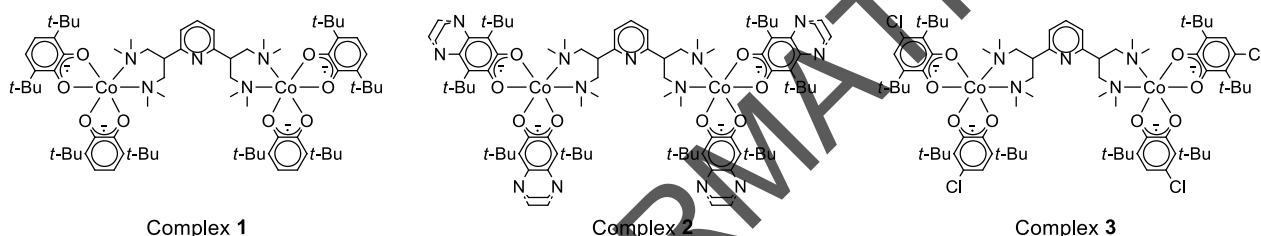
### THERMODYNAMICS OF NOVEL DINUCLEAR REDOX-ISOMERIC COMPLEXES WITH A TETRAPODAL PYRIDINE-BASED LIGAND

A.A. Zolotukhin<sup>1</sup>, A.V. Arapova<sup>1</sup>, M.P. Bubnov<sup>1,2</sup>, N.N. Smirnova<sup>2</sup>,  
N.A. Skorodumova<sup>1</sup> and G.A. Abakumov<sup>1,2</sup>

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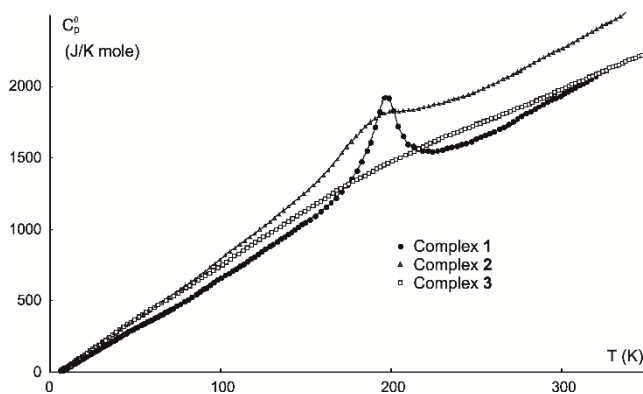
Three novel dinuclear cobalt compounds of general formula (OMP)[CoQ<sub>2</sub>]<sub>2</sub>, where OMP = 2,2'-(pyridine-2,6-di-yl)bis(N<sup>1</sup>,N<sup>1</sup>,N<sup>3</sup>,N<sup>3</sup>-tetramethylpropane-1,3-diamine), Q = mono- or dianion of 3,6-di-tert-butyl-*o*-benzoquinone (complex 1) and its derivatives: 3,6-di-tert-butyl-4,5-N,N'-piperazino-*o*-benzoquinone (complex 2), 3,6-di-tert-butyl-4-Cl-*o*-benzoquinone (complex 3)



were studied calorimetrically. Their heat capacities ( $C_p^0$ ) were obtained over the range 7–330(350) K in the adiabatic vacuum calorimeter with an uncertainty, mainly, of 0.2%. The experimental results of EPR and magnetochemical investigations show that complexes 1–3 in the solid state undergo thermally driven redox-isomeric transformations, which is accompanied by phase transition [1] (Figure).

Thermodynamic parameters of phase transitions of complexes 1–3 were determined.

Thermodynamic functions: enthalpy, entropy and Gibbs energy were calculated from the experimental data in the temperature range from  $T \rightarrow 0$  to  $T = 330(350)$  K.



**Figure:** The heat capacity of studied complexes.

[1] Bubnov, M.P.; Skorodumova, N.A.; Zolotukhin, A.A.; et al. *Z. Anorg. Allg. Chem.*, 2014, 640, 11, 2177-2182.

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### THERMOPHYSICAL PROPERTIES (HEAT CAPACITY, THERMAL EXPANSION, THERMAL CONDUCTIVITY) OF THE FRAMEWORK STRUCTURE PHOSPHATES

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The compounds of kosnarite  $\text{KZr}_2(\text{PO}_4)_3$  type structure (also known as  $\text{NaZr}_2(\text{PO}_4)_3$ , NZP, NASICON) and related types have been widely investigated since their discovery for practical applications as low thermal expansion materials, solid electrolytes for battery materials and sensors, ceramic forms for nuclear waste immobilization, catalysts, luminescent materials and some others [1]. The kosnarite compound variety can be achieved based on the general crystal-chemical formula  $[\text{M1}][\text{M2}]_3\{\text{L}_2(\text{PO}_4)_3\}_{3\infty}$ , where M1 and M2 – cavity cations, L – framework-forming cations. In the present study, the thermophysical properties (heat capacity, thermal expansion, thermal conductivity) data for the crystalline kosnarite-type structure compounds  $\text{A}_x\text{D}_{2.25-0.25x}(\text{PO}_4)_3$  (A – alkali metal; D – Ti, Zr, Hf;  $x = 0, 1$  and 5) and  $\text{M}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  (M – alkali-earth metal) are reported.

The samples were synthesized by the sol-gel method and characterized by means of X-ray diffraction, IR-spectroscopy, electron microprobe and chemical analysis.

The heat capacities of the phosphates were measured using adiabatic and differential scanning calorimetry in the temperature range (6–650) K. Solid-to-solid phase transitions of  $\text{LiZr}_2(\text{PO}_4)_3$ ,  $\text{Na}_5\text{Zr}(\text{PO}_4)_3$  and  $\text{Na}_5\text{Hf}(\text{PO}_4)_3$  were found. The transition functions (temperatures, enthalpies and entropies), molar heat capacities, enthalpies  $[H^0(T) - H^0(0)]$ , entropies  $S^0(T)$  and Gibbs energies  $[G^0(T) - H^0(0)]$  were calculated. The standard entropies of formation at 298.15 K were estimated. From the solution reaction calorimetry, the standard enthalpies of formation of  $\text{Zr}_3(\text{PO}_4)_4$ ,  $\text{NaZr}_2(\text{PO}_4)_3$ ,  $\text{CsZr}_2(\text{PO}_4)_3$  and  $\text{Na}_5\text{Zr}(\text{PO}_4)_3$  were derived. By combining these data, their Gibbs energies of formation at 298.15 K were obtained. Thermodynamic functions of the compounds solid-state synthesis reactions were calculated.

To predict application areas for the ceramics and improve their production technologies, one has to know the rate of temperature change in the product under heat treatment or during service, i.e., its thermal conductivity. So the temperature dependences of the thermal conductivity of the studied ceramic samples of different porosity were experimentally obtained. For low-density materials the thermal conductivity with zero porosity were estimated. The calculated values were in the interval (0.4–1.1) W/(m·K) at the temperatures (298–673) K. These results agree with the data on the thermal conductivity of high-density kosnarite type ceramics.

As the thermal expansion is the most characteristic property of the compound, which depends on the distribution of the chemical bonds forces, the compounds  $\text{AD}_2(\text{PO}_4)_3$  ( $x = 1$ ) and  $\text{M}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  were characterized by high-temperature X-ray diffraction in the region (298–1073) K. The obtained results were combined with the literature data and varying of  $\text{A}^+$  cations radii was used to predict and obtain the material with near zero thermal expansion anisotropy [1]. Considering the results of our framework phosphates study and taking into account the known crystal-chemical data, we can predict the developing new kosnarite-based ceramics, which are characterized by thermal shock resistance and the required level of thermophysical parameters.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMODYNAMIC PROPERTIES OF $\text{Ba}_{1.5}\text{Fe}_2(\text{PO}_4)_3$ AND $\text{Rb}_2\text{FeTi}(\text{PO}_4)_3$ – THE REPRESENTATIVES OF THE LANGBEINITE TYPE PHOSPHATES

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Double and triple phosphates, containing IV group d-elements, are of interest for the purpose of creating new practically useful materials. Some of these substances are considered as hi-tech ceramics basis due to their stability to the extreme environmental conditions (high temperature and pressure, aggressive media, radiation), near-zero thermal expansion parameters and etc. Such compounds are usually characterized by framework structures with  $\{[\text{L}_2(\text{PO}_4)_3]^{2-}\}_x$  frameworks (L are octahedrally coordinated cations). Among them, the structural type of  $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$  (langbeinite) is well-known.

The langbeinite structure is typical of the phosphates, containing large cations (more than 1.5 Å) with low oxidation degrees (+1 and +2) in the cavity sites. Nowadays, there are many scientific works, devoted to synthesis and structural study of langbeinite type phosphates. And yet, despite this fact, the thermodynamic properties of the langbeinite structure phosphates have not been investigated. In the present study the results of thermodynamic investigation of two representatives of this structural family –  $\text{Ba}_{1.5}\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Rb}_2\text{FeTi}(\text{PO}_4)_3$  – are presented.

The compounds were synthesized by precipitating method, starting from the aqueous solutions of  $\text{RbCl}$ ,  $\text{BaCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{TiOCl}_2$  and  $\text{H}_3\text{PO}_4$ . The obtained samples were polycrystalline powders of brown color. The formation of the desired compounds was confirmed on a Shimadzu XRD-6000 diffractometer. The amorphous impurities absence was shown by IR spectra of the samples, which were recorded on an IR-Fourier-spectrometer FSM-1201. The homogeneity and chemical composition of the samples were checked by electron microprobe analysis on a JSM-7600F Schottky Field Emission Scanning Electron Microscope (JEOL) equipped with microanalysis system. The results of electron microprobe analysis have shown that the samples are homogeneous and their compositions are close to the theoretical values calculated for the formulas  $\text{Ba}_{1.5}\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Rb}_2\text{FeTi}(\text{PO}_4)_3$ . A precision automatic adiabatic calorimeter (BCT-3) was used to measure heat capacities over the temperature range (6–350) K. A differential scanning calorimeter DSC 204 F1 Phoenix was used to measure the heat capacities over the temperature range (330–650) K.

Phase transitions, connected with magnetic contribution of heat capacity, were observed for both compounds at temperatures  $T < 12$  K. Except for this region, the heat capacities of the phosphates  $\text{Ba}_{1.5}\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Rb}_2\text{FeTi}(\text{PO}_4)_3$  raised gradually with increasing temperature. The experimental points of  $C_p^0$  at  $T > 12$  K were fitted by means of the least-squares method using power and semilogarithmic polynomial dependences. The phosphate heat capacities at high temperatures were estimated as  $C_p^0 \rightarrow 3Rm$ , where  $R$  is the gas constant,  $m$  is the number of atoms in the formulae unit. The calculated values were 461 and 474 J/(mol·K) for  $\text{Ba}_{1.5}\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Rb}_2\text{FeTi}(\text{PO}_4)_3$ , respectively. Experimental  $C_p^0$  points for the studied phosphates at high temperatures were close to the above values. The experimental data were used to calculate the standard thermodynamic functions:  $C_p^0$ ,  $H^0(T) - H^0(0)$ ,  $S^0(T)$  and  $G^0(T) - H^0(0)$ . Standard entropies of formation at 298.15 K were estimated for the phosphates.

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## INVESTIGATION OF PHASE TRANSITIONS AND THERMODYNAMIC PROPERTIES OF $\text{Ag}_8\text{B}^{\text{IV}}\text{X}_6$ ( $\text{B}^{\text{IV}} - \text{Ge, Sn, X-S, Se}$ ) BY EMF AND DSC METHODS

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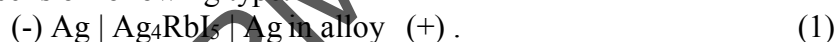
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The compounds of the general formula  $\text{Ag}_8\text{B}^{\text{IV}}\text{X}_6$  ( $\text{B}^{\text{IV}} - \text{Ge, Sn; X-S, Se}$ ) possess ionic conductivity and are prospective materials for photoelectrodes, electrochemical converters of solar energy, ionselective sensors, photoelectro-chemical imaging etc. The existence of a low-temperature phase transition is typical for these phases; the high-temperature modifications crystallize in the cubic structure and possess high ionic conductivity of  $\text{Ag}^+$  ions [1, 2]. In the given work, the results of thermodynamic studies of both modification of  $\text{Ag}_8\text{B}^{\text{IV}}\text{X}_6$  and their transformations are present.

The  $\text{Ag}_8\text{B}^{\text{IV}}\text{X}_6$  compounds were synthesized from high-purity elements (at least 99.999 mass% purity). The mixtures were placed into quartz ampoules, being evacuated to  $\sim 10^{-2}$  Pa and fused. Synthesis was carried out in a two-zone furnace.

The investigations were carried out by using DSC (NETZSCH 404 F1 Pegasus system) and EMF measurements of the reversible cells of following type:



In the cell (1), the solid-state superionic conductor  $\text{Ag}_4\text{RbI}_5$  was used as the electrolyte, while equilibrium alloys of the systems  $\text{Ag-B}^{\text{IV}}\text{-X}$  were served as right electrodes. Right electrode compositions were selected based on the phase diagram.

EMF measurements were done by the compensation method in the temperature range of (290–390) K (sulphides) or (290–430) K (selenides) with the accuracy of  $\pm 0.1$  mV using the high-resistance universal B7-34A digital voltmeter. The assembly of an electrochemical cell and measurements are described in detail elsewhere [3].

At first, the EMF measurements were carried out in the temperature interval of existence of the low-temperature modification of each compound, and then in the range of existence of its high-temperature one.

From the EMF measurements, the partial molar functions of silver in alloys were calculated.

Based on constructed solid state phase equilibria diagrams potential-forming reactions for ternary compounds are found, from which thermodynamic functions of formation and entropies of both modifications of  $\text{Ag}_8\text{B}^{\text{IV}}\text{X}_6$  compounds were calculated. Corresponding thermodynamic data for germanium and tin chalcogenides have been used in the calculations.

The heats of polymorph transitions were calculated using respective thermodynamic functions of both modifications of  $\text{Ag}_8\text{B}^{\text{IV}}\text{X}_6$  compounds while the entropies of polymorph transitions – using the formula  $\Delta S_{\text{p.t.}} = \Delta H_{\text{p.t.}} / T_{\text{p.t.}}$

Thermodynamic functions of polymorph transformations of the above mentioned compounds also were determined by DSC, having higher accuracy. Obtained by both methods dates were in agreement within experimental error.

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## Section 2. Thermodynamics of individual chemical compounds

### SYSTEMATIC ANALYSIS OF ENTHALPY OF THE ACTINIDE OXIDES FORMATION

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Available literature data on the formation enthalpy ( $\Delta_f H_{298}^0$ ) of actinide oxides ( $An_xO_y$ ) are incomplete and fragmentary. Values of  $\Delta_f H_{298}^0$  AnO for Th, U, Np, Pu and Am, also some oxides of actinides (+3), (+4) are known [1–3].

This work is devoted to obtaining more complete information about  $\Delta_f H_{298}^0$   $An_xO_y$ . The calculation was performed by semiempirical method of Poluektov N.S. by this formula

$$\Delta_f H_{298, M'_x O_y}^0 = \Delta_f H_{298, M''_x O_y}^0 + \alpha N_f + \beta S + \gamma' (L_A) (\gamma'' (L_B)),$$

which takes into account the number of f-electrons, S and L - values of spin- and orbital angular momentum of the An ions basic condition motion. Coefficients  $\alpha$ ,  $\beta$ ,  $\gamma'$  and  $\gamma''$  determine the contribution of each of the components in the value of the enthalpy of formation of oxides. By the method of differences of Kireyev V.A. we evaluated the enthalpy of formation of reference compounds of Ac, Cm and Lr, needed for calculation by semi-empirical method. The calculation was made by the formula  $\Delta(\Delta_f H_{298}) = \Delta_f H_{(An_2O_3)} - \Delta_f H_{(AnO_2)} = 450$ . Results of calculations are shown in Table.

**Table.** The enthalpy of formation of oxides of actinides

An	$-\Delta_f H_{298}^0$ , kJ/mol		(a – literature, b – calculation)			
	AnO		An <sub>2</sub> O <sub>3</sub>		AnO <sub>2</sub>	
	(a)	(b)	(a)	(b)	(a)	(b)
Ac	168	168	1756	1756	-	1306
Th	-47	225	-	1660	1226	1205
Pa	30	258	-	1592	1109	1133
U	81	282	1456	1552	1085	1092
Np	174	296	1522	1542	1074	1081
Pu	329	302	1656	1560	1056	1101
Am	398	384	1690	1650	932	1214
Cm	270	270	1682	1682	911	1232
Bk	354	385	1694	1674	1021	1006
Cf	461	457	1653	1672	858	859
Es	496	500	1696	1677	763	792
Fm	512	513	1694	1689	-	804
Md	528	497	1595	1708	-	895
No	548	550	1260	1660	-	1210
Lr	363	363	1766	1766	-	1316

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THE ENERGY OF THE CRYSTAL LATTICE OF BORO- AND ALUMINUM HYDRIDE OF LANTHANIDES

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The obtained data about thermodynamic characteristics of the lanthanides borohydrides (Ln) [1, 2] allowed us to calculate the energy of the crystal lattice ( $U$ ) and set the regularities in the changes of the thermodynamic characteristics of the entire series borogid-borides by the nature of the lanthanide (Ln).

In this research work we present the values of U boro- and aluminum hydride of lanthanide - calculated by Born-Haber cycle (1), according to the equation of A.F. Kapustinskiy (2)

$$U = \frac{1200.5 \cdot V \cdot Z_k \cdot Z_a}{r_k + r_a} \left[ 1 - \frac{0.345}{r_k + r_a} + 0.00435 (r_k + r_a) \right],$$

where  $V$  – number of ions in one formula unit,  $Z$  – charge of the cation and anion, and  $r$  – their radius. Radius of the  $\text{Ln}^{3+}$  cations with coordination number 8 was used, which is typical for these compounds. It was used as semi-empirical method of N.S. Poluektov (3). The results are shown in the Table.

**Table.** Energy of the crystal lattice of complex lanthanides hydrides, kJ/mol

Ln(EH <sub>4</sub> ) <sub>3</sub> E–B, Al	Ln(BH <sub>4</sub> ) <sub>3</sub>			Ln(AlH <sub>4</sub> ) <sub>3</sub>
	Calculation Method			Calculation
	(1)	(2)	(3)	(2)
La	3664.1	3811.09	3664.1	3406.5
Ce	3747.5	3788.56	3751.6	3422.0
Pr	3794.4	3840.22	3814.3	3437.6
Nd	3843.9	3850.02	3845.2	3445.4
Pm	3840.0	3879.75	3866.5	3453.3
Sm	3849.6	3889.76	3871.5	3461.2
Eu	3905.1	3899.82	3901.5	3469.2
Gd	3811.1	3920.10	3811.1	3477.2
Tb	3875.0	3930.32	3883.0	3493.3
Dy	3913.3	3940.59	3923.9	3501.4
Ho	3947.5	3950.92	3957.7	3509.5
Er	3971.4	3971.73	3984.5	3517.7
Tm	3996.2	3982.22	4004.3	3525.9
Yb	4047.8	3982.22	4057.0	3437.6
Lu	3998.8	4003.37	3998.8	3542.5

By the method of differences of Kireyev we assess the unknown value of  $r_{(\text{AlH}_4)^-} = 0.29$  nm.

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## Section 2. Thermodynamics of individual chemical compounds

### MOLECULAR DYNAMICS INVESTIGATION OF STABILITY AND NUCLEATION IN A STRETCHED (SUPERHEATED) FCC CRYSTAL

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The molecular dynamics method has been used to investigate the thermodynamic and the mechanical stability of a Lennard-Jones crystal, and also nucleation in a crystal of the liquid and gas phases. Calculations have been made in the  $NVE$  ensemble in systems containing from  $N = 2048$  to 500 000 particles at reduced temperatures  $T^* = k_B T/\epsilon = 0.3; 0.4; 0.55; 0.7; 0.85$ , the first four of which refer to the region of negative pressures. Here  $k_B$  is the Boltzman constant,  $\epsilon$  is the potential parameter. The thermal and caloric equations of state for a Lennard-Jones crystal have been built up by the results of calculation of pressure and internal energy. The spinodal of a superheated crystal has been determined from the condition  $(\partial p/\partial \rho)_T = 0$ . At temperatures  $T^* > 0.55$  limiting stretches of the crystal phase achieved in computer experiments were smaller than spinodal ones. At lower temperatures in the process of an isothermal crystal stretch one could observe a transition through the spinodal on retention of the initial crystal structure (the FCC lattice). The crystal phase stretched to such a state for a finite time remained stable with respect to infinitesimal perturbations.

The tensors of isothermal moduli of elasticity and isothermal moduli of elastic rigidity have been calculated. Calculations were made in the region of positive and negative pressures. The contributions of attractive and repulsive forces to the virial have been determined at  $T = 0$ . The variable character of the density dependence of these contributions has been shown, which leads to the appearance of a pressure minimum point on the isotherm. For  $T = 0$  this point, the spinodal point, corresponds to the reduced density  $\rho^*_{\min} = \rho \sigma^3 = 0.845$ . Here the zero value is taken by the bulk modulus of elastic rigidity. The shear modulus becomes zero at a lower density  $\rho^* = 0.649$ . In investigating nucleation it has been found that at  $T^* \geq 0.55$  a decomposition of the crystal order begins with the formation of a liquid-phase nucleus and is accompanied by a decrease in the temperature and an increase in the pressure. At  $T^* < 0.55$  cavitation (discontinuity) took place in the system. The appearance of a cavity resulted in increasing temperature and pressure in the system.

At  $T^* > 0.4$  a decomposition of the regular structure was observed in the region of states with the derivative  $(\partial p/\partial \rho)_T > 0$ , and at lower temperatures, close to the density where  $(\partial p/\partial \rho)_T = 0$  and in the region where  $(\partial p/\partial \rho)_T < 0$ . In all cases the crystal decomposition proceeded by the activation mechanism, through the nucleation and growth of a competitive phase. Nuclei of the liquid and gas phases had a form close to spherical.

The method of metastable-phase lifetime measurement has been used to obtain the density dependence of the nucleation rate in a superheated (stretched) crystal. The problems of describing the nucleation kinetics in a stretched crystal in the framework of classical nucleation theory are discussed. The characteristic dimensions of critical nuclei of liquid and gas phases have been calculated.

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NEW THERMODYNAMIC DATA FOR  $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{4-\delta}$ 

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The lanthanum barium cuprate  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-\delta}$  with  $\text{K}_2\text{NiF}_4$  structure is known as the first high-temperature superconductor. The barium has a high ability for carbonate contamination that can influence on sample properties. The introduction of carbonates in the crystal structure may take place from start reagents or atmosphere air.

In order to avoid the carbon contamination the special precautions were taken in solid-state preparation of  $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{4-\delta}$ . The starting reagents  $\text{CuO}$ ,  $\text{La}_2\text{O}_3$ ,  $\text{BaO}_2$  with purity degree of more than 99.99% (metals basis) were ground in an agate ball mill and heated at  $1150^\circ\text{C}$  for 24 h with subsequent thermal treatment in oxygen flow at  $600^\circ\text{C}$  for 24 hours. For comparison the synthesis was repeated in the same condition using  $\text{BaCO}_3$  instead  $\text{BaO}_2$  as in [1]. In both cases the single phase samples were obtained differ in  $c$  cell parameters, but according to FTIR study the introducing of carbonate groups in crystal lattice may take place when  $\text{BaCO}_3$  was used. The use of pure  $\text{BaO}_2$  allowed obtaining the  $\text{La}_{1.8}\text{Ba}_{0.2}\text{Cu}_{3.91}$  sample without carbon contamination.

The measurements of the reaction heat of  $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{4-\delta}$  with 1 M HCl were performed at 298.15 K in a sealed swinging calorimeter with an isothermal jacket. The powdered substances (0.05–0.1 g) were placed in glass ampoules and sealed, weighted with accuracy  $\pm 0.00002$  g and placed into titanium calorimetric vessel ( $V = 112 \text{ cm}^3$ ), filled with  $80.000 \pm 0.003$  g of 1 M hydrochloric acid, and then hermetically closed. The rise of temperature in the experiments was measured by a platinum resistance thermometer. The energy equivalent was determined electrically by potentiometric circuit.

**Table.** The enthalpies of  $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{4-\delta}$  formation from oxides [ $\Delta_{\text{ox}}H^\circ(298)$ ] and elements [ $\Delta_f H^\circ(298)$ ]

Compound	$-\Delta_{\text{ox}}H^\circ(298)$ (kJ/mol)	$-\Delta_f H^\circ(298)$ (kJ/mol)	Cell parameters (Å)		Remarks
			$a$	$b$	
$\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{3.91}$	$50.5 \pm 2.5$	$1929.6 \pm 3.2$	3.79520(4)	13.3441(2)	from $\text{BaO}_2$
$\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{3.91}$	$36.4 \pm 2.7$	$1915.5 \pm 3.4$	3.79550(4)	13.3574(2)	from $\text{BaCO}_3$
$\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{3.976}$	$35.0 \pm 1.6$	$1917.3 \pm 1.6$	–	–	[1]

The enthalpy of  $\text{La}_{1.8}\text{Ba}_{0.2}\text{Cu}_{3.91}$  formation obtained from  $\text{BaO}_2$  is differ from known reference data (Table) almost on 14 kJ/mol, while the enthalpy of carbonate contaminated sample formation is close to them. So, the carbonate contamination, which undetectable by X-ray study, may significantly influences on thermodynamic properties of barium-containing compounds.

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## Section 2. Thermodynamics of individual chemical compounds

### LOW-TEMPERATURE THERMODYNAMIC PROPERTIES OF Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>

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Bis(2,4-pentanedionato)platinum, Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>, belongs to the class of beta-diketonates of metals. Beta-diketonates platinum are used as precursors to the modern technologies for production of functional materials (nanoparticles, thin films, alloys, etc.), which are important for electronics, catalysis and medicine. For optimization of processes requires detailed information on the various physicochemical properties of precursors, including the thermodynamic properties.

The results of experimental research of heat capacity of bis(2,4-pentanedionato)platinum in the temperature range from 6 to 310 K are presented in this work. The data obtained were used to calculate its thermodynamic functions (entropy, enthalpy, reduced Gibbs energy).

A sample of Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> at room temperature is a yellow crystalline powder with a typical crystallite size of ~ 0.2 mm. The melting temperature of the produced sample determined on a Kofler bench is ~513 K which agrees with the data presented in [1]. The chemical analysis of the refined compound showed its composition for C and H corresponds to the calculated one within the accuracy of the analysis (C, H – 0.2%). According to the X-ray phase analysis, the compound is singlephase; the structure of the obtained crystals corresponds to the Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> structure determined in the paper [2].

The heat capacity  $C_{p,m}(T)$  of the sample Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> was measured in the range (6–310) K by the adiabatic method on the installation described in reference [3]. A sample of 4.7595 g was loaded into the calorimetric ampoule. The molar mass used in the calculation of the molar heat capacity was determined from the formula Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> as 393.299 g·mol<sup>-1</sup>. The analysis of the functional dependence of the heat capacity has not revealed any thermal anomaly in its behavior. The smoothed  $C_{p,m}(T)$  dependence over the temperature range 6–310 K was used to calculate the thermodynamic functions, including entropy  $\Delta_0^T S_m^\circ$ , enthalpy  $\Delta_0^T H_m^\circ$ , and reduced Gibbs energy  $\Phi_m^\circ(T)$ . The values of these functions at the reference temperature 298.15 K are:  $C_p^\circ = (292.8 \pm 0.5) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $\Delta_0^{298.15} S_m^\circ = (361.4 \pm 0.9) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $\Delta_0^{298.15} H_m^\circ = (51.35 \pm 0.09) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Phi_m^\circ = (189.2 \pm 0.7) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The uncertainties are due to measurement errors and the account of extrapolation of heat capacity to 0 K.

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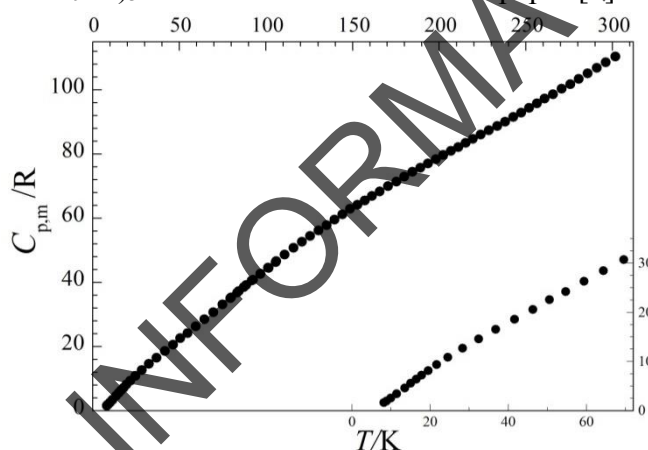
LOW-TEMPERATURE HEAT CAPACITY OF  $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ 

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Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) cobalt,  $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ , belongs to the class of beta-diketonates of metals. Cobalt beta-diketonates are widely used as precursors for chemical vapor deposition of different coatings and films at moderate temperatures. Presented in this work are the results of the experimental research on the heat capacity of  $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  in the temperature range of (8 to 300) K.

Synthesized sample  $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  is a crystalline powder of dark-green color with an average crystallite size  $\sim 0.2$  mm. The chemical analysis of the refined compound showed its composition for C and H corresponds to the calculated one within the accuracy of the analysis. According to the X-ray phase analysis, the compound is singlephase; the structure of the obtained crystals corresponds to the  $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  structure determined in the paper [1].



**Figure:** Experimental heat capacity for  $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  in the range of (8–300) K

The heat capacity  $C_{p,m}(T)$  of the sample  $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  was measured by the adiabatic method on the installation described in reference [2]. The measurement results of standard substance (benzoic acid) heat capacity which characterize a systematic error deviate from the standard data by less than 1% in the range of (5–20) K, less than 0.3% in the range of (20–80) K, and less than 0.15% in the range of (80–300) K. A sample of 4.1161 g was loaded into the calorimetric ampoule. The molar mass used in the calculation of the molar heat capacity was determined from the formula  $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  as  $608.72 \text{ g}\cdot\text{mol}^{-1}$ . The heat capacity has been measured at 78 points in the range (8–300) K. The obtained data are presented in Figure.

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## Section 2. Thermodynamics of individual chemical compounds

### FRACTAL DIMENSIONS OF MIXED LANTHANUM AND ALKALI-EARTH TUNGSTATES

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A fractal model for describing the heat capacity of solids at low temperatures, based on the Debye model, is more precise and demonstrates good applicability for determining structural and dimensional parameters of various natural and inorganic compounds. This approach has been used in the present work for the samples previously synthesized by the method "sol-gel" from the systems of ternary oxides based on lanthanum and tungsten with general formula of  $MeLa_2WO_7$ , where Me is Mg, Ca, Sr, Ba.

The calculation of fractal dimension  $D$  over the range of (5–300) K has been made based on the smoothed values of the heat capacity experimental data obtained by low-temperature adiabatic calorimetry over the range of (4.2–300) K and the generalized equation for these compounds. The numerical method of successive iterations was used when solving the equation. The fixed values of the Debye temperature with increments of 100 K and in some cases 50 K were set to determine the nature of the change of fractal dimension depending on the temperature in the initial equation.

As a result, the sets of values of the fractal dimension of the studied mixed lanthanum tungstates and alkaline earth elements have been obtained. The obtained dependences after extrapolation to absolute zero have a tendency to converge at a point corresponding to the value of the fractal dimension of the given compound. For  $MgLa_2WO_7$  these curves show the convergence at the value of the fractal dimension close to  $D = 3$ , which bears witness to the presence of a three-dimensional-ordered structure and agrees with the data on indexing, indicating the cubic system with the space group of symmetry  $I2_13$ . In the sample of  $CaLa_2WO_7$  the curves of fractal dimension converge at the value of  $D = 3-3.5$ , indicating the presence of an additional contribution to the heat capacity at low temperatures, along with three-dimensional dynamics of the space group  $P2_1/n$ . The sample of  $SrLa_2WO_7$  shows convergence at  $D = 2$ , which bears witness to predominantly two-dimensional type of the crystal lattice dynamics.

Beyond that, at 13 K, a notable peak is observed in fractal dimension curves of this sample which indicates a change of mode of the crystal structure dynamics at this temperature. For the sample of  $BaLa_2WO_7$  the calculations also showed the value of fractal dimension close to 2. In this case there is a flat wide peak in the range of (100–200) K, indicating a change in the dynamics of the sample in the field of liquid nitrogen. The indexing of the two samples has showed the same space group of symmetry  $P112_1/b$ , which coincides with the experimental data previously obtained [1, 2].

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LOW-TEMPERATURE HEAT CAPACITY OF TUNGSTATES OF LANTHANUM  
AND ALKALI-EARTH METALS  $MeLa_2WO_7$

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The systems of oxides based on rare earth elements and transition metals with alkaline earth elements have a number of interesting properties and are widely used in various branches of modern industry. This work presents the results of calorimetric studies of thermodynamic properties of the compounds from ternary oxide systems of lanthanum and tungsten with general formula  $MeLa_2WO_7$ , where Me is Mg, Ca, Sr and Ba. Synthesis of the samples was carried out by the "sol-gel" method using oxides and salts of the brand "chemically pure". Starting materials taken in stoichiometric amounts were dissolved with citric acid and evaporated to obtain citrate precursors which were exposed to a stagewise high temperature annealing with the final stage at 1150°C. The formation of new phases was controlled by the X-ray diffraction. The results of indexing of diffraction patterns of the samples showed the best agreement with space groups of symmetry:  $MgLa_2WO_7 - I2_13$ ,  $CaLa_2WO_7 - P2_1/n$ ,  $SrLa_2WO_7$  and  $BaLa_2WO_7 - P112_1/b$ . The results of two last samples are in agreement with the crystallographic data obtained by other authors [1, 2].

The low-temperature heat capacity of the studied compounds was measured over the temperature range of (4.2–320) K by adiabatic calorimetry on installation of the company «Termax» (Moscow, Russia) [3]. The weighted portions of about (1–1.5) g were placed in a titanium container (1 cm<sup>3</sup>), which then was filled with the heat exchange gas helium and sealed with indium foil. The measured dependences of the heat capacity of the samples over the range from temperature of liquid helium to room temperature showed no deviations from the normal course of the curve. The experimental data were processed by the spline-approximation method. The values of the coefficients of polynomials of the third degree have been obtained and thermodynamic functions of the substances have been calculated over the range of (5–320) K. The values obtained at 298.15 K are given in Table.

**Table.** Heat capacity and related thermodynamic functions of the samples

Compound	$C_p^\circ(298)$ (J/(mol·K))	$S^\circ(298)$ (J/(mol·K))	$\Delta H^\circ(298)$ (kJ/mol)	$\Phi^\circ(298)$ (J/(mol·K))
$MgLa_2WO_7$	233.25±0.25	252.79±1.25	40.302±0.015	117.61±1.02
$CaLa_2WO_7$	224.23±0.24	245.59±0.66	39.074±0.007	114.53±0.52
$SrLa_2WO_7$	222.97±0.24	254.13±1.23	39.566±0.016	121.43±1.08
$BaLa_2WO_7$	277.82±0.30	313.91±1.60	49.186±0.020	148.94±1.36

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## Section 2. Thermodynamics of individual chemical compounds

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### LOW-TEMPERATURE HEAT CAPACITY OF SILICATE APATITE $\text{SrPr}_4(\text{SiO}_4)_3\text{O}$

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Oxide ion conductors have been extensively studied due to their wide applications in solid oxide fuel cells (SOFCs), which is a critical technology that could help to solve current energy supply demand and environmental pollution problems.

Recently, a class of these conductors, apatite-type rare earth silicates, has attracted increasing attention. It has been found to have the low activation energy in the ionic conduction, and thus it is suitable for an intermediate-temperature (IT) SOFC electrolyte operated in the range of (500–900) °C.

The goal of this work includes calorimetric determination of the temperature dependences of the heat capacity of  $\text{SrPr}_4(\text{SiO}_4)_3\text{O}$  from 6 to 330 K. We also present results of high-temperature X-ray diffraction studies in order to obtain information about properties.

For structural investigations, an X-ray diffraction pattern of samples were recorded on a Shimadzu X-ray diffractometer XRD-6000 in the  $2\theta$  range from  $10^\circ$  to  $120^\circ$  with scan increment of  $0.02^\circ$ . The high-temperature X-ray diffraction was carried out on a Shimadzu X-ray diffractometer XRD-6000 using Sample Heating Attachment HA-1001. To measure the heat capacity of the tested substances in the range from 6 to 336 K a BKT-3.0 automatic precision adiabatic vacuum calorimeter with discrete heating was used.

There was obtained 233 experimental  $C_p$  values in two series of experiments. The experimental data were used to calculate standard thermodynamic functions, namely the heat capacity  $C_p(T)$ , enthalpy  $H^\circ(T) - H^\circ(0)$ , entropy  $S^\circ(T) - S^\circ(0)$ , and Gibbs energy  $-[G^\circ(T) - H^\circ(0)]$  of  $\text{SrPr}_4(\text{SiO}_4)_3\text{O}$ . To calculate the standard thermodynamic functions of  $\text{SrPr}_4(\text{SiO}_4)_3\text{O}$ , its values were extrapolated from the temperature of the measurement beginning at approximately 6 K to 0 K by graphic method. The heat capacity of this substance in interval from 6 to 350 K gradually increases with rising temperature and does not show any peculiarities.

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### THERMODYNAMIC SUBLIMATION OF ANTITUBERCULAR DRUGS: PYRAZINAMIDE AND HYDRAZIDES ISONICOTINIC ACID

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The hydrazides of carbonic acids are widely used in science, engineering and medicine. The antituberculous action of isonicotinic hydrazide and its derivatives as first-line drugs is of special importance. Hydrazides structural modification in order to generate new biologically active substances is a current trend of ongoing scientific research. The antituberculous drug compounds: pyrazinamide, isoniazid, salinazid, and vanilin isoniazid were investigated. The saturated vapor pressures of these nitrogen-containing cyclic hydrocarbons were measured using the transpiration method within the temperature range (358–410) K. The temperatures and molar fusion enthalpies were derived using a differential scanning calorimeter. The standard molar enthalpies, entropies and Gibbs energies of sublimation at 298.15 K were calculated.

Essential differences between the saturated vapor pressures of pyrazinamide and isoniazide have been revealed, whereas salinazide and vanilin isoniazid had close vapor pressures values. From the sublimation enthalpies of the studied compounds it can be assumed that the presence of large substituents in the molecular structures of salinazid and vaniline isoniazid should cause a decrease in the molecular package density and, as a consequence, a reduction of van-der-waals interactions. Nevertheless, an increase in the molecular weight of the studied isonicotinic acid derivatives makes the substance crystal lattice energies more stable. And the electron-seeking methoxy-group substantially increases the crystal lattice energy. This may be caused by the formation of dimeric structures of vanillin isoniazide molecules in the crystal. The analysis of the thermodynamic functions shows a linear correlation between the sublimation and vaporization enthalpies of the studied substances. The observed linearity indicates that during the fusion process the flexibility of the molecules increases when the chemical nature of the intermolecular interactions is constant.

The HYBOT descriptors for the biologically active compounds were calculated. It was shown that a sublimation Gibbs energy growth is observed when the polarizability and hydrogen bonding ability of the studied compounds molecules increases.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMODYNAMIC PROPERTIES OF STACKED-CUP MULTIWALL CARBON NANOTUBES

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This work presents the results of the investigation of physico-chemical properties for stacked-cup multiwall carbon nanotubes (MCNT) supplied by Vision Development (Japan) and synthesized by the gas-phase catalytic pyrolysis of hydrocarbons according to the method [1]. It was shown in [2] that the apparent density of MCNT ( $2210 \pm 22$ )  $\text{kg}\cdot\text{m}^{-3}$  at  $T = 293$  K determined in water, toluene, and  $[\text{C}_4\text{mim}]\text{PF}_6$  and the distance between the layers of 0.36 nm are close to the corresponding values for hexagonal graphite being  $2260 \text{ kg}\cdot\text{m}^{-3}$  and 0.3635 nm, respectively.

The heat capacities of MCNT samples in the temperature range from 5 to 370 K have been measured and their energies of combustion have been determined. The thermodynamic parameters of pure (without encapsulated Ni) MCNT were evaluated. The average energy of combustion for pure MCNT is close to the corresponding value for graphite (Table). The difference between their energies of combustion is only  $\sim 170 \text{ J}\cdot\text{g}^{-1}$ . Thus, we can conclude that MCNT and graphite are similar not only geometrically, but also thermodynamically. From the table, it also follows that graphite and MCNT are much more thermochemically stable (about  $3 \text{ kJ}\cdot\text{g}^{-1}$ ) forms of carbon compared to fullerenes  $\text{C}_{60}$  and  $\text{C}_{70}$ .

**Table.** The energy of combustion for some carbon materials at  $T = 298.15 \text{ K}$

Compound	Graphite	MCNT*	$\text{C}_{60}$	$\text{C}_{70}$
$-\Delta_c u_{298}^\circ (\text{J}\cdot\text{g}^{-1})$	$32764 \pm 4$ [3]	$32595 \pm 13$	$36017 \pm 17$ [4]	$35802 \pm 26$ [4]

\* For pure (without encapsulated Ni) sample.

It was found that the heat capacities of MCNT, graphite and fullerenes  $\text{C}_{60}$  and  $\text{C}_{70}$  per one mole of carbon atoms are consistent within  $\pm 3\%$  in the temperature interval from 300 to 350 K. Taking into account this fact the extrapolation of the heat capacity of MCNT was carried out up to  $T = 2000$  K and thermodynamic properties of nanotubes in the temperature range from 0 to 2000 K were calculated.

Thermodynamic analysis of reactions for the synthesis of graphite and MCNT by pyrolysis of carbon-containing gases ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ) was performed. It was found that:

- hydrogen  $\text{H}_2$  ( $\sim 82 \text{ mol}\cdot\text{kg}^{-1}$ ) and solid graphite and MCNT ( $\sim 65 \text{ mol}\cdot\text{kg}^{-1}$ ) are the main components of the equilibrium mixtures obtained by the pyrolysis of hydrocarbons  $\text{C}_n\text{H}_{2n+2}$  at  $T \geq 1300 \text{ K}$  ( $P = 1 \text{ бар}$ );

- the equilibrium of the reaction  $2\text{CO}_{(\text{gas})} \rightleftharpoons \text{CO}_{2(\text{gas})} + \text{C}_{(\text{graphite})}$  ( $\text{C}_{(\text{MCNT})}$ ) is almost completely shifted to the right side of the equation in the range (298–900) K;

- the synthesis of fullerenes  $\text{C}_{60}$  and  $\text{C}_{70}$  from graphite is thermodynamically possible only through the high temperature ( $T > 3000 \text{ K}$ ) sublimation of carbon.

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## THERMODYNAMIC PROPERTIES OF LANTHANIDE ORTHOPHOSPHATE

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Dimensionality plays an important role in determining the properties of nanomaterials. Nanowires and nanobelts representing a class of one-dimensional (1D) nanostructures are the focus of much attention because of their physical, thermal, thermodynamic properties that are quite different from those of their corresponding bulk/sphere (3D) materials [1, 2]. Recently, some studies have been reported on the synthesis of lanthanide orthophosphates nanowires/nanorods and nanotubes by hydrothermal method [3, 4]. Structural and chemical stability, long-term resistance to corrosion, and high melting point of rare earth orthophosphate make these materials suitable for use as heat-resistant and ceramic materials, and as a primary medium for disposal of radioactive wastes. The properties of lanthanide compounds depend strongly on the compositions and structure, which are sensitive to the shape and size of particles. It is known that LnPO<sub>4</sub> compounds have either a monoclinic structure (monazite-type, space group P2<sub>1</sub>/n) for the lighter REE (from La to Gd) or a tetragonal one (xenotime-type, space group I4<sub>1</sub>/amd) for the heavier REE (from Tb to Lu). The goal of this research was the experimental study of the heat capacity in the low temperature range from 4 to 380 K of LnPO<sub>4</sub> (Ln=La,Pr,Nd,Sm) and Am(III) sorption on the samples with various shape and size of particles. The task of present work was to preparation of lanthanide orthophosphates with controlled dimensionality, morphology, shape, chemical composition and crystal structure. LnPO<sub>4</sub> nanowires and particles with sphere-like morphology were synthesized by controlled hydrothermal method and precipitation from the solution, respectively. Optimum synthesis conditions were selected. Structural characteristic of samples was investigated by complex of methods. It is found that dimensionality affects heat capacity in the low temperature range. Sorption experiments show that kinetics of Am(III) sorption onto nanowires is faster than onto particles with microsphere-like morphology. At the same time the steady-state Am(III) sorption onto orthophosphate samples with similar crystal structure is the same.

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## Section 2. Thermodynamics of individual chemical compounds

### CRYSTAL STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF $\text{BaFe}_{1-y-x}\text{Y}_y\text{Me}_x\text{O}_{3-\delta}$ (Me = Co, Ni, Cu)

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Polycrystalline  $\text{BaFe}_{0.9-x}\text{Y}_{0.1}\text{Me}_x\text{O}_{3-\delta}$  (Me = Co, Ni, Cu) with  $0.0 \leq x \leq 0.2$  samples were synthesized by a conventional route and glycerol–nitrate technique. Final annealing was performed at 1373 K in air with subsequent slow cooling to room temperature.

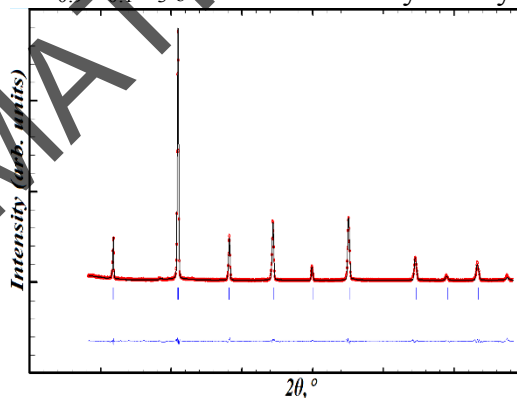
XRD analysis of  $\text{BaFe}_{0.9}\text{Y}_{0.1}\text{O}_{2.62}$  slowly cooled from 1373 K to room temperature in air showed formation of single phases with the perovskite structure. According to the TGA results, the oxygen content at 298 K in air can be represented as  $\text{BaFe}_{0.9}\text{Y}_{0.1}\text{O}_{2.62}$ , which agrees with data reported in [1]. XRD pattern for the  $\text{BaFe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  refined by Rietveld method within the cubic structure (sp.gr.  $Pm\bar{3}m$ ) is shown in Figure.

The temperature effect on the crystal structure of  $\text{BaFe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  was studied by X-ray diffraction in the temperature range 298–1273 K in air.

According to obtained data,  $\text{BaFe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  is stable in air at all temperatures and has cubic structure.

In order to determine the homogeneity range of the  $\text{BaFe}_{0.9-x}\text{Y}_{0.1}\text{Me}_x\text{O}_{3-\delta}$  (Me = Co, Ni, Cu) solid solution, the samples with  $0.0 \leq x \leq 0.2$  were prepared using a ceramic technique and glycerol–nitrate technique. According to the XRD results for slowly cooled samples, single phase  $\text{BaFe}_{0.9-x}\text{Y}_{0.1}\text{Co}_x\text{O}_{3-\delta}$  solid solutions formed in air within  $0 \leq x \leq 0.15$ . Beyond this composition range, the major impurity phase is  $\text{BaCoO}_{3-\delta}$ . The substitution of nickel or copper for iron doesn't lead to the formation of solid solutions in investigation conditions. According to XRD patterns of single phase solid solutions  $\text{BaFe}_{0.9-x}\text{Y}_{0.1}\text{Co}_x\text{O}_{3-\delta}$  ( $0.0 \leq x \leq 0.15$ ) were indexed using  $Pm\bar{3}m$  space group. The unit cell parameters were refined using Rietveld full-profile analysis. The substitution of cobalt for iron leads to the monotonous decrease of the unit cell parameters and the unit cell volume and as a result decrease bond length B–O, since the ionic radius of cobalt are less than ionic radius of iron.

The oxygen content decreases with decrease temperature and mass saturation occurs at  $T < 630$  K upon cooling. The substitution of cobalt for iron sites results in a decrease of oxygen content. Such behavior can be explained by the fact that cobalt is more electronegative element in comparison to iron. All thermal expansion curves of the  $\text{BaFe}_{0.9-x}\text{Y}_{0.1}\text{Co}_x\text{O}_{3-\delta}$  have nonlinear shape. Two extremum points are observed on thermal expansion curve of  $\text{BaFe}_{0.9-x}\text{Y}_{0.1}\text{Co}_x\text{O}_{3-\delta}$  ( $x = 0, 0.05, 0.1, 0.15$ ) sample. From room temperature to about 473 K TEC values was found to decrease to 0 with increasing temperature. At temperature range from 473 K up to 757 K TEC values show sharp increase. This behavior might associate with magnetic changes, because TGA researches are not show to be anomalies and high-temperature X-ray data were no observed structural changes within all temperature range studied with light compression cubic cell at about 573 K.



**Figure:** X-ray diffraction pattern of the  $\text{BaFe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  oxide.

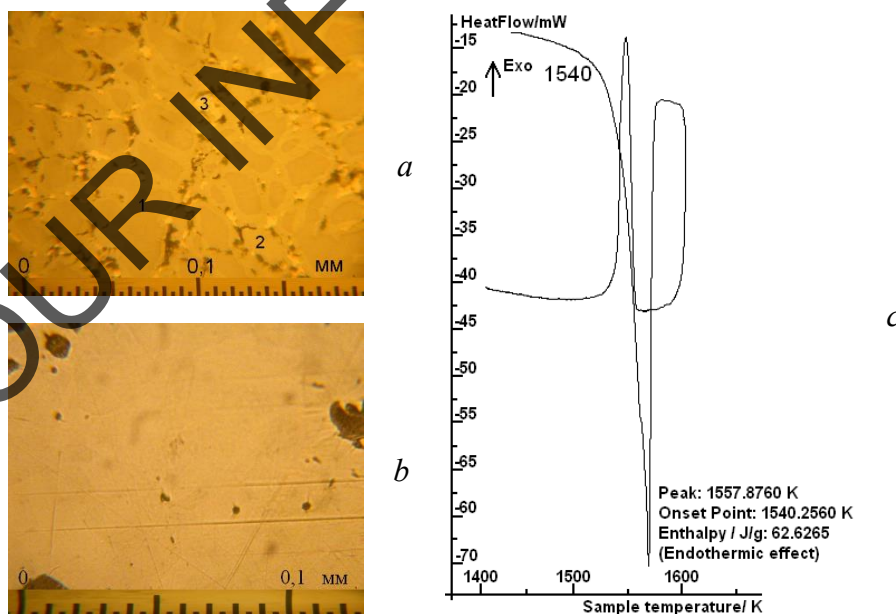
[1] Lu, S.; Long, G.; Ji, Y. *J. Hydrogen Energy*, 2010, 35, 7930-7935.

*This work was supported by the Russian Foundation for Basic Researches (Project No. 13-03-00958\_a).*

DETERMINATION OF THE TEMPERATURE AND ENTHALPY OF  $\text{BaLa}_2\text{FeS}_5$  MELTINGT.M. Burkhanova<sup>1</sup>, A.V. Solovyeva<sup>2</sup><sup>1</sup>Chemistry Institute, Tyumen State University, Semakova Str. 10, 625003 Tyumen, Russia<sup>2</sup>Laboratory of NMR and X-ray Department, Physics Department of the reservoir «KERN» JSC «Siberian Research Institute of Petroleum Industry», 625013 Tyumen, Russia

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$\text{BaLa}_2\text{FeS}_5$  has been synthesized by melting  $\text{BaS}$ ,  $\text{FeS}$ ,  $\text{La}_2\text{S}_3$  in a graphite crucible in a full vacuum quartz vial in a high-frequency current unit. This compound is paramagnetic [1]. Incongruent type of the melting has been observed. In the microstructure of the sample obtained, primary crystallized dark brown grains  $\gamma\text{-La}_2\text{S}_3$  with microhardness of 4800 MPa have been observed. Along the perimeter of  $\gamma\text{-La}_2\text{S}_3$  a lighter phase  $\text{BaLa}_2\text{FeS}_5$  ( $H = 3100$  MPa) is represented. Between the crystals of  $\text{BaLa}_2\text{FeS}_5$  phase constituting a chain of grains eutectic between  $\text{FeS}$  and  $\text{BaLa}_2\text{FeS}_5$  occurs (Figure a). Location of  $\text{BaLa}_2\text{FeS}_5$  phase along the perimeter of  $\gamma$ -phase grains and the formation of eutectic between  $\text{FeS}$  and  $\text{BaLa}_2\text{FeS}_5$  indicates the peritectic type of  $\text{BaLa}_2\text{FeS}_5$  formation. Samples containing 1  $\text{BaS}$  : 1  $\text{FeS}$  : 1  $\text{La}_2\text{S}_3$ , have been annealed at 1070 K for 900 h. The homogeneity of the annealed samples was confirmed by microstructure (Figure b) and X-ray analysis.  $\gamma$ -phase reflexes and  $\text{FeS}$  have not been detected on the diffraction pattern of the annealed sample. The temperature of the incongruent melting of  $\text{BaLa}_2\text{FeS}_5$ , proved by visual-polythermal analysis is 1590 K; by differential scanning calorimetry (DSC) at Setsys Evolution 1750 (TGA – DSC 1600) – 1540 K; the melting enthalpy is equal to 39.5 kJ/mol (Figure c).



**Figure:** a, b – photograph of the microstructure of samples of composition 1 $\text{BaS}$  : 1 $\text{FeS}$  : 1 $\text{La}_2\text{S}_3$ ; b – cooling of the melt; a – the sample annealed at 1070 K; c – curve of differential thermal analysis of the sample  $\text{BaLa}_2\text{FeS}_5$ .

[1] Wakeshima, M.; Ino, K.; Hinatsu, Y. Solid State Comm., 2001, 120, 145-148.

## Section 2. Thermodynamics of individual chemical compounds

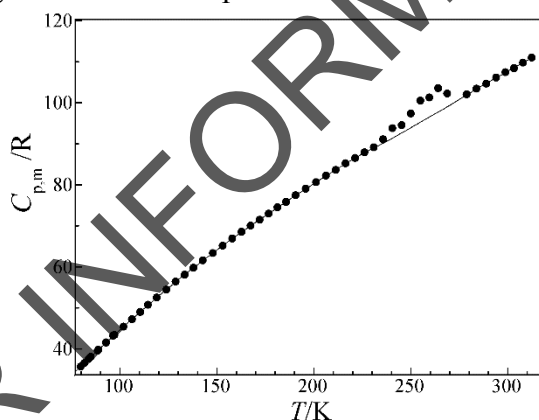
### LOW-TEMPERATURE THERMODYNAMIC PROPERTIES OF $\text{Eu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$

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Rare-earth beta-diketonates are perspective materials for OLED (organic light-emitting device) technology. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium ( $\text{Eu}(\text{thd})_3$ ) belong to this class of compounds. In present work the results of an experimental study of heat capacity  $\text{Eu}(\text{thd})_3$  in the temperature range from 5 to 310 K are given. On the basis of these data, the thermodynamic functions in the above temperature range are calculated.

Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium was obtained as described in [1]. After synthesis, using of gradient furnace the product was additionally purified by double sublimation in a vacuum. X-ray analysis showed single-phase, structure of the crystals corresponded to the structure of  $\text{Eu}(\text{thd})_3$ . The chemical analysis of the refined compound showed that its composition on C and N corresponds to the calculated one within the accuracy of the analysis (C, H – 0.2%). ICP-AES analysis was used to determine the purity of the crystals  $\text{Eu}(\text{thd})_3$ . For the determination of impurities in the sample a high resolution spectrometer iCAP-6500 (Thermo Scientific) was used. Purity of the final compound is not lower than 99.9%.



**Figure:** Experimental heat capacity of  $\text{Eu}(\text{thd})_3$  in the range of (80–310) K.

The heat capacity  $C_{p,m}(T)$  of the  $\text{Eu}(\text{thd})_3$  sample was measured by the adiabatic method on the installation described in [2]. A sample of 4.947 g was loaded into the calorimetric ampoule. The molar mass used in the calculation of the molar heat capacity was determined from the formula  $\text{Eu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  as  $701.77 \text{ g}\cdot\text{mol}^{-1}$ . The heat capacity was measured at 80 points in the range (5–310) K. The smoothed  $C_{p,m}(T)$  dependence was used to calculate the thermodynamic functions. In the temperature range (240–280) K anomaly in the heat capacity with a maximum at  $T \sim 265$  K was revealed (Figure). The anomalous part in a maximum accounts for 6% of the regular heat capacity. The appearance of the anomaly testifies about the phase transformation in  $\text{Eu}(\text{thd})_3$ . The nature of the detected phase transition will be studied in the future.

[1] Stabnikov, P.A.; Zharkova, G.I.; et al. J. Struct. Chem., 2011, 52, 577.

[2] Naumov, V.N.; Nogteva, V.V. Instrum. Exp. Tech., 1985, 28, 1194-1199.

*The reported study was supported by the Russian Foundation for Basic Research (Project No. 14-08-31764 mol\_a).*

### REGULARITIES IN THE BEHAVIOR THE LOW-TEMPERATURE THERMODYNAMIC PROPERTIES OF METAL DIPIVALOYLMETHANATES

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Metal dipivaloylmethanates have high vapor pressures at moderate temperatures and are therefore used as precursors in the deposition of metallic and oxide coatings from the vapor phase. Many properties of these compounds, including thermodynamic properties, have been studied insufficiently. The accumulation of experimental data on thermodynamic properties substantially lags behind practical demands. This is especially true of low-temperature thermodynamic properties, which are necessary for studies of the nature of volatility, equilibrium conditions for crystal–gas systems, and other properties of compounds. The possibility of calculating the thermodynamic characteristics of complex objects by theoretical simulations is currently limited because of the absence of data on many force constants and reliable data on interatomic interaction potential parameters. For this reason, along with the experimental determination of the thermodynamic properties of particular substances, the search for empirical and semiempirical relations for estimating and approximately calculating these properties is necessary.

In the present analysis we have considered all nowadays available experimental data on low temperature heat capacity for metal dipivaloylmethanates ( $\text{Al}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ ,  $\text{Fe}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ ,  $\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ ,  $\text{Ru}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ ,  $\text{Eu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ ) in order to detect regularities in thermodynamic properties behaviour and interrelation of such properties with structural characteristics of these materials. A correlation between heat capacity and the effective molecule volume was detected for metal dipivaloylmethanates. This correlation reflects the intensity of intermolecular interactions. It was shown that universal heat capacity behavior is observed for metal beta-diketonates with identical ligands in the wide range of temperatures. The explanation of the detected regularities in the isoligand row is linked to the identical structural organization in short range ordering, which in its turn determines the coincidence of objects' vibrational spectra in the high frequencies range. A simple equation was put forward that allowed us, in the frame work of detected regularities, to describe the behavior of heat capacity in compounds under study in a wide range of temperatures. The results obtained can be used to calculate thermodynamic characteristics of not studied objects for which the structural data are known. The detected regularities present a general character due to the fact that revealed features that initiate such behavior are connected with identical structure organization in other classes of molecular crystals.

*The reported study was supported by the Russian Foundation for Basic Research (Project No. 14-08-31764 mol\_a).*

## Section 2. Thermodynamics of individual chemical compounds

### HIGH-TEMPERATURE HEAT CAPACITY OF HEAVY RARE EARTH ORTHOVANADATES $RVO_4$

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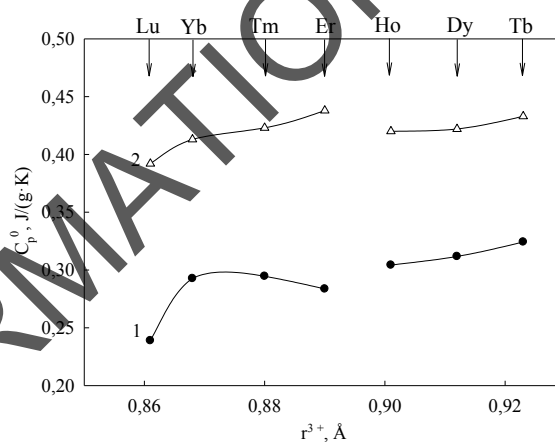
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Heavy rare earth orthovanadates  $RVO_4$  ( $R = Tb, Dy, Ho, Er, Tm, Lu$ ) are the promising materials for creation of diode-pumped solid-state lasers. Also they are applied as a cathodoluminescent material, thermophosphors and scintillators. These materials exhibit excellent catalytic, electric and magnetocaloric properties [1]. There is data about the structure and low-temperature heat capacity of  $RVO_4$ . The aim of this work was a high-temperature heat capacity of  $RVO_4$  ( $R = Tb-Lu$ ) measuring.

Heavy rare earth orthovanadates  $RVO_4$  were prepared by a solid-phase reaction from  $R_2O_3$  and  $V_2O_5$ . Stoichiometric mixtures of the reactants were pelletized and heated in air in the range (873–953) K in increments of 20 K and duration of 15 h at each temperature, then in the range (973–1273) K in increments of 100 K and duration 10 h. Compositions of the samples were controlled by X-ray analysis. The heat capacity was measured by differential scanning calorimetry (NETZSCH STA 449 C Jupiter).

An experimental data of the temperature dependences can be described by the equation  $C_p = f(T)$ . Resulting  $C_p$  coefficients are given in Table.

The properties of rare-earth elements are discussed with due regard for tetrads (or W-effect), considering four groups of rare-earth elements such as La–Nd, Pm–Gd, Gd–Ho and Er–Lu. Figure shows a dependence of standard heat capacity  $C_p^0$  for compounds  $RVO_4$  and oxides  $R_2O_3$  ( $R = Tb-Lu$ ) on the ionic radius  $r^{3+}$  within the third and the fourth tetrads. These curves are of the similar behavior. Hence, it can be concluded, that the heat capacity of these compounds significantly is affected by the interaction of  $R^{3+}-V^{5+}$  and characteristics of the rare earth ions.



**Figure:** The specific heat capacities  $R_2O_3$  (1) and  $RVO_4$  (2) compounds at 298 K versus ionic radius  $r^{3+}$ .

**Table.** The coefficients of approximate equations  $C_p = f(T)$  for  $RVO_4$  ( $R = Tb-Lu$ ) compounds

Compound	Temperature interval (K)	Coefficients				
		$a$	$b \cdot 10^{-3}$	$c \cdot 10^5$	$d \cdot 10^{-5}$	$g \cdot 10$
$TbVO_4$	352–1050	127.6	30.9	-15.2	-	-
$DyVO_4$	346–981	127.1	0.2	-14.2	-	-
$HoVO_4$	336–1039	133.9	10.5	-16.6	-	-
$ErVO_4$	376–1154	121.5	29.3	-5.6	-	-
$TmVO_4$	351–1024	13.0	129.3	-21.2	-4.6	172.9
$YbVO_4$	371–1126	144.9	18.5	-4.7	-	40.9
$LuVO_4$	404–908	134.4	11.6	-21.4	-	-

[1] Huang, Z.; Zhang, L.; Pan, W. J. Solid State Chem., 2013, 205, 97-103.



PHASE-TRANSITION ENTHALPIES AND TEMPERATURES SHIFTS FOR  $\text{EuLnCuS}_3$  (Ln = Tb–Lu)

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Differential scanning calorimetry investigation of incongruent melting  $\text{EuLnCuS}_3$  (Ln = Tb–Lu) compounds was performed for the first time. Being heated to 1840 K all samples are entirely molten. There are difficult behavior of solid–liquid field, that is alike in every sample: there are three non-variant thermal effects  $\Delta H_1 \geq \Delta H_3 > \Delta H_2$  (Figure, Table) and fourth mono-variant peak, besides two another thermal effects on the cooling curve. There is regular increase for temperatures of non-variant phase transformations from Tb to Er, i.e. there is increase thermal stability for  $\text{EuLnCuS}_3$ .

There is a singular value for  $\text{Er}^{3+}$ – $\text{Yr}^{3+}$  ionic radiuses – phase transformations temperatures relationship. Existence of that is conformed to previous structural type change in the number of  $\text{EuLnCuS}_3$  compounds. Sample scanning was carried out in order to match the effect (third or fourth peak) with the melting of  $\text{EuLnCuS}_3$ . The scanning was in progress until the compound temperature reached the third non-variant peak's heat absorption closing level (1560–1640 K). After high-heat treatment all samples retained initial form. Single-phase of compounds was confirmed by microstructure analysis. A conclusion that compounds  $\text{EuLnCuS}_3$  (Ln = Tb–Lu) offer high-temperature polymorphic transformations can be drawn based on:

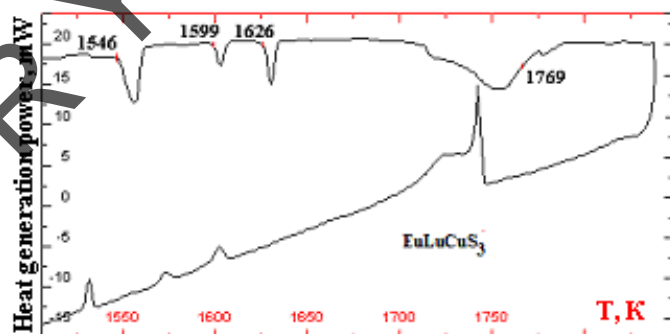
- fidelity of newly received data of non-variant peaks (replicated experiments),
- being sample in solid after thermal analysis,
- exhibiting of thermal effects while heating or cooling.

Postheating afford  $\text{EuS}$  and  $\text{EuLnS}_2$  new phases. That means incongruent melting peak of compounds isn't pronounced, but appears in the process of cooling.

**Table.** Phase transitions temperatures and enthalpies of phase transitions for  $\text{EuLnCuS}_3$

Compound	Temperatures (K) and enthalpies (J/g) of phase transition							
	$T_1$	$\Delta H_1$	$T_2$	$\Delta H_2$	$T_3$	$\Delta H_3$	$T_{\text{melting}}^1$	$T_{\text{liquid}}$
$\text{EuTbCuS}_3$	1478±5	3.3±0.4	1516±3	1.9±0.2	1548±4	3.3±0.3	1722±6	1764±2
$\text{EuDyCuS}_3$	1500±1	9.3±0.6	1543±1	2.2±0.8	1568±2	4.3±0.5	1727±4	1772±3
$\text{EuHoCuS}_3$	1516±1	7.8±0.7	1562±2	2.5±0.8	1591±2	4.6±1.9	1751±5	1774±4
$\text{EuErCuS}_3$	1524±2	4.9±0.5	1575±3	1.5±0.2	1602±3	2.8±0.3	1743±4	1771±3
$\text{EuYbCuS}_3$	1513±4	4.7±0.5	1564±4	2.8±0.3	1594±3	4.9±0.5	1745±4	1778±4
$\text{EuLuCuS}_3$	1549±3	10.8±1.6	1601±2	3.0±1.2	1628±2	4.9±1.7	1746±5	1797±2

<sup>1</sup>Melting temperatures are determined approximately from cooling curve.



**Figure:** Differential thermal analysis of  $\text{EuLuCuS}_3$  sample, stoved at 970 K for 3000 hours. Scanning conditions: thermocouple PtRh 6% – PtRh 30%, scanning rates 5 °C/min, argon flow rate 25 ml/min, crucibles with a volume 100  $\mu\text{l}$ .

This work was supported by Research and Development government task No. 2014/228, No.996.

## Section 2. Thermodynamics of individual chemical compounds

### HIGH-TEMPERATURE HEAT CAPACITY OF THE LIGHT RARE-EARTH ORTHOVANADATES

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Rare-earth orthovanadates crystals ( $RVO_4$ ,  $R = \text{La} - \text{Gd}$ ) are used as laser materials. These lasers are widely employed in different fields of science, technology, and medicine. Despite the intense interest in  $RVO_4$  compounds, properties of some of them have been studied insufficiently.

The properties of rare-earth elements and their compounds are analyzed taking into account the tetrad-effect for four groups of rare-earth elements: La–Nd, Pm–Gd, Gd–Ho, and Er–Lu. Oxides of light rare-earth elements form compounds with  $V_2O_5$ , such as  $RVO_4$ , we consider the first (La–Nd) and second (Pm–Gd) tetrads. Since the heat capacity is a characteristic of the material, which is related to the specific features of its composition and structure, the purpose of this work is to obtain data on the heat capacity of  $RVO_4$  ( $R = \text{La} - \text{Gd}$ ) orthovanadates.

Rare-earth orthovanadates was prepared by solid state reaction. The phase composition of the samples thus prepared was determined by X-ray diffraction on a PANalytical X'Pert Pro MPD diffractometer. The heat capacity  $C_p$  was measured in platinum crucibles by differential scanning calorimetry with an STA449 C Jupiter (NETZSCH). Figure 1 depicts the data on the influence of temperature on the heat capacity of the light rare-earth orthovanadates. Lest the difference of molar masses of these orthovanadates be taken into account, the heat capacity is given in J/(g K). It can be seen that  $C_p$  of these compounds increases regularly with increasing temperature. Temperature dependence of the molar heat capacity can be represented as the classical Maier–Kelley equation (in units of J/(mol K)):

$$\text{GdVO}_4 : C_p = (120,7 \pm 0,7) + (36,2 \pm 0,7)10^{-3}T - (10,51 \pm 0,84)10^5 T^{-2},$$

$$\text{EuVO}_4 : C_p = (131,7 \pm 0,4) + (29,0 \pm 0,4)10^{-3}T - (7,28 \pm 0,55)10^5 T^{-2},$$

$$\text{SmVO}_4 : C_p = (136,3 \pm 0,3) + (26,4 \pm 0,7)10^{-3}T - (21,05 \pm 0,68)10^5 T^{-2},$$

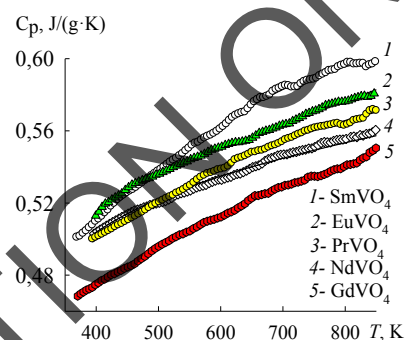
$$\text{NdVO}_4 : C_p = (127,7 \pm 0,7) + (22,7 \pm 0,7)10^{-3}T - (17,77 \pm 0,81)10^5 T^{-2},$$

$$\text{PrVO}_4 : C_p = (131,6 \pm 0,5) + (15,2 \pm 0,5)10^{-3}T - (14,07 \pm 0,60)10^5 T^{-2}.$$

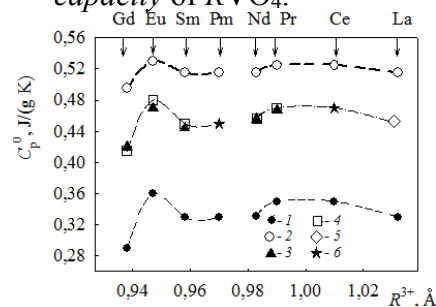
Based on the above data (Figure 2), it can be concluded that the dependences  $(R_2O_3) = f(R^{3+})$  and  $(RVO_4) = f(R^{3+})$  are similar to each other. It should be noted that the values of calculated from formula Neumann–Kopp additive are higher than the experimental values. Figure 2 also presents data of other authors for Rare-earth orthovanadates. It can be concluded that, on the whole, these data agree with our results.

[1] Sirota, N.N.; Novikov, A.V.; Novikova, V.V.; et al. *Rus. J. Phys. Chem. A*, 1990, 7, 1750–1753.

[2] Gavrichev, K.S.; Ryumin, M.A.; Tyurin, A.V.; et al. *Inorganic Materials*, 2010, 7, 77.



**Figure 1:** The temperature dependence of heat capacity of  $RVO_4$ .



**Figure 2:** Change in the standard heat capacity of  $R_2O_3$  (1) and compounds  $RVO_4$  (2–6) as a function of the  $R^{3+}$  ionic radius; 2 – calculation using Neumann – Kopp additive, 3 – data taken from [1], 4 – experiment, 5 – data taken from [2], 6 – estimates.

### CRYSTAL AND DEFECT STRUCTURE, OXYGEN NONSTOICHIOMETRY AND CONDUCTIVITY OF THE COMPLEX OXIDES $\text{SmBa}(\text{Me,Fe})_2\text{O}_{6-\delta}$ (Me = Co, Cu)

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The samples  $\text{SmBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  and  $\text{SmBaCu}_{2-y}\text{Fe}_y\text{O}_{6-\delta}$  were prepared using a glycerin nitrate technique. Final annealing was performed at (1000–1100)°C for 120 h in air with intermediate grindings and slowly cooled to room temperature at the rate of about 100°C/h.

According to the results of X-ray diffraction analysis the homogeneity range for the  $\text{SmBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  and  $\text{SmBaCu}_{2-y}\text{Fe}_y\text{O}_{6-\delta}$  solid solutions at studied conditions appears within 0–1.1 and 0.8–1.2 respectively. The crystal structure of  $\text{SmBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  ( $0 \leq x \leq 0.5$ ) was identified as orthorhombic ( $Pmmm$  sp. gr.), while the samples  $\text{SmBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  with  $0.6 \leq x \leq 1.1$  and  $\text{SmBaCu}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  with  $0.8 \leq y \leq 1.2$  crystallized in tetragonal structure ( $P4/mmm$  sp. gr.).

The changes of oxygen content in the  $\text{SmBa}(\text{Me,Fe})_2\text{O}_{6-\delta}$  solid solutions were measured by thermogravimetric analysis within the temperature range  $25 \leq T, ^\circ\text{C} \leq 1100$  in air. The absolute oxygen content in the samples was determined using a direct reduction of the samples in the TG cell by hydrogen and iodometric titration. It was shown that the oxygen content increases with increasing iron concentration in both systems.

The defect structure of  $\text{SmBaCo}_2\text{O}_{6-\delta}$  and  $\text{SmBaCo}_{1.4}\text{Fe}_{0.6}\text{O}_{6-\delta}$  oxides with double perovskite structure was described using the model based on the simple cubic perovskite  $\text{SmCoO}_3$  as a reference state. Oxygen vacancies ordering in the  $\text{SmBaCo}_2\text{O}_{6-\delta}$  can be introduced by the formation of  $(V_o^{\bullet\bullet} \text{Ba}'_{sm})^{\bullet}$  clusters. Equilibrium constants and enthalpies of the reactions for the point defects formation were refined. The concentrations of all defect species were calculated as functions of temperature and oxygen nonstoichiometry.

Total conductivity and Seebeck coefficient of  $\text{SmBaCo}_2\text{O}_{6-\delta}$ ,  $\text{SmBaCo}_{1.4}\text{Fe}_{0.6}\text{O}_{6-\delta}$  and  $\text{SmBaCuFeO}_{6-\delta}$  were measured simultaneously using a 4-probe technique as a function of oxygen partial pressure  $P_{\text{O}_2}$ , in temperature range  $700 \leq T, ^\circ\text{C} \leq 1100$ . The temperature dependencies of the total conductivity of  $\text{SmBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  possess maxima at approximately (300–350)°C in air. The partial substitution of iron for cobalt leads to decrease the conductivity value.

Seebeck coefficient for all compounds reveals positive values within the entire temperature and oxygen partial pressure ranges that indicate predominant  $p$ -type conductivity.

The dependencies of electrical conductivity  $\log(\sigma)_T = f(\delta)$  and Seebeck coefficient  $Q_T = f(\delta)$  versus oxygen nonstoichiometry were discussed on the basis of the defect structure models. The values of activation energy for fixed oxygen content values were calculated.

Chemical stability of the  $\text{SmBa}(\text{Me,Fe})_2\text{O}_{6-\delta}$  relative to the electrolyte materials  $\text{Zr}_{0.85}\text{Y}_{0.15}\text{O}_2$  and  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$  has been checked within the temperature range (800–1100)°C, by means of annealing of the corresponding mixtures with 1:1 mass ratio during 24 h in air with following XRD analysis. It was found that all samples interact with the  $\text{Zr}_{0.85}\text{Y}_{0.15}\text{O}_2$  even at 900°C and cannot be recommended as electrode materials for this electrolyte. In contrast  $\text{SmBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  and  $\text{SmBaCuFeO}_{6-\delta}$  solid solutions were chemically stable in contact with  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$  to  $T = 1100^\circ\text{C}$  and to  $T = 1050^\circ\text{C}$ , respectively.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMODYNAMIC PROPERTIES OF 4-*tert*-BUTYL-DIPHENYL OXIDE

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The derivatives of diphenyl oxide are from the series of the bicycle aromatic compounds, they find ever increasing application in technology and medicine (semiconducting nanomaterials, liquid crystals, drugs). The diphenyl oxide is the most studied compound of the series. The literature data on thermodynamic properties of the diphenyl oxide derivatives are scanty that delays working up the science basis of the production and application of these compounds. This work is devoted to experimental studying of thermodynamic properties of 4-*tert*-butyl-diphenyl oxide [(CH<sub>3</sub>)<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>-O-C<sub>6</sub>H<sub>5</sub>, 4-TBDPhO]. Data on thermodynamic properties of this substance in the literature are missing.

The sample was synthesized and purified for reliable experimental investigation.

The heat capacities of 4-TBDPhO was measured by vacuum adiabatic calorimetry in the temperature range (8–371) K. The errors in the determination of heat capacities are on average (0.2–0.3)%. The temperature, the enthalpy and the entropy of fusion and purity were determined. The energy of combustion,  $\Delta_c U_m^o(cr)$ , of the sample was determined by static-bomb combustion calorimetry. The error in the determination of energy of combustion is about 0.03%.

The saturation vapor pressures of the substance were measured by dynamic transpiration method in the temperature and pressure intervals (298–325) K and (0.05–1.2) Pa. Vapor pressures were reliable within (1–3)%. The enthalpy and entropy of sublimation at  $T = 298.15$  K were derived.

**Table 1.** Thermodynamic characteristics of 4-TBDPhO

$T_{tp}$ (K)	$N_2$ (mole fraction)	$\Delta_c H_m^o(T_{tp})$	$\Delta_{cr}^g H_m(298)$	$\Delta_c U_m^o(cr)(298)$
			kJ·mol <sup>-1</sup>	
327.84±0.02	0.0030±0.0003	21.99±0.14	100.1±1.0	-8695.3±2.2

The standard thermodynamic functions (changes of the entropy, enthalpy, and Gibbs energy) were obtained for the crystal and liquid states in the studied temperature intervals and for the ideal gas state at  $T = 298.15$  K. The functions of the formation  $\Delta_f H_m^o(298)$ ,  $\Delta_f S_m^o(298)$  and  $\Delta_f G_m^o(298)$  were also calculated for the crystal and ideal gas states.

**Table 2.** Thermodynamic functions of formation for 4-TBDPhO in the crystal and ideal gas states at  $T = 298.15$  K

$\Delta_f H_m^o(cr)$ (kJ·mol <sup>-1</sup> )	$\Delta_f S_m^o(cr)$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$\Delta_f G_m^o(cr)$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^o(g)$ (kJ·mol <sup>-1</sup> )	$\Delta_f S_m^o(g)$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$\Delta_f G_m^o(g)$ (kJ·mol <sup>-1</sup> )
-163.4±2.8	-1032.3±2.4	144.4±2.9	-63.3±3.0	-818.1±3.9	180.6±3.2

For comparison of the thermodynamic data obtained for 4-TBDPhO with the available literature data, the contribution of the *O*-(2*C<sub>b</sub>*) group in the gas state (where *C<sub>b</sub>* is the carbon atom in a benzene ring) into the absolute entropy was determined,  $\Delta S_m^o(g)[O-(2C_b)] = 48.1$  J·K<sup>-1</sup>·mol<sup>-1</sup>. Using the obtaining value  $\Delta S_m^o(g)[O-(2C_b)]$ , the value of the absolute entropy of diphenyl oxide was calculated. The resulting value of absolute entropy of diphenyl oxide agrees with the literature value within 1.0%.

## THERMOCHEMISTRY OF URACIL AND THYMINE

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Thermochemical properties of uracil and thymine have been evaluated using additional experiments. Standard ( $p^0 = 0.1$  MPa) molar enthalpies of formation in the gas phase at  $T = 298.15$  K for uracil  $(-298.2 \pm 0.6)$  and for thymine  $(-337.6 \pm 0.9)$  kJ·mol<sup>-1</sup> have been derived from energies of combustion measured by static bomb combustion calorimetry, and molar enthalpies of sublimation determined using the transpiration method. Results of the G3 and G4 quantum-chemical methods, used for calculations of theoretical enthalpies of formation in ideal gas state, are in very good agreement with the remeasured experimental values.

**Table.** Thermochemical data at  $T = 298.15$  K ( $p^0 = 0.1$  MPa) for uracil and thymine (kJ·mol<sup>-1</sup>)<sup>a</sup>

Nucleoside	$\Delta_c H_m^\circ$ (cr)	$\Delta_f H_m^\circ$ (cr)	$\Delta_{cr}^\circ H_m$	$\Delta_f H_m^\circ$ (g) exp	$\Delta_f H_m^\circ$ (g) calc
Uracil	-1716.1±0.3 [1]	-429.6±0.6 [1]			
	-1721.3±2.2 [4]	-424.4±2.5 [4]			-299.2 (G3)
	-1715.2±1.0 [3]	-430.5±1.1 [3]			-299.5 (G4)
	-1716.3±0.9	-429.4±1.0			-299.8 (F-W)
		<b>-429.5±0.5<sup>c</sup></b>	<b>131.4±0.4</b>	<b>-298.1±0.6</b>	<b>-299.5<sup>f</sup></b>
Thymine	-2362.2±0.8 [1]	-462.8±1.6 [1]			
	-2371.2±1.0 [2]	-453.8±1.1 [2]			
	-2369.0 [5]	-456.0 [5]			
	-2367.3 [6]	-457.7 [6]			-338.1 (G3)
	-2359.3±1.0 [3]	-465.7±1.2 [3]			-337.9 (G4)
	-2359.8±1.4	-465.2±1.6			-336.7 (F-W)
	<b>-464.8±0.8<sup>e</sup></b>	<b>127.2±0.3</b>	<b>-337.6±0.9</b>	<b>-337.6<sup>f</sup></b>	

<sup>a</sup> Uncertainties correspond to expanded uncertainties of the mean (0.95 level of confidence). Data in bold is from this work.

<sup>c</sup> Weighted mean value from this work and refs. [1, 3, 4].

<sup>e</sup> Weighted mean value from this work and refs. [1, 3].

<sup>f</sup> Mean value.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMODYNAMIC PROPERTIES OF THE GASEOUS TIN SALTS

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In present work the thermal stability and thermodynamic properties of gaseous tin borates  $\text{SnB}_2\text{O}_4$ ,  $\text{Sn}_2\text{B}_2\text{O}_5$ , molybdates  $\text{SnMoO}_4$ ,  $\text{SnMo}_2\text{O}_7$ ,  $\text{Sn}_2\text{MoO}_5$  and vanadate  $\text{SnV}_2\text{O}_6$  were studied.

The mass spectrometer MS-1301 was used. The gaseous salts were synthesized directly in molybdenum or zirconia Knudsen cells. The cells were heated by an electron bombardment. The temperature was measured by the optical pyrometer EOP-66.

In order to obtain the standard formation enthalpies of the gaseous tin salts the equilibrium constants of reactions (1)–(6) in the gas phase were measured:



In order to determine vapor composition, appearance energies of the ions were measured using vanishing current method with Au as energy standard. The partial pressures of these vapor species were obtained using the ion current comparison method using Au and Ag as the internal pressure standards. The calculations of reaction enthalpies were made by the second- and third-law procedure. In order to lead obtained values to standard conditions the thermodynamic functions for tin, boron, molybdenum and vanadium oxides were taken from the literature and for gaseous salts were calculated by the statistical thermodynamic method in “rigid rotor – harmonic oscillator” approximation. In order to obtain molecular parameters of gaseous salts quantum-chemistry computation were carrying out. Thermodynamic properties of gaseous tin salts obtained in this work are presented in table below.

*Table. The standard formation enthalpies of gaseous tin oxyacid salts*

Substance	$-\Delta_f H^\circ_{298}$ (kJ/mol)
$\text{SnB}_2\text{O}_4$	1166±22
$\text{Sn}_2\text{B}_2\text{O}_5$	1469±28
$\text{SnMoO}_4$	693±43
$\text{SnMo}_2\text{O}_7$	1444±46
$\text{Sn}_2\text{MoO}_5$	989±32
$\text{SnV}_2\text{O}_6$	1520±43

SYNTHESIS AND PROPERTIES OF LANTHANIDE ZIRCONATE  
WITH PYROCHLORE STRUCTURE

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Samples of lanthanum, praseodymium, neodymium and gadolinium zirconate were synthesized by reverse precipitation for further thermodynamic study. The solution of dissolved lanthanides and zirconium chlorides combined in stoichiometric ratios was added to an aqueous solution of ammonia. The resulting precipitates were centrifuged, washed with hot water and dried at 100°C in air during 24 hours. According to XRD data the structure of the samples was actually amorphous with a pronounced halo at the position of the main X-ray reflections. Part of the sample was annealed at a temperature of (1172–1273) K to obtain a fluorite phase. Ceramic with pyrochlore structure was synthesized at 1823 K for (2–10) hours in air.

The amorphous samples were investigated by DSC. Two phase transitions were observed with temperature increases. The first transition is from amorphous to fluorite structure at about 1000 K, and second one – in a pyrochlore structure – above 1373 K. It was determined that the temperature of formation of the crystalline structure and the temperature of phase transition rise with the increasing of a lanthanide atomic number. The observed thermal effects of zirconate crystallization at ~ 1000 K are much less than values of enthalpy of formation of these compounds. And that means the formation of short-range order of the crystal structure occurs at the time of deposition and drying of precipitation.

To study the thermodynamic properties of lanthanum zirconate with a pyrochlore structure the required for adiabatic calorimetry amount of sample with lattice parameter  $a = 1.08019$  (13) nm was synthesized. The obtained values of heat capacity has a good correlation with those of earlier published for lanthanum zirconate [1].

For the first time, measurements of low-temperature heat capacity of praseodymium zirconate were made. For these purposes, the pyrochlore structure sample with the lattice parameter  $a = 1.07020$  (20) nm was synthesized.

The  $C_p(T)$  data were smoothed by spline fitting using the software of IVTANTERMO Database [2]. The thermodynamic functions (entropy, enthalpy increment and reduced Gibbs energy) were calculated.

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## Section 2. Thermodynamics of individual chemical compounds

### PHASE EQUILIBRIA AND CRYSTAL STRUCTURE OF THE COMPLEX OXIDES IN THE Sm–Fe–Co–O AND Sm–Ca–Co–O SYSTEMS

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Since the complex oxides with the perovskite type structure based on the rare earth, alkali earth and 3d-transition metals (Co, Fe) are considered as promising electrode materials for the solid oxide fuel cells the knowledge of phase equilibria of related systems and information about the crystal structure, oxygen nonstoichiometry and functional properties is the subject of vital importance. This study focuses on the phase equilibria in the Sm – Ca – Co – O and Sm – Co – Fe – O systems at 1100°C in air and the crystal structure of intermediate phases.

The samples were prepared using a glycerin nitrate technique. All powders were annealed at 1100°C during 120–240 h with intermediate grindings with following quenching to room temperature (cooling rate ~500°/min). The homogeneity ranges and crystal structure of the solid solutions were determined by X-ray diffraction. The unit cell parameters were refined using Rietveld full-profile analysis.

#### Sm – Co – Fe – O system:

Results of XRD showed the existence of solid solutions  $\text{SmFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$  with homogeneity ranging within  $0 \leq x \leq 1$ . All complex oxides  $\text{SmFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$  are crystallized in orthorhombic structure (*Pbnm* sp. gr.). Unit cell parameters and atomic positions are defined for all samples of this type. It was found that the increase of cobalt concentration leads to gradual decrease of parameters and volume of unit cells that may be explained by the dimension effects. Oxygen nonstoichiometry in the  $\text{SmCo}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$  was determined using TG method by the reduction in hydrogen flow at 1200°C and dicromatometric titration. The value of oxygen content recalculated to the room temperature was equal to 3. Oxygen nonstoichiometry of complex oxide was investigated by TGA method as temperature function. It was shown that oxygen content in  $\text{SmFe}_{0.5}\text{Co}_{0.5}\text{O}_3$  is similar to stoichiometry in the whole considered temperature range.

#### Sm – Ca – Co – O system:

According to XRD patterns the intermediate phases formed in this system at 1100°C in air were  $\text{Ca}_{3-y}\text{Sm}_y\text{Co}_2\text{O}_{6-\delta}$  ( $0.6 < y < 0.7$ ) and  $\text{SmCaCoO}_{4-\delta}$ . All solid solutions  $\text{Ca}_{3-y}\text{Sm}_y\text{Co}_2\text{O}_{6-\delta}$  ( $0.6 < y < 0.7$ ) were found to have rhombohedral structure (*R-3c* sp. gr.). Unit cell parameters and atomic positions for all samples are found. Formation of complex oxide  $\text{SmCaCoO}_{4-\delta}$  with the structure type  $\text{K}_2\text{NiF}_4$  was determined within the research of dopants influence on the stability of the compositions with spinel structure  $\text{Sm}_2\text{CoO}_4$ . According to the results of XRD analysis this complex oxide was found to be tetragonal (*I4/mmm* sp. gr.).

The values of oxygen content for the slowly cooled samples at room temperature were estimated from the dicromatometric titration results as  $(6-\delta) = 5.88$  for  $\text{Ca}_{2.3}\text{Sm}_{0.7}\text{Co}_2\text{O}_{6-\delta}$ , and  $(4-\delta) = 3.95$  for  $\text{SmCaCoO}_{4-\delta}$ .

The projections of isothermal–isobaric phase diagrams for the Sm – Ca – Co – O and Sm – Co – Fe – O systems to the compositional triangle of metallic components were presented.

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THERMOCHEMICAL CHARACTERISTICS OF COPOLYMERS OF CHITOSAN AND POLYLACTIDE

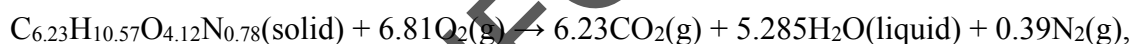
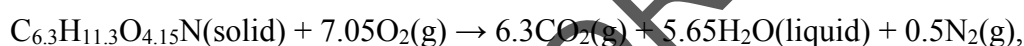
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Perspective direction in creating of biodegradable and biocompatible polymer functionality is using of synthetic polyesters – polylactide, polyglycolide and natural polysaccharides. Representative of a class of natural polysaccharides is chitosan. It has unique properties: high reactivity and sorption capacity, hypoallergenic, non-toxic, it is biodegradable and biocompatible. There is an acute question of obtaining biodegradable, biocompatible polymeric materials and composites for implants. Chitosan should be modified for using it in the manufacture of implants, because it is fragile polymer.

The purpose of our research is investigating thermochemical properties compositions of chitosan and polylactide with different ratios of components. We used the following reagents: chitosan with molecular mass  $1.2 \times 10^5$  and the degree of deacetylation 0.82 and polylactide with a molecular mass  $6 \times 10^4$ .

The combustion enthalpy of copolymers was determined in an updated V-08MA calorimeter with a static calorimetric bomb. Calculations were performed for the following combustion reactions of chitosan and copolymers, containing 16, 20, 30 mass.% of polylactide, respectively:



The combustion energy of the substance under study,  $\Delta_c U$ , was determined under the conditions of calorimetric bomb. Standard values for  $\Delta_c U^\circ$  and  $\Delta_c H^\circ$  were calculated for the combustion of chitosan and copolymers based on the mean value of  $\Delta_c U$ , molar mass and assuming a Washburn correction and a correction determined by the change in the number of moles of the gases.

According to the obtained standard enthalpy of combustion  $\Delta_c H^\circ$ , enthalpy of formation  $\Delta_f H^\circ$  for each copolymer in the solid state at 298.15 K was calculated (Table).

**Table.** Standard energies and the enthalpies of combustion and formation of samples at 298.15 K

Compound	$-\Delta_c U^\circ$ , kJ/mol	$-\Delta_c H^\circ$ , kJ/mol	$-\Delta_f H^\circ$ , kJ/mol
Chitosan	$3291.8 \pm 2.5$	$3292.4 \pm 2.5$	$801.7 \pm 2.5$
Chitosan + PLA (16% PLA)	$3187.2 \pm 2.3$	$3186.7 \pm 2.3$	$802.0 \pm 2.3$
Chitosan + PLA (20% PLA)	$3161.0 \pm 2.4$	$3161.5 \pm 2.4$	$800.8 \pm 2.4$
Chitosan + PLA (30% PLA)	$3097.2 \pm 2.3$	$3097.6 \pm 2.3$	$799.9 \pm 2.3$

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## Section 2. Thermodynamics of individual chemical compounds

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### TRANSFORMATION OF THERMAL PROPERTIES OF FROZEN WATER IN THE HUMID STARCHES UPON DENATURATION

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Calorimetric investigations of the phase transition in water that freezes at cooling below 0°C are of non-vanishing interest. In the work the melting of frozen water (FW) in starches (rice, wheat, potato) that have crystal lattices of A- and B-types has been studied by means of differential scanning calorimetry (DSC). The dependences of the melting temperatures ( $T_m$ ) and heats ( $Q_m$ ) for FW have been determined for the native and amorphous states of the humid starches. It has been shown that water nanoclusters with the  $T_m$  significantly below 0°C can be formed at low content of FW in all starches studied in their native state. The size effect which is mostly pronounced when the amount of FW in a starch-water system is small – up to 10% of the entire sample mass has been observed. The decrease of the peak temperature of the melting curve of FW with respect to that of bulk water can serve as a measure of water dispersion in starch granules. Further, the starting melting temperatures correspond to melting of the water clusters with minimal sizes, whereas  $T_{max}$  of the curve corresponds to melting of the clusters with the most probable sizes. The estimate of the formed water clusters' sizes has been performed.

In contrast to the native starches, this size effect has not been observed in the denatured starches with low water content. It has been found that it is masked by the appearance of additional FW resulting from a high-temperature heating necessary for a thermal destruction of the native granule in this case. Nonetheless, the experiment has shown that the transformation of water clusters, as a result of the starch denaturation, takes place. This transformation leads to an increase of the average size of the water clusters in the denatured starches as well as to a decrease of initial heterogeneity of the water distribution over the whole volume of a sample.

The dependences of the melting heat of FW on humidity obtained for both starch types evidence the redistribution of the relative amounts of frozen and unfrozen water (UFW) as a result of thermal destruction of native crystals. It has been shown that an increase of UFW in amorphous starches takes place. The non-linear character of the  $Q_m$  dependence of FW on the starch humidity, very pronounced in the denatured state and barely visible in the native one, allows one to conclude that there exist water nanoclusters in the investigated systems that have not only  $T_m$  but also  $Q_m$  lower than that of bulk water.

THERMODYNAMIC PROPERTIES OF KAOLINITE  $tr\text{-Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$   
AND DICKITE  $m\text{-Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  IN THE RANGE OF (0–350) K

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The investigation of mutual relations of the couple kaolinite-dickite [ $tr\text{-Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  and  $m\text{-Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ] has a great theoretical significance. The kaolinite-dickite stability region has been defined by geologists and chemists are contradictory. It is need to know the reliable thermodynamic properties of these minerals to resolve the contradictions. Our investigation is the contribution to the solution of this problem.

Heat capacities of kaolinite and dickite were measured by methods of adiabatic and relax calorimetry in the range 4.16–347.15 and 4.92–349.84 K, accordingly. Thermodynamic functions of these minerals were evaluated on the basis of experimental data in the temperature range 0–350 K. The specimens of kaolinite and dickite have the next compositions:  $\text{Al}_{2.017}\text{Si}_{1.969}\text{O}_5(\text{H}_{1.037}\text{O})_4$  and  $\text{Al}_{2.017}\text{Si}_{1.957}\text{O}_5(\text{H}_{1.034}\text{O})_4$ , respectively. Deviations of real compositions from ideal chemical formula can be attributed to errors of chemical analysis. Therefore calculations were carried out on the basis of the theoretical formula –  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . Thermodynamic functions of kaolinite and dickite at  $T = 298.15$  K are represented in Table. Our temperature dependence of kaolinite heat capacity  $C_p^0(T)$  is in good agreement with literature results [1]. The values of absolute entropy  $S^0(298\text{ K})$  are deviated by 1% ( $200.9 \pm 0.5$  and  $202.93 \pm 0.07$  J/(mol·K), accordingly). Thermodynamic properties of dickite compared with King and Weller data [2] have the considerable deviations. Discrepancies have systematic character. Our  $C_p^0(T)$  values are higher by 3–4%. Our and King's absolute entropies  $S^0(298\text{ K})$  values differ on 4%:  $204.96 \pm 0.20$  and  $197.1 \pm 1.3$  J/(mol·K). These deviations can be explained by a large amount of impurities in the King's sample.

**Table.** Thermodynamic functions of kaolinite and dickite at  $T = 298.15\text{ K}^*$

Compound	$C_p^0(298\text{ K})$ (J/(mol·K))	$S^0(298\text{ K})$ (J/(mol·K))	$H^0(298\text{ K}) - H^0(0)$ (kJ/mol)	$\Phi^0(298\text{ K})$ (J/(mol·K))
$tr\text{-Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	$244.94 \pm 0.06$	$202.93 \pm 0.07$	$35.833 \pm 0.006$	$82.75 \pm 0.07$
$m\text{-Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	$247.05 \pm 0.16$	$204.96 \pm 0.20$	$35.974 \pm 0.015$	$84.30 \pm 0.21$

\*Uncertainties of values are random errors.

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## Section 2. Thermodynamics of individual chemical compounds

### GIBBS ENERGY AND DISSOCIATION ENERGY OF Ti<sub>2</sub>

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The only experimental determination of the dissociation energy of the molecule Ti<sub>2</sub> given in the work [1], made by combination of the Knudsen method with the mass spectrometric analysis of evaporation products. The main result is a statement of the fact of registration in the saturated vapor of titanium not only atoms but also Ti<sub>2</sub> molecules (about 10<sup>-6</sup> of the total vapor pressure in the temperature interval 2122–337 K). Unfortunately, there was no information about the molecular constants for Ti<sub>2</sub>, and to calculate the Gibbs energy for Ti<sub>2</sub>(g), and to determine the dissociation energy with the III law of the thermodynamics, the authors [1] used estimations:  $\omega_e = 288 \text{ cm}^{-1}$  and  $r_e = 2.65 \text{ \AA}$ . Besides, the type of the electronic ground state for Ti<sub>2</sub> was not known. In [1] the calculations have been made with <sup>7</sup>Δ, values obtained using the II and III laws of thermodynamics are:  $D^{\circ}_0(\text{Ti}_2) = 118 \pm 17$  (II) and  $137 \pm 21$  (III) kJ·mol<sup>-1</sup>.

We performed the calculation of the thermodynamic functions for Ti<sub>2</sub>(g) on the basis of currently available data on the molecule Ti<sub>2</sub>: ground state <sup>3</sup>Δ [2–5], vibrational frequency 432 cm<sup>-1</sup> (matrix data [6, 7] and our estimation of matrix shift), equilibrium internuclear distance 1.94 Å [2, 3]. Spin-orbit splitting of the ground state, anharmonicity, centrifugal distortion, and vibration-rotation interaction were taken into account in the calculation of the thermodynamic functions, in accordance with the method described in the reference book "Thermodynamic properties of individual substances" [8]. Sixteen excited electronic states with energies < 10500 cm<sup>-1</sup>, observed experimentally and/or received in the quantum-mechanical calculations [5], are included in the calculation in addition to the ground state.

Recalculation of data [1] using the calculated thermodynamic functions leads to the values of  $D_0(\text{Ti}_2) = 146 \pm 40$  (II) and  $156 \pm 10$  (III) kJ·mol<sup>-1</sup>. Last value is recommended for using as more accurate. A serious difference in the errors of II law values obtained by us and in [1] can be explained by different estimation of the error. We have agreed on the level of confidence is 0.95; in [1] this value was not described. The difference in the III law dissociation energies obtained by us and in [1], largely due to the difference in the values of the Ti<sub>2</sub>(g) Gibbs energy.

The work [9] (registration of predissociation threshold in photodissociation spectra) provides value  $D_0(\text{Ti}_2) = 149 \pm 18 \text{ kJ}\cdot\text{mol}^{-1}$  from a combination of their own measurements of  $D_0(\text{Ti}_2^+) = 234.9 \pm 0.2 \text{ kJ}\cdot\text{mol}^{-1}$  with the values  $D_0(\text{Ti}_2) \geq 130.2 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\text{IE}(\text{Ti}_2) \leq 591.0 \pm 10 \text{ kJ}\cdot\text{mol}^{-1}$ , taken from [2] (resonant two-photon ionization spectroscopy).

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## SYNTHESIS, STRUCTURE AND PROPERTIES OF TRIPHENYLELEMENT CARBOXYLATES OF Sb(V) AND Bi(V)

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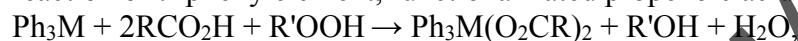
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Triphenylbismuth(V)- and triphenylantimony(V)-derivatives like acrylates, methacrylates, cinnamates, futylacrylates, nitrocinnamates, methoxycinnamates, crotonates contain two double C=C bonds within acrylate fragment. They can participate in polymerization process with polystyrene and polymethylmethacrylate to give metal-containing polymers.

Organometallic compounds mentioned above were synthesized according to oxidation addition reaction of triphenylelement, functionalized propenoic acid and peroxide [1]:



where  $\text{RCO}_2\text{H}$  = functionalized propenoic acid.  $\text{R}' = t\text{-Bu, H}$ .

The composition and the structure of  $\text{Ph}_3\text{Bi}(\text{O}_2\text{CR})_2$  were investigated with the methods of IR- and NMR-spectroscopy and X-ray diffraction. These organometallic compounds as a rule have structure of trigonal bipyramid with three phenyl groups in equatorial position and two acrylate fragments in axial positions [2].

Thermodynamic properties of some triphenylelement diacrylates have been studied [3, 4]. The thermal stability of the samples under study was investigated with the microbalance TG 209 *F1 Iris* (Netzsch, Germany). The significant mass lost was observed since  $T = 385$  K. Heat capacity of  $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCMe}=\text{CH}_2)_2$  was measured over the range from 6.31 to 331.76 K in a BKT-3.0 fully automatic adiabatic vacuum calorimeter. Liquid helium and nitrogen were used as cooling agents. The differential scanning calorimeter (DSC 204 F1 *Phoenix*, Netzsch, Germany) was used to investigate the thermal behavior of the compound under study over the range from 310 to 450 K. Heat capacity of triphenylantimony dimethacrylate was measured by precision adiabatic vacuum calorimetry over the temperature range from 6 to 335 K and by differential scanning calorimetry over the temperature range from 300 to 470 K. The melting of the sample was observed within the above temperature range. The melting was

accompanied by a compound decomposition. On the obtained data, the standard thermodynamic functions of molar heat capacity, enthalpy, entropy and Gibbs energy were calculated over the range from  $T \rightarrow 0$  to 400 K.

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## Section 2. Thermodynamics of individual chemical compounds

### PHASE TRANSITION, THERMAL BEHAVIOUR AND VIBRATIONAL DYNAMICS IN $[\text{Zn}(\text{NH}_3)_4](\text{ReO}_4)_2$

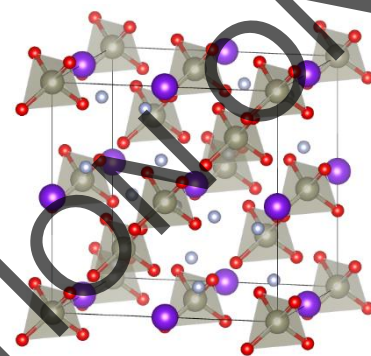
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Compounds of the type  $[\text{M}(\text{NH}_3)_4](\text{XY}_4)_2$  (where M = divalent metal cation, and  $\text{XY}_4$  = tetrahedral anion) are particularly interesting molecular materials because of the occurrence of different reorientational motions of the complex cations,  $\text{NH}_3$  ligands and anions. In these compounds the formation of hydrogen bonds is observed. Such compounds exhibit also an interesting polymorphism. At room temperature tetraamminazinc(II) rhenate(VII) crystallizes in cubic crystal system, space group  $Fm\bar{3}m$  (space group No. 216) with lattice parameter  $a = 10.53$  Å and four molecules per unit cell [1]. The high symmetry of the crystal lattice is possible because the  $\text{NH}_3$  groups, surrounding the central metal ion perform fast reorientational motions (measurable in picoseconds) around their threefold axis. Thus these crystals belong to the so-called dynamically, orientationally disordered crystals (ODIC). The differential scanning calorimetry revealed that tetraamminezinc(II) rhenate(VII) exhibits, in the temperature range of 595–100 K, one reversible phase transition at ca.  $T_C^h = 397.3$  K (upon heating) and at  $T_C^c = 388.0$  K (upon cooling). The following thermodynamic parameters for phase I  $\leftrightarrow$  phase II transition were obtained:  $\Delta H = 3.22 \pm 0.17$  kJ·mol<sup>-1</sup> and  $\Delta S = 8.10 \pm 0.43$  J·mol<sup>-1</sup>·K<sup>-1</sup>. The presence of 9.3 K hysteresis of the phase transition temperature at  $T_C$  and sharpness of the anomaly attests that the detected phase transition is of the first-order type. Decomposition of  $[\text{Zn}(\text{NH}_3)_4](\text{ReO}_4)_2$  compound can be divided into two main steps. The first step connected with the deammination can be further divided into two sub-steps. It is completed up to ca. 595 K. In the second step, the  $\text{Re}_2\text{O}_7$  is released above ca. 1220 K and zinc oxide is formed as a final product of decomposition. The variation of the activation energies of the deammination and decomposition steps of  $[\text{Zn}(\text{NH}_3)_4](\text{ReO}_4)_2$  was calculated through the model-free isoconversional Kissinger–Akahira–Sunose method and model-free Kissinger method. The model-free methods employed in this work are based on dynamic TG/DTG analysis as recommended by ICTAC Kinetics Committee [3]. The X-ray powder diffraction measurements performed by us revealed that down to 100 K crystal structure does not change. However in the middle infrared spectra (registered in the 300–9 K range) we have observed splitting of bands connected with internal vibration of  $\text{NH}_3$  groups in the low temperatures. Moreover splitting of lattice vibration mode was registered in the far infrared spectra. Appearing of a new band during cooling at ca. 3188 cm<sup>-1</sup> may be connected with slowing down of the  $\text{NH}_3$  reorientational motion and with the formation of a hydrogen bond at the low temperatures.



**Figure:** Unit cell of  $[\text{Zn}(\text{NH}_3)_4](\text{ReO}_4)_2$  at room temperature.

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HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF  $\text{Bi}_2\text{Sn}_2\text{O}_7$ 

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Pyrochlore-type bismuth tin oxide  $\text{Bi}_2\text{Sn}_2\text{O}_7$  is a material with well established and important catalytic and gas sensing properties, while information about their properties including thermal properties is extremely scarce.

The aim of this work was to study the high temperature heat capacity of  $\text{Bi}_2\text{Sn}_2\text{O}_7$  and to determine its thermodynamic properties on the basis of these data.

The  $\text{Bi}_2\text{Sn}_2\text{O}_7$  sample was synthesized by the solid-phase reaction method from the initial oxides  $\text{Bi}_2\text{O}_3$  and  $\text{SnO}$ . After preliminary annealing, these oxides were converted to a stoichiometric mixture, which after pressing was annealed in air at 1003 K for 30 h, intermittently with grinding and pressing every 5 h.

The samples were subjected to X-ray powder diffraction analysis using an X'Pert Pro instrument (Panalytical, The Netherlands) with  $\text{CuK}_\alpha$  radiation. At room temperature, a  $\text{Bi}_2\text{Sn}_2\text{O}_7$  sample had the lattice parameters:  $a = b = 15.1026(9)$  Å,  $c = 21.515(2)$  Å (sp. gr.  $I-4c2$ ).

The heat capacity  $C_p$  was measured in platinum crucibles by differential scanning calorimetry with an STA 449 C Jupiter (NETZSCH) in an inert atmosphere over the temperature interval (400–950) K.

The effect of temperature on the molar heat capacity of  $\text{Bi}_2\text{Sn}_2\text{O}_7$  crystals is illustrated graphically in Figure. The values of  $C_p$  grow regularly with increasing temperature, the  $C_p = f(T)$  curve exhibits an extremum which passes through a maximum at 898 K. In view of the literature data it was suggested, that in this region there is a transition  $\beta\text{-Bi}_2\text{Sn}_2\text{O}_7 \rightarrow \gamma\text{-Bi}_2\text{Sn}_2\text{O}_7$ . The clearly pronounced  $\lambda$ -shaped extremum may be evidence of second order transition. According to the experimental data the entropy of this phase transition was calculated, its value  $\approx 0.4$  J/(mol K).

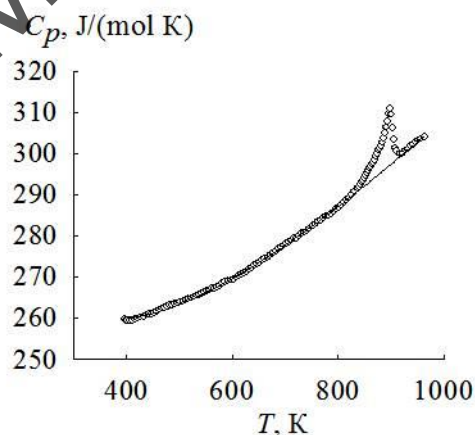
The dependence of heat capacity from temperature without phase transition (400–950 K) can be described by equation

$$C_p = 94.82 + 0.146 T - 0.0015 T^{-2} + 2133.53 T^{-0.5}$$

The presence of a temperature dependence of  $C_p$  allows to find the enthalpy  $H^0(T) - H^0(400 \text{ K})$ , entropy  $S^0(T) - S^0(400 \text{ K})$  and Gibbs reduced energy  $\Phi^0(T)$  according to the known thermodynamic equations. The calculation results are presented in Table.

**Table.** Thermodynamic functions of  $\text{Bi}_2\text{Sn}_2\text{O}_7$

$T, \text{ K}$	$C_p$ (J/(mol·K))	$H^0(T) - H^0(400 \text{ K})$ (kJ/mol)	$S^0(T) - S^0(400 \text{ K})$ (J/(mol·K))	$\Phi^0(T)$ (J/(mol·K))
500	263.2	26.12	58.28	6.04
600	269.5	52.74	106.8	18.90
700	277.6	80.09	148.9	34.52
800	287.0	108.3	186.6	51.23
900	297.3	137.5	221.0	68.22



**Figure:** Temperature dependence of the heat capacity of  $\text{Bi}_2\text{Sn}_2\text{O}_7$ .

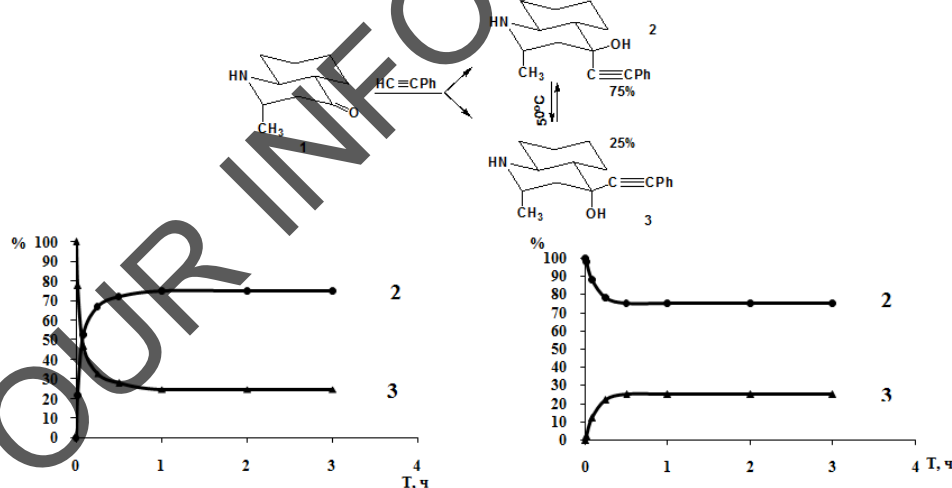
## Section 2. Thermodynamics of individual chemical compounds

### ISOMERIZATION-EQUILIBRATION IS THE METHOD OF THE DETERMINING OF SPATIAL STRUCTURES OF CYCLIC ETHYNYLCARBINOLS

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We previously elaborated the conditions of equilibration of stereoisomeric cyclic ethynylcarbinols, epimeric at the carbinol center [1]. It has been shown that the epimerization of stereoisomeric ethynylcarbinols can be used as a method of determination of the configuration of the quaternary carbinol center. It is known that the reaction of  $\beta$ -axial substituted saturated six-membered cyclic ketones with ethynyls leads to axial alcohols and the thermodynamically more stable equatorial alcohols are not formed or are obtained in very low yields. We have studied the isomerization-equilibration of 2a-methyl-4-phenylethynyl-4-hydroxy-decahydroquinoline (m.p. 151°C). According to the stereochemical rule of ethynylation of steric hindered cyclic ketones we proposed that phenylethynyl group in the structure of observed alcohol was situated in equatorial position and hydroxyl one was located in axial site. However the resulting mixture obtained after isomerization consisted of 75% alcohol (m.p. 151°C) and 25% of its epimer. This result indicated on the alcohol (m.p. 151°C) is the thermodynamically more stable isomer with equatorial hydroxy group. Therefore, it became necessary to revise its structure. Thus epimeric alcohol (m.p. 143°C) was preparatively isolated after isomerization of alcohol (m.p. 151°C) and both isomers were studied.



To establish the structure of 2a-methyl-4-phenylethynyldecahydroquinolinols-4 the complex methods were used. It has been shown that, the alcohol 2 (m.p. 151°C) is an equatorial, as opposed to the known rule of the preferred formation of axial alcohols in the case of hindered ketones ethynylation. And the alcohol 3 (m.p. 143°C) is its epimer at C<sub>4</sub> center. Furthermore, the isomerization of decahydroquinolinol 3 gave an equilibrium mixture in the same ratio (75% of the equatorial alcohol 2 and 25% of the axial epimer 3).

Thus, the reaction of isomerization-equilibration of ethynylcarbinols represents the developed methods of obtaining of minor stereoisomers. And equilibration of ethynylcarbinols can be used for determining of the configuration of quaternary carbinol center.

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## SOME UNRESOLVED PROBLEMS OF CRITICAL PHENOMENA

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In 1982 K.G. Wilson was awarded the Nobel Prize "for his theory for critical phenomena in connection with phase transitions". The theory exists, however, the deep unresolved issues remain. The key problem among them is the role of critical fluctuations. It is well known that there are two approaches to the problem of phase transitions and critical phenomena: the classic one (all theories named "mean-field"), in which the fluctuations of the order parameter (density in pure liquids) do not taken into account, and the second one (modern theories: Ising model, scaling and renormalization group), where the fluctuations play a decisive role. It is logically to assume that the first type of theories must be valid far from the critical point where there are no fluctuations, and the second type – near it, where the critical opalescence gives an evidence of multiple light scattering on large-scale density fluctuations. The transition from one theory to another is given, as is well known, by the Ginzburg criterion [1].

An analysis of the literature  $p\rho T$ -precision data showed, however, that this crossover in pure liquids has not been observed experimentally [2]. The system demonstrates a monotonic behavior of thermodynamic parameters: critical indices do not undergo any change, remaining precisely the same in the wide range of temperature and density changes. The critical indices here too show an universal behavior that differs, however, both from classical and Ising one [2]. Such a behavior was detected as early as 1900 [3]. Afterward, Guggenheim plotted the generalized coexistence curve of 8 pure liquids and paid attention that it was not agreed with the van-der-Waals equation, being not square-law and more likely a cubic parabola [4]. However, neither Guggenheim himself for whom this result was only a by-product of his analysis of the "principle of corresponding states", nor, unfortunately, those who subsequently quoted his work, have ignored the other surprising fact: the generalized coexistence curve was well approximated by a simple power dependence so far from the critical point that it captures both areas – fluctuation's area and distant from it [2].

It seems, that this "principle of corresponding states", apparently, gives to the critical point the special status, singled out by the Nature itself. This "principle" means that a system "feels" the own critical point very far from it. Another surprising fact: the thermal conductivity critical enhancement which is observed on the critical isochore for hundreds degrees from a critical point. The nature of these effects and feasible mechanisms of their realization are not clear up to now.

The change of static critical exponents in the immediate vicinity of the critical point towards their classical values has been discovered experimentally [5]. Later the similar results were obtained in the [6]. This transition was named the *second crossover* (to distinguish it from Ginzburg's crossover that sends the system toward the opposite direction) [2, 7, 8].

All these considered above unexpected facts are beyond any consistent theory of second order phase transitions and strongly call for further investigation.

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## Section 2. Thermodynamics of individual chemical compounds

### INTERACTION OF COMPONENTS IN THE Sb–Bi–Sm SYSTEM

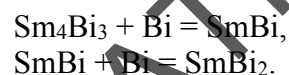
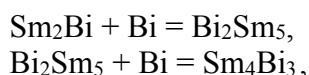
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The Sb–Bi–Sm ternary system is promising in terms of creating new thermoelectric materials. Isostructurality  $\text{SmSb}_2$  ( $\text{LaSb}_2$  structure type,  $t_m = 1372^\circ\text{C}$ ) and  $\text{SmBi}_2$  ( $\text{LaBi}_2$  structure type,  $t_m = 1297^\circ\text{C}$ ) compounds predetermine the formation of extended solid solutions in the system.

Interaction of components in the Sb–Bi–Sm system in sealed evacuated quartz ampoules was studied by DSC (Differential scanning calorimetry)-method. DSC was performed using the STA 449 F3 Jupiter with a heating rate of 5 K/min and in argon atmosphere. The accuracy of determines the melting enthalpy is 10–15%.

Interaction of components when they are in polycrystall state not occurs. Transition of bismuth in the liquid phase cause interaction with samarium crystal phase forming the  $\text{Sm}_2\text{Bi}$ . These reactions proceed with increasing of temperature:



In the sample composition Sm : Bi is 1 : 2 samarium is remain, which forms eutectic with  $\text{SmBi}_2$  phase.

Interaction between antimony and samarium at temperatures (680–800) $^\circ\text{C}$  proceeds as self-propagating high-temperature synthesis (SHS) and predominantly leads to the formation of a phase with given ratio of chemical elements in the charge (Figure).

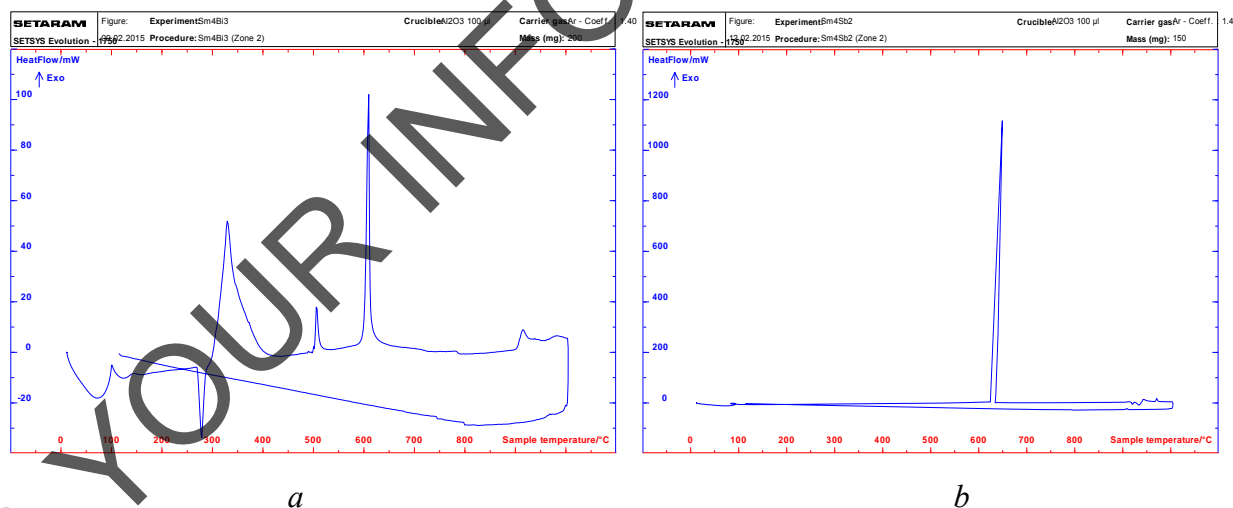


Figure: Thermograms of interaction between the elements Sm and Bi (a, 4 : 3) and Sm and Sb (b, 4 : 3).

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## THERMODYNAMIC PROPERTIES OF TRIPHENYLBISMUTH DICROTONATE

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The title compound belongs to the family of triphenylbismuth diacylates. Triphenylbismuth diacylates and triphenylantimony diacylates contain two double C=C bonds. Due to these bonds they can be used for copolymerization with polystyrene and polymethylmethacrylate. Triphenylbismuth dicrotonate is a very promising monomer for developing of metalcontaining organic scintillators which recently attracted much attention in the field of high-energy physics. It was found that the participation of both acrylate groups in polymerization leads to cross-linking considerably decreasing the thermooxidative destruction of the resulting polymer [1]. Thermodynamic properties of the triphenylantimony diacylates have been studied [2, 3]. The synthesis was carried out on the oxidation addition reaction of triphenylbismuth, crotonic acid and *tert*-butyl hydroperoxide:



The yellow crystals of triphenylbismuth dicrotonate were filtered off and dried. The yield was 73%. The product was recrystallized twice from chloroform–hexane mixture, m.p. 153°C. A crystal for X-ray diffraction analysis was obtained from benzene solution [4].

The temperature dependence of heat capacity of triphenylbismuth dicrotonate was studied by precision adiabatic vacuum calorimetry and differential scanning calorimetry over the temperature range from 6 to 450 K. It was revealed that above 350 K this compound melts. The melting was accompanied by a partial polymerization with subsequent decomposition of the sample. The low-temperature ( $20 \text{ K} \leq T \leq 50 \text{ K}$ ) heat capacity was analyzed using the Debye's heat capacity theory of solids and its multifractal version.

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## Section 2. Thermodynamics of individual chemical compounds

### HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF NOVEL NICKELITE-MANGANITE $\text{LaMg}_2\text{NiMnO}_6$ OVER THE RANGE OF (298.15-673) K

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The aim of this work is to study the thermodynamic properties of a novel nickelite-manganite composition  $\text{LaMg}_2\text{NiMnO}_6$ . The compound of the above composition was synthesized by ceramic technology with lanthanum oxide (III), which of "chemically pure", manganese oxide (III) and magnesium carbonate of qualification "analytical grade".

The isobaric heat capacity of compounds was investigated in a batch calorimeter IT-S-400. At each temperature (increments of 25 degrees) five experiments were conducted. The results are averaged. Standard deviation ( $\bar{\delta}$ ) and random error component ( $\Delta$ ) were calculated for the average values of the specific and molar heat capacities at each temperature. Table 1 shows that near 373 K and 573 K  $\text{LaMg}_2\text{NiMnO}_6$  has  $\lambda$ -shaped phase transitions of the second order.

**Table 1.** Experimental values of the heat capacity of cobalt-manganite  $\text{LaMg}_2\text{NiMnO}_6$  [ $C_{p(\text{spec.})} \pm \bar{\delta}$ , J/(g·K);  $C_p^{\circ(m)} \pm \Delta$ , J/(mol·K)]

T, K	$C_p \pm \bar{\delta}$	$C_p^{\circ} \pm \Delta$	T, K	$C_p \pm \bar{\delta}$	$C_p^{\circ} \pm \Delta$
298.15	0.828±0.0162	232±18	498	0.4476±0.0071	178±8
323	0.6447±0.0089	256±10	523	0.4911±0.0121	195±13
348	0.6716±0.0121	267±13	548	0.5478±0.0090	218±10
373	0.7012±0.0103	279±11	573	0.6234±0.0122	248±14
398	0.3352±0.0093	133±10	598	0.5228±0.0086	208±10
423	0.3712±0.0097	147±11	623	0.4744±0.0113	188±13
448	0.3956±0.0081	157±9	648	0.4881±0.0087	194±10
473	0.4133±0.0126	164±14	673	0.5152±0.0098	205±11

Taking into account the experimental data presented in Table 1, the equations of the temperature dependence of nickelite-manganite heat capacity were derived (Table 2).

**Table 2.** The equations of temperature dependence of the heat capacity of  $\text{LaMg}_2\text{NiMnO}_6$

Coefficients of the equation $C_p^{\circ} = a + bT + cT^2$ , J/(mol·K)			$\Delta T$ , K
a	$b \cdot 10^{-3}$	$-c \cdot 10^5$	
815.6±47.2	-(898.0±52.0)	-(281.0±16.3)	298-373
2447.3±141.5	-(5814.4±33.2)	-	373-398
-(817.4±47.3)	1591.6±92.1	502.2±29.0	398-573
925.9±53.6	-(1183.8±68.5)	-	573-623
-(13.7±0.8)	324.4±18.8	-	623-673

Then the temperature dependence of the thermodynamic functions  $S^{\circ}(T)$ ,  $H^{\circ}(T) - H^{\circ}(298.15)$  and  $\Phi^{\text{xx}}(T)$  were calculated.  $\Phi^{\text{xx}}(T)$  is a reduced Gibbs potential, which was calculated from 298.15 K.

STANDARD ENTHALPY OF SOLUTION OF THE BIOLOGICALLY ACTIVE  
SUBSTANCE COUMARIN – PEUTSEDANIN IN 96% ETHANOLSh.B. Kasenova<sup>1</sup>, G.K. Mukusheva<sup>2</sup>, B.K. Kasenov<sup>1</sup>, Zh.I. Sagintaeva<sup>1</sup>,  
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Among biologically active substances coumarins have been little studied. In this connection this work presents the results of calorimetric studies of the dissolution enthalpy of the biologically active substance coumarin – peutsedanin C<sub>15</sub>H<sub>14</sub>O<sub>4</sub> in 96% ethanol solution, which were obtained on a calorimeter DAK-I-IA. The ratio of moles of substance and ethanol were equal to 1 : 9000, 1 : 18000 and 1 : 36000. At each dilution five parallel experiments were performed. The results were averaged. The results of calorimetric studies are shown in Table.

**Table.** Enthalpy of dissolution of peutsedanin at various dilutions

№	Mass, g	$\Delta H_{\text{diss}}$ , J	$\Delta H^m_{\text{diss}}$ , kJ/mol
Peutsedanin in 96 % ethanol solution			
1:9000			
1	0.0024	0.316	34.00
2	0.0024	0.322	34.65
3	0.0024	0.323	34.76
4	0.0024	0.317	34.11
5	0.0024	0.328	35.30
Mean	$\Delta H^m_{\text{diss(I)}} = 34.56 \pm 0.66$		
1:18000			
1	0.0012	0.250	53.81
2	0.0012	0.246	52.95
3	0.0012	0.250	53.81
4	0.0012	0.254	54.67
5	0.0012	0.253	54.45
Mean	$\Delta H^m_{\text{diss(II)}} = 53.94 \pm 0.84$		
1:36000			
1	0.0006	0.179	77.05
2	0.0006	0.180	77.48
3	0.0006	0.177	76.19
4	0.0006	0.182	78.34
5	0.0006	0.181	77.91
Mean	$\Delta H^m_{\text{diss(III)}} = 77.39 \pm 1.03$		

From results of  $\Delta H^m_{\text{diss}}$ , shown in the Table, based on the known of dependence  $\Delta H^m_{\text{diss}} = a + e\sqrt{m}$  the dependence [J/mol] is derived:

$$\Delta H^m_{\text{diss}}(\text{C}_{15}\text{H}_{14}\text{O}_4) = 117.37 - 1734.03\sqrt{m}, \quad (1)$$

where  $m$  – molal concentration of peutsedanin C<sub>15</sub>H<sub>14</sub>O<sub>4</sub> at 96% ethanol solution.

The standard enthalpy of peutsedanin dissolution was calculated using equation (1). It is equal to 117.4±1.3 kJ/mole.



## Section 2. Thermodynamics of individual chemical compounds

### HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF NOVEL ZINCATE-MANGANITE $\text{LaCa}_2\text{ZnMnO}_6$ OVER THE RANGE OF (298.15–673) K

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This work presents the results of calorimetric studies of the heat capacity of novel zincate-manganite  $\text{LaCa}_2\text{ZnMnO}_6$ . The research was carried out with calorimeter IT-S-400 over the range of (298.15–673) K. Five parallel experiments were done at each temperature (increments of 25 degrees). The results were averaged and processed by the methods of mathematical statistics. The isobaric heat capacity of compounds was investigated in a batch calorimeter IT-S-400. At each temperature (increments of 25 degrees) five experiments were conducted. The results are averaged. Standard deviation ( $\bar{\delta}$ ) and random error component ( $\overset{\circ}{\Delta}$ ) were calculated for the average values of the specific and molar heat capacities at each temperature. Table 1 shows that near 348 K  $\text{LaCa}_2\text{ZnMnO}_6$  has a  $\lambda$ -shaped phase transition of the second order.

**Table 1.** Experimental values of the heat capacity of zincate-manganite  $\text{LaCa}_2\text{ZnMnO}_6$

$[C_{p(\text{spec.})} \pm \bar{\delta}, \text{J}/(\text{g} \cdot \text{K}); C_p^{\circ}(\text{m}) \pm \overset{\circ}{\Delta}, \text{J}/(\text{mol} \cdot \text{K})]$

$T$ (K)	$C_p \pm \bar{\delta}$	$C_p^{\circ} \pm \overset{\circ}{\Delta}$	$T$ (K)	$C_p \pm \bar{\delta}$	$C_p^{\circ} \pm \overset{\circ}{\Delta}$
298.15	0.4911 ± 0.041	214 ± 14	498	0.4474 ± 0.0116	195 ± 14
323	0.5365 ± 0.0183	236 ± 22	523	0.4848 ± 0.0166	211 ± 20
348	0.5803 ± 0.0139	253 ± 17	548	0.5076 ± 0.0140	221 ± 17
373	0.5684 ± 0.0175	248 ± 21	573	0.5245 ± 0.0142	228 ± 17
398	0.5466 ± 0.0171	238 ± 21	598	0.5498 ± 0.0139	239 ± 17
423	0.5102 ± 0.0159	222 ± 19	623	0.5758 ± 0.0144	251 ± 17
448	0.4570 ± 0.0141	199 ± 17	648	0.5811 ± 0.0116	253 ± 14
473	0.4075 ± 0.0144	177 ± 18	673	0.5991 ± 0.0123	261 ± 15

Taking into account the experimental data presented in Table 1, the equations of the temperature dependence of zincate-manganite heat capacity were derived (Table 2).

**Table 2.** The equations of temperature dependence of the heat capacity of  $\text{LaCa}_2\text{ZnMnO}_6$

Coefficients of the equation $C_p^{\circ} = a + bT + cT^2$ (J/(mol·K))			$\Delta T$ (K)
$a$	$b \cdot 10^{-3}$	$-c \cdot 10^5$	
-(17.5 ± 1.4)	776.3 ± 60.2	-	298–348
1156.9 ± 89.7	-(1721.7 ± 133.5)	-(369.5 ± 28.7)	348–473
395 ± 30.6	-(60.7 ± 4.7)	-(422.5 ± 32.8)	473–673

Then the temperature dependence of the thermodynamic functions  $S^{\circ}(T)$ ,  $H^{\circ}(T) - H^{\circ}(298.15)$  and  $\Phi^{\text{xx}}(T)$  were calculated.  $\Phi^{\text{xx}}(T)$  is a reduced Gibbs potential, which was calculated from 298.15 K.

HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF  
COBALT-MANGANITE  $\text{LaNa}_2\text{CoMnO}_5$  OVER THE RANGE OF (298.15–673) KB.K. Kasenov<sup>1</sup>, M.O. Turtubaeva<sup>2</sup>, Sh.K. Amerkhanova<sup>1</sup>,  
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This work presents the results of calorimetric studies of the heat capacity of novel cobalt-manganite  $\text{LaNa}_2\text{CoMnO}_5$ . The research was carried out with calorimeter IT-S-400 over the range of (298.15–673) K. Five parallel experiments were done at each temperature (increments of 25 degrees). The results were averaged and processed by the methods of mathematical statistics [1].

**Table 1.** Experimental values of the heat capacity of cobalt-manganite  $\text{LaNa}_2\text{CoMnO}_5$  [ $C_{p(\text{spec.})} \pm \bar{\delta}$ ,  $J/(g \cdot K)$ ;  $C_p^0 \pm \Delta$ ,  $J/(mol \cdot K)$ ];  $\bar{\delta}$  is a standard deviation,  $\Delta$  is a random error component

$T$ (K)	$C_p \pm \bar{\delta}$	$C_p^0 \pm \Delta$	$T$ (K)	$C_p \pm \bar{\delta}$	$C_p^0 \pm \Delta$
298.15	0.5957±0.0130	226±14	498	0.7147±0.0107	271±11
323	0.6322±0.0081	240±9	523	0.6459±0.0163	245±17
348	0.6450±0.0121	244±13	548	0.6078±0.0182	230±19
373	0.6789±0.0104	257±11	573	0.5711±0.0098	216±10
398	0.6964±0.0153	264±16	598	0.5401±0.0095	205±10
423	0.7420±0.0117	281±12	623	0.5696±0.0051	216±5
448	0.7801±0.0099	296±10	648	0.6185±0.0120	234±13
473	0.8181±0.0173	310±18	673	0.6882±0.0115	261±12

Near 473 K  $\text{LaNa}_2\text{CoMnO}_5$  has a  $\lambda$ -shaped phase transition of the second order. The equations of temperature dependence of the heat capacity have been derived (Table 2), taking into account our experimental data.

**Table 2.** The equations of temperature dependence of the heat capacity of  $\text{LaNa}_2\text{CoMnO}_5$

Coefficients of the equation $C_p^0 = a + bT + cT^2$ , J/(mol·K)			$\Delta T$ (K)
$a$	$b \cdot 10^{-3}$	$-c \cdot 10^5$	
(7.7±0.4)	634.0±32.0	39.4±2.0	298–473
(405.2±20.4)	537.6±27.1	1030.9±51.9	473–598
(2799.0±141.0)	3426.4±172.6	3413.4±171.9	598–673

Further, the temperature dependences of thermodynamic functions  $S^\circ(T)$ ,  $H^\circ(T) - H^\circ(298.15)$  and  $\Phi^{\text{xx}}(T)$  of cobalt-manganite  $\text{LaNa}_2\text{CoMnO}_5$  were calculated from the experimental data of  $C_p^0 \sim f(T)$  and the calculated value of  $S^\circ(298.15)$ . When evaluating the errors of functions  $S^\circ(T)$  and  $\Phi^{\text{xx}}(T)$  the estimation error of  $S^\circ(298.15)$  ( $\sim 3.0$ ) were taken into account.  $\Phi^{\text{xx}}(T)$  – reduced Gibbs potential, which was calculated from 298.15 K.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMODYNAMIC CHARACTERISTICS OF PHASE TRANSITIONS IN THE SPINELS

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Materials with the spinel structure have been extensively studied for a range of applications including their use as inorganic pigments [1], component of Mixed-Oxide (MOX) fuel for atomic energy, ion conductors, Li-battery electrodes, and for production of heat-insulated materials and materials for microelectronics. The goal of this work includes calorimetric determination of the temperature dependences of the heat capacity of  $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  and  $\text{Co}_{7/3}\text{Sb}_{2/3}\text{O}_4$  from 6 to 330 K, detection of the possible phase transitions, and calculation of the standard thermodynamic functions in the range from 0 to 330 K. To measure the heat capacity of the tested substances in the range from 6 to 330 K a BKT-3.0 automatic precision adiabatic vacuum calorimeter with discrete heating was used. The heat capacity of  $\text{LiMn}_2\text{O}_4$  in intervals from 6 to 240 and from 304 to 347 K gradually increases with rising temperature and does not show any peculiarities, but from 240 to 304 K there is seen an anomalous heat capacity ( $T_{\text{tr}} = 286.0 \pm 0.1$  K) [2]. The standard enthalpy and entropy of phase transition are  $\Delta_{\text{tr}}H^\circ = 1157 \pm 2$  J/mol and  $\Delta_{\text{tr}}S^\circ = 4.045 \pm 0.040$  J/(mol·K). A reversible phase transition is associated with partial charge ordering and accompanied orbital ordering due to the Jahn–Teller effect in  $\text{Mn}^{3+}$  ions. The observed changes in the Raman and IR spectra as function of temperature indicate that  $\text{LiMn}_2\text{O}_4$  undergoes a phase transition into a lower symmetric phase. Indeed, our X-ray diffraction data show clear evidence of the cubic to orthorhombic phase transition around 286 K. The heat capacity of  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  in interval from 12 to 670 K gradually increases with rising temperature and does not show any peculiarities, but over the range from 6 to 12 K there is seen an anomalous heat capacity ( $T_{\text{tr}} = 7.5 \pm 0.1$  K) [3]. The heat capacity of  $\text{Co}_{7/3}\text{Sb}_{2/3}\text{O}_4$  in intervals from 6 to 55 and from 70 to 327 K gradually increases with rising temperature and does not show any peculiarities, but from 55 to 70 K there is seen an anomalous heat capacity ( $T_{\text{tr}} = 60.3 \pm 0.1$  K) [4]. The standard enthalpy and entropy of phase transition are  $\Delta_{\text{tr}}H^\circ = 15.8 \pm 0.5$  J/mol and  $\Delta_{\text{tr}}S^\circ = 0.258 \pm 0.007$  J/(mol·K). The magnetization measurements of the  $\text{Co}_{7/3}\text{Sb}_{2/3}\text{O}_4$  compounds revealed the presence of a spin-glass transition, which should be a result of the competition between several magnetic interactions depending on the  $\text{Co}^{2+}$  site occupation. It should be noted that the spinel, containing *d*-metals in their composition, often observed transitions at temperatures below 70 K. There are at least two factors related to the spin-glass transition: (a) a competition between the diamagnetic  $\text{Sb}^{5+}$  and the ferromagnetic  $\text{Co}^{2+}$  ions both occupying the same crystallographic site; (b) the different crystallographic sites occupied by the  $\text{Co}^{2+}$  ions, as we observe in the structural analysis.

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## THERMODYNAMICS OF COMPOUNDS WITH RADIONUCLIDES

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Since the inception of chemical thermodynamics one of the most important tasks of this science is to determine the standard thermodynamic functions of individual substances. Such data are required primarily for calculating equilibrium chemical reactions at various temperatures and pressures. The enthalpies of formation of about 250 inorganic compounds containing uranium were experimentally determined for the first time using a reaction adiabatic calorimeter. The temperature dependences of heat capacities at constant pressure for more than 50 compounds in a temperature interval from 7 to 350 K were studied in an adiabatic vacuum calorimeter [1–6]. The obtained data allowed describing possible phase transitions and calculating standard entropies of formation of the compounds. It is significant to note that heat capacities at constant pressure of the majority complex oxides monotonously grow with rising temperature without any visible anomalies. On the contrary, the physical transitions are observed in uranylcarbonates, uranylsulfates, potassium dithorium trisphosphate, several tungstates and spinels. The description of transitions was made by means of McCallaf–Vestrum classification of physical transitions. According to this classification phenomenological all phase transitions in solids can be categorized into seven types (I, 2I, 3I, 2N, 3N, G, H). The most widespread type of transitions in the layered compounds is isothermal (I) transitions connected with polymorphic transitions in the crystal. The polymorphism is caused by possible shifts or rotations of layers relatively to each other in the crystalline structure. Isothermal transitions are seen as “peaks” on the curve of heat capacity; the area of “peaks” is numerically equal to the enthalpy of phase transition. The physical transitions, which are more rarely met with, are H-transitions and they are observed as “humps” on the curve of heat capacity. According to physical point of view the given anomaly may be connected with “defreezing” of rotations around M–OH<sub>2</sub> bond in structures of the appropriate crystallohydrates. The compounds Na<sub>4</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and K<sub>2</sub>Fe<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub> show the G-type (glass-like) of physical transitions. The nature of this anomaly is, probably, related to the presence of cation–cation interactions in the structure of this compound that is confirmed by us using Voronoi – Dirichle calculations of polyhedra with program complex TOPOS. Thus, the calorimetric methods allowed estimating all necessary thermodynamic functions of some inorganic compounds with radionuclides.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMODYNAMIC PROPERTIES OF SOME CESIUM CONTAINING PHOSPHATES OF TRIDYMITE STRUCTURE TYPE

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Interest in  $\beta$ -tridymite structure type phosphates  $\text{CsM}^{\text{II}}\text{PO}_4$  ( $\text{M}^{\text{II}}$  – divalent metal with a tetrahedral coordination), containing cesium in a high concentration and possessing chemical and radiation stability, is conditioned by an opportunity to use them as ceramic for  $^{137}\text{Cs}$   $\gamma$ -radiation sources of commercial and medical applications. Physical, chemical and thermodynamic properties of all these types of compounds depend strongly on their crystal structure. Only  $\beta$ -tridymite structure type is of interest in this study.  $\beta$ -tridymite crystal structures are three-dimensional frameworks composed of six-membered rings of vertex-sharing  $\text{M}^{\text{II}}\text{O}_4$  and  $\text{PO}_4$  tetrahedra and large cavities occupied by  $\text{Cs}^+$  cations [1]. As it is known [2], cesium containing phosphates with a  $\beta$ -tridymite structure have four polymorphs with analogous frameworks and different unit cell symmetries (two monoclinic with space groups  $P2_1$  and  $P2_1/a$ ; and two orthorhombic with space groups  $Pna2_1$  and  $Pnma$ ). An increase in temperature is often accompanied by phase transitions with an increase in symmetry:  $P2_1 \rightarrow P2_1/a \rightarrow Pna2_1 \rightarrow Pnma$ ; and the phase transformations between two monoclinic forms frequently occur below room temperature. Some of these compounds exhibit magnetic transitions at low temperatures. In the work the thermodynamic properties for the crystalline phosphates  $\text{CsM}^{\text{II}}\text{PO}_4$  ( $\text{M}^{\text{II}} = \text{Ni}, \text{Co}, \text{Mn}$ ) with  $\beta$ -tridymite structure type are reported. The samples were synthesized by the co-precipitation method. The phase purity of the sample was checked by powder X-ray diffraction. The homogeneity and chemical composition of the sample were confirmed by electron microprobe analysis. The heat capacities of the phosphates were measured using adiabatic and differential scanning calorimetry in the temperature range (6–650) K. Phase transitions of phosphates  $\text{CsM}^{\text{II}}\text{PO}_4$  ( $\text{M}^{\text{II}} = \text{Ni}, \text{Co}, \text{Mn}$ ) were discovered. The temperature dependence of the heat capacity of crystalline  $\text{CsMnPO}_4$  showed that for the phosphate two phase transitions were found at temperatures 6.9 and 127 K. They correspond to the order–disorder transition and the transition between monoclinic and orthorhombic modifications of  $\text{CsMnPO}_4$ , respectively. Three phase transitions were found at temperatures 311, 481 and 512 K for the  $\text{CsCoPO}_4$  phosphate. They correspond to the transitions between monoclinic and orthorhombic modifications of  $\text{CsCoPO}_4$  ( $P2_1 \leftrightarrow P2_1/a$ ,  $P2_1/a \leftrightarrow Pna2_1$ ,  $Pna2_1 \leftrightarrow Pnma$ , respectively). The investigation of samples by high-temperature X-ray powder diffraction and measurement of temperature dependence of the magnetic susceptibility of  $\text{CsMnPO}_4$  crystalline phosphate [3] allowed us to describe their nature. The transition functions (temperatures, enthalpies and entropies),  $C_{p,m}^{\circ}/R$ ,  $\Delta_0^T H_m^{\circ}/RT$ ,  $\Delta_0^T S_m^{\circ}/R$  and  $\Phi_m^{\circ}/R$  were calculated over the range of  $T = (0 \text{ and } 650)$  K from experimental data. Thermodynamic properties of all researched cesium containing  $\beta$ -tridymite structure type phosphates  $\text{CsM}^{\text{II}}\text{PO}_4$  ( $\text{M}^{\text{II}} = \text{Zn}, \text{Mg}, \text{Ni}, \text{Co}, \text{Mn}$ ), including literature data [1–3], were compared.

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**LOW-TEMPERATURE HEAT CAPACITY OF SYNTHETIC  
CARACOLITE  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$**

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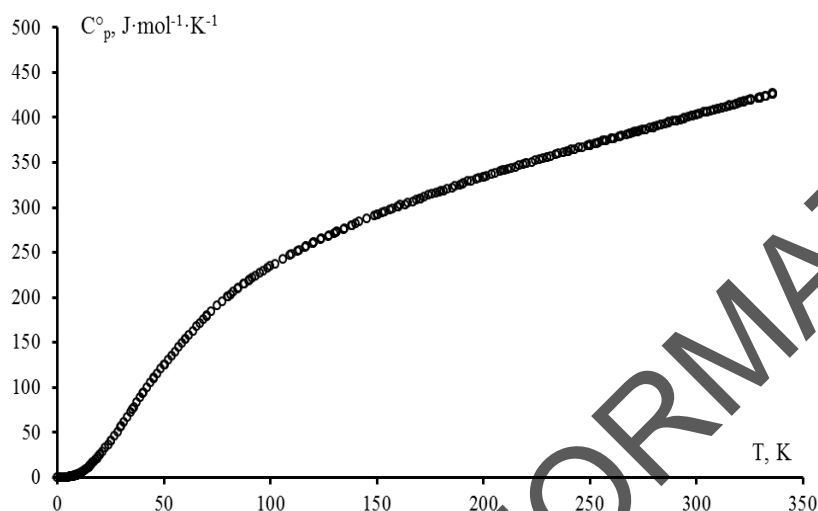
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The temperature dependences of trisodium dilead tris(sulfate(VI)) chloride  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$  heat capacity have been measured for the first time in the range from 6 to 336 K.  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$  is a synthetic analog of nature mineral caracolite of apatite structural class [1].

Last year apatites are of interest due to their huge range of possible applications. The most



**Figure:** Temperature dependence of heat capacity of caracolite  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$ .

important areas of using of apatites are production of bioceramic materials [2], solid oxide fuel cells (SOFC) [3], and sensors [4]. For structural investigations, an X-ray diffraction pattern of a  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$  sample was recorded on a Shimadzu X-ray diffractometer XRD-6000 ( $\text{CuK}_\alpha$  radiation, geometry  $\theta$ - $2\theta$ ) in the  $2\theta$  range from  $10^\circ$  to  $60^\circ$  with scan increment of  $0.02^\circ$ . The X-ray data and

estimated impurity content (0.5–1 % mass) in the substance led us to conclude that the studied sample was an individual crystalline compound. Thermal experiments were carried out on a LABSYS Setaram with a heating rate of  $10 \text{ K} \cdot \text{min}^{-1}$ . To determine the elemental (cation) composition of the solution of  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$  in nitric acid atomic absorption spectrophotometer AA-6300 Shimadzu with graphite atomizer GFA-EX7i Shimadzu and the automatic feed samples ASC-6100 Shimadzu was used. To measure the heat capacity  $C_p^\circ$  of the tested substance in the range from 6 to 336 K a BKT-3.0 automatic precision adiabatic vacuum calorimeter with discrete heating was used.

There was obtained 233 experimental  $C_p^\circ$  values in two series of experiments. To calculate the standard thermodynamic functions (heat capacity  $C_p^\circ(298.15) = 401.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , enthalpy  $H^\circ(298.15) - H^\circ(0) = 76.81 \text{ kJ} \cdot \text{mol}^{-1}$ , entropy  $S^\circ(298.15) = 540 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , and Gibbs energy  $-[G^\circ(298.15) - H^\circ(0)] = 84.21 \text{ kJ} \cdot \text{mol}^{-1}$ ) of trisodium dilead tris(sulfate(VI)) chloride, its  $C_p^\circ$  values were extrapolated from the starting temperature of the measurement to  $T \rightarrow 0 \text{ K}$  by Debye's function of heat capacity ( $\theta_D(\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}) = 120 \text{ K}$ ). The absolute entropies of  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$  and the corresponding simple substances  $\text{Na}(\text{cr})$ ,  $\text{Pb}(\text{cr})$ ,  $\text{S}(\text{cr})$ ,  $\text{O}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$  were used to calculate the standard entropy of formation of the compound under study at 298.15 K:  $\Delta_f S^\circ(298.15, \text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}, \text{cr}) = -1182.1 \pm 1.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .

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## Section 2. Thermodynamics of individual chemical compounds

### ENTHALPIES OF FORMATION OF ACYCLIC SATURATED HALOGEN-CONTAINING RADICALS

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Enthalpy of formation at normal conditions ( $\Delta_f H^0$ ) is a key thermodynamic attribute of chemical compounds. At present time, the extensive database of  $\Delta_f H^0$  of molecules has been created. In many biological and technological processes the free radicals ( $R^\bullet$ ) play a very important role. Unlike molecules, in most cases, radicals  $R^\bullet$  possess a high reactivities and short lifetimes. Such properties of  $R^\bullet$  make difficult to measure their physicochemical properties.

The classical method of finding  $\Delta_f H^0$  of the substances is the calorimetric method, but it is practically unusable for finding  $\Delta_f H^0(R^\bullet)$  because of high reactivity of  $R^\bullet$ . Under such conditions, the use of the theoretical methods of prediction  $\Delta_f H^0$  (for example, quantum-chemical calculations) becomes very relevant. Nevertheless, the employing of the quantum chemistry in order to determine  $\Delta_f H^0(R^\bullet)$  has some drawbacks. So, when the number of atoms increases as well as the heavy atoms are added to the compounds (from III or next periods of the periodic table) the accuracy of the calculation is significantly reduced and that calculation becomes more expensive. Therefore, such methods is unusable for computing of the  $\Delta_f H^0$  big compounds.

Series of the free halogen-containing radicals were examined in this work. To data, the existing fund of the  $\Delta_f H^0$  acyclic saturated halogen-containing organic radicals has more than 85 values [1, 2]. During our work we have calculated  $\Delta_f H^0(R^\bullet)$  for some new halogen-containing organic radicals and have refined the known values of  $\Delta_f H^0(R^\bullet)$ .

All calculations were performed by the equation (1):

$$\Delta_f H^0(R^\bullet) = D(R-X) - \Delta_f H^0(X) + \Delta_f H^0(RX), \quad (1)$$

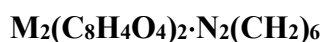
where X = H, F, Cl, Br, I, their atomic enthalpies of formation at 298° K are equal to:  $\Delta_f H^0(\text{H}) = 218$  kJ/mol,  $\Delta_f H^0(\text{F}) = 79.39$  kJ/mol,  $\Delta_f H^0(\text{Cl}) = 121.3$  kJ/mol,  $\Delta_f H^0(\text{Br}) = 111.87$  kJ/mol,  $\Delta_f H^0(\text{I}) = 106.76$  kJ/mol. Set of the auxiliary  $\Delta_f H^0(RX)$  values has been specified. So, the values of 26 enthalpy of formation of halogen-containing organic radicals have been found, that resulted in increasing in more than 30% the database of this compounds.

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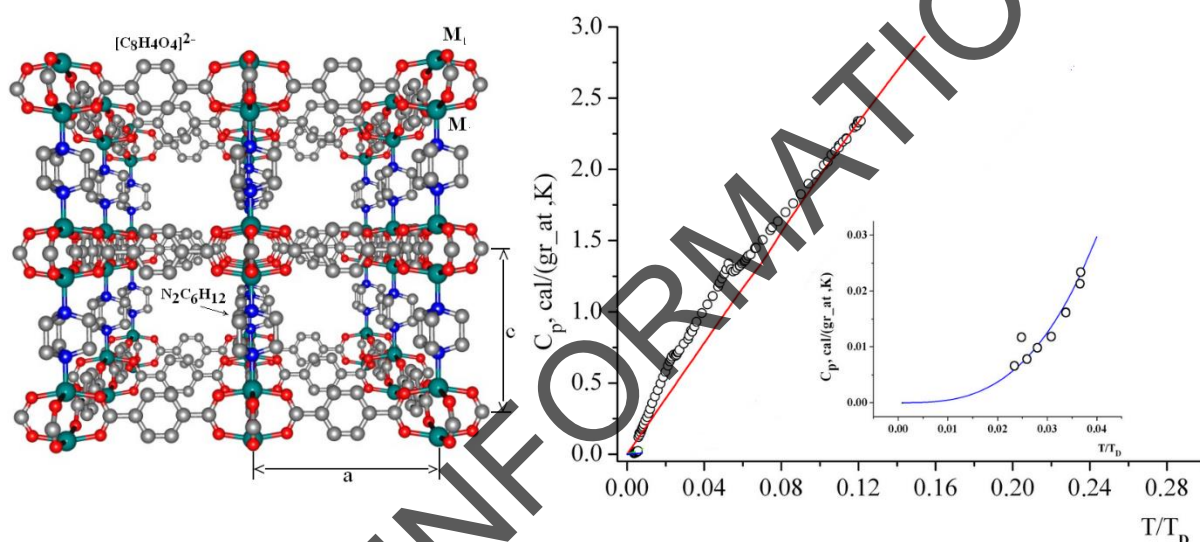
## THERMODYNAMIC PROPERTIES OF HIGH POROUS COMPOUND



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Crystal structure of high-porous metal-organic sorbent  $M_2(C_8H_4O_4)_2 \cdot N_2(CH_2)_6$  is made up of tetragonal 2D-layers  $M(C_8H_4O_4)$  intermitted by molecular ligands  $N_2(CH_2)_6$  ( $M = Co, Ni, Cu, Zn$ ). The crystal symmetry is tetragonal, space group  $P4/mmm$ ,  $a = 10.929$  and  $c = 9.608$  Å,  $Z = 1$  [1]. The figure shows the arrangement of metal  $M^{2+}$  cations, terephthalate anions  $[C_8H_4O_4]^{2-}$ , and ligand molecules of 1,4-diazabicyclo[2,2,2]octane  $N_2(CH_2)_6$ .



**Figure:** The structure of  $M_2(C_8H_4O_4)_2 \cdot N_2(CH_2)_6$  (left) and specific heat ( $C_p$ ) of the compound  $Zn_2(C_8H_4O_4)_2 \cdot N_2(CH_2)_6$  (right).

In this work we report data on thermodynamic properties of  $M_2(C_8H_4O_4)_2 \cdot N_2(CH_2)_6$  studied at (8–300) K using low-temperature adiabatic calorimetry. Three phase transitions were observed at low temperatures. It is shown that specific heat of the compound obeys the classical Debye law  $C_p \sim T^3$  only below 20 K, whereas above 20 K it is proportional to the first degree of temperature,  $C_p \sim T$ , to indicate strong anisotropy of crystal vibrations corresponding to 1D vibration continuum. The observed linear dependence of heat capacity may be related to the influence of vibrations in chains of  $-M-M-N_2(CH_2)_6-M-M-$ . The interaction between chains of  $-M-M-N_2(CH_2)_6-M-M-$  via  $[C_8H_4O_4]^{2-}$  terephthalate anions leads to formation of a three-dimensional structure of the crystal below 20 K. The discovered phase transitions are related to the order–disorder processes in the sublattice of twisted and untwisted  $N_2(CH_2)_6$  molecules.

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## Section 2. Thermodynamics of individual chemical compounds

### PHASE TRANSITION AND THERMODYNAMIC PROPERTIES OF SOME AURIVILLIUS PHASES

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Bismuth-containing layered ferroelectrics are known as the Aurivillius phases have been the subject of researchers' increasing attention for their ferroelectric properties. The general formula of such compounds can be represented as  $A_{m-1}Bi_2B_mO_{3m+3}$ , where  $m$  is typically from 1 to 5 and can take fractional values. Their structure have studied in detail in [1]. Most of them undergo phase transition from ferroelectric (with several symmetry-equivalent versions of structure) into paraelectric phase (with only type of structure) on heating. Last phase transition correspond to the Curie temperature. The compounds  $Bi_2MoO_6$  ( $m = 1$ ),  $Bi_3NbTiO_9$  ( $m = 2$ ),  $Bi_4Ti_3O_{12}$  ( $m = 3$ ),  $BaBi_4Ti_4O_{15}$  ( $m = 4$ ),  $Ba_2Bi_4Ti_5O_{18}$  ( $m = 5$ ) and  $Bi_5Nb_3O_{15}$  ( $m = 1.5$ ),  $Bi_7Ti_4NbO_{21}$  ( $m = 2.5$ ),  $CaBi_8Ti_7O_{27}$  ( $m = 3.5$ ) have been synthesized by solid state reactions.  $Bi_4V_2O_{11}$  is the corresponding intrinsic oxygen deficient compound  $(Bi_2O_2)(VO_{3.5}\square_{0.5})$  and exhibits, versus temperature, three main polymorphs:  $\alpha$  monoclinic,  $\beta$  orthorhombic and  $\gamma$  tetragonal. The  $\alpha$ -polymorph is stable from room temperature up to 723 K,  $\beta$  between 790 K and 850 K and  $\gamma$  - above 850 K up to the melting point around 1140 K. Phase transitions have been studied with differential scanning calorimetry together with high-temperature X-ray diffraction. For  $Bi_4Ti_3O_{12}$  were carried out calorimetric determination of the

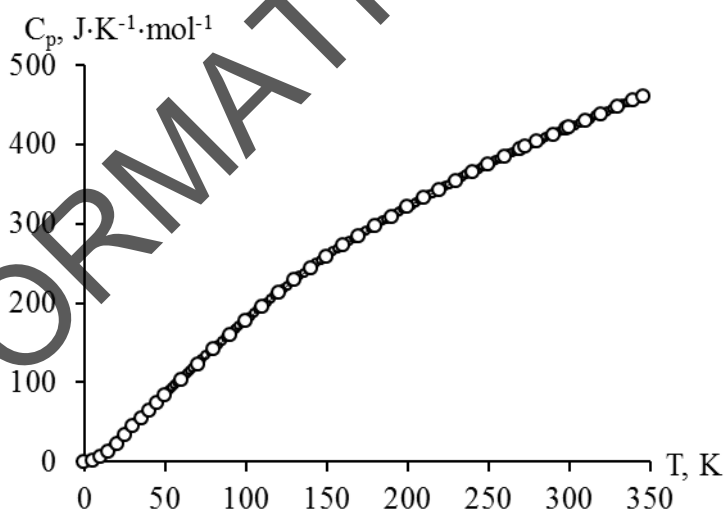


Figure: Temperature dependence of heat capacity of  $Bi_4Ti_3O_{12}$ .

temperature dependence of the heat capacity  $C_p^o = f(T)$  from 7 to 346 K (Figure), and calculation of the standard thermodynamic functions in the range from  $T \rightarrow 0$  to 346 K. The heat capacity of this substance in interval from 7 to 346 K gradually increases with rising temperature and does not show any peculiarities. To calculate the standard thermodynamic functions of the tetrabismuth trititanium oxide, its  $C_p^o$  values were extrapolated from the temperature of the measurement beginning (approximately 7 K) to 0 K by graphic method. The absolute entropies of tetrabismuth trititanium oxide and the corresponding simple substances ( $Bi(cr)$ ,  $Ti(cr)$  and  $O_2(g)$ ) were used to calculate the standard entropy of formation of the compound under study at 298.15 K:

$$\Delta_f S^o(298.15, Bi_4Ti_3O_{12}, cr) = -1086.6 \pm 0.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

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FEATURES OF PHASE TRANSITIONS TERMODINAMIC  
IN LANTANIDOMESOGENS

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Thermotropic liquid crystals (LC) are widely used as anisotropic liquid medium in various optical devices. Introduction of lanthanide ion into the liquid crystal molecules lets to enlarge the possibility of using of liquid crystalline mesophases orientation behavior and approach to the creation of multifunctional materials with unusual magnetic and optical properties.

In this work we have studied a series of lanthanide complexes (Figure 1) showing the smectic mesomorphism in the temperature range from 140 to 240°C.

Thermodynamics of phase transitions was studied by methods of polarized polythermal microscopy and differential scanning calorimetry. Upon cooling, the complexes form a vitrified film with saved molecular packing defined in the mesophase [1]. This is evidenced by the absence of peaks in the DSC curve upon cooling (Figure 2) and the observation of vitrified smectic mesophase texture by polarized microscope at room temperature. The obtained complexes of europium and samarium have effective luminescence with a peak wavelength of 613 and 650 nm (at  $T = 25^\circ\text{C}$ ), respectively. Thus, the possibility of the creation of supramolecular-organized luminescent materials with specific packing of the molecules in a wide range of temperatures, including room temperature was shown.

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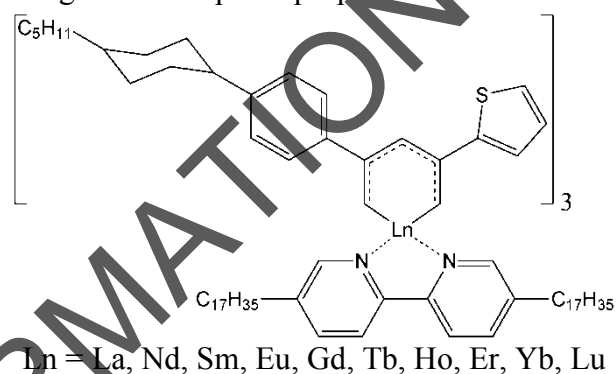


Figure 1: The structure of LC lanthanide complexes.

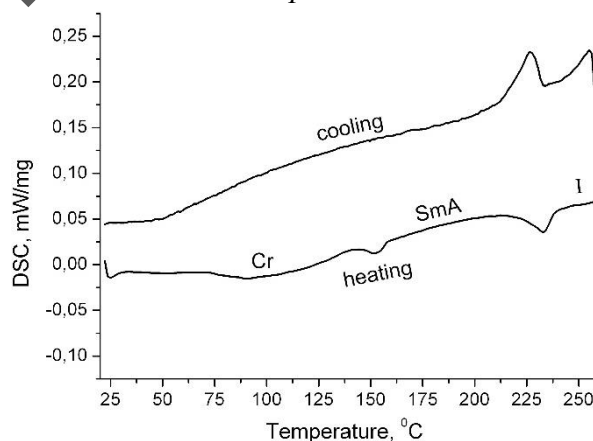


Figure 2: Typical DSC thermogram of the gadolinium(III) complex during heating and cooling.

## Section 2. Thermodynamics of individual chemical compounds

### MOLECULAR AND ION SUBLIMATION OF HALIDE LANTHANIDE. THERMODYNAMIC PROPERTIES

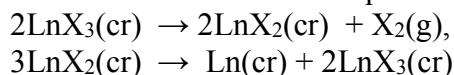
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Determination of thermodynamic properties of lanthanide halides for several decades remains a priority of research in the chemistry of lanthanides. Activity in this area has increased significantly at the beginning twenty-first century in connection with the more and more expanding fields of application of these promising compounds.

A present report provides a review of available literature data on the vaporization thermodynamics of the di- and trichloride, bromide and iodide lanthanides together with the new systematic investigations, carried out in the high temperature mass spectrometry laboratory of Ivanovo State University of Chemistry and Technology.

Most of lanthanide compounds are in the trivalent state, but some of them are stable in two and four valence state. Unusual oxidation degree of lanthanide leads to the fact that at high temperatures the reaction of decomposition and disproportionation



may occur. As a result, the composition of the gas and condensed phase does not remain constant and therefore the use of the traditional approach on the base of the second and third laws of thermodynamics for determining the sublimation enthalpies for thermally unstable compounds becomes problematic. Most authors, who have studied the vaporization of  $\text{LnX}_2$  and  $\text{LnX}_3$ , did not pay this enough attention. But ignoring these reactions can leads to errors in the thermodynamic data obtained. To clarify this problem, along with traditional research the special experiments have been also conducted in our laboratory.

A magnetic sector-type mass spectrometer MI1201 ( $\angle 90^\circ$ , curvature radius of 200 mm), modified for high temperature studies, was used. A unique ion source allowed work in two regimes: 1) the regime of ionization by electrons (for analysis of neutral species) and 2) the regime of thermionic emission (analysis of charged vapor components). In the latter case the ions are formed at the working temperatures inside the effusion cell and extracted from it by a weak electric field (about  $10^5$  V/m). Samples of lanthanide halides were evaporated from the molybdenum or graphite effusion cells (the ratio of evaporation area to the area of the effusion orifice was about 400).

The peculiarity of the given cycle works, in contrast to the previous ones, are as follows:

- the study not only the molecular, but the ion sublimation has been also carried out,
- determination of the thermodynamic characteristics of molecules and ions for the thermally unstable lanthanides has been made using alternative technique, based on the measurement of the ion appearance energies,
- the molecular and ion sublimation under conditions of evaporation from the open surface (Langmuir's method) has been performed additionally.

Proposed method of determining the thermodynamic parameters of molecules and ions for thermally unstable compounds is based on measuring the ion appearance energy by the modified extrapolated difference technique. Using a suitable standard, method permits determine the ion appearance energy and then calculate the energy characteristics (energy dissociation, atomization energy, enthalpy formation et al.) molecules and ions.

## MELTING CURVE ESTIMATION FOR REFRACTORY METALS

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The approach to melting curves estimation for refractory metals is proposed. The pertinent procedure starts from the dataset on caloric properties of the solid phase. Here this method was used for platinum metals group (Ru, Ir, Os), because of high precision measurements of enthalpy  $H_T^0 - H_{298}^0$  for the main elements of this group have been carried out at the Institute for High Temperatures [1]. First of all we applied the quasi thermodynamic relation following from the Debye–Grüneisen theory of the crystal lattice [2] for the correlation between the metal caloric properties and its thermal expansion coefficient

$$\beta(T) = \frac{C_p^0(T)}{Q_0 \left[ 1 - 2(H_T^0 - H_0^0) / \Delta H_{subl}^0 \right]}, \quad (1)$$

involving only one adjustable constant  $Q_0$  and the measured values of the isobaric heat capacity and the enthalpy. By this means, thermal expansion coefficient and volume of solid phase up to melting point have been estimated. The correlation of the volume jump at the melting point with a number of other variables

$$\frac{\beta(T_m) V_s(T_m) T_m \Delta S_m}{C_p^0(T_m) \Delta V_m} = \mu = 0.6 \quad (2)$$

may be used taking into account the similarity within the platinum metals group, i.e. between the refractory metals and metals with low melting point (Pt, Pd, Rh). Both correlations [(1), (2)] provide thermodynamic consistency of the thermal properties of refractory metals. As a result, the Clausius–Clapeyron equation provides the rigorous value of the melting curve initial slope (Table).

**Table.** Basic parameters of melting point, including MCIS\*

Metal	$T_m$ (K)	$\Delta V_m$ (cm <sup>3</sup> /mol)	$\Delta S_m$ (J/(mol·K))	MCIS (K/GPa)
Ru	2606	0.630	14.68	42.9
Ir	2707	0.703	15.20	46.2
Os	3320	0.833	19.14	40.4

\*MCIS – melting curve initial slope.

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## Section 2. Thermodynamics of individual chemical compounds

### HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF $\text{Ru}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ IN THE TEMPERATURE RANGE FROM 6 K TO 488 K

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Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) Ruthenium,  $\text{Ru}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  (or  $\text{Ru}(\text{thd})_3$ ), is classified as a metal beta-diketonate and is a typical representative of molecular crystals.  $\text{Ru}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  is used to obtain thin films by MOCVD method. The thermodynamic properties of  $\text{Ru}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$  in the temperature range from 6 K to melting point) are not well studied.

Three phase transitions in the temperature range from 310 K to melting point detected by DSC method. Temperatures of phase transitions are

$434.8 \pm 2.0$  K,  $452.2 \pm 1.0$  K and  $461.1 \pm 1.0$  K. Melting point has been established by DSC method and it is  $487.8 \pm 1.0$  K.

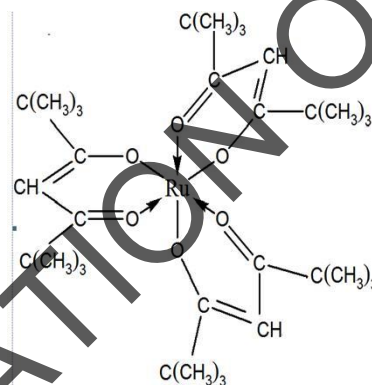
Enthalpies of phase transitions were calculated, and they are  $121 \pm 1$  kJ/mol,  $103 \pm 3$  kJ/mol and  $101 \pm 5$  kJ/mol. The melting enthalpy is  $86 \pm 2$  kJ/mol. Heat capacity of  $\text{Ru}(\text{thd})_3$  was measured at low temperature (6 - 310 K). We found the anomaly at 35 K.

We calculated thermodynamic functions: enthalpy, entropy and Gibbs energy at low temperature (6 - 310 K).

The vibrational spectrum of  $\text{Ru}(\text{thd})_3$  was reconstructed and its heat capacity was calculated for the entire range of solid phase existence (6 - 432 K) [1] based on the experimental data on heat capacity obtained by adiabatic method within the range of 6 - 310 K and knowledge about temperature of first phase transitions. Integral thermodynamic functions (entropy, internal energy, and Helmholtz energy) were calculated in range 6 - 432 K.

[1] Kuzin T. M.; Bespyatov M. A.; Naumov V. N.; Musikhin A. E.; Gelfond N. V. *Therm. Acta*, 2015, 602, 49-52.

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**Figure 1:** Scheme of the molecule  $\text{Ru}(\text{C}_5\text{H}_7\text{O}_2)_3$ .

THE THERMODYNAMIC CHARACTERISTICS OF LANTHANIDE  
PENTAFLUOROPHENOLATES

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The lanthanide complexes  $\text{Ln}(\text{OC}_6\text{F}_5)_3$  are the most promising as emitters in the OLED-devices, because they don't contain the ancillary groups with luminescence quenching C–H, N–H or O–H fragments. However, the low thermal stability and high hygroscopicity of these compounds don't allow to use them by making organic electroluminescent diodes. To solve this problem, the phenolates, containing 1,10-phenantroline  $\text{Ln}(\text{OC}_6\text{F}_5)_3(\text{Phen})_x$  as neutral ancillary ligands, were synthesized in Razuvaev Institute of Organometallic Chemistry [1, 2]. As expected, the introduction of additional groups into the coordination sphere of the lanthanides significantly increased the thermal and hygroscopic stability of the complexes. However, there is no quantitative data about the volatility of these compounds in the literature.

The aim of this study was investigation of thermochemical properties and vapor phase composition of complexes  $\text{Ln}(\text{OC}_6\text{F}_5)_3(\text{Phen})_x$  ( $\text{Ln} = \text{Li}$  (I),  $\text{Zn}$  (II),  $\text{Pr}$  (III),  $\text{Eu}$  (IV),  $\text{Dy}$  (V),  $\text{Er}$  (VI);  $\text{Phen} = 1,10\text{-phenantroline}$ ).

The composition and structure of complexes were confirmed with elemental analysis, IR-spectroscopy, as well as X-ray diffraction study was carried out. The composition of the vapor phase was investigated with mass-spectrometry.

The vapor pressure of these complexes I–VI was studied with the Knudsen effusion method in the temperature range from 75 to 170°C and the thermodynamic parameters of the processes of vaporization were determined. The vaporization temperature interval was chosen according to the DSC data (25–200)°C. The complexes I–VI are stable according to the mass-spectrometry data, there is no aggregation of molecules. Consequently, the calculation of vapor pressure was performed for the process of sublimation to monomeric vapor.

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## Section 2. Thermodynamics of individual chemical compounds

### CALORIMETRIC AND THERMODYNAMIC INVESTIGATION OF ALKALI-METAL URANYL MOLYBDATES AND URANYL TUNGSTATES WITH GENERAL COMPOSITION $M^I_2[(UO_2)(M^{VI}O_4)_2]$ AND $M^I_2[(UO_2)_2(M^{VI}O_4)O_2]$ ( $M^I - Li, Na, K, Rb, Cs$ ; $M^{VI} - Mo, W$ )

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A calorimetric and thermodynamic investigation of seven alkali-metal uranyl molybdates  $Li_2[(UO_2)(MoO_4)_2]$  (1),  $Na_2[(UO_2)(MoO_4)_2]$  (2),  $K_2[(UO_2)(MoO_4)_2]$  (3),  $Rb_2[(UO_2)(MoO_4)_2]$  (4), and  $Cs_2[(UO_2)(MoO_4)_2]$  (5) ( $M^I:U:M^{VI} = 2:1:2$ ),  $K_2[(UO_2)_2(MoO_4)O_2]$  (6), and  $Rb_2[(UO_2)_2(MoO_4)O_2]$  (7) ( $M^I:U:M^{VI} = 2:2:1$ ) and six uranyl tungstates  $Na_2[(UO_2)(W_2O_8)]$  (8),  $K_2[(UO_2)(W_2O_8)]$  (9), and  $Rb_2[(UO_2)(W_2O_8)]$  (10) ( $M^I:U:M^{VI} = 2:1:2$ ),  $K_2[(UO_2)_2(WO_4)O_2]$  (11),  $Rb_2[(UO_2)_2(WO_4)O_2]$  (12), and  $Cs_2[(UO_2)_2(WO_4)O_2]$  (13) ( $M^I:U:M^{VI} = 2:2:1$ ), was undertaken. The various phases were synthesized by high-temperature solid-state reaction. The synthetic products were characterized by X-ray powder diffraction and X-ray fluorescence methods. The low-temperature heat capacity,  $C_p$ , was measured using adiabatic calorimetry from  $T = (6 \text{ to } 335) \text{ K}$ . Based on these data, the third law entropy for all studied compounds was calculated. The enthalpy of formation of all uranyl tungstates and two uranyl molybdates was determined using HF solution calorimetry. Using these new experimental results, together with literature data, the Gibbs free energy of formation of each compound was calculated.

**Table 1.** Standard thermodynamic functions for studied compounds at  $T = 298 \text{ K}$  and pressure  $p = 0.1 \text{ MPa}$

$M^{VI}$	$M^I:U:M^{VI}$	Compound	$C_p^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$H^\circ(T) - H^\circ(0) / \text{kJ}\cdot\text{mol}^{-1}$	$S^\circ(T) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$-[G^\circ(T) - H^\circ(0)] / \text{kJ}\cdot\text{mol}^{-1}$	$-\Delta_f H^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$-\Delta_f S^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$-\Delta_f G^\circ / \text{kJ}\cdot\text{mol}^{-1}$
Mo	2:1:2	1	310.1	53.91	344.5	48.81	$(3456 \pm 9)$	$846 \pm 1$	$3204 \pm 9$
		2	308.6	56.53	373.2	54.74	$(3500 \pm 2)^a$	$862 \pm 1$	$3243 \pm 2$
		3	311.8	58.62	389.8	57.61	$(3529 \pm 3)^a$	$872 \pm 1$	$3269 \pm 3$
		4	300.7	56.85	377.3	55.64	$(3533 \pm 3)^a$	$909 \pm 1$	$3262 \pm 3$
		5	302.5	57.67	393.8	59.73	$(3530 \pm 3)^a$	$909 \pm 1$	$3259 \pm 3$
	2:2:1	6	308.5	57.44	374.1	54.10	$(4018 \pm 5)^a$	$909 \pm 1$	$3746 \pm 5$
		7	310.8	58.09	390.4	58.29	$(4009 \pm 5)$	$917 \pm 1$	$3735 \pm 5$
W	2:1:2	8	289.6	52.23	333.4	47.18	$3755 \pm 13$	$910 \pm 1$	$3484 \pm 13$
		9	353.7	64.91	423.3	61.29	$3897 \pm 10$	$847 \pm 1$	$3645 \pm 10$
		10	290.5	53.62	354.4	52.05	$3861 \pm 14$	$940 \pm 1$	$3581 \pm 14$
	2:2:1	11	309.8	57.33	379.6	55.84	$4185 \pm 8$	$908 \pm 1$	$3914 \pm 8$
		12	338.9	61.03	405.7	59.94	$4210 \pm 10$	$906 \pm 1$	$3940 \pm 10$
		13	336.1	61.64	418.0	62.99	$4227 \pm 10$	$911 \pm 1$	$3956 \pm 10$

**Table 2.** Standard thermodynamic functions of formation for studied compounds at  $T = 298 \text{ K}$  and pressure  $p = 0.1 \text{ MPa}$

<sup>a</sup> Value was determined previously.

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## THERMODYNAMIC PROPERTIES OF $\text{Ph}_3\text{Sb}(\text{OC}(\text{O})\text{Ph})_2$ AND $\text{Ph}_3\text{Bi}(\text{OC}(\text{O})\text{Ph})_2$

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Coordination chemistry of triphenylantimony  $\text{Ph}_3\text{SbX}_2$  and triphenylbismuth  $\text{Ph}_3\text{BiX}_2$  (X is oxygen containing functional group) attract particular interest of the researchers. The investigations of the synthesis and physicochemical properties of this kind of compounds are in progress, since the obtaining of the regularities of their changes with the compound composition and structure is an actual and essential task.

In the present research, the temperature dependences of heat capacity of triphenylantimony dibenzoate  $\text{Ph}_3\text{Sb}(\text{OC}(\text{O})\text{Ph})_2$  (**I**) and triphenylbismuth dibenzoate  $\text{Ph}_3\text{Bi}(\text{OC}(\text{O})\text{Ph})_2$  (**II**) were studied with the precision adiabatic vacuum calorimeter BKT-3.0 (Russia) and differential scanning calorimeter DSC 204 *FI Phoenix*<sup>®</sup> over the temperature range from  $T = (6 \text{ to } 490) \text{ K}$ . The thermal stability of the compounds was studied by the thermogravimetric analysis with the thermo-microbalance TG 209 *FI Iris*<sup>®</sup> (Netzsch, Germany).

It was revealed that the compound **I** melted over the indicated temperature range. The melting was accompanied with the partial decomposition of the sample. The temperature of the melting was estimated according to the method of the Netzsch *Proteus*<sup>®</sup> Software. The enthalpy and the entropy of the melting were impossible to establish.

An intensive exothermal effect was observed over the range from  $T = (417 \text{ to } 430) \text{ K}$  for the sample **II**, the signal wasn't reproduced on subsequent recooling and reheating. The transition was probably caused by the decomposition with the polymerization.

The multifractal treatment was carried out for low-temperature ( $20 \text{ K} \leq T \leq 50 \text{ K}$ ) heat capacity data, and the crystal structure topology was established for the compounds under study.

The experimental data were used to calculate the standard thermodynamic functions: heat capacity  $C_p^\circ$ , enthalpy  $H^\circ(T) - H^\circ(0)$ , entropy  $S^\circ(T)$ , and Gibbs function  $G^\circ(T) - H^\circ(0)$  in the range from  $T \rightarrow 0$  to the temperatures of the destruction beginning of the samples. Also for the compounds under study the values of the standard entropy of formation were calculated at  $T = 298.15 \text{ K}$ .

The thermodynamic properties of the organic compounds of Sb(V) and Bi(V) under study were compared with those for pentaphenylantimony  $\text{Ph}_5\text{Sb}$  and other antimony- and bismuth-organic derivatives.

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## Section 2. Thermodynamics of individual chemical compounds

### CALORIMETRIC STUDY OF TRIPHENYLANTIMONY DIPROPIONATE $\text{Ph}_3\text{Sb}(\text{OC}(\text{O})\text{C}_2\text{H}_5)_2$

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The synthesis and investigations of physicochemical properties of organoantimony(V) complexes have attracted considerable interest of researches recently. There are a lot of investigations on their biological and optical properties, and their thermal-oxidative stability [1, 2]. Organic derivatives of pentavalent antimony find an application in different fields of practice, e.g. as reagents and catalysts in fine organic synthesis, pharmaceutical composition, biocides and fungicides.

In the present research the temperature dependence of heat capacity of triphenylantimony dipropionate  $\text{Ph}_3\text{Sb}(\text{OC}(\text{O})\text{C}_2\text{H}_5)_2$  was measured by precision adiabatic vacuum calorimetry and differential scanning calorimetry over the temperature range from  $T = (6 \text{ to } 480) \text{ K}$ . It was revealed that compound under study exists in crystalline and liquid states. The standard thermodynamic characteristics of fusion were determined and analyzed. The purity of the investigated organoantimony(V) compound was estimated from experimental calorimetric data about its fusion. The thermal stability of the investigated compound was studied by TG analysis (TG 209 *Fl Iris*, Netzsch-Geratebau).

The experimental results were used to calculate the standard ( $p^\circ = 0.1 \text{ MPa}$ ) thermodynamic functions (heat capacity  $C_p^\circ(T)$ , enthalpy  $H^\circ(T) - H^\circ(0)$ , entropy  $S^\circ(T)$ , and Gibbs energy  $G^\circ(T) - H^\circ(0)$ ) of triphenylantimony dipropionate in crystalline and liquid states from  $T \rightarrow 0$  to 480 K.

The low-temperature ( $T < 50 \text{ K}$ ) heat capacity dependence was analyzed on the basis of Debye's heat capacity theory of solids and its multifractal model, so the characteristic temperature and the fractal dimension were determined, and chain-layered structure topology was established.

The standard thermodynamic properties of triphenylantimony dipropionate were discussed and compared with literature data for other organic derivatives of antimony(V) studied earlier.

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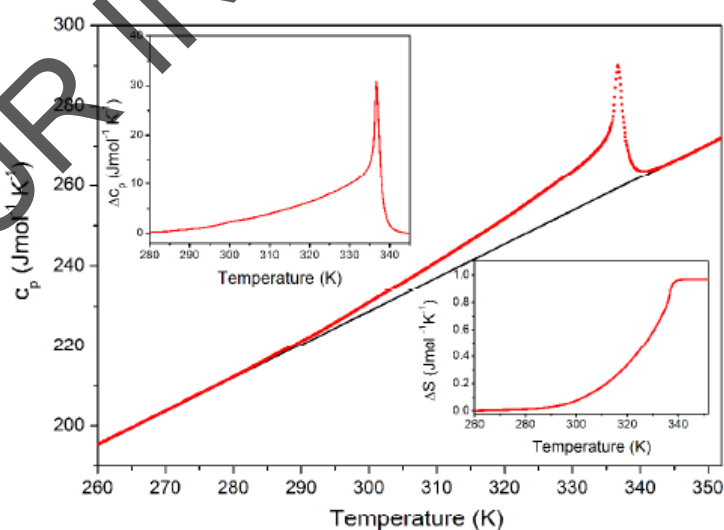
*This work was performed with the financial support of the Ministry of Education and Science of the Russian Federation (Contract No. 4.1275.2014/K) and the Russian Foundation for Basic Research (Project No. 14-03-31038 mol\_a).*

## CALORIMETRIC INVESTIGATION OF PHASE TRANSITIONS IN SOME METAL FORMATE FRAMEWORKS TEMPLATED BY ALKYLAMMONIUM CATIONS

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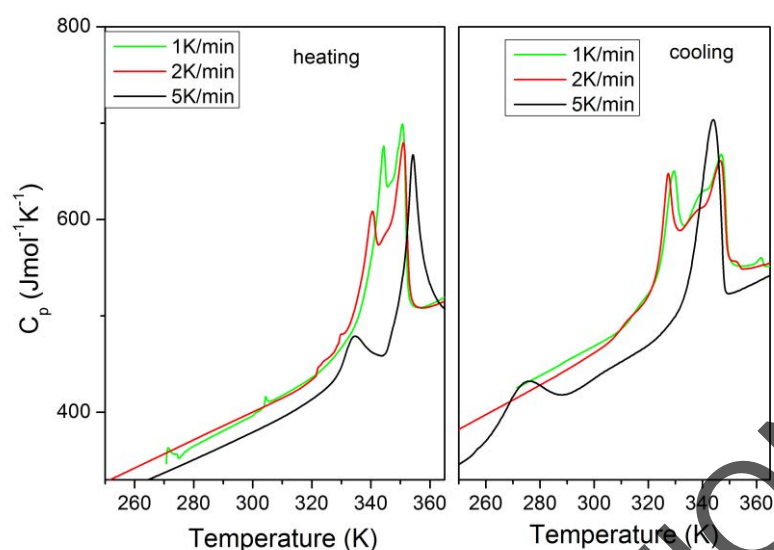
Metal-organic frameworks (MOFs) are known to possess various functionalities, which can be tuned by using different organic ligands and metal ions [1]. Among this huge class of MOFs, metal formate frameworks attracted a lot of attention in recent years since the HCOO<sup>-</sup> ion is capable of mediating ferro- or antiferromagnetic coupling between metal ions due to its small size [2]. As a result, many metal formate frameworks exhibit interesting magnetic properties [2]. Furthermore, some of the metal formate frameworks of general formula [cat][M(HCOO)<sub>3</sub>] with M = Mg, Zn, Mn, Ni, Co, Fe, and cat = ammonium, dimethylammonium (DMA) etc., were shown to exhibit multiferroic properties [3, 4]. Coexistence of magnetic and electric orders was also reported for mixed-valence [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Fe<sup>III</sup>Fe<sup>II</sup>(HCOO)<sub>6</sub>] crystallizing in the niccolite-like structure [5].

In the present work, we report results of DSC studies for [NH<sub>2</sub>-CH<sup>+</sup>-NH<sub>2</sub>][Mn(HCOO)<sub>3</sub>] (FMDMn) and [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Na<sub>0.5</sub>Fe<sub>0.5</sub>(HCOO)<sub>3</sub>] perovskites as well as [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Fe<sup>III</sup>Fe<sup>II</sup>(HCOO)<sub>6</sub>] mixed-valence niccolite. We will also present DSC data for a few novel amine-templated metal formates not reported in literature. We will show that these compounds exhibit rich polymorphism and we will discuss nature of the observed phase transitions. These studies are part of our investigations of structural, dielectric and phonon properties in this wide group of ferroic and multiferroic MOFs.



**Figure 1:** The heat capacity of FMDMn measured in a heating mode. The insets show change in  $C_p$  and  $S$  related to the phase transition. This compound crystallizes in the monoclinic space group  $C2/c$  at room temperature. Upon heating, a structural phase transition occurs around 335 K to the rhombohedral phase, space group  $R-3C$ . The phase transition has a slightly-first order character with the  $\Delta H \sim 0.360 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta S \sim 0.97 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$ .

## Section 2. Thermodynamics of individual chemical compounds



**Figure 2:** The heat capacity of novel  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Mn}_2(\text{HCOO})_6]$  niccolite showing large thermal hysteresis of the lower temperature phase transition.

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**THE STUDY OF THERMAL STABILITY  
OF THE BISMUTH- AND ANTIMONYCONTAINING POLYMERS**

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The triphenylbismuth- and triphenylantimony derivatives of unsaturated carbonic acids are useful for metalcontaining polystyrene and polymethylmethacrylate syntheses.

In this study the thermal stability of polymethylmethacrylate containing various amounts of triphenylantimony dicrotonate was investigated using the DSC method.

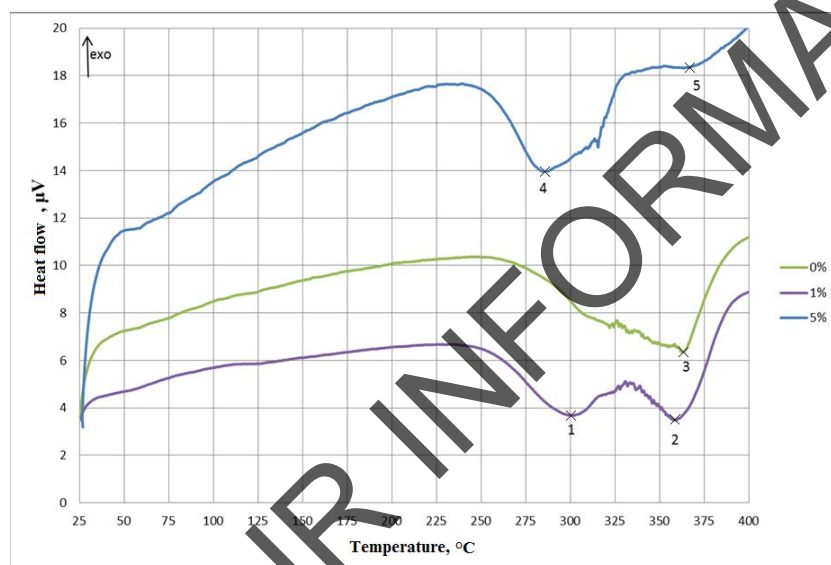
Triphenylbismuth dicrotonate is a very promising monomer for developing of metalcontaining organic scintillators which recently attracted much attention in the field of high-energy physics. It was found that the participation of both acrylate groups in polymerization leads to cross-linking considerably decreasing the thermooxidative destruction of the resulting polymer [1].

Organic glasses based on triphenylantimony diacrylate and methylmethacrylate having increased fungal resistance are available now [1].

Thermodynamic properties of the triphenylantimony diacrylates have been studied [2, 3].

The polymers were obtained by the of block polymerization method in degassed sealed tubes. Concentration of triphenylantimony dicrotonate was ranged from 0 to 5 mass%. The DSC curves were obtained using a differential scanning calorimeter LABSYS (TGA, DTA, DSC), Setaram (France).

Thus, riphenylantimony dicrotonate additives increase the thermostability of polymethylmethacrylate.



**Figure:** The DSC analysis curves for polymethylmethacrylate with 0, 1 and 5% of triphenylantimony dicrotonate. The values of the minima on the curves: 1 – 300.4°C, 2 – 358.5°C, 3 – 363.2°C, 4 – 315.5°C, 5 – 367.8°C.

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 [3] Letyanina, I.A.; Markin, A.V.; Smirnova, N.N.; Gushchin, A.V.; Shashkin, D.V. Russ. J. Phys. Chem. A, 2012, 86, 1189-1195.

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## Section 2. Thermodynamics of individual chemical compounds

### DIAGRAM OF THE ELECTROCHEMICAL EQUILIBRIUM STEEL 20KT

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When modeling electrochemical equilibrium diagram of steel 20KT (GOST 633-80) that the alloy contains iron (mass%): carbon (0.2), silicon (0.2), manganese (0.5), and copper (0.14). Traces of chromium (0.06), and nickel (0.15) practically do not affect the electrochemical corrosion behavior of steel [1]. Aluminum (0.01), sulfur (0.003), together with the finishing of the melt and the Si–Ca synthetic slag, specify the number and composition of the metal remaining in the so-called corrosive nonmetallic inclusions [1].

The main phases of steel 20KT are ferrite ( $\alpha$ -phase (Fe)) and cementite ( $(\text{FeMn})_3\text{C}$ ). Solubility of copper in iron at 25°C is  $\sim 10^{-5}$  mol.% [2], so 20KT copper in steel is present as a dispersion of inclusions distributed substantially pure copper ( $\epsilon$ -phase (Cu)) [1]. Thus, the overall electrochemical equilibrium diagram of steel includes diagrams potential E–pH steel metallic matrix ( $\alpha$ -phase (Fe) +  $\epsilon$ -phase (Cu)), cementite ( $(\text{FeMn})_3\text{C}$ ) and nonmetallic inclusions, thermodynamics, chemical and electrochemical stability which has been considered previously [1].

Thermodynamic properties of ferrite ( $\alpha$ -phase (Fe)) described in terms of a generalized model of "regular" solution [1]. Active components ferrite steel 20KT at 25°C made:  $a_{\text{Fe}}(\alpha) \approx 0.985$ ;  $a_{\text{Mn}}(\alpha) \approx 0.025$ ;  $a_{\text{Si}}(\alpha) \approx 4.0 \cdot 10^{-26}$  (standard state – pure component with bcc lattice). The diagram of the electrochemical balance of the metal matrix steel 20KT allocated 60 areas the prevalence of the various phases and phase components; the diagram of the electrochemical equilibrium cementite ( $(\text{FeMn})_3\text{C}$ ) – 20 areas dominance.

Content of Si, Mn and Cu in the steel 20KT such that they are not enough to form a solid oxide film with the participation of these elements; locally they can enter into the inner sublayer passivation film of iron oxides [1]. Phase equilibria involving mixed carbide ( $(\text{FeMn})_3\text{C}$ ) are metastable in the steel structure 20KT,  $\epsilon$ -phase (Cu) and graphite, as a product of the electrochemical dissolution of cementite acts as a cathode areas that facilitate steel passivation due to the formation of the oxide film on the basis of magnetite  $\text{Fe}_3\text{O}_4$ . This is thermodynamically possible only weakly acidic, neutral or alkaline aqueous media. The thermodynamic stability of the main phase steel 20KT throughout the pH range is reduced as follows:  $\epsilon$ -phase (Cu)  $\rightarrow$  cementite ( $(\text{FeMn})_3\text{C}$ )  $\rightarrow$   $\alpha$ -phase (ferrite).

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## SUBLIMATION AND FUSION PROCESSES AND THEIR RELATION WITH CRYSTAL STRUCTURES OF ACETAMIDOBENZOIC ACID ISOMERS

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Experimental determination of organic compounds thermochemical properties in the gas phase requires the knowledge of the sublimation enthalpy. The enthalpy of sublimation is also significant information on the estimative of intermolecular hydrogen bonds energies. This characteristic also assists with solvation processes analysis of investigated materials in various solvents. Inert gas flow method was chosen by us to study sublimation process by measuring saturation vapor pressure and calculation of sublimation thermodynamic parameters of investigated species. This work is a continuation of our previous studies focused on correlations between thermodynamic parameters of sublimation, solvation, partitioning processes with structure feature of the investigated compounds [1, 2].

In the present work we have investigated the thermodynamic functions of sublimation and fusion processes of the acetamidobenzoic acid isomers. The standard ( $p^\circ = 0.1$  MPa) molar enthalpies of sublimation of those three isomers were obtained from temperature dependencies of vapor pressure measured by inert gas flow method. The investigated species are related with acetaminophens, phenacetin, acetanilide and hydroxybenzoic acid isomers, which were studied by us in previous works [1, 2]. For acetamidobenzoic acid isomers no experimental values on the vapor pressure and enthalpies of sublimation are reported in the literature.

The thermodynamic aspects of the acetamidobenzoic acid isomers sublimation processes have been studied by investigation of the temperature dependence of vapor pressure by means of transpiration method. Temperature dependencies of saturated vapor pressure for *i*-acetamidobenzoic acids ( $i = 2, 3$  and  $4$ ) were obtained by flow inert gas-carrier transfer method. Thermodynamic parameters of sublimation were calculated for 2-acetamidobenzoic acid (2-AcAmBA), 3-acetamidobenzoic acid (3-AcAmBA) and 4-acetamidobenzoic acid (4-AcAmBA) (2-AcAmBA:  $\Delta G_{\text{sub}}^{298} = 54.4 \text{ kJ}\cdot\text{mol}^{-1}$ ;  $\Delta H_{\text{sub}}^{298} = 116 \pm 1 \text{ kJ}\cdot\text{mol}^{-1}$ ;  $\Delta S_{\text{sub}}^{298} = 205 \pm 4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ; 3-AcAmBA:  $\Delta G_{\text{sub}}^{298} = 73.2 \text{ kJ}\cdot\text{mol}^{-1}$ ;  $\Delta H_{\text{sub}}^{298} = 137 \pm 1 \text{ kJ}\cdot\text{mol}^{-1}$ ;  $\Delta S_{\text{sub}}^{298} = 215 \pm 4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ; 4-AcAmBA:  $\Delta G_{\text{sub}}^{298} = 72.3 \text{ kJ}\cdot\text{mol}^{-1}$ ;  $\Delta H_{\text{sub}}^{298} = 138 \pm 1 \text{ kJ}\cdot\text{mol}^{-1}$ ;  $\Delta S_{\text{sub}}^{298} = 221 \pm 8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ). Sublimation enthalpy of ortho-acetamidobenzoic acid is the lowest of three isomers. It is cause of presence one intramolecular hydrogen bond in ortho-isomer, which is not breaking in the sublimation process. At the same time, the crystal lattice energies of meta- and para-acetamidobenzoic acid isomers are almost equal. The values of the sublimation enthalpies of these compounds were compared with other benzoic acid derivatives. The influence of size and nature of the substituent on thermodynamic properties has been analyzed. The dependence between the sublimation enthalpy and fusion temperature was found.

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## Section 2. Thermodynamics of individual chemical compounds

### CALORIMETRIC AND HIGH-TEMPERATURE INVESTIGATION OF SOME THORIUM PHOSPHATES AND SILICATES

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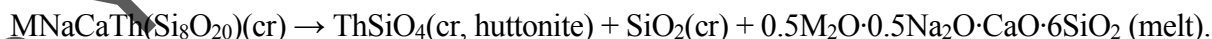
At the present time, decision radiochemical problems is impossible without fundamental information about the oxygen-containing compounds of thorium. The knowing of dependences “composition – structure – properties” is of great importance. One of the most widespread minerals of thorium are phosphates and silicates.

Double thorium phosphates  $M_kTh_{3-k}(PO_4)_{4-k}$  ( $M^I = Li, Na, Ag, K, Rb, Tl, Cs$ ;  $M^{II} = Cd, Ca, Sr, Pb$ ) crystallize in the monoclinic system (space group  $C2/c$  for  $M^ITh_2(PO_4)_3$  and  $P2_1/n$  for  $M^{II}Th(PO_4)_2$ ) [1]. Several stoichiometric composition are known today for thorium-containing silicates:  $ThSiO_4$  (Th : Si = 1 : 1),  $MM'CaTh(Si_8O_{20})$  (Th : Si = 1 : 8),  $Ca_2Th_4(SiO_4)_6O_2$  (Th : Si = 2 : 3),  $Na_{12}Th_3(Si_8O_{19})_4 \cdot 18H_2O$  (Th : Si = 3 : 32). Among the mineral containing Th and Si, the most diverse are minerals with the general formula  $MM'CaTh(Si_8O_{20})$  (M - □, Li, Na, K, Rb, Cs; M' – Na, Ca) [2, 3]. In ekanite (space group  $I422$ ), the M' positions are occupied by Ca ions. In turkestanite minerals (space group  $P4/mcc$ ), the M positions are occupied by Na and K atoms.

All of this substances were synthesized by a high-temperature solid-phase reaction.

The experimental values of the molar heat capacity of  $KNaCaTh(Si_8O_{20})$  has been measured for the first time in the range from 5.5 to 350 K by precision adiabatic vacuum calorimetry and does not show any peculiarities. The experimental data were used to calculate standard thermodynamic functions, namely the heat capacity, enthalpy, entropy and Gibbs energy for the range from  $T \rightarrow 0$  to 350 K. The value of the fractal dimension D in the function of multifractal generalization of Debye's theory of the heat capacity of solids was estimated and the character of heterodynamics of structure was detected. To calculate the standard thermodynamic functions of the  $KNaCaTh(Si_8O_{20})$ , its values were extrapolated from the temperature of the measurement beginning at approximately 5.5 K to 0 K by graphic method. The absolute entropies of turkestanite and the corresponding simple substances were used to calculate the standard entropy of formation of the compound under study at 298.15 K.

Thermal analysis of the compounds  $M_kTh_{3-k}(PO_4)_{4-k}$  showed that they are stable up to 1723 K, except for  $CsTh_2(PO_4)_3$  whose thermogram exhibits an endothermic effect at 1588 K. This compound irreversibly decomposes without melting. A study of the thermal stability of  $MM'CaTh(Si_8O_{20})$  showed that  $Ca_2Th(Si_8O_{20})$  is stable up to 1723 K, whereas turkestanite group compound incongruently melts at 1437 - 1524 K. The reaction scheme can be presented as follows:



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**THERMODYNAMIC PROPERTIES OF 1H,1H,5H-OCTAFLUOROPENTYL  
ACRYLATE OVER THE RANGE FROM  $T \rightarrow (0 \text{ TO } 345) \text{ K}$**

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Fluorine-containing monomers are used in a variety of coatings applications because of their heat and chemical resistance, weatherability, low refractive index, non-cohesiveness, water and oil repellency, and electric insulating properties. The investigation of the standard thermodynamic properties of 1H,1H,5H-octafluoropentyl acrylate in a wide temperature range by precision calorimetry allows to determine the thermochemical parameters of polymerization processes at different temperatures and to estimate the ceiling temperature.

In the present work the temperature dependence of heat capacity of 1H,1H,5H-octafluoropentyl acrylate in crystalline and liquid states was obtained in the temperature range from  $T = (6 \text{ to } 345) \text{ K}$  by precision adiabatic vacuum calorimetry. The standard thermodynamic quantities of fusion namely temperature, enthalpy and entropy for 1H,1H,5H-octafluoropentyl acrylate as the estimation of sample purity under study were obtained. Using low-temperature heat capacity data the structure topology of monomer was established as a linear-planar. From experimental data the standard thermodynamic functions of 1H,1H,5H-octafluoropentyl acrylate, namely, the heat capacity  $C_p^\circ(T)$ , enthalpy  $H^\circ(T) - H^\circ(0)$ , entropy  $S^\circ(T)$  and Gibbs energy  $G^\circ(T) - H^\circ(0)$  have been calculated for the range from  $T \rightarrow 0$  to 345 K for crystalline and liquid states. Using literature data [1] for poly-1H,1H,5H-octafluoropentyl acrylate and results of present work the thermodynamic characteristics of polymerization processes have been calculated and discussed.

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## Section 2. Thermodynamics of individual chemical compounds

### SUBLIMATION ENTHALPIES OF FURANE DERIVATIVES

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Furan derivatives are used as starting materials in the synthesis of biologically active compounds, which are the base for the synthesis of antioxidants, cardiovascular, antifungal and antimicrobial preparations. Considering the wide range of uses of furane derivatives, it is important to examine the thermodynamic properties, the complex of which includes the enthalpy of sublimation ( $\Delta_{sub}H$ ), knowledge of which allows the optimization of the processes of synthesis and purification of the desired products.

The study used a sample of industrial furan acid (I) of the company MERCK purified by repeated recrystallization from hot water. Samples of 3-(2-furyl)-2-propenoic acid (II), furfural oxime (III), ethyl-2-cyano-3-(2-furyl)-2-propenoate (IV) and 2-furyl,2-cyano-2-propenamide (V) were purified by repeated recrystallization from benzene (II), from mixture of ethanol and dimethylformamide (IV–V), by vacuum distillation (III).

The investigated compounds under normal conditions are crystalline substances whose identity was confirmed by the elemental analysis and IR spectroscopy. The spectra showed no bonds that are not inherent in the substances studied. The purity of the studied compounds was confirmed by TLC.

The temperature dependence of the saturated vapor pressure of the compounds was determined by integral Knudsen effusion method. The design of the experimental setup and the check of the reliability of its operation are described in [1]. The vacuum system installation ensures the achievement of residual pressure for 0.1 Pa in 35±5 s. The accuracy of temperature control, temperature and time of effusion were: ±0.1 K, ±0.05 K and ±5 s, respectively. The effective time of the effusion was 75 s. The mass change of the substance was determined by the weight difference between effusion chamber mass before and after the experiment with the accuracy of ±5·10<sup>-5</sup> g, the standard deviation of the values was calculated based on the Student coefficient for the 5% level of significance.

The coefficients of the temperature dependence of the saturated vapor pressure, temperature range and default values of  $\Delta_{sub}H$  and  $\Delta_{vap}H$  of the studied compounds are shown in Table. Also the results of the conversion enthalpy of vaporization from an average temperature of the range to 298 K according to the equations proposed in [1] are shown.

**Table.** Parameters of the process of vaporization of the studied compounds

Compound	$T_1-T_2$ (K)	$A$	$-B \cdot 10^{-2}$ (K)	$\Delta_{sub(vap)}H^\circ(T_m)$ (kJ/mol)	$\Delta_{sub(vap)}H^\circ_{298}$ (kJ/mol)
I (cr)	324.0–373.0	34.65±0.29	110.49±0.99	91.86±0.82	93.1 ±1.0
II (cr)	347.7–377.9	36.0±1.5	123.0±5.6	102.2±4.7	104.4±5.0
III (cr)	318.8–336.0	40.71±0.75	120.8±2.5	100.4±2.0	101.2±2.1
IV* (l)	375.6–405.6	29.2±1.2	93.0±4.6	77.3±3.8	87.7±4.1
IV (cr)	326.8–335.2	36.1±2.7	122.4±8.8	101.7±7.3	101.9±7.5
V (cr)	398.8–374.6	35.9±1.8	134.9±7.1	112.1±5.9	115.8±6.0

\* $T_{fus} = 364.7$  K.

[1] Sobechko, I.B.; Van-Chin-Syan, Yu.Ya.; et al. Rus. J. Phys. Chem., 2014, 12, 2046-2053.

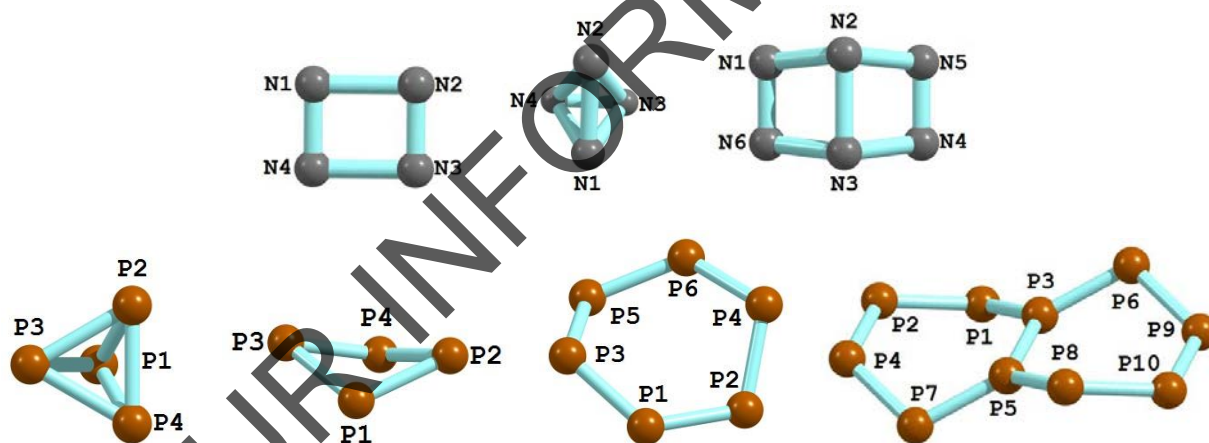
## THERMODYNAMICS OF POLYATOMIC NITROGEN, PHOSPHORUS AND ARSENIC MOLECULES ACCORDING TO CALCULATION BY DFT METHOD

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Quantum-chemical calculations of polyatomic nitrogen, phosphorus and arsenic molecules having even numbers of atoms and  $E_4$ ,  $E_6$ ,  $E_8$  and  $E_{10}$  general formulas ( $E - N, P, As$ ), have been carried out by QCISD method. On the basis of data of these calculations, the conclusion about possibility of existence of two types of nitrogen molecules, namely tetranitrogen  $N_4$  having form of symmetrical tetrahedron and of rectangle, and hexanitrogen having form of “opened book” has been made. In the cases of phosphorus and arsenic, a possibility of existence of three types of molecules having four, six and ten atoms of the given chemical elements:  $E_4$  (in form of symmetrical tetrahedron and of non-coplanar, quasi-equilateral quadrangle),  $E_6$  (in form of non-coplanar quasi-equilateral hexagon) and  $E_{10}$  (in form of two non-coplanar quasi-equilateral hexagons connected to each other along the common side). The molecular structures of some of them are shown in Figure:



**Figure:** Molecular structures of some polyatomic nitrogen and phosphorus compounds.

Thermodynamic characteristics [namely, standard enthalpy of formation  $\Delta_f H^\circ(298)$ , standard entropy of formation  $\Delta_f S^\circ(298)$  and standard Gibbs's energy of formation  $\Delta_f G^\circ(298)$ ] have been calculated for all these simple substances by G3 method. It has been shown with using of the given data for  $N_4$  and  $N_6$  that indicated polyatomic nitrogen compounds unlike  $N_2$  are able to reacting with molecular oxygen  $O_2$  with formation of nitrogen monoxide NO and a significant amount of thermal energy. Calculated per mole of the initial substance  $\Delta H^\circ(298)$  value for such a reaction in the case of tetrahedral  $N_4$  is  $-410.0$  kJ, in the case of “rectangular”  $N_4$  is  $-409.4$  kJ; in the case of  $N_6$  it is  $-343.7$  kJ. Besides, and it is extremely noteworthy, the values of entropy  $\Delta S^\circ(298)$  as a result of such an interaction in the each of these three cases are positive (201.5, 183.8 and 356.3 J/K, respectively). With consideration of the given circumstance, the conclusion that, unlike of  $N_2$  oxidation by molecular oxygen reaction, which is reversible and the possibility of realization of which is caused by entropy factor,  $N_4$  oxidation reaction as well as  $N_6$  oxidation one is thermodynamically irreversible, has been made.

## Section 2. Thermodynamics of individual chemical compounds

### THERMODYNAMIC PROPERTIES OF SOME BIPHENYLS. ENTHALPIES OF FORMATION OF AROMATIC RADICALS

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Derivatives of biphenyls (DBP) find ever increasing applications in technology and medicine as liquid crystals, semiconducting nanomaterials and drugs. Temperature dependences of the vaporization enthalpies,  $\Delta_{\text{vap}}H_m^{\circ}$ , were determined for three biphenyls, namely 1,1'-biphenyl (BP), 4-nitrobiphenyl (4-NBP) and 3-*iso*-propylbiphenyl (3-IPBP) on an isothermal heat conducting Calvet micro calorimeter with an estimated accuracy of  $\leq 1.0$  per cent in the (323–373) K range. The average values  $\Delta_{\text{vap}}H_m^{\circ}$  were adjusted to 298.15 K. Treatment of the data for DBP was carried out by the least square method to get the analytical dependence of vaporization enthalpy on temperature,  $\Delta_{\text{vap}}H_m^{\circ}/\text{kJ}\cdot\text{mol}^{-1} = \alpha + \beta (T/\text{K})$ . Formation enthalpies of some biphenyl derivatives have been determined in a gas phase. On the base of “double the difference” method the novel scheme for enthalpies of formation of aromatic radicals calculations has been suggested. The scheme allows to exclude the energies of reorganization of molecules fragments into radicals and to determine the enthalpies of formation for radicals and energies of dissociation for chemical bonds using the enthalpies of atomization. On the basis of the proposed scheme the enthalpy of formation for biphenyl-4-yl has been calculated. The values obtained for investigated compounds are listed in Tables 1 and 2.

**Table 1.** Enthalpies of vaporization (kJ/mol), 298.15 K

BP sublimation	4-NBP sublimation	3-IPBP evaporation
81.5 ± 0.8	108.4 ± 0.9	76.6 ± 0.5
81.52 [1]	–	76.4 ± 0.8 [2]

**Table 2.** Enthalpies of formation of DBP and radical of biphenyl-4-yl, kJ/mol

Compound	$\Delta_f H^{\circ}(\text{g})$	$\Delta_f H_{\text{BP}\cdot}(\text{NO}_2)$	$\Delta_f H_{\text{BP}\cdot}(\text{H})$
BP	179.9 ± 2.9	432.6	–
4-NBP	154.4 ± 7.1	–	425.9
4-MeBP	143.3 ± 1.3	429.7	429.7
4-IPBP [3]	97.2 ± 2.5	430.1	430.1
4- <i>tert</i> -BBΦ	72.0 ± 2.8	431.8	431.8

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[2] Nazmutdinov, A.G; et al. Fluid Phase Equil., 2012, 335, 88-98.

[3] Pimenova, S.M.; Nesterov, I.A.; Sikachov, F.Yu. Rus. J. Phys. Chem. A, 2013, 87, 2154-2158.

## SOLUTION CALORIMETRY METHOD FOR DETERMINATION VAPORIZATION/SUBLIMATION ENTHALPY OF POLYAROMATIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES AT 298.15 K

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Thermochemical properties of polycyclic hydrocarbons and their derivatives provide essential information for predicting the combustion behavior of fossil fuels, as well as for prediction of their environmental behavior. Experimental determination of vaporization/sublimation enthalpies of low volatile and thermally unstable compounds using conventional methods is a challenging task. Results available in the literature are very often in disarray. That's why, the purpose of our work was development of new solution calorimetry approach for determination vaporization/sublimation enthalpy of low volatile and thermally unstable organic compounds.

In comparison to conventional methods, where experiment is performed at elevated temperatures, the solution calorimetry based approach has some crucial advantages. Firstly, calorimetric measurements are usually carried out directly at the reference temperature 298.15 K. Following, this method is highly suitable for studies of thermally unstable compounds. Moreover, the solution calorimetry based method is free from difficulties connected with proper temperature adjustment of experimental data to 298.15 K.

In this work a new solution calorimetry based approach for determination enthalpies of sublimation and enthalpies of vaporization of low volatile compounds is proposed. The approach is based on the measurements of solution enthalpy of a substance of interest in benzene and its molar refraction:

$$\Delta_{cr(l)}^g H_m^{A_i} = \Delta_{soln} H_m^{A_i/C_6H_6} + 6.86 + 1.088 \cdot MR^{A_i} \quad (1)$$

Using Eq. (1), we can calculate enthalpy of vaporization  $\Delta_1^g H_m^{A_i}$  of the solute  $A_i$  (for the liquid solutes) or the enthalpy of sublimation,  $\Delta_{cr}^g H_m^{A_i}$ , for the solid solutes. Enthalpies of solution at infinite dilution in benzene for a set of 34 polyaromatic hydrocarbons and their halogen derivatives were measured at 298.15 K [1, 2]. For validation of the literature data an additional sublimation experiments were performed for phenanthrene, 1-phenylnaphthalene, 1,2-diphenylbenzene, 1,2,3,4-tetraphenylnaphthalene, hexaphenylbenzene, 1,2-, 1,3-, 1,4-dibromobenzenes, 4-bromobiphenyl, 4,4'-dibromobiphenyl and rubrene [1, 2] by using transpiration, quartz crystal microbalance, and thermogravimetry techniques. Vaporization/sublimation enthalpies derived from the solution calorimetry approach were in good agreement with those measured by conventional methods. The solution calorimetry approach gives the reliable and quick appraisal of vaporization/sublimation enthalpies. Unlike conventional methods, the solution calorimetry approach provides results directly at the reference temperature without heat capacity adjustments.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMODYNAMICS OF INTERMOLECULAR INTERACTIONS OF N-ALKYLBENZOATES

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Alkylbenzoates are widely used in different fields of industry. Some of them act as drugs and stabilizing agents. Properties of alkylbenzoates in condensed phase and in solution are largely determined by the intermolecular interactions. Information about strength of intermolecular interactions and its effect on the structure of alkyl benzoates is not available in the literature. Experimental techniques like solution calorimetry, transpiration, IR spectroscopy as well as quantum chemical calculations were used to resolve this task.

In this work thermochemical data on dissolution, vaporization and intermolecular interactions of *n*-alkylbenzoates (with alkyl groups C1–C4) were obtained. Enthalpies of solution at infinite dilution of *n*-alkylbenzoates in different organic solvents and water were measured at 298.15 K. Energies of intermolecular interactions between *n*-alkylbenzoates and various proton donors were calculated by Solomonov method [1].

Enthalpies of vaporization of *n*-alkylbenzoates at 298.15 K were determined from the temperature measurements of vapor pressure by transpiration method. Enthalpies of solvation of *n*-alkylbenzoates in different solvents were determined based on experimental data. These values were compared with different solvent scales in order to analysis the solute–solvent intermolecular interactions. Enthalpies of hydrogen bonding of *n*-alkylbenzoates with proton donor solvents were obtained from the calorimetric data. Effect of alkyl group length on the enthalpy of intermolecular interaction of *n*-alkylbenzoates with alcohols and chloroform were analyzed. FTIR-spectra of *n*-alkylbenzoates in studied solvents were measured to find the structure of molecules in solution and calculate their association degree with solvent. Enthalpies of formation of alkylbenzoates in the gas phase were calculated using G3MP2 methods. These values are in good agreement with the experimental enthalpies of formation.

Based on obtained experimental results some relationships between thermochemical data and structure of *n*-alkylbenzoates were found. These relationships can be used for the prediction of properties of *n*-alkylbenzoates in standard state, gas phase and in solution.

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## EQUILIBRIA OF INTERCONVERSIONS, THERMODYNAMIC PROPERTIES OF *TERT*-BUTYLDIPHENYLOXIDES

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Diphenyloxide (DPO) derivatives are important products for modern industry, science and technology. On their base polymers with unique mechanical and optical properties are being developed. AlkylDPO with different functional groups have abilities of substance self-organization and liquid crystals properties, also they able to control plant pathogenic fungi. In spite of useful properties variety of DPO derivatives there are lack of thermodynamic data and fundamental physicochemical properties for them. Up to date references contain data only for diphenyloxide and some nitro-derivatives.

At this time we accomplished consequent studies of diphenyloxides.

- Liquid phase equilibrium of mono-, di- and tri-ring-substituted *tert*-butylDPO (TBDPO) interconversions were studied. Values of equilibrium constants over the temperature range from 354.4 to 469.2 K were determined for ten unrelated reactions. Enthalpy and entropy effects were calculated with use of the obtained equilibrium constants. It was found that for TBDPO there are selective processes which can be implemented in the systems represented either only “ortho–para” conversions, or whole complex of “ortho–meta–para” conversions. Dependencies of equilibrium mixture composition, which formed due to the liquid phase alkylation, on temperature and compounds ratio were investigated.
- 4-*tert*-Butyldiphenyloxide was synthesized, separated and purified. Saturated vapor pressures for condensed and solid state for that compound were determined by the transpiration method. The enthalpy of vaporization and sublimation were estimated. Adjustments for prediction methods of those properties were made for alkylDPO.
- The heat capacities of 4-*tert*-butyldiphenyloxide were measured by vacuum adiabatic calorimetry in the temperature range (8–371) K. The temperature, the enthalpy and the entropy of fusion were determined. The energy of combustion of the sample was determined by static-bomb combustion calorimetry.
- Kovats indices were obtained for 13 TBDPO, normal boiling temperatures were calculated on base of that indices. Critical properties and saturated vapor pressures for all chemical reactions participants were estimated by modern prediction methods. On the base of obtained data a transition to thermodynamic properties of gas phase conversions was carried out.
- The main thermodynamic functions (the changes of entropy, enthalpy, and Gibbs energy) and functions of formation at  $T = 298.15$  K of 4-*tert*-butyldiphenyloxide in condensed and ideal gas states were computed on the basis of the obtained experimental data.

The all studied phases will be presented in the report. Also possible structure–properties relationships will be assumed.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMODYNAMIC PROPERTIES OF ALUMINIUM OXYNITRIDE

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A polycrystalline ceramic material based on the cubic spinel phase in the  $\text{Al}_2\text{O}_3 - \text{AlN}$  system possess a unique combination of mechanical properties, making this material a candidate for applications which require relatively light weight, high strength, chemical inertness, broad electromagnetic transparency and resistance to radiation damage. It is transparent in the near-ultraviolet and visible through the mid-infrared spectrum. A cubic structure of aluminum oxynitride provides it with isotropic optical properties and the absence of birefringence yet. It gives the material certain advantage over sapphire.

Aluminum oxynitride has a cubic spinel crystal structure, where the anion sites are randomly occupied by 5 N atoms and 27 O atoms, and the cations are distributed between octahedral and tetrahedral coordination. There are 8 Al cations in tetrahedral sites, and 15 Al and one vacancy in the 16 octahedral sites. Owing to random O/N distribution the width of the homogeneity region of aluminum oxynitride varies with temperature and is 60–80 mol.%  $\text{Al}_2\text{O}_3$  at 1800°C. And the chemical formula of aluminium oxynitride can be expressed as  $\text{Al}_{23-1/3x}\text{O}_{27+x}\text{N}_{5-x}$  ( $0.429 < x < 2$ ) [1].

Thermodynamic stability of aluminum oxynitride has been discussed on the basis of the calculated data. It was estimated that aluminum oxynitride is stable only under a small region of oxygen and nitrogen pressures and that it is metastable below 1640°C. Investigation of thermodynamic properties of aluminum oxynitride will contribute to optimize the synthesis process.

Synthesis of aluminum oxynitride was performed by direct sintering of pressed mixture of  $\text{Al}_2\text{O}_3$  and AlN in the ratio of 9:5 at the temperature of 1800°C. X-ray diffraction was used to confirm the phase composition and to determine the  $\text{Al}_2\text{O}_3/\text{AlN}$  ratio in the prepared compound. And in that way the single-phase semitransparent sample of aluminum oxynitride with lattice parameter  $a = 7.943(6)$  Å was synthesized. According to the dependence of the lattice parameter of aluminum oxynitride on its composition [2] the exact element ratio was defined as 73 mol.%  $\text{Al}_2\text{O}_3$  / 26 mol.% AlN (or  $\text{Al}_{22.7}\text{O}_{28.5}\text{N}_{3.5}$ ).

The heat capacity of aluminum oxynitride was measured in the temperature range from 5 to 350 K by the adiabatic calorimetry. The experimental data were compared with the heat capacity of ALON™ Optical Ceramic (Surmet Corp.) that had been measured in the temperature range of (-50–700) K [3]. Smoothed heat capacity values were used to calculated temperature dependences of thermodynamic functions (entropy, enthalpy change and reduced Gibbs energy). Standard thermodynamic properties of aluminum oxynitride (73 mol.%  $\text{Al}_2\text{O}_3$ ) were first calculated:  $C_p^\circ(298.15) = 891.0 \pm 1.8$  J/(mol·K),  $S^\circ(298.15) = 614.4 \pm 1.2$  J/(mol·K),  $H^\circ(298.15) - H^\circ(0) = 117.3 \pm 0.2$  kJ/mol.

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**CRITICAL PROPERTIES OF COMPONENTS OF BIODIESEL.  
n-ALKANOIC ACID METHYL ESTERS**

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Biodiesel is a blend of methyl or ethyl esters of fatty acids made from vegetable oils and animal fat. Biodiesel is a renewable energy resource and has some advantages over petroleum fuels. The vapour-liquid critical properties are important characteristics of pure compounds because a knowledge of the critical parameters allows building equations of state, estimating thermophysical properties by the application of the principle of corresponding states.

In this work, we report the experimental critical temperatures  $T_c$  and pressures  $p_c$  of seven  $n$ -alkanoic acid methyl esters  $C_nH_{2n-1}O_2CH_3$  with  $n = 6, 7, 8, 9, 10, 11, 12$ . Methyl esters of  $n$ -alkanoic acids beginning from methyl heptanoate are thermally unstable at their critical point [1]. To measure the critical properties of  $n$ -alkanoic acid methyl esters, we used the pulse-heating method which is applicable to thermally unstable compounds [2]. The residence times were from 0.03 to 1.0 ms. The samples of the esters were purchased from Alfa Aesar and Sigma-Aldrich and had the purities from 98.6 to 99.9 mol.%. The uncertainties of the critical constants measured in this study are  $\delta p_c = 0.03 p_c$  and  $\delta T_c = 0.01 T_c$ . Here  $T_c$  is the absolute temperature; the uncertainties are a combined expanded uncertainty at the 95% level of confidence.

The critical properties of  $n$ -alkanoic acid methyl esters measured in this work are given in Table. These values together with the results of the previous measurements [3, 4] were processed and the following equations were obtained:

$$T_c / K = 1293.03 - 2853.91n^{-1/2} + 2881.52n^{-1},$$

$$p_c / MPa = 151.264n^{-3/2} - 364.294n^{-2} + 237.351n^{-5/2}.$$

These equations describe the experimental critical properties of methyl esters of  $n$ -alkanoic acids for  $5 \leq n \leq 18$  and can be used for a prudent extrapolation.

**Table.** Critical temperatures and pressures of  $n$ -alkanoic acid methyl esters  $C_nH_{2n-1}O_2CH_3$

$n$	$T_c$ (K)	$p_c$ (MPa)
6	612 ± 6	2.88 ± 0.09
7	626 ± 6	2.53 ± 0.08
8	646 ± 6	2.34 ± 0.07
9	662 ± 7	1.87 ± 0.06
10	675 ± 7	1.93 ± 0.06
11	694 ± 7	1.78 ± 0.05
12	709 ± 7	1.43 ± 0.04

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## Section 2. Thermodynamics of individual chemical compounds

### EFFECTS OF DOPING AND TEMPERATURE ON CRYSTAL STRUCTURE OF DOUBLE PEROVSKITE $\text{Sr}_2\text{NiMoO}_6$

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Complex oxide materials with double perovskite structure  $\text{A}_2\text{MMoO}_6$  ( $\text{A} = \text{Sr}, \text{Ba}$ ;  $\text{M} = \text{Ni}, \text{Zn}$ ) are attracting the attention of scientists due to their potential application as anode materials for solid-oxide fuel cells (SOFC). Aim of the present work was to study the doping and temperature effects on crystal structure of  $\text{Sr}_2\text{NiMoO}_6$ . Substitution in  $\text{Sr}_2\text{NiMoO}_6$  was carried out by  $\text{Ba}^{2+}$ -ions at Sr-sublattice and  $\text{Zn}^{2+}$ -ions at Ni-sublattice.

The samples  $\text{Sr}_{2-x}\text{Ba}_x\text{NiMoO}_6$  ( $x = 0.0; 0.25; 0.5; 0.75; 1.0; 1.25; 1.5; 1.75; 2.0$ ) and  $\text{Sr}_2\text{Ni}_{1-y}\text{Zn}_y\text{MoO}_6$  ( $y = 0.25; 0.5; 0.75; 1.0$ ) were obtained by wet-chemical route. The phase purity was investigated by means of X-ray diffraction on Inel Equinox 3000 diffractometer using  $\text{CuK}_\alpha$ -radiation supplied with high-temperature attachment HDK S1 (Edmund Buechler GmbH). XRD data were refined by the Rietveld method using FullProf software.

According to the XRD data at 298 K  $\text{Sr}_{2-x}\text{Ba}_x\text{NiMoO}_6$  samples in the composition range  $0.0 \leq x \leq 0.25$  possessed tetragonal ( $I4/m$  Space group) double perovskite lattice isostructural to boundary  $\text{Sr}_2\text{NiMoO}_6$  whereas in the range of  $0.25 < x \leq 2.0$  samples possessed cubic ( $Fm3m$  Space group) double perovskite lattice isostructural to  $\text{Ba}_2\text{NiMoO}_6$ . On the basis of the composition dependences of lattice parameters it was shown that substitution of strontium on barium in  $\text{Sr}_2\text{NiMoO}_6$  increased the lattice volume owing to dimensional effect. The analysis of temperature dependences of  $\text{Sr}_{1.75}\text{Ba}_{0.25}\text{NiMoO}_6$  lattice parameters in the temperature range  $298 \leq T, \text{K} \leq 523$  allowed to conclude about existence of crystal structure transition from tetragonal to cubic lattice near  $T = 380 \text{ K}$ . That is why substitution of strontium on barium in  $\text{Sr}_{2-x}\text{Ba}_x\text{NiMoO}_6$  caused the decreasing of transition temperature with comparison with un-doped  $\text{Sr}_2\text{NiMoO}_6$  (508 K).

Analysis of  $\text{Sr}_2\text{Ni}_{1-y}\text{Zn}_y\text{MoO}_6$  lattice parameters allowed to establish that at 298 K all samples having tetragonal structure are isostructural to boundaries  $\text{Sr}_2\text{NiMoO}_6$  and  $\text{Sr}_2\text{ZnMoO}_6$ . On the basis of lattice volumes composition dependences at 298 K for  $\text{Sr}_2\text{Ni}_{1-y}\text{Zn}_y\text{MoO}_6$  it was stated that substitution of nickel on zinc in  $\text{Sr}_2\text{NiMoO}_6$  caused lattice volume increasing due to dimensional effect. The analysis of temperature dependences of  $\text{Sr}_2\text{Ni}_{1-y}\text{Zn}_y\text{MoO}_6$  lattice parameters in the temperature range  $298 \leq T, \text{K} \leq 673$  allowed to establish that temperature of crystal structure transition from tetragonal to cubic phase for  $\text{Sr}_2\text{Ni}_{1-y}\text{Zn}_y\text{MoO}_6$  samples increased with zinc content increasing: for  $y = 0.25$  sample transition occurred at  $T = 540 \text{ K}$ , for  $y = 0.5$  sample – at  $T = 570 \text{ K}$ , for  $y = 0.75$  sample – at  $T = 640 \text{ K}$ . That is why substitution of nickel on zinc in  $\text{Sr}_2\text{Ni}_{1-y}\text{Zn}_y\text{MoO}_6$  caused the increasing of transition temperature with comparison with un-doped  $\text{Sr}_2\text{NiMoO}_6$

It was stated that thermal expansion coefficients (TEC) of  $\text{Ba}_2\text{NiMoO}_6$ ,  $\text{Sr}_{1.75}\text{Ba}_{0.25}\text{NiMoO}_6$ ,  $\text{Sr}_2\text{Ni}_{1-y}\text{Zn}_y\text{MoO}_6$  samples calculated from high-temperature X-Ray powder diffraction data in temperature range  $303 \leq T, \text{K} \leq 673$  were close to TEC of traditional electrolyte materials which allowed recommending those compounds as promising anode materials for high-temperature fuel cells.

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## THERMODYNAMICS OF NATURAL CALCIUM AMPHIBOLE – ACTINOLITE

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Actinolites are widespread rock-forming minerals of the calcium amphibole group of tremolite  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  – ferroactinolite  $\text{Ca}_2\text{Fe}^{2+}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  isomorphic series. Actinolite formula appears as  $\text{Ca}_2(\text{Mg,Fe})_5[\text{Si}_8\text{O}_{22}](\text{OH})_2$ . Available in the literature the thermodynamic properties of actinolite were limited by the data estimated or calculated from the equilibrium.

The actinolite from Shabry talc deposit (Central Urals, Russia) was used for the first calorimetric study. The sample was presented as needle crystals of light green color of a few centimeters size. In this work the mineral was studied using different diagnostic methods. The chemical formula was calculated on the basis of electron microprobe analysis (Camebax SX-50, France) data and had the form  $\text{Ca}_2(\text{Mg}_{4.5}\text{Fe}^{2+}_{0.5})[\text{Si}_8\text{O}_{22}](\text{OH})_2$ . Results of X-ray study (STOE-STADI MP, Germany) confirmed the monomineral composition of the sample. IR absorption spectra (Fourier spectrometer FSM-1201, Russia) showed the absence of impurities in the examined substance also. Thermal and thermogravimetric studies in the range from room temperature to 1200°C (Derivatograph Q-1500D, Hungary) demonstrated the characteristic behavior of amphibole, DTA curves showed endothermic effect corresponding to the removal of constitutional water (dehydroxylation process) at 1000–1150°C ( $t_{\text{max}} = 1090^\circ\text{C}$ ). The total mass loss was  $\sim 2.2\%$ .

The thermochemical investigations were performed on Calvet microcalorimeter (Setaram, France) using two experimental techniques: the enthalpy of formation was determined by the solution calorimetry in melt of composition  $2\text{PbO}\cdot\text{B}_2\text{O}_3$  at  $T = 973\text{ K}$ , the enthalpy increments of actinolite were measured at  $T = 507, 630, 778, \text{ and } 973\text{ K}$  by dropping samples into calorimeter without melt. The specimen masses were 4–20 ( $\pm 2\cdot 10^{-3}$ ) mg. Calibration of the calorimeter was performed by dropping pieces of reference substances – platinum wire and corundum  $\alpha\text{-Al}_2\text{O}_3$  using their reference enthalpy increments data [1].

The value of the standard enthalpy of formation from the simple substances for actinolite studied was obtained using a thermochemical cycle, taking into account the dissolution of the mineral and its constituent components (oxides and magnesium hydroxide), and was found to be  $\Delta_f H^\circ(298) = -12054 \pm 18\text{ kJ/mol}$ .

Results of enthalpy increment measurements were fitted by least-squares yielding and the equation of the heat capacity of actinolite was found as  $C_p = 889.9 + 130.9 \cdot 10^{-3}T - 246.8 \cdot 10^{-5}T^2\text{ J/(K}\cdot\text{mol)}$ , the maximum approximation error was 0.48%.

To calculate the Gibbs energy of formation of studied mineral we estimated the value of its standard entropy, which is unknown in the current literature. An evaluation was made on the basis of the value of entropy of similar in composition and structure tremolite  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  [1], this value was obtained from low-temperature heat capacity measurements [2]. The  $S^\circ(298) = 565.8 \pm 1.6\text{ J/(K}\cdot\text{mol)}$  and  $\Delta_f G^\circ(298) = -11331 \pm 18\text{ kJ/mol}$  values were calculated for actinolite  $\text{Ca}_2(\text{Mg}_{4.5}\text{Fe}^{2+}_{0.5})[\text{Si}_8\text{O}_{22}](\text{OH})_2$ .

The new thermodynamic data for actinolite can be used for the physico-chemical quantitative modeling of the natural processes involving this mineral.

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## Section 2. Thermodynamics of individual chemical compounds

### ENTHALPY OF FORMATION OF ALKYL RADICALS

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Enthalpies of formation of alkyl radicals ( $R^\bullet$ ) ( $\Delta_f H^\circ(R^\bullet)$  at 298.15 K and 0.1 MPa) are among the key values in thermochemistry [1]. They are basis for testing of various methods of  $\Delta_f H^\circ(R^\bullet)$  forecasting and specify the reference set for verification of the quantitative correlations "structure – property". A lot of different values in organic compounds such as the strength of the chemical bonds are estimated by means of  $\Delta_f H^\circ(R^\bullet)$ .

In this work we have critically analyzed the literature data on enthalpies of formation of alkyl radicals and classified them by the criteria of strictness. The  $\Delta_f H^\circ(R^\bullet)$  errors were discussed as well. Taking into account the C–X (X = H, Cl) bond cleavage enthalpies in alkanes and monochlorine alkanes the enthalpies for fifteen alkyl radicals have been defined. On the basis of quantitative correlations "structure – property" within the additive-group model the obtained values of  $\Delta_f H^\circ(R^\bullet)$  were analyzed.

The electron density distribution (including spin density) of radicals was studied in the framework of the "quantum theory of atoms in molecules" (QTAIM). The influence of the unpaired electron on the electron density distribution in *n*-alkyl radical groups was considered, and it was shown the effect is extended onto the nearest two CH<sub>2</sub>-groups. In accordance with this conclusion it should distinguish the radical groups having unpaired electron and its two neighboring; the remaining groups have to be considered the same as in alkane molecules. Therefore, in order to simulate the alkyl radicals the 19 groups were introduced, and also the 11 group increments have been determined; addition eight parameters were taken from the Benson's model for alkanes (as consequence of electron density distribution).

Based on these data the new expanded set of molecular fragments was offered. The proposed model of forecasting of  $\Delta_f H^\circ$  radicals under consideration includes eleven descriptors: C<sup>•</sup>-(C)(H)<sub>2</sub>, C<sup>•</sup>-(C)<sub>2</sub>(H), C<sup>•</sup>-(C)<sub>3</sub>, C-(C<sup>•</sup>)(H)<sub>3</sub>, C-(C<sup>•</sup>)(C)(H)<sub>2</sub>, C-(C<sup>•</sup>)(C)<sub>2</sub>(H), C-(C<sup>•</sup>)(C)<sub>3</sub>, C-(C)(H)<sub>3</sub>, C-(C)<sub>2</sub>(H)<sub>2</sub>, C-(C)<sub>3</sub>(H), C-(C)<sub>4</sub>.

For the first time the  $\Delta_f H^\circ$  for 13 alkyl radicals were defined, thus the data fund on  $\Delta_f H^\circ$  of alkyl radicals was revised, updated and expanded by more than 25%.

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## THERMODYNAMIC PROPERTIES OF YTTRIUM TRIHALIDE MOLECULES

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Yttrium trihalide vapors mainly consist of  $YX_3$  monomeric molecules. In lower concentrations more complex species are present. Thus thermodynamic functions for monomeric molecules are needed for thermodynamic modeling of high-temperature processes in systems containing yttrium halide. Experimental information on the structure and spectra necessary for calculation of thermodynamic functions for these molecules is extremely scarce, because the experimental study of such compounds is very difficult. These compounds have very low volatility. High temperatures must be used to produce sufficient vapor pressure. High temperatures necessarily excite many quanta of the low-frequency bending motions, leading to large shrinkage effects. The vapor composition is unlikely to be simple; depending on the temperature and pressure, a fairly complex mixture of monomers, dimers and possibly trimers will be present. Recently published new experimental data and results of quantum-chemical ab initio and DFT calculations have expanded the information on the structure and vibration frequencies for yttrium trihalides. From this data, we estimated molecular constants for the whole  $YX_3$  series. For all  $YX_3$  molecules  $D_{3h}$  planar structure is accepted in this work, according to the results obtained in the recent quantum-mechanical computations [1, 2] and experimental data for  $YF_3$  and  $YCl_3$  [2, 3]. The vibrational frequencies taken on the basis of experimental and theoretical data are available in the literature. For  $YX_3(g)$  calculations were carried out using "rigid rotator – harmonic oscillator" approximation in the temperature range (298.15–6000) K. Yttrium trihalides have a closed electron shell, so the calculation of the thermodynamic functions are carried out without taking into account the excited electronic states. In all cases, thermodynamic quantities errors values are recommended. The calculated data is recorded in the database of information system IVTANTHERMO. As an illustration, the thermodynamic functions of  $YCl_3(g)$  for the temperatures 298.15, 1000, 1500, 2000, 3000 K are presented in Table. We believe that the results of this work are reliable being based on sufficiently more broad information published in recent time.

**Table.** Thermodynamic properties of  $YF_3(g)$  molecule

Temperature (K)	$C_p^\circ(T)$ (J/(mol·K))	$\Phi^\circ(T)$ (J/(mol·K))	$S^\circ(T)$ (J/(mol·K))	$H^\circ(T)-H^\circ(0)$ (kJ/mol)
298.15	70.744	257.856	314.283	16.824
1000	81.636	336.243	408.304	72.060
1500	82.461	366.176	441.593	113.125
2000	82.757	388.142	465.362	154.440
3000	82.971	419.858	498.966	237.325

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The work was supported by the Russian Science Foundation (Project No. 14-50-00124).

## Section 2. Thermodynamics of individual chemical compounds

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### BENCHMARK THERMODYNAMIC PROPERTIES OF ALKYLBIHENYLS: COMPREHENSIVE EXPERIMENTAL AND THEORETICAL STUDY

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Thermochemical properties of biphenyls are in disarray. New standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation at the temperature  $T = 298.15$  K of biphenyl, 4-tert-butyl-biphenyl, 3,3'-di-methyl-biphenyl, and 4,4'-di-tert-butyl-biphenyl were determined using combustion calorimetry. New molar enthalpy of vaporization of biphenyl was derived from the vapor pressure temperature dependence measured by the transpiration method. Thermodynamic data on alkyl substituted biphenyls available in the literature were collected, evaluated, and combined with own experimental results. This collection together with the new experimental results reported here has helped to resolve contradictions in the available enthalpies of formation data and to recommend the set of vaporization, sublimation, fusion, and formation enthalpies for alkylbiphenyls as the reliable benchmark properties for further thermochemical calculations. Quantum-chemical calculations of the gas phase molar enthalpy of formation of alkylbiphenyls have been performed using the G3MP2 method and results were in excellent agreement with the recommended experimental data. The standard molar entropies, molar heat capacities at the constant pressure, molar heat contents and the standard molar Gibbs function of formation have been calculated.

THERMODYNAMIC PROPERTIES OF NEODYMIUM CHLORIDE  
LOWEST HYDRATES

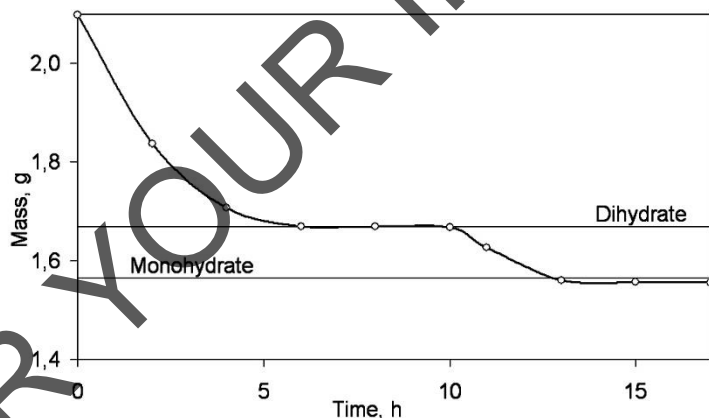
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Thermal stability and thermodynamics of the lowest hydrates of neodymium chloride are of great interest for the processes of anhydrous salt preparation and for its reduction to the metal. Precise measurements of the water vapour pressure over salt hydrates are often limited by the low-speed equilibration, formation of metastable, highly disperse and amorphous phases, by hydrolysis reactions. Therefore several tensimetric methods are usually used to obtain the reliable data. However for practical use of such thermodynamic results and for preliminary calculations it is often enough to have approximate data. Such data may be obtained with a method, proposed earlier [1], which is based on two main principles. First, a special glass or quartz vessel with a thin capillary is used for derivatographic measurements, allowing to determine quite accurately the temperature, at which the dissociation pressure of a hydrate achieves 1 atm; second, the estimated value of the standard entropy of a hydrate dissociation is used (146.8 J/mol·K). This method was particularly used to obtain the standard enthalpies of formation and standard entropies of the lowest hydrates of lanthanum chloride and sulfate [2, 3].

Two chemically pure samples of neodymium chloride hexahydrate of different origin were analyzed for neodymium content using a precise volumetric method to give practically identical results, the mean value  $\text{NdCl}_3 \cdot (6.08 \pm 0.04)\text{H}_2\text{O}$  was used for calculations. The main temperatures observed on heating (°C) are the following: 120 – incongruent melting, 154 – boiling of the saturated solution, 167 – decomposition of tetrahydrate, 201 – decomposition of dihydrate, 265 – decomposition of monohydrate. The residue was sintered, so the obtained temperatures of the lowest hydrates decomposition may be too high, as was observed for  $\text{LaCl}_3$  monohydrate [2].

To minimize kinetic inhibition of the decomposition process, powdery dihydrate was obtained by the method of controlled isothermal drying of hexahydrate at the temperature 100°C (Figure).



**Figure:** Air-drying of  $\text{NdCl}_3 \cdot 6.08\text{H}_2\text{O}$ .

This dihydrate did not melt on heating, and the end product of decomposition was also powdery. The following temperatures (°C) of decomposition were obtained at the heating rates 4.5 and 2.3 K/min: 178 (dihydrate) and 264 (monohydrate). Comparison of the observed mass loss with the theoretical values indicated that the resulting monohydrate and anhydrous chloride contained some percent of solid hydrolysis products –  $\text{NdOCl}$  or  $\text{Nd}(\text{OH})_2\text{Cl}$ . No indication of solid solutions was obtained, and it is the advantage of the used method that such products and a slow hydrolysis reaction do not influence substantially on the accuracy of the obtained values of  $\Delta_f H^\circ(298)$  (kJ/mol) and  $S^\circ(298)$  (J/(mol·K)):  $\text{NdCl}_3 \cdot \text{H}_2\text{O}$  ( $-1360.6 \pm 5$  and  $194.9 \pm 5$ );  $\text{NdCl}_3 \cdot 2\text{H}_2\text{O}$  ( $-1668.5 \pm 9$  and  $236.8 \pm 9$ ).

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## Section 2. Thermodynamics of individual chemical compounds

### DETERMINATION OF STABILITY CONSTANTS OF CYCLODEXTRIN INCLUSION COMPLEXES WITH BETULIN DERIVATIVES BY CAPILLARY ELECTROPHORESIS

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Betulin derivatives are pentacyclic triterpenoids of plant origin, which possess many pharmacological effects, such as antiviral, anti-inflammatory, antitumor activities. However, their medical use is very limited due to low solubility in water [1]. It is known that the solubility of these compounds can be substantially increased by means of complexation with cyclodextrins (CD). CDs are torus-shape oligosaccharides built up from glucopyranose units obtained by fermentation of starch. Cyclodextrins are able to form inclusion complexes with a great number of compounds, which may improve the guest solubility, bioavailability, physicochemical stability, both in solid state and in solution [2]. Capillary electrophoresis (CE) is not only an excellent separation technique but also well known as a suitable tool for determination of equilibrium physicochemical parameters such as stability constants [3]. For practically insoluble compounds, capillary electrophoresis has not been used.

The aim of this study was to determine the stability constants of the inclusion complexes between cyclodextrins ( $\beta$ -cyclodextrin, hydroxypropyl- $\beta$ -cyclodextrin and hydroxypropyl- $\gamma$ -cyclodextrin) and the betulin derivatives (betulinic acid and betulonic acid) using a capillary electrophoresis method.

The all measurements were performed using a Krasnoyarsk Regional Center of Research Equipment SB RAS capillary electrophoresis system with a diode array detector Agilent <sup>3D</sup>CE G 1600A (Agilent Technologies, Germany). An unmodified silica capillary with inner diameter 50  $\mu\text{m}$ , total length 64.5 cm, and effective length 56 cm was used. Capillary was thermostatted at 25°C. Detection was performed in the UV region at 200 nm. All solution in the experiments were filtered with a syringe filter, pore size 0.45  $\mu\text{m}$ . The samples were injected hydrodynamically for 2500 mbar·s. The applied voltage was +10 kV (cathode at the detector side). The results were processed using an embedded HP ChemStation software rev.10.02.

CE was firstly applied to determine the stability constants of water insoluble compounds. The solubility of betulin derivatives into solutions with different concentrations of cyclodextrins was measured by CE. Stability constants were obtained on the basis of solubility diagrams. In this case the stability constant can be calculated from the following equation:

$$S = K \cdot S_0 \cdot [CD] + S_0,$$

where  $S$  and  $S_0$  are solubility of derivatives betulin in buffer solution with and without CD, respectively;  $K$  is stability constant;  $[CD]$  is CD concentration. The stability constants of studied inclusion complexes were in the range from 250 to 500  $\text{M}^{-1}$ .

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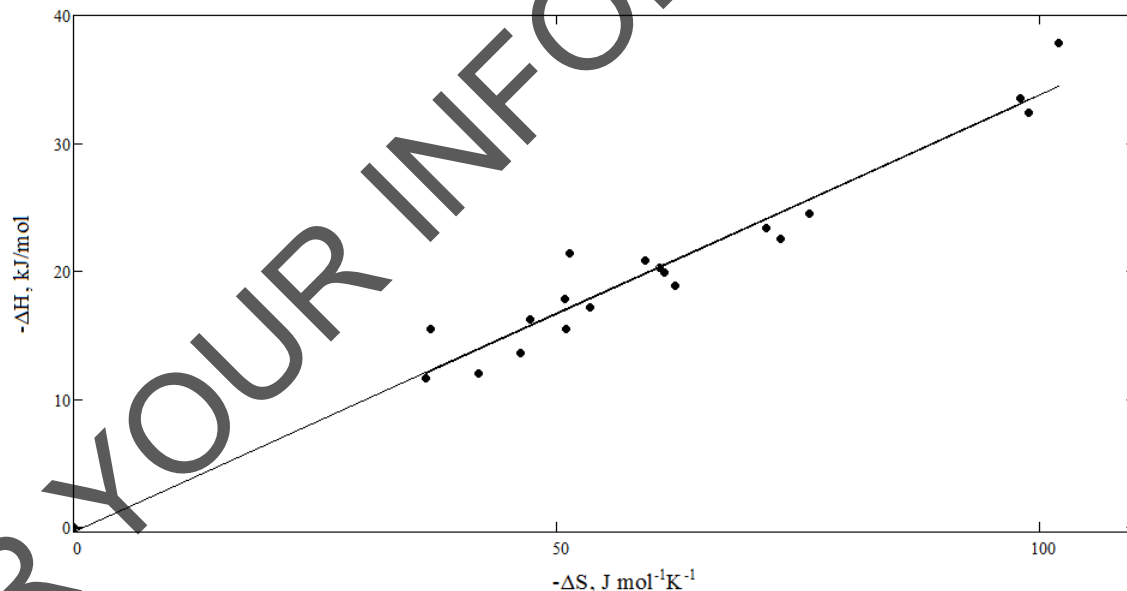
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COMPENSATION AND COOPERATIVE EFFECTS IN H-BOND  
THERMODYNAMICS OF HYDROPEROXIDESA.B. Remizov<sup>1</sup>, R.A. Skochilov<sup>1</sup>, O.V. Mikhailov<sup>2</sup><sup>1</sup>General Chemical Technology Department, Kazan National Research Technological University  
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Self-association of cumyl (CUH), tertiary butyl and 3-phenylmethyl hydroperoxides in various solvents and hetero-association of CUH with acetone and acetophenone in *n*-decane solutions were studied by FTIR spectroscopy.

We have developed a new approach in factor analysis frameworks which allows to determine concentrations and spectra of each H-bonded associate in solutions by their IR spectra [1]. With use this technique the temperature dependences of equilibrium constants of self-association of cumyl  $C_6H_5(CH_3)_2C(OOH)$  (CUH), *tert*-butyl  $(CH_3)_3C(OOH)$  (TBH) and 3-phenylmethyl  $(C_6H_5)_3C(OOH)$  (PMH) hydroperoxides in various solvents (*n*-decane ( $n-C_{10}H_{22}$ ), carbon tetrachloride ( $CCl_4$ ) and chlorobenzene ( $C_6H_5Cl$ )) were investigated by FTIR spectroscopy. The concentrations of hydroperoxides were varied from 0.01 up to 0.25 mol/l. The heteroassociates of CUH with acetone  $(CH_3)_2C=O$  (AC) and acetophenone  $C_6H_5(CH_3)C=O$  (AP) in *n*-decane solutions were investigated by the same methods. Thermodynamic parameters ( $\Delta H_i$ ,  $\Delta S_i$  and  $\Delta G_i$ ) of self- and heteroassociate formation were determined.



**Figure:** Common enthalpy–entropy compensation plot for all series of self- and hetero-association of hydroperoxides.

The obtained results were analyzed in combination with *ab initio* calculations DFT data on linear and cyclic CUH self-associates. The analysis data of the compensation enthalpies and entropies revealed compensation and cooperative effects.

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## Section 2. Thermodynamics of individual chemical compounds

### ADDITIVE CALCULATION OF VAPOR PRESSURE VALUES AND DETERMINATION OF ALIPHATIC HYDROCARBONS CRITICAL PARAMETERS ON ITS BASIS

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Calculation procedure for organic compounds saturated vapour pressure values based on the additive determination the coefficients in Riedel equation (1) describing the vapour pressure values temperature dependence within a wide range of temperatures [1]:

$$\ln P = A + \frac{B}{T} + C \cdot \ln T + D \cdot T^6, \quad (1)$$

where A, B, C, D are the equation coefficients.

For additive calculation the coefficients in Riedel equation a modified systematization of certain method of group contributions was used. Instead of Gauche interaction considering 1,4-intramolecular interactions partially a direct number account of all 1,4-intramolecular interactions of various type including the farther one was introduced.

The database NIST-TRC was used as a source of experimental information on the vapor pressures of alkanes, alkenes, alkynes, alkadienes, allenes needed to determine the numerical values of the parameters of the calculation method.

An algorithm is developed to determine the critical temperature, critical pressure and Riedel coefficient at the critical point in the temperature dependence of the compound vapour pressure. To calculate these substances critical parameters it was used Riedel equation with the reduced parameters. The coefficients  $A^+$ ,  $B^+$ ,  $C^+$ ,  $D^+$  can be expressed through the Riedel coefficient at the critical point  $\alpha_c$  [1]:

$$\begin{aligned} \ln P = \ln P_c - 35 \cdot 0,0838 \cdot (3,758 - \alpha_c) + 36 \cdot 0,0838 \cdot (3,758 - \alpha_c) \cdot \frac{T_c}{T} + \\ + (42 \cdot 0,0838 \cdot (3,758 - \alpha_c) + \alpha_c) \cdot \ln \left( \frac{T}{T_c} \right) - 0,0838 \cdot (3,758 - \alpha_c) \cdot \left( \frac{T}{T_c} \right)^6 \end{aligned}$$

The temperature dependence of saturated vapour pressure with three unknown random parameters  $T_c$ ,  $P_c$  and the  $\alpha_c$  was solved as the General form regression. Its solution is reduced to nonlinear equations system [2]. The determination of the individual constants  $T_c$ ,  $P_c$  and the  $\alpha_c$  values for hydrocarbon series in the temperature dependence saturated vapor pressure was carried out with the system Mathcad processing source ( $P, T$ )-data using the least squares method using three alternative functions Minerr, Find and Genfit conducting an independent search the nonlinear regression model parameters.

The average relative deviation of the calculated values of the vapor pressures in a wide range of temperature from the experimental values for 117 aliphatic hydrocarbons of the classes mentioned above amounted to 0.26%.

The average relative deviation of the calculated values of  $T_c$  and  $P_c$ , from the measured and calculated values of the  $\alpha_c$  found from the experimental data for 60 aliphatic hydrocarbons of various types, amounted 0.21; 2.26 and 0.31% respectively.

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THERMODYNAMIC PROPERTIES OF POLY(TRIFLUOROMETHYL)FULLERENES  
 $C_{60}(CF_3)_n$ ,  $n = 2-18$ N.A. Romanova, A.I. Druzhinina, R.M. Varuschenko, T.S. Papina, V.A. Luk'yanova,  
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Investigations of thermodynamic properties of trifluoromethylfullerenes are significantly hampered by the fact that preparation of pure compounds in amounts required for thermodynamic studying is a rather difficult task [1, 2]. But in this work a trifluoromethylfullerene  $S_6-C_{60}(CF_3)_{12}$  (Figure) was synthesized as described in [3] using a three-section glass ampoule in gramme-scale amount sufficient for reliable experimental investigation. Sample of  $S_6-C_{60}(CF_3)_{12}$  was characterized by elemental analysis, IR, UV/Vis, NMR  $^{19}F$ , Raman spectra and X-ray powder diffraction data.

The energy of combustion of  $S_6-C_{60}(CF_3)_{12}$  in oxygen was determined in a rotating-bomb isoperibolic calorimeter. The apparatus, calorimetric procedure, and analysis of combustion products were described in details in [4]. The heat capacity of  $S_6-C_{60}(CF_3)_{12}$  was determined in a fully automated set-up – a vacuum adiabatic calorimeter. This system was also used for processing and collecting the heat capacity data. Construction of the calorimeter and experimental procedure were described in [5]. We determined the enthalpy of combustion of  $S_6-C_{60}(CF_3)_{12}$  in oxygen and its heat capacity, which made possible to derive the thermodynamic functions of  $S_6-C_{60}(CF_3)_{12}$ , namely enthalpy, entropy and Gibbs energy of formation at 298.15 K (Table).

The enthalpy of formation of  $C_{60}(CF_3)_n$ ,  $n = (2-18)$  were estimated by method of isodesmic reactions according to equation:

$$\Delta_f H_m(C_{60}(CF_3)_n) = [n/12 \cdot \Delta_f H_m^{\text{exp}}(C_{60}(CF_3)_{12}) + (1-n/12) \cdot \Delta_f H_m^{\text{exp}}(C_{60})] - \Delta_r H^{\text{th}}, \quad (1)$$

where  $\Delta_r H^{\text{th}}$  value is DFT calculated enthalpy of reaction of disproportionation:

$$C_{60}(CF_3)_n = n/12 \cdot (S_6-C_{60}(CF_3)_{12}) + (1-n/12) \cdot C_{60}. \quad (2)$$

These experimental thermochemical data enabled estimation of the formation energy for a broad range of other trifluoromethylated compounds  $C_{60}(CF_3)_n$ , with  $n = (2-18)$ , on the basis of their DFT calculated relative energies.

**Table.** Thermodynamic functions of  $S_6-C_{60}(CF_3)_{12}$  at  $T = 298.15$  K

Physical state	$-\Delta_c H_m^\circ$ (kJ/mol)	$-\Delta_f H_m^\circ$ (kJ/mol)	$S_m^\circ$ (J/mol K)	$-\Delta_f S_m^\circ$ (J/mol K)	$-\Delta_f G_m^\circ$ (kJ/mol)
Crystalline	28704 ± 146	6072 ± 148	1397 ± 14	2665 ± 14	5278 ± 148
Ideal gas	28853 ± 146	5923 ± 148	1582 ± 14	2480 ± 14	5184 ± 148

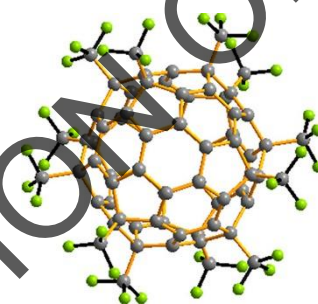
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**Figure:** Top view of the  $S_6-C_{60}(CF_3)_{12}$  molecule.

## Section 2. Thermodynamics of individual chemical compounds

### PHASE EQUILIBRIA IN THE Y – Sr – Fe – O SYSTEM AND PHYSICOCHEMICAL PROPERTIES OF $Sr_{1-x}Y_xFeO_{3-\delta}$

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Powder samples of the ferrites under investigation were synthesized by means of conventional glycerol-nitrate method. Final annealing was performed at 1373 K in air with subsequent quenched to room temperature.

The phase equilibria in the Y – Sr – Fe – O system were systematically studied at 1373 K in air. The intermediate phases formed in the Y – Sr – Fe – O system at 1373 K in air were solid solutions  $Sr_{1-x}Y_xFeO_{3-\delta}$  with  $0.0 \leq x \leq 0.1$  and  $0.05 \leq x \leq 0.25$  (Figure). It was shown that  $Sr_{1-x}Y_xFeO_{3-\delta}$  with  $0.0 \leq x \leq 0.1$  possesses orthorhombic structure (sp. gr.  $Pnma$ ). According to the results of X-ray diffraction analysis the homogeneity range for the  $Sr_{1-x}Y_xFeO_{3-\delta}$  solid solutions at studied conditions appears within  $0.05 \leq x \leq 0.25$ . XRD patterns for all single phase samples were refined by Rietveld method within the cubic structure ( $Pm\bar{3}m$  space group).

The refined unit cell parameters and unit cell volumes of  $Sr_{1-x}Y_xFeO_{3-\delta}$  were increased with the increase of yttrium content probably due to larger ionic radius of  $Y^{3+}$  compared to that of  $Fe^{3+}/Fe^{4+}$ .

Oxygen nonstoichiometry of  $Sr_{1-x}Y_xFeO_{3-\delta}$  solid solutions with  $0.05 \leq x \leq 0.25$  was measured by means of thermogravimetric technique within the temperature range (298–1273) K in air. The absolute values of oxygen content were determined using iodometric titration (Table).

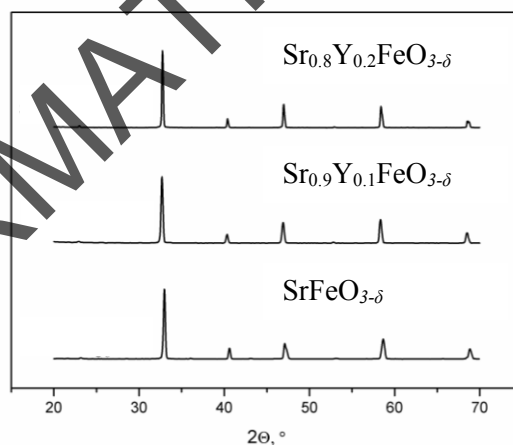


Figure: X-ray patterns of the  $Sr_{1-x}Y_xFeO_{3-\delta}$ .

Table. The values of the unit cell parameters and oxygen content for the  $Sr_{1-x}Y_xFeO_{3-\delta}$

Composition	Space group	a, Å	b, Å	c, Å	Oxygen content (3- $\delta$ )
$Sr_{0.8}Y_{0.2}FeO_{3-\delta}$	nPmP		3.861		2.65±0.04
$Sr_{0.9}Y_{0.1}FeO_{3-\delta}$			3.868		2.74±0.04
$SrFeO_{3-\delta}$	mmPP	10.9m5		7.701	2.87±0.04

The oxygen content of  $Sr_{1-x}Y_xFeO_{3-\delta}$  was decreased with the increase of yttrium content (Table).

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## PHASE COMPOSITION OF OXIDE SYSTEM $Ce_{1-x}M_xO_{2-\delta}$ AND ITS EFFECT ON CATALYTIC ACTIVITY

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Systems on the basis of complex oxides are increasingly used in the present time. On the one hand they are used as components of catalytic systems for atmosphere protection from emissions of toxic substances. These catalytic systems can be used for both mobile (transport) and stationary pollutants, for example, various manufacturing processes. On the other hand complex oxides are used as components for promising energy sources such as fuel cells, devices of flameless oxidation. Complex oxide systems on the basis of cerium oxide (fluorite structure) and lanthanum manganite (perovskite structure) are among promising materials in this regard. Prospectivity of complex oxides is a possibility of their properties controlling by introducing dopants with different nature in their structure. For example, alkaline and transition metals (copper, silver, iron and others) are the dopants which significantly change the characteristics of the above-mentioned complex oxides. It should be noted that variation of chemical composition is not the only way for complex oxides' properties controlling. Either homogeneous, due to the formation of solid solutions, or heterogeneous systems containing additional phase (in metal or oxidized form) are formed during synthesis of complex oxides. In the second case the additional phase may favorably affect catalytic activity.

The present work is devoted to the study of the correlation of chemical and phase composition of complex oxide components with their activity and stability. Complex oxides on the basis of cerium oxide  $Ce_{1-x}M_xO_{2-\delta}$  ( $M = Cs, K, Ag, Fe, Ni, Cu$ ) were synthesized by pyrolysis of polymer-salt compositions [1]. Nitrates of the respective metals and polyvinyl alcohol were used as initial substances. This method allows to obtain nanosized particles of complex oxides. The obtained materials possess high activity in the reaction of catalytic oxidation of carbon-containing substances.

By the x-ray phase analysis ( $CuK\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ,  $2\Theta = 20^\circ - 70^\circ$ ) it was found that the introduction of such dopants as K, Cs, Fe (up to  $x = 0.3$ ) in fluorite structure results in the formation of solid solutions. So, the smooth change of the lattice parameter of the basis oxide was observed. While the introduction of Ag, Ni, Cu leads to the formation of heterogeneous systems, which contain metallic silver or oxides of nickel and copper, respectively, in addition to the main phase.

It is shown that cerium oxide doped with alkaline and transition metals has significantly higher catalytic activity in the reaction of soot oxidation by oxygen in comparison with pure  $CeO_{2-\delta}$ . Model soot (Degussa) was used for experiments. Four-fold excess of oxide materials were taken. Carbon black and catalyst were carefully grinded to achieve tight contact between particles. Soot oxidation was performed in air, in an open reactor under isothermal conditions. The temperature interval was (300–350)°C.

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## Section 2. Thermodynamics of individual chemical compounds

### HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF DyVO<sub>4</sub>

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Possessing an advantageous combination of physicochemical and functional properties, rare earth orthovanadates are widely used to produce a variety of materials: phosphors for high and low-pressure mercury lamps, catalysts, and others. It is known from the literature that dysprosium orthovanadate has a crystal lattice with the xenotime structure (*I41/amd*) and is isostructural with zircon (ZrSiO<sub>4</sub>). The purpose of this work was to obtain reliable data on the low-temperature thermodynamic functions of DyVO<sub>4</sub> from experimental heat capacity data measured by adiabatic calorimetry.

Dysprosium orthovanadate was prepared by reacting stoichiometric amounts of analytical grade NH<sub>4</sub>VO<sub>3</sub> and Dy<sub>2</sub>O<sub>3</sub> at 570, 770, and 1170 K for at least 24 h at each temperature. Single phase of samples was confirmed by the powder X-ray diffraction method. The low-temperature heat capacity of DyVO<sub>4</sub> was measured in the range (6.12–343.26) K using a BKT-3 calorimeter (LLC Termis). The sample studied had the form of fine white powder.

According to studies of dysprosium orthovanadate at very low temperatures, on heating this compound undergoes both an antiferromagnetic to paramagnetic phase transition [1] ( $T = 2.93$  K) and an orthorhombic to tetragonal structural transformation ( $T = 14.4$  K). The latter transition is due to the cooperative Jahn–Teller effect, arising from the interaction of orbital states of electrons and crystal field distortions. This effect in DyVO<sub>4</sub> was described in detail: the  $a$  and  $b$  parameters of the orthorhombic structure vary gradually starting above 7 K and become equal at 13.8 K [2] which corresponds to a second-order phase transition. Above 14 K, the  $a$  and  $c$  parameters of the tetragonal structure vary systematically. The anomaly found in this study has the following characteristics: transition temperature  $T = 14.42$  K,  $\Delta S_{tr} = 7.93$  J/(mol K),  $\Delta H_{tr} = 98.8$  J/mol. The anomalous heat capacity values  $C_{p,tr}(T)$  were measured from the baseline obtained by extrapolating the smoothing curve for the experimental heat capacity data in the range 42.63–343.26 K.

The anomalous Schottky contribution was evaluated as the difference between the measured heat capacity  $C_p(T)(\text{DyVO}_4)$  and the normal heat capacity  $C_n(T)(\text{DyVO}_4)$ .  $C_n(T)$  of DyVO<sub>4</sub> was calculated from the heat capacities of GdVO<sub>4</sub> and diamagnetic LuVO<sub>4</sub>.

Entropy, change of enthalpy and derived Gibbs's energy were calculated by the equation with use of functions of Debye, Einstein and Kiffer. Thermodynamic functions of RE orthophosphates in area (2–1600) K were obtained using the experimental data. Using the  $S^0(298.15$  K) found in this study, we calculated the standard Gibbs energy of formation of DyVO<sub>4</sub> from its constituent elements. To this end we used the  $\Delta H_f^0(\text{DyVO}_4, 298.15$  K) reported in [3].

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THERMODYNAMIC BASIS OF PROCESSES FOR TREATMENT OF  
 $\text{Ln}_2(\text{SO}_4)_3$  ( $\text{Ln} = \text{La} - \text{Lu}$ ) IN THE HYDROGEN STREAM

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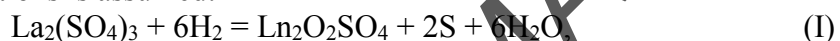
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Oxysulfides of rare earth elements (REE) of  $\text{Ln}_2\text{O}_2\text{S}$  ( $\text{Ln} = \text{La} - \text{Lu}$ ) and yttrium are studied as phosphors, laser and optical materials [1]. Solid solution of  $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  is a new prospective probe for biomarking [2].

The aim of this work is to study the thermodynamic formation of reaction products in competing processes: 1)  $\text{La}_2(\text{SO}_4)_3 \rightarrow \text{La}_2\text{O}_2\text{S}$ ; 2)  $\text{La}_2(\text{SO}_4)_3 \rightarrow \text{La}_2\text{O}_3$ .

Method of obtaining  $\text{Ln}_2\text{O}_2\text{S}$  compounds at impact on REE sulfates of hydrogen stream is technological, without contamination of batch, operating time of the product takes place in one step without the use of additional reagents [3].

The thermodynamics of the processes occurring in the interaction of sulfates of rare earth elements with hydrogen at (600–1150)°C is considered on the example of lanthanum sulphate. The chemical reactions is assumed:



It was established, that the formation of a homogeneous  $\text{Ln}_2\text{O}_2\text{S}$  in a stream of hydrogen at (500–850)°C is occurred at treatment of  $\text{Ln}_2(\text{SO}_4)_3$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ ), but mix of  $\text{Ln}_2\text{O}_2\text{S}$  and  $\text{Ln}_2\text{O}_3$  compounds is occurred at the same temperature as a result of the experiment with  $\text{Ln}_2(\text{SO}_4)_3$  ( $\text{Ln} = \text{Gd} - \text{Lu}$ ). Thermodynamic data are available in literature [1, 4] for  $\text{Ln}_2\text{O}_2\text{S}$  and  $\text{Ln}_2\text{O}_3$  compounds. The phenomenon is explained by preferential formation of oxysulfides at the treatment of lanthanide sulphates from lanthanum to samarium, but increase of stability of oxide in comparison with oxysulfides is observed from gadolinium to lutetium, according to values of Gibbs energy (Table).

**Table.** The values of Gibbs energy (kJ/mol) for oxysulfides and oxides of REE

Compound	$-\Delta G^\circ(298)$	Compound	$-\Delta G^\circ(298)$
$\text{La}_2\text{O}_2\text{S}$	1539 [1]	$\text{La}_2\text{O}_3$	1705 [4]
$\text{Sm}_2\text{O}_2\text{S}$	1518 [1]	$\text{Sm}_2\text{O}_3$	1727 [4]
$\text{Gd}_2\text{O}_2\text{S}$	1520 [1]	$\text{Gd}_2\text{O}_3$	1729 [4]

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[4] Lidin, R.A. The constants of inorganic substances: a handbook. M.: Drofa, 2006, 685.

## Section 2. Thermodynamics of individual chemical compounds

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### INVESTIGATION OF THERMODYNAMIC PROPERTIES OF LIQUID-CRYSTALLINE DENDRIMERS

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Dendrimers are special class of high-molecular compounds whose molecules are highly ordered spatially hyperbranched topologically completely acyclic compositions with structure of continuously branching tree. Liquid-crystalline (LC) dendrimers, which molecules combine structural units capable to impart the liquid-crystalline properties with amorphous dendritic architecture have attracted progressively growing attention of researchers engaged in the chemistry and physics of liquid crystals, physical chemistry of polymers, and supramolecular chemistry. Carbosilane liquid-crystalline dendrimers hold a particular position among the large quantity of dendrimers. This is connected with their kinetic and thermodynamic stability and vast possibilities to change their dendritic architecture via specific reactions typical for silicon.

For the first time the temperature dependences of the heat capacity of liquid-crystalline carbosilane dendrimers with terminal methoxyphenylbenzoate groups from the first to the fourth generation have been determined over the range from 6 to 370 K by the method of precision adiabatic vacuum calorimetry. In the above temperature range the physical transformations have been detected and their standard thermodynamic characteristics have been estimated and analyzed. Particularly, the phase transitions in liquid-crystalline state have been detected and their thermodynamic quantities were interpreted with structural parameters. The enthalpies and entropies of transformations have been found in inclined type smectic crystals.

The experimental data were used to calculate standard thermodynamic functions, namely the heat capacity  $C_p^0(T)$ , enthalpy  $H^0(T) - H^0(0)$ , entropy  $S^0(T)$  and Gibbs energy over the range from  $T \rightarrow 0$  to 370 K for different states. The standard entropies of formation of dendrimers in liquid-crystalline state at  $T = 298.15$  K and the standard entropies of its hypothetical synthesis at the same temperature were estimated. The standard thermodynamic properties of studied dendrimers have been compared and some dependences on their composition were obtained. Thus, it was shown that thermodynamic properties dendrimers under study do not depend on generation number and are defined of the nature of terminal groups.

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## LOW-TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF LAYERED PEROVSKITE-TYPE OXIDES

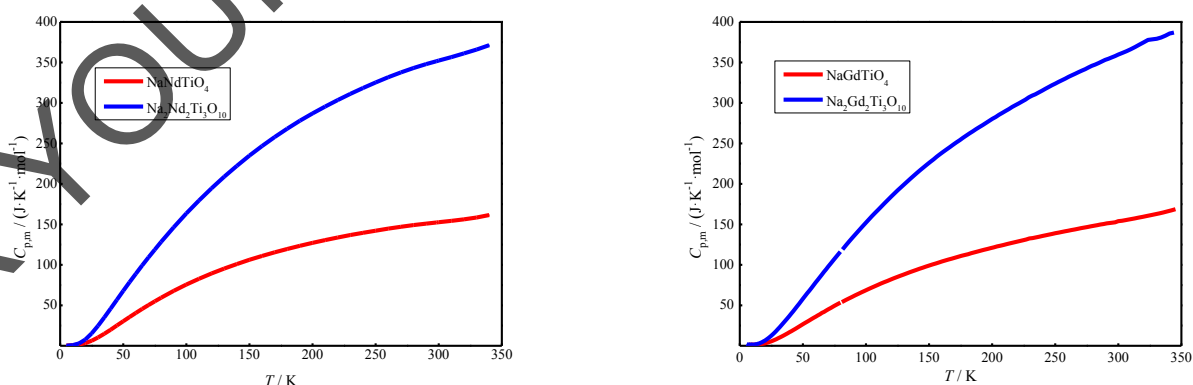
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Layered perovskite-type oxides represent one of the most perspective classes of ceramic materials. Owing to the particularities of their crystal structure, these compounds exert important physical and chemical properties (electric, magnetic, catalytic) and find application in the newest areas of science and equipment.

In the report results of calorimetric investigation of titanates  $\text{NaLnTiO}_4$  and  $\text{Na}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$  ( $\text{Ln} = \text{Nd, Gd}$ ), which belong to the Ruddlesden–Popper phases, are presented. These compounds are constructed by the intergrowth of alternating perovskite-type blocks ( $P$ ) and rock-salt type slabs ( $RS$ ) with various thickness of perovskite blocks.

Isobaric heat capacity of the complex oxides was measured in an adiabatic calorimeter in the temperature range of (6–340) K. Heat capacities of the samples rise gradually with temperature increase over the main temperature interval (Figure). At the same time, heat capacities of three compounds were found to increase with temperature decrease in the range of (6–7.5) K for  $\text{Na}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ , (6–8) K for  $\text{NaGdTiO}_4$ , and (6–10) K for  $\text{Na}_2\text{Gd}_2\text{Ti}_3\text{O}_{10}$ . Such anomalies observed in the heat capacity curves are likely to be descending branches for magnetic disorder–order phase transitions, which lie outside the measuring range of the calorimeter. Standard thermodynamic properties (heat capacity, enthalpy, entropy, and Gibbs energy) of the oxides were evaluated from the experimental heat capacity temperature dependencies.

The heat capacity data of Gd-containing complex oxides in the range of (20–50) K were analyzed using the multifractal model of heat capacity of solids. According to the multifractal model,  $D = 2.8$ ,  $\Theta_{\text{max}} = 262.5$  K for  $\text{NaGdTiO}_4$ , and  $D = 2.8$ ,  $\Theta_{\text{max}} = 251.0$  K for  $\text{Na}_2\text{Gd}_2\text{Ti}_3\text{O}_{10}$ . The obtained values of  $D$  indicate the layered-spatial structure of Gd-containing oxides, which are in agreement with structural features of compounds under consideration.



**Figure:** Molar heat capacities of  $\text{NaLnTiO}_4$  and  $\text{Na}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$  ( $\text{Ln} = \text{Nd, Gd}$ ) as function of temperature.

This work was supported by the Russian Foundation for Basic Research (Project No. 14-33-0676) and Saint Petersburg State University research grant (reg. No. 12.0.105.2010).

## Section 2. Thermodynamics of individual chemical compounds

### INVESTIGATION OF LOW-TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF $KTh_2(PO_4)_3$

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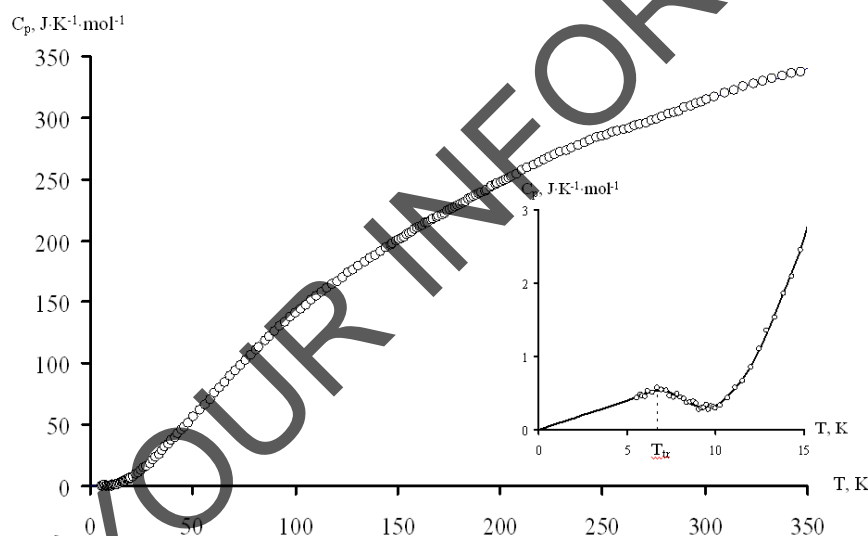
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The widespread minerals of thorium are oxide, silicates and phosphates. In the orthophosphates and orthoarsenates, only two structure-types host actinides in ninefold coordination: the monoclinic  $KTh_2(PO_4)_3$  structure, and the monazite structure, but these two are amongst the most important as they show the widest range of chemical composition.

The experimental values of the molar heat capacity of  $KTh_2(PO_4)_3$  over the range from 5.5 to 350 K and the smooth  $C_p = f(T)$  plot are presented in Figure. The heat capacity of this substance in interval from 10 to 350 K gradually increases with rising temperature and does not show any peculiarities, but over the range from 5.5 to 10 K there is seen an anomalous heat capacity [1]. The transition temperature of the sample under study  $T_{tr} = 6.7 \pm 0.2$  K was estimated as the temperature of maximal  $C_p$  value within the temperature interval of the transition. In the literature, there are practically no results of a study of the temperature dependences of the heat



**Figure:** Temperature dependence of heat capacity of  $KTh_2(PO_4)_3$ .

capacity of thorium compounds at liquid-helium temperatures. However, it is known that thorium metal is diamagnetic. It becomes superconductor at temperatures below 1.4 K. Perhaps the presence of thorium in studied compound contributed to this transition.

To calculate the standard thermodynamic functions of the potassium dithorium trisphosphate, its  $C_p$  values were extrapolated from the temperature of the measurement beginning at approximately 5.5 K to

0 K by graphic method. The absolute entropies of potassium dithorium trisphosphate and the corresponding simple substances were used to calculate the standard entropy of formation of the compound under study at 298.15 K,  $\Delta_f S^\circ(298.15, KTh_2(PO_4)_3, cr) = -1186.3 \pm 1.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

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THERMODYNAMIC INVESTIGATION OF RIBOFLAVIN,  
CYANOCOBALAMIN AND NICOTINIC ACID

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Riboflavin, cyanocobalamin and nicotinic acid are water-soluble B vitamins that play important role in cell metabolism. They have a key role in the normal functioning of the brain and nervous system. B vitamins are widely used in medicine, in food industry, in production of cosmetics. The goal of this work includes calorimetric determination of the standard thermodynamic functions of the B vitamins to describe biochemical and industrial processes with its participation.

The temperature dependences of heat capacity of riboflavin ( $C_{17}H_{20}N_4O_6$ ), cyanocobalamin ( $C_{63}H_{89}CoN_{14}O_{14}P$ ) and nicotinic acid ( $C_5H_4N-COOH$ ) have been measured in the range from 7 to 330 K, from 6 to 343 K and from 5 to 346 K, respectively. The heat capacity for all substances gradually increases with rising temperature and does not show any peculiarities. The experimental data were used to calculate standard thermodynamic functions, namely the heat capacity, enthalpy

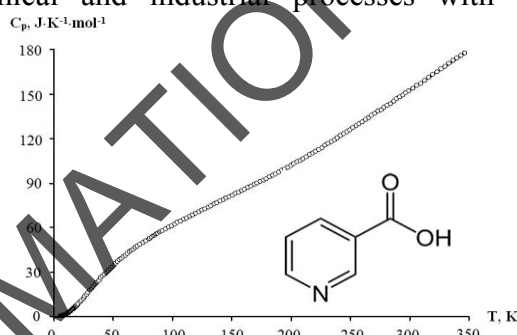


Figure: Temperature dependence of heat capacity of nicotinic acid.

$H^\circ(T) - H^\circ(0)$ , entropy  $S^\circ(T) - S^\circ(0)$  and Gibbs energy  $G^\circ(T) - H^\circ(0)$  for the range from 0 to 330 K. The value of the fractal dimension  $D$  in the function of multifractal generalization of Debye's theory of the heat capacity of solids was estimated and the character of heterodynamics of structure was detected. The  $D$ -value points to the layer structure of compounds. In a calorimeter with a static bomb and an isothermal shield, the energies of combustion of the riboflavin and cyanocobalamin have been measured at 298.15 K. The enthalpies of combustion  $\Delta_c H^\circ$  and the thermodynamic parameters of formation  $\Delta_f H^\circ$ ,  $\Delta_f S^\circ$ ,  $\Delta_f G^\circ$  of the vitamins ( $B_2$ ,  $B_{12}$ ) from the simple substances at  $T = 298.15$  K and  $p = 0.1$  MPa have been calculated [1, 2]. The enthalpy of formation of nicotinic acid was experimentally determined in work [3]. These values of standard enthalpy and entropy of formation were used to calculate the standard Gibbs energy of formation nicotinic acid at 298.15 K [4]. For the tested substances the decomposition temperatures were determined by differential scanning calorimetry.

Table. Enthalpies of combustions and thermodynamic characteristics of formation of vitamins

Compound	$-\Delta_c H^\circ$ (kJ·mol <sup>-1</sup> )	$-\Delta_f H^\circ(298)$ (kJ·mol <sup>-1</sup> )	$-\Delta_f S^\circ(298)$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$-\Delta_f G^\circ(298)$ (kJ·mol <sup>-1</sup> )
$C_{17}H_{20}N_4O_6$	8116 ± 13	1432 ± 13	1961 ± 3	847 ± 14
$C_5H_4N-COOH$	-	344.9 ± 0.9	503 ± 3	195 ± 2
$C_{63}H_{89}CoN_{14}O_{14}P$	33459 ± 14	5017 ± 15	7281 ± 5	2846 ± 15

- [1] Knyazev, A.V.; Smirnova, N.N.; Plesovskikh (Shipilova), A.S.; Shushunov, A.N.; Knyazeva, S.S. *Thermochim. Acta*, 2014, 582, 35-39.  
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## Section 2. Thermodynamics of individual chemical compounds

### REGULARITIES IN THE CHANGES OF THE THERMAL EXPANSION PARAMETERS OF SOLID SOLUTIONS OF ARSENATE– AND VANADATE– PHOSPHATE OF ZIRCONIUM AND ALKALI METALS. TEMPERATURE DEPENDENCE OF THE HEAT CAPACITY OF $\text{NaZr}_2(\text{AsO}_4)_3$

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Crystalline compounds with NZP-structure and ceramics on their basis have high stability with regard to destructive factors of natural and technogenic character, and resistance to the thermal stresses. The ability of solid solution formation makes it possible to vary their thermophysical properties. Thermophysical properties, such as thermal expansion and heat capacity, have fundamental significance in all application areas of these materials.

The goal of the research is to explore behavior of arsenates  $\text{MZr}_2(\text{AsO}_4)_3$  ( $M = \text{Li, Na, K, Rb, Cs}$ ) and complex phosphates  $\text{MZr}_2(\text{TO}_4)_x(\text{PO}_4)_{3-x}$  ( $T = \text{As, V}$ ) with NZP-structure under heating.

X-ray diffraction patterns were obtained on a Shimadzu XRD-6000 diffractometer. High-temperature measurements were made in temperature range 293–1073 K on the same apparatus using a Shimadzu HA-1001 thermal accessory. The temperature dependence of the heat capacity of  $\text{NaZr}_2(\text{AsO}_4)_3$  was measured over the temperature range from 7 to 340 K with BKT-3.07 thermophysical unit and from 300 to 650 K using DSC 204 F1 Phoenix calorimeter.

The crystalline phosphates were synthesized with the sol-gel method based on reactions in aqueous solution. The phase purity of the synthesized samples was checked with powder X-ray diffraction. The results of electron microprobe analysis have shown that the samples are homogeneous and their compositions are close to the theoretical values calculated for the formulas  $\text{MZr}_2(\text{AsO}_4)_3$  and  $\text{MZr}_2(\text{TO}_4)_x(\text{PO}_4)_{3-x}$ .

In the studied systems there is a characteristic picture of temperature dependence of the changes in the unit cell parameters: structure expansion along “c” axis and structure compression along “a” axis. Thermal expansion data show different behavior of arsenates  $\text{MZr}_2(\text{AsO}_4)_3$  and the solid solutions of arsenate-phosphates  $\text{MZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$  and vanadate-phosphates  $\text{MZr}_2(\text{VO}_4)_x(\text{PO}_4)_{3-x}$  in regard to anisotropy and volumetric thermal expansion. The size increasing of an alkali metal cation of the arsenates leads to the decrease of absolute values of volumetric thermal expansion coefficients and anisotropy. Owing to composition changing ( $x$ ) of solid solution, anisotropy decrease effect can be accompanied either by an increase or decrease of average linear thermal expansion coefficient (LTEC) value. Thermal expansion anisotropy and LTEC are minimal for  $\text{CsZr}(\text{AsO}_4)_3$  ( $\alpha_{\text{av}} = 2 \cdot 10^{-6} \text{ K}^{-1}$ ),  $\text{CsZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$  ( $\alpha_{\text{av}} = 3 \cdot 10^{-6} \text{ K}^{-1}$ ) and  $\text{CsZr}_2(\text{VO}_4)_{0.2}(\text{PO}_4)_{2.8}$  ( $\alpha_{\text{av}} = 0.7 \cdot 10^{-6} \text{ K}^{-1}$ ).

The curve  $C_p^0$  of arsenate  $\text{NaZr}_2(\text{AsO}_4)_3$  does not have any features in the temperature range (7–650) K. The absence of polymorphic transformation on the curve  $C_p^0 = f(T)$  is caused by crystalline arsenate stability. For the arsenate the thermodynamic functions  $C_p^0$ ,  $H^\circ(T) - H^\circ(0)$ ,  $S^\circ(T)$ ,  $G^\circ(T) - H^\circ(0)$  from  $T \rightarrow 0$  to 650 K are calculated. The standard entropy of its formation from elements is  $\Delta_f S^\circ(\text{NaZr}_2(\text{AsO}_4)_3, \text{cr}, 298.15 \text{ K}) = -1087 \pm 2 \text{ J}/(\text{mol K})$ .

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## THERMODYNAMICS AND STRUCTURES OF GASEOUS GERMANIUM SALTS

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In present study the stability of tree new gaseous oxyacid salts of germanium was shown. Thermodynamic properties and structures for  $\text{GeB}_2\text{O}_4$ ,  $\text{GeMo}_2\text{O}_7$  and  $\text{GeV}_2\text{O}_6$  were obtained by high temperature mass spectrometry and M06 DFT calculations.

The mass spectrometer MS-1301 was used. The gaseous salts were synthesized directly in molybdenum or zirconia Knudsen cells. The cells were heated by an electron bombardment. The temperature was measured by the optical pyrometer EOP-66. Localization of energy stationary points and subsequent vibrational analysis were performed in the framework of DFT M06 method. Def2-TZVP basis sets with the corresponding effective core potential for tin were chosen.

The interpretation of mass spectra was done by ordinary for low-resolution mass spectrometry scheme including the comprasion  $m/z$  ratio with theoretical for all peaks in mass spectrum, calculations of the isotopic abundances for each gropus of peacks and determination of apparent energy for all ions. At the final we conclude that vapor above germanium oxide-containing systems consist of gaseous oxides and geseous germanium oxyacid salts. In order to obtain the standard formation enthalpies of the gaseous germanium salts the equilibrium constants of reactions (1)–(4) in gaseous phase were measured:



The calculations of reaction enthalpies were made by the third-law procedure. In order to lead obtained values to standard conditions the thermodynamic functions for germanium, boron, molybdenum and vanadium oxides were taken from literature and for gaseous salts were calculated by the statistical thermodynamic method in “rigid rotor – harmonic oscillator” approximation. The obtained standard formation enthalpies for gaseous germanium salts listed in table below.

*Table. The standard formation enthalpies of gaseous germanium oxyacid salts*

Substance	$-\Delta_f H^\circ_{298}$ (kJ/mol)
$\text{GeB}_2\text{O}_4$	1101±18
$\text{GeMo}_2\text{O}_7$	1449±41
$\text{GeV}_2\text{O}_6$	1520±42

## Section 2. Thermodynamics of individual chemical compounds

### CALORIMETRIC AND MAGNETIC STUDY OF SYNTHETIC $\text{Ca}_2\text{Ge}_{(1-x)}\text{Cr}_x\text{O}_4$ MIXED CRYSTALS

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Materials with olivine structure are widely used in various fields of science and technology as the basic material for solar systems [1] and laser medium [2, 3]. Preparation of these materials with specified properties and effects is often associated with the presence of transition metal ions in the structure. These ions can be a structural unit or a dopant in the crystal lattice. Usually, the study of thermodynamic properties of substances with a similar structure was carrying out for the samples with high doping level. At the same time, there is lack of thermodynamic properties data of low doped compounds with olivine structure. The goal of this research was calorimetric and magnetic study of synthetic  $\text{Ca}_2\text{Ge}_{(1-x)}\text{Cr}_x\text{O}_4$  solid solutions with low level of doping by Cr ions in compound. A choice of objects for investigation was made in favor of this compound because  $\text{Ca}_2\text{Ge}_{(1-x)}\text{Cr}_x\text{O}_4$  is promising as a material for creating on its basis amplifiers for fiber links, operating at wavelengths of about 1.4 microns. Moreover, chromium ions are incorporated into crystal structure of  $\text{Ca}_2\text{GeO}_4$  in charge state as only +4. For comparison, Cr ions, as dopant, are entered into crystal structure widely known forsterite ( $\text{Mg}_2\text{SiO}_4$ ) in two charges state +3 and +4. The latter circumstance is largely determined the difficulty in studying the properties of  $\text{Mg}_2\text{SiO}_4$  doped by chromium ions. Olivine-type mixed crystals  $\text{Ca}_2\text{Ge}_{(1-x)}\text{Cr}_x\text{O}_4$  were prepared as a result the solid state reaction of CaO,  $\text{GeO}_2$ ,  $\text{Cr}_2\text{O}_3$  in appropriate molar ratios. Five samples of turquoise-green powders were obtained and their purity were varied in the range from  $x = 0.04$  to 0.2. Analysis of final product of the reaction was performed by XRD method. By vacuum adiabatic calorimetry it has been found, that the temperature dependence of heat capacity of samples shows two anomalies in the temperature regions around  $T = 11$  K and from  $T = (230 \text{ to } 245)$  K. Earlier [4], it was shown that there are only contribution due to lattice vibrations to the heat capacity of the synthetic  $\text{Ca}_2\text{GeO}_4$  (without impurities) and phase transitions were not found. The X-ray analysis of  $\text{Ca}_2\text{GeO}_4$  confirms the constancy of olivine crystal structure in the temperature region from  $T = (100 \text{ to } 300)$  K. It should be noted that changing in chemical composition of  $\text{Ca}_2\text{Ge}_{(1-x)}\text{Cr}_x\text{O}_4$  leads to decreasing value of  $C_p^\circ = f(T)$  with increasing concentration of chromium ions ( $x$ ). It is known, that anomalies in general direction  $C_p^\circ = f(T)$  of similar materials are associated with the emergence of order in the magnetic sublattice structure of the compounds [1, 5]. We assumed that investigated material has properties which are close to the antiferromagnetic. Magnetic properties were characterized using an automated physical characterization system, Quantum Design PPMS-9. Magnetization was measured as a function of temperature between 2 and 300 K in a magnetic field of up to 5 kOe. The magnetic nature of anomalies in heat capacity of compounds under study was confirmed by the temperature dependence of magnetic susceptibility. It is shown, that the results of calorimetric and magnetic studies are in good agreement with each other in temperature region of anomalies.

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PHASE RELATIONS AND PHYSICOCHEMICAL PROPERTIES OF INDIVIDUAL PHASES IN QUATERNARY OXIDE SYSTEM  $\text{LaMnO}_3\text{--BaMnO}_3\text{--BaFeO}_{2.5}\text{--LaFeO}_3$ L.S. Skutina<sup>1</sup>, V.E. Sheveleva<sup>1</sup>, E.Yu. Pikalova<sup>2</sup>, E.A. Filonova<sup>1</sup><sup>1</sup>Ural Federal University named after the first President of Russia B.N. Yeltsin  
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The most using method allowing to achieve desired properties of complex oxide material is doping with donor and acceptor elements. In present work influence of properties and concentration of dopant on crystal structure and physicochemical properties of lanthanum manganite  $\text{LaMnO}_3$  was studied. Doping was performed in *A*-site (by substitution for  $\text{La}^{3+}$  by  $\text{Ba}^{2+}$ ) and in *B*-site (by substitution for  $\text{Mn}^{3+}$  by  $\text{Fe}^{3+}$ ) at the same time.

The samples of  $\text{La}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$  were synthesized by standard ceramic route in three 24h-steps in temperature range of  $1123 \leq T, \text{K} \leq 1373$  followed by quenching to room temperature. The phase purity was investigated by means of X-ray diffraction on a DRON-3 UM diffractometer using  $\text{CuK}\alpha$ -radiation. XRD data were refined by the Rietveld method using *FullProf* software. As a result,

phase composition data allowed to propose a fragment of phase diagram for  $\text{LaMnO}_3\text{--BaMnO}_3\text{--BaFeO}_{2.5}\text{--LaFeO}_3$  system at 1373 K in air (Figure). The phase diagram is divided into the 8 phase areas: 1 – orthorhombic perovskite phase (*O*)  $\text{La}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$  formation; 2 – the two-phase (*O+R*) area; 3 – rhombohedral perovskite phase (*R*)  $\text{La}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$  formation; 4 – *O*- $\text{La}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$  and rhombohedral  $\text{La}_{0.4}\text{Ba}_{0.6}\text{FeO}_3$ ; 5 – *R*- $\text{La}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3\text{+BaMnO}_3$ ; 6 – *R*- $\text{La}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3\text{+BaMnO}_3\text{+BaFeO}_{2.5}$ ; 7 –  $\text{BaFeO}_{2.5}\text{+R-La}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3\text{+O-La}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$ ; 8 –  $\text{La}_{0.4}\text{Ba}_{0.6}\text{FeO}_3\text{+BaFeO}_{2.5}$ .

For the physicochemical properties investigation, the samples of  $\text{La}_{1-x}\text{Ba}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$  were pressed into films and annealed at 1623 and 1723 K. Relative expansion measurements were carried out by means of a high-temperature dilatometer in temperature range of  $303 \leq T, \text{K} \leq 1173$  and heating/cooling speed of 573 K/hour. It was stated that thermal expansion coefficients of  $\text{La}_{0.9}\text{Ba}_{0.1}\text{Mn}_{0.1}\text{Fe}_{0.9}\text{O}_3$  and  $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$  phases calculated from dilatometric data in temperature range of  $303 \leq T, \text{K} \leq 1173$  are close to TEC of YSZ which allows recommending those compounds as promising cathode materials for high-temperature fuel cells. Due to electric conductivity measurements of  $\text{LaMnO}_3$ ,  $\text{La}_{0.9}\text{Ba}_{0.1}\text{Mn}_{0.1}\text{Fe}_{0.9}\text{O}_3$  and  $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$  samples at temperature range  $303 \leq T, \text{K} \leq 1173$  in air those were carried out by standard four-probe technique it was concluded that Ba-doping of  $\text{LaMnO}_3$  increases the total conductivity owing to increasing charge carriers  $\text{Mn}^{4+}$  ions. The chemical compatibility of  $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$  with traditional electrolyte materials we also studied.

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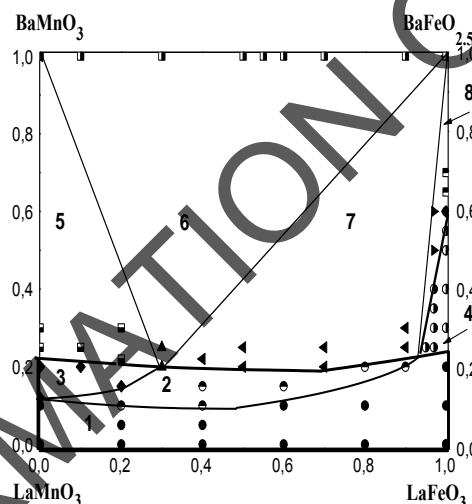


Figure: The phase diagram of system  $\text{LaMnO}_3\text{--BaMnO}_3\text{--BaFeO}_{2.5}\text{--LaFeO}_3$  at  $T = 1373 \text{ K}$  in air.

## Section 2. Thermodynamics of individual chemical compounds

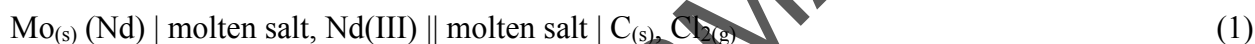
### THERMODYNAMICS OF NEODYMIUM BETWEEN GALLIUM–ALUMINUM LIQUID ALLOY AND LiCl–KCl MOLTEN SALT PHASES

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Actinides recycling by separation and transmutation are considered worldwide as one of the most promising strategies for more efficient use of the nuclear fuel as well as for nuclear waste minimization, thus contributing to make nuclear energy sustainable. With this purpose, two major fuel reprocessing technologies have been explored so far to separate the actinides from the fission products arising from nuclear energy production: hydrometallurgical and pyrometallurgical processes. The actinide – lanthanide separation efficiency can be estimated from the thermodynamic equilibrium constants and the activity coefficients which give the idea of the interactions between the elements and molten salts or liquid metals.

The formal standard potentials of  $E_{Nd(III)/Nd(0)}^*$  and  $E_{Nd(Ga-Al)}^{**}$  vs.  $Cl/Cl_2$  reference electrode has been obtained by measuring the electromotive force of the galvanic or semi-galvanic cells (1) and (2) by using potentiometry at zero current method on Autolab 30.



The results of calculations are the following:

$$E_{Nd(III)/Nd}^* = -(3.750 \pm 0.005) + (8.82 \pm 0.12) \cdot 10^{-4} \cdot T \pm 0.003 \quad V, \quad (3)$$

$$E_{Nd(III)/Nd(Ga-Al)}^{**} = -(2.860 \pm 0.17) + (5.25 \pm 0.19) \cdot 10^{-4} \cdot T \pm 0.009 \quad V, \quad (4)$$

$$\lg \gamma_{Nd(Ga-Al)} = \frac{3F}{2.3RT} (E_{Nd(III)/Nd}^* - E_{Nd(III)/Nd(Ga-Al)}^{**}). \quad (5)$$

The temperature dependence of the activity coefficient of solid  $\alpha$ -Nd in metal liquid gallium – aluminum alloy was determined in fused 3LiCl–2KCl eutectic using expression (5):

$$\lg \gamma_{\alpha-Nd(Ga-Al)} = 5.37 - \frac{13467}{T} \pm 0.23. \quad (6)$$

Partial excess Gibbs energy of  $\alpha$ -Nd in liquid Ga–Al alloy was calculated according by equation (8) using expression (6):

$$\Delta G_{Nd(Ga-Al)}^{ex} = \Delta H_{Nd(Ga-Al)}^{ex} - T\Delta S_{Nd(Ga-Al)}^{ex} \quad (7)$$

$$\Delta G_{Nd(Ga-Al)}^{ex} = 2.303RT \log \gamma_{Nd(Ga-Al)} \quad (8)$$

$$\Delta G_{Nd(Ga-Al)}^{ex} = -257.4 + 102.6 \cdot 10^{-3} T \pm 3.6 \quad kJ/mol. \quad (9)$$

The obtained data of the temperature dependences of the activity coefficient and partial excess Gibbs energy of neodymium in liquid gallium–aluminum eutectic alloy over the temperature investigation range (723–823) K showed the promise of using this system in future innovation method of recovery of nuclear waste.

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CALORIMETRIC STUDY OF CARBOSILANE DENDRIMERS OF THE THIRD AND SIXTH GENERATIONS WITH DIFFERENT TERMINAL GROUPS

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Dendrimers are nanosized, three-dimensional, highly-branched, monodispersed (in the ideal case) macromolecules of perfectly regular structure with a large number of terminal functional groups. Together with the hyperbranched polymers they represent a new class of polymeric materials, called macromolecular nanoobjects [1, 2]. The combination of structural perfection of dendrimers and possibilities of modification of their outer surface layers enable to control the properties of dendrimers in wide ranges, and it is necessary for development up-to-date nanotechnologies.

The investigation of the standard thermodynamic properties of carbosilane dendrimers in a wide temperature range by precision calorimetry allows us to reveal and analyze practically important dependences of thermodynamic properties of dendrimers on their composition.

In the present research the temperature dependences of heat capacities of carbosilane dendrimers of the third and sixth generations with ethyleneoxide and phenylethyl terminal groups, denoted as **G3**[(OCH<sub>2</sub>CH<sub>2</sub>)<sub>1</sub>OCH<sub>3</sub>]<sub>32</sub>, **G6**[(OCH<sub>2</sub>CH<sub>2</sub>)<sub>1</sub>OCH<sub>3</sub>]<sub>256</sub>, **G3**[CH<sub>2</sub>CH<sub>2</sub>Ph]<sub>32</sub> and **G6**[CH<sub>2</sub>CH<sub>2</sub>Ph]<sub>256</sub>, were measured in the temperature range from  $T = (6 \text{ to } 560) \text{ K}$  by precision adiabatic vacuum calorimetry and differential scanning calorimetry.

The physical transformations, such as anomalies of heat capacities (for dendrimers of the third generation), high-temperature relaxation transition – "nanosized effect" (for dendrimers of the sixth generation), and glass transition (for all investigated dendrimers) were detected in the above temperature range. The standard thermodynamic characteristics of the revealed transformations were estimated and analyzed based on composition and structure of dendrimers under study.

The standard thermodynamic functions, namely, heat capacity  $C_p^{\circ}(T)$ , enthalpy  $H^{\circ}(T) - H^{\circ}(0)$ , entropy  $S^{\circ}(T) - S^{\circ}(0)$ , and Gibbs energy  $G^{\circ}(T) - H^{\circ}(0)$  from  $T \rightarrow 0$  to 560 K, and the standard entropies of formation  $\Delta S_f^{\circ}$  at  $T = 298.15 \text{ K}$  of the investigated dendrimers were calculated per corresponding conditional moles of selected repeating units.

The standard thermodynamic properties of dendrimers under study were discussed and compared with literature data for carbosilane dendrimers with different functional terminal groups [3, 4]. It was established that the thermodynamic properties of dendrimers are more dependent on the nature and structure of the outer layer, than on the number of generation.

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## Section 2. Thermodynamics of individual chemical compounds

### CALORIMETRIC STUDY OF MONOETHANOLAMINE

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Monoethanolamine (MEA) is the first in a class of amino alcohols, which is widely used in cryobiology at present. The structure of its molecule enables suggesting the presence of a spatial network of hydrogen bonds in the condensed state that affects its physical and chemical properties such as low compressibility, low thermal coefficient of volume expansion, a large overcooling of liquid phase and the readiness for glass formation [1].

In the gaseous phase the MEA molecule adopts preferably the gauche conformation and in crystal it adopts a trans conformation. The conformation of the molecules in the liquid MEA depends on the temperature. Crystal X-ray diffraction study of MEA described in [2]. On the results of this work is built crystal defined conformation of molecules, hydrogen bonds and the mechanism of crystal melting [3].

X-ray diffraction study of crystalline MEA was carried out in [2]. As a result of this work the crystal is built, the conformation of molecules and the hydrogen bonds are determined, and the crystal melting mechanism is proposed [3].

The difficulties in the MEA study at low temperatures are connected with special network of H-bonds stability in liquid MEA and a high hygroscopicity of the substance.

We have determined the overcooling value, temperatures of crystallization melting and devitrification of MEA at various cooling and heating rates of the sample by DSC method [4]. As it was shown in [2] the only crystalline form of MEA was found by DSC. However, our dielectric studies of MEA at low temperatures have shown polymorphism of solid MEA. Therefore, we studied the heat capacity of MEA in a wide temperature range of 120K - 345K on the adiabatic vacuum calorimeter BKT-3 (AVK). The melting points of the two crystalline forms and a solid phase transition between them at 208K (maxima on the temperature dependence of the heat capacity), and the devitrification temperature at 159K (146K - data DSC) were found.

Thus, calorimetric data confirmed the presence of the two crystalline forms of MEA, which were not detected by DSC method. Previously, two crystalline forms were found in 3-amino-1-propanol [5].

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STANDARD ENTHALPIES OF DISSOLUTION OF FULLEREN C<sub>60</sub> IN BENZENE, TOLUENE, *o*-XYLENE, *o*-DICHLOROBENZENE AT 298.15 K

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Fullerene C<sub>60</sub> was obtained in scientific centre "Kurchatovsky institute" from the products of vaporization of carbon and consisted of main component not less 99.9 mass%

The enthalpies of solution were measured at 298.15 K in an isothermic-shell calorimeter with next characteristics: the thermometric sensitivity was 8·10<sup>-6</sup> K; calorimetric sensitivity was 6·10<sup>3</sup> J; accuracy of the support constant of temperature of the isothermal jacket was ±0.002 K. The energy equivalent of the calorimeter was determined by the electric method with a systematic error of less then 0.1%. The reliability of the calorimeter was verified by measuring the enthalpy of the solution of KCl(cr) in water.

The enthalpies of solution C<sub>60</sub> in organic solvents were measured at small concentrations; the amount of heat put together (0.1–1.0) J, the samples weight were (0.01–0.05) g.

The concentration dependence was small; we used linear extrapolation to find the standard enthalpies of dissolution; these values are listed in the Table.

**Table.** Standard enthalpies of solution C<sub>60</sub> in organic solvents

Solvent	Benzene	Toluene	<i>o</i> -Xylene	<i>o</i> -Dchloro- benzene
$\Delta H^0_\infty$ (kJ/mol)	-6.80±0.12	-8.65±0.10	-10.00±0.10	-12.90±0.12

The standard values of Gibbs energies of dissolution C<sub>60</sub> in investigated solvents are positive (very small solubility); the standard values of entropy of solution negative for all investigated systems. For substances, that do not enter into chemical interaction with solvent, the positive values of entropy of dissolution are expected. Probably, that C<sub>60</sub> interacts with solvent and forms the strong solvates.

## Section 2. Thermodynamics of individual chemical compounds

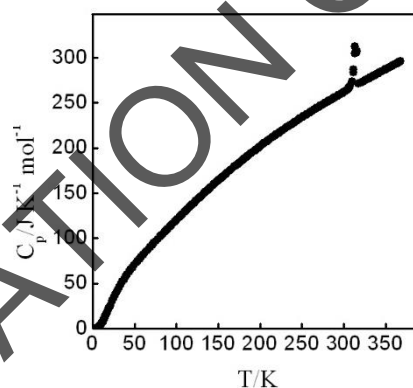
### THERMODYNAMIC PROPERTIES OF LITHIUM *BIS*(TRIFLUOROMETHANESULPHONYL)IMIDE

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Lithium *bis*(trifluoromethanesulphonyl)imide ( $\text{LiNTf}_2$ ) is used as an intermediate in synthesis of  $\text{NTf}_2$ -containing ionic liquids (ILs) and as a component of electrolytes for lithium batteries. Since  $\text{LiNTf}_2$  is one of the simplest compounds containing  $\text{NTf}_2$  anion, its investigation can give a key to unique properties of  $\text{NTf}_2$  containing ILs. In this work we report the results of investigation of  $\text{LiNTf}_2$  by the adiabatic calorimetry and the Knudsen effusion method.

Heat capacity of the substance in the crystalline state in the range of (5–370) K and parameters of its solid-phase transition were determined in a TAU-10 vacuum adiabatic calorimeter (Termis, Moscow, Russia). The uncertainty of the heat capacity measurements was  $\pm 0.4\%$  over the main temperature range (20–370) K and did not exceed  $\pm 2.0\%$  near 5 K. The only anomaly in the temperature dependence of the heat capacity of compound was a solid-phase transition ( $T_{\text{tr}} = 314.7 \text{ K}$ ;  $\Delta_{\text{tr}}H = 205 \pm 7 \text{ J}\cdot\text{mol}^{-1}$ ;  $\Delta_{\text{tr}}S = 0.65 \pm 0.02 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ). The standard thermodynamic functions of the compound in the condensed state in the range (5–370) K were calculated based on the obtained results.



**Figure:** Experimental  $C_p$  of  $\text{LiNTf}_2$ .

**Table.** Standard thermodynamic function of crystalline  $\text{LiNTf}_2$  at  $T = 298.15 \text{ K}$ ,  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$C_{p,m}$	$\Delta_0^T S_m^\circ$	$\Delta_0^T H_m^\circ / T$	$-(G_m^\circ(T) - H_m^\circ(0)) / T$
$260.6 \pm 1.0$	$318.4 \pm 1.9$	$152.7 \pm 0.7$	$165.6 \pm 2.0$

The temperature dependence of the saturated vapor pressure for  $\text{LiNTf}_2$  was obtained by the Knudsen effusion method, and the enthalpy of sublimation was derived. The experimental data obtained in this work allowed us to find the entropy of the compound in the gas state.

### TESTING OF ACCURACY OF EXPERIMENTAL ENTHALPIES OF FORMATION OF NITROGEN-CONTAINING COMPOUNDS BY QUANTUM CHEMICAL CALCULATIONS

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The heat of formation is a key property of a compound, which permits the quantification of its thermochemistry. This is particularly important in the area of energetic materials, for which the heat release upon decomposition or combustion is an essential factor in determining detonation or propellant performance. Numerous high-nitrogen compounds have explosive properties and attract great attention in the modeling of new high energy materials with projected characteristics. Although heats of formation can be found experimentally, certain nitrogen-containing compounds are difficult to synthesize and some of them are highly unstable. Thus the enthalpies of formation are often unknown or determined with relatively large uncertainties. Today quantum chemical calculations can be used successfully for analyzing of experimental data and prediction of thermochemical properties.

The Gaussian-n family methods (G4 and G4(MP2)) and some DFT potentials combined with atomization reaction were tested in their possibilities to quantitatively estimate the values of enthalpy of formation. To get the accurate gas-phase enthalpies of formation, the quantum chemical calculations combined with isodesmic reaction scheme were used in this study. A set of internally consistent values of enthalpies of formation of nitrogen-containing compounds has been obtained. Among these are nitrocompounds, nitramines, N-oxides, amines, heterocycles, and azides with different architecture and functional groups.

The experimental condensed phase enthalpies of formation and enthalpies of sublimation/vaporization were analyzed based on recommended values of the gas phase enthalpies of formation. In some cases a possible inaccuracy of the experimental values has been suggested. The reliable experimental enthalpies of sublimation were used to parameterize the Politzer's equation [1] for prediction of heats of sublimation of high-nitrogen compounds.

- [1] Politzer, P.; Murray, J.S.; Grice, M.E.; DeSalvo, M.; Miller, E. *Mol. Phys.*, 1997, 91, 923-928.

## Section 2. Thermodynamics of individual chemical compounds

### CRYSTAL STRUCTURE AND PHASE TRANSITION IN COBALT-DEFICIENT LAYERED PEROVSKITE $\text{EuBaCo}_{2-x}\text{O}_{6-\delta}$

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The layered rare-earth cobaltites  $\text{LnBaCo}_2\text{O}_{6-\delta}$  (Ln – rare earth element) are of great interest since they have a charge order, metal-insulator and many magnetic transitions depending on the nature of lanthanide and the oxygen content  $\delta$  [1]. Recently, it was found that the introduction of vacancies in the cobalt sublattice changes the magnetic properties and the magnetic phase diagram of  $\text{GdBaCo}_{1.86}\text{O}_{5.32}$  [2]. In this respect it is interesting to investigate the influence of vacancies in the cobalt sublattice on the oxygen content and physical properties of  $\text{LnBaCo}_{2-x}\text{O}_{6-\delta}$ .

The  $\text{EuBaCo}_{2-x}\text{O}_{6-\delta}$  ceramics were prepared by the standard ceramic technology in platinum crucibles at (900–1150)°C. The phase composition and structure of the samples were checked by X-ray diffraction analysis at room temperature and in the range (400–500)°C. Differential scanning calorimetric measurements (DSC) were performed in the temperature range (30–600)°C (Figure).

DSC showed heat effects corresponding to the structural transition from tetragonal symmetry ( $P4/mmm$ ) to orthorhombic ( $Pmmm$ ) (Figure). The parameters of this phase transition are presented in Table. As seen the heat effect in  $\text{EuBaCo}_{1.9}\text{O}_{6-\delta}$  has complex shape by comparing with one for  $\text{EuBaCo}_2\text{O}_{6-\delta}$  [3]. It can indicate more complex behavior of cobalt-deficient double perovskites during  $P4/mmm$ - $Pmmm$  transition.

By analyzing the obtained results we can suppose the formation of clusters of several unit cells around cobalt and oxygen vacancies in positions with an octahedral environment.

**Table.** Temperature and energy of structural phase transition  $P4/mmm - Pmmm$

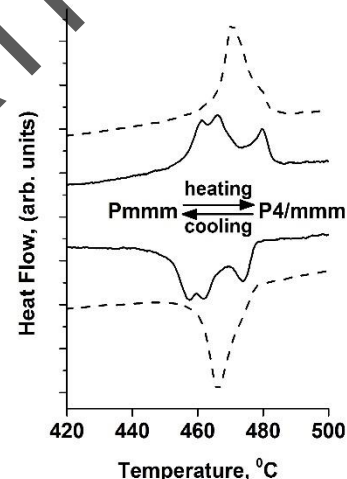
Compound	$E$ (J/g)	$T$ (°C)
$\text{EuBaCo}_2\text{O}_{6-\delta}$	-3.1	466
$\text{EuBaCo}_{1.9}\text{O}_{6-\delta}$	-3.0	469/462/458

[1] Martin, C.; Maignan, A.; Pelloquin, D.; et al. Appl. Phys. Lett., 1997, 71, 1421.

[2] Arbuzova, T.I.; Telegin, S.V.; Naumov, S.V.; Patrakov, E.L.; Reznitskih, O.G. Solid State Phenomena, 2014, 215, 83.

[3] Tarancon, A.; Marrero-Lopez, D.; Pena-Martinez, J.; et al. Solid State Ionics, 2008, 179, 611-618.

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**Figure:** Fragment of DSC of  $\text{EuBaCo}_2\text{O}_{6-\delta}$  (dash line) and  $\text{EuBaCo}_{1.9}\text{O}_{6-\delta}$  (solid line).

THERMOCHEMICAL PROPERTIES OF SOME RARE-EARTH  
AND BARIUM COBALTITES

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This work continues systematic investigations of thermodynamic properties of perspective oxides materials. It is carried out at Luginin's thermochemistry and Chemical Thermodynamics Laboratories of Physical Chemistry division of MSU. It is devoted to the study of thermochemical properties of  $\text{Ln}_2\text{BaCoO}_5$  ( $\text{Ln} = \text{Nd, Gd, Dy, Ho}$ ). The choice of object of research is caused by its application as precursors for complex cobaltites and cuprocobaltites ( $(\text{Ln}_{1-x}\text{Ba}_x)_2\text{Co}_2\text{O}_{6-\delta}$  and  $\text{LnBaCoCuO}_5$ , which are colossal magnetic resistance (CMR) materials. The reproducible synthesis of such compounds and application of materials based on them, require knowledge of their thermodynamic properties. There is no literature data on enthalpies of formations of  $\text{Ln}_2\text{BaCoO}_5$ .

Samples of  $\text{Ln}_2\text{BaCoO}_5$  were obtained by method of solid state synthesis from barium carbonate, cobalt oxide and corresponding rare-earth oxides in quartz ampoules under continuous evacuation at residual gas pressure of 1.33 Pa and 1303 K for 120 h with two intermediate grindings. The preliminary annealing of cobaltites was performed in air (1223 K, 50 h). The synthesized compounds were tested by TG–DSC methods and X-ray analysis.

The enthalpies of reactions  $\text{Ln}_2\text{BaCoO}_5$  with 1 M hydrochloric acid were measured at 298.15 K in a hermetically sealed swinging calorimeter with an isothermal coat. Temperature rise in each run was measured by platinum resistance thermometer. Thermometric sensitivity of circuit was  $3 \cdot 10^{-5}$  K. The energy equivalent of calorimeter was determined by electric technique. The obtained and reliable literature data on thermochemistry of barium, cobalt and rare-earth compounds were used to calculate the enthalpies of formation of specified phase from elements and binary oxides according to thermochemical cycles. The results are given in Table.

The dependence of the  $\text{Ln}_2\text{BaCoO}_5$  enthalpies of formation on ionic radii of rare-earth elements has a complicated character so it is impossible to find a strong correlation between the thermochemical properties of the studied cobaltites and the ionic radii of rare-earth elements. A similar dependence of enthalpies of formation was also observed for cuprates  $\text{Ln}_2\text{BaCuO}_5$  [1–3]. Note that there is a similar dependence for the enthalpies of formation for binary oxides  $\text{Ln}_2\text{O}_3$ . It seems that the thermochemical properties of complex rare-earth cuprates and cobaltites are generally determined by their rare-earth elements.

All of  $\text{Ln}_2\text{BaCoO}_5$  thermochemical parameters were obtained for first time in this work. They can be used to construct phase diagrams and optimize the targeted synthesis of these compounds.

**Table.** The enthalpies of reactions and formation of  $\text{Ln}_2\text{BaCoO}_5$

Compound	$-\Delta_f H^\circ(298)$ (kJ/mol)	$-\Delta_{\text{ox}} H^\circ(298)$ (kJ/mol)	$-\Delta_f H^\circ(298)$ (kJ/mol)
$\text{Nd}_2\text{BaCoO}_5$	$728.1 \pm 2.0$	$76.3 \pm 6.3$	$2670.2 \pm 5.1$
$\text{Gd}_2\text{BaCoO}_5$	$716.2 \pm 2.4$	$86.0 \pm 5.9$	$2692.7 \pm 4.1$
$\text{Dy}_2\text{BaCoO}_5$	$666.9 \pm 2.3$	$103.9 \pm 6.3$	$2754.2 \pm 3.7$
$\text{Ho}_2\text{BaCoO}_5$	$680.9 \pm 2.6$	$77.0 \pm 10.9$	$2747.2 \pm 6.7$

[1] Efremova, M.; Popova, A.; Monayenkova, A.; et al. *J. Alloys Compd.*, 2008, 452, 99-101.

[2] Uspenskaya, I.; Tiphlova, L.; Popova, A.; et al. *J. Alloys Compd.*, 2009, 470, 241-244.

[3] Kovba, M.; Monayenkova, A.; Tiflova, L.; et al. *Russ. J. Phys. Chem.*, 2012, 86, 1307-1310.

## Section 2. Thermodynamics of individual chemical compounds

### CALORIMETRIC STUDY OF POLY(PHENYLENE-PYRIDYL) DENDRON OF THE THIRD GENERATIONS WITH DODECYL TERMINAL GROUPS IN THE REGION FROM $T \rightarrow 0$ TO 500 K

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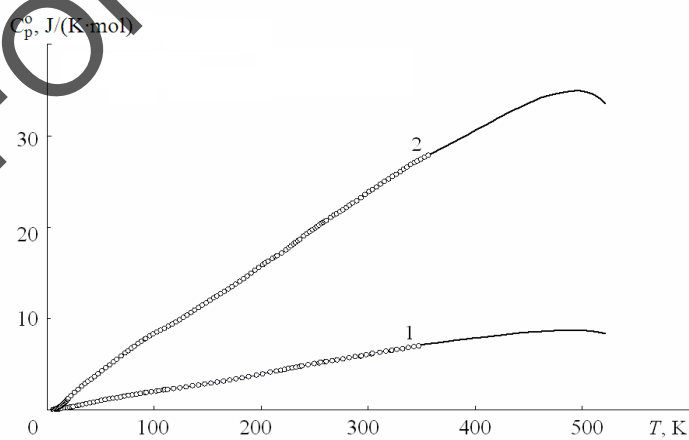
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Polyphenylene dendrimers possess high chemical and thermal stability similar to linear polyphenylenes, but with greatly increased solubility due to the prevention of intermolecular packing. To date, the thermodynamic characteristics of some polyphenylene dendrimers of different generations were studied in a wide range of temperatures. However, there is no similar data for the appropriate dendrons, from which dendrimers are built, while the study of the thermodynamic properties of dendrimers and appropriate dendrons is of great interest not only because of their reference standard thermodynamic data, but also for the analysis of the changing these properties on composition and structure of above mentioned compounds.

In the present work we have studied over interval (6–500) K the heat capacity of third generation dendron with carboxyl focal point, decorated with dodecyl groups at the periphery (D3-C<sub>12</sub>H<sub>25</sub>) (Figure).

On the basis of experimental data the dendron standard thermodynamic functions, namely, heat capacity  $C_p^{\circ}(T)$ , enthalpy  $H^{\circ}(T) - H^{\circ}(0)$ , entropy  $S^{\circ}(T) - S^{\circ}(0)$ , and Gibbs energy  $G^{\circ}(T) - H^{\circ}(0)$  in the investigated temperature interval, and the standard entropy of formation at  $T = 298.15$  K, have been calculated; the thermodynamic characteristics of investigated dendron and studied by us earlier [1] corresponding poly(phenylene-pyridyl) dendrimer of the third generation (G3-C<sub>12</sub>H<sub>25</sub>) were compared (Figure).



**Figure:** Heat capacities of dendron D3-C<sub>12</sub>H<sub>25</sub> (1) and appropriate dendrimer G3-C<sub>12</sub>H<sub>25</sub> (2).

[1] Zakharova, Yu.A.; Smirnova, N.N.; Shifrina, Z.B.; Yuzik-Klimova, E.Yu. Vestnik of Lobachevsky state university of Nizhni Novgorod, 2014, 1, 79-84 (in Russian).

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## CALCULATION OF THERMODYNAMIC PROPERTIES OF DIMETHYLENECYCLOURETHANE IN ANHARMONIC APPROXIMATION

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Dimethylene urethane (DMU, C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>N<sub>1</sub>) is an important monomer used for the preparation of polyurethane rubbers, lacquers and fibers. This compound is widely applied in pharmacy, medicine and cosmetics.

The combustion energy of DMU was measured in a modified B-08MA calorimeter with isothermal shell and a stationary bomb. The enthalpy of DMU sublimation was obtained by transpiration method [1]; the melting temperature and melting enthalpy were found with DSC. The temperature dependence of the saturated vapor pressure was measured in the range (323–353) K.

DMU geometry was optimized by mPW2PLYP/6-311++G(3df, 3pd), B3LYP/6-311++G(3df, 3pd) and MP2/6-311++G(3df, 3pd) using the Gaussian 09 software. The total electronic energy  $E_{total}$  and harmonic frequencies  $\omega_{harm}$  were found, and using B3LYP/6-311++G(3df, 3pd) within of the second order vibration perturbation theory in the quartic force field (VPT2 QFF) anharmonic frequencies  $\omega_{anharm}$  were obtained. A scanning of the potential energy surface along the dihedral angle NCCO was performed, and on the basis of  $E_{total}$  the barrier between the enantiomers was estimated as 2.9 kJ/mol.

In the framework of the "rigid rotator – anharmonic oscillator" [2] thermodynamic functions in the ideal gas state in the range of (298.15–1500) K were calculated. The enthalpy of ring strain was evaluated as 50.1 kJ/mol.

**Table.** Thermodynamic properties of dimethylene urethane in the range of (298.15–1500) K

$T$ (K)	$H^{\circ}_T - H^{\circ}_0$ (kJ/mol)	$S^{\circ}$ (J/(mol·K))	$G^{\circ}_T - H^{\circ}_0$ (kJ/mol)	$C^{\circ}_p$ (J/(mol·K))	$\Delta_f H^{\circ}$ (kJ/mol)	$\Delta_f G^{\circ}$ (kJ/mol)
298.15	14.8	306.2	-76.4	77.9	-345.6	-244.6
300	15.0	306.7	-77.0	78.4	-345.7	-244.0
400	24.1	332.8	-109.0	104.1	-351.4	-209.2
500	35.7	358.5	-143.6	127.1	-355.6	-173.1
600	49.4	383.5	-180.7	146.4	-358.6	-136.2
700	64.9	407.3	-220.2	162.2	-360.4	-98.9
800	81.8	429.8	-262.1	175.0	-361.5	-61.5
900	99.8	451.0	-306.1	185.5	-362.0	-24.0
1000	118.8	471.0	-352.2	194.1	-362.0	13.6
1100	138.6	489.9	-400.3	201.1	-361.6	51.0
1200	159.0	507.6	-450.2	206.9	-360.9	88.5
1300	179.9	524.4	-501.8	211.7	-360.1	125.7
1400	201.3	540.2	-555.0	215.7	-359.0	163.1
1500	223.0	555.2	-609.8	219.2	-357.8	200.3

[1] Verevkin, S.P.; Emel'yanenko, V.N. Fluid Phase Equilib., 2008, 266, 64-75.

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## Section 2. Thermodynamics of individual chemical compounds

### MOLAR HEAT CAPACITY AND THERMODYNAMIC PARAMETERS OF CRYSTALLINE DIPEPTIDES

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Thermodynamic studies of crystalline peptides attracted a lot of attention, since these systems can be used as molecular materials, drugs and biomimetics. They are zwitterions linked with each other by dipole-dipole interactions, hydrogen bonds and Van der Waals interactions. The crystals of some amino acids and peptides were previously studied at 298–348 K using DSC technique [1]. The aim of the present work was to determine the heat capacities of DL-alanyl-DL-norvaline and L-alanyl-L-tryptophan. Heat capacity is the important parameter because it is related to the intermolecular cohesion energy in the crystal arrangement, which provide insight into the solid phase energy and structure.

The behavior of the samples as a function of temperature was studied by DSC 204 F1 Phoenix differential scanning heat flux calorimeter (NETZSCH, Germany) with a high sensitivity  $\mu$ -sensor. The sample was heated at the rate of 10 K min<sup>-1</sup> in an argon atmosphere and cooled with gaseous nitrogen. The heat capacity calibration was done by running a standard sapphire ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) measurement at the experimental temperatures. The analysis of the results showed that measurements error of the specific heat capacity of the crystalline substance was within  $\pm 0.003$  J g<sup>-1</sup>K<sup>-1</sup>.

The specific heat capacities ( $C_p^0$ ) measurements were carried out between 288.15 and 348.15 K. The  $C_p^0$  values were obtained in two series of experiments. The experimental values of the molar heat capacity ( $C_{p,m}^0(\text{cr})$ ) of the dipeptides studied are presented in Table. The measured  $C_p^0$  values were used to calculate the thermodynamic functions of the dipeptides:  $S^0(T) - S^0(T_0)$ ,  $H^0(T) - H^0(T_0)$ .

The molar heat capacities of the substances studied increase with rising temperature and does not show any peculiarities in the range (288.15–348.15) K. Comparison of the this results with the published data on the molar heat capacity of some crystalline aliphatic peptides [1] showed that the  $C_{p,m}^0(\text{cr})$  values increase when the Van der Waals volumes rise. The van der Waals volumes ( $V_w$ ) of the peptide molecules were calculated by using the increments of the atom volumes ( $\delta V_i$ ) obtained previously by numerical integration method [2]. It has been shown that the molecular packing densities in crystals follow the order: L-Ala-L-Trp < L-Ala-L-Ala < Gly-L-Ala < DL-Ala-DL-Val < DL-Ala-DL-Nvl.

**Table.** Molar isobaric heat capacities of crystalline peptides at various temperatures

Substances	$C_{p,m}^0(\text{cr})$ (J mol <sup>-1</sup> K <sup>-1</sup> ) at temperatures $T$ (K)				
	288.15	298.15	313.15	333.15	348.15
DL-alanyl-DL-norvaline	255.4±0.5	277.0±0.6	291.1±0.8	308.6±0.5	315.4±0.6
L-alanyl-L-tryptophan	328.9±0.9	340.5±0.8	363.6±0.9	443.0±1.0	564.2±1.0

[1] Badelin, V.; Kulikov, O.; Vatagin, V.; et al. *Thermochim. Acta*, 1990, 169, 81-93.

[2] Kuz'min, V.S.; Katser, S.B. *Izv. Akad. Nauk. Ser. Khim.*, 1992, 41, 922.

## THERMODYNAMIC PROPERTIES OF CHALCOGENIDES OF INDIUM AND GALLIUM IN THE WIDE TEMPERATURE RANGE

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Compounds of  $A^{III}B^{VI}$  attract attention due to their unique optical properties. On the basis of  $In_2Te_3$  semiconductors can be created radiation resistant measuring instruments of exclusively high doses and intensity of ionizing radiation. Measuring instruments can be applied in nuclear reactors and behind the first wall, in a zone of biological protection, in burials of radioactive waste, in research and industrial accelerators of big capacities for monitoring and automation of protection and operation.

In our laboratory, two investigations have been done for the first time. Firstly, systematic research of heat capacity of polytypes of six selenides and tellurides of indium and gallium, stable at the room temperatures, has been done in the range of temperatures (4–350) K. Secondary, values of standard thermodynamic functions (heat capacity, entropy, derived Gibbs energy, change of enthalpy and Gibbs energy of formation) in the field of low temperatures have been calculated. Using a method of differential scanning calorimetry temperature dependences of heat capacity of GaSe,  $Ga_2Te_3$ , InSe, InTe in the range of (300–700) K was determined for the first time. For telluride of gallium  $Ga_2Te_3$  the additional study of heat capacity in the region of helium temperatures was carried out using the method of relaxation calorimetry in system for research of physical properties of the materials Quantum Design PPMS 9. Good agreement with data of low-temperature adiabatic calorimetry and lack of phase transitions in the interval lower than 2 K and higher than 600 K were noted.

The heat capacity of six studied compounds represents monotonously increasing smooth curve without any anomalies. It is found that in the field of the lowest temperatures dependence of  $C_p/T = f(T^2)$  for semiconductor compounds  $A^{III}B^{VI}$  is linear which allows the use of Debye's model for extrapolation to absolute zero temperature and calculation of standard thermodynamic functions.

On the basis of multifractal treatment of experimental data for low-temperature heat capacity the primary motives in structure of the studied compounds are established. For GaSe,  $Ga_2Se_3$ , GaTe,  $Ga_2Te_3$ , InSe, InTe is shown that fractal model of temperature dependence of a heat capacity is applicable. Model parameters, such as characteristic temperature and temperature dependence of fractal dimension are determined. As distinction of electronegativity of atoms of metal and chalcogen increases, forces between layers that make fractal dimension became larger, amplify.

The standard values of  $\Delta_f H^0(298.15\text{ K})$  and  $\Delta_f G^0(298.15\text{ K})$  and the thermodynamic stability are decreased as atomic numbers of elements from Ga to In in the set of the similar compounds increase. With increasing of molecular mass of compounds there is a natural growth of standard entropy, for example, from  $70.17 \pm 0.14\text{ J K}^{-1}\text{ mol}^{-1}$  for GaSe to  $102.2 \pm 0.2\text{ J K}^{-1}\text{ mol}^{-1}$  for InTe.

## Section 2. Thermodynamics of individual chemical compounds

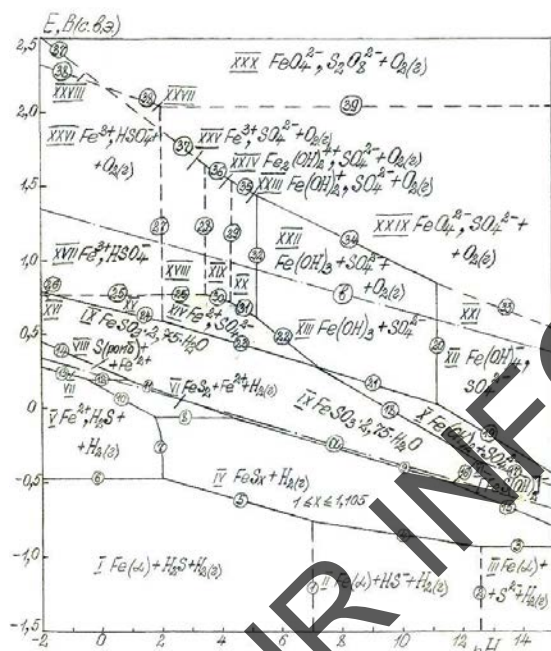
### DIAGRAMS OF THE ELECTROCHEMICAL EQUILIBRIUM $E - pH$ SYSTEMS HYDROXIDES (OXIDES) Fe(III) – $H_2SO_4$ – $SO_3^{2-}$ – $H_2O$

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The authors [1, 2] developed technological scheme of conversion ferrous cake – waste copper–nickel production in sulfite  $FeSO_3 \cdot 2.75H_2O$ . Processing is based on a study of the cake of hydroxides (oxides) of iron –  $H_2SO_4$  –  $SO_3^{2-}$  –  $H_2O$ , which flow together red-ox processes Fe(III) / Fe(II) and S(IV) / S(VI), as well as deposition iron from solution as sulfite Fe(II). In



**Figure:** Diagram  $E - pH$  of  $Fe(OH)_3 - H_2SO_4 - SO_3^{2-} - H_2O$  at  $25^\circ C$ ,  $P = 1$  bar (air) and  $a_i = 0.1$  mol/l

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## CALORIMETRIC STUDY OF TRIPHENYLBISMUTH DIMETHACRYLATE $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCMe}=\text{CH}_2)_2$

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Organic derivatives of pentavalent bismuth, their synthesis and investigation of their properties are of considerable interest in view of the fact they find an application in different fields of practice, e.g. as reagents and catalysts in fine organic synthesis, pharmaceutical composition, biocides and fungicides. Some researchers note that bismuth and its compounds are the least toxic among the heavy metals [1, 2], and it can lead to increasing of their use in pharmaceutical and cosmetic industry.

The synthesis of triphenylbismuth dimethacrylate was carried out similarly to the synthesis of triphenylantimony dimethacrylate [3]. It was based on the oxidation addition reaction of triphenylbismuth with methacrylic acid in the presence of hydrogen peroxide:



In the present research, the temperature dependence of heat capacity  $C_p^\circ = f(T)$  of triphenylbismuth dimethacrylate  $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCMe}=\text{CH}_2)_2$  was measured between 5.3 and 330 K in the precision adiabatic vacuum calorimeter, and the thermal behavior of this compound was studied within the range from 310 to 450 K by the differential scanning calorimetry. There were revealed reproducible anomaly from 150 to 170 K caused by structural changes in the crystal lattice, and intensive exothermic transition over the range from 385 to 450 K caused by the reductive decomposition with the polymerization of the sample under study. The experimental results were used to calculate the standard ( $p^\circ = 0.1$  MPa) thermodynamic functions (heat capacity  $C_p^\circ$ , enthalpy  $H^\circ(T) - H^\circ(0)$ , entropy  $S^\circ(T)$ , and Gibbs function  $G^\circ(T) - H^\circ(0)$ ) of triphenylbismuth dimethacrylate from  $T \rightarrow 0$  to 385 K. The chain-layer structure topology was established for the compound under study using the multifractal treatment of low-temperature heat capacity. The standard entropy of formation of the compound under study at  $T = 298.15$  K was calculated. Obtained for  $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCMe}=\text{CH}_2)_2$  results were compared with ones for  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CCMe}=\text{CH}_2)_2$ .

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## Section 2. Thermodynamics of individual chemical compounds

### THERMAL INVESTIGATION OF VOLATILE MAGNESIUM β-DIKETONATE DERIVATIVES

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The present work is devoted to investigation the influence of various ligand type on the thermal properties of magnesium β-diketonate derivatives as potential precursors for MgO film chemical vapor deposition. For this purposed, the series of mixed-ligand complexes with β-diketonate and diamine ligands  $\text{Mg}(\text{L}_1)(\text{thd})_2$ , thd =  ${}^t\text{BuCOCHCO}{}^t\text{Bu}$ ,  $\text{L}_1 = \text{NH}_2(\text{CH}_2)_2\text{NH}_2$  (en) (**1**) [1],  $\text{NMe}_2(\text{CH}_2)_2\text{NMe}_2$  (tmeda) (**2**) [1],  $\text{NH}_2(\text{CH}_2)_3\text{NH}_2$  (pda) (**3**),  $\text{NMe}_2(\text{CH}_2)_3\text{NMe}_2$  (tmpda) (**4**), 1,10-phenanthroline (phen) (**5**), 2,2'-bipyridile (**6**),  $\text{Mg}(\text{tmeda})(\text{L}_2)_2$ ,  $\text{L}_2 = \text{RCOCHCOR}'$ ,  $\text{R}=\text{R}'=\text{CF}_3$  (hfac) (**7**) [2],  $\text{R}=\text{CF}_3$ ,  $\text{R}'=\text{Me}$  (tfac) (**8**) и  $\text{R}=\text{CF}_3$ ,  $\text{R}'={}^t\text{Bu}$  (ptac) (**9**),  $\text{Mg}(\text{Q})(\text{hfac})$ ,  $\text{Q} = \text{phen}$  (**10**), bipy (**11**) and β-iminoketonate complexes  $[\text{Mg}(\text{L}_3)_2]_n$ ,  $\text{L}_3 = \text{RC}(\text{NR}_1)\text{CHCOR}$ ,  $\text{R} = \text{Me}$ ,  $\text{R}_1 = \text{H}$  (*i*-acac) (**12**),  $\text{Me}$  (*Mei*-acac) (**13**);  $\text{R} = {}^t\text{Bu}$ ,  $\text{R}_1 = \text{H}$  (*i*-thd) (**14**) were synthesized. The obtained compounds were characterized by elemental analysis, mass-spectrometry, IR- and <sup>1</sup>H-NMR spectroscopy, single-crystal X-ray diffraction.

The thermal properties of the complexes in condensed phase were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The qualitative volatility rows were created on the base of TG data: mixed-ligand complexes with aromatic diamines are less volatile than compounds with aliphatic ones. It was shown that introducing of CH<sub>2</sub>-group in diamine ligand led to the decrease of thermal stability (complexes **1** and **2** vs. **3** and **4**). Compounds **12** and **13** with β-iminoketonate ligands are more stable under heating compared to their β-diketonate analog  $[\text{Mg}(\text{acac})_2]_3$ . As a result of DSC investigation, the temperatures and thermodynamic parameters of phase transitions were obtained, some correlations between these parameters and crystal structure were revealed.

The temperature dependencies of saturated vapor pressure for complexes **2**, **7**, **8**, **9**, **14** and  $[\text{Mg}(\text{thd})_2]_2$  **15** were measured by static (S), transpiration (T) or Knudsen's effusion (K) methods. The results and calculated thermodynamic parameters of vaporization processes are presented in the Table.

**Table.** The thermodynamic parameters of vaporization processes of magnesium complexes

Complex	Process	Method	ΔT (K)	n	$\ln(p/p_0)=A-B/(T, \text{K})$		ΔH <sub>T</sub> <sup>*</sup> (kJ/mol)	ΔS <sub>T</sub> <sup>*</sup> (J/mol K)
					A	B		
<b>15</b>	Subl.	K	346 – 400	8	30.4	17088	142 ± 2	253 ± 6
<b>14</b>	Subl.	K	387 – 428	6	35.9	20457	170 ± 6	298 ± 15
<b>2</b>	Subl.	S	422 – 475	30	13.5	8233	68.4 ± 0.8	112 ± 2
		T	373 – 413	9	24.3	13327	111 ± 2	202 ± 5
<b>8</b>	Subl.	T	333 – 363	9	25.4	12028	100 ± 3	211 ± 7
		Evap.	368 – 403	10	17.1	9141	76 ± 4	142 ± 10
<b>9</b>	Subl.	S	335 – 428	41	9.8	6325	53 ± 2	82 ± 6
<b>7</b>	Evap.	S	359 – 473	40	13.6	7351	61.0 ± 0.4	113.2 ± 0.9

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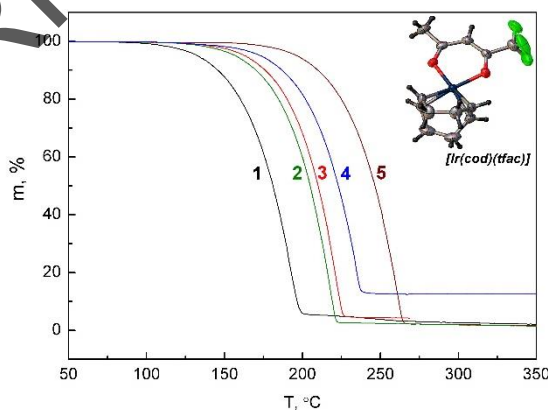
THERMOCHEMICAL INVESTIGATION OF IRIIDIUM(I) COMPLEXES WITH  $\beta$ -DIKETONATE AND CYCLOOCTADIENYL LIGANDSE.S. Vikulova<sup>1</sup>, I.Yu. Ilyin<sup>1</sup>, L.N. Zelenina<sup>1,2</sup>, A.E. Turgambaeva<sup>1</sup>, S.V. Sysoev<sup>1</sup>, N.B. Morozova<sup>1</sup><sup>1</sup>*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Lavrentiev Av. 3, 630090 Novosibirsk, Russia*<sup>2</sup>*Novosibirsk State University, Pirogova Str. 2, 630090 Novosibirsk, Russia*  
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Iridium and iridium oxide are perspective materials for coating of electrical poles of cathodes and anodes on diagnostic and ablation endocardial electrodes. The MOCVD (Metal Organic Chemical Vapor Deposition) seems to be the most reasonable method to obtain such coatings. The iridium(I) complexes are considered as promising MOCVD precursors because of their good characteristics of volatility and more useful synthetic methods in comparison with compounds of iridium(III). Nevertheless, the systematic investigations of thermal properties of such complexes are needed for the most successful their MOCVD application.

According to the above, this work is devoted to thermochemical study of the series of iridium(I) complexes  $[\text{Ir}(\text{cod})(\text{L})]$  ( $\text{L} = \text{RC}(\text{O})\text{CHC}(\text{O})\text{R}'$ ,  $\text{R} = \text{R}' = \text{Me}$  (acac),  $^t\text{Bu}$  (thd),  $\text{CF}_3$  (hfac);  $\text{R} = \text{CF}_3$ ,  $\text{R}' = \text{Me}$  (tfac),  $^t\text{Bu}$  (ptac); cod = cyclooctadiene-1,5)). The complexes were synthesized and characterized by elemental analysis,  $^1\text{H-NMR}$ -, IR- and Raman spectroscopy, mass-spectrometry and X-ray diffraction.

The thermal properties of the complexes in condensed phase were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC); the thermodynamic parameters of melting were obtained. The following qualitative volatility row of  $[\text{Ir}(\text{cod})(\text{L})]$  could be created on the TG data:  $\text{L} = \text{hfac} > \text{tfac} \approx \text{ptac} > \text{acac} > \text{thd}$  (Figure). The calculations of the energy of intermolecular interactions in crystal lattice were performed in order to explain this volatility order.

The results of measurements of temperature dependencies of saturated vapour pressure and investigation of thermodecomposition of vapours for some compounds will be also presented.



**Figure:** Mass loss curves of  $[\text{Ir}(\text{cod})(\text{L})]$ ,  $\text{L} = \text{hfac}$  1,  $\text{tfac}$  2,  $\text{ptac}$  3,  $\text{acac}$  4,  $\text{thd}$  5 (He).

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## Section 2. Thermodynamics of individual chemical compounds

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### SUBLIMATION THERMODYNAMICS OF AMINOBENZOIC ACID, NICOTINIC ACID AND RELATED AMIDO-DERIVATIVES

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The investigation of the sublimation of biologically active compounds is of great interest for the prediction of pharmaceutically important properties of drugs on their basis. The class of compounds including aminobenzoic acid, nicotinic acid and related amido-derivatives can be often considered either as a basis or additional components of the pharmaceutical formulations and have been successfully used in pharmacology for a long time.

The inert gas transpiration technique was used for measuring the vapor pressures of the following biologically active compounds: 4-aminobenzoic acid, nicotinic acid, 4-aminobenzamide, 4-pyridinecarboxamide and 3-pyridinecarboxamide in the temperature range from 347.15 to 403.15 K. Differential scanning calorimetric analysis was applied to obtain the temperature and molar enthalpy of fusion of the compounds studied. The analysis of the relationship between the vapor pressure values and the molecular structure of the substances shows that for the benzene derivatives the substitution of the amido-group by the hydroxyl one results in an approximately tenfold vapor pressure growth. For 3-substituted pyridine compounds nicotinamide and nicotinic acid such structural change causes twofold decrease of the vapor pressure. At the same time, the change of the position of the carbamide substituent in the pyridine derivatives does not affect strongly the volatility of the structural isomers. The thermodynamic sublimation parameters: enthalpy, entropy and Gibbs energy were derived from the temperature dependences of the saturated vapor pressure. The obtained results allowed the estimation of the relationship between the sublimation thermodynamic parameters and the thermophysical properties of the substances. A linear correlation between the sublimation and vaporization enthalpies was revealed that means the main intermolecular interactions in the crystal and liquid states to be the same for the substances studied.

The correlation equations were applied to calculating the saturated vapor pressure of the investigated compounds on the basis of the fusion temperatures, and sublimation enthalpies. We employ the model approach based on the HYBOT descriptors for the biologically active substances to determine the correlation between the molecular structure and sublimation enthalpy. The descriptors which best reflect the main types of interactions in the molecular crystals are the molecular polarizability, the sum of all H-bond acceptor and donor factors. The close values of the experimental and calculated parameters testify to the possibility of the prediction of the volatility of the investigated compounds using the proposed equations.

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## THE CRITICAL TEMPERATURE OF BINARY MIXTURES. THEORY AND PRACTICE

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Information about the critical temperatures of binary mixtures is a keystone for the design of supercritical technologies. Development of the prediction methods based upon the experimental data for the mixtures of industrial importance is an essential step towards the application of such data to practical use. For this reason, the results of primary experiment must have a high degree of validity.

Nowadays, isochoric method is the most extensively used for the determination of critical properties. It is known that critical density reached is a very important criterion for the critical temperatures determination by isochoric method. Previously we have shown [1–3] that for each mixture the critical density has to be found experimentally by plotting an experimental phase « $T - \rho$ » diagram. In this case the maximum temperature of coexistence of vapour and liquid phases is determined along with the critical temperature.

In this work we proposed a method for the determination of critical properties of binary mixtures by plotting an experimental phase surface in the coordinates "temperature–density–composition".

Mathematical treatment of surface of phase transition was tested on literature data for binary mixtures of alkanes. Types of mathematical functions to describe the surface of phase transition were selected on the basis of information that has been obtained by us in [3].

The experimental procedure was tested on binary mixtures of alkanes and alkenes with aromatic hydrocarbons.

The experiment was carried out in an air bath oven by the ampoule method. The phase transition was determined visually by the appearance of the phase boundary. For the each ampoule the filling point and composition of the mixture were adjusted individually based on the previous experience of the authors in the study of critical and maximum temperatures of coexistence of liquid and vapor phases of binary mixtures of hydrocarbons [3].

It was found that the determination of the critical properties of mixtures by experimental surfaces of phase transition can significantly reduce the time needed for the experiment in order to get reliable information about the critical properties of the mixture in the whole composition range.

It has been shown that necessary precision of the description of the surface of phase transition was achieved if the extrema points (areas in the near of the critical and maximum temperature) are obtained experimentally over a wide range of variation of the composition of the mixture.

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## Section 2. Thermodynamics of individual chemical compounds

### CALORIMETRIC STUDY OF *TRIS*(PENTAFLUOROPHENYL)-4-PYRIDYLETHYLGERMANE

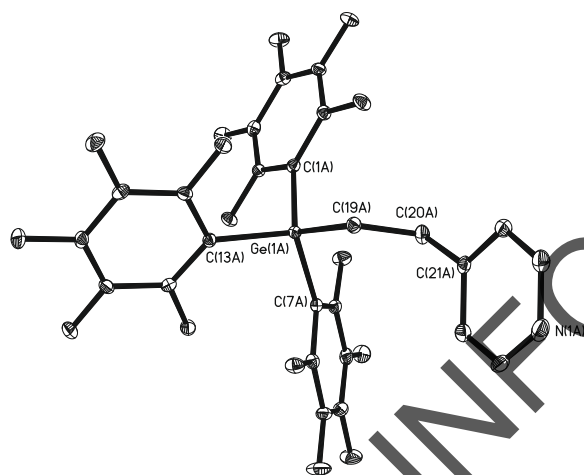
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Fluorinated amphiphilic compounds are of interest because they behave at interfaces as surfactants. Already developed a variety of methods for synthesis of such compounds and actual is the study of their thermodynamic properties.

*Tris*(pentafluorophenyl)-4-pyridylethylgermane was prepared by reaction of *tris*(pentafluorophenyl)germane and 4-vinylpyridine at room temperature in THF under argon. The structure was proved by IR, NMR and X-ray analysis (Figure).



**Figure:** Structure of *tris*(pentafluorophenyl)-4-pyridylethylgermane.

The thermal stability of *tris*(pentafluorophenyl)-4-pyridylethylgermane was studied using TG 209 F1 thermal microscopes (Netzsch Geratebau, Germany). We determined that a considerable (2%) loss in mass related to the destruction of the sample is observed at  $T = 472$  K. The melting of the sample was studied by DSC (DSC 204 F1 Phoenix, Netzsch Geratebau, Germany). It was established that compound under study melts without destruction. The standard thermodynamic characteristics of fusion have been determined from obtained experimental data. The onset temperature of fusion, enthalpy and entropy of fusion were determined. Also, the impurities content in tested sample was estimated from DSC-results.

## THERMODYNAMIC PROPERTIES OF SAMARIUM, GADOLINIUM AND DYSPROSIUM POLYSELENIDES

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Specificity of rare-earth polyselenides of  $LnSe_x$  composition ( $1.5 < x < 2.0$ ) is caused by features of stereochemical behavior of the selenium atoms forming extended bonds and creating low-dimensional structures in anion sublattice. The structure-forming role of selenium clusters is revealed in a rich variety of superstructures whose period grows with increase of a non-stoichiometry. The displacement of selenium atoms in new positions of superstructures results to electron density redistribution and charge density wave formation. Under external fields the electronic-structural transitions can take place in such superstructures. Thanks to this phenomenon rare-earth polyselenides show anisotropy of physical properties and have ability to the same interesting behavior, as the compounds with cationic clusters. But experimental investigation of this effect is not realized owing to lack of high-quality crystals of rare-earth polyselenides. These crystals are difficult to obtain without knowing the thermodynamic parameters ( $p_{Se}-T-x$ ) which define the conditions of their growth. Literary data on phase diagrams of rare-earth polyselenides have sketchy and contradictory character both about the number of phases, and their real composition.

Earlier we have investigated light (La, Ce, Nd, Pr) rare-earth polyselenides and revealed the regularity in the change of solid phase compositions under stepwise removing the selenium atoms from anionic lattice:  $Ln_nSe_{2n-1}$  where  $n$  is equal to 5, 7, 10, 20 [1]. The aim of this work is to clarify the implementation of this regularity for heavy (Sm, Gd, Dy) rare-earth polyselenides and to obtain a set of standard thermodynamic functions for these polyselenides.

The initial samples for investigation were the single crystals of higher polyselenides of Sm, Gd and Dy:  $SmSe_{1.90}$  and  $LnSe_{1.875}$  ( $Ln = Gd, Dy$ ). The selenium vapour pressure over studied samples has been measured by static method with quartz membrane-gauge manometers using an isothermic and anisothermic procedure. The limiting errors in values of pressure, temperature and solid phase composition were 0.5 Torr, 1 K and 0.01 formula units, accordingly. The measurements have been realized in wide intervals of temperature ( $758 \leq T/K \leq 1298$ ), pressure ( $1 \leq p/\text{Torr} \leq 760$ ) and composition ( $1.5 \leq x/\text{f. u.} \leq 1.9$ ).

The detailed thermodynamic study has revealed that the phase regions in the studied composition intervals consist of discrete intermediate phases whose stoichiometric composition can be described by the same general formula  $Ln_nSe_{2n-1}$  found earlier for light rare-earth polyselenides but with somewhat another set of  $n$  values ( $n = 3, 4, 5, 7, 8$ ). The main result of this study is the thermodynamic parameters ( $p_{Se}, T$ ) which define the fields of stability and the growth conditions of homogeneous polyselenide phases. These fields are very narrow for the polyselenides with small  $n$  values therefore it isn't surprising that they still weren't synthesized. A set of thermodynamic characteristics ( $\Delta_f H_{298}^\circ, S_{298}^\circ, \Delta_f G_{298}^\circ$ ) obtained in this work can be used for thermodynamic simulation of crystal growth processes of Sm, Gd and Dy polyselenides.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMOCHEMICAL PROPERTIES OF Cu(II) $\beta$ -IMINOKETANATES

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Layers of metallic copper are widely used in modern microelectronics due to their thermal, electrical and physical characteristics. One of the perspective applications of copper is the use of it as dopant of active layer in a palladium membrane for hydrogen extraction and purification. An effective method for the deposition of functional layers is MOCVD (Metal Organic Chemical Vapor Deposition). Actual task is the search of available volatile compounds of copper promising as MOCVD precursors. Due to the high affinity of copper to oxygen MOCVD is complicated by formation of oxide phase impurities. A possible solution of this problem is the synthesis of precursors with a minimum content of oxygen atoms in the ligand. One of such classes of compounds is  $\beta$ -iminoketanates of Cu(II). It is known that the introduction of fluorinated groups in the ligand structure increases the volatility of precursors, so it is advisable to use fluorinated analogues of  $\beta$ -iminoketanates.

Six different complexes of Cu(II) with various ligands by general formula  $\text{Cu}(\text{R}^1\text{C}(\text{NR})\text{CHC}(\text{O})\text{R}^2)_2$  ( $\text{R} = \text{H}$ ,  $\text{R}^1 = \text{R}^2 = \text{Me}$  (i-acac) **1**;  $\text{R} = \text{H}$ ,  $\text{R}^1 = \text{CF}_3$ ,  $\text{R}^2 = \text{Me}$  (i-tfac) **3**;  $\text{R} = \text{Me}$ ,  $\text{R}^1 = \text{R}^2 = \text{Me}$  (mi-acac) **4**;  $\text{R} = \text{Me}$ ,  $\text{R}^1 = \text{CF}_3$ ,  $\text{R}^2 = \text{Me}$  (mi-tfac) **6**) were synthesized by the reaction between  $\text{Cu}(\text{OH})_2$  and corresponding  $\beta$ -iminoketone. The obtained samples were identified by elemental analysis, IR-spectroscopy and single-crystal X-ray analysis.

The thermal properties of above mentioned compounds have been investigated by the thermogravimetric analysis (NETZSCH TG 209). The data of mass loss have shown that complex **3** ( $\text{Cu}(\text{i-tfac})_2$ ) is the most volatile while complex **2** ( $\text{Cu}(\text{i-thd})_2$ ) is the least volatile.

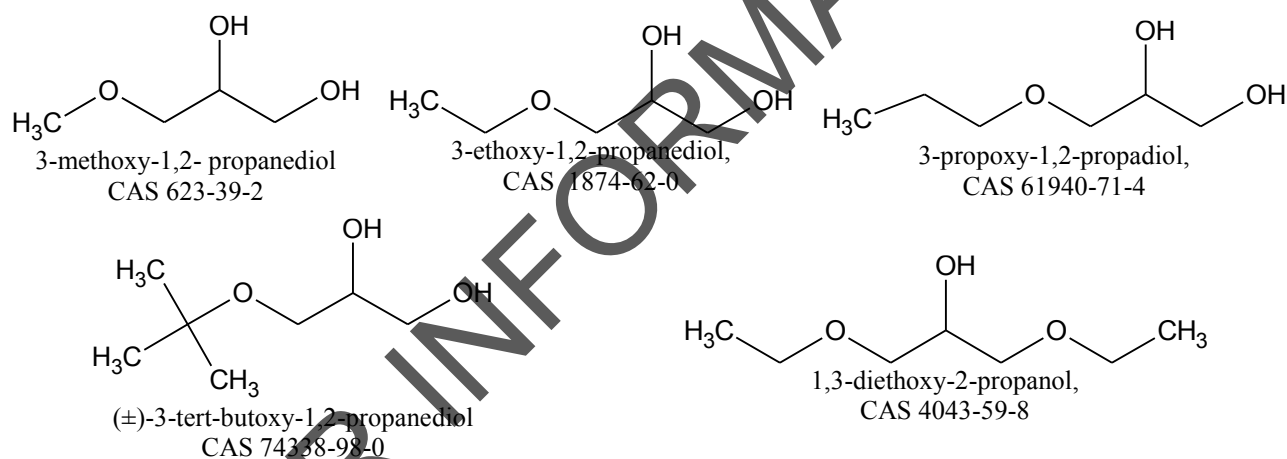
The method of differential scanning calorimetry (SETARAM 111) was used to determine the thermodynamic characteristics of melting process ( $T_{\text{melt}}$ ,  $\Delta_{\text{melt}}H_{T_{\text{melt}}}$ ,  $\Delta_{\text{melt}}S_{T_{\text{melt}}}$ ). Calorimetric measurements were performed in vacuum at heating rates of 1–2 K/min for all complexes. The samples exhibited the only phase transition (melting) in the studied temperature range ( $T_{\text{room}} - T_{\text{melt}}$ ). It follows that the samples were individual phases in the limit of the sensitivity of method. The uncertainties in the measurement of heat effects were less than 1.5%.

The data on volatilities and melting allowed us to choose the most optimum conditions for carrying out MOCVD processes.

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ENTHALPIES OF VAPORIZATION AND VAPOR PRESSURES  
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In the previous work we have described a method of a glycerol utilization by etherification with linear and branched out alcohols [1]. Due to the implementation of “green” policies in production, these substances can have a great commercial interest as eco-friendly solvents or oxygenates to diesel fuel, biodiesel or their mixture [2–4]. We need reliable thermodynamic data to create a technology of their producing. Five glycerol ethers were studied in this work. Liquid samples of (3-methoxy-1,2-propanediol, (±)-3-tert-butoxy-1,2-propanediol and 1,3-diethoxy-2-propanol) were of a commercial origin. Samples of 3-ethoxy-1,2-propanediol and 3-propoxy-1,2-propadiol were synthesized and purified in our laboratory.

**Figure:** Glycerol ethers.

In this work we have determined enthalpies of vaporization of glycerol ethers from the temperature dependence of the vapor pressure measured by the transpiration method. The static method was used for 1,3-diethoxy-2-propanol for validation of our results. Previous studies of oxygen-containing substances described in the work [5] were combined with new data for glycerol ethers to improve a prediction scheme for enthalpy of vaporization.

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## Section 2. Thermodynamics of individual chemical compounds

### THERMAL PROPERTIES OF PRECURSORS AS A KEY TO SUCCESSFUL CVD OF OXIDE COATINGS

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Chemical Vapour Deposition (CVD) is widely applied to fabricate several functional materials (high-k dielectrics, enhanced emission materials, SOFC etc.). It is a multivariable complicated process and one of the essential conditions of its successful realization is the “right” selection of source compounds (precursors). The precursor should satisfy a set of requirements, the main being a sufficiently high vapour pressure at relatively low temperatures (“volatility”) and stability in the solid and gas phases. Besides forming composite material, the used compounds should certainly be experimentally compatible: they should decompose at the same temperature range.

Since almost all metals of the Periodic Table are subject to interest of science and a great number of organic compounds are available, volatile metal compounds with organic ligands possess an undoubted advantage over inorganic ones, the accessibility of practically any combinations of metal–ligand makes it possible to obtain an “ideal” precursor suitable for certain tasks and satisfying the requirements on both the saturated vapour pressure and thermal stability. The vast majority of the precursors currently known is characterized only by TG/DTA. These data are very useful for determining phase transitions and qualitative assessment of the “volatility” of the precursors but uninformative for obtaining quantitative characteristics of their vaporization processes. In addition, they provide no information on thermal behaviour of the gas phase. The lack of fundamental information about mechanisms of the precursors’ vaporization and decomposition leads to the fact that the basis for the development of film deposition processes is an empirical approach to establishing the optimum technological parameters that determine the desired functional properties of the resulting materials.

The present work demonstrates the significance of complex approach to the investigation of precursors’ thermal properties in developing technical procedure to obtain mono- and composite oxide films by CVD.

We carried out the systematic study of row of different metal (Cs(I), Mg(II), Sc(III), Hf(IV)) complexes containing (O, C, N)-ligands of various organic classes (beta-diketones, ketoimines, diamines, cyclic dienes). Thermal properties and decomposition mechanisms were investigated by DSC, *in-situ* high temperature mass spectrometry, tensimetric methods (Knudsen effusion method with mass spectrometric registration of gas phase, flow method and static method with membrane-gauge manometer). As a result, data on vapour pressure and thermal stability of the compounds and temperature dependencies of the gas phase composition by their thermolysis were obtained. The research allowed us to retrace the changes in chelate thermal properties during both the metal substitute and the organic component variation. Based on this information the suitable precursors were selected and the deposition regimes were determined to form mono- and composite oxide films (Cs<sub>2</sub>O, MgO, Sc<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>) by CVD.

## THERMODYNAMIC PROPERTIES AND THERMAL DECOMPOSITION OF VANADYL ACETYLACETONATE

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Vanadyl acetylacetonate  $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$  is a precursor for the synthesis of vanadium dioxide films which are used in the recording, storing optical information elements, visualizers, detectors, laser technology and other devices. Selection of the optimal conditions of synthesis requires knowledge of the thermodynamic properties and thermal stability of  $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ . Here are presented the results of the heat capacity and thermodynamic functions determinations as well as some features of the thermal decomposition of  $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ .

Sample of  $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$  was synthesized from vanadyl sulfate and acetylacetonone. The phase composition of sample was proved by XRD and IR spectroscopy measurements.

Heat capacity  $C_p^\circ$  was measured in the range (5–345) K by the adiabatic method and includes 119 measured points. There are no abnormalities of the heat capacity in the entire temperature range.  $C_p^\circ(298.15 \text{ K}) = 316.33 \text{ J mol}^{-1}\text{K}^{-1}$ . Thermodynamic functions are calculated:  $S^\circ(298.15 \text{ K}) = 383.42 \text{ J mol}^{-1}\text{K}^{-1}$ ,  $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 55520 \text{ J mol}^{-1}$ .

Thermal decomposition of  $\text{VO}(\text{acac})_2$  has been studied by thermogravimetric (TGA), X-Ray phase analysis (XRD), mass spectrometry and Fourier transform infrared spectroscopy in the atmosphere of dry and wet inert gas. The obtained results suggest the following sequence of breaking bonds in solid  $\text{VO}(\text{acac})_2$  by heating.

Above 180°C the mechanism proton-assisted thermolysis starts



with cleavage one of the chelate ligand. It is consistent with the data on the two-stage hydrolysis [1] and oxidation [2] of solid  $\text{VO}(\text{acac})_2$ . The ligand cleavage is not associated with its opening the original disclosure, as by heating the acid bands disappear before the VOH band appears [3]. At 260°C  $\text{VO}(\text{acac})_2$  melts with decomposition. The disappearance of the C–C–C and C–O bands above (430–480)°C show further decomposition of the ligands:



with the evolving of gaseous  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , propadiene  $\text{C}_3\text{H}_4$  [3] and solid vanadium hydroxide  $\text{VO}(\text{OH})_2$ . Above 330°C the last decomposes to solid  $\text{VO}_2$ .

The results of XRD and FTIR spectroscopy of samples of  $\text{VO}(\text{acac})_2$ , annealed in a wet inert atmosphere [4], show that if the destruction of chelate cycles ends at 480°C, the crystallization is completed at (550–600)°C.

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## Section 2. Thermodynamics of individual chemical compounds

### PHASE EQUILIBRIA IN THE Sm – Sr – Co - Fe – O SYSTEMS

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Phase equilibria in the Sm – Sr – Co – O and Sm – Sr – Fe – O systems were systematically studied at 1100°C in air.

Polycrystalline samples in Sm–Sr–Co–Fe–O systems were synthesized using a conventional ceramic route and glycerin nitrate technique. Phase identification was performed by X-ray diffraction (XRD) analysis using a DRON-6.0 diffractometer with  $\text{CuK}\alpha$  radiation. Unit cell parameters were refined using the Fullprof package. The changes of oxygen content of the single phase samples were measured by thermogravimetric analysis within the temperature range  $25 \leq T, ^\circ\text{C} \leq 1100$  in air. The absolute oxygen content in the samples was determined using a direct reduction of the samples in the TG cell by hydrogen and red-ox titration. Thermal expansion of samples was studied within the temperature range (25–1100)°C in air.

According to the results of XRD analysis three types of solid solutions:  $\text{Sr}_{1-x}\text{Sm}_x\text{MeO}_{3-\delta}$ ,  $\text{Sr}_{2-y}\text{Sm}_y\text{MeO}_{4\pm\delta}$  (Me = Co, Fe),  $\text{Sr}_{3-z}\text{Sm}_z\text{Fe}_2\text{O}_{7-\delta}$  exist in the systems.

It was found that single-phase  $\text{Sr}_{1-x}\text{Sm}_x\text{MeO}_{3-\delta}$  (Me = Fe, Co) samples were obtained within the ranges  $0.05 \leq x \leq 0.50$  (tetragonal structure  $I4/mmm$  sp. gr.) for Me = Co and  $0.0 \leq x \leq 0.5$  (cubic structure  $Fm\bar{3}m$  sp. gr.) and  $0.85 \leq x \leq 1.00$  (orthorhombic structure  $Pbnm$  sp. gr.) for Me = Fe. XRD patterns of the single phase samples were refined by Rietveld method within the cubic structure ( $Fm\bar{3}m$  sp. gr.) for Me = Fe. Gradual substitution of strontium by samarium leads to the decrease of the unit cell parameters and unit cell volume, that can be explained by the size factor ( $r_{\text{Sm}^{3+}} = 1.38 \text{ \AA}$ ;  $r_{\text{Sr}^{2+}} = 1.58 \text{ \AA}$ , CN 12). An introduction of samarium into the strontium cobaltate and strontium ferrite increases the oxygen content. Thermal expansion of  $\text{Sr}_{1-x}\text{Sm}_x\text{MeO}_{3-\delta}$  (Me = Fe, Co) samples was studied within the temperature range (25–1100)°C in air. The bend on the  $\Delta L/L = f(T)$  curve for the  $\text{Sr}_{0.9}\text{Sm}_{0.1}\text{CoO}_{3-\delta}$  sample indicates the presence of phase transition at temperature  $\sim 335^\circ\text{C}$ . The decrease of average values of TEC with the increase of Sm content is probably related to the reduction of the unit cell volume and diminishing of oxygen exchange.

According to the results of XRD analysis single phase samples  $\text{Sr}_{2-y}\text{Sm}_y\text{MeO}_{4\pm\delta}$  were formed within the range  $0.7 \leq x \leq 1.1$  for Me = Co and  $0.7 \leq x \leq 0.8$  for Me = Fe. X-ray diffraction patterns obtained for all single phase samples were indexed in the orthorhombic structure, sp. gr  $I4/mmm$ . The values of oxygen content in the  $\text{Sr}_{2-x}\text{Sm}_x\text{MeO}_{4\pm\delta}$  solid solutions recalculated to the room temperature were nearly equal to 4.0.

The homogeneity range of the  $\text{Sr}_{3-z}\text{Sm}_z\text{Fe}_2\text{O}_{7\pm\delta}$  solid solutions was found to be  $0.0 \leq z \leq 0.3$  and  $z = 1.2$ . Single phase samples based on strontium ferrite possess tetragonal structure,  $I4/mmm$  space group ( $0.0 \leq z \leq 0.3$ ) or  $P4_2/mmm$  space group ( $z = 1.2$ ). The value of oxygen content in the  $\text{Sr}_{1.2}\text{Sm}_{1.8}\text{Fe}_2\text{O}_{7\pm\delta}$  was nearly equal to 6.96 at 25°C.

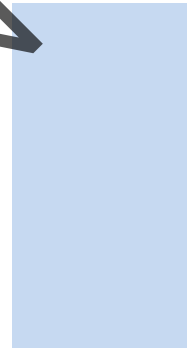
The projections of isothermal–isobaric phase diagrams for the Sm – Sr – Co – O and Sm – Sr – Fe – O systems to the compositional triangle of metallic components were presented.

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FOR YOUR INFORMATION ONLY

**Section 3**  
**Thermodynamics of solutions  
and heterogeneous systems**



## Section 3. Thermodynamics of solutions and heterogeneous systems

### MOLECULAR INTERACTIONS AND FEATURES OF STRUCTURE OF TETRACHLOROMETHANE–ACETONITRILE SOLUTIONS

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The present work is a follow-up on our recent study of microheterogeneous structure of binary solutions containing chlorine component [1–5]. Here we report a study of solutions system  $\text{CCl}_4 - \text{C}_2\text{H}_3\text{N}$ . Notably, chlorine-aggregation is an important feature of organochlorines substances. It is caused by the interaction between the chlorine atoms of several molecules by unshared pairs *np*- and free *nd*-orbitals. In the liquid acetonitrile, molecules can form dimers due to the donor – acceptor interactions between atoms C and N. In addition, more complex structures can be formed due to the interaction of a nitrile group nitrogen with a  $\text{CH}_3$ -group hydrogen.  $\text{C}_2\text{H}_3\text{N}$  molecule has large dipole moment, whereas  $\text{CCl}_4$  molecule has no dipole moment.

The molecular interactions between identical or different molecules were calculated. The speed of ultrasound was measured and adiabatic compressibility was calculated. Moreover, we computed the excess parameters – molar volume, adiabatic compressibility, molar refraction and the effective polarizability. In addition we analyzed the concentration dependence of these parameters. All the dependences show complex behavior and the parameters change sign at certain concentrations.

We have shown that the entire interval of solutions existence can be divided into three regions that differ in structure: 0–0.1, 0.1–0.45 and 0.45–1 mole fractions of acetonitrile. We assume that the structure of solutions in the first region can be explained by chlorine-aggregation of  $\text{CCl}_4$  molecules and solvates formation. In the second region it can be explained by an agglomeration of  $\text{CCl}_4$  molecules and conglomeration of  $\text{CCl}_4$  and  $\text{C}_2\text{H}_3\text{N}$  molecules by formation of  $\text{Cl} \cdots \text{H}$  bonds. Finally, solutions structure in the third region can be explained by an agglomeration of acetonitrile molecules, by donor-acceptor interactions and by formation of  $\text{N} \cdots \text{H}$  bonds.

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ENTHALPIES OF SOLUTION AND ENTHALPIES OF TRANSFER  
OF IMIDAZOLIUM-BASED IONIC LIQUIDS IN TETRAHYDROFURAN  
AND CHOLOROFORM: PROTON ACCEPTOR SCALE

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Ionic liquids are organic salts with melting point lower than 100°C. Due to their unique properties, they can be used as universal catalysts, solvents and coolants. Ionic liquids have low vapor pressure, high chemical and thermal stability, the ability to dissolve many organic and inorganic substances. It allowed them to be widely adopted in catalysis, synthesis, electrochemistry, nanotechnology and etc. However, their thermodynamic properties haven't been extensively studied. Especially, there is lack information about energies of intermolecular interactions in solutions of ionic liquids with different solvents.

In this work we studied the thermodynamics of dissolution of aprotic ionic liquids in chloroform and tetrahydrofuran at 298.15 K. The objects of our study were ionic liquids with the imidazolium cation, different anions and different length of alkyl groups. Tetrahydrofuran and chloroform were taken as solvents due to several reasons. First, they have equal parameters of van der Waals interactions. Secondly, tetrahydrofuran is proton acceptor and chloroform is proton donor. So, difference between enthalpies of solution of ionic liquids in these two solvents (enthalpy of transfer) can be a measure of hydrogen bonding strength. Also, depending the sign of this difference one can say that studied ionic liquids have higher proton donor or proton acceptor ability. In order to obtain thermodynamic data at infinite dilution concentration effect on the heat of dissolution was studied. It was shown based on calorimetric data that studied ionic liquids exhibit predominantly proton acceptor abilities. The strength of hydrogen bonding increase in the range  $\text{Trif} < (\text{CN})_2\text{N} < \text{SCN} < \text{BuSO}_4 < \text{EtSO}_4 < \text{MeSO}_4$ . Also we have observed that proton acceptor ability of studied ionic liquids slightly depend on the length of alkyl group. Obtained calorimetric data were confirmed by FTIR-spectroscopic results.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### BINODAL SURFACES OF QUATERNARY SYSTEM WITH TWO PAIRS OF SPLITTING COMPONENTS

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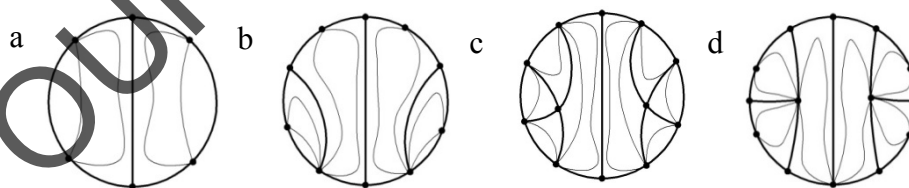
Mathematical modeling is one of the most effective and rapid methods of multicomponent multiphase systems studying. The adequacy of the mathematical modeling is determined not only by quantitative reproduction of system characteristics (boiling temperature and composition of azeotropes, the solubility of the components), but also by reproduction of the variety of the thermodynamic behavior of the system. It is necessary to develop criteria of mathematical modeling adequacy specially in conditions of limited experimental data on liquid–liquid–vapor equilibrium of multicomponent systems.

The atlas of bimodal surfaces digraphs for quaternary systems with two pairs of splitting components is proposed as such criterion, namely the compliance of the bimodal surface digraph of quaternary system to one of the structures from the atlas. The tops of the digraph are the points corresponding to equilibrium compositions of liquid phases of azeotropes and critical points. The edges of digraph are oriented in accordance with the boiling temperature of the points corresponding to digraph tops. The procedure of binodal surface digraph construction is discussed in details in [1].

The digraphs atlas numbering 31 structure was obtained on the basis of analysis of all possible scans of vapor–liquid equilibrium diagrams of quaternary systems under the following conditions: there is at least one binary heteroazeotrope in splitting area; if the system contains ternary azeotropes in splitting ternary constituent, they are heterogeneous; if the system contains quaternary azeotrope, it is located in splitting area. All digraphs obey the algebraic sum of the indices of singular points. As binodal surface is of the second dimension, the digraphs are described by equation [2]

$$\sum N^f - \sum C^f = 2.$$

Examples of digraphs of real quaternary systems are presented in Figure.



**Figure:** Examples of digraphs of real quaternary systems: a – acetone–hexane–water–toluene; b – chlorobenzene–butyl alcohol–water–ethanol; c – acetone–hexane–chloroform–water; d – ethanol–benzene–water–cyclohexane.

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### MELAMIN AND PHENOZAN DERIVATIVES ACTIONS ON THERMODYNAMIC AND STRUCTURAL PARAMETERS OF MULTILAMMELAR LIPOSOMES

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The examining of mechanism of biological active substances (BAS) – melamine and phenozan derivatives, influencing to the biomembranes structural parameters was held. As the simple models of animal cellular biomembranes, being by the primary target for BAS, the phospholipid multilammelar liposomes were used. With aid of DSC and small-angle X-ray scattering (SAXS) the thermodynamic and structural properties of models was tested. Liposomes were consisted of numerous bilayer phospholipid membranes that were formed from individual synthetic DMPC (dimyristoilphosphatidylcholine) or natural phospholipid mixture – egg lecithin. DMPC molecules have the shape as cylinder because contain two residues of saturated myristic acid as hydrocarbon chains and the size of phosphate head is small. DMPC form the bilayer liposomes with short crook of membrane, when thin films were acted by hydration in phosphate buffer when neutral pH and temperature above of main phase transition. Subtle films on the walls of flask were acquired when DMPC was dried under vacuum. These multilayer films were acted by hydration consistently as – the stratum for stratum. Such method allowed to education of multilayer vesicular structures, composed of bilayer membranes, by the overall size up to 2000 Å from data of electron microscopy. Examining of BAS action on thermally induced transitions of lipid phase is the most important link in circuit test of biological effects of BAS. Because thermally induced phase main transition, i.e. the transition from solid – gel state in rank order to the liquid state – liquid crystal, play a major role in membranes of living organism. When liquid phase all conformational rearrangements of proteins occur easily: oligomers formation, lipids flip-flop moving, and lateral shifting. In solid membranes all these species of mobility have been hampered, and all structural-functional activities are inhibited. The membrane structures and functions were remained, when liquid crystal state of membrane exists. And the braking of all conformation processes is lacking when studying BAS effects on the experimental objects. We used the aqueous solutions of hydrophilic substances or ethanol–aqueous emulsion of hydrophobic ones from ultra small concentrations up to large ones ( $10^{-21}$  –  $10^{-3}$  M). For test of melafen solution actions to the membrane structures the specific approach was applied: different speed of heating: from 1 to 0.125 degree/min to cells with samples. Such approach was used in order to educe some eventual restructuring of additive cooperative units in membrane microdomains. And second DSC approach was – the reheating under the different rates that indicate of some relaxation processes in microdomains organization. The structural membrane changes, both in lipid and protein components, under BAS, identified by DSC, are supported by changes in membranes microviscosity by SPR with introduction of spin-labeled probes to erythrocytes at the 2–4 Å; 6–8 Å of membranes depths. In cells BAS change the membranes permeability: passive (hemolysis) and active (channel conductance). During ripple-phase the nana-size short-lived pores arise at membranes, thus BAS penetrate, and modify structure and function, as was shown early on erythrocytes and by us on SOC channels of EAC cells. The integral structural changes (period and degree of order) did not were found by SAXS at lecithin liposomes under hydrophilic BAS, opportunely under hydrophobic phenozan derivatives.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### ENTHALPIES OF PHASE TRANSFORMATIONS IN THE YSE – Y<sub>2</sub>SE<sub>3</sub> SYSTEM

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Enthalpies of phase transformations in the Yse – Y<sub>2</sub>Se<sub>3</sub> system determined differential scanning calorimetry (DSC) method for sample mass about 100 mg. DSC was conducted on STA 449 F3 Jupiter unit, rate of heating was 10 K/min, the experiment was held in helium atmosphere (grade 7.0; 99.99999%). The unit was calibrated according to the melting enthalpy of the referring marks ( $\Delta H_{\text{melt}}(\text{SrF}_2) = 142 \text{ J/g}$ ,  $\Delta H_{\text{melt}}(\text{Au}) = 62.3 \text{ J/g}$ ,  $\Delta H_{\text{melt}}(\text{Cu}_2\text{S}) = 145 \text{ J/g}$ ), the accuracy of deducting enthalpy of melting is 10–15%.

Phase diagram of the Yse – Y<sub>2</sub>Se<sub>3</sub> system is of eutectic type. The YSe and Y<sub>2</sub>Se<sub>3</sub> compounds melt congruently ( $T_{\text{melt}}(\text{Yse}) = 2390 \text{ K}$ ,  $T_{\text{melt}}(\text{Y}_2\text{Se}_3) = 1780 \text{ K}$ ). DSC of Y<sub>2</sub>Se<sub>3</sub> sample shows endoeffect at 1575 K (1305 °C),  $\Delta H = 9.7 \text{ J/g}$ .

The sample of Y<sub>2</sub>Se<sub>3</sub> heated to 1650 K is in solid state. The peaks of thermal effect are reproduced with cooling at the temperature of 1560 K. The character of thermal effect peak lets us conclusively claim that the noted phase change in the system diagram corresponds to non-variant phase equilibrium, polymorphic transition  $\varepsilon\text{-Y}_2\text{Se}_3 \leftrightarrow \xi\text{-Y}_2\text{Se}_3$ ,  $T = 1575 \text{ K}$ ,  $\Delta H = 4 \pm 0.4 \text{ kJ/mol}$ . Phase transition is classified as fast, and high temperature modification is not fixed by hardening.

In the range of solid solution based on Y<sub>2</sub>Se<sub>3</sub> the temperature of polymorphic transformation decreases to the temperature of eutectoid phase transformation at  $1575 \pm 5 \text{ K}$ , that can be proved by constructing Tamman triangle (Table).

**Table.** Temperatures and enthalpies of phase transformation in the YSe – Y<sub>2</sub>Se<sub>3</sub> system

Sample composition, at.% Se	Phase composition of sample	T and $\Delta H$ of polymorphic change	T and $\Delta H$ of eutectic crystals	$\Delta T$ and $\Delta H$ of primary crystals of phases
57	SS YSe + eutectic	–	1622 K; 22 J/g	(SS YSe) 1662–1676 K; 75 J/g
57.5	SS YSe + eutectic	1530 K; 1.3 J/g	1628 K; 43 J/g	–
58	SS Y <sub>2</sub> Se <sub>3</sub> + eutectic	1540 K; 8.1 J/g	1623 K; 28 J/g	(SS Y <sub>2</sub> Se <sub>3</sub> ) 1622–1666 K; 49 J/g
Sm <sub>2</sub> Se <sub>3-x</sub> (59.8–60)	Y <sub>2</sub> Se <sub>3-x</sub>	1575 K; 9.7 J/g	–	(SS Y <sub>2</sub> Se <sub>3</sub> ) 1678–755 K; 158 J/g

On DSC-curves of the samples (57; 57.5; 58; 60 at.% Se) thermal effects of solidus and liquidus lines are observed (Table). The melting point of Y<sub>2</sub>Se<sub>3</sub> compound determined as the extrapolation of the liquidus line according to DSC data, and assumed to be equal 1780 K.

The melting temperature of eutectics between the phases YSe and Y<sub>2</sub>Se<sub>3</sub> according to DSC is  $1625 \pm 7 \text{ K}$ . Eutectic composition is taken equal to 57.5 at.% Se, this corresponds to ratio of phases 0.425Yse : 0.575Y<sub>2</sub>Se<sub>3</sub>. Melting enthalpy of eutectic composition according to DSC is 43 J/g.

Fusion heat of the phase YSe calculated by linearized form of the van Laar equation [1] on the liquidus line from YSe to eutectics is 37 kJ/mol.

[1] Khritokhin, N.A.; Andreev, O.V.; Burkhanov, T.M. Russian Journal of Inorganic Chemistry, 2002, 47, 1, 122-125.

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## THERMODYNAMIC STUDIES OF RIFABUTIN – CYCLODEXTRIN INTERACTIONS IN WATER

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Cyclodextrins (CDs) are hydrophilic cyclic oligosaccharides used as solubilizers for poorly soluble substances. Solubilization occurs via hydrogen bonding between a lipophilic moiety of a molecule and the hydrophobic cavity of CD, which leads to the formation of water-soluble associates. It was shown previously that aqueous solubility of antituberculosis antibiotic rifabutin (RB) (BCS Class II;  $c_s = 0.19$  mg/ml) is increased 2.5-fold in the presence of hydroxypropyl- $\beta$ -CD (hp- $\beta$ -CD) [1] due to the formation of nanosized (1–10 nm) and submicron (100–600 nm) aggregates of the drug and hp- $\beta$ -CD.

Molecular interactions in [RB-(hp- $\beta$ -CD)] system in water were evaluated by calculation of the thermodynamic properties using the inverse gas chromatography (IGC) method.

RB substance was obtained from Luohe Nanjiecun Pharmaceutical Group Pharmacy CO., LTD (China); hp- $\beta$ -CD was purchased from Sigma-Aldrich (USA).

The measurements were carried out using a gas chromatograph (Crystal 200M, Chromatec, Russia) equipped with a katharometer detector. Helium was used as a carrier gas with a flow rate of 30 ml/min. The analyzed samples of RB, hp- $\beta$ -CD, and their composition [RB-(hp- $\beta$ -CD)], prepared using the dry co-grinding technique, were packed into the glass columns. Test solvent (water) was injected into a GC vaporizer via gas tight microsyringe. RB, hp- $\beta$ -CD and the composition [RB-(hp- $\beta$ -CD)] chromatograms were obtained at 30-70°C.

The following constants were calculated: activity coefficients of water into the stationary phase, excess Gibbs energy ( $G^E$ ), enthalpy ( $H^E$ ), entropy ( $S^E$ ), and Flory–Huggins interaction parameter ( $\chi$ ).

Obtained negative values of the excess Gibbs energy of hp- $\beta$ -CD-water mixing ( $G^E$ ) at different temperatures correspond to the system thermodynamic stability and high solubility of hp- $\beta$ -CD in water (500 mg/ml). On the contrary, the values of  $G^E$  of the RB solution are positive in the whole temperature range, confirming the poor water solubility of RB.

The calculated value of  $G^E$  for the solution of the [RB-(hp- $\beta$ -CD)] composition was negative, but its absolute value was higher than the  $G^E$  of the CD – water system.

It was shown that the systems (hp- $\beta$ -CD) – water, [RB-(hp- $\beta$ -CD)] – water had the lowest values of  $\chi$ -parameter, whereas the RB - water system was characterised by the highest value of  $\chi$ -parameter. Therefore, it can be concluded that the solubility of RB in aqueous medium was enhanced in the presence of hp- $\beta$ -CD, which is in agreement with the previously obtained data on the weak interaction in this system.

**Table.** Thermodynamic parameters of mixing at 303 K

Compound/water	$H^E$ (J/mol)	$S^E$ (J/(mol·K))	$G^E$ (J/mol)	$\chi$
RB	10660	34,3	261	3.27
hp- $\beta$ -CD	6591	37,0	-4634	1.86
[RB-(hp- $\beta$ -CD)]	11901	49,6	-3116	2.26

[1] Anshakova, A.V.; Yermolenko, J.V.; Gelperina, S.E.; Maksimenko, O.O.; Mezhev, Ya.O. Uspekhi v Khimii i Khimicheskoi Tekhnologii [Successes in Chemistry and Chemical Technology], 2012, 26, 2, 58-62.

### Section 3. Thermodynamics of solutions and heterogeneous systems

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#### THERMODYNAMICS OF SYSTEMS WITH BIOLOGICALLY ACTIVE COMPLEXES OF PLATINUM AND PALLADIUM

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In this work the results of calculation of thermodynamic parameters and study the properties of new materials with biologically active complexes of platinum and palladium are presented.

The results of the experiments associated with biologically active complexes of platinum and palladium, in particular,  $[C_{24}H_{60}O_{12}S_{12}Pd_6]$  are considered. Using the determined structural formula and programs such as PASS, it is possible to evaluate the pharmacological effects, the mechanism of action and the specific toxicity of the substance.

Ligands and palladium salts alone show low biological activity in studied systems, while complexes derived from them exhibit significant activity. We have studied the influence of composition, structure and presence of ligands in the functional groups on the properties of new biologically active complexes.

When obtaining the mercaptoethanol complex with palladium, the hexanuclear cluster complex was formed. Palladium atoms form a molecular structure with each other through a disulphide bridge. We considered methods of a quantitative content assessment of an active component. Spectroscopic parameters were defined and dispersive analysis of derived materials was carried out.

Comparability of the obtained data was estimated by difference and similarity coefficient based on the solute concentration. We used potentiometric system to determine properties of the substances in solution. The maximum degree of reaction proceeding was derived from change in dilution factor taking into account volumes of solution of the substance complexes, the added water and the titrant. The equilibrium concentrations and the equilibrium constants have been defined.



## THERMODYNAMICS OF BINARY SYSTEMS GRAPHITE OXIDE – POLAR SOLVENT

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The unique properties of graphite oxide (GO) have recently been suggested as a basis for some unusual applications, e.g., for fabrication of supercapacitors using laser-induced reductive patterning or as a material for membranes which are permeable for water but not for ethanol or other polar solvents. The main feature of graphite oxide solvation is significant lattice expansion due to insertion of solvent between oxidized graphene layers.

In this study GO prepared according to Brodie (B-GO) and Hummers (H-GO) methods were used for measurements.

Sorption of solvents (S) by graphite oxide was studied using differential scanning calorimetry (DSC) and XR diffraction (XRD) in the binary systems GO – water, methanol, dimethylformamide (DMF), tetrahydrofurane (THF), *o*-xylene and *N*-methylpyrrolidone. The amount of solvent sorbed and corresponding heats of sorption were determined using DSC, isopiestic and thermogravimetric methods. The corresponding changes in XRD patterns were recorded.

The results obtained by various methods agreed within the limits of experimental errors. It was shown that sorption of solvents by H-GO, B-GO may be considered as formation of bulk phases, namely, solid solutions/ solvates with the compositions (GO)<sub>S0.12-0.5</sub> and typical interplane distances ( $d = 9-12 \text{ \AA}$ ). One or two solvent layers are incorporated within the inter space.

First order phase transformation of (GO)<sub>S0.36-0.28</sub> into (GO)<sub>S0.18-0.12</sub> (incongruent melting) was observed in the systems B-GO – methanol and B-GO –DMF. It corresponds to transition from two to one solvent layers between GO planes.

The endothermic effects, measured by DSC were  $10.0 \pm 1.5$  and  $5 \pm 1$  J per gram of GO for methanol and DMF, respectively. These effects were 2–3 times less than those measured for fullerene solvates.

*o*-Xylene is not sorbed by GO.

Schreder effect was not observed in H-GO and B-GO – water sorption.

Thermal effects corresponding to melting/freezing of sorbed solvents were not detected.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC INVESTIGATION OF $Tl_5Te_{3-x}Cl_x$ SOLID SOLUTIONS

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Chalcogenides and chalcogenides of heavy *p* metals are considered perspective functional materials possessing semiconductor, thermoelectric, photoelectric properties. According to recent investigations, some of thallium chalcogenides are promising materials for efficient X-ray and  $\gamma$ -ray detection.

Due to the crystal structure features,  $Tl_5Te_3$  has both cation- and anion-substitution analogues. Among cation-substitution analogues,  $Tl_9BiTe_6$  distinguishes with extreme high thermoelectric indicators.

The experimental results of phase equilibria in the ternary T–Te–Hal (Hal – Cl, Br, I) systems show that they are characterized by formation of ternary compounds of type  $Tl_5Te_2Hal$ , which are non-stoichiometric phases with a wide range of homogeneity.

This work is devoted to the elaboration of homogeneity area of  $Tl_5Te_2Cl$  and thermodynamic properties of  $Tl_5Te_{3-x}Cl_x$  solid solutions using electromotive force (EMF) measurements. For the EMF measurements, the following concentration chains were assembled:



The assembly of an electrochemical cell and measurements were similar to those reported elsewhere. In the chains of type (1), metallic thallium was used as the left electrode, while equilibrium alloys of the system Tl–Te–Cl were exploited as the right electrode. A saturated glycerin solution of KCl with the addition of 0.1 mass% TlCl was used as an electrolyte. EMF was measured by the compensation method in the temperature range of (300–430) K.

The results of the EMF measurements of the chains (1) are consistent with the solid-state phase diagram of the system. The analysis showed the linearity of the EMF dependences upon temperature for all alloys.

From EMF measurements for various compositions of right electrode temperature–concentration dependences of EMF values and relative partial thermodynamic functions of thallium in the alloys are obtained, which showed that  $Tl_5Te_2Cl$  compound has a wide homogeneity region, almost completely covering  $Tl_2Te$ – $Tl_5Te_3$ – $Tl_5Te_2Cl$  subsystem.

The integral thermodynamic functions of the solid solutions  $Tl_5Te_{3-x}Cl_x$  were calculated by integration of the Gibbs–Duhem equation (Table).

**Table.** The standard integral thermodynamic functions of  $Tl_5Te_3$ ,  $Tl_5Te_2Cl$  and  $Tl_5Te_{3-x}Cl_x$  solid solutions

Phase	$-\Delta_f G^0(298\text{ K})$	$-\Delta_f H^0(298\text{ K})$	$S^0(298\text{ K})$ ( $J \cdot K^{-1} \text{ mol}^{-1}$ )
	$\text{kJ} \cdot \text{mol}^{-1}$		
$Tl_5Te_2Cl$	$355.9 \pm 1.1$	$377.1 \pm 5.0$	$474.1 \pm 6.8$
$Tl_5Te_{2.2}Cl_{0.8}$	$329.7 \pm 1.2$	$345.8 \pm 4.8$	$471.7 \pm 7.2$
$Tl_5Te_{2.4}Cl_{0.6}$	$302.5 \pm 1.3$	$313.7 \pm 4.6$	$468.3 \pm 7.5$
$Tl_5Te_{2.6}Cl_{0.4}$	$274.3 \pm 1.4$	$281.2 \pm 4.0$	$465.6 \pm 7.8$
$Tl_5Te_{2.8}Cl_{0.2}$	$244.5 \pm 1.5$	$248.5 \pm 3.4$	$462.8 \pm 8.0$
$Tl_5Te_3$	$213.5 \pm 1.4$	$216.6 \pm 2.4$	$459.1 \pm 8.1$

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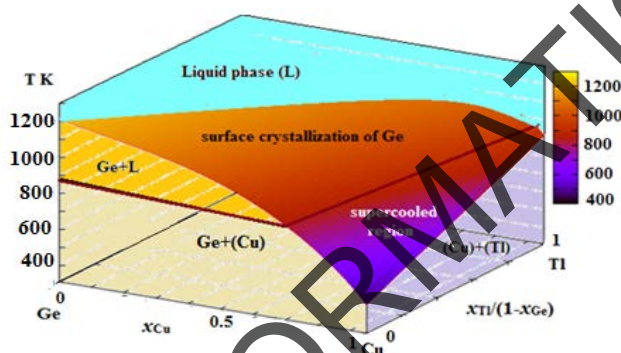
**THERMODYNAMIC CALCULATION AND 3D VISUALIZATION  
OF THE LIQUIDUS AND IMMISCIBILITY SURFACES  
OF THE CU–TI–GE (SN, PB) SYSTEMS**

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The solid solutions and intermetallic phases of ternary systems Cu–Ti–Ge (Sn, Pb) are perspective materials. The phase diagrams of these systems were studied in details. This work devoted to the thermodynamic analysis of phase equilibria in systems Cu–Ti–Ge (Sn, Pb).



**Figure:** The thermodynamic 3D computer modeling of surface crystallization of the Ge.

For determining and modeling these properties thermodynamic equations were used which were solved based on thermodynamic information obtained from the phase diagram of the binary boundary systems by using a limited number of experimental data for the ternary system [1, 2]:

$$T = \left[ \Delta H_1^m + y \overline{\Delta G}_{1(12)}^{\text{exs},l} + (1-y) \overline{\Delta G}_{1(13)}^{\text{exs},l} + bx_1(1-x_1)y(1-y) \right] / (\Delta S_1^m - RT \ln x_1),$$

where  $x_1, T$  – are mole fraction and temperature;  $y = x_2 / (1-x_1)$ ;  $T^m, \Delta H_1^m, \Delta S_1^m$  – are temperature, molar enthalpy and entropy of melting;  $\overline{\Delta G}_{i(i,j)}^{\text{exs}}$  – is the partial excess free energy of component  $i$  for binary system  $i-j$ ; constant  $b$  is defined according to the data of symmetrically arranged compositions. The value  $\overline{\Delta G}_i^{\text{exs}}$  associated with the thermodynamic activity and activity coefficient on the relation  $\overline{\Delta G}_i^{\text{exs}} = RT \ln \gamma_i = RT \ln(a_i / x_i)$ .

The calculation and visualization of immiscibility and crystallization surfaces of phases in the above state systems were performed by the program [grafikus.ru/plot3d](http://grafikus.ru/plot3d).

In Figure the liquidus surface of Ge in Cu–Ti–Ge system is presented. At the calculations the limited number of experimental data [3] for the liquidus surface of Ge was used.

[1] Mammadov, A.N.; Salimov, Z.E.; Babanly, M.B. *Az. Chem. J.*, 2014, 4, 12-15.

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[3] Babanly, M.B.; Salimov, Z.E.; Aliev, Z.S.; Imamalieva, S.Z. *Russian Journal of Inorganic Chemistry*, 2012, 57, 3, 443-448.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### PHASE EQUILIBRIA IN THE YbTe–SnTe–PbTe AND THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS

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Lead and tin tellurides and complex phases based on them are narrow band-gap semiconductors, and can be used in developing of new-generation of high-performance materials for thermoelectric convertors, mid- and far-IR detectors, and IR lasers [1].

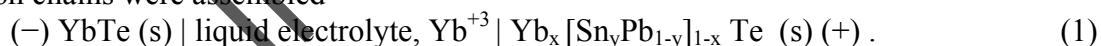
In order to create and develop modern preparative methods and controlled synthesis of novel complex materials it is necessary to investigate phase equilibria and thermodynamic properties of the respective systems.

The aim of this work is to study the phase equilibria and thermodynamic properties of the YbTe–SnTe–PbTe system.

Taking into account that all starting compounds of this system are isostructural (NaCl type cubic structure) and the lattice parameters are very close, the formation of cation substitutional solid solutions is expected. However, according to the literature data the YbTe–SnTe(PbTe) include ternary YbSnTe<sub>2</sub> and YbPbTe<sub>2</sub> compounds.

The preparation of all samples was performed in sealed (~10<sup>-2</sup> Pa) silica ampoules with preliminary synthesized compounds. In order to achieve maximal equilibrium state all alloys were ground into fine powders, mixed and pressed into pellets, and then annealed at 1000 K for 600 h.

Differential thermal analysis (DTA) was performed using the NETZSCH 404 F1 Pegasus system while X-ray powder diffraction (XRD) analysis was done with the Bruker D8 ADVANCE diffractometer (CuK<sub>α</sub> radiation). For the electromotive force (EMF) measurements, the following concentration chains were assembled



In the chains (1), saturated glycerin solution of KCl with the addition of YbCl<sub>3</sub> was used as the electrolyte. EMF was measured by the compensation method in the temperature range of (300–400) K.

However, ternary compounds YbSnTe<sub>2</sub> and YbPbTe<sub>2</sub> which reported earlier were not confirmed during present investigation. That is why, we have decided to refine the phase diagrams of boundary systems and plot the T–x–y diagram of this quasiternary system in the (300–1400) K temperature interval. According to collected data, the boundary binary YbTe–SnTe and YbTe–PbTe are characterized by the formation of high-temperature continuous cation substitutional solid solutions with a NaCl-type cubic structure, which are undergo spinodal-type phase decomposition below 950 K.

The maximum solubility at room temperature, based on YbTe equal to about 3 mol.%, while based on SnTe and PbTe found equal to 30 and 35 mol.%, respectively.

From EMF measurement the partial thermodynamic functions of YbTe "component" in the solid solutions were calculated. By integration of the Gibbs–Duhem equation the thermodynamic functions of dissolution of YbTe in SnTe, PbTe and Sn<sub>y</sub>Pb<sub>1-y</sub>Te solid solutions were calculated.

[1] Volkov, B.A.; Ryabova, L.I.; Khokhlov, D.R. Phys. Usp., 2002, 45, 819-846.

## THERMOCHEMICAL CHARACTERISTICS OF THE INTERACTION OF L-CYSTEINE WITH SODIUM DODECYL SULFATE IN AQUEOUS SOLUTIONS

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Amino acids are useful probe molecules for determining functional group contributions to biopolymer conformational stability. Interactions between surfactant and protein molecules are a subject of intensive research because they can modulate the functional properties of protein molecules. However, details of the interactions remain unclear.

Integral enthalpies of dissolution  $\Delta_{\text{sol}}H^0$  of L-cysteine (L-Cys) in mixed solutions of water with sodium dodecyl sulfate (SDS) were measured using a sealed variable temperature four ampoule calorimeter equipped with an isothermal shell of our own design to make consecutive measurements of a series of thermal effects during the dissolution of several weighed portions of a substance in the same amount as the solvent without refilling the calorimeter cell. The amino acid concentration was varied in the range of (0.007–0.009) mol/kg. The concentration dependence of enthalpies of transfer obtained was discussed using a common approach based on the analysis of different types of interactions that occur during the dissolution of crystalline substances in a solvent.

The transfer enthalpies are positive and increase with increasing surfactant concentration up to 0.05 mol/kg. The positive values of  $\Delta_{\text{tr}}H^0$  can be interpreted as due to the release of structured water molecules from the hydration co-spheres into the bulk. Partial dehydration of amino acid or surfactant molecules is an endothermic process. The hydration shells of ammonium and carboxylate groups are large enough to overlap the side chains of amino acid molecules and the charged groups strongly disrupt the structure of water up to a considerable distance [1]. L-cysteine inserts into the micelles and interacts with the hydrophobic tails of the surfactant molecules. There are three kinds of factors: a) ion–hydrophobic interactions between zwitterions of amino acid molecules and alkyl chain of surfactant molecules; b) hydrophilic–hydrophobic interactions between hydrophilic side chain of amino acid molecules and hydrophobic chain of surfactant molecules; c) hydrophobic–hydrophobic interactions between hydrophobic side chain of amino acid molecules and ethylene tail of surfactant molecules. According to the hydration co-sphere overlap model, these three types of interactions are endothermic. Therefore, the transfer enthalpies increase with increasing surfactant concentration. The interparticle interactions in aqueous solutions were quantitatively estimated via regression analysis using terms of the McMillan–Mayer theory [2] by calculating the enthalpy coefficient of pair interactions ( $h_{xy}$ ) between amino acid and molecules of sodium dodecyl sulfate. The enthalpy coefficient of pair interactions  $h_{xy}$  for the investigated amino acid had positive value, suggesting that the endothermic processes associated with the structural rearrangement of a ternary solution and the release of water molecules from the hydration shells of amino acid and sodium dodecyl sulfate dominate over direct interactions between the solvated polar groups of the interacting molecules.

[1] Ide, M.; Maeda, Y.; Kitano, H. *J. Phys. Chem. B*, 1997, 101, 7022-7026.

[2] McMillan, W.G.; Mayer, J.E. *J. Chem. Phys.*, 1945, 13, 276-305.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### SOLUBILITY OF CHENODEOXYCHOLIC ACID IN VARIOUS SOLVENTS AT DIFFERENT TEMPERATURES

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Solubility behavior of drugs in different solvents at variable temperature plays a crucial role in purification, pre-formulation, dose selection in pharmaceutical field. Chenodeoxycholic acid (CDCA) is a naturally occurring human bile acid with IUPAC name 3 $\alpha$ , 7 $\alpha$ -dihydroxy-5 $\beta$ -cholanic acid. The structure of CDCA is given in Figure 1. It is a tumor promoter in animal models, which enhances cell transformation *in vitro*.

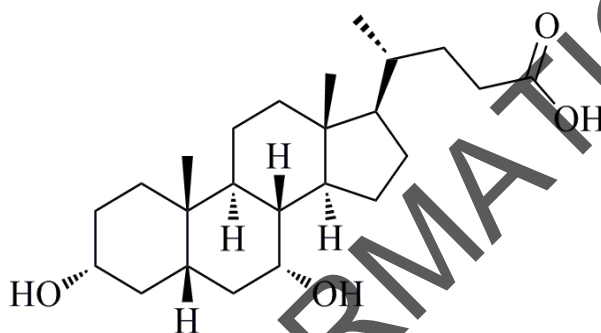


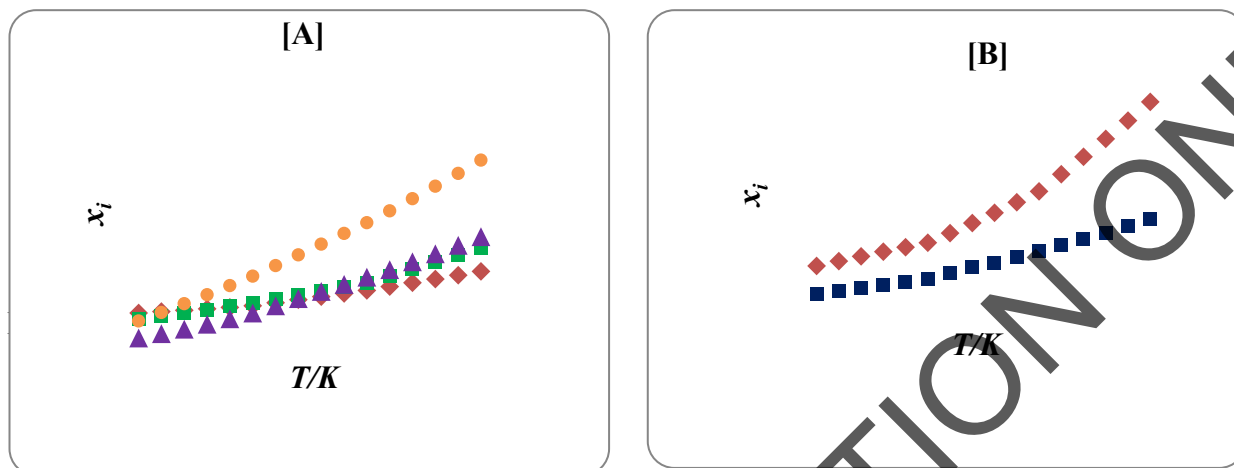
Figure 1: Chemical structure of CDCA.

In the present work, solubility of Chenodeoxycholic acid were determined in methanol, ethanol, propan-1-ol, butan-1-ol, tetrahydrofuran and 1,4-dioxane over the temperature range from 298.15 to 328.15 K by using gravimetric method. Figure 2 shows that in each solvent, the solubility of CDCA increases nonlinearly with temperature. In alcoholic solvents, at 298.15 K, the order of mole fraction solubility is: butan-1-ol > ethanol > methanol > propan-1-ol. However, when temperature increases to 314.15 K, the solubility order changes as butan-1-ol > propan-1-ol > ethanol > methanol. The comparison of solubility data with dielectric constants of the solvents suggests that above 314.15 K, solubility of CDCA decreases with increase in dielectric constant of alcoholic solvents. However, at lower temperatures, this trend is not followed which suggests that polarity is not the only factor responsible for the solubility of a substance in a solvent. Thus, at higher temperatures, among the studied alcohols, solubility increases with increase of CH<sub>2</sub> groups. In other two non-alcoholic solvents, solubility is higher in tetrahydrofuran than in 1,4-dioxane which is in the same order as their dielectric constants.

The temperature dependence of solubility in pure solvents has been described by the modified Apelblat [1, 2] and Buchowski–Ksiazczak  $\lambda h$  equations [3, 4]. It is observed that the calculated solubility values by the modified Apelblat equation are in good agreement with the experimental values. However, the values evaluated by Buchowski–Ksiazczak  $\lambda h$  equation deviate considerably from the experimental values.

Further, some thermodynamic parameters such as dissolution enthalpy ( $\Delta H_{sol}$ ), Gibb's free energy ( $\Delta G_{sol}$ ) and entropy of dissolution ( $\Delta S_{sol}$ ) of chenodeoxycholic acid in studied solvents were evaluated from the solubility data using modified Van't Hoff equation. The positive dissolution enthalpy and Gibbs energy of dissolution for all the studied solvents suggest that dissolution process for chenodeoxycholic acid is endothermic and spontaneous. The entropy of dissolution ( $\Delta S_{sol}$ ) is also positive indicating thereby favorable entropy of solubilization for

CDCA in solution. Thus, higher positive  $\Delta S_{sol}$  values suggest entropy-driving dissolution process. This may be due to different molecular structures and space conformations between solute (CDCA) and solvent molecules.



**Figure 2:** Variation of experimental mole fraction solubilities ( $x_i$ ) of CDCA with temperatures, for [A] in alcoholic solvents, methanol (♦), ethanol (■), propan-1-ol (▲), butan-1-ol (●) and [B] in non alcoholic solvents tetrahydrofuran (♦) and 1,4-dioxane (■).

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### RESEARCH OF DIFFERENT ISO-MANIFOLDS IN TERNARY SYSTEM WITH BIAZEOTROPIC CONSTITUENT

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The study of various iso-manifolds is one of directions for development of thermodynamic-topological analysis of multicomponent mixtures phase diagrams. On the one hand, the rigorous approach to separating agent (entrainer) selection in the separation of complex biazotropic mixtures by extractive distillation is based on the building in the concentration simplex mutual course of number of iso-manifolds [1]. On the other hand, the study of isotherm-isobars,  $K$ - and  $\alpha$  – manifolds equal to 1 ( $K$  – distribution factor of a component between the vapor and liquid phases;  $\alpha$  – coefficient of components relative volatility) allows to uniquely determine the structure of the residue curve map of the system. The most informative is the investigation of  $K = 1$  and  $\alpha = 1$  manifolds behavior, the intersection of which allows localizing azeotropes of any composition, which is especially hard to do in systems containing biazotropic components. As is well known, biazotropic mixtures have a complex physico-chemical nature and are characterized by the relative volatility of the components, close to 1, as well as little difference between the boiling points of the components and azeotropes.

In this work the object of research is the system butyl propionate (BP) – propionic acid (PA) – butyl butyrate (BB), containing biazotropic component BP–PA. This constituent is the boundary element of the concentration tetrahedron of butyl propionate – propionic acid – butyl butyrate – butyric acid (BA) system, that has commercial value and which includes homologues of carboxylic acids and their butyl esters. Computational experiment on determination of vapor–liquid equilibrium (VLE) at 40 kPa in the system under study is selected as a research method; NRTL model with non-ideal vapor phase is used.

On the basis of experimental and pseudo experimental (UNIFAC-DMD) data for systems BP–PA, BP–BB and PA–BB NRTL equation parameters are evaluated. For biazotropic system butyl propionate – propionic acid 14 sets of parameters are obtained. Parameters that produced the least error in the description of experimental data are selected for further calculations.

We have determined the characteristics of positive and negative azeotropes BP–PA, positive azeotrope PA–BB; it is shown that BP–BB is a zeotropic. Complete VLE data in the system BP – PA – BB are obtained, they have been processed to build the isotherm-isobars,  $K = 1$  and  $\alpha = 1$  lines in the concentration triangle. After analyzing the obtained iso-manifolds, we established, that ternary azeotropes are absent in the system and uniquely determined the structure of the residue curve map for the system butyl propionate – propionic acid – butyl butyrate. We have set the class, type and subtype of this graph according to the classification given in the article [2]: 3.[2.1.0]-3a. It should be noticed, that the real three-component system phase diagram, which belongs to the specified class, found for the first time.

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PHASE EQUILIBRIA IN SOME SULFONES SYSTEMS:  
EXPERIMENT AND CALCULATIONS

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Sulfones can be used as solvents for batteries, as intermediate in oil desulfurization and as extracting agent. Any industrial application requires phase diagrams of the substances mixtures, e.g. to choose compositions acceptable for process temperatures. The purpose of this work was to determine melting point data (temperature and enthalpy) of some pure sulfones (*i*-BuSO<sub>2</sub>Bu (I), (*i*-Bu)<sub>2</sub>SO<sub>2</sub> (II), AmSO<sub>2</sub>*i*-Bu (III)) and their mixtures and to compute binary and ternary phase diagrams.

The measurements were performed by DSC at the 204 F1 calorimeter in argon atmosphere. For most of samples, the following scanning program was used: cooling to -80°C with cooling rate 5 K·min<sup>-1</sup>, and registration while heated up to 30°C with scanning rate 10 K·min<sup>-1</sup>. For some samples an isotherm before crystallization and cooling rate 2 K·min<sup>-1</sup> were used to remove overcooling effects if glass transition was observed or difference between crystallization and melting was too high. The results obtained for pure substances are shown in Table. Stability parameters of pure sulfones were used to the thermodynamic assessment of phase equilibria in binary and ternary systems.

Temperatures of solidus and liquidus in binary systems were measured by DSC-method. Results of experiment and thermodynamic calculations with PhDi and Ternapi programs [1, 2] were compared. It was shown that nonvariant points in subsystems I – II and I – III can be reproduced assuming the ideal behavior of liquids but for correct description of (*i*-Bu)<sub>2</sub>SO<sub>2</sub> and AmSO<sub>2</sub>*i*-Bu mixture more complex model is necessary. Ternary surface of crystallization was calculated with a Redlich–Kister model and coordinates of eutectic point were determined.

The work was performed at the User Facilities Center of Lomonosov Moscow State University.

**Table.** Enthalpies and temperatures of melting of pure sulfones

Compound	$\Delta_{\text{fus}}H^\circ$ (kJ/mol)	$T_{\text{fus}}$ (K)
<i>i</i> -BuSO <sub>2</sub> Bu (I)	13.6	265.3±0.1
( <i>i</i> -Bu) <sub>2</sub> SO <sub>2</sub> (II)	17.5	284.5±0.1
AmSO <sub>2</sub> <i>i</i> -Bu (III)	18.4	270.3±0.2

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## Section 3. Thermodynamics of solutions and heterogeneous systems

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### THE LOCAL PHASE TRANSITIONS OF THE SOLVENT IN THE NEIGHBORHOOD OF A SOLVOPHOBIC POLYMER AT HIGH PRESSURES

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In 2002, ten Wolde and Chandler proposed a very elegant idea [1] stating that a hydrophobic polymer chain immersed in an aqueous medium can undergo a coil-globule transition when in a neighborhood of the polymer a surface dewetting transition occurs. The authors speculated, based on the results of computer simulations, that this effect is reminiscent of the first-order phase transition.

In order to describe the above mentioned mechanism within statistical thermodynamics it is therefore necessary to take the solvent explicitly into account. However, most theoretical models describe the solvent only implicitly, i.e., its influence on the macromolecule is taken into account through an effective monomer–monomer interaction. Such an approach simplifies the model, however the details of the solvent behavior – in particular phase transitions in the bulk solution, heterogeneity of the solvent near the polymer chain, and the dependence of the solvent quality on the pressure – are not taken into account.

In this work we investigate local phase transitions of the solvent in the neighborhood of a solvophobic polymer chain which are induced by a change of the polymer–solvent repulsion and the solvent pressure in the bulk solution [2]. We describe the polymer in solution by the Edwards model [3], where the conditional partition function of the polymer chain at a fixed radius of gyration is described by a mean-field theory. The contributions of the polymer–solvent and the solvent–solvent interactions to the total free energy are described within the mean-field approximation [4]. We obtain the total free energy of the solution as a function of the radius of gyration and the average solvent number density within the gyration volume. The resulting system of coupled equations is solved varying the polymer–solvent repulsion strength at high solvent pressure in the bulk. We show that the coil-globule (globule-coil) transition is accompanied by a local solvent evaporation (condensation) within the gyration volume.

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THERMODYNAMICS OF COMPLEX FORMATION OF LEFLUNOMIDE WITH CYCLODEXTRINS

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Leflunomide is one of the drugs which are used in the basic therapy of rheumatoid arthritis. Leflunomide action is very important since this medicine reduces inflammation in the joints that is responsible for both the symptoms of rheumatoid arthritis and the destruction of joints. However, practical application of leflunomide and preparation of leflunomide containing pharmaceutical formulations are complicated due to poor aqueous solubility ( $10^{-5}$  M) and low bioavailability of this drug. Aqueous solubility can be enhanced through the encapsulation of leflunomide by cyclic oligosaccharides (cyclodextrins). As it is well known, inclusion complex formation of cyclodextrins with drugs can significantly improve their solubility, dissolution rate, absorption and bioavailability as well as reduce side effects and toxicity.

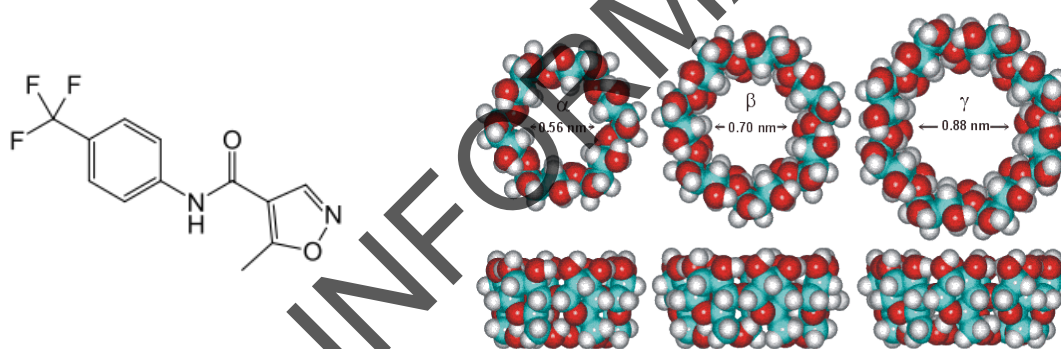


Figure: Structures of leflunomide and  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins.

In this work, complex formation of leflunomide with  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins was studied by UV-vis spectroscopy and solubility methods at 298.15 K. It was shown that aqueous solubility of leflunomide is considerably increased in the presence of cyclodextrins. This is caused by the placement of hydrophobic part of leflunomide molecule inside the cyclodextrin cavity. The obtained solubility diagrams are linear and correspond to 1:1 inclusion complex formation occurring between cyclodextrins and leflunomide. Stability constants of the complexes calculated from the solubility diagrams and UV-titration experiments were analyzed in terms of influence of cyclodextrin cavity size on the complexation process. Solubilizing effect of cyclodextrins towards leflunomide was demonstrated and discussed.

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### Section 3. Thermodynamics of solutions and heterogeneous systems

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#### THERMODYNAMIC STUDY OF EFFECTS OF INORGANIC CATIONS ON COMPLEX FORMATION OF CYCLODEXTRINS WITH *p*-AMINOBENZOIC AND BENZOIC ACIDS

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Inclusion complexes of cyclodextrins with biologically active molecules and drugs have received numerous applications in pharmacy, cosmetic and food industries. In this connection, the various aspects of inclusion complex formation of cyclodextrins are successfully considered. However, only a limited number of works was devoted to study of salt effects in complexation of cyclodextrins. Influence of biologically relevant inorganic salts should be taken into account since these salts compose physiological liquids and can affect the behavior of inclusion compounds in the course of their practical usage.

In the present study, we attempted to examine in detail the effects of various inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) on the inclusion complex formation of  $\alpha$ - and  $\beta$ -cyclodextrins with *p*-aminobenzoic and benzoic acids. Choice of *p*-aminobenzoic acid (vitamin B<sub>10</sub>) and benzoic acid as guest molecules was determined by their biological role and application in medicine and cosmetic industry. Study of complex formation of cyclodextrins with benzoic and *p*-aminobenzoic acids in water and saline solutions (0.2M) with pH 8 was carried out by means of <sup>1</sup>H NMR and UV-spectroscopy.

Comparative analysis of the obtained stability constants (K) of the complexes showed, that binding affinity of cyclodextrins to the acids is weaker in the salt solutions. More significant decrease of K values was observed in the presence of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . It was demonstrated that in comparison with  $\text{K}^+$ , all other cations under consideration are able to form stable ion pairs with the ionized carboxylic group of the acids. Ion pairing being in competition with inclusion complex formation is the main reason of specific salt effects, manifestation of which depends on the nature and properties of cations, size of cyclodextrin cavity and acid structure.

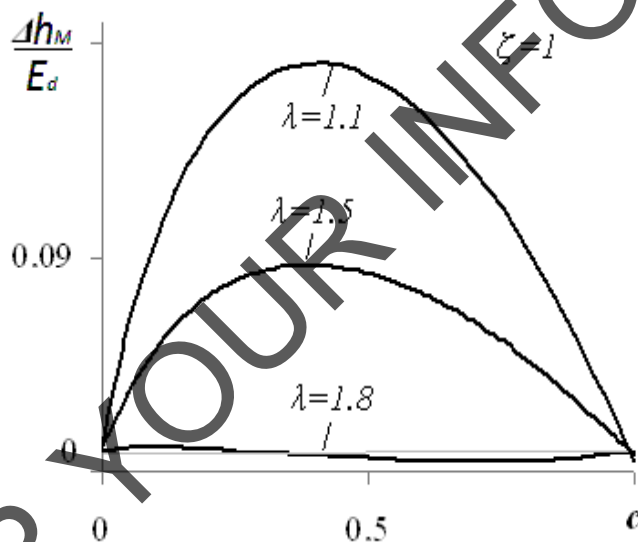
*This work was supported by the Russian Foundation for Basic Research (Project No. 13-03-97516-r-center-a). We thank "The upper Volga region centre of physico-chemical research" for scientific equipment provided.*

## STATISTICAL THERMODYNAMICS OF BINARY SOLUTION WITH DIMERISING OF ONE OR BOTH COMPONENTS WITHIN HARD-SPHERE MODEL

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Evaluation of chemical equilibrium in non-ideal systems is one of the most difficult issues in physical chemistry because activities of reaction participants depend on forces between particles at the microscopic level. A problem related to dimerization in hard sphere systems can be considered as the simplest theoretical task if some model pair potential of interparticle interactions is taken into account [1].

In this work we present a statistical-thermodynamic analysis for two theoretical models of the dimerization equilibrium in binary mixtures  $A_cB_{1-c}$  within the hard sphere model: dimerisation of the only A-component, or the task of the indifferent solvent effect, and self-dimerisation in both components A and B, the effect of mutual influence at self-association, on the thermodynamic properties. The calculation of the dimerization equilibrium at constant temperature and pressure leads to the solution of two equations, the mass action law (MAL) and the equation of state (EOS), since any shift in the chemical equilibrium results in the system density change and vice versa [2]. Thermal effects vary from pure endothermic to alternating with exothermic effect at moderate and high concentrations depended on the ratio of the dimerizing particles diameter and



the solvent ones. It was determined that the change of the thermal effect types from pure endothermic to alternating with exothermic effect at moderate and high concentrations depended on the ratio of the dimerizing particles diameter and the solvent molecules occurs. We shall present the effect of self-dimerisation on the thermodynamics as well.

**Figure:** Reduced enthalpy of mixing at three values of the dimer length ( $\lambda$ ) and fixed value of the indifferent solvent particle size ( $\xi$ ).

Thus, both positive and negative deviations from the ideality in the dimerizing hard sphere system with the presence of the indifferent solvent can be simply described with a minimal number of parameters characterizing the ratio of particles size of the mixture components.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### PHASE TRANSITION THERMODYNAMICS OF $\text{Ag}_{2-x}\text{S}$ – $\text{SrS}$ SYSTEM

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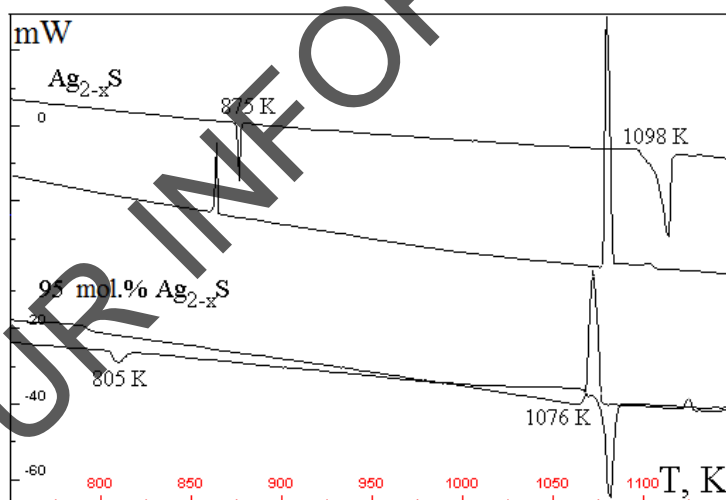
The diagram based on optical microscopy, X-ray diffraction analysis and differential scanning calorimetry data was first time constructed for  $\text{Ag}_{2-x}\text{S}$ – $\text{SrS}$  system. This diagram is eutectic with bounded domain of solid solution based on primary components.

Based on thermal analysis data (samples 1–90 mol.% of  $\text{SrS}$ ) determined variations of eutectoid phase transition peak area were fixed (Figure):

1.04 (1 mol.% of  $\text{SrS}$ ) → 1.98 (2%) → 2.32 (3%) → 2.27 (4%) → 1.98 (6%) → 1.27 (10%) → 0.4 (90%) J/g. Average of eutectoid temperatures over 10 diff. compositions samples is  $804 \pm 8$  K. Composition 2.5 mol.% of  $\text{SrS}$  was taken as eutectoid point. Equations for eutectoid reactions into  $\text{Ag}_{1.985}\text{S}$ -based solid solution (S.S.):

$0.979\text{S.S. } \beta\text{-Ag}_{1.985}\text{S} (0.005 \text{ SrS}; 0.995 \text{ Ag}_{1.985}\text{S}) + 0.021\text{S.S. } \text{SrS} (0.94 \text{ SrS}; 0.06 \text{ Ag}_{1.985}\text{S}) \leftrightarrow$   
 $\text{S.S. } \gamma\text{-Ag}_{1.985}\text{S} (0.025 \text{ SrS}; 0.975 \text{ Ag}_{1.985}\text{S}); \Delta H_r = 2.3 \pm 0.3 \text{ J/g}$

Average of eutectic melting thermal effect demonstration onset temperatures over 11 samples is  $1075 \pm 5$  K. Peak area rises: 15.76 (4 mol.% of  $\text{SrS}$ ) → 18.50 (5%) → 19.35 (8%), then it decreases: 19.35 (8%) → 14.70 (12%) → 13.08 (15%) → 7.69 (33.4%) → 1.19 (90%) J/g. Based on optical microscopy, DSC data and constructed Tamman triangle the conclusion was drawn that eutectic composition is 10 mol.%  $\text{SrS}$ .



**Figure:** Differential thermal curves of  $\text{Ag}_{2-x}\text{S}$ – $\text{SrS}$  system samples. Scanning conditions: Setsys Evolution 1750 (TG-DSC 1600),  $v_{\text{heating}} = 5 \text{ K/min}$ ,  $v_{\text{argon flowing}} = 25 \text{ ml/min}$ ,  $V_{\text{crucible}} = 100 \mu\text{l}$ .

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## CONCENTRATION EFFECT ON HYDRATION STRUCTURE OF PROLINE ZWITTERION

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It is known that amino acids are the constituents of a number of proteins and biologically active compounds and are involved in the regulation of various physiological functions of living organisms. L-proline (L-Pro) is the only imino acid of the natural proteinogenic amino acids with  $\alpha$ -amino group as a moiety of five-membered pyrrolidine ring. Its accumulation in the living cells helps to preserve the native conformation of proteins under abiotic stresses. However, the mechanism of the protective effect of L-Pro preventing denaturation of the protein is not fully understood till now. It is assumed [1–3] that this mechanism is determined largely by the hydration of the amino acid.

The aim of this contribution is to study of L-Pro zwitterion (L-Pro-ZW) hydration structure in aqueous solution in the concentration range 0–6 M at 298 K and 0.1 MPa. The calculations were performed by the integral equation method in the framework of the 1D-RISM (Reference Interaction Site Model) approach using the computer program from the AmberTools package (version 1.5) [4]. The geometrical parameters of L-Pro-ZW structure were taken from PubChem Structure DataBase [5]. The corresponding Lennard-Jones parameters were adopted from the General Amber Force Field [6]. The modified version of the SPC/E model (MSPC/E) was used for water [7].

According to the data obtained, an increase of L-Pro content in solution leads to significant changes in its hydration structure. With the concentration change of solute from 0 to 6 M the hydration number of carboxyl group is reduced almost by two times (from  $\sim 8.5$  to  $\sim 4$ ). At the same time,  $-\text{COO}^-$  group in infinite diluted aqueous solution and in 6 M solution forms  $\sim 4$  and  $\sim 3$  H-bonds correspondingly (a decrease is  $\sim 25\%$ ). The nitrogen atom of  $-\text{NH}_2^+$  group does not form hydrogen bonds with the solvent in the whole concentration range. The hydration number of  $-\text{NH}_2^+$  group in infinite diluted aqueous solution is  $\sim 4.5$ . The solution concentration growth to 6 M leads to reduction of this hydration number to 2.8 (a decrease is 36.6%). The number of H-bonds formed by hydrogen atoms of  $-\text{NH}_2^+$  group at infinite dilution is  $\sim 1.7$ . With the increasing of the solution concentration to 6 M the number of H-bonds of  $-\text{NH}_2^+$  is decreased to  $\sim 1.2$  (by 29.5%). The data obtained show a weak hydration for pyrrolidine ring of L-Pro-ZW in the whole concentration range of solute.

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### Section 3. Thermodynamics of solutions and heterogeneous systems

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#### QUASI-CHEMICAL APPROACH – NOVEL POWERFUL TOOL TO STUDY SUPRAMOLECULAR ORGANIZATION AND MICROSCOPIC EQUILIBRIUM AND NON-EQUILIBRIUM PROPERTIES OF NON-IDEAL LIQUID SYSTEMS.

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The recent results on using quasi-chemical approach for studying polymorphic supramolecular organization, dynamics of molecular thermal motion, and a set of physicochemical properties both equilibrium and non-equilibrium ones, which are based on the concepts of polymorphic supramolecular assemblies and extended quasichemical variables processes in matter are reviewed [1-5].

The methods to investigating supramolecular ordering in liquids due to non-covalent molecular interactions like H-bonds, and to describing structure and properties of aggregates, those which are polymorphic both on structure and composition, thermodynamics of its formation, and integral and differential parameters of aggregation are discussed for the wide temperature range [1-5].

The models for thermodynamic, dielectric, optic, and relaxation properties of liquid non-ideal systems, which are defined by molecular parameters of different nature, have been constructed on the basis of . Quasi-chemical approach to describing structure molecular thermal motion and series of macroscopic properties of liquids and mixtures has been developed and discussed.

For the first time the long-range molecular correlation in liquids in the common parameters of state were revealed. The structure, properties, and thermodynamics of formation of supramolecular forms, consisted from tens of molecules, were studied. Thus the models developed allow us to study structure of disordered condensed systems far more than nearest coordination shells. The comparison of the models developed with diffraction, spectroscopic, simulation methods for studying of liquids are discussed.

The macroscopic manifestations of polymorphic supramolecular ordering in physicochemical properties of liquid mixtures are considered. The molecular models of polymorphism in liquids are discussed

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*This work was supported by the Russian Foundation for Basic Research (Project No. 10-03-01164) and by the Program of Ministry of Education and Science of the Russian Federation "Development of scientific potential of higher education institutions (2009-2010)" (Project No. 2.1.1/3305).*



THERMODYNAMICS OF SORPTION BENZOTRIAZOLE DERIVATIVES  
IN CONDITIONS RP HPLC

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High performance liquid chromatography (HPLC) is a powerful and promising tool for the study of biologically active compounds mixtures, that allows not only to separate and identify the components of such mixtures, and also to obtain information about the mechanisms of their sorption, determine the thermodynamic parameters of sorption on the basis of the temperature dependence of the retention values. Calculation of thermodynamic characteristics such as enthalpy, entropy and Gibbs energy, in turn creates the possibility of purposeful regulation and optimization of the chromatographic process.

In this work we investigated the thermodynamics of sorption of benzotriazole derivatives on the surface of the hypercrosslinked polystyrene from acetonitrile - water solutions of different composition in the temperature range (298–343) K. The change of the enthalpy formation, entropy and Gibbs energy formation in the transition sorbate from volume solution to the surface layer of sorbent depending on changes in the content of the modifier in the eluent are illustrated. It is shown that different temperature factor affects the sorption characteristics in depending on the structure of the benzotriazole derivatives. In particular, the transition from the hydroxy-derivatives (1*H*- or 2*H*-benzotriazol-1-yl-methanol) to the corresponding chlorinated derivatives enhances temperature influence on the retention as well as the composition of the eluent. Wherein, the absolute value of the Gibbs energy in chlorinated derivatives substantially higher than the hydroxy, which is probably the presence of lone electron pairs of the chlorine atom, the reinforcing  $\pi$ - $\pi$ -interaction of aromatic molecules of sorbates with HCPS surface and lead to increasing of sorption. For derivatives with two benzotriazole fragments the sorption is sufficiently high, moderately decreasing with increasing temperature. The obtained negative standard molar enthalpy values indicate about exothermic sorption process, and the modifier content increases in eluent thermal effect process for all the considered compounds according to the absolute value to increase. The obtained negative standard molar enthalpy values indicates about exothermicity of sorption process, and the modifier content increase in eluent thermal effect process for all the considered compounds according to the absolute value increases. Entropy values are also negative, apparently due to the process of releasing a certain amount of acetonitrile molecules from the surface of the sorbent in the bulk phase of the interaction of molecules sorbate with aromatic fragments of polystyrene. Smaller values of  $|\Delta G|$  for the rest of benzotriazole derivatives possible due to a greater ability of these compounds to form solvate complexes with electron center of the component of the mobile phase. On the base of the calculated difference values molar energy sorption standard and test substances (benzotriazole) set the contribution of individual functional groups and substituents in the sorption by hypercrosslinked polystyrene at the transition of molecules sorbate from the volume solution to the surface of the sorbent layer according to the change in the content of modifier in the eluent.

*This work was supported by the Ministry of Education and Science of the Russian Federation within the state assignment grant No. 4.110.2014/K.*

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMICS OF PHASE TRANSITIONS IN SUPRAMOLECULAR LIQUID CRYSTAL SYSTEMS

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Liquid crystals prepared by self-assembly processes via formation of intermolecular interactions such as hydrogen bonding, are promising materials for fabrication of new functional materials. Alkoxybenzoic acids (AOBA) – liquid crystals formed by hydrogen bonded molecules, they are successfully used as quasicomponents.

In order to identify the regularities of influence of H-bonds on the thermodynamics of phase transitions in systems based on homologues AOBA the T–X phase diagram were obtained for systems of *p-n*-heptyloxybenzoic (**I**) and *p-n*-undecyloxybenzoic (**II**); *p-n*-hexyloxybenzoic-*p-n*-pentyloxybenzoic; *p-n*-hexyloxybenzoic-*p-n*-octyloxybenzoic; *p-n*-hexyloxybenzoic-*p-n*-dodecyloxybenzoic acids. The main regularities of interaction of components were identified using thermal methods, X-ray diffraction, dilatometry and dielectricometry. Temperature dependence of volumetric characteristics, the dielectric anisotropy of pure components and concentration dependence of these properties were obtained.  $G^E$ ,  $\Delta_{mix}H$  have been calculated and constructed depending on the concentration. Deviation from ideal behavior of mixtures can be attributed to formation of different kinds of molecular associates due to the interaction of electroanatomic fragments of molecules. The binary phase diagrams of acids bearing different alkoxy-chain lengths indicated that molecular length plays an important role in the formation of new liquid crystalline complex. At the 2:1 ratio of **I** to **II** an intermediate phase – co-crystal  $\gamma$  - is formed and proved his individuality [1]. Based on these data, we propose a model according to which, mesogens strongly differing in molecular length (more than 2 atom of C) take place in cocrystallization, but in systems with close in length terminal substituents and molecular structure (such as nematogen + nematogen or smektogen + smektogen) form a solid solution of substitution. Earlier, it was shown that in a system different in molecular structure (nematogen + smektogen) with close in length terminal substituents tend to the formation of new supramolecular complex [2].

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## THERMODYNAMIC PROPERTIES OF WATER + HYDRAZINE MIXTURE OVER THE WIDE RANGE OF STATE PARAMETERS

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Hydrazine (diamide)  $\text{H}_2\text{N}-\text{NH}_2$  is widely used in different fields of science and technology as a fuel for jet engines and rockets, as a reaction medium in analytical and organic chemistry, in pharmaceutical industry, for polymers production, and for the corrosion protection systems.

Aqueous solutions of hydrazine are basic ones. The first dissociation constant of hydrazine is equal to  $8.5 \cdot 10^{-7}$  at 298.15 K. At low temperatures the solid hydrazine forms two hydrates with water:  $\text{N}_2\text{H}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ; in liquid phase the presence of these hydrates has not been established.

Thermal and baric characteristics of volume properties of a liquid binary system over the wide range of temperatures and pressures result in important information on the components interactions. Water + hydrazine mixtures are model solutions as only amino-groups participate in the interaction with water molecules.

Using the experimental values of density,  $\rho$ , measured at atmospheric pressure, and compressibility coefficients,  $k = (v_0 - v)/v_0$ , the molar isothermal compressions,  $K_T$ , molar isobaric expansions,  $E_p$ , molar isochoric elasticities,  $\beta$ , internal pressure,  $p_{\text{int}}$ , apparent molar volumes,  $V_{\phi,i}$ , and partial molar volumes,  $\bar{V}_i$ , as well as their limiting values,  $\bar{V}_i^\infty$ , were calculated over the temperature range of (278.15–323.15) K and at pressures from 1 to 1000 bar. It was shown that the concentration dependences of water + hydrazine density passed through the extreme at  $x_2 \approx 0.5$  (hydrazine molar fraction), which position weakly shifted with temperature growth under all pressures studied. The compressibility coefficients,  $k$ , decreased exponentially with the hydrazine concentration rising. The changes of the limiting partial volumes of hydrazine on pressure were opposite in sign at 278 and 323 K. For isobars of the mixture molar isobaric expansion on hydrazine concentration the inversion region, shifting to the lower  $\text{N}_2\text{H}_2$  concentrations with temperature rising, was observed.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### INTERACTION OF NANOCLUSTER POLYOXOMETALATES WITH VAPORS OF LOW-MOLECULAR LIQUIDS

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Nanocluster polyoxometalates (POMs) with a buckyball and a toroidal structure are a subject of much interest to inorganic chemists owing to their layered framework structure, which has an inner cavity and "windows" for exchange of different molecules with the environment. These compounds are promising as the sensor, catalytic, and sorption materials and as the agents for addressed delivery of substances, which is ensured by the fact that POMs are multicharged ones capable of complexation. To understand the mechanisms of these processes it is necessary interaction studies POM with low-molecular liquids (LML) different nature.

The purpose of the present work is to study of sorption properties of nanocluster polyoxometallates based on molybdenum different structure to the vapor of methanol and benzene, the determination of thermodynamic and kinetic parameters of the interaction of these components, the assessment of stability POM among low-molecular liquids.

The objects of research were used nanoclusters:

Mo<sub>132</sub>: (NH<sub>4</sub>)<sub>42</sub>[Mo<sup>VI</sup><sub>72</sub>Mo<sup>V</sup><sub>60</sub>O<sub>372</sub>(CH<sub>3</sub>COO)<sub>30</sub>(H<sub>2</sub>O)<sub>72</sub>]•300H<sub>2</sub>O•10CH<sub>3</sub>COONH<sub>4</sub> – buckyball structure,

Mo<sub>72</sub>Fe<sub>30</sub>: [Mo<sub>72</sub>Fe<sub>30</sub>O<sub>252</sub>(CH<sub>3</sub>COO)<sub>12</sub>{Mo<sub>2</sub>O<sub>7</sub>(H<sub>2</sub>O)}<sub>2</sub>{H<sub>2</sub>Mo<sub>2</sub>O<sub>8</sub>(H<sub>2</sub>O)}(H<sub>2</sub>O)<sub>91</sub>]•150H<sub>2</sub>O – buckyball,

Mo<sub>138</sub>: (NH<sub>4</sub>)<sub>32</sub>[Mo<sup>VI</sup><sub>110</sub>Mo<sup>V</sup><sub>28</sub>O<sub>416</sub>H<sub>6</sub>(H<sub>2</sub>O)<sub>58</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>6</sub>]•250H<sub>2</sub>O – toroidal structure.

Preparation polyoxometallates accomplished by synthesis and subsequent crystallization from aqueous solutions.

The isothermal equilibrium sorption of vapors of methanol and benzene at the 298 K was studied. The gravimetric version of the sorption method was used. The chemical potentials of LML  $\Delta\mu_1$ , polyoxometallates  $\Delta\mu_2$ , Gibbs energy of interaction components  $\Delta g^m$  were calculated. The kinetics of sorption Mo<sub>132</sub> was studied. Stability of the structure of POM in the vapor sorbates was investigated by vibrational spectroscopy.

All sorption isotherms have the stepped character associated with a complex mechanism of the process. Differences in the sorption behavior for POM with a different structure were found. The samples have greater sorption capacity and greater thermodynamic affinity to methanol than to benzene. This is due to the polarity of methanol molecules that have a higher thermodynamic affinity to the surface of POM. The results correlate with the enthalpy of interaction of the POM and LML  $\Delta H$ :  $\Delta H < 0$  for polar liquids,  $\Delta H > 0$  for non-polar. The maximum affinity to sorbates shows Mo<sub>132</sub>, the smallest – Mo<sub>72</sub>Fe<sub>30</sub>, Mo<sub>138</sub> takes an intermediate position.

It is established that for all samples  $\Delta g^m < 0$ . They correlate with sorption isotherms and decreased with the increase in the sorption capacity. The anomalous step type of kinetic curves of sorption for Mo<sub>132</sub> was found. It can be connected with the complex structure of POM and the possibility of sorption by both an external, and internal surface of a buckyball, and also a relaxation of structure of POM in the course of sorption.

It is established that samples of Mo<sub>132</sub> and Mo<sub>138</sub> are stable in the course of sorption, unlike unstable Mo<sub>72</sub>Fe<sub>30</sub> which structure collapses under the influence of low-molecular liquids.

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OBSERVATION OF OSCILLATIONS OF SOLUTION – CRYSTAL PHASE  
TRANSITION

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Kinetic features of phase transitions in systems of small volume have been observed at microscopic research of size effects. The experimental procedure is described in [1]. A subject of the study was finding metastable states and phases in the pico- and femtolitre volume. We have seen oscillations during the phase transition "solution-crystal" in an ensemble of droplets of solution KCl – NaCl – H<sub>2</sub>O. We have found conditions under which the oscillating phase transitions may be observed. Our studies have revealed the reproducibility of the phenomena. The duration and number of oscillations may be large enough.

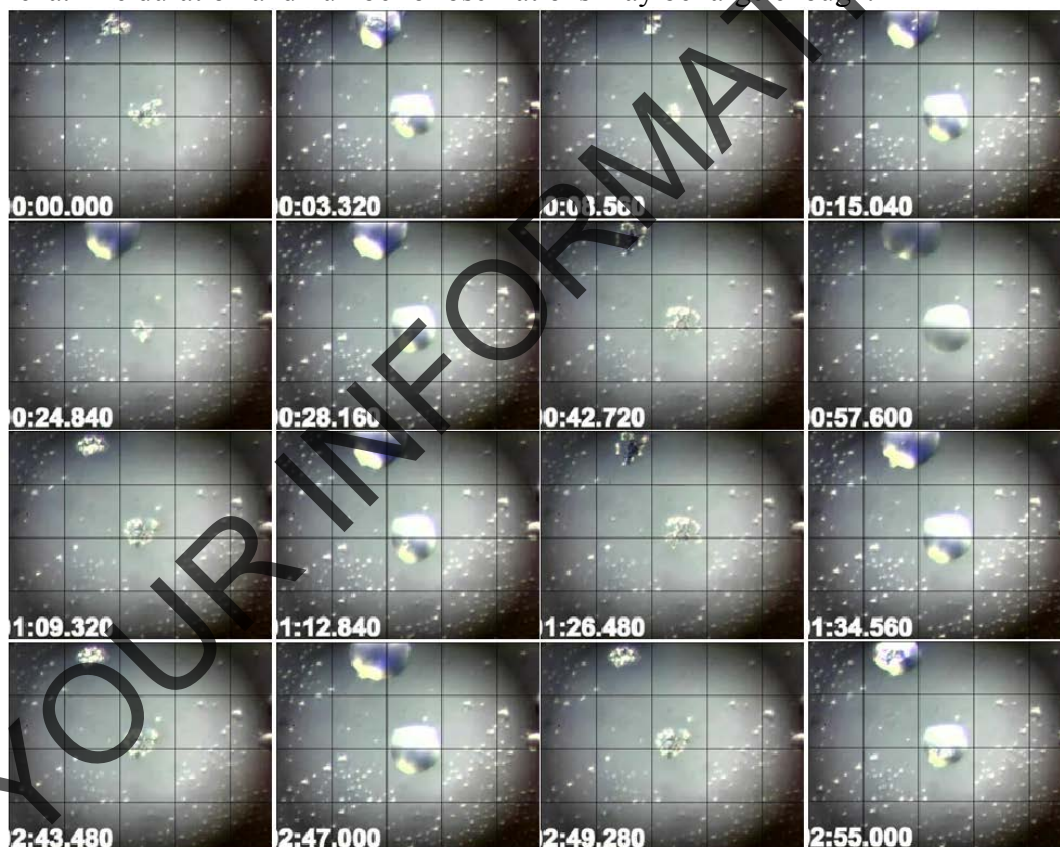


Figure: Sequence of frames shows oscillating phase transitions in the system KCl – NaCl – H<sub>2</sub>O. Grid spacing – 100 mcm.

The average frequency of the oscillation crystal-drop was up to 4–6 per minute in the above experiment during several minutes under stationary conditions (at constant humidity and room temperature).

[1] Titaeva, E.K.; Fedoseev, V.B. Crystallogr. Rep., 2014, 59, 437-441.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### AMBIGUITY OF PHASE DIAGRAMS IN NANOSCALE SYSTEMS

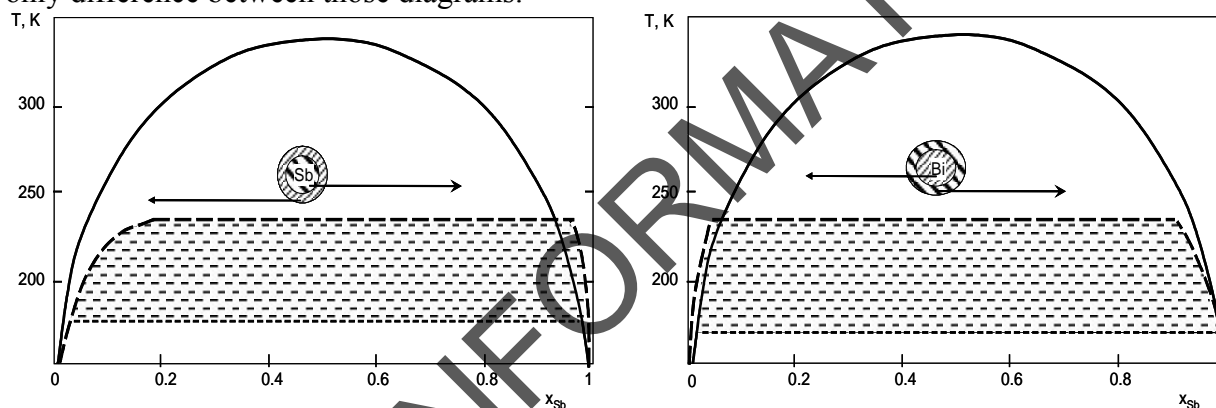
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Classical chemical thermodynamics allows to model size effects during phase changes. The calculations show the essential difference between phase transitions in microscopic and bulk systems. The differences appear in the phase diagrams as a shift and deformation of heterogeneity regions, binodal and spinodal lines. The report discusses another factor which influences on the form of phase diagrams. It is the shape and location of the phases. Systems with the core-shell configuration demonstrate this phenomenon most clearly.

For example the figure shows a fragment of the phase diagram of the alloy Bi–Sb ( $x_{\text{Sb}} = 0.5$ ) for the core-shell system with radius 100 nm. The composition of the solid solution in the core is the only difference between those diagrams.



**Figure:** The solid line describes the heterogeneity region (stratification) of macroscopic system Bi–Sb, the dashed line separates the heterogeneity area for nanoscale systems with different placement of coexisting solid solutions, the shaded area is the metastability region of heterogeneous state of nanoscale systems.

The important feature of a small size system is the dependence of phase diagrams on a concentration. The changing of concentration is also accompanied by the change of the upper critical temperature, deformation of the metastable region and heterogeneity region. Homogeneous state is the only equilibrium state for smaller systems. Articles [1–3] describe some thermodynamic aspects associated with the appearance of metastable states and their stability.

Obviously, the shape of a system is not limited by the core-shell configuration. The system may exhibit multiple various phase diagrams when the coexisting phases are of different form and/or all phases are in contact with an external boundary.

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[2] Fedoseev, V.B.; Fedoseeva, E.N. JETP Lett., 2013, 97, 408-412.

[3] Fedoseev, V.B. Fizika Tverdogo Tela, 2015, 57, 585-589.

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**DIAGRAMS OF PHASE EQUILIBRIA OF TERNARY SYSTEMS  
CONTAINING ANILINE, WATER AND SATURATED HYDROCARBONS**

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The study of phase equilibrium of ternary systems containing a component – a member of the homologous series allows to determine the regularities of properties changes and to predict properties of systems with a component with a large or intermediate number of carbons in the hydrocarbon chain.

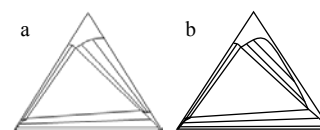
The objects of present research are ternary systems containing water, aniline and saturated hydrocarbon ( $C_6H_{14}$  –  $C_{10}H_{22}$ ). Some systems have been already studied experimentally in [1]. Liquid–liquid–vapor phase equilibrium was studied using mathematical modeling and NRTL equation. The relative error of the liquid phase composition description was 1.8%, of the temperature description was 0.99%. Liquid-vapor equilibrium diagram was studied at 760 mm Hg and splitting diagram – at boiling temperature and at 20°C.

Phase diagrams contain three-phase splitting regions and have the structure presented in Figure 1. A decrease of splitting region is observed (the area of the region is reduced by 12.8%) with increasing the number of carbons in the hydrocarbon chain. Transformation of the splitting diagram at boiling temperature is observed. The structure of phase diagram for two last members of systems considered is presented in Figure 1b.

All binary constituents of ternary systems are heterogeneous at 20°C. Solubility in the binary systems containing water and hydrocarbon mostly doesn't change with increasing temperature up to the boiling point and in systems containing aniline and hydrocarbon solubility increases and in systems with  $C_9H_{20}$  and  $C_{10}H_{22}$  these components are completely soluble in each other (Figure 1b).

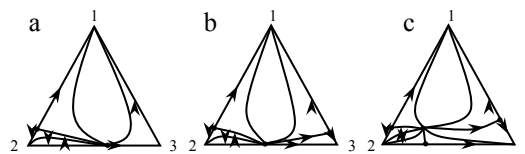
In aniline – water – saturated hydrocarbon ternary systems changes in the structure of liquid–vapor equilibrium diagram are also observed (Figure 2). Binary azeotrope water – hydrocarbon enriches with water and azeotrope aniline – hydrocarbon – with aniline.

Analyzing dependences obtained it can be assumed that increasing the number of carbons in the hydrocarbon chain in aniline – water – saturated hydrocarbon ternary systems the structure vapor–liquid equilibrium diagram will change (assuming the disappearance of two binary azeotropes), and the region of the three-phase splitting will remain at the boiling point of the mixture and at 20°C.



**Figure 1:** Qualitative splitting diagrams of ternary systems:

a – at 20°C; b – at boiling.



**Figure 2:** Changes of vapor–liquid phase diagram in aniline (1) – water (2) – saturated hydrocarbon (3) ternary systems at 760 mm Hg.

(a) –  $C_6H_{14}$ ; (b) –  $C_8H_{18}$ ; (c) –  $C_{10}H_{22}$ .

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## Section 3. Thermodynamics of solutions and heterogeneous systems

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### METHODOLOGY AND RESULTS OF QUANTITATIVE SIMULATION OF BOROSILICATE GLASS STRUCTURE

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Vibrational spectroscopy and NMR spectroscopy experimental study provides detailed information about features of the anionic structure of borate and silicate glasses. The study of the borosilicate systems faced significant problems. Borosilicate glasses are characterized by non-uniform distribution of cations modifiers between borate and silicate components as well as these glasses have a large number of structural units. A large amount of experimental studies of glasses with a wide range of composition is necessary. Also ambiguity of spectral data's interpretation due to the mutual influence of the different structural units' fluctuations takes place.

These problems can be partially solved with a thermodynamic modeling of the anions' interconversion process depending on the temperature and the composition of the system. That approach is based on the available spectral studies data and will give the possibility of harmonizing the concepts of structure of the borate, silicate and borosilicate glasses and extrapolating the results in previously unexplored and intermediate glass compositions.

The thermodynamics model was worked out as a result of experimental data processing. The model describes correlation and interaction of different structural units in the alkaline borosilicate systems with a wide variation their composition.

This model combines a complex of reaction equations for interaction between structural units and the values of equilibrium constants for these reactions. Results of the research allow to model the structure of the solid oxide alloys  $\text{Me}_2\text{O}-\text{SiO}_2$ ,  $\text{Me}_2\text{O}-\text{B}_2\text{O}_3$  (where Me – Na or K) and can be applied for the  $\text{Me}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  systems with any ratio  $[\text{Me}_2\text{O}]/[\text{B}_2\text{O}_3]$ .

According to the data of studies of binary and ternary systems by methods of Raman spectroscopy and NMR spectroscopy quantitative values of model parameters were chosen. Also the results of thermodynamic calculations in other models were used for determination of parameters for our model. The modeling results qualitatively and quantitatively (in some cases) coincides with the experimental data. It provides the possibility of extrapolating the observed structural changes for the glasses of previously unexplored compositions.

*The research has been supported by the Russian Foundation for Basic Research (Project No. 14-08-00323).*



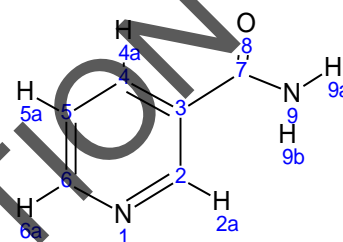
THERMOCHEMICAL STUDY OF NICOTINAMIDE COMPLEXATION  
WITH NICKEL(II) ION IN BINARY SOLVENTSG.A. Gamov<sup>1</sup>, M.N. Zavalishin<sup>1</sup>, S.V. Dushina<sup>1</sup>, V.A. Sharnin<sup>1,2</sup><sup>1</sup>Research Institute of Thermodynamics and Kinetics of Chemical Processes,  
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Pyridinecarboxamide-3 (nicotinamide, B<sub>3</sub> vitamin) is known as agent preventing pellagra together with nicotinic acid. In the living tissues both these compounds are included in composition of NAD and NADP coenzymes. The nicotinamide also effects on protein and RNA biosynthesis.

Nickel acts in a few of biological reactions having significance in vital functions of some protozoa and bacteria. The metal provides the molecular hydrogen oxidation and is included in urease composition (in fungi and plants as well). At the same time, the harmful (in particular, allergenic and carcinogenic) effect of nickel compounds on human health must be noted.

The aim of presented work is to study the influence of aqueous ethanol and aqueous dimethyl sulfoxide solvent composition on reaction exothermicity of nickel(II) complexation with nicotinamide. To reach this goal, the solvation–thermodynamics approach accounting the contribution of thermodynamic functions of ligand, central ion and complex into the thermodynamic characteristic change of reaction transfer is used.

The experimentally determined enthalpy changes of complexation reaction between nickel(II) and nicotinamide in aqueous ethanol and dimethyl sulfoxide are given in Table.



**Figure:** Structural formula of nicotinamide.

**Table.** Enthalpy changes of complexation reaction between nickel(II) and nicotinamide in binary solvents

$X_{\text{EtOH}}$ m.f.	0	0.1	0.3	0.5	0.7	0.85
$-\Delta_r H^\circ(298.2)$ (kJ/mol)	12.63±0.53	13.80±0.60	9.74±0.02	11.21±0.45	17.37±0.60	19.07±0.32
$X_{\text{DMSO}}$ m.f.	0	0.1	0.3	0.5	0.7	0.85
$-\Delta_r H^\circ(298.2)$ (kJ/mol)	12.63±0.53	13.01±0.28	16.51±0.54	14.03±0.27	13.88±0.11	14.56±0.19

Study was carried out in the framework of State Task of the Ministry of Education and Science of the Russian Federation (Project No. 2293) and with financial support of Council on Grants of the President of the Russian Federation (Grant No. 14.Z56.14.5963-MK).

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC MODELLING OF SYSTEMS CONTAINING LIQUID CRYSTALLINE BENZOIC ACIDS

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Liquid crystals (LC) are widely used in display technologies. Liquid crystalline materials (LCM) are multicomponent mixtures having a wide temperature range of the certain mesophase type. Unfortunately, thermodynamic modelling of systems containing LC is restricted by the ideal solution method [1]. For check-up of different thermodynamic models we choose systems with liquid crystals that form networks of hydrogen bonds. *p*-Hexyl- and *p*-alkyloxybenzoic acids ( $n$ AOBA,  $C_nH_{2n+1}-O-C_6H_4-COOH$ ) are purified by crystallization; *p*-hexyl- and *p*-alkyloxybenzoic acids ( $n = 3-6$ , 3OBA-6OBA) are nematic LC. 16OBA is smectic  $S_c$  LC. LC having alkyl chains of 7 to 12 carbon atoms (7OBA – 12OBA) are smectic-nematic LC.

Systems containing *p*-hexyl- and *p*-alkyloxybenzoic acids are studied by polarizing microscopy, thermal analysis, visual analysis and solubility methods. Complete phase diagrams are obtained for systems with non-mesogenic toluene, phenyl benzoate, *n*-octane and *n*-decane.

Typical phase diagram is shown in Figure.

Solubility curves of LC with solvents that belong to different homologues series (alkanes, cyclohexane, aromatics, chlorinated alkanes, alcohols, esters, acetonitrile) are investigated. Tests for miscibility are made. The thermodynamic models based on the solubility parameter approach (Hildebrand and Hansen solubility parameters) are applied for the demixing prognosis. Applicability of the group-contribution methods for the activity coefficients of components estimation (ASOG, UNIFAC models) is checked basing on the solubility curves calculation. Restrictions and advantages of the considered thermodynamic methods are discussed.

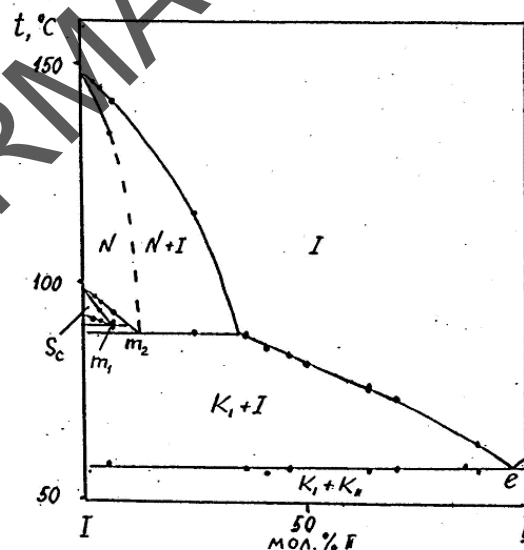


Figure:  $T$ - $x$ -diagram of 7OBA (I) – toluene (II) system.

Data on thermodynamic and physical properties for mesogens are taken from [2] or calculated using the quantum-chemical methods and the group-contribution schemes [3]. Comparison of results obtained with the systems of “model” benzoic acid is made. Influence of alkyl chains of LC on the excess thermodynamic functions is discussed.

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## LIQUID-VAPOR EQUILIBRIUM, VOLUMETRIC AND TRANSPORT PROPERTIES OF DIMETHYLSULFOXIDE – ACETONITRILE SYSTEM

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The study of volumetric properties, viscosities and liquid–vapor phase equilibrium for dimethylsulfoxide (DMSO) – acetonitrile (ACN) binary system has been fundamental and practical interests. Fundamental importance is caused by the fact that the components of this system are capable both to self-association, and to interact with each other. Obviously, that the presence of such competing interactions considerably influences on the thermodynamic properties of this solution. Moreover, DMSO and acetonitrile have a wide application as solvents or as important fine chemicals in biology and medicine [1, 2].

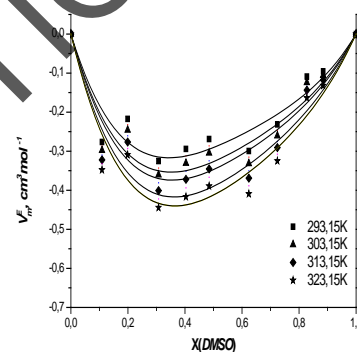
The densities of binary DMSO–ACN mixtures have been measured on a DMA 4500 vibrating-tube densimeter over the (293.15–323.15) K temperature range at the atmospheric pressure.

Viscosity measurements were carried out with an Ubbelohde-type suspended-level viscometer at temperatures from (298.15 to 318.15) K.

Saturated vapor pressures of solutions were measured above liquid with the use of a static method in the whole concentration interval at different temperatures from 293.15 to 323.15 K. Partial pressures of components were calculated by integrating the Gibbs – Duhem equation.

Excess molar thermodynamic quantities such as excess molar volumes, viscosities and Gibbs energies were calculated and described by the Redlich – Kister equation. Correlation parameters and standard deviations were calculated as well.

It was found that the above mentioned excess molar thermodynamic quantities are negative over the whole range of composition of this system (Figure). The negative deviation from ideality testifies that very strong molecular interactions take place between DMSO and ACN.



**Figure:** Excess molar volumes,  $V_m^E$ , plotted against  $x(\text{DMSO})$  for DMSO–ACN mixture at different temperatures.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC REGULARITIES OF CALCIUM OXALATE CRYSTALLIZATION IN THE PRESENCE OF AMINO ACIDS

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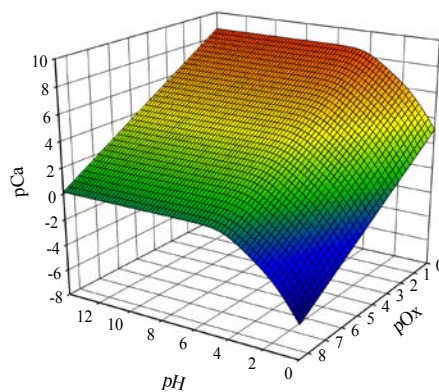
The problem of stone formation is becoming more prominent and a real threat to the modern residents of all countries. Pathogenic organo-mineral aggregates are of complex and heterogeneous composition. Overall, however, the most common of urinary stones are calcium oxalate stones, composed of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (whewellite) and  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (weddelite). These minerals may also be a part of dental stones, gallstones, salivary gland calculus, and others. This explains the importance of studying the crystallization of calcium oxalate in conditions close to physiological. Organic materials of proteinic nature, which are components of physiological fluids, have a great influence on the character of the crystallization process of minerals, particularly calcium oxalate. The aim of this work is to establish the thermodynamic regularities of formation of calcium oxalate in the presence of a number of amino acids.

Model solution, mineral composition (inorganic macro components), temperature, ionic strength and pH of urine corresponding to that of a healthy adult average person were taken in the construction of a thermodynamic model of processes of phase formation (in the system  $\text{Ca}^{2+} - \text{C}_2\text{O}_4^{2-} - \text{H}_2\text{O} - \text{amino acid}$ , as prototype body fluid). This set of amino acids was chosen due to their high content both in physiological salt solution and in urinary stones; as well as differences in the structure.

Based on the available data on the thermodynamic values of solubility products at 310 K, functional dependence was determined  $p\text{Ca}^{2+} = f(p\text{C}_2\text{O}_4^{2-}, \text{pH})$ , and constructed in the form of a three-dimensional diagram ("stability field") for calcium oxalate monohydrate  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (Figure).

To evaluate the effect of acidity and concentration of amino acid additives on the possible formation of sparingly soluble compounds in solution, we showed graphical dependences of the index of oversaturation of these factors:  $\text{SI} = f(\text{pH})$  and  $\text{SI} = f(p\text{C}_{\text{amino acid}})$ . It is assumed that if the  $\text{SI} > 0$ , then these conditions are thermodynamically more probably to result of precipitation from the solution phase.

Medium acidity has the greatest influence on the thermodynamic stability of the substances, the state of the system and processes of crystallization. Thus, with increasing pH values the driving force of crystallization of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  is greatly increased. The described pattern is explained by the fact that the pH increases with an increase in the relative concentration of  $\text{C}_2\text{O}_4^{2-}$  in the system, so there is a positive correlation between the supersaturation of the medium and pH. It was established that the introduction of amino acids in concentrations corresponding to saline has little effect on the formation of mineral solids due to low values of stability constants of complexes with calcium ions for all the considered amino acids. It should be noted that the constructed thermodynamic model reflects the possibility of formation of phases, only on the basis of data on their thermodynamic stability in the standard state, and does not take into account, in particular, kinetic factors influencing on formation of the solid phase in the real world.



**Figure:** Stability field of the system  $\text{Ca}^{2+} - \text{C}_2\text{O}_4^{2-} - \text{H}_2\text{O}$ .

## COMPLETE SCALING FOR MULTICOMPONENT FLUIDS

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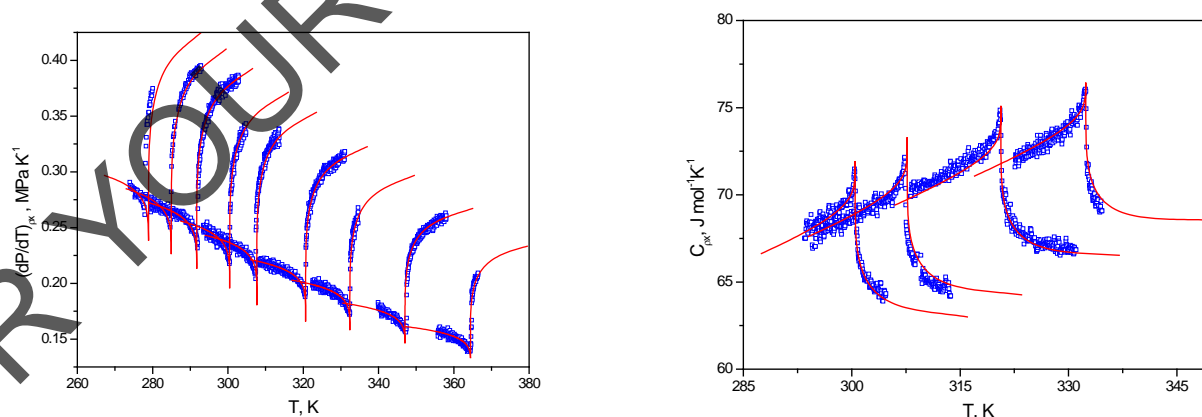
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The theoretical model based on the concept of so-called “complete scaling” has been elaborated for multicomponent mixtures. As a result, the equation of state (EOS) for near-critical mixture with given composition has been formulated. It has been shown that the isochoric heat capacity  $C_{V,x}$  as well as the temperature derivative of the pressure  $(\partial P/\partial T)_{\rho,x}$  demonstrate the cusp-like anomalies at mixture critical point. In the framework of the proposed EOS the explicit equation of dew-bubble curves in the vicinity of vapor-liquid critical points in mixtures has been derived. It is shown that along these curves the pressure and the temperature depend non-analytically on the mixture density. As a consequence, the second derivatives  $(d^2T/d\rho^2)_{\text{DBC}}$  and  $(d^2P/d\rho^2)_{\text{DBC}}$  (taken along the dew-bubble curves) reveal cusp-like anomalies at the critical point. This specific feature enables one an easy estimation of the critical parameters of multicomponent mixtures directly from fitting a polynomial to dew-bubble-curve experimental data. To verify the validity of the obtained EOS, it was applied for the description of thermodynamic properties of several binary and multicomponent mixtures which have been studied experimentally in our laboratory by the adiabatic calorimetry method. The measurements of the temperature dependencies of pressure, and heat capacity were carried out for all systems along different isochores in wide vicinity of their critical points. It has been demonstrated that the proposed EOS describes adequately the experimental data in one- and two-phase region of the mixtures with the sufficiently high accuracy. As an example, Figure illustrates the description of the behaviour of the derivative  $(\partial P/\partial T)_{\rho,x}$  and isochoric heat capacity  $C_{V,x}$  in multicomponent mixture within the scope of the developed EOS.



**Figure:** The behavior of the derivative  $(\partial P/\partial T)_{\rho,x}$  and isochoric heat capacity  $C_{V,x}$  in multicomponent mixture along the isochores in one- and two-phase region. Experimental points are denoted by open squares. The solid red lines indicate the calculated dependencies.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMICS OF THE $\text{In}_2\text{O}_3$ – $\text{ZnO}$ SYSTEM

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Samples of the system in the whole composition range were prepared from mixtures of  $\text{ZnO}$  and  $\text{In}_2\text{O}_3$  (both Merck, reagent grade) by solid-state synthesis at 1323 K in air for 180 h with intermittent grindings in a jasper mortar.

As determined by XRD analysis, the samples of the heterogeneous phase regions [ $\text{ZnO} + \text{Zn}_7\text{In}_2\text{O}_{10}$ ] (I), [ $\text{Zn}_7\text{In}_2\text{O}_{10} + \text{Zn}_5\text{In}_2\text{O}_8$ ] (II), [ $\text{Zn}_5\text{In}_2\text{O}_8 + \text{In}_2\text{O}_3$ ] (III) and the individual mixed oxides were synthesized.

Vaporization processes in the  $\text{In}_2\text{O}_3$ — $\text{ZnO}$  system have been studied by the Knudsen effusion technique in combination with mass spectrometric analysis of the vapor phase in the temperature range from 1380 to 1460 K. An MS-1301 high-temperature mass spectrometer was used in the experiments and quartz effusion cells with the sublimation surface-to-effusion orifice area ratio of about 3000 were employed.

The vapor above the system consists of  $\text{Zn}(\text{g})$ , and  $\text{O}_2$ , which corresponds to the incongruent vaporization of  $\text{Zn}_7\text{In}_2\text{O}_{10}$  and  $\text{Zn}_5\text{In}_2\text{O}_8$ . This means that, during the effusion experiments, the system figurative point moves toward less volatile  $\text{In}_2\text{O}_3$ , which is confirmed by the elemental analysis of the nonvolatile residue in all heterogeneous regions. The partial pressures of the vapor species obtained are presented in Table. The change in the Zn partial pressure upon the transition from pure  $\text{ZnO}$  to heterogeneous region I was beyond the sensitivity of the mass-spectral experiment.

**Table.** Partial and total pressures of the vapor over species  $\text{ZnO} - \text{In}_2\text{O}_3$  system at 1428 K

Solid phase	$p$ (Pa)		
	Zn	$\text{O}_2$	total
ZnO	8.86	3.10	11.96
ZnO + $\text{Zn}_7\text{In}_2\text{O}_{10}$	8.80	3.08	11.88
$\text{Zn}_7\text{In}_2\text{O}_{10} + \text{Zn}_5\text{In}_2\text{O}_8$	6.47	2.27	8.74
$\text{Zn}_5\text{In}_2\text{O}_8 + \text{In}_2\text{O}_3$	4.11	1.44	5.55

The pressure values are given with the precision required for a correct calculation of equilibrium constants.

The  $\text{ZnO}$  activity in heterogeneous regions II and III was found to be 0.64 and 0.32, respectively.

**THERMODYNAMIC PARAMETERS OF PROTOLYTIC EQUILIBRIA  
FOR SOME DIPEPTIDES IN AN AQUEOUS SOLUTION**

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The heats of interaction between solutions of D,L-leucyl-glycine, L-leucyl-L-leucine, L-valyl-L-valine, D,L-valyl-D,L-leucine, glycyl-D,L-leucine, and glycyl-D,L-valine, and solutions of nitric acid and potassium hydroxide have been measured calorimetrically at 298.15 K and at ionic strength values from 0.1 up to 1.0 mol/l. The influence of "background" electrolyte character and concentration on the stepwise dissociation heats for the dipeptides was under consideration. The relevant thermodynamic parameters for the standard solution have been evaluated (Table).

The results obtained were compared with the corresponding data on related compounds (D,L-alanyl-D,L-serine, D,L-alanyl-D,L-leucine, D,L-alanyl-D,L-valine, D,L-alanyl-D,L-alanine, D,L-alanyl-glycine, D,L-alanyl-D,L-asparagine, D-asparagine, L-serine, glycine, L-leucine, D,L-alanine,  $\beta$ -alanine,  $\beta$ -alanyl- $\beta$ -alanine,  $\beta$ -alanyl-glycine, glycyl-glycine, glycyl- $\beta$ -alanine, glycyl-L-asparagine) investigated earlier in this laboratory using the same experimental procedures. Dependences of the reaction thermodynamic quantities on a side substituent hydrophobicity of the C- and N-terminal amino acid residue in series  $\text{CH}_2\text{CONH}_2 < \text{CH}_2\text{OH} < \text{H} < \text{CH}_3 < \text{CH}(\text{CH}_3)_2 < \text{CH}_2\text{CH}(\text{CH}_3)_2$  and on the distance between the carries of positive and negative charges have been discussed. As ancillary part of this study, the spatial, electronic and energy parameters for isolated molecules and ions of some dipeptides and amino acids have been computed.

**Table.** The standard thermodynamic parameters of the dissociation reactions

$T = 298.15 \text{ K}, I = 0$	$\text{p}K^{\circ}$	$\Delta G^{\circ}$ (kJ/mol)	$\Delta H^{\circ}$ (kJ/mol)	$-\Delta S^{\circ}$ (J/mol·K)
D,L-leucyl-glycine				
$\text{H}_2\text{L}^+ = \text{H}^+ + \text{HL}$	$3.34 \pm 0.05$	$19.06 \pm 0.29$	$0.59 \pm 0.12$	$62.0 \pm 1.0$
$\text{HL} = \text{H}^+ + \text{L}^-$	$8.29 \pm 0.05$	$47.32 \pm 0.29$	$45.34 \pm 0.24$	$6.6 \pm 1.2$
L-leucyl-L-leucine				
$\text{H}_2\text{L}^+ = \text{H}^+ + \text{HL}$	$3.45 \pm 0.01$	$19.69 \pm 0.06$	$-1.97 \pm 0.22$	$72.7 \pm 0.8$
$\text{HL} = \text{H}^+ + \text{L}^-$	$8.12 \pm 0.01$	$46.35 \pm 0.06$	$45.01 \pm 0.30$	$4.5 \pm 1.0$
L-valyl-L-valine				
$\text{H}_2\text{L}^+ = \text{H}^+ + \text{HL}$	$3.38 \pm 0.01$	$19.29 \pm 0.06$	$-1.89 \pm 0.26$	$71.0 \pm 0.9$
$\text{HL} = \text{H}^+ + \text{L}^-$	$8.18 \pm 0.03$	$46.69 \pm 0.17$	$46.04 \pm 0.40$	$2.2 \pm 1.5$
D,L-valyl-D,L-leucine				
$\text{H}_2\text{L}^+ = \text{H}^+ + \text{HL}$	$3.19 \pm 0.01$	$18.21 \pm 0.06$	$-2.31 \pm 0.15$	$68.8 \pm 0.5$
$\text{HL} = \text{H}^+ + \text{L}^-$	$8.33 \pm 0.01$	$47.55 \pm 0.06$	$45.82 \pm 0.28$	$5.8 \pm 0.9$
Glycyl-D,L-leucine				
$\text{H}_2\text{L}^+ = \text{H}^+ + \text{HL}$	$3.17 \pm 0.02$	$18.09 \pm 0.11$	$-2.60 \pm 0.13$	$69.4 \pm 0.6$
$\text{HL} = \text{H}^+ + \text{L}^-$	$8.49 \pm 0.01$	$48.46 \pm 0.06$	$45.18 \pm 0.18$	$11.0 \pm 0.8$
Glycyl-D,L-valine				
$\text{H}_2\text{L}^+ = \text{H}^+ + \text{HL}$	$3.11 \pm 0.02$	$17.75 \pm 0.11$	$-2.16 \pm 0.11$	$66.8 \pm 0.5$
$\text{HL} = \text{H}^+ + \text{L}^-$	$8.48 \pm 0.02$	$48.40 \pm 0.11$	$44.60 \pm 0.18$	$12.7 \pm 0.7$

*This work was supported by the Russian Foundation for Basic Research (Project No. 14-03-00360-a).*



## Section 3. Thermodynamics of solutions and heterogeneous systems

### CONSTRUCTION OF THE TERNARY Fe–Co–S SYSTEM

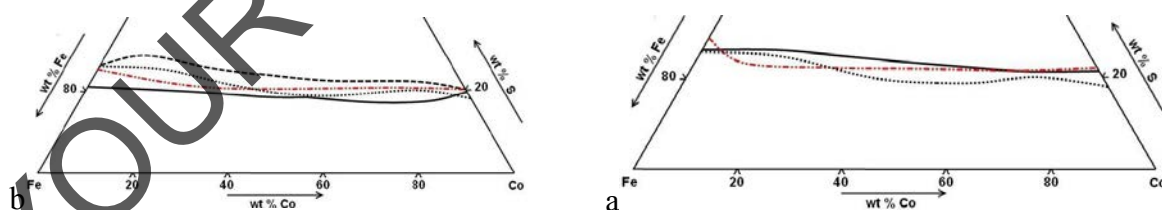
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Cobalt is extracted as a byproduct of oxidizing nickel and copper-cobalt ores during pyrometallurgical processing. Received matte contains up to 12 mass% of cobalt. Technological problems associated with the recovery of cobalt mattes indicate investigation relevance of physic-chemical properties of Fe–Co–S system. In addition, there are thermodynamic methods to calculate liquidus and solidus surfaces of multicomponent systems using modern software package. However, the experimental results mainly obtained by the method of thermal analysis are the necessary parameters to create different thermodynamic models.

Vogel and Hillner [1] applied thermal analysis and electron probe microanalysis (EPMA) for the first time to receive the liquidus surface. The data of Moleva and co-workers [2] practically coincide with the experimental results of Vogel [1]. Later, Raghavan [3] offered a reaction scheme for the Fe–Co–S system. It is based on the Vogel's results, however, some corrections were made taking into account the accepted binary phase diagrams. And liquidus temperatures obtained by Soltanieh et al. [4] are slightly higher than the data in [1]. Based on the available literature data of the Fe–S, Co–S and Fe–Co systems, the thermodynamic data for the Fe–Co–S ternary system was calculated by Kongoli and Pelton [5]. Furthermore, the resulting liquidus temperatures and tie-lines from Kongoli's model are in good agreement with the result of Soltanieh's investigation.

The combined usage differential scanning calorimetry, thermogravimetry, scanning electronic microscopy and EPMA has allowed the prediction of phase transformations parameters in the volume of the ternary system. Mathematical treatment of the obtained results allowed the visualization of phase transformations of the Fe–Co–S system as the liquidus and solidus projections. In particular, Figure shows the isothermal sections of the ternary Fe–Co–S system at 1100 and 1200°C. Comparison of the data obtained by the authors of present work with the results presented in [1, 4–6] showed satisfactory agreement.



**Figure:** Liquidus data for the Fe–Co–S system at 1100°C (a) and 1200°C (b).  
Dotted line – [1], dashed line – [4], solid line – [6], dash-dot line – present work.

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## THERMODYNAMIC MODELING OF AL-REM-TM ALLOYS

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Thermodynamic modeling of ternary Al-REM-TM (REM = Ce, Gd, TM = Ni) alloys was performed using TERRA software (created in MSTU named after N. Bauman) [1].

The modeling was executed at the common pressure of  $P = 10^5$  Pa in argon atmosphere and temperature range (300–4000) K. The modeling systems were taken as condensed phases and gas phase above it. Initial contents of ternary systems (at.%) : Al – 86, Ni – 8, Gd (Ce) – 6.

According to literature data [2–6], the formation of ternary compounds, such as  $Gd_3Ni_5Al_{19}$ ,  $Gd_4Ni_6Al_{23}$ ,  $GdNi_3Al_9$ ,  $GdNiAl_4$ ,  $GdNiAl_3$ ,  $Gd_3Ni_7Al_{14}$ ,  $GdNiAl_2$ ,  $GdNi_2Al_3$ ,  $\tau_1(AlCeNi)$ ,  $\tau_2(Al_2CeNi)$ ,  $\tau_3(Al_5Ce_2Ni_5)$ ,  $\tau_4(Al_3CeNi_2)$ ,  $\tau_5(Al_4CeNi)$ ,  $\tau_6(Al_5CeNi_2)$ ,  $\tau_7(Al_7CeNi_2)$ ,  $\tau_8(Al_{23}Ce_4Ni_6)$ ,  $\tau_9(Al_{0.85}Ce_2Ni_{2.15})$ ,  $\tau_{11}(Al_{59.8}Ce_{12.1}Ni_{28.1})$ ,  $\tau_{12}(Al_{40.3}Ce_{30.4}Ni_{29.3})$  is possible in Al–Ni–Gd and Al–Ni–Ce systems. Among them, information about thermodynamic properties of these compounds is lack. It is known, that some compounds are unstable or metastable. For example, in Al–Ni–Gd system only  $Gd_4Ni_6Al_{23}$  compound is thermodynamically stable. Moreover, after appropriate annealing at elevated temperature only binary compounds and pure aluminum are observed. That's why the modeling was executed taking into account the possibility of formation of binary compounds only. The following condensed pure substances and compounds were taken into account:

*Al–Ni–Ce system:* NiAl,  $Ni_2Al_3$ ,  $NiAl_3$ ,  $Ni_3Al$ ,  $Ni_5Al_3$ , AlCe,  $Al_{11}Ce_3$ ,  $Al_3Ce$ ,  $Al_2Ce$ ,  $AlCe_3$ .

*Al–Ni–Gd system:* NiAl,  $Ni_2Al_3$ ,  $NiAl_3$ ,  $Ni_3Al$ ,  $Ni_5Al_3$ , AlGd,  $Al_2Gd_3$ ,  $Al_3Gd$ ,  $Al_2Gd$ ,  $AlGd_2$ .

The temperature dependencies of alloys equilibrium composition, activities of the components, the integral and partial excess thermodynamic characteristics (enthalpy, entropy and Gibbs energy) were calculated.

Using subprogram TRIANGLE [1] the phase diagrams were constructed at the temperatures, which correspond to solid and liquid state, respectively: 800 K and 2273 K for Al–Ni–Gd system; 800 K and 2173 K for Al–Ni–Ce system.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC MODELING OF A<sup>III</sup>B<sup>V</sup> MELTS

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Nowadays the materials used in the electronic engineering consist of several elements (more than 5 as a rule) and that is why it is correctly to speak not about the separate material phases, but about the formation of the complex structures.

In different fields of industry the binary and ternary A<sup>III</sup> – B<sup>V</sup> semiconductor solid solutions and their intermetallic compounds are widely used. A<sup>III</sup>B<sup>V</sup> compounds are the nearest electronic analogous of silicon and germanium compounds. They belong to diamond-like group of semiconductor materials. Most of the known A<sup>III</sup>B<sup>V</sup> compounds crystallize in a cubic system, zinc blend type (ZnS), except the nitrides of aluminum, gallium, indium and thallium, which present a hexagonal cell, wurtzite type (ZnS).

The preliminary thermodynamic estimation is necessary to predict and check the semiconductor multifunctional structures of complex composition and to create the flexible technologies, that determine the general technical progress of electronic engineering.

Presented work is devoted to the investigation and reassessment of the composition and thermodynamic characteristics of binary A<sup>III</sup>B<sup>V</sup> alloys, such as Ga–Sb, Al–Sb, In–Sb, In–P, Ga–P, B–P, Al–P, In–As, Al–As, Ga–As, using optimized thermodynamic functions of the A<sup>III</sup>–B<sup>V</sup> compounds [1] and thermodynamic modeling method [2]. As a software the program complex TERRA was used [3]. Modeling was executed in atmosphere of argon at the common pressure of  $P = 10^5$  Pa and temperature and concentration intervals, corresponding to the regions of liquid state on the phase diagrams of above-indicated binary systems according to [4].

The activities of components, equilibrium composition of melts, integral excess enthalpies, entropies, integral and partial excess Gibbs energies were obtained. It was established, that the activities of the components have big negative deviations from Raoult's law. Concentration dependencies of integral excess Gibbs energies, entropies and enthalpies are not monotonous. These facts justify, that strong interaction between atoms of different sorts takes place.

Using subprogram RECTANGLE [1] the phase diagrams for all above-indicated systems were constructed. On these diagrams the temperature and concentration regions of existence of the components of the condensed phase and the gas phase are shown.

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[2] Vatolin, N.A.; Moiseev, G.K.; Trusov, B.G. Thermodynamic modeling in high-temperature inorganic systems, Moscow: Metallurgia, 1994 (in Russian).

[3] Trusov, B.G. Vestnik of Bauman Moscow State Technological University, 2012, 2 (Special Issue), 240-249 (in Russian).

[4] Phase diagrams of binary metallic systems: Handbook. In 3 vol. Ed. N.P. Ljakishev, Moscow: Mashinostroenie, 1997 (in Russian).

**THERMODYNAMIC CHARACTERISTICS OF NICKEL(II)  
COMPLEX FORMATION REACTIONS WITH GLYCYLGLYCINATE-ION  
IN WATER – DIMETHYLSULFOXIDE SOLVENTS**

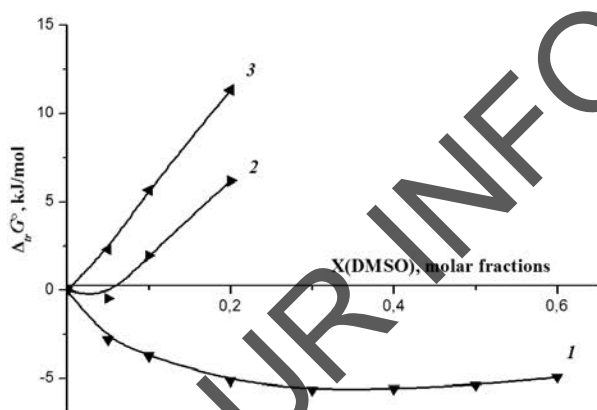
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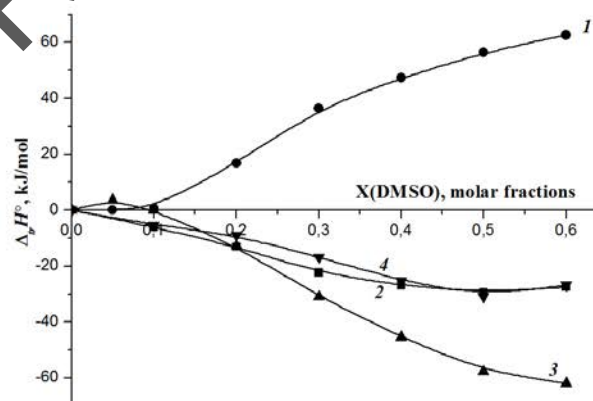
The constants of equilibria and thermal effects of complexformation reactions nickel(II) with glycyglycinate-ion to form 1:1, 1:2, 1:3 complexes were determined by potentiometric and calorimetric methods in the composition range of 0.00 to 0.60 molar fractions of dimethylsulfoxide at 298.15 K and ionic strength 0.1 M (NaClO<sub>4</sub>).

The stability of these complexes in water – dimethylsulfoxide solvent is higher than in water. At the same time the increase of constants stability occurs at 0.00–0.30 molar fractions DMSO. Exothermicity of mono- and biscomplex formation reactions is increases with rising content of DMSO in solution. The coordination of third glycyglycinate-anion accompanied by a non-monotonic change of exothermicity.

Analysis of reagents solvation effects in the change of thermodynamics characteristics of reactions suggests that hardening of the complex is determined mainly by the weakening of the ligand solvation at partial compensation  $\Delta G^\circ$  of complex- and central-ions resolution (Figure 1, 2).



**Figure 1:** Influence of H<sub>2</sub>O–DMSO on  $\Delta_r G^\circ$  of complexformation reaction nickel(II) with glycyglycinate-ion (1) and solvation reagents: 2 –  $\{\Delta_r G^\circ([NiGG]^+) - \Delta_r G^\circ(Ni^{2+})\}$ , 3 –  $\Delta_r G^\circ(GG^-)$ .



**Figure 2:** Enthalpies characteristics of monocomplexformation reaction nickel(II) with glycyglycinate-ion in H<sub>2</sub>O–DMSO: 1 –  $\Delta_r H^\circ(GG^-)$ , 2 –  $\Delta_r H_r^\circ$ , 3 –  $\Delta_r H^\circ(Ni^{2+})$  [1], 4 –  $\Delta_r H^\circ([NiGG]^+)$ .

The complexformation of nickel(II) with glycyglycinate-ion is determined mainly by energetic component while the change of complex stability in water – dimethylsulfoxide solutions is related by both components.

[1] Hefter, G.; Marcus, Y.; Wagborne, W.E. Chem. Rev., 2002, 102, 8, 2773-2836.

*Study was carried out in the framework of State Task of the Ministry of Education and Science of the Russian Federation (Project No. 2293).*

## Section 3. Thermodynamics of solutions and heterogeneous systems

### H<sub>2</sub>O–D<sub>2</sub>O SOLVENT ISOTOPE EFFECTS ON THE THERMODYNAMIC CHARACTERISTICS OF BICARET HYDRATION: A COMPARATIVE ANALYSIS

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The alkyl-*N*-substituted glycolurils (bicyclic bisureas of the octane series) have found the applications in the field of construction of self-assembling molecular entities and preparation of pharmaceuticals. Among such derivatives, the tetra-*N*(2,4,6,8)-substituted ones (see Figure) are the most active. The psychotropic drug *mebicar* is well-known tranquilizer at present. Other representative of the specified bioactive achiral compounds, *bicaret* (or 2,4,6,8-tetraethylglycoluril), is much less studied. The glycolurils compared have the same molecular bicyclic framework, adopting a conformation of “half-open book”. But, the alkyl-*N*-substituents of bicaret have a more bulk-branched structure compared to that of mebicar. When the specified glycoluril derivatives are subjected to dissolution in water H/D-isotopologues, this leads to the substantially differing thermodynamic effects, including D<sub>2</sub>O–H<sub>2</sub>O solvent isotopic those. Hence the aim of this report is to assess the influence of further lengthening of peripheral hydrocarbon chains of mebicar, to form bicaret (see in Figure), on both energy-related and structure-packing changes in the H/D isotopically distinguishable aqueous media.

The results of experimental study (using the calorimetry and precise densimetry) of solutions of bicaret in heavy and ordinary water at various temperatures are summarized in Table. Being based on the results obtained, we conclude that a hydrophobic constituent of the bicaret hydration is the predominant and this is enhanced in heavy water. The hydration of mebicar is also treated as a superposition of two mechanisms, hydrophobic and hydrophilic, with the latter being predominating. In this report, the dissolution heat capacities and enthalpy-/volume-related interaction parameters for the glycoluril-derivatives compared in H<sub>2</sub>O and D<sub>2</sub>O are discussed too.

**Table.** The thermodynamic characteristics of dissolution of the compared glycoluril-derivatives in water with the corresponding solvent isotope effects:  $\delta Y (H_2O \rightarrow D_2O) = Y (D_2O) - Y (H_2O)^*$

Temperature	Bicaret		Mebicar [1]		Bicaret		Mebicar [2]	
	$\Delta_{\text{sol}} H_m^0$	$\delta \Delta_{\text{sol}} H_m^0$	$\Delta_{\text{sol}} H_m^0$	$\delta \Delta_{\text{sol}} H_m^0$	$d$	$\delta d$	$d$	$\delta d$
278.15 K	-15.66	-1.01	1.96	0.41	0.6307	0.0022	-	-
298.15 K	-6.83	-0.85	3.67	0.20	0.6197	0.0009	0.6377	0.0018
318.15 K	-1.97	-0.64	7.03	-0.03	0.6096	0.0002	0.6278	0.0001

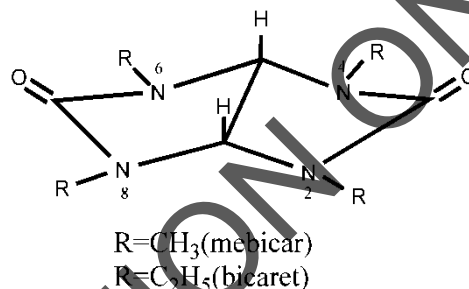
\*  $\Delta_{\text{sol}} H_m^0 / (\text{kJ} \cdot \text{mol}^{-1})$  is the standard molar enthalpy of solution;  $d = V_{\text{vdw}} / V_m^0$  is the “packing density”

where  $V_{\text{vdw}}$  is the van-der-Waals volume (per 1 mol) and  $V_m^0$  is the standard molar volume of the solute.

[1] Ivanov, E.V.; Abrosimov, V.K.; Batov, D.V. Russ. Chem. Bull., 2006, 55, 741-743.

[2] Ivanov, E.V.; Abrosimov, V.K. J. Solution Chem., 2007, 36, 313-325.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 13-03-00716-a).



**Figure:** A schematically simplified molecular structure of the tetra-*N*-alkylated derivative of glycoluril.

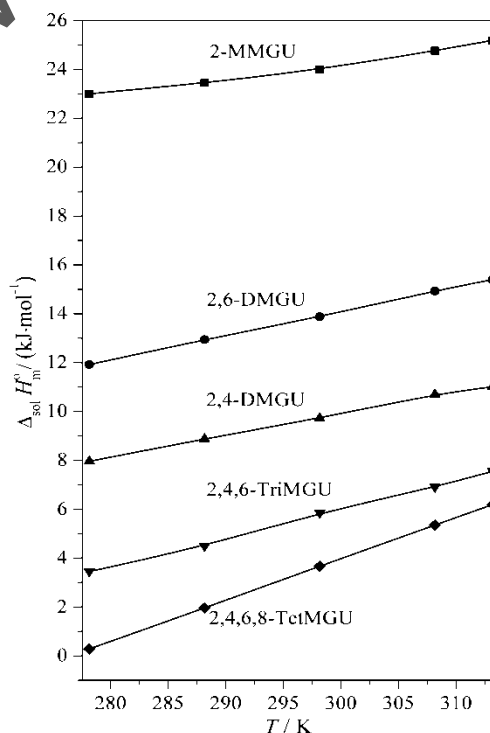
SOME TEMPERATURE-DEPENDENT FEATURES OF A GLYCOLURIL HYDRATION DURING THE SEQUENTIAL *N*-METHYLATION OF ITS MOLECULES

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The molecules of a general formula  $(\text{CH})_2[(\text{NR})_2\text{CO}]_2$ , where  $\text{R} \equiv \text{H}$  or  $\text{CH}_3$ , consisting of two close-to-planar five-membered heterocycles, are known as the methyl-*N*-substituted glycoluril derivatives. Glycoluril (2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione or tetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione) and its methyl-*N*-substituted derivatives have found a number of useful applications including the supramolecular chemistry, pharmaceutical chemistry and drug development. Herewith each of such glycoluril derivatives has the certain geometric features of the molecular bicyclic framework. Similar to the unsubstituted glycoluril (GU), 2,4-dimethyl- (2,4-DMGU), 2,8-dimethyl- (2,8-DMGU) and 2,4,6,8-tetramethylglycoluril (2,4,6,8-TetMGU) are structurally achiral. In turn, monomethyl- (2-MMGU), 2,6-dimethyl- (2,6-DMGU) and 2,4,6-trimethylglycoluril (2,4,6-TriMGU) were found to be in the racemate (chiral) form. The existing structural differences are reflected on the character of interaction of these bicyclic compounds with the aqueous surroundings, a fact that should be manifested in the enthalpic and volumetric effects of their dissolution (hydration).

Figure illustrates the trend of changing of standard molar enthalpies of the glycoluril dissolution during the sequential *N*-methylation of its molecules. As seen the dissolution process becomes decreasingly endothermic on going from mono- to di- and further to tri- and tetra-*N*-substituted derivatives. Noteworthy is also the fact that the  $\Delta_{\text{sol}}H_{\text{m}}^{\circ}$  values for 2,4-DMGU (*N*-CH<sub>3</sub> groups are sited in the same ring) and 2,6-DMGU (these groups are sited in different rings) differ by *ca.* 4 kJ·mol<sup>-1</sup>. At the same time to compare the hydration effects of these derivatives, the energy spent to destroy the structural packing of each of them (*i.e.*, the molar enthalpies of their sublimation) must be taking into account. However such data were obtained only for the certain derivatives. This problem is avoided partly if the values of standard solution heat capacity,  $\Delta_{\text{sol}}C_{p,m}^{\circ} = (\partial\Delta_{\text{sol}}H_{\text{m}}^{\circ}/\partial T)_p$ , will be considered as a criterion for the hydration nature of the solute. We derived the following series of  $\Delta_{\text{sol}}C_{p,m}^{\circ} / (\text{J mol}^{-1}\cdot\text{K}^{-1})$  at  $T = 298.15$  K: 66.5 (2-MMGU) < 90.4 (2,4-DMGU) < 99.5 (2,6-DMGU) < 123 (2,4,6-TriMGU) < 168 (2,4,6,8-TetMGU). This corresponds presumably to the increase in hydrophobic constituent of the solute hydration. Such a conclusion is confirmed by the results of studying the volume-related properties of aqueous glycoluril derivatives under consideration.



**Figure:** Standard molar enthalpies of solution of the methyl-substituted glycolurils in water as a function of temperature.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 13-03-00716-a).

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THE STATE DIAGRAMS OF THE SURFACE LAYERS IN THE PROCESSES OF PHENOL ADSORPTION BY ACTIVE COAL

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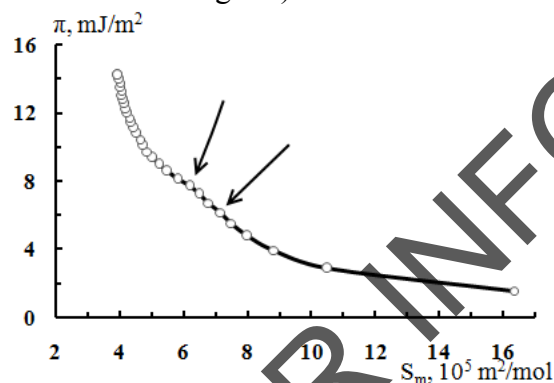
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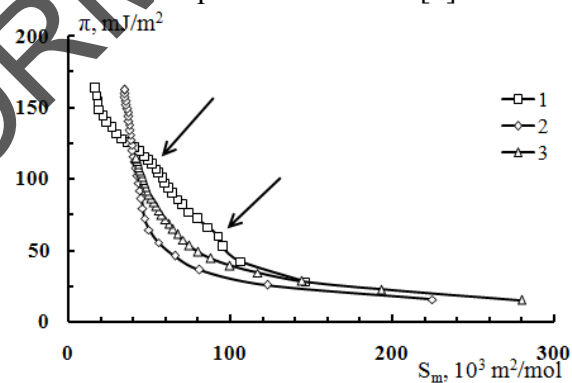
The studies of different nature adsorption systems have a great importance for the development of the adsorption theory, as well as for resolving of various application tasks. For example, some results may be useful in questions of valuable components extraction from solutions and wastewater purification from pollutants.

In the present work the mathematical investigations of the phenol adsorption from aqueous solutions on active coal [1] have been performed. The active coal was obtained by thermolysis of brown coal at 800°C within 1 hour in the presence of potassium hydroxide in ratio 1:1 to the dry coal mass [1].

The treatment of the experimental isotherms by the numerical method allowed getting a dependence of the two-dimensional surface pressure from of the molar area value – a two-dimensional diagram of the surface layer state (Figure 1). The curve shape in Figure 1 has similar type as a phase diagrams of surface films (Figure 2). By analogy with the processes in the surface films [2] it was established that the kinks on the obtained dependence (marked by arrows in the diagram) can be correlated with two-dimensional phase transitions [3].



**Figure 1:** Two-dimensional diagram of surface layer state in phenol adsorption from water solution on active coal at 293 K.



**Figure 2:** Two-dimensional diagrams of surface layer state in styrene adsorption on skeleton nickel from water-2-propanol solution at 293 K with 2-propanol mole fraction  $x_2$ : 1 – 0.073; 2 – 0.192, 3 – 0.681 [2].

Thus, the character of  $\pi = f(S_m)$  dependence allows to assert, that the adsorbate state in the surface layer is determined not only by the degree of adsorption space filling, but also by the interactions of the adsorbate-adsorbent and by aspects of solvation of the adsorption process participants.

[1] Isaeva, L.N.; Tamarkin, Y.C.; et al. J. Siberian Fed. Univ. Chem., 2009, 2, 25-32.

[2] Sharonov, N.Y.; Ulitin, M.C.; Budanov, M.A. Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol., 2009, 52, 4, 11-14.

[3] Frolov, Yu. Course of colloid chemistry, M.: Khimiya, 1989, 463.

Present work was done in the Laboratory of adsorption processes and heterogeneous catalysis of Research Institute of Thermodynamics and Kinetics of chemical processes of ISUCT.

THE COMMON REGULARITIES OF ADSORPTION PROCESSES  
AT SOLID AND LIQUID SURFACES

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The surface layers formation at interfaces is stipulated by solutes solvation interactions with solutions components in bulk phase and in surface layers. Therefore the aim of the present work was to study the peculiarities of surface layers formation processes at the liquid/gas and solid/liquid interfaces. That aim is resolved on basis of investigation results of I, I-electrolytes adsorption from solutions and organic compounds adsorption at the hydrogenation catalyst.

By using of Rebinder's and capillary rise methods at 30°C the surface tensions isotherms of hydrogen, sodium and potassium chlorides aqueous solutions and ethanol-water solutions have been obtained. And by using of adsorption-calorimetric method the adsorption isotherms and the adsorption enthalpies of sterol, acetone and sodium maleat at the skeleton nickel from solutions have been obtained under condition of liquid phase catalytic hydrogenation reactions.

It was found that surface tension and Gibbs adsorption isotherms of electrolytes have polyextremes character. In dilute solutions electrolyte shows surface-activity and surface-inactivity properties, and basis changes in surface layers formation in I, I-electrolytes solutions is occurred in the low concentrations area (over ~0.7 mol/kg).

The full adsorption values, adsorption heats and entropies have been calculated using the developed ions adsorption models. It was established that adsorption values of chlorides in surface layer are increased with temperature, and ones are decreased with transfer to water-organic solvents. The isotherms of full adsorptions have a maximum. The dependencies of adsorption heats and entropies from electrolyte concentrations in water solutions have a polyextreme character.

With increasing of ethanol mole fraction in solution the transfer to more monotonous curves is observed. Moreover, it is shown that the character of dissolving enthalpies changes with solutes concentration or ethanol content rise in solutions qualitatively agrees with surface tension isotherms. That is why the behavior of values of adsorption thermodynamic characteristic with increasing of ethanol concentration is determined by solvation interactions in bulk phase.

The adsorption isotherms of organic compounds on skeleton nickel from solutions are related to 3L- and 4L-types by Gibbs classification.

The two-dimensional diagrams of surface layers state of skeleton nickel at the organic compounds adsorption have a typical parts, which is related to changing of surface layer state. It is shown that dependencies of differential enthalpies of sodium maleate, sterol and acetone adsorption from concentration have maximums. Second-order phase transitions and maximums of adsorption enthalpies answer to the same values of adsorption, what may be explain by changing of composition and structure of skeleton nickel surface layers. Assignment these extremes to the features of solvation interactions are adjusted with solvation energies of this class compounds with solvents.

The obtained results allow concluding that in the case of adsorption at the liquid/gas surface the displacement of solvent molecules from surface layer by solvated electrolyte molecules is occurred. And in the case of adsorption on metals surface adsorbat solvated state is changed.

The processes of adsorption layers formation at the liquid /gas and solid/liquid have a one-type regularities, which is stipulated by solvation interaction both in bulk phase and in surface layer.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### NEW NATIONAL STANDARD OF RUSSIA IN THE FIELD OF SOLUTION CALORIMETRY

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D.I. Mendeleev Institute for Metrology (VNIIM, Saint Petersburg) is the oldest metrological institution in Russia, where 53 State Primary Standards are established, successfully used and continuously improved. One of them is a new generation of the National Primary Special Standard of solution heat unit, which was improved and studied in a period from 2010 to 2012 in the Laboratory of Calorimetry and High-purity Organic Substances for Metrology Purposes. Many years of experience of researchers from the N.N. Semenov Institute for Chemical Physics of Russian Academy of Sciences allowed to develop and create this Standard. Constructional defects, which were found in many of previously developed precision calorimetric systems (both domestic and foreign) have been taken into account.

The following metrological characteristics of the new National Primary Special Standard were realized:

- measurement range is  $5 \div 1200$  J;
- standard measurement uncertainty: type A is  $(1.0 \div 3.0) \cdot 10^{-4}$ ; type B  $(0.6 \div 1.2) \cdot 10^{-4}$  and expanded measurement uncertainty is  $(2.4 \div 6.5) \cdot 10^{-4}$  ( $k = 2$ ).

The Standard consists of the following measuring systems:

- the new precision calorimeter of solution “KR-1”;
- the apparatus for electrical calibration;
- the system for collection, processing and keeping the measuring information;
- the system for calorimetric samples preparation;
- the precision electronic balance.

The precision calorimeter contains hermetically sealed calorimetric vessel (volume  $110 \text{ cm}^3$ , horizontally disposed), with the mechanism for mixing a liquids inside this vessel and the mechanism for breaking ampoules. The calorimetric samples are solid or liquid substance, weight is about 1 g, placed into thin-walls glass ampoules volume  $1 \div 2 \text{ cm}^3$ .

The measuring system consists of a resistance thermometer (1000 Ohm) for measurements of an average-surface temperature of the calorimetric vessel (thermometer is bifilar reeled up on a surface of the vessel), and the high-precision multi-bit analog-digital converters for high-precision temperature measurements.

Electrical calibration can be performed using an electric calibration heater, because these techniques are precise and convenient, and measurements of electrical power and energy can be easily made with a high accuracy that needed for various practical calorimetric experiments.

Calibration system consists of a heater, with resistance 64 ohm, material – thermostable cuprum-based alloy (manganin) placed inside the calorimetric vessel, the precision power supply, and the high-precision multimeter (by Agilent Technologies) for measuring of electrical power during a calibration process.

More detailed researching of metrological characteristics of the new solution calorimeter is planning in near future using the samples based on the potassium chloride (similar to NIST SRM 1655 – KCl samples). We are also planning to approve the high-purity potassium chloride as the CRM for Solution Calorimetry. Currently it is an actual metrological problem in various areas in Russian thermochemistry researches.



ENTHALPIES OF SOLUTION AND ENTHALPIES OF SOLVATION  
OF 1-ETHYL-3-METHYL-IMIDAZOLIUM BASED IONIC LIQUIDS IN WATER

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Ionic liquids (ILs) belong to a class of molten salts which are liquid below the decomposition temperature. They usually consist of bulky asymmetric organic cations and different anions. Unique properties of ionic liquids such as high thermal stability, negligible vapor pressure, non-flammability, and good solvation ability for different types of chemicals allow their use in various fields of chemical industry such as organic synthesis, pharmacy, electrochemistry, and cellulose processing. ILs can be also applied in separation processes, biphasic transfer, and extraction. In practical applications, water is often used as the second solvent. It was shown, that ILs were effective for the removal of organics from aqueous stream. Moreover, water as a cosolvent additionally increases solubility of organic compounds in ILs. Thus, areas of practical applications of IL–water mixtures significantly depend on their mutual solubility.

In this work we studied dissolution of several imidazolium based ionic liquids in water by using solution calorimetry at 298.15 K [1]. We selected ILs with the common cation (1-ethyl-3-methylimidazolium) connected to eight different anions. In the focus of our study was to assess an impact of the anion on the values of limiting enthalpies of solution and enthalpies of solvation in terms of intensity of intermolecular interactions in aqueous solutions of ionic liquids. Some dependences between thermochemical data and ILs parameters responsible for different types of intermolecular interactions were analyzed.

Highly accurate and consistent values of solution enthalpies for five ionic liquids in water were directly measured at 298.15 K using two different calorimeters. These results could be useful for prediction of ILs solubility in aqueous solutions at elevated temperatures and validation of solution enthalpies calculated indirectly from the solubility temperature dependence. Enthalpies of solvation were calculated from solution enthalpies measured in this work and vaporization enthalpies available from the literature. The linear correlation of solvation enthalpies with the hydrogen-bonding interaction energies revealed the importance of this type of intermolecular interactions in ionic liquid aqueous solutions, as well as provided useful empirical equation for a quick appraisal of solvation enthalpies.

[1] Varfolomeev, M.A.; Khachatryan, A.A.; Akhmadeev, B.S.; Solomonov, B. N.; Yermalayeu, A.V.; Verevkin, S.P. *J. Sol. Chem.*, accepted, JOSL-D-14-00302R1.

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### Section 3. Thermodynamics of solutions and heterogeneous systems

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#### EFFECT OF ALKYL GROUP LENGTH ON THE ENTHALPIES OF HYDROGEN BONDING AND VAN DER WAALS INTERACTIONS OF ORGANIC SOLUTES WITH 1-ALKYL-3-METHYLIMIDAZOLIUM *BIS*(TRIFLUOROMETHYLSULFONYL)IMIDE

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Ionic liquids (ILs) belong to a class of molten salts which are liquid below the decomposition temperature. They are capable of dissolving different types of compounds such as usual organic molecules, polymers, lignin and etc. Their solvent power depends on ability to interact with solute's molecules and also on temperature. In order to predict solubility of some compounds in ILs we need to know strength of intermolecular interactions and temperature coefficient. Enthalpies of solution and enthalpies of solvation could be used as a measure of these properties. Consequently, determination and analysis of thermochemical data present an actual task.

Nowadays, enthalpies of solution and solvation of different compounds in ILs are usually determined by indirect methods, mostly by gas chromatography. In this work we have studied thermochemistry of solution of organic compounds in ILs using direct solution calorimetry technique in order to check available data and to get new values. 1-Alkyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquids with linear alkyl group length C<sub>1</sub>–C<sub>8</sub> were taken as objects of this investigation. We have collected literature values of limiting activity coefficients of organic molecules in studied ILs at different temperatures and used them for calculation of solution enthalpies. Also we have carried out dissolution experiments for polar and non-polar solutes in 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid. We have shown that enthalpies of solution of polar compounds in studied ILs determined by different authors from temperature dependences of activity coefficients and using direct calorimetric technique are in good agreement. For non-polar solutes (alkanes and etc.) we observed disarray in solution enthalpies obtained by various research groups from chromatographic measurements.

The enthalpies of solution of *n*-alkanes in imidazolium based ionic liquids linearly depend on the volume of the solute molecules. The scale of the van der Waals interactions of ionic liquids has been proposed on the basis of these linear dependencies. Obtained parameter of van der Waals interactions of studied ionic liquids decreases with increasing the length of alkyl group.

Hydrogen bond enthalpies of organic solutes with 1-alkyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquids were determined using modified method for non-electrolytes [1]. It was shown that the enthalpy of hydrogen bond in studied systems does not depend on the length of alkyl group.

[1] Solomonov, B.; Novikov, V.; Varfolomeev, M.; Milesenko, N. J. Phys. Org. Chem., 2005, 18, 49-61.

*This work has been supported by MK-7126.2015.3 and has been performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.*

### CONSTRUCTION OF PHASE EQUILIBRIUM DIAGRAMS WITH VOLATILE AND AGGRESSIVE COMPONENTS: CONSTRUCTION OF LIQUIDUS AND SOLIDUS PROJECTIONS OF TERNARY Fe–Sn–S SYSTEM

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This work is devoted to research and construction of phase equilibrium diagram of ternary Fe–Sn–S system. Previously, the authors researched the phase transformations in Me1–Me2–S systems [1–3]. So, extensive methodical experience was applied in experimental studies of reactions in multicomponent systems using the modern physico-chemical methods of analysis (DSC, TGA, SEM, RSMA, and XRD). The presence of volatile components such as Sn, S and chemical compound SnS creates the additional methodological difficulty in the framework of this study. In addition, the vapors of tin are aggressive towards most metals, including platinum–rhodium thermocouples, which used in the basis of the measuring cell (with using of DSC method). We proposed the usage of ampoule technique for work with volatile compounds and elimination the interaction of corrosive vapors Sn and the measuring cell. Although ampoule technique was used in the study of multicomponent systems previously, including systems with aggressive and volatile components [4], under performing of this work the combination of ampoule technique and standard DSC cell was designed. Under implementing of these technical solutions sealed quartz ampoule is placed directly in the alumina crucible for the DSC-analysis, which volume is 80  $\mu\text{l}$ . Thus, the mass of the investigated material is minimizing, allowing receiving more correct results due to the decreasing of thermal gradient on the sample volume. This method of combining a standard cell for DSC analysis and quartz ampoule was used in the study of phase transformations in ternary Fe–Sn–S system. The main results are the liquidus and solidus surface projections of the discussed system in a wide range of compositions.

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### Section 3. Thermodynamics of solutions and heterogeneous systems

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#### ACOUSTIC AND THERMODYNAMIC PROPERTIES OF LIQUID BINARY MIXTURE OF CYCLOHEXANE + *n*-HEXADECANE

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An evaluation of current state of experimental studies and theoretical calculations of thermodynamic properties of binary mixtures of cyclohexane with *n*-alkanes has been carried out. The overview showed that experimental data were scarce and unsystematic. It seems not to have been subjected to overall analysis. The measurements were carried out only for some types of mixtures and compounds. To determine thermodynamic properties of mixtures the acoustic method has been used.

The subject of the study was the binary mixture of cyclohexane with *n*-hexadecane. The speed of sound in liquid mixture has been measured using technique of direct determination of transit time of acoustic pulses through known distance. The measurements were made at temperatures from 298 to 433 K and pressures from 0.1 to 100.1 MPa. Experimental speed of sound data have been obtained for the first time.

The own speed of sound data obtained at atmospheric and elevated pressures along with literature values of density and isobaric heat capacity at atmospheric pressure have been used to calculate the different thermodynamic properties in a wide range of parameters. As a result, the values of density, isobaric and isochoric heat capacity, adiabatic and isothermal compressibility, excess molar volume become available. The temperature, pressure and mixture composition dependences of thermodynamic and excess properties have been discussed.

Comparison between our calculated values of density and those available in the literature has revealed good agreement.

The computed values of density were generalized by the Tait equation. We have determined the coefficients of the Tait equation for individual compositions and for the entire mixture in the indicated interval of state parameters. This equation possesses good extrapolation potentialities as far as pressure is concerned. Above mentioned equation reproduces available literature data with uncertainty, not worse that accuracy of the direct determination of density at pressures above 100 MPa.

FRactal SKEYLING OF REACTIONS SELF-ASSEMBLY  
ON THE NANOCOMPOSITE SORBENT WITH QUANTUM POINTS

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Fractal modeling of the reactions of self-assembly [1] proceeding on a nanocomposite sorbent was carried out. The sorbent represents the nanostructured composite from organic molecules with the set structure and thickness on a colorchrom (nanofilm). The sorbent contains the proton heterojunction capable to provide a heterophase exchange not only electrons, but also protons. Thus, the two-phase heteroborder can be also used as the technical device. An important region application of nanocomposites – a catalysis of chemical reactions. Process of sorption is connected with the return solyubilization, i.e. the phenomenon of inclusion in structure of the third component (the occluded gas). Process of a solyubilization proceeds spontaneously, with absorption of heat. The chemical model of self-assembly of molecular complexes consists of a few stages. Basic formulas according to which carried out modeling [2]:

$$L_m = n \cdot \lambda, \quad (1)$$

$$L_m = N_m 2r_m, \quad (2)$$

$$L_m = N_m^D \cdot \lambda^{2-D}, \quad (3)$$

where  $L_m$  – the linear size of a fractal;  $N_m$  – quantity of the micelles belonging to a fractal;  $\lambda$  – length of free run;  $D$  – fractal dimension. Size  $D$  – 1.1–1.4.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### HEAT EFFECTS OF AMMONIUM CATION SORPTION BY ION-EXCHANGE MEMBRANE MK-40 AND SULFONIC CATION-EXCHANGE RESIN KU-2\*8 OUT OF WATER SOLUTIONS

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Ion-exchange materials are widely used for division and purification of water solutions. At the sorption of ions on ion-exchangers the aggregate of the interactions of different origin reflecting on energy and structural qualities of the system *ion-water-ion-exchanger* must be taken into account.

As the objects of the research have been chosen the heterogeneous ion-exchange membrane MK-40 and the cation exchanger KU-2\*8 of helium type containing the sulfonate groups  $-\text{SO}_3\text{H}$ . The research was conducted at  $25^\circ\text{C}$  on a differential heat-conducting microcalorimeter MID-200. Into the boat swimming on the surface the mass of the ion exchanger and  $2\text{ cm}^3$  of water were set for its swelling. After thermostating during 24 h the ion exchanger and the saline solution were mixed up and the heat power values of their interaction were registered.

From the results of calorimetric measurements the thermokinetic curves of the sorption of the ammonium ions by the cation exchanger KU-2\*8 and the membrane MK-40 were got. It is established that the interaction of the cation exchanger KU-2\*8 with the ammonium ions is conducted by heat release while for the membrane MK-40 this process is sign-changing. On the thermokinetic curves there is the only expressive maximum. The intensity of heat release for the KU-2\*8 reaches the maximum at 6–15 min of the beginning of sorption process, and for the membrane MK-40 – at 3–12 min. It should be noted that the value of the maximum of heat release sorption depends on the structure of the ion-exchanger. For the sulfonic cation-exchange resin KU-2\*8 it is nearly two times as big as for the membrane. It can be connected with bigger concentration of sulfonate groups in the cation exchanger KU-2\*8 in comparison with the membrane. The duration of the sorption process for the KU-2\*8 is 1.4–2.8 h, and the MK-40 – 2.5–3.8 h.

From the thermokinetic curves the enthalpies of the process were calculated. The enthalpy of the sorption process of the ions  $\text{NH}_4^+$  by the cation exchanger KU-2\*8 increases for the concentrations of ammonium nitrate 0.1–0.25 mol/dm<sup>3</sup>. The further increase of concentration 0.25–0.9 mol/dm<sup>3</sup> leads to the gradual decrease of the enthalpy. This can be probably connected with decreasing quantity of the functional groups available for exchange with increasing concentration of saline solution. For the membrane MK-40 the decrease of exothermicity with the increase of salt concentration and the transition to endothermic area are observed. Such change of the enthalpy of the process is probably conditioned by big expenditure of energy on the dehydration of ion-exchange groups of the membrane MK-40 in comparison with the KU-2\*8 and the redistribution of water in the system. The total heat effect of the sorption process of the ammonium cations by the ion exchangers is calculated from the heat effects of several running processes of the ammonium ions interaction with the ion exchanger functional groups, ion hydration, dehydration of ion-exchanger sulfonate groups and ammonium cations, rearrangement of water molecules in the solution and in the phase of the cation exchanger and the membrane, deformation of the polymerous matrix during the formation of sorption centres. We also should take into account that with the increase of ammonium salt concentration in the solution, formation of ion pairs is possible on whose destruction expenditures of energy are necessary.

## A STATISTICAL THEORY OF COSOLVENT-INDUCED COIL-GLOBULE TRANSITIONS IN DILUTE POLYMER SOLUTION

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The coil-globule transition in dilute polymer solutions is one of the most interesting phenomena in physical chemistry of polymers. The mechanism of conformational transition of a chain molecule upon a change of environment has found many applications in recent technological advances ranging from encapsulation of drug molecules in a polymer coil and targeted delivery to smart materials changing their properties in response to the environment [1, 2].

There were some approaches which describe a coil-globule transition but solvent is considering implicitly. It has been shown that, as the solvent becomes poorer, the polymer coil shrinks leading eventually to a collapse of the polymer coil. Up to now only a few attempts considering the cosolvent explicitly have been reported.

We present a statistical model of a dilute polymer solution in good solvent in the presence of low molecular weight cosolvent [3]. Polymer in solution is described by the Edwards model [4], where the partition function of the polymer chain with a fixed radius of gyration is described in the framework of the mean-field approximation. The contributions of polymer-cosolvent and the cosolvent-cosolvent interactions in the total free energy are treated also within the mean-field approximation. For convenience we separate the system volume on two parts: the volume occupied by the polymer chain expressed through its gyration volume and the bulk solution. Considering the equilibrium between the two subvolumes we obtain the total free energy of the solution as a function of radius of gyration and the cosolvent concentration within gyration volume.

We investigated the conformational changes of the polymer induced by a change of the cosolvent concentration and the type of interaction between the cosolvent and the polymer. Varying the interaction strength between polymer and cosolvent we showed that the polymer collapse occurs in two cases – either when the interaction between polymer and cosolvent is repulsive or when the interaction is attractive.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### CALCULATION OF IMPURITY DISTRIBUTION DURING DIRECTED CRYSTALLIZATION WITH PRESENCE OF GAS PHASE

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The two-phase variant of the process with possible neglect of the effect of the third (gas) phase of the purified substance is considered in detail in the theory of normal directed crystallization as a method for ultra purification of substances. However, the effect of the gas phase on distribution of impurities in three phases can be significant in substances with sufficiently high values of vapor pressure at their melting temperature. Germanium tetrafluoride can be an example of this substance.

The solution to the problem on distribution of impurity substance by the solid and the fluid phases at temperature close to the triple-point temperature is found. The assumptions are made that the impurity is distributed uniformly in the liquid and the gas phases, the impurity diffusion is absent in the solid phase and the concentration being in equilibrium with liquid is observed only in the surface layer.

The differential equation of mass balance of the crystallization process follows from the condition of mass maintaining of the impurity substance redistributed between three phases due to increase of the total mass of the solid phase by  $dN_S$  value

$$N_L dy + x dN_L + \alpha x dN_G + \alpha N_G dx = -K x dN_S,$$

where  $N_L$ ,  $N_G$ ,  $N_S$  is the amount of purified substance in the liquid, vapor and solid phases (mole), respectively;  $x$  is the molar fraction of impurity in liquid;  $\alpha$ ,  $K$  are the coefficients of impurity distribution between liquid–vapor and liquid–crystal phases. The equation is solved by analytical and numerical methods. The expression found for the molar fraction of impurity in the liquid phase  $x$  is of the form

$$x = \frac{X_0}{(1-\alpha) \frac{v_G N_0 - V_0}{N_0 (v_G - v_L)} + \alpha \left\{ \frac{N_L + \frac{\alpha (V_0 - v_S N_0)}{v_G - v_S - \alpha (v_L - v_S)}}{v_G N_0 - V_0 + \frac{\alpha (V_0 - v_S N_0)}{v_G - v_S - \alpha (v_L - v_S)}} \right\}^{\frac{K (v_G - v_L)}{v_G - v_S - \alpha (v_L - v_S)} - 1}}$$

where  $X_0$  is the molar fraction of impurity in the initial substance in amount of  $N_0$  moles,  $V_0$  is the volume of container,  $v_S$ ,  $v_L$ ,  $v_G$  are the molar volumes of the main substance in the crystalline, liquid and vapor phases. The molar fractions of impurities in the gas phase and surface layer of crystal can be calculated using the values of  $\alpha$  and  $K$ .

The theoretical estimations of thermodynamically ultimate possibilities of the three-phase method are made. The coefficients of distribution of impurities  $K$ ,  $\alpha$  in two-phase  $\text{GeF}_4$  – impurity component systems are calculated by the equations of statistical thermodynamics of the diluted solutions.

The calculation results indicated that the directed crystallization is a potentially highly efficient method for purification of  $\text{GeF}_4$  from impurity substances.



THE DEFINITION OF CHANGES OF THE ACTIVATION ENERGIES  
OF RELAXATION PROCESSES DURING THE FILLING  
OF THE LOW-DENSITY POLYETHYLENE

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When systems containing the polymer matrix are heated, there is a relaxation process associated with the serial "unfreezing" of various forms of molecular mobility. There are the transitions that are associated with the increased mobility of large sections of molecules segments, cooperative with the movement of the neighboring molecules, and the transitions that determine the increase in the mobility of the relatively small areas of the macromolecules of the polymer. The occurrence of these processes is associated with a particular value system temperatures  $T_\alpha$  and  $T_\beta$ , respectively.  $T_\alpha$  is called the "glass transition temperature", because when it happens the transition from the glassy to the highly elastic state takes place. Both transitions have been characterized for a specific system specific temperatures or temperature intervals are due to the local energy fluctuations that contribute to overcoming the energy barriers in the elementary acts of transitions. The magnitude of these barriers is the effective activation energy of relaxation processes. Knowledge of the values of activation energy and its influencing parameters allows us to quantitatively characterize the elementary acts of the process. Relaxation nature  $\alpha$ - and  $\beta$ -transitions are manifested depending on the values of the corresponding temperature on the rate of heating or cooling system, i.e., the scanning speed temperature  $V_T = dT/dt$ . From the slope of the dependences of  $T_\alpha(V_T)$  and  $T_\beta(V_T)$  determine the activation energy study of relaxation processes.

When the energy barrier of the transition does not change with temperature a plot of  $\ln V_T(1/T)$  should be a straight line, where the extrapolation to  $1/T = 0$  gives the value  $\ln V_{0f} = 19.4$  or  $V_{0f} = 2.7 \cdot 10^8$  K/s for full technical carbon LDPE. This value is less than the unfilled polymer, is about  $10^{13}$  K/s.

In the case of the dependence of the energy barrier from the temperature slope  $\ln V_T(1/T_i)$  is determined not only by the magnitude of the barrier, but the derived values of the barrier on the temperature. If  $U_i(T) = \left(\frac{dU_i(T)}{dT}\right)_{T_i} < 0$  the slope exceeds the value  $U_i/k$  and the value calculated

from the tilt angle exceeds the value of the energy barrier, the value of  $V_0$  is greater. Therefore, if the value  $\ln V_0$  more 30–32 K/s, it means that the activation energy of the process changes with temperature. This case is observed in the study of the temperature relaxation transitions for LDPE filled with carbon. From the difference  $\ln V_{0f} - \ln V_0$  – is possible to evaluate the temperature derivative of the height of the barrier at the transition temperature. The value of

activation energy can be calculated from the relation  $U_i(T)_i = kT \ln \frac{V_0}{V_T(T_i)}$ .

For 200°C  $U = 8.6 \cdot 10^{-5}$  eV/K, 473 K,  $\ln(2.7 \cdot 10^8/0.03) = 0.932$  eV; for as 210°C  $U = 8.6 \cdot 10^{-5}$  eV/K, 483 K,  $\ln(2.7 \cdot 10^8/0.07) = 0.916$  eV; for as 230°C  $U = 8.6 \cdot 10^{-5}$  eV/K, 503 K,  $\ln(2.7 \cdot 10^8/0.13) = 0.928$  eV,  $U_{cp} = 0.925$  eV, which is very close to the value found in the first case.

From these calculations it follows that the relaxation processes in the filled system is substantially different from similar processes in homopolymer and so filled system should be described taking into account such differences.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC PROPERTIES OF UREA – AMMONIUM SULFAMATE – WATER SYSTEM

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Urea ((NH<sub>2</sub>)<sub>2</sub>CO) is one of the most popular nitrogen fertilizers and ecologically benign component of de-icers. Addition of salts containing sulfur and other elements to solid urea or its solutions allows developing new complex fertilizers and de-icers. In this work we investigate ammonium sulfamate (NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub> or AMS) as possible urea additive. This substance is high soluble in water [1, 2], decomposes to common salts over the time and can be used for developing new mixtures stable in a wide range of temperature and composition.

So, the aim of present work was to study the thermodynamic properties of (NH<sub>2</sub>)<sub>2</sub>CO – NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub> – H<sub>2</sub>O ternary system. Experiments and thermodynamic modelling were applied to solve the problem.

Experimental part of the work includes density measurements of AMS and urea – ammonium sulfamate aqueous solutions in a wide concentration range at various temperatures (15, 25 and 50°C). Some data on phase boundaries in the ternary system were obtained also using DSC method. These data were used for the verification of phase equilibria calculations.

Critical review and thermodynamic modeling of binary Urea – Water subsystem was made in [3]. Phase relations in Ammonium Sulfamate – Water subsystem were presented in [1, 2, 4]. Ammonium Sulfamate – Urea binary subsystem was studied previously by us [5]. Thermodynamic modeling of Ammonium Sulfamate – Urea and Ammonium Sulfamate – Water subsystem was made on the results of present and cited works [1–5]. Polynomial representation of excess Gibbs energy of binary solutions was used. Thermodynamic model of the ternary system was constructed on the basis of data in binary subsystems only. The pressure–composition dependence of Gibbs energy of liquid was considered additionally and expanded caloric equation of state was obtained.

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### TRENDS IN THE EXTRACTION OF LIGHT AND MEDIUM LANTHANIDES BY TRIBUTYL PHOSPHATE FROM NITRIC ACID SOLUTIONS

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The continuously increasing world market demand for rare earth elements (REE) forces the intense development of new technologies of processing REE, as well as improvement of existing technologies. Usually pure rare earth elements are obtained by liquid extraction. As an example, research and collection of the data on phase equilibria in the lanthanides – nitric acid – organic extractant (in our case – tributyl phosphate (TBP)) systems are necessary to construct an accurate model of extraction cascades. Available publications on the similar subject give a very limited knowledge on the distribution coefficients in the multi-component system, and lack the information on the complete composition of the equilibrium phases. For closing this gap new experimental data are needed.

The purpose of the current research was to study trends in the extraction of light and medium REE (neodymium and samarium) by tributyl phosphate from nitric acid solutions. The work consists of two parts: extraction experiments and determination of the equilibrium phases composition.

Extraction experiments were conducted at 298 K. For preparing initial mixtures for extraction experiments lanthanide nitrate hydrates, TBP, water and nitric acid were used. Our research covered a wide range of concentration of REE nitrates and nitric acid. The mixtures under study were placed in separating funnels, then the content of funnels was mixed using shaker for 1 hour and the mixtures were left in the air thermostat for at least ten hours. After separating by decantation liquid phases were analyzed. The content of lanthanides in the aqueous phase was determined by ICP-AES and spectrophotometry methods. For determination of REE in the organic phase multistage re-extraction was used with further analysis of the extract. The content of nitric acid in the aqueous phase and water in the organic phase were determined by acid-base potentiometric and Fischer titration accordingly. Also densities of both phases were measured at 298 K.

As a result liquid-liquid equilibria data in the neodymium (samarium) nitrate – nitric acid – water – tributyl phosphate system were obtained and REE partition coefficients between aqueous and organic phases have been calculated. The current research is a part of the project devoted to the thermodynamic investigation of liquid extraction which is realized at the Laboratory of Chemical Thermodynamics, Lomonosov Moscow State University. And obtained liquid-liquid equilibria data in the next step of the work will be used for construction of the thermodynamic model of the water – nitric acid – lanthanide (Nd, Sm) nitrate – TBP system.

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### Section 3. Thermodynamics of solutions and heterogeneous systems

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#### THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS IN LANTHANUM ORTHOVANADATE – LANTHANUM ORTHOPHOSPHATE SYSTEM

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Rare-earth compounds have always been of interest because of such properties as high-temperature stability,  $\alpha$ -decay resistance and intriguing luminescent behavior. The ability to incorporate large amounts of ions and to form wide range of solid solutions allows flexible alteration of composition in order to change desired physico-chemical properties. For rare earth orthovanadates and orthophosphates aforesaid ability is partially due to their typical structure types: monazite and xenotime. While being basically quite similar, these structures differ in coordination number because of shift of planes in monazite occurring in order to accommodate larger RE ion and therefore a new RE–O bond appearing [1].

Accordingly, the conjunction of these anions in one structure can be of two variants: when unsubstituted substances tend to have one structure type or different types. Since complex rare earth vanadates–phosphates can be used in the elaboration of new advanced materials possible complications in preparation are undesirable. Thus, the possible predicting of target compound existence based on thermodynamic calculations should be studied. While reliable thermodynamic data for heat capacity measurement for unsubstituted compounds have begun to be rapidly acquired nowadays, these for solid solutions are still mostly missing.

Lanthanum orthovanadate – lanthanum orthophosphate system was chosen as a subject matter of the study. Continuous solid solution was obtained using solid state synthesis at 1000°C. Samples were characterized by means of XRD. Heat capacity of samples containing 25, 50 and 75 mol. % of vanadate anion was studied in low-temperature range by means of adiabatic calorimetry. The data acquired were then compared with these of pure  $\text{LaVO}_4$  [2] and  $\text{LaPO}_4$  [3]. Thermodynamic functions of 25, 50 and 75 mol. % solid solutions were determined.

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## CALPHAD ASSESSMENT OF AU–PD SYSTEM: A SIMPLE SYSTEM?

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Thermodynamic description of Au–Pd binary system is necessary for thermodynamic modeling of high-order systems containing gold and palladium.

Thermodynamic assessment of the system [1] does not account for last thermodynamic data, including the only experimental thermodynamic investigation of the liquid [2]. Calculations performed by authors of [2, 3] are based only on their own thermodynamic data. No new experimental works on phase equilibria or thermodynamics seem to appear after 1990.

The stable phases in the Au–Pd binary are liquid and fcc solid solution [1, 4]. Ordered phases AuPd<sub>3</sub>, AuPd and Au<sub>3</sub>Pd mentioned in published reference books were either observed in thin films (never in bulk samples) or inferred indirectly from short-range order data. Recent *ab initio* calculations (see, e.g., [5]) consistently give for those phases critical temperatures of disordering not exceeding (200–400)°C. So, those are hardly accessible for experiment and were not included in our assessment.

New assessment of the system is based on published data for both phase equilibria (liquidus and solidus data) and thermodynamics (enthalpies and activities of components in fcc phase and activities of components in the melt). We used PARROT module of the Thermo-Calc software system. For the fcc phase subregular model was dictated by thermodynamic data, whereas for liquid phase the Redlich–Kister polynomial expanded to quadratic term was inferred from [2]. For both phases the absence of temperature dependence of  $\Delta H$  and  $\Delta S$ , *i.e.* applicability of Neuman-Kopp's rule, was accepted.

Several sets of parameter values were obtained depending on relative weights ascribed to different thermodynamic data. Those are essentially indistinguishable as concerns to phase equilibria, but differ somewhat in the values of thermodynamic functions. The final choice was rather difficult; it was done by comparing results of extrapolation to calculation of liquidus surface of the Au–Cu–Pd ternary where sufficient experimental data exist [6].

Unusual and somewhat unexpected feature of Au–Pd system is the necessity of rather complicated model for the liquid phase. Indeed, the data for the binary itself could be described by subregular model with nearly the same precision but results extrapolating markedly worse.

Our attempts to describe the data for solid phase by physico-empirical model are also discussed.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC MODELING OF $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ SYSTEM

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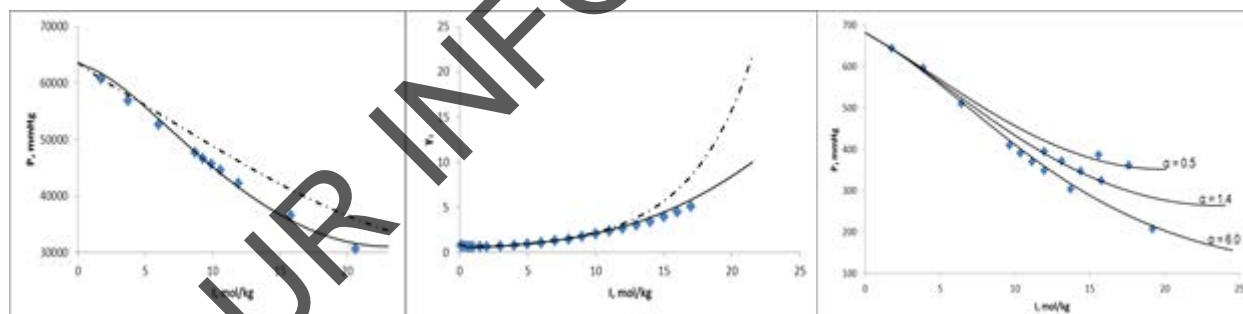
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The Bayer process is the first stage of the production of pure aluminum from bauxite. This process consists of several steps, the main result of which is the obtaining of aluminum. One of the problems of the Bayer process is to find out efficient methods for returning active alkali and aluminum to the cycle. The thermodynamic properties of liquid phase of the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  system are of great importance, because alkali and aluminum are the main components of aluminate solution of the Bayer process.

The aim of this work is to optimize parameters of thermodynamic model of  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  system liquid phase. The Pitzer model was used for the description of thermodynamic properties of solutions. Its parameters were obtained during the fitting of experimental data for  $\text{Na}_2\text{O}-\text{H}_2\text{O}$  and  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  systems separately.

**$\text{Na}_2\text{O}-\text{H}_2\text{O}$  system.** Parameters of the Pitzer model for the alkali concentration range 0 – 10 mol/kg and the temperature range (0–350)°C are presented in the literature [1], but alkali concentration can reach 15 mol/kg in the Bayer process. Therefore, the model parameters were optimized over a large number of experimental data. The results of optimization of Pitzer model parameters are shown in Figures 1,2. It should be noted, that 19 parameters were used in [1], while we were able to reduce this number to 11 statistically significant parameters in the present study.

**$\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  system.** Parameters of the Pitzer model were optimized in two steps: at the first step parameters were fitted to the vapor pressure data [2] and then to the solubility of gibbsite. The results of optimization are shown in Figure 3.



**Figure 1:** Vapor pressure over NaOH solutions, points – experimental data [2], dotted line – [1], solid line – present work.

**Figure 2:** Mean ionic activity coefficient of NaOH solutions, points – experimental data [3], dotted line – [1], solid line – present work.

**Figure 3:** Vapor pressure over NaOH–NaAl(OH)<sub>4</sub> solutions,  $\alpha$  – mole ratio NaOH to NaAl(OH)<sub>4</sub>, points – experimental data [2], solid line – present work.

The main result of this work is the thermodynamic model of the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  system which adequately describes available literature data on vapor pressure, activity coefficients, osmotic coefficients and solubilities in the ionic strength range (0–20) mol/kg and temperature (0–350)°C.

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## EXCESS ENTHALPY OF TERNARY SYSTEMS (*N*-PROPANOL + ACETIC ACID + WATER OR *N*-PROPYL ACETATE) AT 313.15 K

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The experimental investigation of thermochemical properties is of great importance because it gives an idea of non-ideality of mixtures, which is important for the development of new theoretical approaches in thermodynamics of heterogeneous systems. Also, the knowledge of such properties is essential for many industrial applications including organic synthesis. For example, the study of systems with esterification reaction is of well-known basic and practical importance, but the thermochemical properties of the quaternary reactive system (alcohol + carboxylic acid + ester + water) and constituent ternary and binary systems have been studied scarcely. The present research is a continuation of complex thermodynamic investigation of the system (*n*-propanol + acetic acid + *n*-propyl acetate + water). Earlier we have studied excess molar enthalpies of binary mixtures (*n*-propanol + acetic acid), (acetic acid + *n*-propyl acetate), and (*n*-propanol + *n*-propyl acetate) at  $T = 313.15$  K [1]. The goal of the present study was to determine excess enthalpies  $H^E$  for two homogeneous ternary systems: (*n*-propanol + acetic acid + water) and (*n*-propanol + acetic acid + *n*-propyl acetate) at  $T = 313.15$  K.

The species used in experiments were additionally purified by distillation. According to the chromatographic and refractometric analysis the content of the main substances in the samples was not less than 99.5 mol.%.

The measurements of the  $H^E$  values were carried out with the C80 calorimeter with membrane mixing cells manufactured by Setaram Instrumentation (France). The C80 calorimeter works on the Tian-Calvet heat flow principle. The apparatus and procedure were tested by determining excess enthalpies for the standard system (hexane + cyclohexane), and the results were found to differ by less than 3%.

The excess molar enthalpy  $H^E_{12+3}$  was determined for several pseudobinary mixtures in which component 3 (acetic acid) was added to binary mixtures of components 1 (*n*-propanol) and 2 (*n*-propyl acetate or water). For this purpose, binaries with fixed mole ratios,  $x_1/x_2$  (1:3, 1:1, 3:1), were prepared by mass. Then, excess molar enthalpy  $H^E_{123}$  of the ternary mixture was obtained from the relationship

$$H^E_{123} = H^E_{12+3} + (1-x_3)H^E_{12},$$

where  $x_3$  represents the mole fraction of acetic acid and  $H^E_{12}$  is the excess molar enthalpy of the particular binary mixture.

The experimental data for the ternary systems were fitted using the Redlich–Kister equation and the NRTL model.

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*Irina Letyanina acknowledges Saint Petersburg State University for a research grant (No. 12.50.1564.2013). Alexander Toikka is also grateful to the Russian Foundation for Basic Research (Project No. 15-03-02131). The experimental study has been carried out using the equipment of the Center of Thermal Analysis and Calorimetry of Saint Petersburg State University.*

## Section 3. Thermodynamics of solutions and heterogeneous systems

### MECHANISM OF CELLULOSE TRIACETATE FILMS STRUCTURE FORMATION IN THE COURSE OF SOLVENT VAPOR SORPTION

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At present the processes of structure formation in cellulose esters that possess increased rigidity of macromolecule chains attract much attention due to their ability to ordering and formation of liquid crystal (LC) state in solutions and melts, and in the presence of organic solvent vapors. Hydrogen bonds and donor-acceptor interactions play a significant role in the formation of the anisotropic state of polymer systems. This work was aimed at studying intra- and intermolecular interactions in cellulose triacetate (CTA) films in the course of sorption of vapors of solvents: dimethylsulfoxide (DMSO), nitromethane (NM) and tetrachloroethane (TCE), and their structures. The phase state of the systems was estimated by polarization microscopy and X-ray diffraction analysis. The mechanism of cellulose triacetate structure formation in the presence of solvents was studied combining the solvent vapors sorption by polymer film and *in situ* recording the IR spectra with a Nicolet 6700 Thermo Scientific Fourier IR spectrometer with following analysis of structure changes in macromolecules. The deconvolution of absorption bands of OH- and C=O-groups of macromolecules into components (by the PEAK RESOLVE program) showed that upon sorption of NM and DMSO vapors by CTA films the redistribution of different in nature intra- and intermolecular H-bonds in macromolecules takes place. The nature and rigidity of interchain associates and solvate complexes in CTA films containing NM and DMSO are discussed. The enthalpy of their formation is determined. The number of intramolecular and various types of intermolecular H-bonds in CTA films at different stages of solvent sorption is calculated. Their role in formation of the new structure of polymer film by solvents action is estimated. At the final stage of sorption, according to phase diagrams, in CTA-NM system at a polymer concentration 77% the crystalline and LC phase can exist, the CTA-DMSO system at 74% corresponds to two-phase region, in which isotropic and LC phases coexist. Anisotropic structures formation is confirmed by CTA films micrographs (in polarized light) before and after sorption of NM and DMSO vapors. The difference in interactions of solvents with CTA leads to changes in polymer films initial structure. Upon sorption of NM and DMSO, in diffraction pattern of CTA film, as opposed to initial film with amorphous structure, the reflections intrinsic to CTA II crystalline modification appear. Upon DMSO sorption, the CTA film has lesser ordering, while at TCE sorption no ordering occurs. The changes in CTA films structure in the course of solvent sorption are discussed from the viewpoint of competing interchain interaction of OH- and C=O-groups of macromolecules and their solvation by solvent molecules. The NM and DMSO molecules, which predominately solvate the polymer OH-groups, break the interchain H-bonds and favor the formation of highly ordered structures in CTA. The lesser ordering in CTA film by strong donor solvent DMSO (donor number  $DN_{SbCl5} = 28.9$ ) compared to NM ( $DN_{SbCl5} = 2.7$ ) is due to breaking the intramolecule H-bonds and  $O_{(3)}-H'_{(3)}\dots O_{(5)}$  and  $O_{(2)}-H_{(2)}\dots O'_{(6)}$  bonds between two neighboring pyranose circles of polymer chain that stabilize the rigid spiral conformations of cellulose esters. The TCE molecules mainly solvate the acetate groups, the content of which in CTA is fairly higher than that of OH-groups, which leads to destruction of the initial CTA structure. Thus, by the solvents action of various chemical nature, the CTA films with amorphous, crystalline, and LC structure remained even after desorption solvent vapors can be obtained.

*The study was performed within the framework of the State Task of the Ministry of Education and Science of the Russian Federation.*



THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS IN THE  $\text{Lu}_2\text{O}_3\text{-ZrO}_2$  SYSTEM STUDIED BY HIGH TEMPERATURE MASS SPECTROMETRY

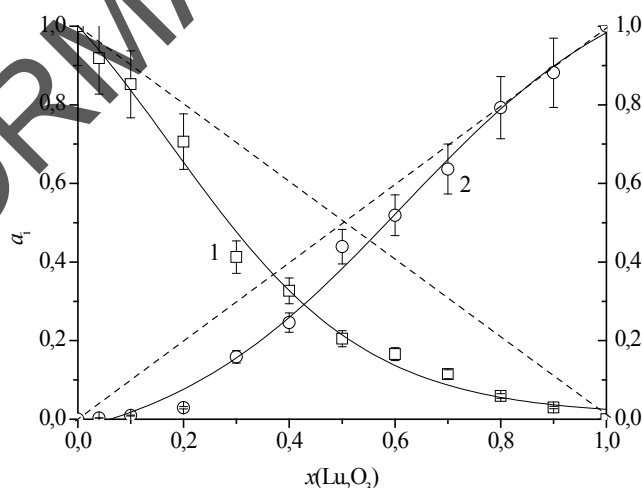
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Study of the vaporization processes and thermodynamic properties of solid solutions in the  $\text{Lu}_2\text{O}_3\text{-ZrO}_2$  system was carried out by the Knudsen effusion mass spectrometric method. Investigation was done using MS 1301 mass spectrometer at the ionization energy equaled to 30 eV. Vaporization of the samples under consideration was carried out from twin tungsten effusion cells heated by the electron bombardment. Temperature was measured by optical pyrometer EOP-66 with the accuracy  $\pm 5$  K over the temperature range (2650–2750) K.

The  $\text{Lu}^+$ ,  $\text{Zr}^+$ ,  $\text{LuO}^+$ ,  $\text{ZrO}^+$  and  $\text{ZrO}_2^+$  ions were detected in mass spectrum above  $\text{Lu}_2\text{O}_3\text{-ZrO}_2$  system. The mass spectrum analyses and appearance energies of ions in mass spectrum shown that the vapor over the  $\text{Lu}_2\text{O}_3\text{-ZrO}_2$  system consist of Lu, LuO, ZrO,  $\text{ZrO}_2$  and O molecules. The partial pressures of these vapor species were obtained using the ion current comparison method. We did not take into account the interactions between the sample and cell material because the products of interactions were observed at the beginning of evaporations only.

The  $\text{Lu}_2\text{O}_3$  activities in the  $\text{Lu}_2\text{O}_3\text{-ZrO}_2$  system at the temperature 2700 K were found by the differential mass spectrometric method using lutetium oxide as the standard of the determination of the component activities. The  $\text{ZrO}_2$  activities in the samples studied were calculated according to the Gibbs–Duhem equation. As seen from Figure the activities of lutetium oxide in all concentration range of condensed phase has low negative deviation from ideal case whereas zirconium dioxide activities has strong negative deviation from ideal case.



**Figure:** The  $\text{ZrO}_2$  (1) and  $\text{Lu}_2\text{O}_3$  (2) activities as the function of the mole fraction of  $\text{Lu}_2\text{O}_3$ . The dotted lines correspond to the ideal case.

## Section 3. Thermodynamics of solutions and heterogeneous systems

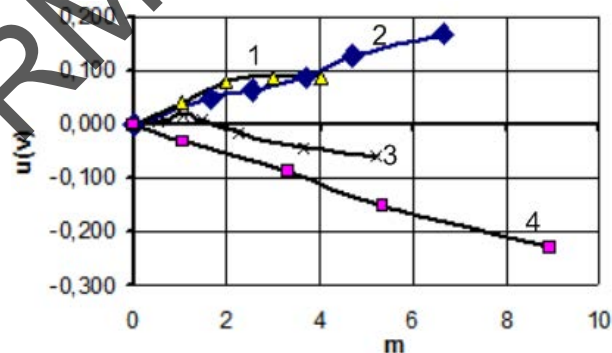
### TERMODYNAMIC AND RADIOBRIGHTNESS TEMPERATURES OF AQUEOUS SALT SOLUTIONS IN MILLIMETER RANGE OF WAVELENGTHS

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Thermodynamic equilibrium field of radiation exists inside a cavity with thermal insulated walls (absolute black body). A concept of radiobrightness temperature is used for real objects. The thermal radiation determines the differences between thermodynamic and radiobrightness temperatures. The radiation parameters are different for various substances (radiobrightness contrasts). They depend on temperature and frequency. In the millimeter frequency range radiobrightness coefficients are connected with ion conductivity and orientation dynamics of water molecules in the solution. As a result these parameters are important in theoretical and practical investigations (the distant monitoring of aqueous surfaces of the Earth). In the laboratory practice the radiobrightness temperatures can be measured more precisely by means of narrow band radiometers of millimeter's range. In our investigation the frequencies of 61.2 and 150 GHz were used. Methods to measure radiation of water and salts solutions were worked out. Some data of measurements at 150 GHz-frequency are presented in Figure. On the ordinate axis  $U(V)$  voltage values proportional to the changes of radiobrightness temperatures of objects are given.  $U(V)$  values are the differences between the radiation effects of a corresponding solution and water. On the absciss axis the molality of solutions is given.



**Figure:** The differences of radiation effects  $U(V) = U(V)_{sol} - U(V)_{water}$  at 150 GHz. Solutions: 1 – KCl, 2 –  $NH_4Cl$ , 3 – NaCl, 4 – LiCl.

The results for water and the solutions of alkali metals, ammonium and magnesium chlorides at frequencies of 61.2 and 150 GHz are presented. It is shown that the radiation of solutions of potassium, rubidium, cesium and ammonium chlorides is stronger than the radiation of the distilled water and the radiation of lithium, magnesium and partly sodium chloride solutions is less than the radiation of distilled water. So the signs of the change of radiation of water in solutions can be different.

The connection of above mentioned parameters and dielectric properties in centimeter and millimeter range of wavelengths is considered. It is determined by hydration effects of different signs (different structural temperature of ions, negative and positive hydration). As a result a new in the laboratory practice method of the researching of aqueous salt solutions and the determining their radiobrightness contrasts is proposed. It is based on the radiation characteristics determined with the help of the highly sensitive radiometers in the millimeter range of wave.

**THERMODYNAMICS OF SOLVATION OF N-OCTANE AND TOLUENE  
IN MIXTURES OF WATER WITH TETRAHYDROFURAN**

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Thermodynamic functions (enthalpies, entropies and Gibbs free energies) of solvation of *n*-octane and toluene in binary mixtures of water with tetrahydrofuran with various compositions have been determined at 298.15 K. Enthalpies of solution were obtained by means of precision titration calorimetry, and the Gibbs free energies of solvation were calculated from limiting activity coefficients determined using headspace analysis technique. The most interesting feature is a sharp maximum on the plot of the enthalpy of solvation against the molar fraction of water. In water-rich mixtures, the enthalpy of solvation is higher than in either pure water or tetrahydrofuran. Possible molecular origins of such behavior were considered. Gibbs free energy vs enthalpy plots were also considered and compared with those for the same solutes in various individual solvents.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC MODELLING OF THE $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ SYSTEM

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The glass forming  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system is one of the most important systems in glass technology due to specific physical and chemical properties (low thermal expansion coefficient, high chemical stability etc.). While melting in industrial glass furnaces, some components (sodium, boron etc.) volatilize from the glass melt surface. This evaporation process could cause some nugatory consequents such as furnace material degradation. Thus an investigation of the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system thermodynamic properties is an actual problem.

The aim of the research is thermodynamic modelling of condensed phases in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system for further description of liquid–vapour data.

An optimization of thermodynamic model parameters in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  ternary system and constituent binary subsystems in the wide temperature range was carried out to obtain self-consistent and reliable description of all thermodynamic data available in the literature. Excess Gibbs energy of the liquid was described by the combination of Redlich-Kister polynomials. Gibbs energies of formation of  $x\text{Na}_2\text{O}\cdot y\text{B}_2\text{O}_3$ ,  $x\text{Na}_2\text{O}\cdot y\text{SiO}_2$  binary compounds were approximated by means of  $\Delta_f G^{\text{ox}}(T) = A + BT + C \ln T$  functions. All optimization subroutines were written in the MATLAB programming language. The software packages PhDi [1] and TernAPI [2] developed in the laboratory of chemical thermodynamics of MSU were applied for plotting binary and ternary phase diagrams.

Obtained thermodynamic models of the phases are in a good agreement with existing data about the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  phase diagram and activity coefficients of  $\text{Na}_2\text{O}$  and  $\text{B}_2\text{O}_3$  in the corresponding binary subsystems.

Optimized model of the liquid phase was used for calculation of vapour–liquid equilibrium by means of FactSage software complex [3]. Obtained results are in a better agreement with the experimental vapour pressures measured in the research laboratory Saint-Gobain Recherche (France) than original data from FactSage databases.

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### THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIA IN THE MIXTURES OF WATER, NITRIC ACID, TRIBUTYL PHOSPHATE AND RARE EARTH NITRATES (Nd, Sm, Pr)

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Nowadays compounds of rare earth elements are widely used in different sectors of industry. Tri-*n*-butyl phosphate extraction in water–organic solvents is one of the most popular method of extraction and separation of lanthanoid compounds. Process conditions usually base on experimental data and are adjusted empirically. To optimize extraction process composition and quantities of coexisting aqueous and organic phases are required. Thermodynamic modelling is quite efficient method for obtaining this type of data. The aim of this work is to construct thermodynamic model of the systems containing water, tributyl phosphate, nitric acid and neodymium, samarium and praseodymium nitrates.

Experimental data for the binary subsystems water – tri-*n*-butyl phosphate, water – nitric acid and water – rare earth nitrate are presented in the literature. Information about thermodynamic properties of the components of ternary subsystems water – nitric acid – rare earth nitrate and water – tributyl phosphate – nitric acid is absent. Therefore, partial vapor pressure of the water was measured in these ternary systems by transpiration method at 298.15 K and water activities were calculated. In addition, liquid–liquid equilibria was studied in the quaternary systems water – tributyl phosphate – nitric acid – rare earth nitrate systems at 298.15 K.

The electrolyte version of generalized local composition model was used for the description of thermodynamic properties of solutions. This model generalizes well-known local composition models such as UNIQUAC, Wilson and Tsuboka – Katayama, effect of electrolytes is taken into account by means of Debye–Huckel and polynomial Pitzer-type terms.

Parameters of the model were fitted using experimental data of the water – tri-*n*-butyl phosphate system (water activities, liquid–liquid equilibria, mixing enthalpies), water – nitric acid system (vapour–liquid equilibria, solid–liquid equilibria, dilution and dissolution enthalpies), water – rare earth nitrate systems (water activities), water – tributyl phosphate – nitric acid system (liquid–liquid equilibria, vapour–liquid equilibria), water – nitric acid – rare earth nitrate systems (vapour–liquid equilibria) and water – tributyl phosphate – nitric acid – rare earth nitrate systems (liquid–liquid equilibria). The estimation of model parameters was performed by minimization sum of squares of residuals. 95% confidence intervals for parameters were calculated, only statistically significant parameters are used.

In this work strict and detailed thermodynamic description of the water – tri-*n*-butyl phosphate, water – tributyl phosphate – nitric acid and water – tributyl phosphate – nitric acid – rare earth nitrate systems was obtained for the first time. These models could be used for prediction phase equilibria in solutions containing several rare earth nitrates, it would be helpful for development of effective technology of rare earth elements compounds separation.

*This research work was financially supported by the URALCHEM Holding.*

## Section 3. Thermodynamics of solutions and heterogeneous systems

### SULFONYL DERIVATIVES OF THE GEWALD-TYPE THIOPHENES AS POTENTIAL COLLECTORS FOR IONIC FLOTATION OF NONFERROUS METALS

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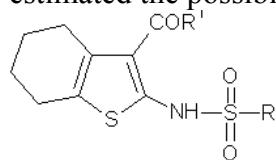
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Ionic flotation (IF) is one of the perspective methods for concentration of nonferrous metals from a different technological solutions [1]. The development of new effective reagents is very important for improving the effectiveness of ion flotation. At this case thiophene derivatives are of great interest.

The *N*-substituted sulfonyl thiophene derivatives of the Gewald (STG) (Figure) were chosen due to the presence of electron-donor atoms (N, O), that were anticipated to form chelates nonferrous metals. STG have also sulfonyl group, which provides surfactant properties of ligands. STG have simple structure and well known method of producing [2].

In this work we have studied process of STG complexing with nonferrous metals as well as we estimated the possibility of their application in flotation technology.



R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>-p), C<sub>6</sub>H<sub>4</sub>Cl-p, C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>-p), C<sub>6</sub>H<sub>4</sub>(NHCOCH<sub>3</sub>-p)  
R' = OC<sub>2</sub>H<sub>5</sub>, NH<sub>2</sub>, OH, NHC<sub>6</sub>H<sub>5</sub>

**Figure:** *N*-substituted sulfonyl thiophene derivatives of the Gewald.

It was found that reagents form ions with Cu(II), Co(II), Ni(II), Cd(II) and Zn(II) in ammoniac solutions complex compounds, ratio [M(II)] : [HL] = 1 : 2, pH values 7.5–9.5. Complexes of STG with nonferrous metals have been isolated and identified. We have calculated the solubility products SP of the prepared complexes:  $K_{sp} \text{ CuL}_2 = 8.4 \cdot 10^{-18}$ ,  $K_{sp} \text{ CoL}_2 = 1.37 \cdot 10^{-14}$ ,  $K_{sp} \text{ NiL}_2 = 9.49 \cdot 10^{-17}$ ,  $K_{sp} \text{ ZnL}_2 = 5.23 \cdot 10^{-18}$ ,  $K_{sp} \text{ CdL}_2 = 5.23 \cdot 10^{-14}$ . The  $-\lg$  SP complexes of compounds was linear with the Hammett constant  $\sigma$ . This dependence allows to predict the solubility of complexes of a number of new reagents.

Low solubility of the complexes in water, good solubility of the reagents in aqueous alkaline solutions and their high hydrolytic stability in alkaline conditions allow to use the studied compounds as promising collectors for ionic flotation of nonferrous metals.

A possibility of using STG reagents as collectors for ionic flotations has been investigated. Optimal conditions of ionic flotation such as pH range, flotation time and consumption of reagents have been studied.

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## INFLUENCE OF LANTHANOID RADIUS ON LATTICE ENERGY OF BISMUTH–RENIUM–LANTHANOID OXIDES

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Compounds on the basis of bismuth oxides possess a wide set of unique properties and are of interest for use in various areas. The delta-form of bismuth oxide ( $\delta$ -Bi<sub>2</sub>O<sub>3</sub>) is a perspective material for applications in electrochemical devices such as high-purity oxygen generators and electrochemical sensors. In pure Bi<sub>2</sub>O<sub>3</sub> the  $\delta$ -phase is only stable over a narrow temperature range (1100–1200 K) and much work has been carried out on stabilization of this phase to room temperature through solid solution formation with other oxides. A new perspective family of composition Bi<sub>12.5</sub>Ln<sub>1.5</sub>ReO<sub>24.5</sub> has been prepared recently. These compounds exhibit exceptionally high oxide ion conductivity at low temperatures.

This work is devoted to the estimation of the dependence of lattice energies for Bi<sub>12.5</sub>Ln<sub>1.5</sub>ReO<sub>24.5</sub> (Ln = La, Nd, Sm, Gd, Dy, Ho, Lu) on  $1/r_{Ln}$  ( $r_{Ln}$  – ionic radius of lanthanoid).

We prepared a series of new compounds with the general formula Bi<sub>12.5</sub>Ln<sub>1.5</sub>ReO<sub>24.5</sub> for Ln = La, Nd, Sm, Gd, Dy, Ho, Lu, Yb. The compounds were synthesized by solid state reactions from mixtures of Bi<sub>2</sub>O<sub>3</sub>, NH<sub>4</sub>ReO<sub>4</sub>, and Ln<sub>2</sub>O<sub>3</sub> or Bi<sub>2</sub>O<sub>3</sub>, Re<sub>2</sub>O<sub>7</sub>, and Ln<sub>2</sub>O<sub>3</sub>. The powders were mixed in an agate mill and then pressed in pellet and treated at 1100 K. Analysis of the obtained samples was performed by X-ray fluorescence analysis, X-ray and neutron diffraction. Thermochemical data were measured by solution calorimetry in a calorimeter with an isothermal jacket.

As there is no data on lattice energy for Bi<sub>12.5</sub>Ln<sub>1.5</sub>ReO<sub>24.5</sub> in literature we calculated the lattice energy for Bi<sub>12.5</sub>Ln<sub>1.5</sub>ReO<sub>24.5</sub> (Ln = La, Nd, Sm, Gd, Dy, Ho, Lu) using our experimental data on standard formation enthalpies. We used a Born–Haber cycle for calculation.

To construct the dependence of the lattice energy on structural parameters we used the Kapustinskii formula which connects lattice energy with structural parameters suggesting that there is ionic binding. After some mathematic transformations for our compounds Bi<sub>12.5</sub>Ln<sub>1.5</sub>ReO<sub>24.5</sub> the Kapustinskii formula can be written as following:  $U = A + B/r_{Ln}$ . On the basis of data calculated by us we constructed the dependence U versus  $1/r_{Ln}$ . For the series of Bi<sub>12.5</sub>Ln<sub>1.5</sub>ReO<sub>24.5</sub> compounds there is practically a linear dependence of lattice energies on  $1/r_{Ln}$ . Using this dependence we calculated the lattice energy of the compound Bi<sub>12.5</sub>Yb<sub>1.5</sub>ReO<sub>24.5</sub>:  $-125020 \text{ kJ}\cdot\text{mol}^{-1}$ . Then we measured formation enthalpy for Bi<sub>12.5</sub>Yb<sub>1.5</sub>ReO<sub>24.5</sub> with solution calorimetry. The lattice energy on the basis of experimental data for Bi<sub>12.5</sub>Yb<sub>1.5</sub>ReO<sub>24.5</sub> was calculated as  $-125063 \text{ kJ}\cdot\text{mol}^{-1}$ .

As it is possible to see the values are the same within limits of 0.03% which demonstrates that the dependence U versus  $1/r_{Ln}$  allows one to estimate the lattice energy for unknown compounds of the Bi<sub>12.5</sub>Ln<sub>1.5</sub>ReO<sub>24.5</sub> series with high accuracy.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### FORMATION ENTHALPY OF STRONTIUM CERATE DOPED BY EUROPIUM

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The most well-known materials for solid oxide fuel cells are perovskite oxides with large basic A cations (Ba, Sr) and tetravalent B cations (Zr, Ce). Doped alkaline earth cerates and zirconates exhibit proton conductivity at elevated temperatures due to the water vapor decomposition and mobile protons formation. Perovskites based on SrCeO<sub>3</sub> doped with Ln offer more moderate levels of proton conductivity in comparison to Ba-containing analogues but with much lower oxygen ion conductivity. This is a principal reason for employing SrCeO<sub>3</sub> system in HTPC-based sensor and membrane applications. In general, the sealing material should be thermally and chemically stable under SOFC operational conditions. Therefore, the study of chemical, thermodynamic and thermal stabilities of HTPC materials is an important task.

This work is devoted to the thermodynamic investigation of SrCeO<sub>3</sub> doped by Lu<sub>2</sub>O<sub>3</sub> to determine the standard formation enthalpy and other thermochemical characteristics.

We synthesized compound SrCe<sub>0.9</sub>Eu<sub>0.1</sub>O<sub>2.95</sub> by solid state reactions from mixtures of SrCO<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>. We characterized the obtained sample by X-ray fluorescence and X-ray diffraction analysis. Sample has orthorhombic structure. We used solution calorimetry for measurement of thermochemical data.

We created two thermochemical cycles to determine formation enthalpy of SrCe<sub>0.9</sub>Eu<sub>0.1</sub>O<sub>2.95</sub>. The first cycle was based on solution of investigated sample in 1 M HCl + 0.1 M KI and comparison obtained solution enthalpy with solution enthalpy of chlorides mixture (SrCl<sub>2</sub>, CeCl<sub>3</sub>, EuCl<sub>3</sub>).

For second cycle we solved SrCe<sub>0.9</sub>Eu<sub>0.1</sub>O<sub>2.95</sub> in above mentioned solvent and compare with solution enthalpy of mixture SrCO<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub>. Standard formation enthalpy for strontium cerate doped by europium was calculated on the basis of experimental data using necessary literature data. The values  $\Delta_f H^\circ(\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{2.95}, 298.15 \text{ K})$  calculated on both cycles are agree within an error of experimental data.

Then we calculated lattice energy of SrCe<sub>0.9</sub>Eu<sub>0.1</sub>O<sub>2.95</sub> on the basis of obtained formation enthalpy using Born–Gaber cycle and compared this value with lattice energy of SrCe<sub>0.9</sub>Lu<sub>0.1</sub>O<sub>2.95</sub> which was investigated earlier by us [1]. Comparison shoed that lattice energy is increased on absolute value with decreasing lanthanides radius, i.e. from SrCe<sub>0.9</sub>Eu<sub>0.1</sub>O<sub>2.95</sub> to SrCe<sub>0.9</sub>Lu<sub>0.1</sub>O<sub>2.95</sub>.

We also discussed the symmetry of the crystal structure of prepared Eu-doped SrCeO<sub>3</sub> (SrCe<sub>0.9</sub>Eu<sub>0.1</sub>O<sub>2.95</sub>) and SrCe<sub>0.9</sub>Lu<sub>0.1</sub>O<sub>2.95</sub>. We compared the lengths of pseudo cubic cell, i.e.  $a:\sqrt{2}$ ,  $b:2$ ,  $c:\sqrt{2}$ , and some functions of them for SrCe<sub>0.9</sub>Eu<sub>0.1</sub>O<sub>2.95</sub> and SrCe<sub>0.9</sub>Lu<sub>0.1</sub>O<sub>2.95</sub>. As it was follows from our analysis that differences of parameters, namely  $(a:\sqrt{2} - b:2)$ ,  $(b:2 - c:\sqrt{2})$ ,  $(c:\sqrt{2} - a:\sqrt{2})$  are smaller for SrCe<sub>0.9</sub>Lu<sub>0.1</sub>O<sub>2.95</sub>. It means that SrCe<sub>0.9</sub>Lu<sub>0.1</sub>O<sub>2.95</sub> has higher crystal symmetry than SrCe<sub>0.9</sub>Eu<sub>0.1</sub>O<sub>2.95</sub>. It correlated with fact that ion radius of Lu<sup>3+</sup> (0.0861 nm) is more close to ion radius of Ce<sup>4+</sup> (0.087 nm) than ion radius of Eu<sup>3+</sup> (0.0947 nm).

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HEAT CAPACITY OF BISMUTH-RENIUM OXIDE DOPED BY LUTETIUM  
IN THE TEMPERATURE RANGE OF (175–740) KN.I. Matskevich<sup>1,2</sup>, Th. Wolf<sup>2</sup>, D.P. Pishchur<sup>1</sup>, S.G. Kozlova<sup>1</sup>, T.P. Adamova<sup>1</sup><sup>1</sup>*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences  
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The stabilized bismuth oxides are ones of the materials to be used for ceramic oxygen generators, electro catalysts and as an electrolyte in fuel cells operated at lower temperatures. They belong to the promising ionic conductors. The conductivity is up to two orders of magnitude greater than that in stabilized zirconia. However, the high conductivity phase is stable over narrow range of temperature (1000–1100 K). The new compounds of general formula  $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$  were discovered earlier. For perspective application of these compounds it is necessary to perform full physico-chemical investigation of above mention materials.

Our work is devoted to determination of  $\text{Bi}_{12.5}\text{Lu}_{1.5}\text{ReO}_{24.5}$  heat capacity in the temperature range of (175–740) K. We measure heat capacity for the first time. We synthesized  $\text{Bi}_{12.5}\text{Lu}_{1.5}\text{ReO}_{24.5}$  by solid state reaction from mixtures of  $\text{Bi}_2\text{O}_3$ ,  $\text{NH}_4\text{ReO}_4$ , and  $\text{Lu}_2\text{O}_3$ . The powder was mixed; pressed in pellet and treated at 1100 K. Analysis of the obtained sample was performed by X-ray fluorescence analysis, X-ray and neutron diffraction. Compound has cubic structure (space group  $\text{Fm}\bar{3}\text{m}$ ). Heat capacity was measured by comparison method using DSC 204 F1 Phoenix in the temperature range of (175–740) K. DSC measurements of sample and standard of  $\text{Al}_2\text{O}_3$  were performed by heat flow measurement method at a constant heating rate of 6 K/min in open aluminum crucible in 25 ml/min Ar flow. The baseline signal obtained by heating 2 empty crucibles was subtracted from the experimental results of samples.  $\text{Al}_2\text{O}_3$  was used as standard to calculate heat capacity. Before measuring  $\text{Bi}_{12.5}\text{Lu}_{1.5}\text{ReO}_{24.5}$  we measured heat capacity of  $\text{Bi}_2\text{O}_3$  to check our method. The measurement was carried out in the temperature range of (175–740) K.  $\text{Al}_2\text{O}_3$  was used as standard for calculation. Then we compare our experimental data on heat capacity with literature data [1, 2]. In paper [1] low temperature heat capacity of  $\text{Bi}_2\text{O}_3$  was measured by adiabatic method in the temperature range of (60–300) K. In paper [2] enthalpy and entropy increments were measured in the temperature range of (300–1070) K by drop calorimeter. Comparison showed that within limits 1.5% our and literature data are agree. Measurement of  $\text{Bi}_{12.5}\text{Lu}_{1.5}\text{ReO}_{24.5}$  heat capacity showed that from 175 up to 560 K the curve of heat capacity is smooth (Figure). Measurements were taken several times and were reproduced. The error of experiment was 2%. We observed anomaly higher than 560 K. We calculated heat capacity of bismuth–rhenium oxide doped by lutetium at standard temperature:  $C_p^\circ(298.15\text{ K}) = 881.2 \pm 17.6\text{ J/K}\cdot\text{mol}$ . Comparison of experimentally obtained value and heat capacity estimated as sum of binary oxides (870.7 J/K·mol) showed that values are agree within 1%.

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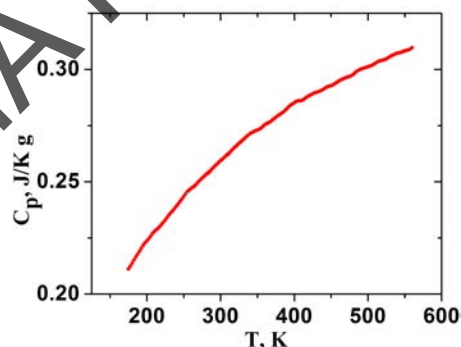


Figure: Heat capacity of  $\text{Bi}_{12.5}\text{Lu}_{1.5}\text{ReO}_{24.5}$ .

## Section 3. Thermodynamics of solutions and heterogeneous systems

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### AZEOTROPE IN BINARY MIXTURE OF *n*-HEPTANE–WATER

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At the ambient conditions, the binary mixture of *n*-heptane – water is heterogeneous, which was having a wide region of separation by temperature and pressure. This is meaning that the system is in three-phase state 11-12-v, with boundary between phases.

Isochoric heat capacity studies were carried out in automated device high-temperature adiabatic calorimeter-piezometer [1].

The temperature dependence of the Isochoric heat capacity and pressure of the system [ $x$  H<sub>2</sub>O + (1- $x$ ) C<sub>7</sub>H<sub>16</sub>] at the  $x = \text{const}$ , were carried by the isochors in the density range (146.0–501.5) kg/m<sup>3</sup> in the temperature range of (373–540) K and pressures up to 10 MPa.

The limited solubility of hydrocarbons and water leads to the mixture of these components has a region three-phase separation. The temperature dependence of the Isochoric heat capacity and pressure along isochors is measured from three-phase state area at the increasing temperature. The two phase transition of liquid–vapor as well as liquid–liquid were observed by isochors at  $\rho = \text{const}$ . These features were fixed by correspondingly jumps on the temperature dependences of isochoric heat capacity and pressure-depend breaks and kinks. For a mixture of [ $x$  H<sub>2</sub>O + (1- $x$ ) C<sub>7</sub>H<sub>16</sub>] with  $x = \text{const}$ , the isochors  $\rho = \rho_{\text{az}}$  on temperature -depend isochoric heat capacity, where occurred one jump of heat capacity, as well as one break on the pressure–temperature dependence was observed. We believe that this density ( $\rho_{\text{az}}$ ) is corresponding to the state of azeotrope.

The parameters of the azeotrope state for *n*-heptane – water system at the studied range were defined. The effect of concentration of polar component on the temperature shifts of azeotrope state was defined. The line of azeotropic equilibrium was plotted.

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## THERMODYNAMIC PROPERTIES OF TERNARY SOLUTIONS IN THE WATER – NITRIC ACID – RARE EARTH NITRATE (PR, ND, SM) SYSTEMS

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Rare Earth Elements (REE) are vital for the manufacturing of modern high-tech products. Commonly high-purity specific REEs are produced by liquid extraction of their salts with an organic extraction agent. However thermodynamic properties of phases in extraction systems described in the literature are odd, estimated and inconsistent even for aqueous ones. Thermodynamic model of multi-component water–organic salt system is relevant for optimization of REE salts separation conditions. A choice of suitable thermodynamic models and optimization of their parameters for binary systems followed by transition to a system of higher order allows simplifying the problem significantly and decreasing time required for its solution. So, the aim of present work is studying the thermodynamic properties of aqueous solutions of nitric acid and light- or medium-REE nitrate (praseodymium, neodymium, samarium). Physico-chemical properties and thermodynamic models of binary water solutions of nitric acid and Pr, Nd, Sm nitrates are presented in the literature [1, 2], but there are no experimental or theoretical investigations of the ternary systems.

A convenient way to obtain thermodynamic properties of the components in any system is vapor pressure measurements. Here we used transpiration method. In this method a current of inert gas is passed over thermostatic saturator filled with the sample at a rate sufficiently low for equilibrium conditions to be established and carries the vapor of the sample away, which is then collected in a cold trap. Partial pressures of the components can be calculated assuming Dalton's law is valid and the weight of condensate, the volume of transporting gas and atmospheric pressure are provided. Experimental unit similar to described in [3] was set up. Vapor pressures over rare earth nitrates and nitric acid aqueous mixtures up to concentrations of 3 and 20 mol.% respectively were measured at  $25 \pm 0.02^\circ\text{C}$  within the accuracy of 1%. The purity of substances was chemical grade. Concentrations of REE nitrates and nitric acid in the initial solution and condensate were determined by acid-base and potentiometric titration and ICP-AES.

The activity of water calculated from measured vapor pressures was compared with the ones estimated using Mikulin–Zdanovsky method and eGLCM (electrolyte version of generalized local composition model). This model is developing in the laboratory of chemical thermodynamics of Lomonosov MSU Chemical Department and generalizes well-known local composition models accounting the effect of electrolytes by means of Debye–Huckel and polynomial Pitzer–type terms. The binary interaction parameters obtained in our lab as a result of recalculation of subsystem properties by eGLCM were utilized only. The difference between our experimental and calculated data was less than 1% in the former case and 2.5% in the latter one.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### THE CALCULATION OF THE COORDINATES EUTECTIC POINT OF MnS – Tb<sub>2</sub>S<sub>3</sub> SYSTEM

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There is complicated interaction in MnS–Tb<sub>2</sub>S<sub>3</sub> system at temperatures below 1400 K. The complex sulphide MnTb<sub>4</sub>S<sub>7</sub> is formed by solid-phase reaction. The subsolidus part of the phase diagram refers to the eutectic type. Therefore it is possible to apply the equations Schroeder–Le Chatelier and Van Laar [1, 2] to system. This equations will allow to calculate the coordinates of the eutectic point and liquidus line the position in high-temperature area. The Schroeder–Le Chatelier equation (1) is used for systems without the formation of solid solutions or with a minimum area of a solid solution, the ions form a solid solution must be isomorphic.

$$T_E = \frac{1}{\left[ \frac{1}{T_m^A} - \frac{R}{\Delta H_m^A} \ln x_A^E \right]} \quad (1)$$

$$T_E = \frac{1}{\left[ \frac{1}{T_m^A} - \frac{R}{\Delta H_m^A} \ln \frac{x^L}{x^S} \right]} \quad (2)$$

where is  $x_A^E$  the mole fraction of component A in eutectic;  $\Delta H_m^A$  is the heat of melting of component A, kJ/mol;  $T_m^A$  is the melting temperature of component A, K; and  $R$  is the universal gas constant (8.31 kJ/(mol K)),  $x^L$  and  $x^S$  the compositions of the solid and liquid phases.

The MnS–Tb<sub>2</sub>S<sub>3</sub> system on the basis of MnS and Tb<sub>2</sub>S<sub>3</sub> forms solid solutions. Solubility at 1570 K on the base manganese monosulfide is 6 mol.% Tb<sub>2</sub>S<sub>3</sub>, on the base  $\gamma$ -Tb<sub>2</sub>S<sub>3</sub> – 16 mol.% MnS. Van Laara's equation (2) includes values of compositions of a liquid and solid phases. Therefore the equation (2) can be applied to systems with formation of areas of homogeneity. The calculation of the eutectic temperature is possible by knowing its composition or on the crossing point the left and right branches of the liquidus line, as calculated according to equations (1) and (2). Calculation of the eutectic temperature carried out separately from the data for MnS and Tb<sub>2</sub>S<sub>3</sub> (Table).

**Table.** The melting point of the eutectic in the MnS–Tb<sub>2</sub>S<sub>3</sub> system, calculated from the equations of Schroeder (1) and Van Laar (2)

Equation for calculate temperature of the eutectic, K	$T_{\text{melt}}$ , K	
	Schroeder	Van Laar
MnS: $x_A^E = 0.73$ , $\Delta H_m^A = 6.1$ kJ/mol [2], $x^L = 0.73$ , $x^S = 0.92$	1584	1645
Tb <sub>2</sub> S <sub>3</sub> : $x_A^E = 0.27$ , $\Delta H_m^A = 94$ kJ/mol [2], $x^L = 0.27$ , $x^S = 0.84$	1656	1700

The melting temperature of the eutectic is 1663 K. It was determined experimentally by differential scanning calorimetry. The closest to the experimental value melting temperature of the eutectic calculations were carried out by Van Laar and Schroeder equations according to the liquidus branches from Tb<sub>2</sub>S<sub>3</sub> (Table).

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CONCENTRATION DEPENDENCE OF THERMODYNAMICAL, STRUCTURAL AND PHYSICAL PROPERTIES OF  $(\text{TlInSe}_2)_{1-x}(\text{TlGaTe}_2)_x$

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Roentgenographic data of source ternary compounds and samples of compositions of  $\text{TlInSe}_2\text{--TlGaTe}_2$  system indicate that both compounds and studied samples crystallize in the  $\text{TlSe}$  type tetragonal syngony, which is consistent with the literature data.

To determine the concentration dependence of the change in Gibbs free energy of the alloys of  $\text{TlInSe}_2\text{--TlGaTe}_2$  system we conducted a thermodynamic analysis based on data of physico-chemical analysis. Equation of temperature and concentration dependence of the Gibbs free energy of formation of alloys is obtained from the Gibbs–Helmholtz equation by using the ideal solution model, including nonmolecular compounds.

Using the thermodynamic quantities and function accounting for configurational entropy of mixing nonmolecular compounds for  $(\text{TlInSe}_2)_{1-x}(\text{TlGaTe}_2)_x$ , gives us:

$$\begin{aligned} \Delta G_T^0 \text{ (kJ/mol)} = & -227(1-x) - 178x + 38 \cdot 10^{-3} T(1-x) + 4.6 \cdot 10^{-3} T \cdot x + \\ & + 24.93 \cdot 10^{-3} T [(1-x) \ln(1-x) + x \ln x] - \\ & - 27x(1-x)^3 \cdot 10^{-3} T \left[ \ln \left( \frac{T}{298.15} \right) + \left( \frac{298.15}{T} \right) - 1 \right]. \end{aligned}$$

Here, the fifth and sixth members represent the Gibbs free energy of mixing of solid solutions  $(\text{TlInSe}_2)_{1-x}(\text{TlGaTe}_2)_x$ , i.e., the Gibbs free energy of formation of solid solutions from ternary compounds.

Experimental data show that  $E_g = f(x)$   $(\text{TlInSe}_2)_{1-x}(\text{TlGaTe}_2)_x$  diagram as well as the lattice constants is characterized by the concave curves. The dependence of band gap on the  $(\text{TlInSe}_2)_{1-x}(\text{TlGaTe}_2)_x$  composition is approximated by the following equation:

$$E_g(x) = xE_g^A + (1-x)E_g^B - x(1-x)E_b,$$

where  $E_b$  is the slope of the energy on the  $E_g = f(x)$  diagram.

### Section 3. Thermodynamics of solutions and heterogeneous systems

#### ENTHALPY OF ACRYLIC GLUE COMPOSITION HARDENING UNDER THE ACTION OF THE INITIATING SYSTEM CONTAINING TRIALKYLBORANE AND AMINES COMPLEXES

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Using microcalorimeter type Calve DAC-1A, the processes of hardening of acrylate glue composition under the influence of the initiating system  $R_3B$  ( $R = Et, Pr$ ) – amine ( $NH_2(CH_2)_6NH_2$  or  $CH_3O(CH_2)_3NH_2$ ), depending on the molar ratio of  $R_3B$  and amine were studied. It is found that for these systems the nature of thermokinetic curves of the process of hardening depends on the type of introduced amine. It is shown that, for example for  $CH_3O(CH_2)_3NH_2$ , a large part of the heat dissipation occurs in the first 30–60 minutes, and in the case of  $NH_2(CH_2)_6NH_2$  – in the first 20 minutes. After 200–250 minutes heat dissipation is set at the level of the background and practically is not observed. For the system  $CH_3O(CH_2)_3NH_2$  (1:1) a small constant heat dissipation yet is observed within 10–15 hours. The change of the ratio of boron and nitrogen in the initiator  $Et_3B \cdot NH_2(CH_2)_6NH_2$  ( $B:N = 1:1, 1:2, 1:1.5$ ) increases the time of hardening of the studied acrylate glue composition. The effect of small additives of quinones (*n*-benzoquinone, naphthoquinone, anthraquinone) and peroxides (dibenzoyl- and dilauroylperoxide, *t*-BuOOH), that provide a high degree of conversion of the monomer acrylate composition, was studied. The enthalpies of hardening of acrylate glue composition under the action of the initiating systems studied are shown in Table.

**Table.** Enthalpies ( $\Delta_r H^\circ$ ) of acrylic glue composition (AGC) hardening under the action of the initiating system containing complexes of trialkylborane and amines,  $T = 298.15 K$

No	The structure of the complex	B:N	$-\Delta_r H^\circ$ , kJ/(rel. mol AGC)
1	$Pr_3B \cdot CH_3O(CH_2)_3NH_2$	1:1	35.4±0.4
2	$Et_3B \cdot CH_3O(CH_2)_3NH_2$	1:1	46.0±0.5
3	$Pr_3B \cdot 0.5NH_2(CH_2)_6NH_2$	1:1	16.0±0.3
4	$Et_3B \cdot 0.5NH_2(CH_2)_6NH_2$	1:1	24.5±0.5
5	$Et_3B \cdot 0.75NH_2(CH_2)_6NH_2$	1:1.5	26.5±0.6
6	$Et_3B \cdot NH_2(CH_2)_6NH_2$	1:2	17.5± 0.7

On the basis of the data obtained, the initiating system  $Et_3B - NH_2(CH_2)_6NH_2$  with a molar ratio of  $B:N = 1:0.5$  is selected for the bonding of thermoplastic materials with low surface energy. It is also shown that small additions of para-benzoquinone, naphthoquinone, anthraquinone, dibenzoylperoxide, *tert*-butylhydroperoxide and dilauroylperoxide (0.05–0.15 mass%) increases the strength of the glue joint.

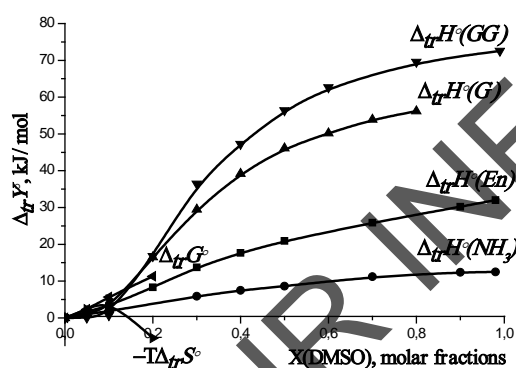
**THERMODYNAMICS OF GLYCYLGLYCINE SOLVATION  
IN WATER – DIMETHYLSULFOXIDE SOLVENT AT 298.15 K**

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This work presents the thermodynamics characteristics of glycylglycine transfer from water to water-dimethylsulfoxide solvent in various range of mixed solvent concentration at 298.15 K. The Gibbs energies of dipeptide transfer are determined by interphase distribution method of the substances between immiscible phases. Enthalpies of glycylglycine transfer are determined by calorimetry.

The solvation of glycylglycinate-ion decreases in the investigated concentration range of water – dimethylsulfoxide solvent (0.00–0.20 molar fractions of DMSO) more than three times compared with the neutral form of the dipeptide. The correlation between the  $\Delta G^\circ$  values of dipeptide anion resolution and autoprotolytic constants of mixed solvent are found. This indicates to the important role of acid-base solvent properties in the solvation state change of dipeptide. Similar solvent effect, but in a wide range of concentrations also found in the case of glycine. Analysis of glycylglycinate-ion  $\Delta_{tr}G^\circ$  changes in water – dimethylsulfoxide solvent demonstrates, that amino- and carboxylate groups contribute different effects in change of anion solvation state while peptide group solvation is absent.



*Figure: Contributions of enthalpy and entropy in change of Gibbs energy transfer of glycylglycinate-ion (GG) and  $\Delta_{tr}H^\circ$  of glycinate-ion (G) [1], ethilendiamine (En) [2] and ammonia (NH<sub>3</sub>) [3] in water solutions of DMSO.*

Calorimetric study of glycylglycine solvation is carried out in a wide range of concentrations (until 0.99 mol. fr. DMSO). It was shown that with increasing content of dimethylsulfoxide in solution

the exothermicity of glycylglycinate-ion solvation decreases sharply and significantly higher than the solvation decrease of ammonia and ethilendiamine. The weakening of glycylglycinate-ion solvation at low solvent concentrations is determined by the increasing of transfer enthalpy values. Probably a weakening of anion solvation will be at higher concentrations of dimethylsulfoxide in water solution which will be determined by  $\Delta_{tr}H^\circ$ .

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### MODELLING OF NITRIC ACID EXTRACTION WITH 12% AND 30% TRIBUTYL PHOSPHATE IN DODECANE

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The fuel reprocessing is based on PUREX process. As Pu concentration is low usually H<sub>2</sub>O–HNO<sub>3</sub>–UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>–TBP–diluent system can be considered as a main one. Usually molar concentrations had been used during the research of this system. An alternative approach using mole fractions and rational activity coefficients has been demonstrated in [1]. The main system is divided into subsystems and every subsystem is calculated through thermodynamic activities. Now the system H<sub>2</sub>O–HNO<sub>3</sub>–TBP–dodecane is considered as a part of the big system. The experimental data were given in [2]. The procedure of the calculation has been changed in comparison with [2]:

1. The maximum level of acid concentration has been restricted to 6.6 mol/L. Therefore the number of points is 29 in 30% TBP series and 23 in 12% TBP series.

2. Effect of water on TBP activity is taken into account.

The formation of solvates from *i* acid molecules and *j* TBP molecules is calculated as

$$x_{ij} = K_{ij} \cdot a_{ai} \cdot a_{tj} / f_{ij}, \quad (1)$$

where  $K_{ij}$  is a formation constant,  $a_{ai}$  is an activity of the acid,  $f_{ij}$  is an activity coefficient of the solvate and can be calculated as

$$f_{ij} = \exp[h_{ij}(a_w - 1)], \quad (2)$$

where  $h_{ij}$  is a hydration ratio of the solvate and  $a_w$  is water activity.

Molar concentrations can be found as

$$c_j = x_j \cdot d \cdot 1000 / \sum x_i \cdot M_i, \quad (3)$$

where  $x_i$  and  $M_i$  are a mole fraction and molar mass of component “*i*”,  $d$  is a density of the organic phase calculated through found empirical equation

$$d = d_0 + 0.226488 \cdot \varphi_{tb} + 0.028843 \cdot c_a, \quad (4)$$

where  $d_0$  is a density of the poor solvent,  $\varphi_{tb}$  is a volume part of TBP:  $\varphi_{tb} = 0.3$  for 30% and  $\varphi_{tb} = 0.12$  for 12% TBP.

Molar concentrations of acid  $c_{ac}$  and TBP  $c_{tc}$  have been calculated as:

$$c_{ac} = c_{11} + c_{12} + 2c_{21}, \quad (5)$$

$$c_{tc} = c_{t1} + c_{11} + 2c_{12} + c_{21}. \quad (6)$$

The equations (5) and (6) are used to estimate average relative deviation of calculated data from experimental ones:

$$\delta_a = \left\{ \sum [(c_{ac} - c_a) / c_a]^2 / (n-1) \right\}^{0.5}, \quad (7)$$

$$\delta_t = \left\{ \sum [(c_{tc} - c_t) / c_t]^2 / (n-1) \right\}^{0.5}, \quad (8)$$

$$\delta_{t+a} = 0.5 \cdot [\delta_a^2 + \delta_t^2]. \quad (9)$$

It is possible to use three criterion of optimization:  $\delta_a$ ,  $\delta_t$  and  $\delta_{t+a}$ . The latter criterion is more usual because the errors of acid and TBP concentration are near.

**Table.** The main results of the calculation

TBP concentrations	$K_{11}$	$K_{12}$	$h_{12}$	$b_2$	$\delta_t$	$\delta_a$	$\delta_{t+a}$	$\delta_{t+a} =$ <b>3.2</b>
30%	0.2692	2.414	2.187	0.6799	1.12	2.20	1.75	
12%	0.2692	2.414	2.187	0.6799	4.99	4.03	4.54	

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**CALORIMETRIC STUDY OF PHASE TRANSFORMATION  
IN THE FLUORIDE–SULFATE GLASS-FORMING SYSTEMS**

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Glasses and glass-ceramics with high ionic conductivity at low and medium temperatures are attracting widespread practical interest. Such glasses can be used in various electrochemical devices, and have a number of advantages over the crystalline compounds of the same composition: higher conductivity, a relatively simple synthesis technology and the manufacture of details with required shapes and sizes, a smooth variation of properties, etc. The aim of this work is to determine the glass formation region in the KF–CdSO<sub>4</sub> system and to study the kinetics of phase transformations in the glasses by differential scanning calorimetry (DSC). The samples synthesis and determination of the glass formation range in the system KF–CdSO<sub>4</sub> were performed according to the procedure as detailed in [1]. The colourless and transparent glass samples were obtained within 40–60 mol.% of CdSO<sub>4</sub>. Calorimetric investigations for the (100–*x*) KF–*x*CdSO<sub>4</sub> (*x* = 40, 45, 50, 55, 60 mol.%) glass samples were carried out on the DSC 204 F1 Phoenix (NETZSCH). The glass transition temperature *T<sub>g</sub>*, the temperature *T<sub>x</sub>* of the crystallization onset, the peak crystallization temperature *T<sub>cr</sub>*, heat capacity change at the glass transition  $\Delta C_p$  and enthalpy of crystallization  $\Delta H$  were directly determined from DSC curves (see Table 1). The kinetics of phase transformations of the glass samples was studied by non-isothermal method at heating rates 2.5, 5, 10, 20, 40 °C/min. The activation energy values for glass transition *E<sub>g</sub>* and crystallization *E<sub>cr</sub>* calculated according to the [2, 3] and [3, 4], respectively are shown in Table 2.

**Table 1.** Values of the *T<sub>g</sub>*, *T<sub>x</sub>*, *T<sub>cr</sub>*,  $\Delta C_p$  and  $\Delta H$  for the glass (100–*x*)KF–*x*CdSO<sub>4</sub> at heating rate 10 °C/min

<i>x</i> (mol.%)	<i>T<sub>g</sub></i> (°C)	<i>T<sub>x</sub></i> (°C)	<i>T<sub>cr</sub></i> (°C)	– $\Delta C_p$ (J/(g·K))	$\Delta H$ (J/g)
40	229.1	257.3	270.0, 293.5	0.51	62.5
45	244.1	297.2	301.3	0.46	62.3
50	257.3	296.1	299.8	0.52	62.5
55	269.0	314.1	317.8	0.51	65.5
60	273.4	334.6	336.2	0.51	62.2

**Table 2.** Values of the *E<sub>g</sub>*, *E<sub>cr</sub>* for the glass (100–*x*)KF–*x*CdSO<sub>4</sub>

<i>x</i> (mol.%)	<i>E<sub>g</sub></i> [2] (kJ/mol)	<i>E<sub>g</sub></i> [3] (kJ/mol)	<i>E<sub>cr</sub></i> [3] (kJ/mol)	<i>E<sub>cr</sub></i> [4] (kJ/mol)
40	-428.8	-437.1	-213.7, -286.2	-217.1, -295.6
45	-395.6	-403.9	-205.7	-215.3
50	-489.5	-498.6	-272.5	-282.0
55	-422.1	-431.3	-254.3	-264.2
60	-496.9	-506.1	-247.0	-257.1

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC EVALUATION OF CHEMICAL AND ELECTROCHEMICAL EQUILIBRIA INVOLVING AQUEOUS SULPHUR SPECIES AT AMBIENT AND ELEVATED TEMPERATURES AND PRESSURES

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Sulphur can form a huge variety of ions in water solution with oxidation degrees ranging from – 2 to +8 [1] including polysulphides ( $S_n^{2-}$  and  $HS_n^-$ ,  $1 \leq n \leq 8$ ), polythiosulphates ( $S_nO_3^{2-}$  and  $HS_nO_3^-$ ,  $2 \leq n \leq 7$ ), polythionates ( $S_nO_6^{2-}$  and  $HS_nO_6^-$ ,  $2 \leq n \leq 6$ ) and other ions ( $S_2O_n^{2-}$  and  $HS_2O_n^-$ ,  $3 \leq n \leq 8$ ,  $SO_n^{2-}$  and  $HSO_n^-$ ,  $3 \leq n \leq 5$ ). Uncharged species like  $SO_2$ ,  $H_2SO_3$ ,  $SO_3$ ,  $H_2SO_4$ ,  $H_2S_2O_3$ ,  $H_2S_2O_4$ ,  $H_2S_2O_8$ , and  $H_2S_n$ ,  $1 \leq n \leq 8$  can also be present in aqueous state. The values of standard Gibbs energy of formation of aqueous sulphur species together with the data on the standard electrode potentials of half-cell reactions and equilibrium constants of chemical reactions involving these species were collected from various sources [2–4], analyzed and verified. The most reliable and self-consistent thermodynamic information were determined and used in calculations.

Thermodynamic properties of basic chemical and electrochemical equilibria in S – H<sub>2</sub>O system at 25°C and air pressure of 1 bar were presented in form of Latimer series, Frost diagrams, predominance diagrams (activity – pH) and Pourbaix diagrams (potential – pH). The domains of thermodynamic stability of various stable and metastable aqueous sulphur species in dependence on potentials, pH and values of thermodynamic activities of ions in solutions were determined.

The dependency of thermodynamic properties of sulphur species on temperature and pressure was estimated using various models [5]. Group contribution method [6] was used to evaluate Gibbs energies of formation of ions for which no information were available. Phase transformations of pure sulphur at various pressures were evaluated using available equation of state [7]. Basic chemical and electrochemical equilibria in S – H<sub>2</sub>O systems at elevated temperatures and pressures were predicted. Latimer, Frost and Pourbaix diagrams of sulphur in high-subcritical and low-supercritical regions of water were constructed.

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### STUDY OF HETEROGENEOUS EQUILIBRIA IN AQUEOUS SOLUTIONS OF INORGANIC COMPOUNDS OF URANIUM(VI)

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Heterogeneous equilibria in aqueous solutions of uranium compounds with formula  $M^k(UO_2An)_k \cdot nH_2O$  (where  $An = VO_4^{3-}, PO_4^{3-}, AsO_4^{3-}, HSiO_4^{3-}, HGeO_4^{3-}$  and  $BO_3^{3-}$ ;  $M^k$  is an alkaline, alkaline-earth and some of the d-transitional and rare earth elements) were investigated depending on the acidity, the anionic composition, ionic strength, temperature, etc.

The state of the uranium (VI) compounds in aqueous solutions depends on medium acidity most significantly. The pH of a saturated solution determines the acid-base intervals of existence of crystalline compounds, the nature of the secondary bottom phases, the solubility of the substances, species of uranium and other structural elements in aqueous solutions.

It is established that the crystal structure of uranylvanadates is the most resistant to aqueous solutions and these compounds retain their individuality in the pH range from 0–2 to 11–14. Uranylborates are chemically unstable, and their structure is destroyed in aqueous solutions regardless of the acidity. Such compounds as  $M^k(UO_2An)_k \cdot nH_2O$  ( $An = VO_4^{3-}, PO_4^{3-}, HSiO_4^{3-}, HGeO_4^{3-}$ ) are stable in a wide acid-base interval spanning from 6 to 10 pH units. The structure of uranylphosphates and uranylarsenates is preserved at a pH-value from 1–3 to 8–12. This interval for uranylsilicates and uranylgermanates is shifted by 2–3 pH units into the region with larger pH values. Stability interval of compounds d-transition and rare earth elements is less than the analogous derivatives of alkali and alkaline earth elements approximately 2–3 pH units.

The dependence of the uranium (VI) compounds solubility from pH has the form of a curve with a minimum. The solubility minimum is observed at pH 6 to 8 for compounds with  $An=VO_4^{3-}, PO_4^{3-}, AsO_4^{3-}$  and pH 9–10 for compounds with  $An=HSiO_4^{3-}, HGeO_4^{3-}$ . At these pH values the solubility of most of the studied compounds of phosphorus (V), arsenic (V), silicon (IV) and germanium (IV) is at the level concentrations ( $10^{-7}$ – $10^{-5}$ ) mol/L. There is a clear trend of increasing solubility in the transition from uranylphosphates to uranylarsenates and from uranylsilicates to uranylgermanates. The minimum solubility of uranylvanadates is slightly lower and it varies depending on the nature of  $M^k$  atom in the interval ( $10^{-9}$ – $10^{-7}$ ) mol/l. It has been observed decrease of solubility of compounds with increasing  $M^k$  oxidation state in the following direction  $A^+ > A^{2+} > A^{3+}$ . In acidic and alkaline media, the solubility of the uranium compounds is increased to  $10^{-4}$  to  $10^{-1}$  mol/l and above.

It is proposed physico-chemical description of heterogeneous systems under study. These description takes into account the heterogeneous dissolution reaction and whole complex of homogeneous equilibria involving different ion-molecular forms of U(VI), P(V), As(V), V(V), Si(IV), Ge(IV), B(III), alkaline, alkaline-earth and d-transition and rare earth elements. Proposed description allowed us to use the experimental data for calculation of solubility products and other thermodynamic constants.

On the basis of the calculated constants and proposed in this work physico-chemical descriptions we conducted modeling of the studied compounds state in aqueous solutions over a wide range of acidity. It was calculated the phase diagrams of aqueous solutions and solid phases, solubility curves, thermodynamic constants. These results are in good agreement with the experimental data set out and confirm the regularities of the processes of conversion and dissolution of the complex uranium (VI) compounds.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC PROPERTIES OF POTASSIUM IODIDE SOLUTIONS IN MIXED N-METHYLPYRROLIDONE – WATER SOLVENT AT 298.15 K

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Heat capacity  $C_p$  and density  $\rho$  of potassium iodide in MP–H<sub>2</sub>O mixtures with  $X_{MP} = 0.025$  and  $0.050$  at  $298,15$  K were experimentally investigated. For measurement the precision calorimetric and densimetric installation were used. The errors of  $C_p$  and  $\rho$  measurements were not more than  $\pm 1 \cdot 10^{-3} \text{ J}(\text{g} \cdot \text{K})^{-1}$  and  $\pm 2 \cdot 10^{-5} \text{ g} \cdot \text{cm}^3$ . Experimental values of  $C_p$  and  $\rho$  were used to calculate the apparent molal heat capacities  $\Phi_c$  and volumes  $\Phi_v$  of potassium iodide in MP–H<sub>2</sub>O mixtures with  $X_{MP} = 0.025$  and  $0.050$ . The standard partial molal heat capacities  $\bar{C}_{P_2}^0$  and volumes  $\bar{V}_2^0$  of KI in MP–H<sub>2</sub>O at  $298.15$  K were determined by the extrapolation of concentration dependences of  $\Phi_c$  and  $\Phi_v$  to the state of infinity dilution.

The system for separating the values of  $\bar{C}_{P_2}^0$  and  $\bar{V}_2^0$  into ionic components  $\bar{C}_{P_i}^0$  and  $\bar{V}_i^0$  in mixed MP–H<sub>2</sub>O solvent at mole fractions of  $X_{MP} = 0.025$ – $0.05$  was not described in the literature. However, a system of standard values for  $\bar{C}_{P_i}^0$  and  $\bar{V}_i^0$  was proposed in [1, 2] for other compositions of MP–H<sub>2</sub>O, based on comparative calculation methods and using the relations:

$$\bar{C}_{P_{2,i}}^0(\text{MP-H}_2\text{O}) = a_C \bar{C}_{P_{2,i}}^0(\text{H}_2\text{O}), \quad (1)$$

$$\bar{V}_{2,i}^0(\text{MP-H}_2\text{O}) = a_V \bar{V}_{2,i}^0(\text{H}_2\text{O}), \quad (2)$$

where  $a_C$  and  $a_V$  are empirical coefficients.

We may assume with a high degree of confidence that such linear dependences are also obeyed for MP–H<sub>2</sub>O mixtures where  $X_{MP} = 0.025$ – $0.050$ . Treating the results for KI and the literature data on  $\bar{C}_{P_2}^0$  and  $\bar{V}_2^0$  for RbI in MP–H<sub>2</sub>O mixtures with  $X_{MP} = 0.025$ – $0.050$  [4] led to the values of coefficients  $a_C$  and  $a_V$  in Eqs. (1) and (2) and allowed us to calculate the  $\bar{C}_{P_i}^0$  and  $\bar{V}_i^0$  values of ions. The results from calculations and the literature data on  $\bar{C}_{P_i}^0$  and  $\bar{V}_i^0$  in water and our MP–H<sub>2</sub>O mixture at  $X_{MP} = 0.10$  are given in Table. The obtained values coincide within the error, confirming once again the negligible effect small additions of MP have on the structure of water and allowing us to use the system of standard values of heat capacity and volumes of ions in aqueous solution for separating  $\bar{C}_{P_2}^0$  and  $\bar{V}_2^0$  into ionic components in the given range of MP–H<sub>2</sub>O compositions.

**Table.** Standard partial molal heat capacities ( $\bar{C}_{P_i}^0$ ,  $\text{J}(\text{mol K})^{-1}$ ) and volumes ( $\bar{V}_i^0$ ,  $\text{cm}^3 \cdot \text{mol}^{-1}$ ) of ions in mixed MP–H<sub>2</sub>O solvent at  $298.15$  K

$X_{MP}$	$\bar{C}_{PK^+}^0$	$\bar{V}_{K^+}^0$	$\bar{C}_{PI^-}^0$	$\bar{V}_{I^-}^0$
0	-56.5	14.3	-73.2	30.9
0.025	-54±10	14.4±0.2	-70±10	31.0±0.2
0.05	-51±10	14.7±0.2	-66±10	31.8±0.2
0.10 [2, 3]	-48	15.2	-62	32.9

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## ION-MOLECULAR INTERACTIONS IN SYSTEM KI – N-METHYLPYRROLIDONE – WATER, ACCORDING TO CALORIMETRY AND DENSITOMETRY DATA

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To explain the character of the changes in heat capacity  $C_p$  and volume  $V$  on the mixing of isomolal binary solutions KI–MP and KI–water, the results from our studies and the available literature data on the properties of solutions KI–MP–H<sub>2</sub>O over the range of mixed solvent composition were used. To accomplish this, additivity coefficients were calculated using the equation:

$$\delta_Y = \frac{Y_{\text{exp}} - Y_{\text{add}}}{Y_{\text{add}}} 100\% ,$$

where  $Y_{\text{exp}}$  denotes the experimental values of  $C_p$  or  $V$  of ternary solutions, and  $Y_{\text{add}}$  represents the additive values of  $C_p$  or  $V$  of solutions

It is noteworthy that  $C_p$  and  $V$  deviate significantly from the additivity and the dependences have extrema located in the range of ~0.3 mole fractions of MP. This character of curves  $\delta = f(X_{\text{MP}})$  indicates that the specific interaction occurring between the components in a binary MP–H<sub>2</sub>O system and leading to the formation of the most stable associates of the MP·2H<sub>2</sub>O composition also determines the formation of ternary KI–MP–H<sub>2</sub>O solutions. The investigations of the MP–H<sub>2</sub>O system in [1] established that the formation of MP·2H<sub>2</sub>O associates in solution leads to rise in heat capacity, a reduction in the volume of the system, and the emergence of extrema on the concentration dependences of the excess thermodynamic functions. The dependences  $\delta = f(X_{\text{MP}})$  confirm that the presence of the electrolyte does not change the sign of deviations of  $C_p$  and  $V$  from additivity; rather, it lowers the magnitude of these deviations and, as follows from Figure, the most dramatic drop occurs in mixtures with  $X_{\text{MP}}$  contents 0.3–0.5.

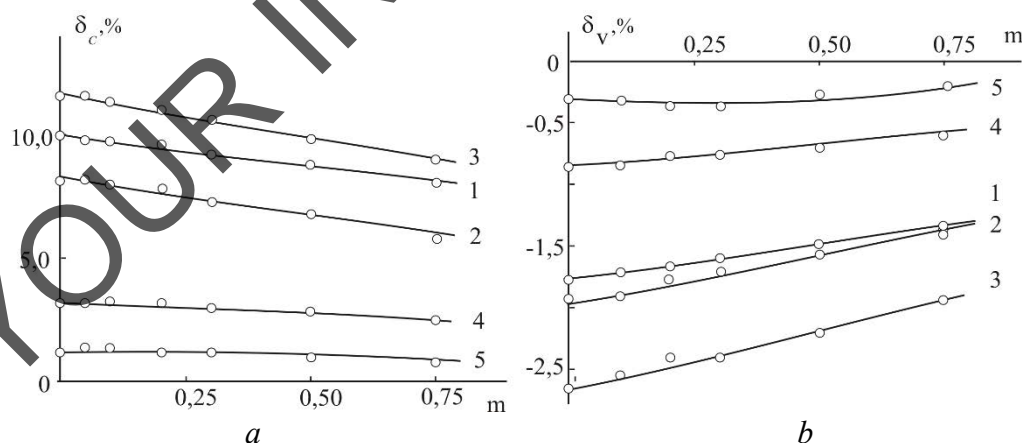


Figure: Concentration dependences of additivity coefficients of the KI–MP–H<sub>2</sub>O system.  $X_{\text{MP}}$ : (1) 0.1, (2) 0.33, (3) 0.50, (4) 0.75, (5) 0.90.

Introducing ions into a solvent of this composition probably leads to the destruction of the hydrogen bonds between the components and associates, and thus to a significant reduction of heat capacity and an increase of volume.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

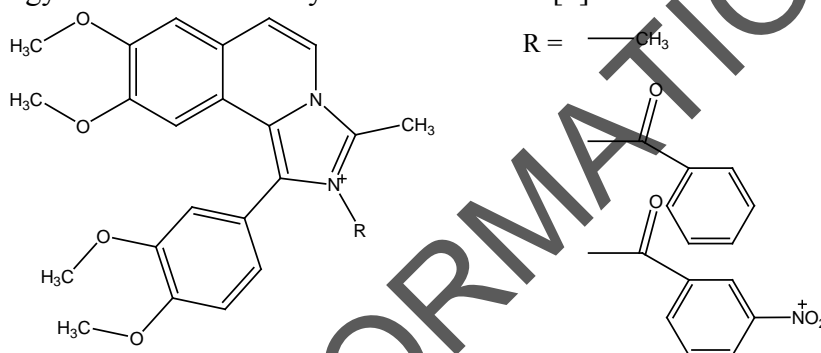
### THERMODYNAMICS OF INTERACTION OF DEOXYRIBONUCLEIC ACID MOLECULE WITH ISOQUINOLINE DERIVATIVES

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The ability of compounds to bind with deoxyribonucleic acid (DNA) and its affect on biological properties is an important factor in determining the possibility of using such compounds for medical purposes. The process of synthesis of novel biologically active compounds on the basis of already known drugs to enhance the effectiveness of the drug is relevant. Papaverine is widely known spasmolytic drug. It has in its structure the core of isoquinoline. Investigated in this work compounds are analogues of papaverine.

The compounds were synthesized in the Research Institute of Hygiene, Occupational Pathology and Human Ecology FMBA of Russia by Krivorotov D.V. [1].



**Figure:** The structure of investigated compounds.

The presence of flat heterocyclic chromophore in the structure allows to suggest the existence of interaction with DNA molecule. One of the main aspects in the study of the interaction of the biologically active compounds with DNA is the determination of thermodynamics parameters of binding. For this purpose, the methods of calorimetry and spectrophotometry were used. Thermodynamic parameters such as enthalpy, the binding constant and the number of places of binding were obtained.

From the calorimetric and spectrophotometric titrations it has been found that the compounds have one type of binding with DNA. The number of places of binding  $n = (0.2-0.4)$ . The interaction of these compounds with DNA is exothermic and enthalpy of interaction  $\Delta H = (-3.5 - -10)$  kcal/mol. However, the binding constants obtained by means of calorimetric titration have values lower than those obtained from spectrophotometric titration. This may be due to different models used in calculation of this parameter during the spectrophotometric and calorimetric titrations [2, 3], as well as different conditions during the titrations.

ITC experiments were performed using a TA Instruments Nano ITC 2G Microcalorimeter at Thermogravimetric and Calorimetric Research Centre Saint Petersburg State University.

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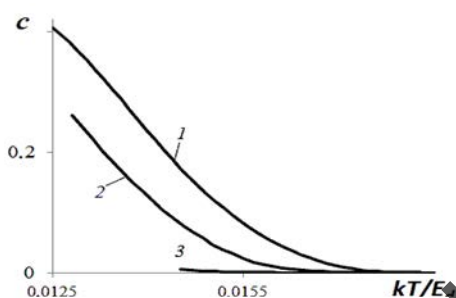
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## STATISTICAL THERMODYNAMIC MODEL OF COMPLEX FORMATION IN DIVALENT METAL SALT MELTS IN THE MEAN-SPHERICAL APPROXIMATION

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Concepts regarding the formation of auto-complex groups in salt melts based mainly on the analysis of optical spectra were proposed in [1]. Concentration of the auto-complexes was considered as the maximum possible when all the simple anions of halogens almost associated in the complexes [2]. This model neglects the electrostatic cooperative effects in the interaction of charged particles, and main attention is given on the relations in the complex. Thus, it was assumed that the ideal mass action law has realised. In our opinion, this theory of auto-complexes is inconsistent with the classical theory of electrolytes [2]. Statistical-thermodynamic theory of complexation in molten salts should operate with activity of ions when deriving mass action law and comprise the method of their calculation from the forces acting between the particles of the ionic melt.



**Figure:** Calculated temperature dependences of the concentration of the complexes  $(MX_4)^{2-}$  type for different energies of dissociation;  $E_d^0 = 9e^2/\epsilon a$  (1);  $E_d = 0.85E_d^0$  (2);  $E_d = 0.75E_d^0$  (3).

can use a generalization of the Van der Waals theory [3–5] or the approximation of Percus–Yevik. The contribution of electrostatic interactions to the free energy can be described in terms of the Debye–Huckel approximation or by using the mean-spherical approximation (MSA). We have developed a model allows one to calculate temperature dependence of the concentration of auto-complexes at different energies of dissociation. It was shown that chemical equilibrium  $M^{2+} + 4X^- = (MX_4)^{2-}$  in halide melts of divalent metal has to be shifted much appreciably toward dissociation due to the electrostatic interactions of charged particles in dense ionic liquid. It was found that the range of temperatures in which auto-complex anions exist shrinks with a reduction in the energy of dissociation and, below a certain threshold of the dissociation energy, this concentration is equal to zero over the whole range of temperatures.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

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### THERMODYNAMIC MODELLING OF SYSTEMS CONTAINING LIQUID CRYSTALS

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Thermotropic liquid crystals (LC) have found a wide application in photonics as well as in display technologies [1, 2]. A huge range of applications sets a lot of requirements to physical properties of liquid crystalline materials (LCM). Modern LCM are multicomponent mixtures needing to have a constant and reproducible composition over the wide temperature range of the certain mesophase type. Physico-chemical basis of LC material science is a phase diagram. Analysis of literature data has shown that more than 70 % of published phase diagrams with LC contain errors in interpretation of thermal analysis and microscopy measurements [3]. The goal of the submitted work is to develop thermodynamic methods to predict the phase diagram type and to obtain reliable data on LCM properties.

More than 200 binary systems containing nematic (smectic-nematic, smectic) LC are investigated. Complete phase diagrams and solubility curves are obtained by DTA, visual analysis, polarizing microscopy and solubility methods. Experimental and literature [3] data on systems for thermodynamic analysis are used. Three main types of systems are analyzed: (1) LC systems, (2) LC – high melting non-mesogen (dichroic dyes, tolane, phenylbenzoate, etc.), (3) LC – low melting non-mesogen (solvent). Liquid crystals belong to different classes: benzylideneanilines, phenylbenzoates, azo- and azoxybenzenes, phenylcyclohexanes, cyanobiphenyls.

Comparative analysis of the existing prediction methods for phase diagrams is made. Different thermodynamic methods (the solubility parameters of Hildebrand and Hansen, UNIFAC model) are used to predict the phase diagram type, to calculate the solubility curves and invariant point position. Data on thermodynamic and physical properties for mesogens are taken from [4] or calculated using the group-contribution methods. Activity coefficients of components and the excess thermodynamic functions for the melting and mesophase formation are estimated.

Correlations between alkyl chain length, crystal structure of mesogens and their solubility in solvents of different polarity are determined. A correlation of the invariant points position on the components properties is revealed. A dependence of the phase diagram type on the excess thermodynamic functions is discussed.

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## THERMODYNAMIC DESCRIPTION OF SYSTEMS CONTAINING LIQUID CRYSTALLINE ESTERS

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Liquid crystals (LC) are widely used in modern technologies. To obtain constant and reproducible properties of LC materials it is necessary to have individual substances of high purity. The typical final stage of purification of LC is a crystallization from a solution. The type of molecular interactions in LC – non-mesogen systems plays the main role in a solvent selection for crystallization. Usage of the thermodynamic methods to predict the phase diagram type, to calculate the solubility curves and invariant point position seems to be very interesting.

Binary LC – non-mesogen systems are investigated by thermal analysis, visual polythermal analysis and solubility methods [1]. Two homologous series of liquid crystalline esters having a common formula  $R_1-O-C_6H_4-COO-C_6H_4-O-R_2$  (where  $C_6H_4$  is 1,4-phenylene,  $R_1 = C_6H_{13}, C_9H_{19}, C_{10}H_{21}$ ,  $R_2 = C_4H_9$ ;  $R_1 = CH_3, C_4H_9, C_8H_{17}, C_{10}H_{21}$ ,  $R_2 = C_6H_{13}$ ) are used as mesogenic components. The last two substances are smectic-nematic liquid crystals. The other LC have nematic phase. Solubility curves of LC in solvents of different polarity (*n*-alkanes, cyclohexane, aromatics, chlorinated alkanes, alcohols, esters, acetonitrile) are obtained.

All phase diagrams of studied systems have a minimal set of non-variant reactions: eutectic and methatectic. If components have different molecular interaction types, it is possible to see a broad demixing region. Excess thermodynamic functions for liquidus curves are calculated. The models based on the solubility parameter (usage of Hildebrand and Hansen solubility parameters, the Flory-Huggins equation) are applied for the demixing prognosis. Hildebrand solubility parameters for LC are estimated basing on equation:  $\delta_i = ((\Delta H_i^v - RT) / V_i)^{0.5}$ , where  $\Delta H_i^v$ ,  $V_i$  are the vaporization enthalpy and the molar volume of components at 298 K. For mesogens the vaporization enthalpies are estimated basing on the group-contribution method (GCM). Data on density of mesogens are taken from [2] or calculated using the group-contribution methods. The average error for density prediction by GCM for LC substances equals 2–3%.

The usage of polar and non-polar contributions of the Hansen solubility parameters [3] gives an opportunity to expand the demixing prediction to the LC – polar solvent systems. Applicability of the group-contribution equation (UNIFAC) is checked for the activity coefficients estimation. Restrictions and advantages of the considered thermodynamic methods are discussed. Correlations between alkyl chain length of LC and their solubility in solvents of different polarity are determined. A dependence of the phase diagram type on the excess thermodynamic functions is discussed.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

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### HYDROGEN ADSORPTION ON PALLADIUM CATALYST FROM SOLUTION

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In work adsorption-calorimetric study of hydrogen adsorption laws on palladium catalysts from an aqueous solution of sodium hydroxide was carried out at 303 K. Used samples of catalysts of palladium supported on activated carbon with a metal content from 1 to 10 mass%. The catalysts are prepared by depositing a transition metal adsorption from solutions of palladium chloride on the carrier surface, followed by chemical reduction of metal ions with sodium formate. Pd/C catalyst are adsorbents with highly developed specific surface area from 607 to 758 cm<sup>2</sup>/g mixed with the porous structure. For the studied catalytic systems the number and the heat of adsorption of hydrogen at different degrees of coverage of the catalyst surface were determined.

It was established that hydrogen adsorption heat depends on the degree of filling associated with the nature of the solvent and the content of catalytically active metal – palladium. For result analysis of the experiment a surface model with discrete heterogeneity in the approximation of an ideal adsorbed layer was used. We prove that the surface model with discrete heterogeneity describes the results of the adsorption-calorimetric experiment in all catalytic systems. With the help of this model were calculated thermodynamic characteristics of adsorption of the three individual forms of hydrogen-related active centers of palladium in solution: maximum adsorption, adsorption coefficients and standard heat of individual forms. The results showed that the amount of weakly adsorbed hydrogen with heat of adsorption 20–30 kJ/mol was reduced from 70–75 to 20–25%, while the amount of strongly adsorbed hydrogen with heat of adsorption from 140–150 kJ/mol increased from 15–10 to 20–25% with increasing pH of the liquid phase from 8 to 11.

Thus, the influence of the content of palladium catalysts, as well as the nature and composition of solvents on the hydrogen adsorption laws is manifested through changes in the values of adsorption heats and adsorption coefficients of individual forms of the adsorbed substance.

*The work was performed as part of the State Task of the Ministry of Education and Science of the Russian Federation (Project No. 1800).*

## FEATURES OF DIAGRAMS COMPOSITION – EXCESS GIBBS ENERGY OF NON-ELECTROLYTE QUARTERNARY MIXTURES

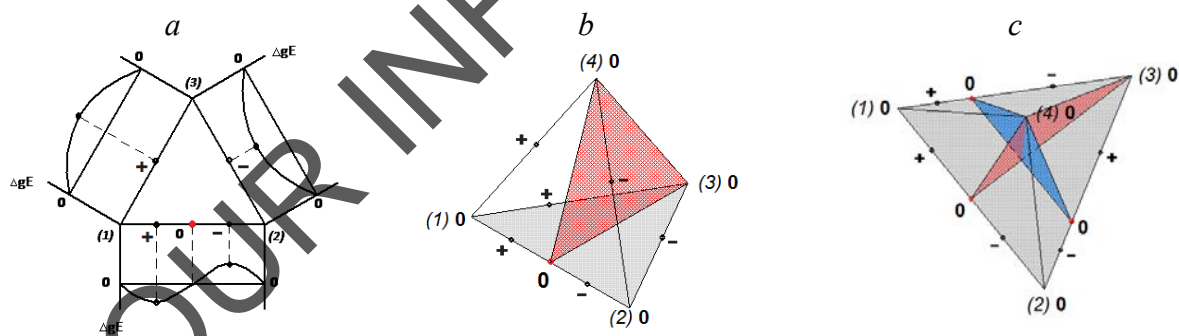
V.M. Raeva, I.A. Velichko

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Excess Gibbs energy ( $\Delta g^E$ ) is one of the most important characteristic of mixtures, it reflects the qualitative and quantitative specificity of intermolecular interactions. The method to choice of selective entrainers for separation of any binary azeotropic system [1] and ternary azeotropic systems of some types [2] has been proposed on the analysis of dependencies  $\Delta g^E$  – composition (x) [2].

This study investigates the quaternary non-ideal systems of non-electrolytes, characterized by various deviations of liquid binary mixtures from ideal behavior: positive ( $\Delta g^E(x) > 0$ ), negative ( $\Delta g^E(x) < 0$ ), mixed ( $\Delta g^E(x) > / < 0$ ). Examples of boundary contours of concentration simplexes which exhibit opposite deviations from the ideal in binary systems are shown below (Figure a). Isomanifold  $\Delta g^E = 0$  can share simplex on the field with opposite (positive or negative) deviations (Figure b). In the case of mixed deviations in binary mixtures isomanifolds  $\Delta g^E = 0$  divide the interior of the simplex to more areas (Figure c).

It is necessary to consider these features diagrams composition – excess Gibbs energy when choosing selective agents (4) for the separation of azeotropic ternary systems (1-2-3) with any character deviations from ideal behavior. It has been found that the presence of mixed deviations in binary solutions i (1, 2 or 3) – 4 (entrainer) may be a critical restriction for the possibility of extractive distillation.



**Figure:** Boundary contours of composition – excess Gibbs energy diagrams for ternary (a) and quaternary (b, c) systems.

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*The work was supported by the Russian Foundation for Basic Research (Project No. 13-03-00222a).*

## Section 3. Thermodynamics of solutions and heterogeneous systems

### PREDICTION AND ANALYSIS OF SOLVATION ENTHALPIES AND HYDROGEN BONDING ENTHALPIES OF ORGANIC SOLUTES IN AROMATIC SOLVENTS BASED ON SOLOMONOV AND ABRAHAM METHODS

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Enthalpies of solvation provide valuable insight regarding solute–solvent interactions and molecular complexation in liquid state. Solvation enthalpies have been applied in chemical kinetic studies to model solvent effects on reaction rate parameters.

First purpose of the present communication is to predict and analyze enthalpies of solvation of different organic solutes in aromatic solvents (mesitylene, *p*-xylene, chlorobenzene and 1,2-dichlorobenzene) using Solomonov and Abraham methods. Second is to illustrate how these values can be used to obtain enthalpies of weak hydrogen bonds between proton donors and aromatic hydrocarbon solvents.

Enthalpies of solution of proton donors, proton acceptors and amphiphilic compounds in the *p*-xylene, mesitylene, chlorobenzene and 1,2-dichlorobenzene were determined. Enthalpies of solvation are calculated by combining the measured enthalpies of solution with literature enthalpies of vaporization and sublimation. Effect of alkyl group and halogen substitution in benzene ring on solvation enthalpies was discussed. Abraham model correlations for the gas were obtained to aromatic solvent solvation enthalpies [1]. The product of the solute and solvent coefficients describe a particular type of solute–solvent interaction. Hydrogen-bond interactions are given by the products ( $a \times A$ ) and ( $b \times B$ ) which take into account the possibility that the solute might be a H-bond donor ( $a$  A) and a H-bond acceptor ( $b$  B). Hydrogen bond enthalpies were calculated for select proton donor solutes with benzene, toluene, mesitylene, *p*-xylene, chlorobenzene and 1,2-dichlorobenzene using the obtained multi-parameter correlations. The same procedure was carried out using Solomonov method [2]. It was shown, that hydrogen bonding enthalpies determined by two independent methods are in good agreement with each other. Enthalpies of hydrogen bond of different proton donor solutes increase in the following order benzene < toluene < *p*-xylene < mesitylene. Investigation of quantitative parameters of X–H... $\pi$  hydrogen bonds play a crucial role in the effect of solvents on the reactivity of dissolved molecules.

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*This work has been performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.*

### THERMODYNAMICS OF HYDROGEN BONDING OF NITROGEN-CONTAINING CYCLIC AND AROMATIC COMPOUNDS WITH PROTON DONORS AND PROTON ACCEPTORS: THE STRUCTURE–PROPERTY RELATIONSHIP

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It is well-known that nitrogen-containing cyclic and aromatic compounds are highly basic organic molecules that can form strong hydrogen bond with proton donors. But some of them are also self-associated by hydrogen bond due to acidic N–H groups. These nitrogen-containing compounds can form stable supramolecular structures with specific properties. Also many of the nitrogen-containing compounds are widely used as dyes and pesticides, they are found in drugs and biologically active compounds. The properties and crystal structure of these compounds are determined by the presence of hydrogen bonds, e.g., secondary structure of proteins, enzymes, and nucleic acids. Therefore, investigation of hydrogen bonds in large molecules is complicated task due to a large number of active sites. So, in this case usually model compounds like amides and etc. are used for these studies.

In present work hydrogen bonding of nitrogen-containing cyclic and aromatic compounds with proton donors and proton acceptors was studied. Enthalpies of solution of pyrrolidine, piperidine, *N*-methylpyrrolidine, *N*-methylpiperidine, pyrazole, imidazole, pyrrole, *N*-methylimidazole, *N*-methylpyrazole, *N*-methylpyrrole, aniline, *N*-methylaniline, *N,N*-dimethylaniline, pyridine, 2-, 3-,4-methylpyridine in ethers, ketones, esters, nitriles, amines and chloroform were determined at infinite dilution using isothermal calorimeter.

Enthalpies of solvation of nitrogen-compounds in organic solvents were calculated based on experimental and literature data. Intermolecular interactions of amines with organic solvents were discussed.

Enthalpies of hydrogen bonding of nitrogen-containing compounds with proton acceptors were determined in accordance with procedure proposed in the work [1]. It is known, that *N*-methylpyrrole, *N*-methylimidazole, *N,N*-dimethylaniline have no acidic proton, so they don't form hydrogen bonds with proton acceptors. It was shown, that pyrrolidine and piperidine have negligible acid properties. However it was revealed, that enthalpies of specific interactions of aniline with proton acceptors aren't equal to double enthalpy value for *N*-methylaniline due to the occurrence of anti-cooperative effects in complexes 1:2 aniline-bases.

Another pattern is observed when nitrogen-containing compounds interact with proton donors. It was shown that proton acceptor abilities of pyrrole, *N*-methylpyrrole, aniline, *N*-methylaniline, *N,N*-dimethylaniline are practically equal. However, in case of *N*-methylimidazole and *N*-methylpyrazole enthalpies of hydrogen bonding are significantly higher due to the formation of complexes with two solvent molecules (1:2).

Also, enthalpies of solution of organic molecules in nitrogen-containing cyclic and aromatic compounds were measured. Obtained from these data enthalpies of hydrogen bonding were compared with the values for opposite systems. It was shown, that in case of pyrrole, aniline, *N*-methylaniline as solvents enthalpies of specific interactions are above zero. This is the result of solvent reorganization (breaking of solvent–solvent hydrogen bonds).

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*This work has been supported by MK-7126.2015.3 and has been performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.*

### Section 3. Thermodynamics of solutions and heterogeneous systems

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#### INTERACTION OF CURCUMIN WITH HUMAN SERUM ALBUMIN: CALORIMETRIC AND SPECTROSCOPIC STUDIES

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The interactions of the anti-angiogenic cancer drug, Curcumin an antioxidant with human serum albumin (HSA) have been examined by the fluorescence, UV-vis, and isothermal titration calorimetry (ITC) techniques. Fluorescence results indicate that in case of HSA-drug complexes the quenching of fluorescence intensity is at 295 nm. Experimental results revealed curcumin have an ability to quench the intrinsic fluorescence of HSA tryptophan through a static quenching procedure. The binding constant is determined using Stern-Volmer modified equation and energy transfer mechanisms of quenching are discussed.  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  values are also calculated. It is found that curcumin remained bound to unfolded state of HSA and facilitates the process by pushing tryptophan moiety to more polar environment in the unfolded state. The curcumin slower down the process of denaturation of reversibly refold the sub-domain IIA, by also recovering fluorescence lifetime loss, but it was slow in the presence of curcumin. The spectroscopic and thermodynamic techniques provide a quantitative understanding of the binding of anti-angiogenic cancer drug with human serum albumin.

**INVESTIGATION OF THERMAL STABILITY OF  $\text{Li}_x\text{TiCh}_2$   
(Ch = S, Se) BY DSC METHOD**

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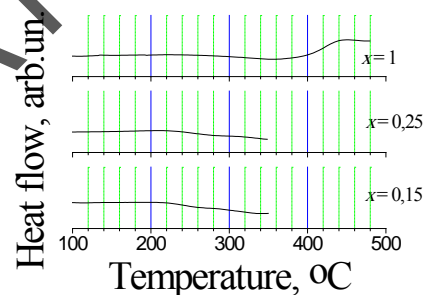
Dichalcogenides of transition metals have been extensively studied for use as cathode materials in ambient temperature high-energy density batteries.  $\text{Li}_x\text{TiCh}_2$  (Ch = S, Se) is the most promising because of its high capacity (up to  $x = 3$ ) for intercalation/deintercalation of lithium ions without significant changes in the basic layered structure exhibiting only a small reversible deformation. Structural stability upon intercalation is due to the presence of strong ionic-covalent bonds between Ti and Ch atoms [1, 2]. Despite of numerous investigations on lithium intercalation into transition metal chalcogenides, phase diagrams of the  $\text{Li}-\text{MX}_2$  ( $X = \text{S, Se}$ ) systems still not reliably established. Therefore the aim of this study was to investigate the thermal stability of the intercalates  $\text{Li}_x\text{TiS}_2$  ( $x = 0.10, 0.25, 1.00$ ) and  $\text{Li}_x\text{TiSe}_2$  ( $x = 0.05; 0.10; 0.25; 1.00$ ) by differential scanning calorimetry (DSC).

Investigations were carried out on the DSC 204 F1 Phoenix (NETZSCH) in the temperature range from 25 to 350°C, heating rate of 10°C/min and subsequent cooling in the same temperature range; the sample cell was purged with argon at a rate of 30 ml/min. The powder samples were placed and compacted into crucibles of high-pressure stainless steel. Then the crucible was thoroughly screwed by the lid with gold seals. These manipulations were carried out in a dry argon atmosphere box UNILAB MBRAUN. In some cases, the analyzed temperature range extended to 500°C. The obtained data were processed using software NETZSCH Proteus.

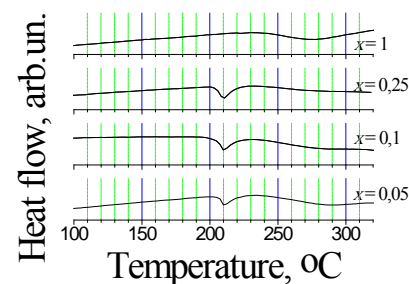
DSC curves for  $\text{Li}_x\text{TiS}_2$  and  $\text{Li}_x\text{TiSe}_2$  samples can be found in Figures 1 and 2, respectively. As can be seen, all investigated intercalates  $\text{Li}_x\text{TiS}_2$  are stable in the temperature range (25–350)°C, whereas among intercalates based on titanium diselenide only  $\text{Li}_1\text{TiSe}_2$  is stable. Heating up to 500°C does not led to any endothermic effects (Figure 1). In this case, there was only a deviation of DSC curve that may have been caused by reversible vaporization of sulfur. The intercalates  $\text{Li}_x\text{TiSe}_2$  ( $x = 0.05; 0.10; 0.25$ ) were less thermally stable: all DSC curves near 200°C display reproducible endothermic effects. This is typical for the first order phase transition. These data provides support for the reversible decomposition of solid solutions  $\text{Li}_x\text{TiSe}_2$  ( $x \leq 0.25$ ) on the matrix phase  $\text{TiSe}_2$  and thermally stable solid solution based on  $\text{Li}_1\text{TiSe}_2$ .

Thus, our investigations of  $\text{Li}_x\text{TiCh}_2$  (Ch = S, Se) compounds shows that the thermal stability of phases with completely filled octahedral positions  $\text{Li}_1\text{TiCh}_2$  is quite high and is limited only by the chalcogen volatility at elevated temperatures. At the same time, the thermal stability of solid solutions  $\text{Li}_x\text{TiCh}_2$  ( $x \leq 0.25$ ) with partially filled octahedral positions is radically different.

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**Figure 1:** DSC data of  $\text{Li}_x\text{TiS}_2$  samples.



**Figure 2:** DSC data of  $\text{Li}_x\text{TiSe}_2$  samples.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### PARTITION BEHAVIOR OF SMALL BIOMOLECULES IN THE AQUEOUS BIPHASIC SYSTEM BASED ON ALKYLIMIDAZOLIUM IONIC LIQUID OR NONIONIC SURFACTANT: EXPERIMENT AND MODELING

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Aqueous biphasic systems (ABS) based on alkylimidazolium ionic liquid or nonionic surfactants were found to be perspective for extraction of hazardous compounds or high valued products, incl. biomolecules [1, 2]. We focused on the aqueous-salt solutions of hydrophilic ionic liquids, 1-alkyl-3-methylimidazolium bromide (or chloride),  $C_n\text{MimBr}$  ( $C_n\text{MimCl}$ ),  $n = 4, 6, 8$ . The other group of systems under study includes mixed surfactant systems containing two nonionic surfactants (Triton, Span) or nonionic-ionic surfactant mixtures (Triton X-114 with cetyltrimethylammonium bromide, CTAB or sodium dodecyl sulfate, SDS).

The systems with hydrophilic ILs splitting into two liquid phases on addition of inorganic salt or other substances due to salting-out effect have been intensively studied experimentally [1]. By using PC-SAFT [3, 4] the liquid-liquid equilibrium in the ternary and quaternary systems  $C_n\text{MimX}$  ( $n = 4, 6$ ;  $X = \text{Cl}, \text{Br}$ ) +  $\text{K}_2\text{HPO}_4$  ( $\text{K}_3\text{PO}_4$ ) + (amino acid) + water was calculated. Model parameters for binary  $C_n\text{MimX} + \text{H}_2\text{O}$  mixtures were estimated using the available literature data on the densities, boiling temperatures and water activity coefficients [5, 6]. The parameters of binary interactions between IL and each of the salts under study were estimated from the phase equilibrium data for the ternary systems IL-salt-water and then these parameters were used to calculate partition coefficients of amino acids (tryptophan, alanine, tyrosine) in the quaternary systems. The comparison of the results of the model calculations with the experimental data of this study and those from [7] was made.

The effects of additives (e.g., salts or ionic surfactants) and variations in temperature or pH on the phase and partition behavior of ABS based on nonionic surfactant (Triton X-114) were studied. The clouding, phase equilibria and solute partitioning behavior for aqueous mixed systems of Triton X-114 + ionic (CTAB or SDS) or nonionic (Span 80) surfactant were investigated. Vanillin was used as a model substance at different pH values, specifically in partly dissociated or non-dissociated states. The experimental data on partition coefficients were compared with the predictions by the thermodynamic model COSMO-RS [8, 9].

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## THERMODYNAMIC STUDY ON HYDRATION OF COPOLYMER HYDROGELS OF ACRYLAMIDE WITH (METH)ACRYLIC ACID

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Polyelectrolyte hydrogels are extensively studied as advanced biocompatible materials with prospective biomedical and biotechnological applications. These materials are often referred to as “smart”, the adjective, which emphasize their ability of a controlled reaction to the variety of external stimuli. In case of hydrogels it means their substantial and reversible volume changes – contraction and swelling in respect to the variation in pH, temperature, ionic composition and the quality of a solvent. Contraction and swelling of gel network in an aqueous medium is a result of a misbalance of several internal thermodynamic forces among which the interaction of macromolecular subchains with water plays a major role. Such information can be obtained via the thermodynamic study of the hydration of polyelectrolyte gels.

We have studied two series of hydrogels: copolymers of acrylamide with acrylic acid (PAAm/PAAc) and copolymers of acrylamide with methacrylic acid (PAAm/PMAC). In both series the concentration of PAAm monomer units was set to 0, 20, 40, 60, 80, 100%. Radical polymerization of hydrogels was performed in 1.6 M water solution of monomer mixture. Cross-linking agent – methylenediacrylamide was added to the mixture in 16 mM and 8 mM concentration to provide network density 1:100 and 1:200, which is the average number of cross-links per number of monomer units in linear subchains. Ammonium persulfate in 3 mM concentration was used as an initiator. Polymerization was performed in PE probe tubes (diameter 10 mm) at 80°C for 2 h. Upon the polymerization gel cylinders were removed from the probe tubes and washed in distilled water for 2 weeks with water renewal every 2 days until constant mass of the gel samples was achieved. The equilibrium swelling degree of copolymeric gels in water was determined gravimetrically. Prior to thermodynamic measurements portions of gels were dried to the constant weight. The enthalpy of gel hydration over the entire range of water content was determined using SETARAM C80 3D Calvet calorimeter. Gibbs energy of hydration was determined via isothermal sorption of water vapors on dried gel samples. Sorption isotherms were obtained using high-vacuum apparatus of a laboratory design. All thermodynamic measurements were performed at 25°C.

The enthalpy of gel swelling strongly depended on the content of water in the gel network. At zero water content the integral enthalpy of swelling was strongly negative. At medium and high water content the partial enthalpy of hydration was positive. PAAm, PMAC and all their copolymers had close values of the enthalpy of hydration. The partial enthalpy of hydration of PAAc and its copolymers with PAAm was much more positive in the range of high and medium water content. The values of Gibbs energy of swelling were negative over the entire range of water content. Based on the obtained thermodynamic data Flory–Huggins parameters the enthalpy and entropy contributions were calculated. The dependence of Flory–Huggins parameter on PAAm/PAAc and PAAm/PMAC composition was discussed on the basis of hydrophilic and hydrophobic interactions in swollen hydrogels. As a whole, the swelling of PAAm/PAAc and PAAm/PMAC gels in water was found to be entropy driven.

*The financial support of the Russian Science Foundation (Project No. 14-19-00989) is acknowledged.*

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THE EXPERIMENTAL DATA ON CHEMICAL EQUILIBRIUM FOR THE SYSTEM ACETIC ACID + *n*-BUTANOL + *n*-BUTYL ACETATE + WATER

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The studies of chemical equilibrium (CE) and liquid–liquid equilibrium (LLE) are important both for basic physico-chemical research and for the development of energy-saving technologies. The object of presented study is acetic acid – *n*-butanol – *n*-butyl acetate – water system. Butyl acetate is a common solvent which is used in various line of industry. During the synthesis of butyl acetate may occur the splitting of solution, which can lead to undesirable consequences in the process. Knowledge of LLE and CE data is necessary for the optimization of esters synthesis process. Liquid phase splitting in reacting systems is relevant also for basic thermodynamic analysis. There is enough experimental data on LLE acetic acid – *n*-butanol – *n*-butyl acetate – water system, but there is a lack of data on the CE under the isothermal conditions. This work is a continuation of the series of studies on thermodynamic properties of multicomponent systems with coupled mass transfer and chemical reaction [1-3].

The experimental study of CE and LLE was carried out at 293.15–313.15 K by gas chromatographic (GC) analysis (Cristal 5000, Chromatec, Russia) with the internal calibration standard detection method. New experimental data on CE were obtained for homogeneous and heterogeneous regions. We also used the data that had been obtained in our recent work [3]. On the base of experimental data the surfaces of phase and chemical equilibrium were constructed in the concentration tetrahedron (Figure). The crossing CE and LLE surfaces (i.e. the establish heterogeneous CE) is discussed.

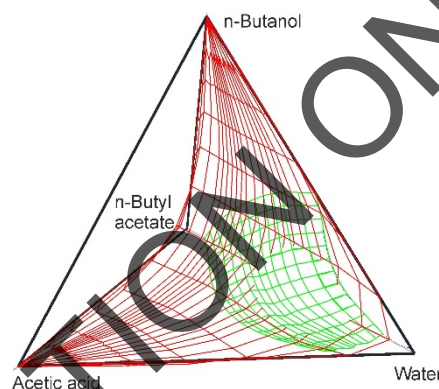
The UNIFAC model was used to calculate CE and to estimate the equilibrium constant. The calculated data were compared with available information in the references. On the base of our results the complete topological structure of the liquid phase diagram of acetic acid – *n*-butanol – *n*-butyl acetate – water system had been obtained.

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**Figure:** Quality appearance of the surface of phase (green) and chemical (red) equilibrium.

## INVESTIGATION OF THE EVOLUTION OF THREE LIQUID PHASES COEXISTENCE REGION IN THE QUARternARY MIXTURE

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When separating multicomponent heterogeneous mixtures in units consisting of distillation column and decanter, the fundamental question is the location of liquid phases coexisting region (LPCR) with different numbers of liquid phases ( $\phi^{\text{liq}}$ ) in a concentration simplex. Solution of this task is based on the vapor-liquid and liquid-liquid equilibrium data of a mixture and its constituents, as well as on the general laws of formation of the topological structure of liquid phases coexistence regions.

This work is devoted to the evolution investigation of three liquid phases coexistence region (LPCR-3) in the four-component mixture, formed by the addition of 2-methyl-1,3-butanediol (1) to the ternary 2-methyl-2-butene (2) – acetonitrile (3) – water (4) mixture. Mathematical modeling of vapor-liquid phase equilibrium of investigated quaternary mixture at the atmospheric pressure, liquid – liquid equilibria and liquid – liquid – liquid equilibria at 293.15 K is produced by AspenPlus 7.3 software. The NRTL equation parameters, using the existing experimental data [1], are regressed. Additional software was specially designed for this study. It allows processing a large amount of input data and presenting the results on a tetrahedral diagram.

A method for studying the evolution of LPCR-3 is proposed. It is built on a combined analysis of the material balance of mixing (the addition of the first component to 2–3–4 mixtures of equimolar composition for obtaining a mixture of  $x^*$  composition (brutto-composition)) and on the equation of a topological invariant separation region  $R + f = n - 1$  [2], where  $n$  – the number of components in the system. Invariant equation is a direct sum of two varieties: linear  $R$ , associated with a number of liquid phases ( $R = \phi^{\text{liq}} - 1$ ), and nonlinear  $f$ , whose dimension is equal to the number of freedom degrees for given LPCR.

When studying the LPCR-3 it is important to have the  $x^*$  composition in this region. In this case  $f = 1$  and this degree of freedom is limited by the setting up (with a particular step) the concentration of added first component. Otherwise, if  $f = 2$  then the point  $x^*$  falls into the two liquid phases coexisting region (LPCR-2), and additional degree of freedom is present. When obtaining such situation, we were changing the  $x^*$  composition in the section where  $x_1 = \text{const}$  (0.46, 0.58, 0.64 mole fraction) in a certain way. By the series of iterations we obtained comprehensive information about the boundaries of the LPCR-3 in a concentration tetrahedron and its transformation into the LPCR-2 due to the disappearance of the acetonitrile layer.

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### Section 3. Thermodynamics of solutions and heterogeneous systems

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#### COMPARATIVE STUDY OF SOLVATION PROPERTIES IN MIXTURES OF WATER WITH ACETONE, TETRAHYDROFURAN AND ACETONITRILE

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The interest to binary and especially to mixed aqueous–organic solvents is due to their unique physico-chemical properties that can be controlled by variation of their composition. Solvation of *n*-octane and toluene in binary mixtures of water with acetonitrile, tetrahydrofuran, and acetone with various compositions was considered. We determined experimentally the magnitudes of thermodynamic functions of dissolution and solvation at 298.15 K. Precision titration calorimetry was used to measure the enthalpies of solution. Limiting activity coefficients and the Gibbs free energies of solvation of the solutes in aqueous–organic mixtures were determined by gas chromatographic headspace analysis method. In addition, molecular dynamics simulations of considered mixtures were performed, and the energies of solvation of a hard sphere solute were calculated using particle insertion method.

Novel data on thermodynamics of solvation of low polar solutes in aqueous–organic mixtures revealed interesting patterns. The solvation shell of hydrocarbons is shown to be enriched with the organic cosolvent. We observed well-pronounced maxima of the dependencies of enthalpies of solvation from the composition of solvent and no maxima for the Gibbs free energies of solvation. The presence of maxima cannot be explained by preferential surrounding of apolar molecules with organic cosolvent if we stay within the framework of averaging the enthalpies of solvation in pure cosolvents. High energy cost of reorganization of binary solvent upon insertion of solute molecules is responsible for such behaviour. Enthalpy–entropy compensation leads to a steady growth of the Gibbs free energies with increasing water content. On the other hand, consideration of the plots of the Gibbs free energy against enthalpy of solvation clearly shows that the solvation properties are changed dramatically after addition of a rather small amount of organic cosolvents. It is found that they suppress the hydrophobic effect very effectively even at low concentration, which leads to the effects like denaturation of proteins or destabilization of micelles and other supramolecular aggregates in the presence of organic compounds. Acetonitrile suppresses the hydrophobic effect less than acetone and tetrahydrofuran.

THE THERMODYNAMICS OF SILVER(I)–2,2'-DIPYRIDYL COMPLEXATION  
IN MeOH–DMSO SOLVENT

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It is necessary to know the main thermodynamics characteristics of complexation reaction and reagents solvation to describe the solvent role in complex formation processes from the standpoint of solvation approach [1]. For this purpose the reaction enthalpies of silver (I) complexes with 2,2'-dipyridyl is identified by the calorimetric way at 298 K throughout the composition of DMSO–MeOH solvent. The analysis of the reactants solvation contributions in the complexation reaction enthalpy change is conducted. The data of silver(I) ion solvation in DMSO–MeOH solvent are not available. From the standpoint of solvation approach the complexation reaction enthalpy change is represented as the ligand solvation and the difference between the complex ion solvation and the silver(I) one:

$$\Delta_t H^\circ_{r1} = (\Delta_t H^\circ_{[AgDipy]^+} - \Delta_t H^\circ_{Ag^+}) - \Delta_t H^\circ_{Dipy} \quad (1)$$

where  $\Delta_t H^\circ_{r1}$  – the transition enthalpy of the silver(I) monocomplex ion formation reaction, kJ/mol;  $(\Delta_t H^\circ_{[AgDipy]^+} - \Delta_t H^\circ_{Ag^+})$  – the difference between the complex ion solvation and the silver(I) ion one, kJ/mol;  $\Delta_t H^\circ_{Dipy}$  – the 2,2'-dipyridyl transition enthalpy change [2], kJ/mol.

It is established that the exothermicity of silver (I) complex formation reaction increases with growing of methanol content in mixed solvent due to positive affect of difference between the complex ion solvation and the silver (I) one. Strengthening of ligand solvation contributes insignificantly effect to the enthalpy of complex formation reaction.

The Gibbs free energy, enthalpy and entropy changes are calculated using the stability constants of silver(I) complexes [3]. In the case of silver(I) monodipiridyl formation growth of negative values of Gibbs energy of the reaction to increase the content of methanol in the mixed solvent is observed due to the influence of both the enthalpy and mainly entropic factors. For complexation reaction to the second stage of coordination step is observed a similar change in the Gibbs energy of complexation reactions due to the advantage of the enthalpy contribution.

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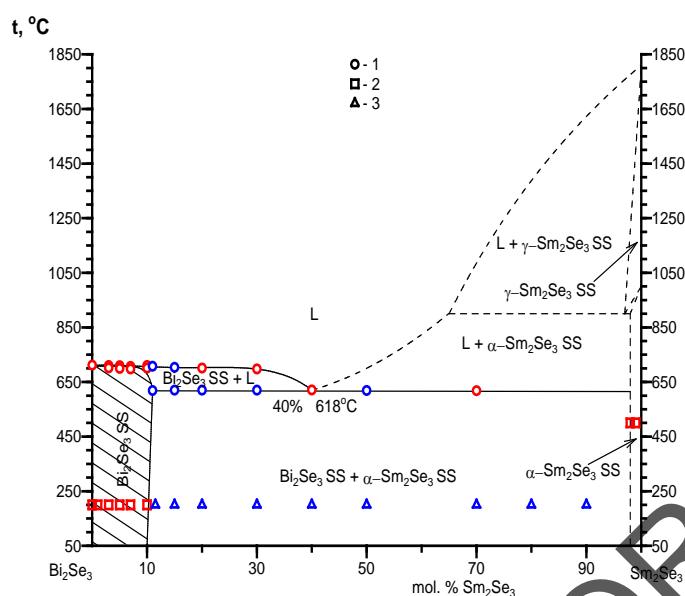
*This study was carried out in the framework of State Task of the Ministry of Education and Science of the Russian Federation (Project No. 2293).*

## Section 3. Thermodynamics of solutions and heterogeneous systems

### CREATING THE PHASE DIAGRAMM OF $\text{Bi}_2\text{Se}_3$ – $\text{Sm}_2\text{Se}_3$ SYSTEM. THERMODYNAMICS OF PHASE TRANSFORMATION

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**Figure:** Phase diagram of  $\text{Bi}_2\text{Se}_3$ – $\text{Sm}_2\text{Se}_3$  system:  
1 – DSC data (experimental aggregate SETSYS Evolution TG-DSC 1600); condition of the samples according to XRD and MSA data; 2 – single-phase sample; 3 – two-phase sample.

The eutectic point composition is 40 mol.%  $\text{Sm}_2\text{Se}_3$ . An interesting feature of the diagram – a slight decrease the liquidus line in the solid solution area, followed by a sharp drop in the two-phase area. The fusion heat of  $\text{Bi}_2\text{Se}_3$  is 51120.72 J/mol was determined. The resulting value is much lower than published data ( $\Delta H_{\text{fus}}(\text{Bi}_2\text{Se}_3) = 85000$  J/mol [2]). Intermolecular interactions of  $\text{Bi}_2\text{Se}_3$ – $\text{Sm}_2\text{Se}_3$  system were analyzed by mixing energy calculation with using the D. S. Kamenetskaya equation [3] for left liquidus line. Mixing energy for selected temperature is less then 2RT. This fact explains the absence of complex selenides in  $\text{Bi}_2\text{Se}_3$ – $\text{Sm}_2\text{Se}_3$  system.

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**PECULIARITIES IN CRYSTALLIZATION KINETICS  
OF SOME CoFeBSiNb BULK AMORPHOUS ALLOYS**

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Co-based bulk metallic glasses are a novel group of engineering materials with unique mechanical, magnetic and corrosion properties. However their industrial application is limited due to low glass forming ability (GFA). In this work we investigated the influence of gallium, tin and zirconium small additions on crystallization of  $\text{Co}_{48}\text{Fe}_{25}\text{B}_{19}\text{Si}_4\text{Nb}_4$  bulk amorphous alloy. The samples in the form of rods 1.5 mm in diameter were prepared by melt injection into a water-cooled cooper mould. DSC curves were obtained at heating-cooling rates of 5, 10, 20 and 40 K/min.

The results are analyzed in the frames of classical JMA model; the glass transition and crystallization temperatures as well as activation energies are determined. It is found, in particular, that in the base composition crystallization goes in one stage with the formation of  $(\text{CoFe})_{23}\text{B}_6$  compound. Introduction of 2 at.% Ga (Zr, Sn) leads to the appearance of the second stage of crystallization with the precipitation of  $\text{MNbB}$  ( $\text{M} = \text{Fe, Ga, Sn, Zr}$ ) metastable borides. The following heating or annealing of the samples cause the decomposition of metastable phase into stable  $\text{Nb}_2\text{B}$  and  $\text{Fe}_2\text{B}$ .

The existing GFA criteria are discussed and it is shown that the new criterion for melts glass forming ability should be introduced.

*The work was partially supported by the Ministry of Education and Science of the Russian Federation (Project No. 4.1177.2014/K) and the Russian Foundation for Basic Research (Project No. 13-03-00598-a).*

## Section 3. Thermodynamics of solutions and heterogeneous systems

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### DSC, ELECTRIC AND MAGNETIC PROPERTIES OF SOME AL–NI–REM AMORPHOUS ALLOYS

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Al–Ni–R amorphous alloys are a novel group of engineering materials with unique physical properties. Nowadays they are going to be used as protecting coatings for the constructions working in corrosive medium. However their physical properties as well as crystallization kinetics are not studied enough. In this works we investigated electrical resistivity, magnetic susceptibility and crystallization path of Al<sub>86</sub>Ni<sub>8</sub>R<sub>6</sub> (R = Gd, Ho, Sm) amorphous ribbons (width – 6 mm, thickness – 30–35 μm) prepared by the standard planar flow method. DSC curves were obtained at heating-cooling rates of 5, 10, 20 and 40 K/min.

It was found that for Sm- and Gd-containing alloys crystallization goes in 4 stages, whereas for ribbon with Ho – in 3 stages: aluminum nanoparticles appear at the first stage; the intermetallic compound Al<sub>3</sub>Ni arises at the second stage independently of the alloy composition; Al<sub>3</sub>R compound comes at the third stage and the eutectic reaction Al + Al<sub>3</sub>Ni + Al<sub>3</sub>R → Al<sub>23</sub>Ni<sub>6</sub>R<sub>4</sub> takes place at the fourth stage. The latest compound seems to be stable: neither annealing at 800 K for several hours nor exposition at room temperatures for several months has destroyed it. It can be decomposed into binary compounds by heating to rather high temperatures only.

Resistivity temperature curves confirm the fact that for the alloys with gadolinium and samarium crystallization goes in 4 stages and for ribbons with holmium – in 3 stages. In amorphous state the resistivity absolute values are at a level of  $\rho = 230\text{--}250\ \mu\text{m}\Omega\cdot\text{cm}$  with practically zero temperature coefficient that allows one to consider these alloys as stable high-resistance materials. During crystallization  $\rho$  decreases for 5 times showing the fact that the contribution of the short-range order is negligible.

Magnetic susceptibility dependences  $\chi(T)$  obtained by Faraday's method were found to follow Curie–Weiss law for ribbons with Gd and Ho and increase in all temperature range for ribbon with Sm. The later is an evidence of Van Fleck magnetism typical for Sm-containing alloys. Some characteristics of electronic structure (effective magnetic moment per atom, paramagnetic Curie temperature, density of states at Fermi level) were calculated from the experimental curves. The results are discussed in supposition of coexistence of paramagnetic aluminum matrix with the embedded branched network consisting of Al<sub>2</sub>R quasimolecules.

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**THE TECHNIQUE OF MULTICOMPONENT PHASE DIAGRAMS  
ONSTRUCTION WITH USAGE OF EXPERIMENTAL METHODS**

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Based on great and longtime experience in construction of phase equilibrium diagrams authors has developed the technique of detailed research of phase transitions with complex usage of modern analytical methods. Proposed technique can be used for investigation of phase transformations and construction the phase diagrams of inorganic systems both with nonvolatile and volatile compounds.

The first step of investigation is analysis of boundary systems and correct choice of the experimental samples after estimation the scheme of phase transitions (Sheil scheme). After this procedure the synthesis of samples under special conditions should be performed. The main synthesis goal is receiving of uniform samples with desired compositions and structure. Last time authors of this work was focused on preparation and experimental research of systems with volatile compounds (such as S, Sn, Zn, etc.), so, more attention will be paid to this problem.

Main experimental methods are Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA). These methods were used for identifications the nature and temperature ranges of thermal effects during the heating. Scanning Electron Microprobe (SEM) and Electron Probe Microanalysis (EPMA) were used for identification the phase compositions and structures of experimental samples. X-ray Diffraction analysis (XRDA) let us defining the crystal structure of equilibria phases. After receiving detailed and approved results about the phase transitions in the volume of investigated system authors have constructed the liquidus and solidus surface projections using mathematical approach for a range of ternary systems, including such compounds, as Cu, Co, Ni, Fe, S, Sn. Some of them will be presented at the conference.

*This work was supported by the Russian Foundation for Basic Research (Projects No. 14-08-31381 мол\_a and No. 14-08-00453 a).*

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC CHARACTERISTICS OF L-PROLINE DISSOLUTION IN THE AQUEOUS SOLUTION OF ORGANIC SOLVENTS AT 298.15 K

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The present study is a continuation of our investigations of the processes of dissolution and solvation of amino acids and peptides in aqueous-organic mixtures. In this context, we want to study the effect of difference physico-chemical properties of organic solvents on the process of dissolution of amino acids in aqueous-organic mixtures using L-proline as an object of study. L-proline is one of the most important amino acids in the proteins of virtually all organisms. The structure of amino acid, specifically, the presence of an aromatic or heterocyclic group in amino acid molecule contributes to the interaction with the components of the water-organic mixtures. Therefore, we determined by a calorimetry method the enthalpies of solution ( $\Delta_{\text{sol}} H^m$ ) of L-proline in aqueous solutions of acetonitrile (AN), 1,4-dioxane (1,4-DO), acetone (AC), formamide (FA), *N*-methylformamide (MFA), *N,N*-dimethylformamide (DMFA), *N,N*-dimethylacetamide (DMA) and *N,N*-dimethylsulfoxide (DMSO) as a function of organic solvent concentration at 298.15 K. Enthalpies of transfer ( $\Delta_{\text{tr}} H^*$ ) of L-proline from water to aqueous organic mixtures as well as the enthalpy coefficients of pairwise interaction ( $h_{xy}$ ) were calculated from these data. The interrelation between enthalpy characteristics of L-proline dissolution (transfer) and the composition of water-organic solvent binary mixtures has been ascertained. By means of a modified Kamlet-Taft equation (1) the contributions of different physico-chemical properties of organic co-solvents to the energy of L-proline – co-solvent intermolecular interactions have been estimated quantitatively:

$$h_{xy} = A_0 + A_1(\delta_1^2/1000)(V_2/100) + A_2(\pi_1^* \pi_2^*) + A_3(\alpha_1\beta_2) + A_4(\beta_1\alpha_2).$$

The analysis of the experimental and calculated data shows that the energy of intermolecular interactions of L-proline with the organic solvent molecules in aqueous solution depends not only on the mixture composition and the structure of the organic solvent, but on their physico-chemical properties as well:

- on energy of the formation of the mixed solvent (weak intermolecular interactions in the mixtures of H<sub>2</sub>O + AN, H<sub>2</sub>O + FA and H<sub>2</sub>O + MFA contributes to the solvation of L-proline, the strong intermolecular interactions in the mixtures of (H<sub>2</sub>O + alcohol) and (H<sub>2</sub>O + dimethylamides) – weakens a solvation);
- on the nature and the concentration of an organic component (the increase in the concentration of organic co-solvent can smoothly increase the exothermicity of the solvation of L-proline both in the case of AN, FA, MFA and can assume extreme character as in the case of alcohols, acetone, 1,4-dioxane, DMF, DMA and DMSO);
- the increase in polarity, polarizability and basicity of the organic co-solvent will strengthen intermolecular interactions with the molecules of L-proline;
- the increase in the cohesion energy density, the molar volume and acidity of organic co-solvent will weaken the energy of pairwise interactions L-proline – organic co-solvent.

CALCULATION OF THERMODYNAMIC PARAMETERS OF CRYSTALLIZATION  
IN SYSTEM  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 

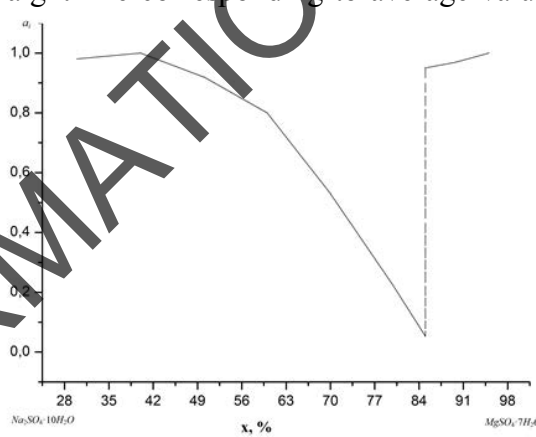
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In this work as method of the cyclic thermal analysis (CTA) the chart of a state in system  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , on which the minimum temperatures in the field of overcooling of  $T_L^{\min}$ , at which spontaneous crystallization, average overcoolings concerning the line of a liquids  $\langle \Delta T_L^- \rangle = T_L - T_L^{\min}$  and lines of a solidus  $\langle \Delta T_S^- \rangle = T_S - T_S^{\min}$  were applied is constructed. Structure of an eutectic  $\sim 85$  mass%  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + 15$  mass%  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . The line corresponding to  $T_S$  temperatures practically is the straight line corresponding to average value of  $-8.0 \pm 1.0^\circ\text{C}$ . Besides for all mixes overcooling  $\Delta T_S^-$  concerning  $T_S$  solidus temperature were fixed. Average values  $\langle \Delta T_S^- \rangle$  lay within  $(2.0 \pm 1.0)^\circ$  and didn't depend on a preliminary overheat of a liquid phase  $\Delta T^+$ . Using Schroder's equation for the line of a liquids as from  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and from  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , eutectic coordinates were found ( $x_E = 0.1498$  and  $T_E = 264.19$  K). By means of the software package of "OriginPro 8" interpolation curves for the  $x \geq 0.15$  and the  $x \leq 0.85$  solutions are received. The function connecting properties of solutions with each other thermodynamic activity of  $a_i$  was offered. Measurements of activity give the chance to estimate deviations in behavior of real solutions from ideal, however don't open the mechanism of interaction of solvent and the dissolved substance. The equation for dependence of real solution on activity of solvent will have an appearance:

$$\ln a_i = \frac{\Delta \bar{H}_{Li}}{RT^2} \left( \frac{1}{T_L} - \frac{1}{T} \right).$$

For definition of  $a_i$  it is necessary to know  $\Delta \bar{H}_{Li}$ ,  $T$  and  $T_L$ . The reasons of formation of mixes of the eutectic type in systems of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  are essential difference of structure of molecules, the content of crystallization water in the corresponding hydrates, configurations of molecules of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , size of hydrogen communications, etc. At incongruent melting of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  saturated solution of salts  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  in own crystallization water turns out, i.e. there is their dehydration according to the scheme  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow \text{MgSO}_4 + 7\text{H}_2\text{O}$ . Thus  $\text{H}_2\text{O}$  molecules in the corresponding crystals form a difficult network of hydrogen communications.



**Figure:** The dependence of thermodynamic activity  $a_i$  on composition of system  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ .

## Section 3. Thermodynamics of solutions and heterogeneous systems

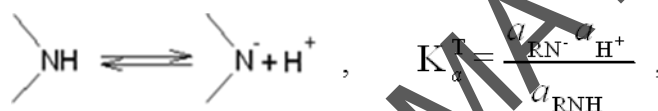
### DETERMINATION OF 5-SUBSTITUTED-1H-TETRAZOLES DISSOCIATION CONSTANTS BY NON-BUFFERED SPECTROPHOTOMETRIC METHOD

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A number of tetrazoles compounds is of interest as these compounds are used as isosteric functional groups of various substituents in the design of biologically active substances. Thus, 5-substituted-1H-tetrazoles are used as isosteric substituents of carboxyl group due to their close values of the acidity constants of carboxylic acids [1]. A number of papers in which tetrazoles successfully applied in the development of new pharmaceuticals is growing. Nevertheless, information of their acidity constant is fragmented.

5-Substituted-1H-tetrazoles are NH-acids. Their dissociation constants depend on the substituent in position 5. The basis for consideration of weak NH-acids is Bronsted–Lowries theory, according to which the acid-base equilibrium is characterized by the thermodynamic dissociation constant  $K_a^T$ :



where  $a_{\text{RN}^-}$ ,  $a_{\text{H}^+}$ ,  $a_{\text{RNH}}$  are the activity of dissociated ions and NH-acids (RNH)

In our recent paper [2] it was proposed an experimental and theoretical approach to determine the thermodynamic dissociation constants of weak organic acids in water and water–organic environment by using the unbuffered spectrophotometric measurements in combination with the numerical extrapolation methods. The proposed method does not require maintaining a constant ionic strength of the electrolyte solution, use of buffer solutions as well as pH measurements. This leads to significantly reduction of the experiment time. Acidity of the environments is created by a test compound with the addition of a strong background electrolyte whose concentration is less than  $10^{-3}$  M. Dissociation constants of weak electrolytes are determined by plotting the optical density of solutions on their concentration, followed by calculation of the concentration of constants using the Law of dilution. The investigations of solutions of weak electrolytes are conducted at the concentrations of  $10^{-5}$ – $10^{-3}$  M. We propose an approach which allows to obtain thermodynamic constants  $K_a^T$  from concentration constants without calculating of the solutions ionic strength and without the concept of activity.

UV spectra of each aqueous solution of 5-substituted-1H-tetrazoles were recorded by spectrophotometer Shimadzu UV-2700. New values of the NH-groups thermodynamic dissociation constants for a 5-substituted-1H-tetrazole in aqueous solutions were obtained. The results of research enable to investigate their biological activity.

[1] Myznikov, L.V.; Koldobskii, G.I.; Hrabalek, A. *Chemistry of Heterocyclic Compounds*, 2007, 43, 1, 1-9.

[2] Lusova, S.S.; Starikova, T.A.; Zevatskii, Yu.E. *Russian Journal of General Chemistry*, 2014, 84, 8, 1634-1635.

**MODELING OF THERMODYNAMIC PROPERTIES  
OF MELTS IN THE  $\text{Bi}_2\text{O}_3$ –( $\text{B}_2\text{O}_3$ ,  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$ )– $\text{SiO}_2$  SYSTEMS**

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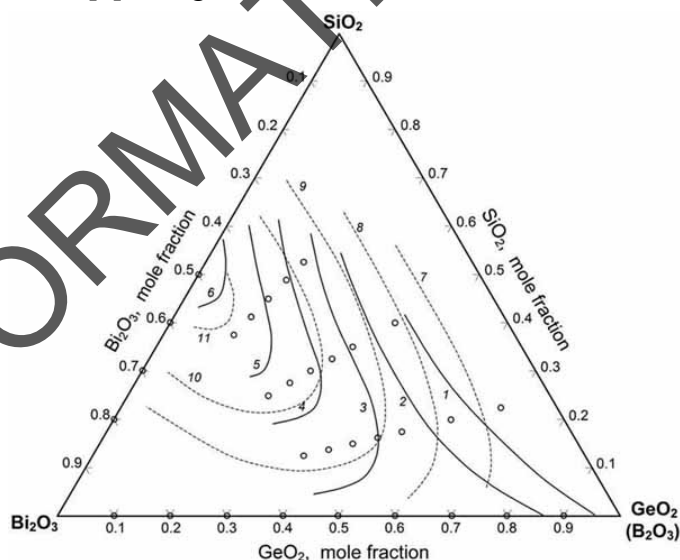
The generalized lattice theory of associated solutions (GLTAS) [1] proved to be valid when applied to modeling of the thermodynamic properties of melts containing  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{BaO}$  and some of other oxides. The aim of the present study was to model the thermodynamic properties of the melts in the  $\text{Bi}_2\text{O}_3$ – $\text{B}_2\text{O}_3$ – $\text{SiO}_2$ ,  $\text{Bi}_2\text{O}_3$ – $\text{GeO}_2$ – $\text{SiO}_2$ , and  $\text{Bi}_2\text{O}_3$ – $\text{P}_2\text{O}_5$ – $\text{SiO}_2$  systems for evaluation and comparison of the integral thermodynamic functions of these systems.

The results of the high temperature Knudsen effusion measurements of activities of components [2] served the experimental basis for the simulation. Only the ranges referring to glass-forming compositions were investigated, the obtained experimental data was reduced to  $T = 1200$  K.

For the given systems calculations closely followed [1]: using available information on the structure of a melt a suitable model lattice and structural units were chosen. The complete set of parameters included the coordination number of the lattice  $z$  (3), numbers of contact points of different types characterizing structural units, numbers of lattice sites occupied by them, and energy parameters attributed to each pair of contact points representing a certain bond formed in the melt. As a result of best-fit procedure approximating the measured activities by the values found by solving an auxiliary system of equations, activities of all components could be determined.

In Figure the computed lines of constant excess Gibbs energy for melts in the  $\text{Bi}_2\text{O}_3$ – $\text{GeO}_2$ – $\text{SiO}_2$  and  $\text{Bi}_2\text{O}_3$ – $\text{B}_2\text{O}_3$ – $\text{SiO}_2$  systems are given as an example. For both systems the only measured value was  $a(\text{Bi}_2\text{O}_3)$ , activities of two other components to be substituted in  $\Delta G^E = RT \sum x_i \ln(a_i/x_i)$  were calculated from the best-fit parameters of the model.

Thus, by the modeling based on GLTAS the experimental values of  $a(\text{Bi}_2\text{O}_3)$  and  $a(\text{P}_2\text{O}_5)$  allowed to assess the activities of other components, Gibbs energies of the melts in the systems studied and relative numbers of bonds of different types formed in these melts.



**Figure:** Excess Gibbs energy of the melts in the  $\text{Bi}_2\text{O}_3$ – $\text{GeO}_2$ – $\text{SiO}_2$  system (solid lines) at  $T=1200$  K obtained using GLTAS compared to  $\Delta G^E$  of the melts in the  $\text{Bi}_2\text{O}_3$ – $\text{B}_2\text{O}_3$ – $\text{SiO}_2$  system (dashed lines). Numbers indicate the values of  $-\Delta G^E$ : 1 – 5, 2 – 10, 3 – 15, 4 – 20, 5 – 25, 6 – 30, 7 – 15, 8 – 20, 9 – 25, 10 – 30, 10 – 35 kJ/mol.

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[2] Stolyarova, V.L., Lopatin, S.I., Shugurov, S.M., Shilov, A.L. Abstracts of XIV Russian Conference (with international participation) on Thermophysical Properties of Substances (RCTP-14), Kazan, Russia, 2014, 2, 252-253.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMIC MASS SPECTROMETRIC STUDIES OF MULTICOMPONENT SILICATE SYSTEMS

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Review on advantages of high temperature mass spectrometric method to study thermodynamic properties and vaporization processes of multicomponent silicate systems up to the temperature 2500 K are presented. In the present study the experimental results as well as modeling of thermodynamic properties of multicomponent silicate systems obtained during last ten years are summarized. The systems under consideration are of great importance in various fields of high temperature materials chemistry and technologies such as glass, ceramics, coatings production, metallurgy, geochemistry, nuclear and space technologies and some others. Data on the vaporization processes and thermodynamic properties of the ternary silicate systems such as  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{Cs}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{MgO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{SrO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{BaO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{PbO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{CdO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ,  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ,  $\text{CaO}-\text{TiO}_2-\text{SiO}_2$ ,  $\text{BaO}-\text{TiO}_2-\text{SiO}_2$ ,  $\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ ,  $\text{Bi}_2\text{O}_3-\text{GeO}_2-\text{SiO}_2$  and  $\text{Bi}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$  are discussed. Some industrial applications of experimental studies and the theoretical approaches for understanding the thermodynamic behavior of multicomponent silicate systems were also illustrated. It was shown that the content of vapor over multicomponent silicate systems was in agreement with the composition of the gaseous phase over the corresponding binary systems where associated, dissociated and polymerized products were found. The regularities of the vaporization of multicomponent silicate systems were discussed from the point of view of the acid-base concept. Results on determination of thermodynamic functions in the silicate systems mentioned were considered taking into account the main requirements for the confirmation of their reliability. Thermodynamic functions of these systems such as activities and chemical potentials of components as well as the Gibbs energies showed various signs of the deviations from the ideal behavior. For modeling of thermodynamic properties of these silicate melts studied the theory of the ideal associated solution and the general lattice theory of associated solutions were used. Using these approaches the different levels of deviation from the ideality in the silicate melts studied were clarified.

It should be noted that further development of high temperature mass spectrometry for the solution of the task "High temperature materials science and processing of silicate systems" has to include mainly consideration of the following important questions:

- to obtain new additional reliable experimental data on thermodynamic properties of silicate systems;
- to create data bases of thermodynamic properties of oxide systems and models for prediction:
  - a) the partial pressures of vapor species over oxide materials,
  - b) thermodynamic properties of oxide materials,
  - c) phase diagrams of the complex oxide systems;
- to predict thermodynamic properties of silicate materials using statistical thermodynamic approaches including the consideration of the correlation between the thermodynamic properties studied and the structure of these materials;
- to find the regularities of vaporization processes of silicate systems and materials at high temperatures.

*The present study was done according to the financial support of the Russian Foundation for Basic Research (Project No. 13-03-00718).*

THE TEMPERATURE DEPENDENCE OF THE COEFFICIENT OF VISCOSITY  
IN AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES

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Dynamic viscosity of the solutions changes noticeably with the changes in the structure of solvated particles under the influence of external actions (changes in concentration and the temperature of the solution). In [1] the equation of the dependence of the relative solution viscosity on the molar fraction of electrolyte is proposed. Graphical analysis of this equation allows to determine the coefficient of viscosity (parameter B) that reflects interaction effect between ions and the solvent. Electronic data processing of a large set of experimental points of dynamic viscosity [2] was used to determine the coefficient of viscosity in aqueous solutions of 45 *s*- and *d*-metal salts. Linear approximation of a specified dependence for electrolyte solutions in small ranges of mass fractions (from 0.02 to 0.04; from 0.04 to 0.06, and so on to saturation) was inferred. When the temperature increases, the interval of mass fractions ranging from 0.02 to 0.04 for all analyzed compounds is characterized by sharp and abrupt changes in parameter B. Similar changes in temperature dependence of the coefficient of viscosity can be seen in aqueous solutions of all examined salts. To illustrate this fact values of parameter B for magnesium perchlorate solutions (although similar temperature dependence is observed in aqueous solutions of lithium chloride, copper sulfate, potassium dichromate and so on) in the range of mass fractions from 0.02 to 0.04 at the temperature (0–100)<sup>o</sup>C are shown in Figure.

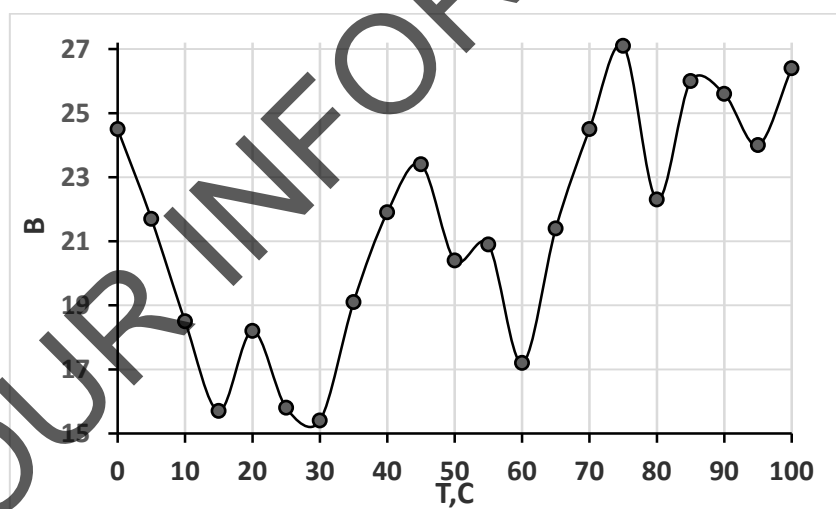


Figure: Dependence of parameter B of magnesium perchlorate on the temperature of solution. Range  $\omega$ : 0.02–0.04.

Temperatures 15, 30, 60 and 80<sup>o</sup>C are of particular interest. Viscosimetric analysis at the described conditions shows a minimum interaction force of the electrolyte ions with water molecules. According to [3] structural changes occur in water at the temperature of 300<sup>o</sup>C. Therefore, structural changes in water occur at 15, 60 and 80<sup>o</sup>C as well. The strongest interaction between electrolyte ions and water molecules is noticed at 45, 75 and 85<sup>o</sup>C.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### PHARMACEUTICAL SALTS AND CO-CRYSTALS OF ASTHMATIC DRUGS

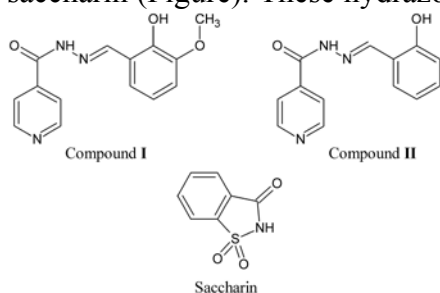
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The development of pharmaceutical salts and co-crystals is one of the hot topics in the field of crystal engineering nowadays as they can fine tune relevant physico-chemical properties of active pharmaceutical ingredients (API). Solubility and bioavailability of an API are important and related properties. APIs have been formulated as salts to change the solubility (increase or decrease) and/or obtain better bioavailability, among other reasons. An estimated half of all drug molecules used in medicine are administered as salts so that the formation and the selection of a suitable salt for a drug candidate are recognized as essential steps in the preclinical phase of modern drug development. In this work, we report pharmaceutical salts of potent asthmatic drugs developed in “Russian research center for safety of bioactive substance” (Staraja Kupavna) with saccharin (Figure). These hydrazone derivatives show antiasthmatic, anti-inflammatory and anti-



**Figure:** Molecular structures of the drug compounds and saccharin.

allergic activities. However, pharmacological activity of the drugs is limited by poor physico-chemical properties. Therefore, the development of novel crystal forms (salt and/or co-crystal) with enhanced physico-chemical profile is highly required. In this case, saccharin was chosen as a coformer because of several important advantages. Firstly it is a GRAS (generally recognized as safe) compound and therefore the API saccharinates do not need exhaustive and separate clinical trials, barring perhaps toxicological studies. The high water solubilities of the saccharinates mean that they can be used in injectible and drop formulations, which is important for asthma treatment. Because saccharin is a potent sweetener, it masks the bitter taste of many drugs and the saccharinates may be used in pediatric medication. Finally, the pH of the saccharinate solutions are higher (pH 5–6) than the corresponding hydrochlorides and other usual salt formulations (pH 2–3). This means that injectible forms of the drug are less likely to cause irritation and other undesirable side effects on the skin.

The crystal structures of I and II salts with saccharin were analyzed by single-crystal X-ray diffraction. Both saccharinates crystallizes in the centrosymmetric space group  $P2_1/n$  with one API cation and one saccharate anion in the asymmetric unit. The main intermolecular interaction in the salts is characterized by an  $N^+-H...O$  hydrogen bond between ions. A second  $N-H...O$  hydrogen bond connects two neighbouring [API+Saccharin] units to form a hydrogen bonded chain across a crystal. The intrinsic dissolution studies show that the saccharinates water dissolution rates are *ca.* 1.5 times higher compared to the initial APIs. In case of a longer-term dissolution experiment, the saccharinate of I shows solubility, which is higher by factor of 3.5 than that of the pure API. For the saccharinate of II, the solubility enhancement is found to be 6.0 times the solubility of the initial II. Therefore, it was established that salt formation of the asthmatic drugs with saccharin is able to enhance their pharmaceutically relevant properties such as aqueous dissolution and intrinsic dissolution rate.

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THERMODYNAMICS OF INTERMOLECULAR INTERACTIONS IN MAGNETIC COMPOSITIONS BASED ON SILICONE RUBBERS

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Development of technologies of production and research of properties of magnetic polymeric materials is one of the actual directions of science. Researches in the field of creation of special magnetic compositions have great importance. Use of silicone rubbers for creation of magnetic compositions does wide prospects of use one in electromagnetic devices for low temperatures and hostile environment. Properties of compositions depend on structure, the nature of components, structure and intermolecular interaction. In this work we studied the thermodynamics of intermolecular interactions in magnetic compositions based on silicone rubbers.

Nickel nanoparticles ( $S_{sp}$  8 m<sup>2</sup>/g) were used. Particles were received by method of electric explosion of a wire of metal at Institute of Electrophysics of Russian Academy of Sciences (Yekaterinburg). Used SKTV copolymers (dimethylsiloksan and 1 mol.% of methylvinilsiloksan), and SKTFT (dimethylsiloksan, 1 mol.% of methylvinilsiloksan and 50 mol.% methylfluorinepropylsiloksan). Magnetic compositions were prepared by mixing the components in solution. Nickel powder with the polymer solution was subjected to ultrasonic treatment and intense mechanical mixing to obtain a uniform distribution of magnetic particles.

Enthalpies of dissolution of copolymers in toluene, chloroform and ethylacetate are measured by isothermal calorimetry method. Enthalpy of surface wetting of nickel nanoparticles is measured. Enthalpies of dissolution of compositions in ethylacetate are measured. The enthalpy of mixture of components of composition in the wide range of concentration is calculated with use of experimental data. The enthalpy of adhesion and parameter of structure are calculated with use of the theory developed by us [1] for description of an enthalpy of mixture in the filled polymeric compositions.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

### THE ENTHALPIES OF FORMATION AND MIXING OF $\text{NH}_4\text{M}^{\text{I}}_{1-x}\text{M}^{\text{II}}_x\text{PO}_4\cdot\text{H}_2\text{O}$ ( $M = \text{Mn, Fe, Co}$ ) SOLID SOLUTIONS

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This work is a part of systematic investigations of the thermodynamic properties of new materials synthesized on the basis of compounds of transition elements. It is carried out at Luginin's Laboratory of Thermochemistry and Inorganic Synthesis Laboratory of Inorganic Chemistry division. It is devoted to the study of thermochemical properties of substitution solid solutions:  $\text{NH}_4\text{Fe}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$  and  $\text{NH}_4\text{Co}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$ . The choice of research object is caused by its application as precursors for synthesis of cathode material in Li-ion batteries. The reproducible synthesis of such compounds and application of materials based on them require knowledge of thermodynamic properties of double lithium and transition elements phosphates and its precursors.

There is no literature data on thermochemical properties of  $\text{NH}_4\text{Fe}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$  and  $\text{NH}_4\text{Co}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$  solid solutions. Only one work [1] was concerned with the determination of the  $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$  enthalpy of formation. According to the IUPAC classification, the data obtained in single work can be considered only as preliminary.

The samples of  $\text{NH}_4\text{Fe}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$  and  $\text{NH}_4\text{Co}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$  ( $x = 0, 0.25, 0.5, 0.75, 1$ ) were prepared by coprecipitation method. The ammonium and phosphates groups are introduced in the  $M(\text{OH})_2$  matrices. The precipitates were washed out by the distilled water and dried up. The synthesized samples were checked by X-ray, ICP-MS and TG analysis. The X-ray examination supported the single-phase nature of samples. It state by using X-ray and TG analysis that investigated solid solutions are monohydrates.

To determinate the enthalpies of formation of studied solid solutions, the enthalpies of reactions of  $\text{NH}_4\text{Fe}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$  and  $\text{NH}_4\text{Co}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$  with 1 M hydrochloric acid were measured at 298.15 K in a hermetically sealed swinging calorimeter with an isothermal coat. Temperature rise in each run was measured by platinum resistance thermometer. Thermometric sensitivity of circuit was  $3\cdot 10^{-5}$  K. The energy equivalent of calorimeter was determined by electric technique. The enthalpies of formation of specified solid solution were calculated on basis of experimental data and the reliable literature data on thermochemical properties of ammonium, iron, cobalt, manganese chlorides and phosphoric acid solutions.

The enthalpies of formation of studied systems depend on type of transition element. These values decrease by an increase of  $x$  (the degree of Mn substitution for Fe and Co). The enthalpies of mixing are negative for Fe–Mn system and the dependence of these values on  $x$  has the minimum at  $x = 0.5$ . The solid solution of  $\text{NH}_4\text{Fe}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$  can be considered as regular solution. The enthalpies of mixing are not near from 0 within measurement errors for Co–Mn systems. The entropy factor can play the role in thermodynamic stability of  $\text{NH}_4\text{Co}_{1-x}\text{Mn}_x\text{PO}_4\cdot\text{H}_2\text{O}$  solution.

The  $\text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O}$  enthalpy of formation found by us coincides with data [1] within measurement errors. All of other thermochemical parameters were obtained for the first time in this work.

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## SPECIFIC FEATURES OF COMPLEX FORMATION IN MULTIVALENT METAL HALIDE MELTS

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Non-standard approach to the problem of dissociation equilibrium in liquid electrolytes goes back to the pioneering work of Debye and Hückel [1]. Electrostatic interaction of ions, their screening, significantly affect the position of the chemical equilibrium. The idea of the existence of auto-complexes in salt melts proposed in [2]. Assumption that rigid bonds between the cation and anions, highly symmetric coordination of ligands around the cation, as well as the availability of relevant comprehensive grouping of normal vibration frequencies allowed on a qualitative level to give an interpretation of spectroscopic experimental data. It is not surprising that such qualitative representation further attempted to extend and on a wide range of thermodynamic and physicochemical variables [3]. At the same time, the interaction of complex anions and single cations and anions was neglected. In other words, it was implicitly assumed that the ideal mass action law (MAL) is valid. In this model the interaction of charged particles in the system was neglected as well as change in volume due to chemical reaction leading to formation of auto-complexes. It is obvious that such an approach is contrary to the classical theory of electrolytes. There is one important fact to construct a correct theory. In dilute electrolytes solutions one can ignore the effect of the volume change associated with chemical reaction due to the overwhelming contribution to the volume of the solvent solution. However, in salt melts formation of large anionic groups with a large volume occupied by the total volume of the corresponding number of free ions is challenged system as a whole, as a result of excessive work to create a large cavity in the liquid, and because of the loss in the screening of electrostatic interactions [4]. Thus, correct MAL must be complemented by the equation of state (EoS) [5, 6]. It is obvious that even the simplest model to analyze the problem of complexation must necessarily take into account different sizes of single and complex ions in salt melt. The proposed work is an analysis of possible reasons for dissociation of auto-complex anions in ionic environment on the example of two statistical theory approximations (Debye–Huckel and MSA). We give description of the Gibbs free energy and derive full equilibrium conditions (MAL and EoS) to analyze the problem of auto-complexes in molten salt. It is shown that the chemical equilibrium towards the formation or dissociation of the complex anions in salt melts is determined by the competition of the dissociation energies inside the complex with the electrostatic interactions of all charged particles in the melt, as well as by the excluded volume effects at high pressures. We discuss possible types of temperature dependence of the complexes concentration for two examples of halide melts with two- and three-valent metals.

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## Section 3. Thermodynamics of solutions and heterogeneous systems

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### THERMODYNAMIC PECULIARITIES OF HETEROGENEOUS FLUID SYSTEMS WITH CHEMICAL INTERACTIONS: NEW EXPERIMENTAL AND THEORETICAL RESULTS

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Peculiarities concerning thermodynamic singularities of reacting systems are an important object of the basic and applied researches. For example the singularities of vapor – liquid phase diagrams in the systems with chemical reactions are the necessary base for the reactive distillation design. The well-known phenomena such as reactive- or chemi-azeotrope are the basic characteristics of topological structure of phase diagrams that is also essential for the design of coupled synthesis and separation processes. In this work we consider cases of non-equilibrium chemical reactions and simultaneous phase and chemical equilibria. The main attention is given to the first case because the thermodynamic studies of the systems in partly nonequilibrium states (i.e. with nonequilibrium chemical reaction) are more limited in comparison with the works on equilibrium data. Nevertheless the new experimental data and theoretical results for simultaneous phase and chemical equilibrium will be considered. The special attention would be paid to the reacting systems with liquid phase splitting: the short description of our experimental results will be presented.

The study of heterogeneous systems in chemically nonequilibrium states gives the additional opportunities for the chemical engineering process design. In these cases one should take into account not only thermodynamic conditions for coupled processes but also some elements of chemical kinetics. In more complex case of miscibility gap the differences of reactions rates in coexisting phases and mass-transfer between phases should be considered. The short discussion of experimental data on kinetics in splitting reactive media will be presented on the base of our recent research. The main objects of our experimental studies are nonequilibrium chemical reactions accompanied by liquid phase splitting in a few water–organic quaternary mixtures (systems with ester synthesis reactions). Experimental results were correlated with using UNIFAC and NRTL models.

In theoretical part the main attention is given to the use of the affinity for thermodynamic and kinetic analysis of processes and equilibria in the systems with immiscibility area. The inclusion in the analysis some additional topological elements – stoichiometric lines, chemical equilibrium and iso-affinity curves, surfaces or hyper surfaces – leads to results that are useful for more precise characteristics of diagrams of heterogeneous reacting systems. Thermodynamic consideration includes the analysis of the dependence of the affinity on reaction extent and composition. The change of the affinity on binodal curves (surfaces) is determined by the run of chemical equilibrium curve (manifolds), tie-lines and stoichiometric lines dispositions in composition space. The conditions of the extremum of the affinity and disposition of chemical equilibrium curves in composition triangle of ternary heterogeneous reacting system are discussed.

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POURBAIX DIAGRAM SYSTEM Zn – SO<sub>4</sub><sup>2-</sup> – H<sub>2</sub>O

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A serious drawback of research into the behavior of metals in sulfuric acid environments is the lack of comprehensive thermodynamic approach to the study of the processes. In particular, there is no diagram of the electrochemical equilibrium, taking into account the effect of electrolyte anions on their passivation associated with the formation on the surface of metal sulfide, sulfite, sulfate and oxide-sulfate films.

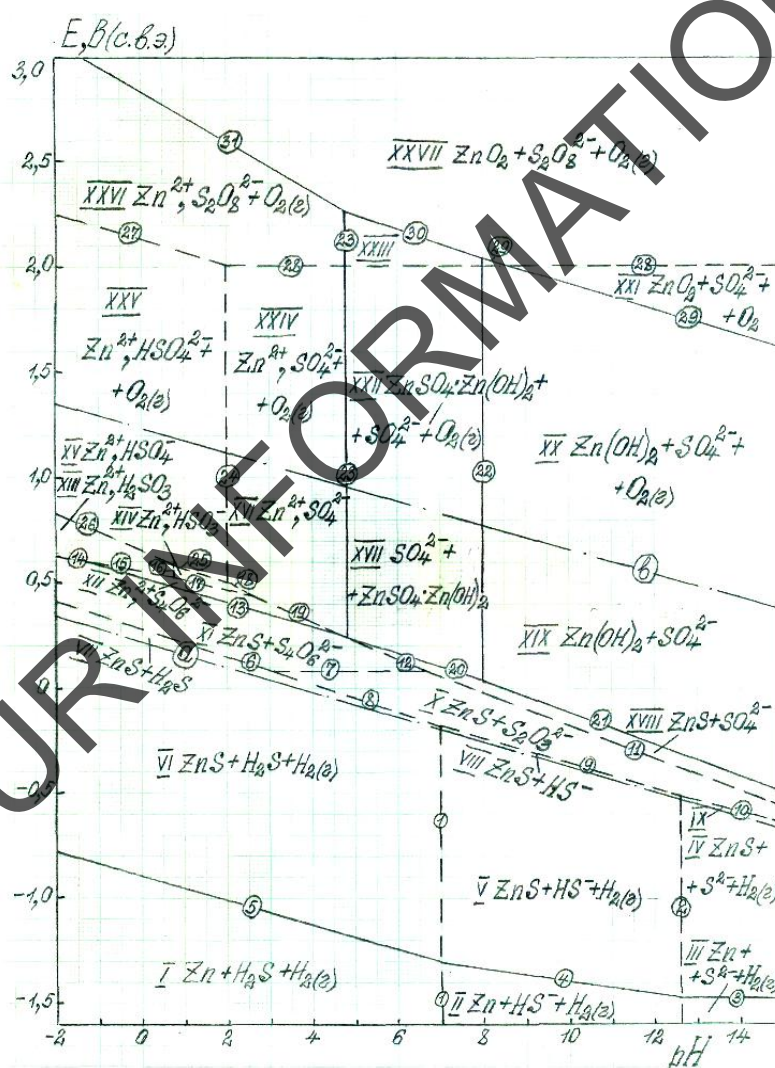


Figure: Diagram E – pH of Zn – SO<sub>4</sub><sup>2-</sup> – H<sub>2</sub>O at 25°C, P = 1 bar (air) and a<sub>i</sub> = 1 mol/l.

Diagram E – pH of Zn – SO<sub>4</sub><sup>2-</sup> – H<sub>2</sub>O is shown in Figure. It is possible to allocate fields of sulfide (area IV – XI and XVIII), sulfate-oxide (area XVII and XXII) and oxide (area XIX and XX) passivity zinc.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### SUPERCRITICAL EQUILIBRIA IN TERNARY SYSTEMS WITH ONE VOLATILE COMPONENT (CRITICAL PHENOMENA, SOLUBILITY AND IMMISCIBILITY)

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There are two main types of binary systems with volatile (1) and non-volatile (2) components, particularly the water – salt systems. Binary systems of type 1 are characterized by continuous increasing of non-volatile (salt) component solubility up to melting temperature and by absence of critical phenomena ( $L=G$ ) in solid saturated solutions. Binary systems of type 2 have the solubility curve ( $L-G-S$ ) with a negative temperature coefficient of solid solubility in subcritical temperature range, the critical phenomena ( $L=G$ ) occur both in not solid saturated and in saturated solutions. The supercritical fluid equilibria takes place above the temperature of critical phenomena ( $L=G-S$ ). The liquid immiscibility phenomena sometimes appear both the systems of types 1 and 2, however usually the available experimental data indicate the immiscibility equilibria in the water – salt systems of type 2 such as  $Na_2SO_4-H_2O$ ,  $K_2SO_4-H_2O$ ,  $Li_2SO_4-H_2O$ ,  $Na_2CO_3-H_2O$ , etc.

A theoretical derivation [1] and experimental studies [2-9] of ternary water – salt systems with binary subsystems of types 1 and 2 show the main regularities of phase transformations taking place in ternary mixtures in a process of heterogenization of homogeneous supercritical fluid spreading from binary subsystems of type 2. Separation of supercritical fluid starts from the critical phenomena in solid saturated solutions and is accompanied (sometimes) with a transition of metastable immiscibility region into the stable equilibria. Negative temperature coefficient of salt solubility (common in the binary subsystems of type 2) is changed to the positive one with increasing of salt 1 concentration in ternary solutions. Investigation of ternary critical equilibria ( $L=G-S$ ) and ( $L_1=L_2-S$ ) show that these monovariant critical curve can have temperature maximum as a result of continuous phase transformation ( $L_1=L_2-S \Leftrightarrow L=G-S$ ) the double homogeneous point (DHP) or in the double critical end-point (DCE) when two critical end-points of the same nature ( $L_1=L_2-S$ ), spreading from the binary subsystems of type 2, coincide. The DCE can also be observed in ternary mixture when two monovariant critical curve of the same nature ( $L=G-S$  or  $L_1=L_2-S$ ), originated in different nonvariant points, coincide at extreme concentration of a salt in ternary solution when gradually changing the nature of the solute from that of type 2 salt into that type 1 salt.

If the appearance of the double homogeneous point (DHP) is the first version of ternary phase diagram for binary subsystems of types 1 and 2, the second version of ternary phase diagram with the same types of binary subsystems is characterized by the emergence of four-phase equilibrium ( $G-L_1-L_2-S$ ) with invariant critical points ( $G=L_1-L_2-S$ ) and ( $G-L_1=L_2-S$ ), from which the monovariant critical curves ( $G=L_1-L_2$ ) and ( $G-L_1=L_2$ ) originate, further going toward higher temperatures and ending at the tricritical invariant end-point ( $G=L_1=L_2$ ).

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### GENERAL APPROACHES FOR PREDICTION AND ANALYSIS OF SOLVATION ENTHALPIES OF DIFFERENT ORGANIC COMPOUNDS IN PURE SOLVENTS

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Enthalpies of solvation provide valuable information regarding solute–solvent interactions in fluid solution. They can be used for analysis of solvent effect on different processes realized in liquid state. Also, measured enthalpies of solvation can be valuable tool for testing solution models and quantum chemical computations. Experimental  $\Delta_{\text{solv}}H^0$  can be utilized to extrapolate gas-to-liquid partition coefficients to system temperatures slightly higher and/or lower than the measurement temperature through standard thermodynamic relationships. Generally, enthalpy of solvation can be presented as a sum of contributions of different intermolecular interactions: enthalpy of non-specific solvation (van der Waals interactions), enthalpy of specific interaction (donor-acceptor interactions, hydrogen bonds) and etc. Another common ratio relates the enthalpy of solvation with the enthalpy of dissolution and the enthalpy of vaporization for liquid solutes or enthalpy of sublimation for solid solutes. These two general relations can be used for determination enthalpies of intermolecular interactions or enthalpies of phase transitions directly at 298.15 K, if enthalpies of solvation and enthalpies of solution are available. Enthalpy of solution is measured using the solution calorimetry or any other indirect techniques (gas chromatography, spectroscopy and etc.). Enthalpy of solvation is not directly available from the experiment, except for gases.

In this work we have carried out systematic study of thermochemistry of solvation of organic compounds in different solvents in order to evaluate general “structure–property” correlations for prediction of these values based on the group contributions and multiparameter scales. Also, obtained in this work enthalpies of solvation were used to develop new methods for determination of enthalpies of hydrogen bonding. These methods are applicable for systems with intermolecular and intramolecular hydrogen bonds as well as for self-associated solvents and ionic liquids. Enthalpies of hydrogen bond for about 1000 solute–solvent systems were calculated and analyzed in this work. Solute and solvent parameters for quantification hydrogen bond basicity and hydrogen bond acidity were generated. Additionally, approach for determination phase transition enthalpies from the enthalpies of solvation was proposed. In comparison to conventional methods, where experiment is performed at elevated temperatures, this approach has some crucial advantages. Firstly, all values are determined directly at the reference temperature 298.15 K. Following, this method is highly suitable for studies of thermally unstable and explosive compounds. Moreover, this method is quick and less demanding compared to the conventional methods. In this work it was successfully applied for determination enthalpies of vaporization and sublimation of different types of organic compounds.

## Section 3. Thermodynamics of solutions and heterogeneous systems

### THERMODYNAMICS OF THE SELF-ASSOCIATION PROCESS AND COMPLEXATION OF WATER-SOLUBLE COBALT(II) PHTHALOCYANINE WITH MULTIDENTATE LIGANDS

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Complexes of water-soluble phthalocyanines with *d*-metals have unique photocatalytic [1], photovoltaic [2] and photosensitive [3] properties. It is explained by possibility to coordinate molecular ligands in fifth and sixth coordination state of central cation. Liquid-phase materials based on such compounds are widely used. Self-association of metallophthalocyanines in solution systems affects their physical and chemical properties greatly. Controlling of formation of associated metallophthalocyanines in solutions allows obtaining functional materials with required properties. Structural-thermodynamic approach to the study of formation of H- and J-aggregates of sulfonated derivatives of cobalt phthalocyanine (Figure) is used in the present work. H-aggregates are formed due to overlapping of conjugated  $\pi$ -electronic systems of two macrocycles, whereas the formation of J-aggregates is connected with central metal cation. The possibility of directed solution restructuring from H-aggregates to J-aggregates is shown in example of complexation of DABCO with creatinine. This process is accompanied by release of great number of monomeric macrocycles. Thermodynamic parameters of the H-aggregates formation and of the additional ligand coordination were calculated. Significant influence of peripheral substituent structure on thermodynamic stability of associates in solution was established. Increasing the number of peripheral functional groups of phthalocyanine macrocycle causes dissociation of H-aggregates. Withal, the stability of molecular complexes DABCO–creatinine has reverse trend. That is why forming sandwich-type dimers are more stable than  $\pi$ – $\pi$ -dimers. Based on obtained data it should be concluded that associates formation process is entropy-controlled.

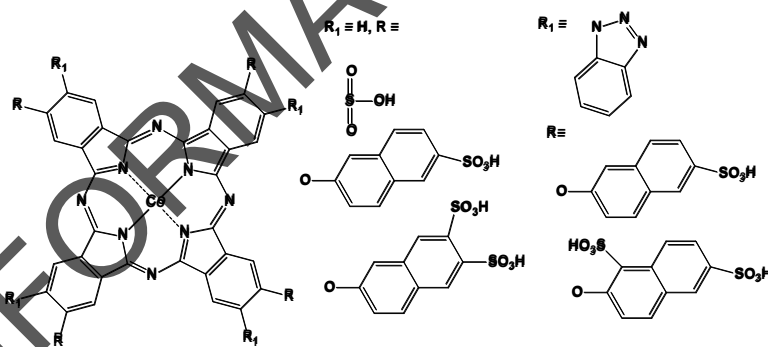


Figure: Scheme of phthalocyanines.

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## THERMODYNAMIC DESCRIPTION OF SYSTEMS WITH CHOLESTERIC LIQUID CRYSTALS

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Liquid crystalline cholesteryl esters have found a wide application in thermography and photonics. Phase diagrams of liquid crystal (LC) – non-mesogen systems are important both for the solvent selection for purification of mesogens and for additives choice for LC mixtures. The knowledge on intermolecular interactions gives a possibility to optimize a selection of non-mesogen.

Binary LC – non-mesogen systems are investigated by thermal analysis, visual analysis and solubility methods. Cholesteryl esters with a common formula R-COO-Chol (where Chol – cholesteryl, R = CH<sub>3</sub>, C<sub>4</sub>H<sub>9</sub>, C<sub>6</sub>H<sub>13</sub> – C<sub>8</sub>H<sub>17</sub>, C<sub>10</sub>H<sub>21</sub>) are used as mesogenic components. Solubility curves of LC in solvents of different polarity (*n*-alkanes, cyclohexane, aromatics, chlorinated alkanes, alcohols, esters, acetonitrile) are obtained.

Usage of the thermodynamic methods to predict the phase diagram type and to calculate the solubility curves seems to be very interesting. The models based on the solubility parameter (usage of Hildebrand and Hansen solubility parameters [1, 2], the Flory–Huggins equation) are applied for the miscibility prognosis. The proposed scheme are tested on “model” substance – cholesterol. Data on solubility of cholesterol are taken from [3].

Solubility parameters of components  $\delta_i$  are calculated by equation

$$\delta_i = ((\Delta_v H_i - RT) / V_i)^{0.5},$$

where  $\Delta_v H_i$ ,  $V_i$  are the vaporization enthalpy and the molar volume of components at 298 K.

For mesogens the vaporization enthalpy can be estimated basing on the group-contribution method (GCM). Data on density of mesogens are taken from [4] or calculated using the group-contribution methods. The average error for density prediction by GCM for LC substances equals 2–3% (the set contained more than 200 mesogens). The different scheme estimations for the solubility parameter are compared.

Correlations between alkyl chain length of LC and their solubility in solvents of different polarity are determined. Statistical analysis of the considered thermodynamic methods is made. Advantages and restrictions of GCM for the solubility curves estimation are discussed.

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[4] Pestov, S.M. *Landolt-Boernstein. N.S. VIII/5A. Physical properties of liquid crystals*, Berlin: Springer, 2003, 492.

## Section 3. Thermodynamics of solutions and heterogeneous systems

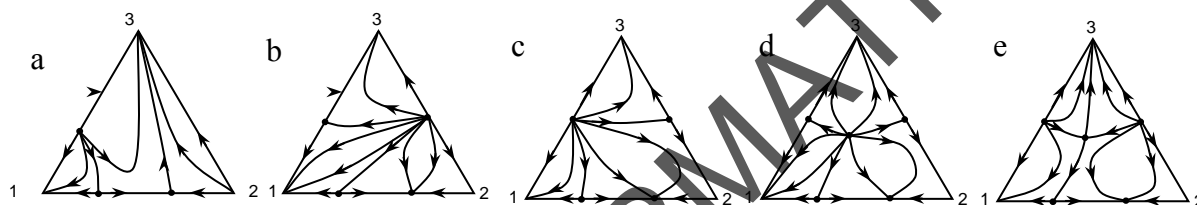
### HETEROAZEOTROPY IN BENZENE – PERFLUOROBENZENE – WATER TERNARY SYSTEM

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The separation of benzene – perfluorobenzene binary system is a complex task because of the presence of two azeotropes [1]. A method of benzene – perfluorobenzene mixture separating by extractive distillation using dimethyl sulfoxide was proposed in [2]. An alternative method of separation on the base of azeotrope forming component adding (water) can be proposed. There are no reliable data about azeotropy in benzene – perfluorobenzene – water ternary system and its constituent perfluorobenzene-water in literature. In this regard, this work is devoted to the study of azeotropy in these systems.

From theoretical analysis of limited literature data on vapor–liquid equilibrium it is possible to predict five variants of topological structure of distillation lines diagram (Figure).



**Figure:** Possible topological structures of phase diagram of benzene (1) – perfluorobenzene (2) – water (3) ternary system.

A boiling temperatures of possible azeotropes were determined using distillation analysis. The experiments at different pressures showed the presence of binary heteroazeotrope in perfluorobenzene – water constituent binary system and ternary heteroazeotrope with a minimum boiling temperature (Table).

**Table.** Azeotropes temperature in benzene (1)–perfluorobenzene (2)–water (3) ternary system

Pressure (mm Hg)	Boiling temperature ( $^{\circ}\text{C}$ )		
	azeotrope 1–3	azeotrope 2–3	azeotrope 1–2–3
200	37.7	37.5	36.3
400	52.7	52.4	50.7
600	62.9	62.8	61.4
760	69.5	69.4	68.8

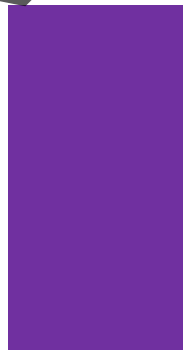
This information is enough to confirm the topological structure of the phase diagram of real ternary system, which corresponds to the diagram *d* in the Figure. The structure is characterized by the presence of three distillation regions, bounded by the separatrices of saddle points. As benzene and perfluorobenzene are characterized by very low mutual solubility in water, concentration simplex is almost completely covered by the splitting area of open type, which allows to move from one distillation region to another. Received physico-chemical information is the basis for developing flowsheet of ternary mixtures separation using a combination of distillation and splitting.

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The work was supported by the Ministry of Education and Science of the Russian Federation (No. 2014/114, project code 2065).

**Section 4.**  
**Thermodynamics of surface  
phenomena and self-  
organization phenomena in  
fluid systems**



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## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### THERMODYNAMIC CHARACTERISTICS OF SORPTION OF METAL-IONS BY BIFUNCTIONAL ION EXCHANGERS

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An advantage of the sorption method is the possibility of ion exchanger reuse in the cycle of "sorption-desorption", that considerably increases the economic efficiency of the sorptive treatment and the possibility of application of this method for extraction of toxins from environmental objects. The aim of this work is to study the sorption equilibrium of copper, zinc, cadmium and lead ions by ion exchangers of Duolite C-467 and Diaion CR-11, to study the rate of its establishment and to calculate the thermodynamic parameters of the systems studied. Thermodynamic description of the sorption of studied ions by ion exchangers is carried out under the assumption of ideal solid phase, i. e. without taking into account the activity coefficients of the ions in the adsorbed state. Studies have been carried out on macroporous chelating ion exchangers Duolite C-467 and Diaion CR-11, designed to extract cations of not very heavy metals from aqueous solutions and brines. Polymeric sorbent matrix is a polystyrene cross-linked with divinylbenzene, grafted with aminophosphonic (Duolite C-467) and iminodiacetic acid (Diaion CR-11) functional groups.

For mathematical processing of sorption isotherms sorption models of Langmuir, Freundlich and Redlich-Peterson have been used. Sorption of metal ions on these sorbents proceeds mainly according to Langmuir's mechanism, i. e. on the surface of polyampholytes monomolecular sorptive layer is formed and all active centers have substantially equal energy and enthalpy of sorption. Selectivity series of sorption of studied ions by the investigated resins at the concentration range of 0,5-5,0 gMe/l are worked out:  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$  (Diaion CR-11) and  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$  (Duolite C-467). Sorption of cations is well described by the linear dependence in coordinates of  $C_{\text{equi}}/A - C_{\text{equi}}$  with a high correlation coefficient ( $R = 0.98-0.99$ ), that allows to determine reliably the value of  $A_{\text{max}}$  and  $K$ . Appropriate equations satisfactorily describing the sorption isotherms are offered.

The enthalpy of the studied processes is determined by the ratio of quantity of released heat to the amount of adsorbed ions. The processes of absorption of ions by ion exchangers in investigated concentration range are exothermic and characterized by the exothermicity fall as far as ions are absorbed. The reason for the subsequent decrease in the intensity of the heat flux may be the need of diffusion of absorbed ions into the interior of the grain, which is associated with additional costs of energy. Also the change of parameters such as activation energy and entropy, free energy of sorption, diffusion coefficients change depending on various factors are considered. The calculated values of activation entropy have negative values in all cases. Experimental data confirm the tendency of reduction of the entropy with increasing of sorption selectivity in the systems studied. In all processes studied with heat release and reduction of entropy in the system selectivity is controlled by enthalpy factor. The lowest value of the calculated activation energy is obtained in the system of  $\text{Cu}^{2+}$ -Diaion CR-11. Indeed, in the case of sorption of copper ions by the mentioned ampholyte process is more energetic than during the sorption of other ions by both ion exchangers.

Ratio of entropy and enthalpy contributions determines magnitude and sign of the Gibbs free energy. Gibbs energy studied by us in all cases is maximal for sodium and minimal for protonated forms of ion exchangers.

Quantitative values of diffusion coefficients, pre-exponential factors, the exchange constant, energy of activation and entropy, Gibbs free energy and enthalpy are given in the report.

## THERMAL PROPERTIES OF THE POLYSTYRENE FILMS FILLED WITH SILICA

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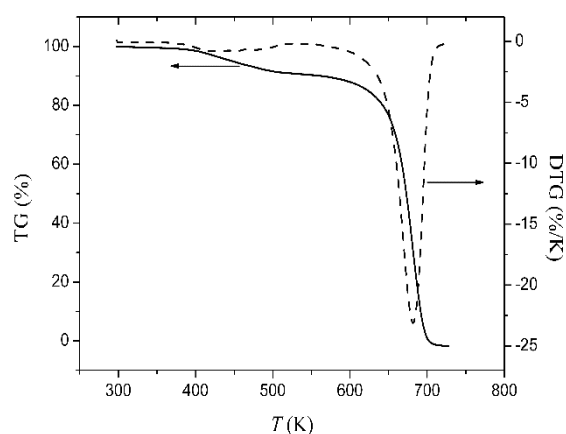
Priority area of the modern chemistry and materials science is development of polymeric nanocomposites with controllable properties. Perspective method for modification of polymers is incorporation of silica into the polymeric matrix. The produced composites get novel physical and chemical properties. In the current study, we have synthesized silica and researched its morphological properties. Also we have fabricated the samples of the polystyrene/silica composite films, and researched an effect of the silica content on the glass transition temperature of composite and its thermal degradation parameters.

Silica has been synthesized by the sol-gel method with tetraethyl orthosilicate (Aldrich, US) as the precursor. The synthesized silica was a white powder. It has been identified by dynamic light scattering that size distribution of the  $\text{SiO}_2$  particles was bimodal with peaks at  $r = 96$  nm, and  $r=535$  nm. To estimate the morphological properties of the material we have used the method of low-temperature nitrogen adsorption-desorption. We have determined the specific surface area, the total pore volume, the pore size distribution, and fractal dimension.

To production of the film composites we have used atactic polystyrene (Aldrich, US; molecular mass of 140000, polydispersity index of 1.64, melt mass flow index of  $6\div 9$  g/10 min), and silica synthesized. A solvent casting of perspective components from solutions has been employed for preparing the mixtures of silica with polymer. Silica batches have been put into o-xylene in different concentration, and resulting suspension has been stirred using magnetic stirrer and ultrasonic bath. Polystyrene has been dissolved in o-xylene too. Then, we have mixed two solutions in the required proportions, casted onto a glass substrate, and kept in air to evaporate the solvent and to form the film.

Fabricated films have been researched by the differential scanning calorimetry and thermogravimetry techniques. We have found the glass transition temperature,  $T_g$ , has influenced by the silica content. Concentration dependence of this value was non-monotonic in range of small additives of  $\text{SiO}_2$  (less than 5 wt.%). The value of  $T_g$  has decreased, as silica content has increased up to 1 wt.%. At higher silica content (up to 5 wt.%), the value of the glass transition temperature has increased with increasing content of  $\text{SiO}_2$ .

By thermogravimetry technique we have obtained that thermal behavior of polymer composites has depended on the filler content. The values of both the onset of polymer degradation and the temperature corresponding to DTG peak have depended non-monotonically on the silica concentration. The highest thermal stability of composite has belonged to the sample with 5 wt.% of  $\text{SiO}_2$ . Van Krevelen method was used to estimate the kinetic parameters of the thermal degradation. It was shown that the activation energy increased with the silica content in composite.



**Figure:** Thermograms for the PS/ $\text{SiO}_2$  (1 wt. %) composite film: TG – straight lines; DTG – dashed lines.

## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### INFLUENCE OF COMPOSITION OF WATER+SODIUM DODECYLSULFATE+1-PENTANOL+TRIETHANOLAMINE+1,2-DIBROMTETRAFLUORETHANE MICROEMULSIONS ON ENTHALPIES OF THEIR FORMATION AND THE MICRODROPS SIZE

D.V. Batov, O.A. Antonova, A.V. Kustov, N.L. Smirnova

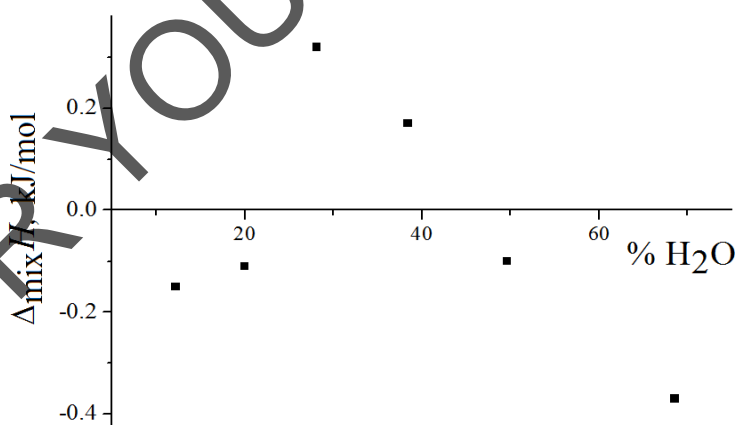
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A perspective direction in respect of creation of the combined means of fire extinction is an application of galogenhydrocarbon microemulsions with water allowing to combine the process of cooling of a flame by water with inhibition of burning reaction by galogenhydrocarbon. Earlier we obtained nonflammable microemulsions of various composition, which contained the water (H<sub>2</sub>O), sodium dodecylsulfate (NaDDS), 1-pentanol (PeOH), and triethanolamine (TEA) as surfactant and co-surfactant, and also 1,2-dibromtetrafluorethan (BFE) as an oil phase. Their viscosities, isobaric heat capacities, the electric conductivities, having a great importance for research of the intermolecular interactions and the microemulsions structure have been studied. The purpose of the present work is the question what is the motive force of formation of the studied microemulsions, that is, what is which contribution, enthalpic or entropic, will be dominating in the general decreasing of a free energy.

For this purpose, the enthalpies of formation and the microdrops size of the microemulsions mentioned above have been determined at standard conditions. The enthalpy of formation of

**Table.** Composition of the investigated microemulsions in mass % of components

ME	NaDDS	H <sub>2</sub> O	TEA	PeOH	BFE
ME-1	8.35	12.22	7.46	5.53	66.43
ME-2	8.41	20.00	7.12	6.02	58.44
ME-3	8.41	28.14	7.55	6.22	49.69
ME-4	8.29	38.44	7.66	6.16	39.44
ME-5	7.82	49.61	7.41	6.11	29.06
ME-6	8.33	68.53	7.01	6.07	10.06



**Figure:** Influence of composition on enthalpies of formation of microemulsions.

microemulsions is accompanied by the endothermic effect.

mixtures or the enthalpy of mixing is a heat effect of simultaneous mixing of the pure components which are at standard pressure and the given temperature. The enthalpies of formation of microemulsions have been obtained using the thermochemical cycle including the enthalpies of dissolution of microemulsions and their components in 2-propanol. It has been shown that the formation of the investigated microemulsions of an oil/water and water/oil types is an exothermic process. Thus, the spontaneous process of formation of microemulsions in the case of oil/water type microemulsions is defined not only by the hydrophobic interactions and entropic effects accompanying them, but also by the strong specific intermolecular interactions which result to the negative enthalpies of formation. The formation of the bicontinual

QUANTUM CHEMICAL APPROACH IN THE DESCRIPTION OF  
1-(N-ALKYL)-IMIDAZOLES CLUSTERIZATION AT THE AIR/WATER INTERFACE

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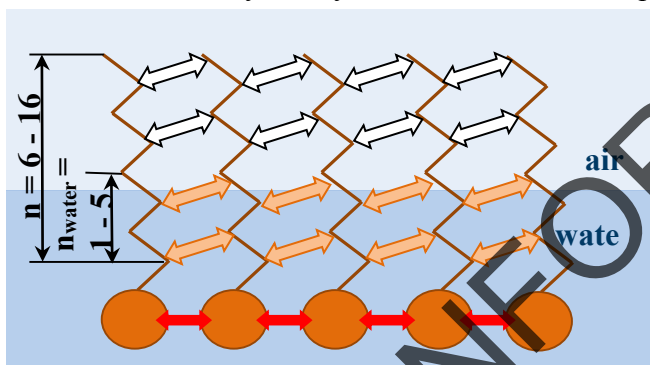
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The studies of self-organization phenomena at the air/water interface are of value not only for understanding the surface properties of aqueous solutions but also for the studies of structural characteristics and self-organization processes in bulk solutions and interfaces. Understanding peculiarities of the formation and the behavior of new phases, modeling their properties, the prediction and control of structural characteristics in dependence of the composition, temperature etc. are of value in the searches of new materials for the needs of science, medicine, industry etc. 1-(N-alkyl)-imidazole and its derivatives are paid special attention in the studies of molecular recognition processes, modeling of cell membranes, etc. The most known and widely used derivatives are alkylmethylimidazolium Ionic Liquids.



**Figure:** Schematic illustration of the monolayer fragment at the air/water.

In this work for the description of the 1-(N-alkyl)-imidazole monolayer formation at the air/water interface we have used the quantum chemical model, proposed earlier [1]. The influence of the phases on the calculated thermodynamic parameters was estimated by carrying out quantum chemical calculations in the both adjusted phases. The nature of the aqueous phase was taken into account through its dielectric permeability in the frames of the continuum model COSMO, program complex Mopac2012, quantum chemical semi-empirical PM3

method. After calculating thermodynamic parameters (enthalpy, entropy and Gibbs' energy of clusterization) of small clusters (dimers, trimers, tetramers etc.) the increments from the intermolecular  $\text{CH}\cdots\text{HC}$  interactions and interactions between functional groups (indicated by the arrows in fig.1) were specified. Using these parameters one can calculate thermodynamic parameters of the clusters formation of any dimension till infinite cluster – monolayer. In the frameworks of this model thermodynamic parameters of the clusterization of 1-(N-alkyl)-imidazoles (6-16 carbon atoms in the chain) at air/water interface were calculated. It is shown that for 1-(N-alkyl)-imidazole formation of two types of monolayers (with hexagonal and oblique unit cell) is equally probable. Parameters of the unit cell for the hexagonal and oblique monolayer are correspondently: 4.6 Å and 7.2 Å; 4.6 Å and 4.6 Å. Enthalpy, entropy, and the Gibbs energy of clusterization were calculated for clusters (dimers-hexamers) which are the structural elements of these monolayers. All increments of the pairwise interactions were obtained within additive scheme corresponding parameters of the monolayers formation were calculated. Spontaneous clusterization for both hexagonal and oblique monolayers at standard conditions takes place when the length of the alkyl chain is equals or exceeds 14-15 carbon atoms.

[1] Vysotsky, Yu.B.; Belyaeva, E.A.; Kartashynska, E.S.; Fainerman, V.B.; Smirnova, N.A. J. Phys. Chem. B, 2015 (in press).

## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### INFLUENCE pH ON SORPTION OF ALIPHATIC AMINO ACIDS CARBOXYL ION EXCHANGERS

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Absorption of amino acids by ion exchangers has the specific character consisting in an essential role of acidity of solution and additional interpartial interactions in a sorbent phase. In work the quantitative assessment of equilibrium characteristics of sorption of aliphatic amino acids – glycine, valin,  $\alpha$ -alanine, D,L-methionine – from solutions with various pH by carboxyl cation exchangers and polyampholytes with application of calorimetric, spectrophotometric, spectroscopic, potentiometric and sorption methods of research is carried out. Taking into account change of ionic forms of amino acids at various hydrogen indicator of the environment the nature of sorption interactions on the protonated and sodium forms of ion exchangers is revealed and the chemical model of heterogeneous equilibriums is offered.

In work it is shown that primary sorption centers of carboxyl ion exchangers are their functional groups possessing equal energy and an enthalpy of sorption, and additional – the absorbed amino acids which take part in various interpartial interactions. At sorption of bipolar ions and anions of amino acids with the protonated ion exchangers the exchanging ion of hydrogen isn't forced out in solution, and passes into structure of carboxyl group of sorbate, neutralizing its negative charge.

Gibbs's energy of sorption at 298 K testify that glycine has bigger affinity to KB-4, than to KB-2, the maximum absorption happens in alkaline area.

**Table.** Gibbs's energy ( $-\Delta_s G$ , J/mol) glycine sorptions by carboxyl cation exchangers

ionic form	pH 2.0		pH 7.0		pH 9.0	
	KB-2	KB-4	KB-2	KB-4	KB-2	KB-4
H <sup>+</sup>	7565 ± 378	11195 ± 280	11555 ± 289	11710 ± 293	10203 ± 255	14185 ± 355
Na <sup>+</sup>	9821 ± 491	12075 ± 302	9113 ± 456	12044 ± 301	10517 ± 263	12587 ± 315

Change of acidity of equilibrium solution leads to change pH in ion exchanger grain that influences the nature of the formed sorption complexes. Besides, it is necessary to consider change of an ionic form of carboxyl ion exchangers at contact with water solutions of various acidity. So in alkaline area there is a penetration of sodium hydroxide into a phase of the protonated sorbent leading to dissociation of carboxyl groups. Therefore interaction of amino acids in alkaline area happens not to a hydrogen form, and to the mixed protonated-deprotonated form of the cation exchanger.

Generally from neutral and alkaline solutions there is mainly molecular sorption, and from sour and alkaline solutions – ionic. Sorption of cations and anions of amino acids respectively happens to the sodium and protonated form of ion exchangers at the expense of the Coulomb attraction and specific interactions between amino acid and a matrix of a sorbent including hydrophilic and hydrophobic effects.

*Work is performed within NIOKR by GK No. 4.2186.2014/K.*



**DYNAMIC SURFACE PROPERTIES OF SPREAD MONOLAYERS OF  
POLYSTYRENE MICROPARTICLES**

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Spread monolayers of charged polystyrene (PS) particles at the air/liquid and liquid/liquid interfaces have been intensively studied during the last decades. Recently the key role of dilational and shear rheological properties of particle monolayers in the stability and dynamics of the foams and emulsions has been emphasized.

In this work the dependence of the dilational surface elasticity on surface pressure of spread monolayers of polystyrene microparticles is studied at the water/air interface [1]. The surface rheological measurements together with the data of optical methods allow dividing the whole range of surface pressures into three zones characterized by different monolayer structures. The formation of ordered structure of PS microparticles even at low surface coverage due to the long range electrostatic repulsion was observed by optical methods. The real part of the dynamic surface elasticity in this case is about 50 mN/m. The dilational surface elasticity increases by one order of magnitude up to 550 mN/m with the increase of particle concentration. The high surface elasticity corresponds to the formation of a closely packed monolayer. Approximately the same dynamic surface elasticity has been observed recently for the adsorption layer of silica nanoparticles [2]. The further increase of the surface coverage results in the monolayer collapse and the surface elasticity drops to almost zero.

The adsorption of charged PS microparticles at the water/air interface strongly depends on ionic strength of solution due to electrostatic barrier. The appearance of particles at the surface layer in presence of 0.1 M NaCl was observed by the optical methods even at low concentration of particles in bulk. In spite of the low adsorption barrier the adsorption of particle was too small and do not lead to the decrease of surface tension of solution.

[1] Bykov, A.G.; Noskov, B.A.; Loglio, G.; Lyadinskaya, V.V.; Miller, R. *Soft Matter*, 2014, 10, 6499-6505.

[2] Yazhgur, P.A.; Noskov, B.A.; Liggieri, L.; Lin, S.-Y.; Loglio, G.; Miller, R.; Ravera, F. *Soft Matter*, 2013, 9, 3305-3314.

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## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### THERMODYNAMIC ASPECTS OF SORPTION AND SEPARATION OF THE ENANTIOMERS OF SOME MONOTERPENES BY GAS-LIQUID CHROMATOGRAPHY USING $\beta$ -DEX 120

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Cyclodextrins is composed of hydrophobic cavity that can trap or encapsulate other molecules. Applications of cyclodextrins and their complexes are found in pharmacy, food, chemistry, chromatography, catalysis, bio-technology, agriculture, cosmetics, medicine. Cyclodextrins and their derivatives are widely used in chromatography as a chiral selectors for stationary phases. In most papers about separations using capillary column, consist of polymer and cyclodextrin, authors usually consider only aspects of selectivity and don't calculate thermodynamic function of sorption. The aim of the work was studying the thermodynamic characteristics of sorption and «host-guest» complexation in the polymer stationary phase of  $\beta$ -DEX 120 for monoterpenes  $C_{10}H_{16}$  (( $\pm$ )-limonene, ( $\pm$ )- $\alpha$ -pinene, ( $\pm$ )-camphene, ( $\pm$ )-menthol), that are widely used in cosmetics, pharmacy and perfumery. Retention factors have been observed for two capillary columns with stationary phases consisting of polydiphenyldimethylsiloxane with additive permethylated  $\beta$ -cyclodextrin (column  $\beta$ -DEX 120) and no chiral additive (DB-35ms) at a temperature range of 80-140°C by capillary gas chromatography. Energetic ( $\Delta\bar{U}^0 = Q_v$ ) and entropy contribution in retention, thermodynamic parameters of «host-guest» complexation between monoterpenes and macromolecular in stationary phase of  $\beta$ -DEX 120 were calculated. By adding in medium polar polymer PPMS 20% mass Me- $\beta$ -CD, the retention of monoterpenes grows, as internal energy is increased because of «host-guest» complexation. The ratio of this increase changes from  $\Delta(\Delta\bar{U}^0) = -8$  kJ (limonenes) to  $\Delta(\Delta\bar{U}^0) = -16$ kJ (menthols). Under the assumption 1:1 stoichiometry of complexes, we calculated the constant of complexation that increases in the sequence limonenes-pinenes-camphenes-menthols. Enthalpy of the exothermic process (+)-isomers of hydrocarbons  $C_{10}H_{16}$  and (-)-isomers of menthol is higher (in absolute) than in the case of enantiomers with the opposite sign of optical rotation that provides for  $\beta$ -DEX 120 moderately expressed enantioselective properties. We submitted a thermodynamic analysis of reasons that lead to a reduction of enantioselectivity with increasing temperature and calculated temperature compensation  $T_{com}$  at which optical isomers eluted from the column at the same time. Revealed that adding macrocycle in polymer leads to an increase in retention because of exothermic contribution in heat of sorption that is due to «host-guest» complexation in stationary phase. Results of this paper have important value for the development of supramolecular chemistry and the design of analytical methods of separation and determination of the enantiomers in natural and synthetic mixtures.

## CLUSTER AND ASSOCIATE MODEL OF TEMPERATURE DEPENDENCY OF SODIUM CHLORIDE DYNAMICAL VISCOSITY

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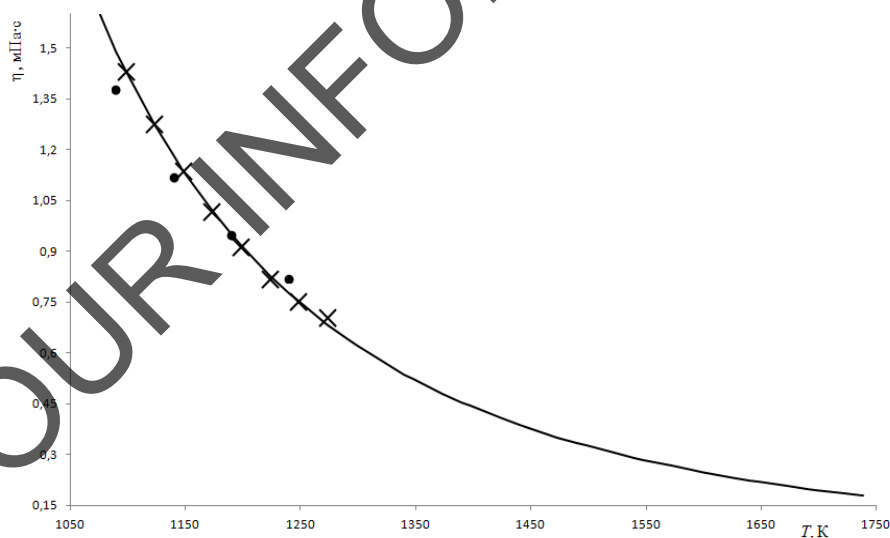
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The authors of Monograph [1] developed the new dependencies of viscosity on temperature in the full range of liquid state for elementary substances based on the chaotic particles conception. According to this conception and the fundamental Boltzmann distribution the viscous flow is regarded as the destruction of the associates by overcoming the van der Waals force between the clusters. In general, this interpretation does not conflict with current understanding of viscous flow and it is governed by the new dependency.

Cluster-associate model of a viscous current of liquid was first used to determine the temperature dependence of the dynamic viscosity of inorganic compounds - sodium chloride:

$$\eta = 1.275(1123/T)^{5,0775}(1190/T)^{0,3124}, \text{ mPa}\cdot\text{s.} \quad (1)$$

The resulting equation adequately describes the experimental data. The advantage of the cluster and associate model is the ability to forecast the viscosity behavior at low and high temperatures up to the boiling temperature. The cluster and associate model of the temperature dependency of dynamic viscosity of liquid sodium chloride allows its application in the whole range of liquid state with the faithful extrapolation to the boiling temperature area and melting temperature area as well.



**Figure:** *Dependency of Dynamic Viscosity of Liquid Sodium Chloride. The dots and crosses are for reference data, and the line is for (1) data.*

The cluster and associate model of the temperature dependency of viscosity does not contain any limitations for the alloys composition. This fact provides the future perspective application of this model for any other substances.

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## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### NONREVERSIBLE RESONANCE ENERGY TRANSFER IN THE SUPRAMOLECULAR STRUCTURE BASED ON THE TOROIDAL NANOCLUSTER $\text{Mo}_{138}$ AND XANTHENE DYE

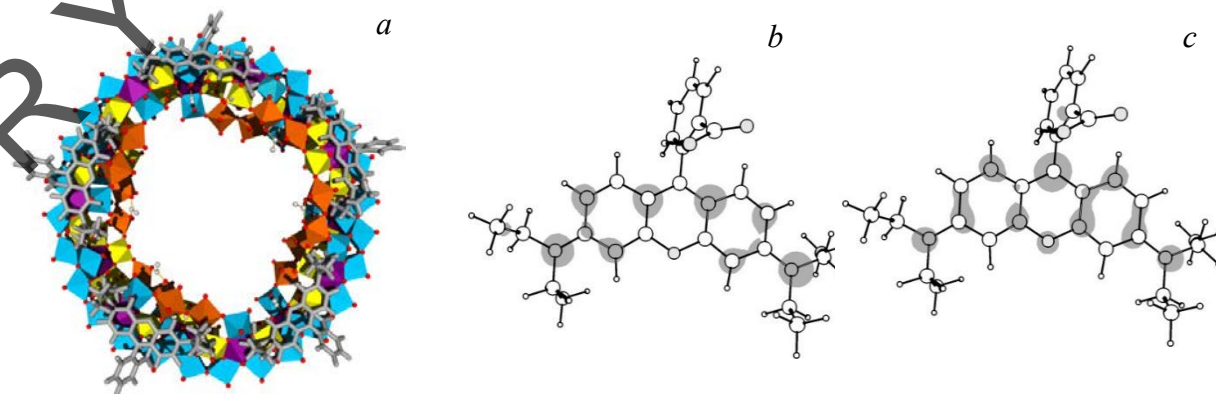
K.V. Grzhegorzhevskii<sup>1</sup>, A.A. Ostroushko<sup>1</sup>, O.V. Koriakova<sup>2</sup>, I.G. Ovchinnikova<sup>2</sup>,  
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The very effective nonreversible fluorescence resonance energy transfer (FRET) was found at the new supramolecular structure  $\text{Mo}_{138}\text{-(RhB)}_n$  (Figure a). This structure is based on the toroid nanoclustered giant polyoxomolybdate (POM)  $\text{Mo}_{138}$  and the xanthene dye – Rhodamine B (RhB). It was produced by the self-assembly method in solution and solid state and it was characterized by the physicochemical methods group at the first time. The nanocluster  $\text{Mo}_{138}$  consists of the oxygen coordination polyhedrons of molybdenum at different states ( $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ ) – that conditions its potential catalytic activities. The POM composition is presented by the formula:  $(\text{NH}_4)_{32}[\text{Mo}^{\text{VI}}_{110}\text{Mo}^{\text{V}}_{28}\text{O}_{416}\text{H}_6(\text{H}_2\text{O})_{58}(\text{CH}_3\text{COO})_6] \cdot x\text{H}_2\text{O}$  ( $x \approx 250$ ). In aqueous solution the  $\text{Mo}_{138}$  forms multicharged anion. In turn they spontaneously aggregate to hollow, single-wall, spherical globules (diameter is  $\sim 300$  nm depending on POM concentration and pH) stabilized by the cations  $\text{NH}_4^+$  and hydrogen bonds. These globules are basis for the supramolecular structure of ion-associates  $\text{Mo}_{138}\text{-(RhB)}_n$  produced by the electrostatic interaction between POM surface and positively charged dye molecules. During the saturation of POM surface by RhB the electric double layer is compressed and the zeta-potential modulo decreases from  $-45\text{mV}$  (for pure  $\text{Mo}_{138}$ ) to zero – at isoelectric point corresponding to components ratio  $\text{Mo}_{138} : \text{RhB} = 1 : 35$  in solution (conc. of  $\text{Mo}_{138}$  is  $4.26 \cdot 10^{-6}$  mol/l). The fluorescence studies of solutions displayed the presence of FRET at excitation in the dye absorbance band – the fluorescence intense was fallen down in  $\sim 100$  times. The FTIR-spectroscopy analysis of ion-associates in solid state proved the integrity of POM structure and revealed the planar location of RhB molecules on POM surface. Taking into account the UV-Vis and Raman spectroscopic data and calculation of the *HOMO-LUMO* electron transition of RhB by the TDDFT (the transition is polarized in plane of condensed aromatic system – Figure b, c) we revealed the presence either radiative and nonradiative energy transfer mechanism conditioned by the overlapping of RhB and  $\text{Mo}_{138}$  molecular orbitals. Thus the produced ion-associates have the potential ability to use for light-controlled catalysis.



**Figure:** a – The ion-associate  $\text{Mo}_{138}\text{-(Rhodamine-B)}_n$ ; b, c – HOMO and LUMO electron states of Rhodamine B molecule calculated by the TDDFT.

### FEATURES OF THE ADSORPTION OF ORGANIC COMPOUNDS FROM THE GAS PHASE BILAYERS «POLYMER – $\beta$ -CYCLODEXTRIN»

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Experimental study of the adsorption properties of monolayers of chiral macrocyclic compounds (eg cyclodextrins) allows us to consider the thermodynamics of complex formation at the interface «gas – solid» and get new materials for sorption and chromatographic techniques. At the same time it is possible to control the orientation of cyclodextrin molecules on the surface of the solid carrier using the sequential application of monolayers of polar polymer and  $\beta$ -cyclodextrin.

We have investigated adsorption of organic compounds of different nature on bilayers «polyethylene glycol – unsubstituted  $\beta$ -cyclodextrin» (PEG/ $\beta$ -CD) and «polyvinylpyrrolidone – unsubstituted  $\beta$ -cyclodextrin» (PVP/ $\beta$ -CD) deposited on graphite carbon support with a flat surface – Carpack Y (CpY) by the method of inverse gas chromatography. Henry adsorption constants  $K_{1,c}$  have been measured. From the temperature dependence of Henry adsorption constants were found differential molar heat of adsorption and the change in molar differential entropy of adsorption.

It was found that assembling of two series of alternating monolayers (PEG and  $\beta$ -CD or PVP and  $\beta$ -CD) layer by layer on the surface of CpY sharp decreases adsorption constants of all studied compounds (with the exception of aliphatic alcohols) than CpY. This effect is observed due to the screening surface graphite substrate bilayer film modifier. However, an increase of the heats of adsorption is observed in the case of aliphatic alcohols for both modified adsorbents. It was found that in the case of the adsorbent CpY/PVP/ $\beta$ -CD the adsorption heat of n-alkanes compared with those in the original adsorbent CpY. On the other hand, adsorbent CpY/PEG/ $\beta$ -CD showed a decrease in adsorption heat with increasing length n-alkane compared to CpY. In general, both adsorbents showed an increase the heat of adsorption of certain cyclic compounds. Found that for all investigated sorbates on the adsorbent bilayer PVP/ $\beta$ -CD to a greater extent observed expression localization adsorption as compared with the original CpY, and in comparison with the adsorbent CpY/PEG/ $\beta$ -CD.

Comparison of the thermodynamic characteristics of adsorption studied compounds on adsorbents with bilayers «polymeric modifier – unsubstituted  $\beta$ -CD» indicates that the PVP gives a more favorable orientation of  $\beta$ -CD molecules in comparison with PEG. Thus, for all studied compounds the values of the thermodynamic characteristics of adsorption in the case of a bilayer of PVP/ $\beta$ -CD larger than in the case of the adsorbent with the bilayer PEG/ $\beta$ -CD. However, for alkanols thermodynamic adsorption characteristics differ little in both adsorbents (CpY/PVP/ $\beta$ -CD and CpY/PEG/ $\beta$ -CD). This is related to the contribution of hydrogen bonding in the intermolecular interaction «adsorbate – macrocyclic component».

*The authors are grateful to the Ministry of Education and Science of the Russian Federation (Grant No. 4.110.2014/K).*

## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### THERMODYNAMICS OF QUASICRYSTAL FORMATION FROM POLYESTERENE MICROSPHERES WITH HEXAGONAL CLOSE PACKING (HCP)

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Quasicrystals from ordered structures of polymeric microspheres, applied and attached on a solid support with diameters 6 – 200  $\mu\text{m}$ , are the practical interest of chemical technologies, *i.e.* catalytic, bioengineering, etc.

One of the formation ways of the ordered structures of polymeric microspheres is their self-organization. As a result, 2D and 3D layers of regularly packed microspheres are formed on the surface of a solid support. We have created a self-organizing structure in the form of a 2D hexagonal packing due to the application of polysterene microspheres (PM) from a water and alcohol blended suspension on the surface of the liquid phase (water) followed by transferring and attachment to the glass surface by using vinyltrimethoxysilane (VTES).

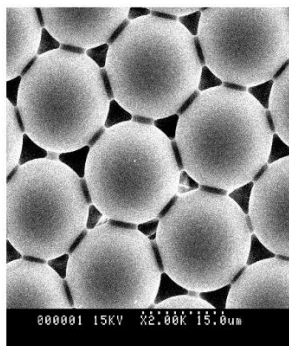
The building mechanism of a self-organizing structure on the water surface includes the following processes:

1. Surface tension and density decrease of liquid's surface layers by using ethanol;
2. Surface tension gradient formation, which results in transfer of substance along the liquid surface (the Gibbs-Marangoni effect);
3. Formation of a "gas cushion" which appears during evaporation of a sufficient amount of ethanol;
4. Formation of capillary waves on the liquid surface.
5. Formation of a convective diffusion of PM in a liquid volume caused by evaporation and dissolution of ethanol.

The ordered structures, obtained on the liquid surface, have a lack of adequate stability and can collapse practically from any physical impact. It is necessary to transfer and attach the packing to a solid surface to increase their stability. The transfer of the PM packing is carried out by its mechanical removal from the water surface onto the glass. The main goal was to preserve the quality of the packing on a solid surface.

For that purpose, a search of substances with good adhesion to glass surfaces and microspheres was carried out. VTES was chosen as an adhesion.

By selecting the necessary concentration of VTES (the concentration ranged between 0.5 – 5% w/w) the size of forming pores was controlled between microspheres and a consolidation was created, in which the pores in the ordered structure would not be closed by the adhesion.



**Figure:** Attached microspheres to a glass surface by using VTES.

PHASE EQUILIBRIA IN SYSTEMS CONTAINING LIQUID CRYSTALLINE  
CHOLESTERYL ESTERS

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Liquid crystalline cholesteryl esters have found a wide application in thermography and photonics. In practice mixtures from liquid crystals (LC) are used. The goal of the present work is to develop methods of the thermodynamic description for the phase diagrams of systems containing cholesteryl substituted liquid crystals.

Cholesteryl (Chol) esters with a common formula R-COO-Chol (where R = CH<sub>3</sub>-, C<sub>4</sub>H<sub>9</sub>-, C<sub>6</sub>H<sub>13</sub>- C<sub>8</sub>H<sub>17</sub>, C<sub>10</sub>H<sub>21</sub>-) are used as mesogenic components. CH<sub>3</sub>-COO-Chol and C<sub>4</sub>H<sub>9</sub>-COO-Chol have nematic N\* phase. Other LC have both nematic N\* and monotropic smectic phases. Systems of these LC substances with tolane, phenylbenzoate and n-decane are investigated by thermal analysis and visual analysis methods. Mesophase types are confirmed by polarizing microscopy. The minimal set of invariant equilibria includes eutectics and metatectics. Influence of carbon number in alkyl chain of LC on coordinates of invariant points is discussed. Excess thermodynamic functions for liquidus are calculated.

The possibility to reveal the solid state polymorphism of mesogens by investigation of LC - non-mesogen systems is demonstrated.

## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

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### APPLICATION OF THE DENSITY FUNCTIONAL APPROACH TO THERMODYNAMICS OF THIN FILM ON CHARGED SOLID PARTICLES

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Adsorption and formation of thin liquid films from vapor phase on electrically charged solid particles is a fundamental phenomenon which is intensively studied both experimentally and theoretically. In this work we will report the results of thermodynamic study of formation of a thin liquid film on charged solid nanoparticle in the case when the electric charge is distributed uniformly over the particle surface. The study has been performed within the local gradient density functional approach. The main thermodynamic characteristics which have been found were the work of the film formation and the chemical potential of the condensate molecule in the film as functions of the radius of the liquid drop and particle, and the magnitude of electric charge of the particle.

Previously we have considered [1] the generalization of the Kelvin-Thomson and the Tohmfor-Volmer thermodynamic formulas for ion-induced nucleation in the case of thin spherical liquid film formed on conducting particle. This generalization was made within the Gibbs method of dividing surfaces and took into account the disjoining pressure of the thin liquid film in the central electric field of the charged particle. Being applied to the nucleation on the nanosized uniformly charged particles, the conventional Kelvin-Thomson formula predicts that the radius of the droplet corresponding to the maximum of the curve of the condensate chemical potential, as well as the radii of equilibrium droplets, can be smaller than the radius of the charged particle. At this the properties of bulk liquid phase are assumed to be reached within the liquid film and the effects of the particle surface wetting are not considered. In previous papers [1, 2], we used several ad hoc approximations for the structural contribution to the disjoining pressure of the liquid film in the generalization of the Kelvin-Thomson formula. However we considered the dielectric permittivity for a substance in the film as constant which was independent of the film thickness.

This study concerns with the following issues. First issue it is the rigorous determination of the disjoining pressure contribution to the chemical potential of the molecule in the film on uncharged particle. The second issue is related to the mutual influence of the disjoining pressure and the electric field on the liquid film characteristics in the case of charged particle. Some ways to resolve the problems associated with the formulated issues can be found within the local gradient density functional approach by direct calculating the density and dielectric permittivity profiles in the film [3]. In this work we have performed such calculations for the liquid water films on uncharged and charged solid particles and have analyzed the profiles of the components of the pressure tensor in these films.

[1] Shchekin, A.K.; Podguzova, T.S. Atmospheric Research, 2011, 101, 493-502.

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## AGREED TEMPERATURE DEPENDENCE OF EVAPORATION, VISCOSITY AND DENSITY OF MERCURY

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Design equations are suggested for evaporation

$$p = 101325 \exp(11,287 - 7109,3/T), \text{ Pa,}$$

dynamic viscosity

$$\eta = 1,692(273/T)^{1,00617(373/T)^{0,38073}}, \text{ mPa}\cdot\text{s,}$$

and density of mercury

$$\rho = 13644,61(273/T)^{0,0590689(413/T)^{-0,568368}}, \text{ kg/m}^3,$$

in all range of its liquid state.

The equations are derived from unified concept of randomized particles subordinate to Boltzmann's distribution taking into account thermal barriers of melting and boiling, that allows to consider from uniform point of view an solid, liquid and gaseous states of matter. Methodical coherence of the received temperature dependences and their high statistical importance is provided to these.

Chaotical (virtually existing) particles are separated into three classes: crystal-mobile with energy not higher than the melting heat ( $\Delta H_m$ )

$$P_{crm} = 1 - \exp[-\Delta H_m/(RT)],$$

liquid-mobile with energy between heat boiling ( $\Delta H_b$ ) and melting one

$$P_{lqm} = \exp[-\Delta H_m/(RT)] - \exp[-\Delta H_b/(RT)]$$

and vapor-mobile with energy not higher than the boiling heat

$$P_{vm} = \exp[-\Delta H_b/(RT)].$$

They were presented in three states and by own are influence on characteristics [1].

So increasing evaporation with increasing temperature is directly related to an increase in the proportion of vapor-mobile particles.

Viscosity reduction is mainly determined by the temperature decreasing proportion of crystal-mobile particles that form virtual clusters and associates, preventing of liquid flow.

The decrease of density is caused by heating and destruction of associates and clusters in composed of crystal-mobile particles as densest virtual entities in a fluid.

Mathematically receiving the calculated equations for evaporation, viscosity and density based on the formulas for  $P_{crm}$ ,  $P_{lqm}$ ,  $P_{vm}$  is achieved by comparing them with experimental data in normalized form.

[1] Malyshev, V.P.; Makasheva, A.M.; Bekturganov, N.S. Viscosity, fluidity and density of substances. Aspect of chaotization. Saarbücken: Lambert Academic Publishing, 2013, 340 p.

## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### THERMODYNAMICS OF ADSORPTION OF CERTAIN ORGANIC COMPOUNDS OF COPPER NANOPARTICLES

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This research describes the adsorption of the test substances, which belong to different classes of organic compounds on the copper nanoparticles.

Copper nanoparticles were obtained by levitation inkjet method [1]. They were applied to inerton in quantity of 15mas.%.

As sorbate were taken organic substances belonging to different classes of compounds: *n*-heptane, *n*-octane, *n*-nonane, methanol, ethanol, benzene, 1-hexyne, 1-hexene.

Adsorption properties of copper nanoparticles were studied by inverse gas chromatography. The gas chromatograph was equipped with a thermal conductivity detector. Helium was used as carrier gas. Chromatography experiments were carried out in a temperature range of 343 – 383 K in steps of 10 degrees.

Some parameters of adsorption were calculated, such as the specific retention volume ( $V_g^T$ ), the heat of adsorption ( $\bar{Q}_1$ ), adsorption entropy components ( $A$ ).

Differential molar heat of adsorption and entropy components sorption test substances are given in Table.

**Table.** Differential molar heat of adsorption and entropy components sorption test substances

sorbate	$\bar{Q}_1$ , (kJ/mol)	-A
<i>n</i> -heptane	13.2	5.9
<i>n</i> -octane	18.8	7.1
<i>n</i> -nonane	25.2	8.5
methanol	20.9	8.7
ethanol	18.4	8.1
benzene	18.6	7.4
1-hexyne	11.4	5.8
1-hexene	7.9	4.8

In a homologous series of *n*-alkanes adsorption heat and entropy component are growing. Methanol, in contrast to ethanol has a higher heat of adsorption. Benzene has a larger heat of adsorption than 1-hexyne, and 1-hexyne greater than 1-hexene. This testifies to the presence of specific interactions of unsaturated and aromatic hydrocarbons with copper nanoparticles. The Calculated proportion of specific interactions decreases in the order: benzene – hexyne-1 – 1-hexene.

[1] Shishkovsky, I.V.; Bulanova, A.V.; Morozov, Y.G. J. Materials Science and Engineering B, 2012, 12, 634-639.

This work was supported by the Russian Foundation for Basic Research (Project No. 13-03-00465\_a).

## THERMODYNAMIC ASPECTS OF COMPLEX FORMATION «HOST-GUEST» IN POLYMER AND LIQUID CRYSTAL SYSTEMS USING INVERSE GAS CHROMATOGRAPHY

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In last years, the considerable attention is paid for synthesis and investigations of properties of compounds with a large molecular cavity in their structures. One of examples of such compounds is cyclodextrins. These macromolecules are widely used as components of chromatographic systems, catalysts, system of additive for drugs. The broad application is due to ability to form inclusion complexes (cavities) between cyclodextrins and different molecules. One of the experimental methods for studying of the thermodynamic of complexation between cyclodextrins and different organic compounds in low molecular weight and high molecular weight solvents is method of gas inverse chromatography (IGC). So, change in Gibbs free energy of formation of cavities in cyclodextrins solutions includes contributions, relating not only with «host-guest» interactions, but with the solvation of a host, a guest, a complex and also with changing in structure of solvents by dissolving compound. It is the main reason of difficulties associated with controversial interpretation of experimental data obtained by various methods including IGC. In this connection, the first part of report is thermodynamic substitution of ability of complexation in solutions with the application of two models – constant volume ( $V, T = \text{const}$ ) and constant pressure ( $p, T = \text{const}$ ), where the interphase redistribution volatile sorbates (guest) takes place. Advantages and disadvantages of both approach, boundaries of applicability of the resulting equations for calculating complexation constants are discussed. It was shown firstly, the formation of cavities also takes place, when the distribution constants between liquid and gas phases in the system with complexation agent lower than in the system without one. Experimental data about complexation process of different classes of organic compounds (also optically active) with  $\beta$ -cyclodextrin and  $\beta$ -cyclodextrin derivatives in polymer (isotropic) and liquid crystal (anisotropic) phases are obtained by IGC. The transition from nonpolar to polar polymer enhances interactions middle polar «guests» with cyclodextrin's cavity and increases selectivity of molecular recognition of enantiomers. In the case of liquid crystals phase, analogical effect is observed, when orientational order parameter are increasing or high polar associated (supramolecular) LC are used.

[1] Atwood, J.L., Steed, J.W. *Supramolecular Chemistry*, 2nd ed., J. Wiley & Sons: Chichester, 2009, 998 p.

*This work was supported by the Russian Foundation for Basic Research (Project No.13-03-01197).*

## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### SORPTION AND SELECTIVE PROPERTIES ISOMER SELECTIVE COMPOSITE SORBENT BASED ON EUTECTIC MIXTURE OF NEMATIC ALKOXYAZOXYBENZENES AND PERBENZOYLATED $\beta$ -CYCLODEXTRIN

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An important area of modern gas chromatography is search of a highly selective universal stationary phases. One way to obtain an universal sorbent is introducing in the liquid crystal (LC) matrix, characterized by highly selective separation of structural isomers, derivatives of cyclodextrins that provide recognition of optical isomers due to the complexation of the type «guest-host». Eutectic mixtures of nematic liquid crystals possess a high structural selectivity than the original individual LC.

We studied mesomorphic, sorption and selective properties of the composite sorbent based on a eutectic mixture of nematic (*N*) liquid crystals of (4-methoxy-4'-etoksiazoksibenzol (MEAB) and 4,4-dietoksiazoksibenzene (AOF) and perbenzoylated  $\beta$ -cyclodextrin (Bz- $\beta$ -CD). Method of thermal polarization microscopy revealed that the introduction of Bz- $\beta$ -CD in the mix «MEAB – AOF» in the amount of 10.0% by weight does not change the type of mesophase, it remains a nematic.

In the temperature range that includes the nematic (*N*) and isotropic (*I*) sorbent phase by gas chromatography determined sorption thermodynamic functions for 30 organic compounds, which are compared with similar functions to the sorbent «MEAB – AOF» (without the addition of the macrocycle). Thermodynamic analysis of the causes of changes in the retention of sorbates were carried out on the basis of the calculation of the difference between the enthalpy and entropy of sorption ( $\Delta(\Delta_{sp}\bar{H}_i^0)$  and  $\Delta(\Delta_{sp}\bar{S}_i^0)$ ) received for LC sorbent with the addition of the macrocycle and without additives.

In the *N*-phase sorbent for all of the investigated sorbates (except camphenes) the following inequalities:  $\Delta(\Delta_{sp}\bar{H}_i^0) \geq 0$  и  $\Delta(\Delta_{sp}\bar{S}_i^0) > 0$ . The implementation of these inequalities shows that the binding of sorbates with the macrocycle occurs athermally or endothermic, and the reason for the increase of  $V_g^T$  is the entropy factor. In an isotropic (*I*) phase of the sorbent solvation effects «LC – macrocycle» weaken, which leads to greater availability of the cavity of the macrocycle and the heat bonding process «sorbate – macrocycle» becomes negative  $\Delta(\Delta_{sp}\bar{H}_i^0) < 0$  for most of sorbates. Negative values of  $\Delta(\Delta_{sp}\bar{H}_i^0)$  correspond to negative values of  $\Delta(\Delta_{sp}\bar{S}_i^0)$ , which indirectly indicates their location due to the formation of a strong complex with the macrocycle. Hence the formation of aggregates «sorbate – macrocycle» largely expressed in phase *I* than in the *N*-phase sorbent.

It was found that investigated sorbent has high structural selectivity ( $\alpha_{p/m} = 1,128-1,059$ , 100-130°C, *N*) and moderately expressed enantioselectivity (1,07-1,02) in a wide temperature range (95-170°C) includes both mesophase and an isotropic sorbent phase. Enantioselectivity of the sorbent is shown as in enhancing retention in making «MEAB – AOF» chiral additive Bz- $\beta$ -CD (lemon, pinenes, camphene), and its reduction (2,3-butanediol).

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INTERGAL EQUATION THEORY FOR THE ELECTRIC DOUBLE LAYER  
BETWEEN THE SURFACES OF MOBILE, ORIENTABLE DIPOLES

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The electrical double layer between the two parallel surfaces in an electrolyte solution is considered. Each surface contains mobile, orientable dipoles. The motivation for this model is the system of two parallel lipid membranes in an electrolyte solution at the physiological conditions, with dipolar approximation of headgroup structure. Then each lipid layer facing the aqueous solution is modeled as a planar surface of dielectric discontinuity at the hydrocarbon/water interface. The headgroup structure of zwitterionic lipids is modeled as a two-dimensional dipolar liquid at this surface. According to the recent theoretical studies of membrane structure and macroion adsorption [1–3], this model succeeds in explaining the major structural and electrostatic properties of membranes.

In this work, we develop for this system the formalism of inhomogeneous Ornstein-Zernike equations with reference hypernetted chain closure (RHNC).

Recently, we have succeeded in constructing the inhomogeneous RHNC theory for the ferrofluid bilayer [4]. A numerical scheme was developed that allowed us to achieve convergent solutions of this theory [4]. In this work, we extend the approach of [4] to include the inhomogeneous electrolyte between the two planar dipolar surfaces. We solve the resulting inhomogeneous RHNC equations. We calculate the orientational densities and pair functions for dipoles (lipid heads); density profiles and pair functions for electrolyte ions; and the dipole-ion pair cross-correlation functions. The results of the RHNC theory are compared with Monte Carlo simulations.

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[2] Haugen, A.; May, S. *J. Chem. Phys.*, 2007, 127, 215104.

[3] Mengistu, D.H.; May, S. *J. Chem. Phys.*, 2008, 129, 121105.

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## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

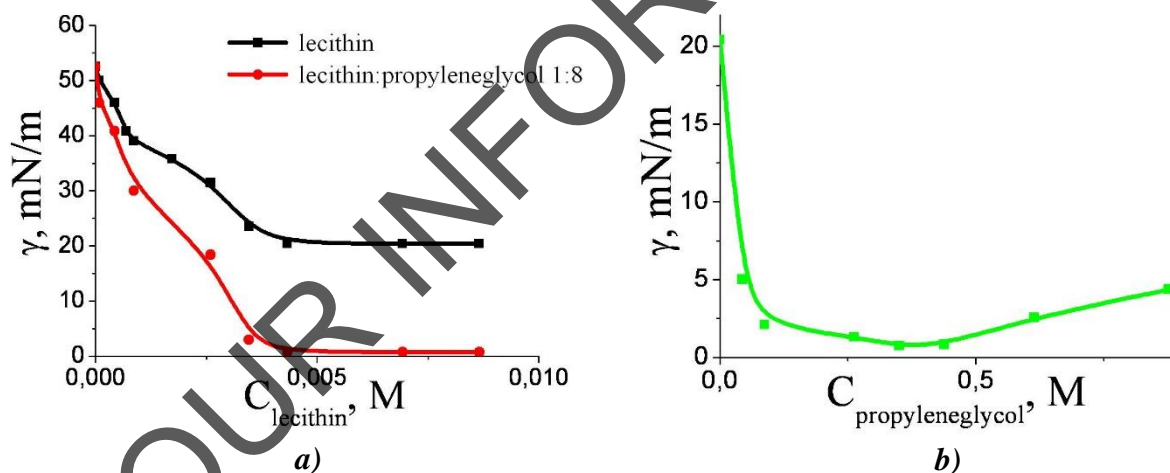
### PHASE DIAGRAM AND INTERFACIAL PROPERTIES OF THE LECITHIN-BASED MICROEMULSION

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The potential applications of microemulsions in the food, cosmetic, and pharmaceutical are linked to their unique properties such as thermodynamic stability, optical clarity and high solubilization capacity. However, the most critical problem of the use of most microemulsions is the toxicity of their partial components. In present study we use of biocompatible microemulsions based on mineral oil as the nonpolar solvent, water as the dispersed phase, and a mixture of lecithin and propyleneglycol as emulsifiers. For preparing the microemulsions necessary to receive low values of interfacial tension between oil and water.

Figure 1 shows the dependence of water/oil interfacial tension on the concentration of lecithin. The smallest value of the interfacial tension  $\gamma = 20.42$  mN/m was found. However, this value is not enough for preparing microemulsion. The addition of alcohol as a result reduce the interfacial tension to 0.73 mN/m (Figure a, b). The main characteristics of adsorption of surfactants has been also calculated. The structure changes in the adsorbed layer has been discussed.



**Figure:** The interfacial tension of the water / oil depending on the concentration of a – lecithin, b – propyleneglycol ( $C_{\text{lecithin}} = 0,004$  M).

Phase diagrams of the four-component systems mineral oil/lecithin:propyleneglycol/water at the ratio surfactant:alcohol 1:8 were constructed. Concentration and temperature region of existence of the microemulsion was identified. Our results showed that the microemulsion area in pseudoternary phase diagrams is wider with increasing temperature from 25 to 37°C. Received microemulsion may be used as effective vehicles for the drugs delivery.

## THE INVESTIGATION OF THICKNESS DEPENDENCE OF REFRACTIVE INDEX FOR NANOSIZED ACETONE FILM ON SILICA BY ELLIPSOMETRIC METHOD

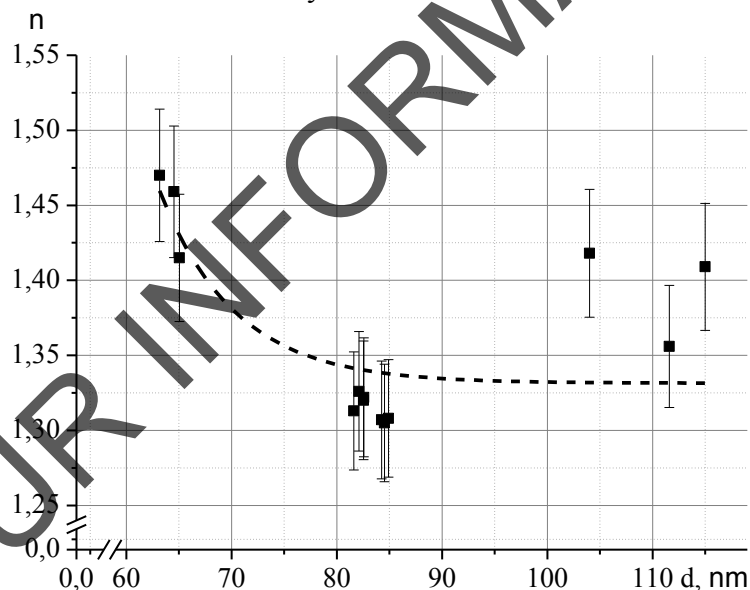
N.Yu. Sdobnyakov, N.V. Novozhilov, A.S. Antonov, E.A. Voronova, O.V. Mikhailova

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Ellipsometry allows investigating not only solid, but also liquid films [1, 2]. Note also that recently technologies using thin film acetone structure as the stabilizer was developed to prepare gold nanoparticles [3], as well as carbon nanotubes [4]. Thus, studies of properties of nanoscale acetone film structures, including their optical properties, are both fundamental and technological interest. On the basis of analysis of the ellipsometric angles spectra ( $\psi$  and  $\Delta$ ) the investigation of thickness dependence of refractive index for nanosized acetone film on silicon surface was carried out using the photometric spectroellipsometer.

The Fig. 1 shows the dependence of the refractive index on the acetone layer thickness on silica substrate. Note, that in this case the refractive index of the film decreases with the increase of its thickness apparently to the macroscopic value. According to [2] the similar result was observed for ethyl alcohol on silica substrate. In our opinion such a monotonic behavior of the effective refractive index indicates the systematic component unrelated to random errors, i.e. determined by the optical properties of the transition layer at the film-substrate interface.



**Figure:** The thickness dependence of refractive index for nanosized acetone film on silica. Error measurement - 3%.

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*The work was supported by Ministry of Education and Science of Russian Federation in frames of the State program in sphere of scientific activity and under support of Russian Foundation for Basic Research (Grant No. 13-03-00119).*

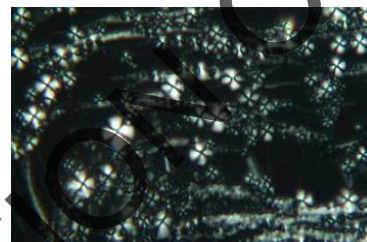
## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### THERMAL PROPERTIES OF LANTHANUM-CONTAINING LYOTROPIC LIQUID CRYSTALS

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The synthesis of nanostructured materials one of the most promising and rapidly developing areas are the use of soft templates. The soft templates are composed of soft compound such as biomolecules, polymer gels, emulsions and lyotropic liquid crystals (LLC). LLC have particular interest: different types of lyotropic mesophases - lamellar, hexagonal and cubic allow obtaining 1D, 2D and 3D ordered arrays exhibit size and shape depended properties. Lyotropic metallomesogens containing trivalent rare-earth metal ions have unique attractive behavior due to combination of some unique optical and magnetic properties of the lanthanide ions with anisotropic supramolecular organization liquid crystal. These multifunctional materials



*Figure: Texture of lamellar mesophase of  $C_{12}EO_4/La(III)/H_2O$  system ( $H_2O-10$  wt %).*

provide new promises in biomedical science and materials science. Lanthanide-containing LLC have been potential applications in areas of porous material templating, as contrast agents in medical imaging, biorelevant systems for drug delivery. In this work presents the study of thermal properties of the LLC on the basis of non-ionic surfactants – dodecyl glycol monododecyl ether ( $C_{12}EO_{10}$ ), tetraethylene glycol monododecyl ether ( $C_{12}EO_4$ ) and hydrated lanthanide nitrates  $La(NO_3)_3 \cdot 6H_2O$ . Using complex methods (POM, SAXS, NMR) the phase diagrams were constructed, the temperature and concentration limits and the type of supramolecular organization were defined [1].

The thermodynamic of phase transition was investigated by differential scanning calorimetry (DSC). By the example of the  $C_{12}EO_4/La(III)/H_2O$  systems with lamellar mesophases (Figure) were shown the variation of thermodynamic parameters of the mesophases depending on the water content in the system.

Measured phase transitions in the lyotropic systems containing water, in contrast to the thermotropic liquid crystals, are wide, because according to the POM results  $\Delta T$  of the lamellar phases is 10-25°C. Therefore, it is quite difficult to obtain well-resolved thermograms. For the all studied systems, endothermic peaks were only detected in the first heating cycle and were not reproduced in any following heating and cooling cycles. This tendency is typical for the lyotropic systems containing water [2]. The obtained phase transition temperatures sufficiently well (within 5-6°C) correlate with the visual observations of these transitions by means of optical microscopy.

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## H-COMPLEXES IN MESOMORPHIC SYSTEMS: PREPARATIONS AND PROPERTIES

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Preparation of new functional nanomaterials using specific intermolecular interactions - a hydrogen bond - is a promising direction of research nowadays. Derivatives of carboxylic acids are often used, as one of the components included in such a material. In most cases the molecules of those compounds can provide mesomorphic units geometric anisotropy and thermal stability of obtained nanomaterials due to their structure and ability to form strong hydrogen bonds. New supramolecular materials demonstrate unique physical and mesomorphic properties.

The systems: p-n-propyloxybenzoic acid - p-n-propyloxy-p'-cyanobiphenyl, p-n-propyloxycinnamonic acid - p-n-propyloxy-p'-cyanobiphenyl were the objects of our research. Mesomorphic properties of the systems were studied by polarization thermomicroscopy and differential scanning calorimetry methods. Complete phase diagrams of the systems were constructed with 10 mol.% concentration step. Two subphases with different mesomorphic and physical properties were found in the nematic phase existence region of both systems. It has been demonstrated that the observable systems have two points of the invariant equilibrium: metatectic and eutectic.

The bulk properties of the systems were investigated by the polythermal dilatometry method. The dielectric properties of the systems were studied by the dielectric method. The analysis of temperature and concentration dependences of systems bulk and dielectric properties was carried out. In both systems, the formation of chain associates between the acid and cyanobiphenyl in a molar ratio of 1: 1 and 2: 1 due to hydrogen bonding was ascertained.

H-complexes 1:1 ratio between p-n-propyloxybenzoic acid and p-n-propyloxy-p'-cyanobiphenyl molecules were modeled. The most energetically favorable conformers were used for complexes modeling. Calculations were carried out by DFT methods B3LYP and B97D with bases 6-311 ++ G \*\* and cc-pVTZ with all molecules parameters optimization. Calculations have shown that the H-complex has angular geometry. Interaction O ... HC arises in the complex in addition to the hydrogen bond O-H ... N. This interaction determines the geometric shape of the complex. The magnitude of a dipole moment of the complex is 6.2 D. The energy of hydrogen bonds is 7 - 8 kcal/mole in the angularly complex. Linear form of the H-complex was also modeled. The magnitude of the dipole moment of H-complex linear form is 7.0 D. The linear and angular forms of the complex have similar values of energy. Thus, these forms can transform into each other under external influences. The formation of two nematic subphases and their mutual transition can be related with this phenomenon.

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## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### DYNAMIC SURFACE PROPERTIES OF LYSOZYME SOLUTIONS: IMPACT OF UREA AND GUANIDINE HYDROCHLORIDE

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The impact of urea and guanidine hydrochloride (GuHCl) on surface properties of lysozyme solutions was investigated by the methods of surface dilational rheology and ellipsometry. Measurements of the kinetic dependencies of the dynamic surface properties and ellipsometric angles of lysozyme/urea and lysozyme/GuHCl solutions show that these two denaturants have different influence on the adsorption layer structure. The increase of GuHCl concentration leads to noticeable changes of the kinetic dependencies of the dynamic surface elasticity and ellipsometric angles while the main effect of urea reduces to a strong drop of the static surface tension. The difference between the effects of these two denaturants on the surface properties of other investigated globular proteins is significantly weaker and is mainly a consequence of a different extent of the globule unfolding in the surface layer at equal concentrations of the denaturants.

The dynamic surface elasticity and surface tension decrease gradually with the increase of urea concentration up to 9 M but the kinetic dependencies of the ellipsometric angle  $\Delta$  and consequently of the adsorbed amount do not display any significant changes. These results are connected with a gradual transformation of the lysozyme globules in the surface layer into the molten globule state without tightly packed interior of the globule and with a dynamic tertiary structure similar to the corresponding transition in the bulk phase at the increase of urea concentration [1]. Lysozyme preserves its molten globule state in the course of adsorption and the interface has no specific effects unlike the case of bovine serum albumin (BSA) and  $\beta$ -lactoglobulin (BLG) solutions [2-4]. On the contrary, the increase of GuHCl concentration leads to an abrupt transition from monotonic to non-monotonic kinetic dependencies of the dynamic surface elasticity of lysozyme solutions in a narrow concentration range and to strong changes of the ellipsometric data. These peculiarities indicate the beginning of the globule unfolding in the surface layer but the observed effect is not as strong as in the case of BSA and BLG solutions. The disulfide bonds between remote aminoacid residues of the protein chain restrict the mobility of the partially unfolded lysozyme molecule and do not allow formation of long loops and tails in the surface layer. The obtained results demonstrate the high sensitivity of the surface dilational rheological properties to protein conformations at the liquid – gas interface.

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## THERMODYNAMICS OF SORPTION OF ORGANIC COMPOUNDS FROM THE GAS PHASE SUPRAMOLECULAR LIQUID CRYSTAL 4-(2-HYDROXYETHYLOXY)-4'-CYANOAZOXYBENZENE

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Liquid crystals are widely used in gas chromatography for the separation of structural isomers of organic compounds due to the orderly arrangement of the molecules in the mesophase temperature range. It is possible to expand the variety of isomer selective stationary phases with the use of supramolecular (associate) liquid crystals, in which the carrier of mesogeneity are not an individual mesogenic molecule, but supermolecule representing associates of two or more molecules, aggregated in nematic and smectic mesophase. Using supramolecular LC as stationary phase leads to a highly selective separation columns with respect to structural isomers in gas-liquid chromatography.

In the work the method of inverse gas chromatography was used to determine the thermodynamic function of the sorption of the gas phase hydrocarbons and alcohols with nematic 4-(2-hydroxyethyloxy)-4'-cyanoazoxybenzene (HEOCAB) and identifies some sorption patterns. It was established that an increased retention of terpene hydrocarbons compared to the corresponding *n*-alkanes is associated with the action of the entropy factor, and less retention of isopropyl alcohol compared with *n*-alcohols is due to the lower contribution enthalpic factor to the constant of sorption, due to steric hindrance. Was calculated the additional contributions (to the dispersion of *n*-alkanes) interactions "sorbate – HEOCAB"  $\Delta_{add}H$ . It was found that *n*-alkanols  $\Delta_{add}H$  value corresponds to the formation of hydrogen bonds with molecules HEOCAB. In the case of aromatic hydrocarbons additional enthalpy contribution arises due to the presence in the structure of arenas and HEOCAB  $\pi$ -conjugated systems, interacting with the embedding of these molecules in the nematic structure of HEOCAB. Positive values of  $\Delta_{add}H$  for limonene indicate that it increased as compared with sorption of *n*-alkanes due entropy factor.

The investigated system shows positive deviations from Raoult's law, which increase in number of alkanols  $\rightarrow$  arena  $\rightarrow$  terpenes  $\rightarrow$  *n*-alkanes. Very high values of the activity coefficients are found for *n*-alkanes  $C_{10} - C_{14}$  ( $\gamma_i^\infty > 60$ ), which testifies to their weak interaction with polar molecules HEOCAB in *N* phase. For all investigated sorbates positive deviations from Raoult's law are due high values of the excess partial enthalpies of these compounds in a solution of LC

( $\bar{H}_i^{E,\infty} \approx 12 - 24$  kJ/mol).

HEOCAB analyzed is a mixture of isomers with different melting points. Low-temperature mixed nematic, containing solid particles inclusions in the range 113 – 135°C, has a high selectivity towards *para*- and *meta*-xylene ( $\alpha_{p/m} = 1.164$ , 115°C). High temperature homogeneous nematic (135 – 175°C) is less associated and able to implementation of dipole-dipole and specific interactions with molecules of sorbates, which leads to a reduction of *meta-para*-selectivity and increase of selectivity for separation of polar and nonpolar compounds with close boiling points.

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## Section 4. Thermodynamics of surface phenomena and self-organization phenomena in fluid systems

### MOLECULAR DYNAMICS STUDY OF NON-IONIC MICELLAR SOLUTION: THERMODYNAMIC AND TRANSPORT PROPERTIES

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Although there is a substantial number of works on the computer simulation of micellar solutions [1], the evaluation of thermodynamic and transport properties of micelles via computer simulations has not yet received a proper attention because of the complexity of related problems. Most of the micellar systems being studied by computer simulations include small numbers of aggregates, often a single micelle, since the simulation of larger systems on relevant time-scales is too computationally expensive. Diffusivities of stable surfactant aggregates play an important role in transport processes in micellar solutions and in dynamics of micellization, solubilization, flotation and micellar relaxation on different time scales. Kinetic phenomena and aggregation processes in micellar solutions are determined by the diffusivities of species constituting the solution because the expressions for the attachment–detachment coefficients in the master kinetic equations for aggregation processes, such as the Becker-Doering difference equations or generalized Smoluchowski equation depend explicitly on these diffusivities [2–8]. All these facts attract attention to experimental and theoretical study of the diffusivities of micelles and monomers in micellar solutions.

The investigation of thermodynamic properties of micellar ensembles requires consideration of large systems comprising tens of aggregates. In order to simulate such ensembles within a reasonable wall-clock time, one should use simpler (coarse-grained) models of both surfactant and solvent. We performed the coarse-grained molecular dynamics simulations of the non-ionic surfactant aqueous solution using CPU and GPU of a single desktop. After the initial process of self-assembly of surfactant molecules, the equilibrium distribution of aggregates by the aggregation number is formed. With the help of this distribution, the work of aggregation of a micelle can be found as a function of aggregation number and surfactant concentration [9]. Besides the work of aggregation, we studied transport properties of the micellar solution, in particular, the self-diffusion coefficients of the micelles as a function of their aggregation number [10].

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INTERACTION OF SHORT-CHAIN OLIGOPEPTIDES WITH VAPORS:  
THERMODYNAMICS AND CHANGE OF THIN FILMS MORPHOLOGY

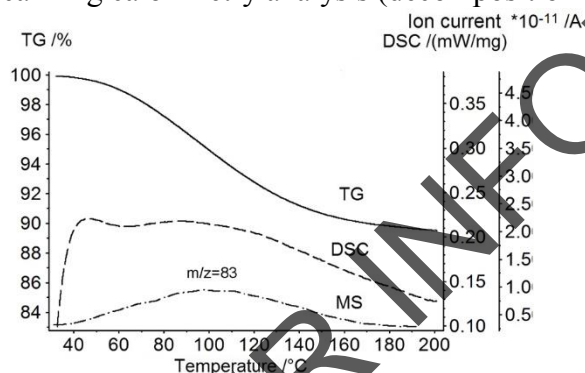
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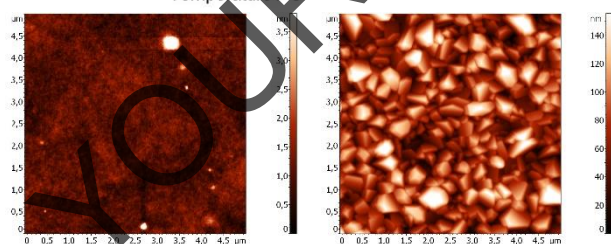
<sup>2</sup>Zavoisky Physical-Technical Institute, Kazan Scientific Center, Russian Academy of Sciences  
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Short-chain oligopeptides are capable to form ordered structures in the result of self-organization. Being of «soft materials», oligopeptides may change the mutual arrangement of fragments under the influence of external factors. This feature is the reason for the changes in the surface morphology of oligopeptide film or the formation of new nanostructures during the interaction with water or organic vapors. From the other hand one can not to predict the type and shape of the oligopeptide nanostructures which will form in the result such interaction, because of insufficient experimental data for such systems.

At present work the interaction of short-chain oligopeptides with water and organic vapors (guest) was studied using atomic force microscopy (surface morphology of thin film), quartz crystal microbalance (sorption capacity) and simultaneous thermogravimetry and differential scanning calorimetry analysis (decomposition of clathrates).



**Figure 1:** Thermoanalysis data of product of dipeptide *L*-alanyl-*L*-valine saturation by vapor of chloroform ( $m/z = 83$ ). Heating rate is 10 K/min.



**Figure 2:** AFM images of the surface of the (a) initial *L*-alanyl-*L*-isoleucine film deposited on HOPG; (b) film saturated with ethanol vapors.

It was found that in generally the sorption capacity of oligopeptide decreases with increase of the molecular size of organic substances. The correlation between the molecular size of guests and the thermal stability of the clathrate was observed. Deviation from this correlation may be due to the formation of hydrogen bonds between guest and oligopeptide. The influence of vapors on morphology of oligopeptide thin film was studied. The correlation between the sorption capacity of oligopeptides and the change of morphology of their films in contact with organic vapors was found.

*This study was supported by the Russian Government Program of Competitive Growth of Kazan Federal University.*

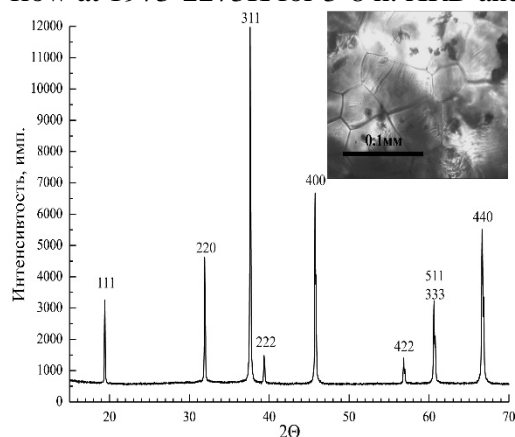
**Section 5**  
**Applied aspects of chemical  
thermodynamics**



FOR YOUR INFORMATION ONLY

THERMODYNAMIC ASPECTS OF Al<sub>2</sub>O<sub>3</sub>-BASED CERAMICS SYNTHESISA.S. Alikhanyan<sup>1</sup>, N.A. Gribchenkova<sup>1</sup>, E.N. Beresnev<sup>1</sup>, T.A. Ivanova<sup>2</sup>, K.G. Smorchkov<sup>1</sup><sup>1</sup>Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences  
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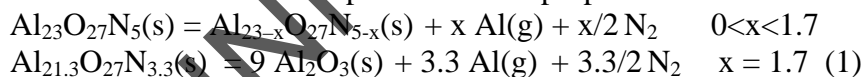
This paper presents the results of synthesis and the investigation of the thermodynamic properties of  $\gamma$ -aluminum oxynitride 9Al<sub>2</sub>O<sub>3</sub>·5AlN (AlON). The synthesis conditions of AlON have been determined. AlON was synthesized by sintering the starting materials at 25 MPa in N<sub>2</sub> flow at 1973-2273K for 3-8 h. XRD and optical micrograph of 9Al<sub>2</sub>O<sub>3</sub>·5AlN are given in Figure.



**Figure:** XRD and optical micrograph of AlON powder synthesized at 2050°C for 4 hrs.

The sublimation the thermodynamics of AlON has been the investigated by the Knudsen-effusion technique with mass-spectrometric analysis of the vapour phase. The mass-spectrometer was a standard model MS 1301. Knudsen-effusion cells were made of tungsten coated with iridium or BN. Temperature was measured by optical pyrometer EOP-66 and stabilized within  $\pm 5$  K. Crystalline AlON was heated from 1930-2000 K. It has been identified by studying the 9Al<sub>2</sub>O<sub>3</sub>·5AlN system in tungsten cells coated BN that its gas phase mainly consists of Al(g) and O<sub>2</sub>. The partial pressures of the vapour species were determined at

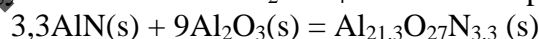
1930 K. These data clearly demonstrate that the sublimation of 9Al<sub>2</sub>O<sub>3</sub>·5AlN (Al<sub>23</sub>O<sub>27</sub>N<sub>5</sub>) a two - step process can be proposed:



The AlN activity in heterogeneous region [Al<sub>21.3</sub>O<sub>27</sub>N<sub>3.3</sub>+ Al<sub>2</sub>O<sub>3</sub>] was found by expressing the pressure of a hypothetical vapour component AlN

$$a_{\text{AlN}} = p_{\text{Al}} \cdot p_{\text{N}_2}^{1/2} / p_{\text{Al}}^{\circ} \cdot p_{\text{N}_2}^{\circ 1/2}$$

The standard Gibbs energy of formation of Zn<sub>2</sub>SnO<sub>4</sub> from the component by the reaction



can be expressed as [1]

$$\Delta G_{1930}^{\circ} = RT \ln a_{\text{AlN}}^{3.3} = RT \ln \{ p_{\text{Al}} \cdot p_{\text{N}_2}^{1/2} / p_{\text{Al}}^{\circ} \cdot p_{\text{N}_2}^{\circ 1/2} \}^{3.3}$$

The enthalpy of reaction (1) was calculated using the temperature-dependent intensities of the corresponding ion currents in the range 1930–1980 K (Table).

**Table.** Thermodynamic parameters of AlON (kJ/mol)

AlON	$a_{\text{AlN}}$ T=1930K	$-\Delta_f G_T^{\circ}$ components	$-\Delta_f G_{1930}^{\circ}$ elements	$\Delta H_{298}^{\circ}(1)$	$\Delta_f H_{298}^{\circ}$ components	$-\Delta_f H_{298}^{\circ}$ elements
9Al <sub>2</sub> O <sub>3</sub> ·3.3AlN	0.83	9.9(1930K)	9878	2096	44.7	16089

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## Section 5. Applied aspects of chemical thermodynamics

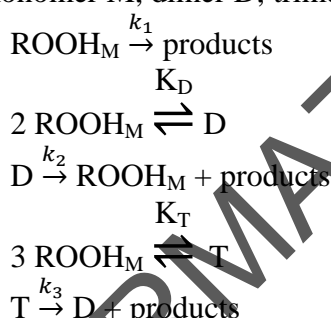
### DECOMPOSITION KINETICS OF ETHYLBENZENE HYDROPEROXIDE IN CCL<sub>4</sub> WITH THE SELF-ASSOCIATION

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Thermal decomposition of hydroperoxides includes simultaneous processes homolytic, molecular and induced free radical decomposition. When changing conditions - temperature, concentration and solvent can vary the ratio of these processes, making it difficult to interpret the results.

Formal kinetic decay scheme hydroperoxide consists of reactions of monomolecular decomposition and decay associates (monomer M, dimer D, trimer T):



The dependence of the initial rate of decay of the total initial  $W_0$  hydroperoxide concentration is linear throughout the range of concentrations, indicating that the first-order reaction of the hydroperoxide. Dependence  $W_0$  of  $[M]$  is close to parabolic, which fully complies with the formal kinetic scheme.

The dependence of the rate of decay of the total monomer concentration is described by a cubic equation

$$W_0 = k_1[M] + k_2K_D[M]^2 + k_3K_T[M]^3,$$

from which we can determine all three constants

$$W_0 = a[M] + b[M]^2 + c[M]^3,$$

where  $a = k_1$ ;  $b = k_2 \cdot K_D$ ;  $c = k_3 \cdot K_T$ .

Data on the kinetics of decay at 110°C are summarized in the Table.

**Table.** The kinetic parameters of decomposition GPEB (110 °C), the solvent carbon tetrachloride

$k_1 \cdot 10^{-5},$ $s^{-1}$	$K_D,$ l/mol	$k_2 \cdot K_D \cdot 10^{-5},$ l/mol·s	$k_2 \cdot 10^{-5}, s^{-1}$	$K_T,$ (l/mol) <sup>2</sup>	$k_3 \cdot K_T \cdot 10^{-5},$ (l/mol) <sup>2</sup> ·s	$K_3 \cdot 10^{-5}, s^{-1}$
58.7	0.75	157	209.5	0.82	76.7	93.7

The table shows that, as would be expected, self-associates ethylbenzene hydroperoxide decay faster monomeric form.

*This work was financially supported by the Russian Ministry of Education and Science as part of the base part of the State job 02.14.*



**THERMODYNAMIC MODELING OF THE BEHAVIOR OF URANIUM WHILE HEATING RADIOACTIVE GRAPHITE IN INERT ATMOSPHERE**

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Nowadays it is become a promising high-temperature treatment of radioactive waste. To date, there are several ways of high-temperature utilization of radioactive graphite [1-3]. The criterion for successful recycling is acceptable emissions of radioactive elements to the environment. Investigations were carried out by means of the thermodynamic modeling.

Distribution of U in the system while radioactive graphite is heated in an argon atmosphere is shown in Figure. The basic elements to a temperature of 2400 K are compounds of the balance condensed uranium carbides. Increasing the temperature to 2900 K leads to higher content of gas U to 98 mol. %. Further heating system reduces the amount of gas U to 82 mol. % And an increase in the content of U + ions up to 17 mol. %.

The minimum basic set of reactions (equilibrium) and in the individual phases at the interface might be written.

UC(s2)+C=UC<sub>2</sub>(s2) (1) 4UC<sub>2</sub>(s2)+2C=2U<sub>2</sub>C<sub>3</sub>(s2) (3) UC(s2)=U+C (5) U=U+ (7)  
2UC(s2)+C=U<sub>2</sub>C<sub>3</sub>(s2) (2) U<sub>2</sub>C<sub>3</sub>(s2)=2U+3C(s2) (4) UC<sub>2</sub>(s2)=U+2C (6)

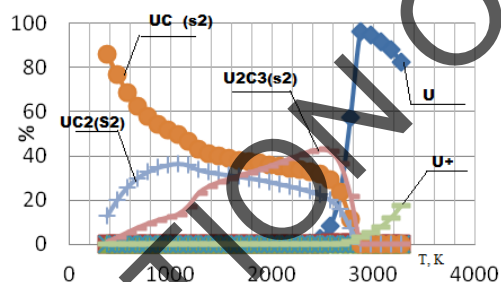
The dependence of the equilibrium constants of reactions (1) - (7) of the temperature is described by the equation of the form:

$$\ln k_i = A + B/T .$$

**Table.** The coefficients in equation constants reaction

Reaction	Temperature range $\Delta T_i$ , K	A	B	The value of the approximation $R^2$
1	373-1173	-897.73	53.68	0.995
2	1173-2573	81386	-4.01	0.999
3	1173-2573	161995	-6.55	0.999
4	2573-2773	419986	110.58	0.999
5	2373-2773	-172092	50.06	0.997
6	2373-2773	-260754	70.03	0.998
7	2873-3273	-43291	11.66	0.999

[1] Kolbin, T.S.; Terentev, D.I.; Barbin, N.M.; Alekseev, S.G. Technosphere safety, 2013, 1, 30.  
[2] Kolbin, T.S.; Terentev, D.I.; Barbin, N.M.; Alekseev, S.G. Technosphere safety, 2013, 2, 40.  
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**Figure:** Distribution of U in the system.

## Section 5. Applied aspects of chemical thermodynamics

### THEORETICAL ASPECTS OF MODERNIZATION OF *PARA-TERT*-BUTYLPHENOL PRODUCTION

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This work was carried out for development of *para-tert*-butylphenol (*p*-TBP) production with high quality answering to the modern requirements to purity of product and, also, for process intensification. To this purpose it was investigated and compared efficiency of several modern sulfur cation-exchange resin, including Amberlyst 36 Dry (A-36 Dry) and Tulsion T-66 MP, with KU-23 and KU 2-8 using early. Determination of kinetic regularities for transalkylation reactions, carried in the “phenol-*tert*-butylphenol” system, could help us to obtain our goals. Industrial process is carried out in relatively mild conditions due to using the sulfur cation-exchange resins. This conditions the presence in reactionary mass the predominance of only four components: phenol (P), *o-tert*-butylphenol (*o*-TBP), *p*-TBP and 2,4-di-*tert*-butylphenol (2,4-diTBP). So it is necessary and sufficiently to know the equilibrium constants  $K_i$  only for two independent reaction for description of equilibrium in this system (in general).

It was found experimentally values of  $K_i$  for chosen conversions:  $o\text{-TBP} + \text{P} \xrightleftharpoons[k_{-1}]{k_1} p\text{-TBP} + \text{P}$  (I) and  $2,4\text{-diTBP} + \text{P} \xrightleftharpoons[k_{-2}]{k_2} p\text{-TBP} + p\text{-TBP}$  (II).  $K_I$  agrees with literature values obtaining in the presence of another kind of catalyst well, and liquid phase equilibrium of reaction (II) is investigated for the first time. Pairwise equality of enthalpy and entropy effects of liquid phase reaction (I) and (II) in the margin of their experimental error was found. Simultaneously it was noticed that between values of  $K_i$  is significant discrepancy. Transition from liquid phase conversions to gas phase ones levels this difference entirely. Thus, the fact that values of  $K_{II}$  are larger than values of  $K_I$  is due to intermolecular, not intramolecular factors. The results of the equilibrium investigation provided a basis for processing of the kinetic data. Its complex analysis allowed to observe:

1. The rate of equilibrium, achieving in the “phenol-*tert*-butylphenol” system, involving concerned sulfur cation-exchange resins increased in the range:  
KU 2-8 < KU-23 << Amberlyst 36 Dry < Tulsion T-66 MP
2. System output on equilibrium state carries out sooner in the presence of A-36 Dry at increasing of moisture content in reactionary mass more than 0.1 %.
3. Under the assumption that the activation energy of the reactions is invariable, values of their preexponential factor are (in the case of water absence): comparable for T-66 MP and A-36 Dry, on passing from T-66 MP to KU-23 and KU 2-8 increase by 15 and 40 times, respectively, for reaction (I); on passing from T-66 MP to A-36 Dry, KU-23 and KU 2-8 increase by 1.5, 2000 and 6000 times, respectively, for reaction (II).
4. Generation of *meta-tert*-butylphenol carries with less rate as compared with main reactions and its concentration in reactionary mass is far from equilibrium value. Nevertheless its presence even in small quantities influences adversary the physicochemical properties of commercial *p*-TBP. It was chosen the synthesis conditions which concentration of *meta*-isomer is minimized at acceptable rates of target reactions in.

*This work was financially supported by the Ministry of education and science of the Russian Federation within the framework of the basic part of governmental tasks of Samara State Technical University (Project code 1708).*

## TG, DSC AND STA-QMS STUDY OF WATER INTERCALATION INTO LAYERED PEROVSKITE-TYPE NIOBATES

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The intensive investigation of photocatalytic properties of layered oxides is explained by the combination of their semiconducting properties with the ability to intercalate water. Water intercalation (reversible process of water molecules introduction into the interlayer space) is regarded as one of the factors influencing the photocatalytic activity. Therefore, modification of intercalation properties of complex oxides by varying their chemical composition opens possibilities to improve their photocatalytic properties.

The aim of this work was to study the intercalation process of water molecules into the structure of layered photocatalysts  $\text{ANdNb}_2\text{O}_7$  (A = H, Li, Na, K, Rb, Cs).

As a result, the perovskite-type niobates  $\text{ANdNb}_2\text{O}_7$  were synthesized by ceramic technique (A = Rb, Cs), by ion-exchange in a melt of alkali metal nitrates (A = Li, Na, K) and by ion exchange in acidic solution (A = H).

The presence of intercalated water in the interlayer space was found only in the structure of oxides with sodium cations and protons. XRD and TGA showed the existence of stable intercalated forms  $\text{HNdNb}_2\text{O}_7 \times 0.89 \text{H}_2\text{O}$  and  $\text{NaNdNb}_2\text{O}_7 \times 1.27 \text{H}_2\text{O}$  compounds in different temperature ranges and determined the content of water. The method of simultaneous thermal analysis (TGA + DSC) combined with mass-spectrometric analysis of the gas phase served as evidence that the weight loss under heating is caused by water liberation (Figure).

Photocatalytic activity of  $\text{ANdNb}_2\text{O}_7$  was measured for photoinduced hydrogen evolution from aqueous isopropyl alcohol solution under UV-irradiation. It was found to be strongly dependant on the cationic composition, the rubidium-containing oxide  $\text{RbNdNb}_2\text{O}_7$  being the most active.

Scientific research were performed at the Center for X-ray Diffraction Methods and the Center for Thermogravimetric and Calorimetric of Research park of St.Petersburg State University.

This work has been supported by the Russian Foundation for Basic Research (Grant No. 15-03-05981) and Saint Petersburg State University (Grant No. 12.38.257.2014).

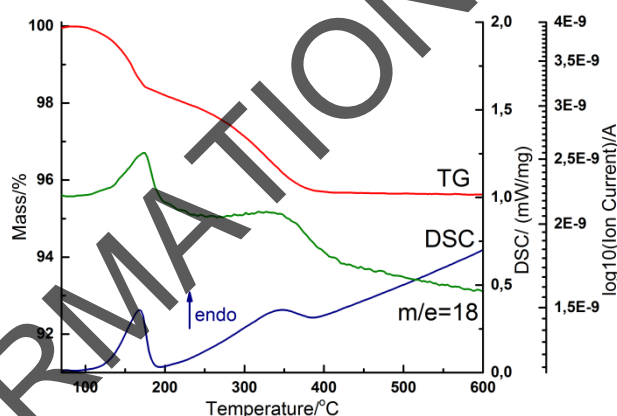


Figure: STA of  $\text{NaNdNb}_2\text{O}_7 \times 1.27 \text{H}_2\text{O}$ .

## Section 5. Applied aspects of chemical thermodynamics

### THE INFLUENCE OF PROCESS VARIABLES IN THE CNTs SYNTHESIS

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The potential use of Carbon Nanotubes (CNTs) in several applications leads to develop different methods to improve their yield and to decrease their cost production. The method of choice to mass production of CNTs is the Chemical Vapor Deposition (CVD) due to their low cost [1]. The principal process variables that affect the length and diameter of the CNTs are the temperature, vapor pressure and the catalyst support [1]. In this study, the analyses were performed varying the temperature in the reaction zone, the argon flow and the organometallic precursor.

A CVD reactor was used with two modifications, the first consist in a quartz tube with 0.02 m diameter and 0.8 m length dimensions and two electric furnaces. The second only used one furnace and decrease the length of the quartz tube to 0.6 m. The organic precursors were ferrocene and benzene and for the case of the reactor modification, instead the ferrocene, an AISI 304 stainless steel concentric core was inserted inside the quartz tube. A constant flow of argon, in the range of 50 and 100 ml/min, was used as gas carrier. The temperatures in the reaction zone were 750, 800 and 900 °C. The reaction time was 1 hr.

The results were analyzed with a JEOL-JSM-5910LV scanning electron microscope for the morphology, and with a Raman Thermo Scientific spectrometer.

The SEM shows that the CNTs with higher lengths were at 800°C (110 µm), however the minor diameters were found at 750°C (55 nm). The argon flow affected the CNTs length, obtaining the higher values with 80 ml/min. The nanotubes obtained with the stainless steel core, had similar characteristics, the major variation was the growth form; the ones with an organometallic precursor were parallel formed in a base, in contrast with the scattered formation of the other CNTs [2].

The Raman analysis showed that the CNTs obtained in the reactor with a stainless steel tube had more defects, nevertheless, the broad of the G band in all the samples suggest similar diameters with the same temperature and flow conditions.

Different process variables analysis showed the temperature and flow to obtain CNTs with high length and small diameter. The organometallic precursor in a CVD process of CNTs synthesis can be replaced by a catalyst support of stainless steel.

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*This investigation was supported by the project of Scientific Research Council of Michoacan University of Saint Nicholas de Hidalgo (Morelia, Mexico) and PRODEP (SEP) Mexico.*

### CFD VALIDATION MODELING OF CNTs SYNTHESIS BY CVD

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E. Huipe Nava<sup>1</sup>, Ma. de L. Mondragon Sanchez<sup>2</sup>

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The Carbon Nanotubes (CNTs) has been researched due to their unique properties and potential applications. The chemical vapor deposition (CVD) is a flexible and economical production method to synthesize CNTs [1]. The Computational Fluid Dynamics (CFD) is useful to study flow dynamics and heat transfer. This investigation showed that CNTs synthesis can be simulated by CFD and the conditions of process can be optimized by this way.

The synthesis of CNTs was in an experimental CVD reactor, with two furnaces, using [2] as reference. A quartz tube with 0.02 m diameter and 0.8 m length dimensions were used. The organic precursors were ferrocene and benzene. Two different (50 and 80 ml/min) argon flows were constant in the experiments as gas carrier. The temperatures in the reaction zone were 850 and 900 °C. The reaction time was 1 hr.

The CFD were performed in the Ansys Fluent Inc 14 software, to obtain the deposition rate inside the quartz tube surface. In this simulation were obtained velocity profiles, turbulence and concentrations of benzene, and the temperatures distribution.

The ferrocene decomposes in the reaction zone forming catalytic particles where the CNTs start its growth; in this area, the benzene pyrolysis allows to deposit carbon to form the CNTs. The simulation model was prepared to consider only the carbon deposition by the benzene on a homogeneous surface.

The simulation results showed that the deposition shouldn't occurred in the first furnace with low temperature (90 °C). Moreover with both high reaction temperatures, the results suggested the highest deposition is in the second furnace inlet, subsequently decreasing to the end of the tube.

The experimental results substantiate the deposition areas, because the largest amount started to deposit in the reaction zone inlet [3]. Also, the results of samples weight obtained by simulation and experimentation were similar with less than 10% variance.

The CFD can be used as a technic to forecast the CNTs deposition area, and the sample weight in a CVD reactor. The data obtained is useful for future work, looking for better synthesis conditions.

[1] Kumar, M.; Ando, Y. *Journal of Nanoscience and Nanotechnology*, 2010, 10, 3739-3758.

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[3] Gomez Sanchez, A.; Domratcheva Lvova, L.; Lopez Garza, V.; Roman Doval, R; Mondragon Sanchez, M. de L. *Materials Research Society Proceedings*, 2012, 1479, 111-116.

*This investigation was supported by the project of Scientific Research Council of Michoacan University of Saint Nicholas de Hidalgo (Morelia, Mexico) and PRODEP (SEP) Mexico.*

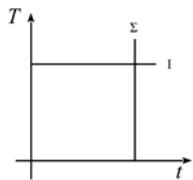
## Section 5. Applied aspects of chemical thermodynamics

### DISCRETE BASIS OF CHEMICAL THERMODYNAMICS PROJECT OF STRUCTURES

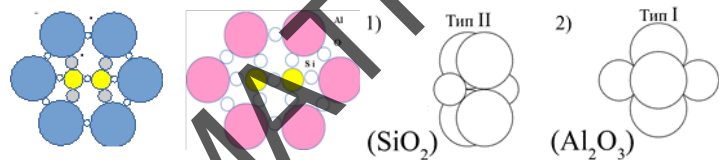
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Non-locality thermodynamics solution by oriented on structural analysis, the presence of a discrete database: this topology two normalization conditions, on *figure 1* their intersection point of the set - discrete volume resulting isothermal discrete scanning – (A,W)IDS; the operator identity to the *ch*-analysis - the chemical-*ch* potential  $\mu$ ; entropy  $S$  - analogue structure. Getting projections solved as a problem of material science analysis. Change properties  $C^e = C^e(C^T, C^c)$  is a  $dC^e = (\partial C^e / \partial C^T)_{C^c} dC^T + (\partial C^e / \partial C^c)_{C^T} dC^c$ , where  $C^e, C^T, C^c$  — property, structure, *ch*-composition - the classes of relevant separate topologies *FCA*. Structure and *ch*-composition respectively to the properties of function  $f$  separately:  $(C^T f_T C^B)$  and  $(C^c f_c C^e)$  [1].



**Figure 1:** The normalization conditions and point the element volume.



**Figure 2:** Starting projection of mullite phase contact zone.

$T_{MA}$  metric (9) applies to the chemical composition on  $f_c$  acts  $VN$  distinction. If the volume at a given point there is no necessary set of atoms assembly structure does not take place. The cell is calculated according to the formulas volume *min* inhomogeneity  $Vn_i, \sum Vn_i$  is homogeneity [1,2]. Its edge over a single atom in a chemical compound to  $\rho$ - $T$  section, *A*-IDS, then the rate of dissolution time enables homogenizing on section  $\rho$ - $t$ , *W*-IDS [1,2]. The sum over  $n_i$  converging to unity  $C^c(\phi_i) = n_i m_i + n_{i-1} m_{i-1} + \dots + 3 m_i + 2 m_{i+1} + 1 m_i = VN$  (1), where  $i$  is the atomic number of the Periodic System *PSM*,  $n_i$  - number,  $m_i$  - molecular weight. Balance -  $C^c(i_\phi)$  (5) for the full amount of  $V = V\phi_i + Vi_\phi$ .

It satisfy the conditions 3 and 4; if original volume  $V = const$  and  $V_i$  of its form, then change  $\{\sum \Delta V_i = 0, \sum V_i + V_{gas} = V\}$  (3), on the diagram is the particle distribution function  $f(n_i, r_i)$  or volumes. Phase compatible if the volume change their joint activity leads to a constant value in accordance with the chemical potential realization at bound areas zone [1]. The contact surface is maximal if  $L_i = n_i r_i$  length  $L = \sum L_i$ , outer and inner surfaces are  $\{L^2_h = L^2_e\}$  (4) the neutralization of internal borders, if not (3) - a form of deformed or separated.

The expressions for the grid/structures and contact zones show diagrams *IDS PSM* elements, their oxides, further compounds. The first type - the conditions of existence of the constituent elements of  $C^c = const$  (pico-, nano-, micro-).

The second type - the numerical relationship of different ways of defining properties. The third type - the coexistence of phases. A single type of registration chart states and transitions  $T_{MA}, \rho(T), \sigma(T)$ , horizontal – transformation,  $\{1\}$ , vertical – state,  $\{\Sigma\}$ , figure 1. [1,2].

Septenary cells allows them to summarize the entire volume of matter of the degeneration states in relation to the environment consistently from the contour to the inner part of it. *Figure 2*. Metric volume is determined only atoms circuit (they active and first interaction), from them draw seven vertical lines. Inside the silicon (two atoms) structures in time before it is spaced relative to the axis  $t$  significantly area *Al* and *Si* to *IDS* are in contact. The oxygen atoms are identical circuit, but only three internal oxygen atoms. Further heating will deform all identical and contour. Oxygen may be larger moving to the edge out of the gap, type I and II.

[1] Doroshko, G.P. Introduction to temperature analysis of material properties. 2007. - 396s.

PHASES AND EXTRACTION EQUILIBRIA  
IN SALT AMMONIUM – OXYPHOS B – WATER SYSTEMS

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Micellar extraction or cloud point extraction is one of perspective methods of trace concentration of contamination in environmental objects analysis. The method allows to exclude toxic and fire-hazardous solvents and to obtain soluble in water extract. For these purposes, non-ionic surfactants such as Triton, Brij, PONPE, are generally used, however, the ionic surfactant may be phase-formation and complexing agents due to availability complementary functional groups. For example, anionic surfactants – Oxyphos B ( $[C_nH_{2n+1}O(C_2H_4O)_m]_2POO^-$ ,  $n = 8-10$ ,  $m = 6$ ). Introduction of inorganic salts or acids can significantly reduce cloud point temperature of surfactant solution, which allows using surfactants with highly hydrophilic and dissociating groups for extraction.

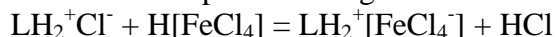
The solubility in sulfate (chloride, nitrate) ammonium – Oxyphos B – water systems in wide temperature range was investigated by visual-polythermal method. All studied systems are characterized by LCST (lower critical point of stratification), which temperature increases in the series  $(NH_4)_2SO_4 > NH_4NO_3 > NH_4Cl$ . Systems containing  $NH_4NO_3$  and  $NH_4Cl$  have stratifying area adjacent to binary system salt-water near apex of water. Sharp (anomalous) decrease in cloud point temperature is accompanied by break curve temperature from the component concentrations.

For exclusion possible interaction of introduced salt with Oxyphos B on salting-out effect potassium sulfate (chloride, nitrate) – Oxyphos B – water systems solubility was studied. Stratification area has the same topology for all salting-out agents. Anomalous effects decrease cloud point temperature in presence of potassium salt expressed lesser than ammonium salts. Descending anomalous decrease of cloud point temperature anions may be arranged in series (irrespective of the cations):  $NO_3^- > Cl^- > SO_4^{2-}$ .

Extraction of number metals in  $NH_4Cl$  – Oxyphos B – water – HCl ( $H_2SO_4$ ) systems at  $75^\circ C$  was studied. Multicharged cations ( $La^{3+}$ ,  $Y^{3+}$ ,  $Fe^{3+}$ , etc.) are extracted by cation-exchange mechanism with formation of insoluble compounds:



Increasing acidity leads to change on mechanism from anion-exchange with protonated form of Oxyphos B. In this cause extraction curve passes through minimum:



Scandium and zirconium form are the most stable chemical compounds with Oxyphos B.  $Zr^{4+}$  are quantitatively extracted into surfactant-rich phase as precipitate, in the presence of  $Sc^{3+}$  stratification are not observed. In the case of doubly charged cations extraction occurs only on anion exchange mechanism.

The distribution of number of organic dyes and their complexes with metals was studied in  $NH_4Cl$  – Oxyphos B – water system at  $75^\circ C$ . Complexes cobalt with PAN and ditizone, passing in surfactant-rich phase quantitatively and which have high color contrast have the greatest interest.

As a result, possibility of application of Oxyphos B as phase-formation agent in micellar extraction method and extractant for number of metals and hydrophilic compounds was shown.

*The work was supported by the Russian Foundation for Basic Research (Grant No. 14-03-96006-r-ural-a).*



## Section 5. Applied aspects of chemical thermodynamics

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### RESEARCH OF POLYMER DESTRUCTION FEATURES USING OF THERMAL ANALYSIS METHODS

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This research represents detailed studying of thermal decomposition processes polymers with use of thermal analysis methods.

Thermal destruction is a process of macromolecules breakdown or release of side chain under the heat influence. Polymer's phase transformations proceed in wide temperature range, as a result the thermal effects of these transformations are weak and difficult detectable. Structural and conformational inhomogeneity of polymers determines thermal dissimilarity of chemically identical reactive groups. These features determine methodical difficulty in providing thermoanalytical experiment and interpretation of received results. Agarwal and Lattimer [1] investigated the gravimetric and energetic behavior of decomposing polymer sample. The standard heat of decomposition of samples is proved to be a constant quantity, independent on the heating rate or the initial mass of the sample. Thus, the standard heat of decomposition is unique energetic property of a sample and can be used for identification of polymer of polymer type.

Regarding the mechanism of dissolution polymers are tentative divide into two types: completely decomposing and destructing with solid residue. These residues can be carbonaceous (char) or originating from other elements contained in the initial sample. Under thermal destruction of these materials the volatiles products must pass through the char to reach the surface. During this process the hot char may cause the occurring of secondary reactions in the volatiles. Owing to carbonaceous chars considerably delayed further thermal decomposition. [2-4]

Poly-methyl methacrylate (PMMA) was selected to represent non-charring materials and poly-vinyl chloride (PVC) was selected to represent charring materials. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used in this research. Analysis was carried out with using simultaneous thermoanalyzer Sestys evo manufactured of SETARAM Instrumentation (France). Interaction between structure and chemical composition of polymer's molecules and their influence on process of thermal decomposition was determined. As well as, the methodical work was carried out to analyze the effect of experimental factors (heating rate, initial mass of sample, atmosphere in furnace chamber, crucible material, etc.) on temperature and heat properties of investigated samples. Mechanisms of thermal decomposition were discussed. Technique of using thermal analysis methods for research of thermal decomposition processes of wide classes polymers was suggested.

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**THERMODYNAMIC CHARACTERIZATION OF THE FORMATION PROCESSES FOR COPPER CARBONATES FROM SULPHIDE AND OXIDE MINERALS**

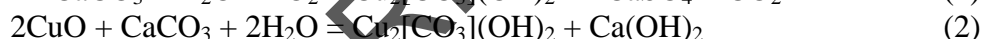
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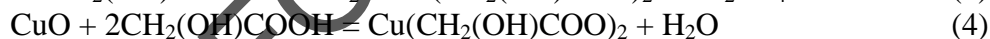
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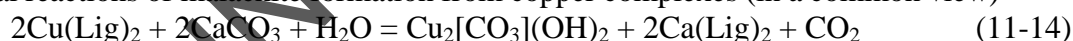
Natural malachite is a valuable decorative and ornamental stone, and also important ore of copper, especially in a zone of the copper field oxidation. For studying thermodynamics of malachite formation reactions a number of thermodynamic calculations of changes of enthalpy, entropy and Gibbs energy of reaction at 273-373 K with participation of complexing agents has been carried out. As a source of copper ions the sulfidic and oxidized minerals were investigated. Under natural conditions the most widespread geochemical complexing substances are humic and fulvic acids. In the work we made thermodynamic estimation of malachite formation probability with participation of primary structural fragments of humus acids such as the simplest  $\alpha$ -hydroxy and  $\alpha$ -amino acids. The following reactions were considered: without complexants



with complexants (in salt forms to neutralize formed acid in reactions with sulfide minerals)



and analogical reactions with participation of Na-lactate (5,6), K-glycinate (7,8) and Ca-alanate (9,10) and final reactions of malachite formation from copper complexes (in a common view)



with participation of glycolates (11), lactates (12), glycines (13) and alanates (14).

The results of the calculations at standard temperature are shown in Table.

**Table.** Thermodynamic functions of the reactions at 298.15 K.

Reaction	$\Delta_r H^\circ(298)$ (kJ/mol)	$\Delta_r S^\circ(298)$ (J/(mol·K))	$\Delta_r G^\circ(298)$ (kJ/mol)	Reaction	$\Delta_r H^\circ(298)$ (kJ/mol)	$\Delta_r S^\circ(298)$ (J/(mol·K))	$\Delta_r G^\circ(298)$ (kJ/mol)
1	-1476.425	-702.328	-1270.538	8	-32.738	-47.463	-18.824
2	50.01	-47.502	64.173	9	-857.51	-490.413	-713.746
3	-815.154	-558.848	-651.327	10	-21.558	-28.425	-13.225
4	-94.366	-228.082	-27.503	11	73.74	293.203	-12.212
5	-810.362	-552.794	-648.311	12	71.899	291.531	-13.563
6	-92.462	-232.806	-24.215	13	196.332	247.18	123.871
7	-843.378	-438.542	-714.819	14	186.457	222.075	121.356

The reactions with participation of copper sulfide are characterized with high values of parameters at direct malachite formation and reactions with intermediate formation of copper complexes. It is seen that complexants promote the transition of oxidized copper into solution. The malachite precipitation from copper complexes with hydroxy acids is thermodynamically probable. The reactions with participation of amino acids have positive magnitudes of Gibbs energy change; nevertheless, it can be marked some tendency to decrease the value at increasing of carbon chain.

## Section 5. Applied aspects of chemical thermodynamics

### THERMODYNAMIC MODELLING OF INTERACTION Ti, Cu AND NITROGEN WITH SiO<sub>2</sub> FOR OPTIMIZATION OF FORMATION CONDITIONS OF NANOCOMPOSITE TiN-Cu ON QUARTZ

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Widely applied in mechanical engineering and metal working the TiN films are characterized by high values of hardness and low factors of a friction. But during too time these films are characterized by considerable fragility which sharply narrows area of their application. For this reason, special interest is called by researches connected with working out of new technologies of reception of composite films with good plasticity and high microhardness. In this work the new formed hybrid technology of composite films in vacuum installation, on a principle of the co-ordinate action vacuum arc and magnetron (planar configuration) categories is offered. In the report the model of layers nanocomposite TiN-Cu layers formation on surface fused quartz SiO<sub>2</sub> is discussed.

Modeling carried out in 2 stages.

At the first stage counted speeds of sedimentation of a film by magnetron material sputtering (Cu) from the ring evaporator and speed of formation at ion-plasma evaporation (Ti). The factor of sputtering and sputtering speed of a target material in the beginning are count. Then it spent construction of a planimetric plotting of thickness distribution films depending on radius of a plate and distance to the evaporator. After that counted distribution of a thickness of the raised dust film on a plate and non-uniformity of this distribution, optimized position of substrate holder with a plate concerning a target and a formation condition nanocomposite Ti-Cu, in particular, composition nitrogen and argon in a gas mix.

At the second stage thermodynamically modeled interaction of nitride TiN, copper with silicon dioxide SiO<sub>2</sub>. For these purposes used multi-purpose complex TERRA. It varied temperature in the range from 273 to 1573 K and pressure from 10<sup>5</sup> to 10<sup>-3</sup> Pa. Possible interactions with participation Ti, Cu, N<sub>2</sub> and SiO<sub>2</sub> are investigated. The special attention is given research phase equilibrium and to revealing of sequence of phase parities and crystallization fields exist phases in system Ti-N<sub>2</sub>-Si-O<sub>2</sub>. In calculations considered following phases: nitrides TiN and Si<sub>3</sub>N<sub>4</sub>, oxides SiO<sub>2</sub>, TiO<sub>2</sub>, Ti<sub>2</sub>O<sub>3</sub>, Ti<sub>4</sub>O<sub>7</sub>, Ti<sub>3</sub>O<sub>5</sub>, TiO and silicides TiSi and Ti<sub>5</sub>Si<sub>3</sub>.

In the report features phase equilibrium in the conditions of high vacuum (10<sup>-2</sup>-10<sup>-4</sup> Pa) in ternary systems are considered: Ti-N<sub>2</sub>-Si, Ti-Si-O<sub>2</sub>, Ti-N<sub>2</sub>-O<sub>2</sub> and Ti-N<sub>2</sub>-Si.

It is shown, that system TiN-SiO<sub>2</sub> characterizing interaction of a layer of nitride TiN with a material of substrate SiO<sub>2</sub>, is a cut in concentration tetrahedron Ti-N<sub>2</sub>-Si-O<sub>2</sub>. The sequence of phase transformations TiN-TiO-Ti<sub>2</sub>O<sub>3</sub>-Ti<sub>3</sub>O<sub>5</sub>-Ti<sub>4</sub>O<sub>7</sub>-TiO<sub>2</sub> in the range of temperatures 1150-1275-1300-1425 K is established at pressure P=10<sup>-3</sup> the Pa. As interaction products occurrence various the titan oxides is possible. There upon fields of crystallization are revealed and established cuts in ternary systems Ti-TiN-O<sub>2</sub>, TiN-Si-O<sub>2</sub>.

Optimum conditions for nanocomposite formation TiN-Cu on surface quartz (SiO<sub>2</sub>) are defined.

THERMOMECHANICAL PROPERTIES OF THE CORUNDUM-REINFORCED  
PORCELAIN BASED ON GEOPOLYMER BODY

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In this paper, corundum porcelain ceramics with low thermal expansion were developed from geopolymer body by the enhanced heat treatment procedures. For preparation of green body, corundum, metakaolin and potassium silicate solution was used formed by vibro-casting method. Granulometry of the system was designed according to the maximum density gradation with granular exponent 0.27 - 0.32 and maximum grain size of corundum particles 0.3 mm. The effect of high temperature treatment in gas kiln with variable atmosphere (oxidized, reduced and neutral) was also discussed.

The microstructure and phase composition, related to the mechanical properties, were systematically investigated by SEM and XRD. In addition, the physical properties (water adsorption, apparent porosity, bulk density, flexure strength) of glass-ceramic material (green and fired body) are measured and discussed. The mathematical approach for inorganic oxide glasses was used according to Appen, Gan Fuxi and Demkina [1-3] to calculation of structural stress between corundum and glass-ceramic phase. The cooling process of glass phase was completely calculated according to Schill [4]. Finally, the flexural strength of fired material (geoporcelain) and dry green body resulted in 70 MPa and 22 MPa, respectively.

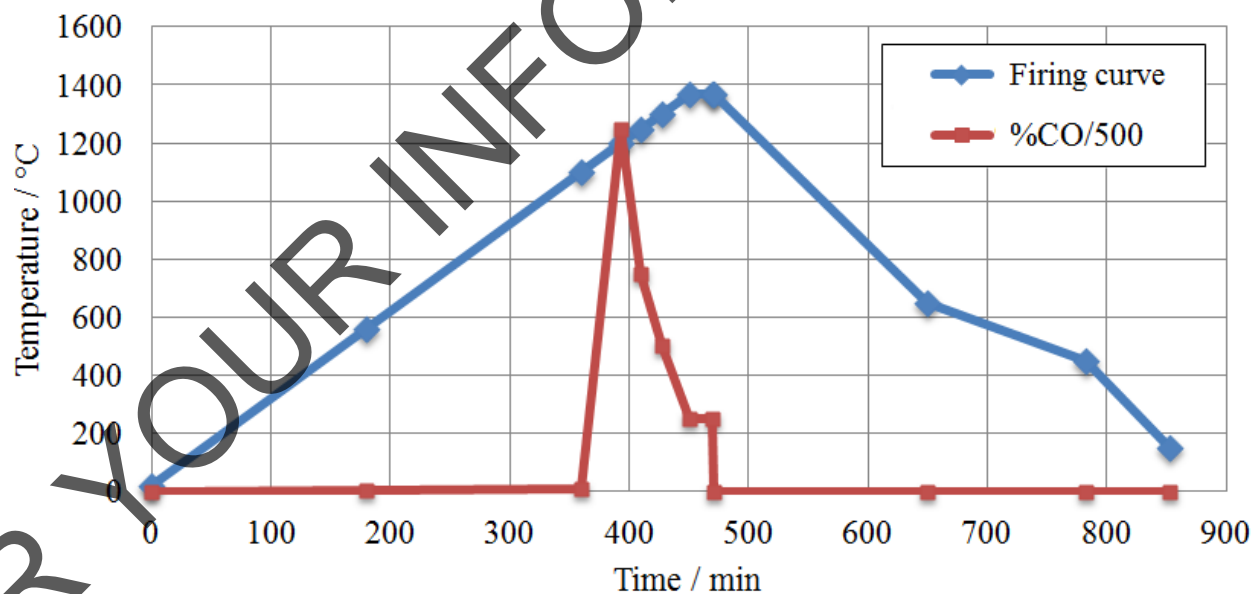


Figure: Geoporcelain firing curve and kiln atmosphere conditions.

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## Section 5. Applied aspects of chemical thermodynamics

### THERMODYNAMICS OF ALKYLATION OF PHENOL WITH HIGH BRANCHED OLEFINS

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High branched alkylphenols (HBAPh) are technically important agents. They are widely used in such industries as from polymeric, general rubber, cosmetic, oil-producing industries to the production of surface-active agents, additive compounds for oil and fuel, polymer stabilizers, medicines and many other substances. With that the properties of end product are determined by a shielding degree of OH-group and/or size and structure of alkyl-substitute in APh molecules.

Currently we know a lot about role and significance of thermodynamics in producing of individual shielding and non-shielding low APh. In many cases we are able to control the process of their selective preparation. But we are not able to control the basics of the process with the use of HBAPh, which has high reactivity and, thereby, it causes a lot of trouble when interpreting the experimental data, forecasting the HBAPh properties and developing the effective technology of its preparation, conversion and the following technical application. The set of studies we carry out in this field of knowledge covers a wide range of issues.

The present article is fully concerned with the equilibrium of reactions proceeding at liquid-phase alkylation of phenol with high branched olefines (C<sub>5</sub>, C<sub>6</sub>, C<sub>8</sub> and C<sub>9</sub>) in the presence of mineral acids and perspective type of strong-acid cation resin (SACR). The temperature range of research is limited by technical capabilities of the used catalysts.

As a result of the research the following is established:

- When the equilibrium is achieved, the alkylphenol ethers are completely isomerized in HBAPh.
- Increase of olefin concentration in base mixture causes side transformations with formation of oligomer and di-alkylphenols
- The prevalence of para-tertiary structures over orto-tertiary ones is typical for all HBAPh in equilibrium
- Orto-secondary APh prevails over para-secondary one in equilibrium system of hexilphenols.
- The increase of process temperature promotes decrease of equilibrium constant in reactions  $o\text{-tert-APh} \leftrightarrow p\text{-tert-APh}$ ,  $di\text{-APh} + Ph \leftrightarrow p\text{-APh} + o\text{-APh}$ , and also promotes disintegration of the alkyl-substitute.

On the base of experimental constants of liquid-phase equilibrium for the independent reactions describing equilibrium of any system in the whole, the enthalpy and entropy effects of the proceeding transformations were determined, compositions of equilibrium compounds as a function of temperature and ratio of reagents were calculated, and the recommendations for realization of the processes focused on receiving specific products in the equilibrium conditions were given.

The experiment results were based upon when forecasting methods of the alkylphenols thermodynamic properties were modified.

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## COMPLEXATION OF RARE EARTH NITRATES WITH DI-(2-ETHYLHEXYL)-PHOSPHORIC ACID IN *O*-XYLENE

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Solvent extraction is most common and effective method for the separation a mixture of lanthanides. The different alkyl phosphoric acids are recommended for separation rare earth elements (REE) from each other within the groups of light, middle or hard elements. One of them is di-(2-ethylhexyl)-phosphoric acid (D2EHPA), which is characterized by high coefficients of separation, does not require a salting-out agent and additional complexing agents. The synthesis of this extractant is cheap, the losses during the extraction are small [1-3]. Because of high viscosity D2EHPA is always used with diluents. The degree of D2EHPA dissociation, the composition of organic complexes formed during extraction, coefficients of separation and distribution of the REE depend on the nature of the diluent.

The purpose of this work is to study the complexation of rare earth nitrates with D2EHPA in *o*-xylene. In this work a set of experimental data required for constructing a thermodynamic model ( $G(T, p, x)$ ) of the liquid phase system  $H_2O - HNO_3 - Ln(NO_3)_3 - o-C_8H_{10} - C_{16}H_{35}O_4P$  ( $Ln =$  light REE) was obtained. Density of solutions and REE distribution coefficient at different temperatures and various composition of mixed solvent and the ratio components were measured. The composition of complex  $Ln^{3+}$  with D2EHPA was determined by  $^{31}P$  NMR.

We can conclude that the mechanism of complexation depends not only on the pH of solution, but also on the concentration of REE and extractant. After measuring densities of initial solutions, aqueous and organic phase after extraction we found density of organic phase changes not linearly with the concentration and temperature (from 15 to 50 °C) of the light REE. Unlike the bulk properties, the REE distribution coefficients do not change with increasing of temperature in the range of 25-50 °C.

The activity coefficients of REE nitrates in nitric acid solutions were estimated by Zdanovsky' rule. The effective and real thermodynamic constants of complexation reactions light REE with D2EHPA in a mixture of water and *o*-xylene at room temperature were calculated.

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## Section 5. Applied aspects of chemical thermodynamics

### FEATURE OF CHEMICAL ACTION OF INTERNAL STRAIN AT THE DIRECT NITROGEN OXIDATION

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Action of internal attraction and repulsion forces leads to total uniform strain of the substance. Alternation of compression and tension appears as an effect of reversing the pressure sign of metastable liquids and crystals. Combination of tension and compression was tested in experiments on interaction of compressed liquid and both tensed and compressed facets of the crystal [1]. The authors do not know studies of mass equilibrium under combined total uniform tension and compression, and the action of internal forces of attraction and repulsion in the substance is for the first time presented as a stable equilibrium of the examined medium under combining  $p_1 = -p_2$  total uniform tension and compression.

Chemical actions of tension and compression forces are compared by effect of reversing sign of the Gibbs' energy change  $\Delta G_{\text{peak}} = \Delta H_{\text{peak}} - T\Delta S_{\text{peak}}$  of supposed chemical reaction: if the sign is positive, the term  $\Delta G_{\text{peak}}$  changes the sign during the transition  $p_1 = -p_2$  due to  $\Delta H_1 = -\Delta H_2$  and  $\Delta S_1 = -\Delta S_2$ , and components of the medium are getting chemical active.

Nitrogen and oxygen are chemically neutral in the standard state, so that the change of the Gibbs' energy  $\Delta G_{\text{peak}}$  of the chemical reaction  $1/2\text{N}_2 + \text{O}_2 \rightarrow \text{NO}_2$  at  $p = 1$  bar and  $T = 298,15$  K is positive and equal 52,29 kJ/mole. The thermodynamic equilibrium constant  $K_a$  of the components in the given reaction may be calculated from the equation  $\Delta G_{\text{peak}} = -RT \ln K_a$ . Its values are  $1.45 \times 10^9$  for extended medium, and  $6.88 \times 10^{-10}$  for the compressed medium. Their ratio  $2.1 \times 10^{18}$  allows hoping for success of chemical air activation and achieving commercial effect in the industrial atmospheric direct nitrogen oxidation because its reserves are  $\tau \sim 10^{16}$  t, and there is no requires of production, transportation, and storage.

Technological accessibility of stable states  $p_1 = -p_2$  is reducing to achieving minimal internal energy of the medium up the Boil temperature, while down the critical and Boil temperature the states  $p_1 = p_2$  are stable. Then the minimal internal energy of mixing nitrogen and oxygen is achievable by isothermal throttling without liquefaction up 406 K at the initial maximal pressure no more than 310 bar. The thermodynamic equilibrium of the medium in the state  $p = p_1 + p_2 = 0$  is possible only under their unchangeable mass ratio. Then the nitrogen oxides excluding allows achieving continuous direct nitrogen oxidation by throttling.

The higher pressures and temperatures in comparison with pressure and temperature necessary for isothermal throttling can also change the sign of  $\Delta G$  for direct nitrogen oxidation, but this way is not commercially profitable: 5%  $\text{NO}_2$  output was achieved at 3000 K. Catalytical direct nitrogen oxidation as well as direct nitrogen oxidation in gas discharge and under explosion had also not achieved technological advantages [2]. Hopefully, the isothermal air throttling without mixture liquefaction proposed in this abstract will allow realizing commercially profitable direct nitrogen oxidation and making the row material base of chemical technology with the ammonia synthesis and the oil and alkane cracking during throttling process also.

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## HIGH-PERFORMANCE BIMETAL/POLYMER ELECTRODES WITH PLATINUM METAL NANOPARTICLES

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Polymer electrolyte membrane fuel cells (PEMFC), which transform fuel chemical energy directly into electricity, have attracted much attention during the last decade, due to the growing interest in the generation of renewable energy for application in stationary and portable devices [1-5]. PEMFC are promising systems to deliver renewable energy because of their low environmental impact when supplied with hydrogen-containing fuels, such as methanol, ethanol, added to the capacity of producing high energy densities [1-5].

Synthesis of bimetallic nanoparticles (NPs) with controlled size, shape, and composition is key to the development of advanced nanocatalysts for chemical power sources (CPS). Platinum-ruthenium (Pt-Ru) and platinum-palladium (Pt-Pd) catalysts are generally regarded as the most popular electrode materials for the electrooxidation of the alcohols and reformat gas such as CO-contaminated H<sub>2</sub> in polymer electrolyte fuel cells [1,4,5]. Because catalysis is a surface effect, the catalyst needs to have the highest possible surface area, so Pt-Ru and Pt-Pd catalysts are commonly used in the form of both unsupported and supported nanoparticles.

One of the main directions of catalytically active, stable and inexpensive catalysts formation for the CPS is the development of nanostructured metals in polymer matrices [1-5]. Proton-exchange perfluorinated polymers with ionogenic sulfo groups (-SO<sub>3</sub>H) of the Nafion type are widely used as solid polymer membrane. In general, Nafion<sup>®</sup> membranes modified by platinum-based mono- and bimetallic catalysts reduce the fuel crossover phenomenon and also allow a self-humidifying condition of the CPS, leading to a high operation temperature with a consequently faster fuel (H<sub>2</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, HCOOH, etc.) oxidation kinetic [2,3,5].

The purpose of research is formation of high active and stable nano-membrane materials with bimetallic platinum metal nanoparticles (Pt-Ru, Pt-Pd) for CPS of new generation with high operating characteristics. Polymer nanocomposites synthesis was carried out by chemical reduction of platinum metal ions in water-organic solutions with ultrasonic treatment. By varying the synthesis conditions one can control the nanoparticles size, content and emerging properties. By means of the electron microscopy, phase analysis, cyclic voltammetry, small-angle x-ray scattering methods it was performed the investigation of nanocomposite functional properties. The obtained bimetal/polymer electrodes containing nanoparticles of different composition, size and shape, can be used as functional membrane-electrode materials for high-performance electrochemical fuel conversion of chemical energy sources.

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### INTERNAL DIAGONALS PROBLEM IN POLYHEDRATION OF RECIPROCAL SYSTEMS

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The algorithm for topological correction of lists of simplexes of different dimensions (TCLSDD) was used for analyzing the published methods for determining internal diagonals in polyhedration of reciprocal systems [1, 2]. Each such diagonal emerges if a stoichiometric compound participates in the polyhedration. Diagonals may compete, which results in several variants of polyhedration. Then, of these variants, the most stable in energy should be selected. TCLSDD algorithm is based on checking all the possible (allowed) combinations of 1D, 2D, and 3D simplexes. The end result of polyhedration should satisfy the formulas relating the numbers of graph vertices and links between them with the numbers of 1D (internal diagonals), 2D (secant planes), and 3D (tetrahedra) simplexes.

For a quaternary reciprocal system, these quantities are related by the expressions [3]:  $L = 3 + 2V_E + 3V_F$ ,  $S_E = 8 + 2V_E + 2V_F$ ,  $S_I = 2 + V_E + V_F - 2V_I + 2L_I$ ,  $T = 3 + V_E + V_F - V_I + L_I$ . Here,  $V_E$ ,  $V_F$ , and  $V_I$  are the numbers of binary, ternary, and quaternary compounds, respectively, which are represented by points on edges and faces of the polyhedron and inside it, respectively;  $L_E$ ,  $L_F$ , and  $L_I$  are the numbers of edges (or their fragments - binary systems without compounds), diagonals on faces, and internal diagonals, respectively;  $S_F$  and  $S_I$  are the numbers of 2D simplexes (triangles) on faces and inside the prism, respectively; and  $T$  is the number of 3D simplexes (tetrahedra).

Because the initial prism of a quaternary reciprocal system has 9 edges and 5 faces (2 triangles and 3 squares), the edges are partitioned by  $V_E$  points into  $L_E = 9 + V_E$  fragments. A quaternary reciprocal system represented as a graph with  $V$  vertices is described by diagonal adjacency matrix  $R$  of dimension  $V \times V$ . The number of nondiagonal elements  $r_{i,j}$  ( $i < j$ ) is  $(V^2 - V)/2$ . The presence of a link between two graph vertices is represented by unity; the absence, by zero; and an unknown link (i.e., a possible internal diagonal), by the question mark ?. From combinations of all the nonzero elements ( $r_{i,j} = 1$  or  $r_{i,j} = ?$ ), taken three or four at a time, the contours of 2D triangular simplexes and 3D tetrahedral simplexes are formed. Further, they are distributed in groups, depending on whether the formation of a given simplex is participated by an element  $r_{i,j} = ?$  - a candidate for an internal diagonal ( $S_I^{**}$ ,  $T^{**}$ ) - or not ( $S_I^*$ ,  $T^*$ ). Then the satisfaction of formulas [3] at various  $L_I$  is checked.

If  $S_I^* = 2 + V_E + V_F - 2V_I$  and  $T^* = 3 + V_E + V_F - V_I$  at  $L_I = 0$ , then none of the internal diagonals participates in the polyhedration. If  $S_I^* < 2 + V_E + V_F - 2V_I$  and  $T^* < 3 + V_E + V_F - V_I$ , then  $L_I \neq 0$ , and the polyhedration is participated by unknowns from the graph link boundary (elements  $r_{i,j} = ?$ ). Then the numbers  $S_I$  and  $T$  of internal planes and tetrahedra, respectively, that are necessary for satisfying formulas [3] is taken from the groups  $S_I^{**}$  and  $T^{**}$ .

Such simple manipulations of all the sets of possible internal planes and tetrahedra, first, are obvious and allow one to fully control the entire process of polyhedration from beginning to end, and second, enable one to consider all the combinations of possible internal diagonals and estimate the probability of the participation of each of them in the polyhedration of the system.

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## THERMODYNAMICS OF BARIUM INTERACTION WITH IRON-BASED MELT COMPONENTS

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In numerous laboratory and industrial experiments a positive effect of barium on steel structure and technological properties was observed. Introduction of barium in steel by means of complex alloys is to reduce the size of primary cast grains. In addition, the nonmetallic inclusions become considerably smaller, linear silicate and aluminate structures practically disappear, and the metal's plasticity, impact strength, and cold strength increase. However, practically no barium is observed in nonmetallic inclusions or in metals.

To elucidate the mechanism of barium modifying effect a thermodynamic analysis of the steel refining by barium, aluminum and silicon was performed.

In connection with it we have developed a model of subregular ionic solutions adapted to oxide systems that are stratified at steel production temperatures. The model applicability is verified in analysis of steel deoxidation and modification of nonmetallic inclusions by barium.

On the basis of available experimental, production, and published data, appropriate parameters for the theory of subregular ionic solutions are determined. Component solubility surfaces are plotted for low alloy and carbon steel and also for multicomponent alloys. Calculations have shown that if Ba content is ~0.001 wt % and the aluminum concentration is also ~0.001 wt %, mainly barium aluminate will be in equilibrium with the metal. At lower Ba concentrations, barium hexaaluminate or even corundum may be formed.

Experiments show that, after the introduction of barium in the steel, it is only present in a few inclusions (mainly aluminates). Most of the barium is concentrated in the slag crust at the surface of crucibles and in the aluminate structures at the surface of corundum crucibles; some is found at the ingot surface. Thanks to the surface-active properties of the barium, the size of the nonmetallic inclusions may be reduced and a cluster-free equilibrium structure of the metal may be formed.

On the basis of solubility surfaces of the metal's components with equilibrium oxide phases, a method has been developed for optimizing compositions of added alloys and mixed reducing agents and modifiers, by plotting consumption of highly active elements. These diagrams allow predicting steel refining. The calculations indicate that with small barium consumption, the refining depth is the greatest when the liquid metal is in equilibrium with barium hexaaluminate and corundum.

The proposed thermodynamic analysis provides information regarding influence of temperature on metal deoxidation and modification, and composition of equilibrium oxide phases.

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## Section 5. Applied aspects of chemical thermodynamics

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### THERMAL ANALYSIS AND COMBUSTION CALORIMETRY OF WOOD LIGNIN AND ITS PYROLYSIS PRODUCTS

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Lignin, along with cellulose, is one of the most prevalent natural organic polymer. Lignin is built from phenylpropane structures and their methoxy and hydroxyl derivatives. Content of lignin in wood is about 20-30% of whole mass, what makes it potential source of different organic compounds. Only wastes from pulp and paper mills contain about 50 million tons per year of lignin. 98% of this amount is just burnt without further processing.

In the near future, development in biotechnological methods of vegetable raw materials conversion into biofuel and biopolymers will increase the amount of lignin wastes. It will require effective technologies of lignin processing for different fields of industry. One of non-selective methods of lignin wastes processing into low molecular weight products is a thermochemical conversion, in particular, pyrolysis.

In this study the thermal decomposition of hydrolysis lignin was carried out and studied using thermal analysis techniques in temperature interval from 300°C to 700°C in inert atmosphere. Amounts of solid (coal like), liquid and gaseous products of decomposition were determined. Higher heating value (HHV) of lignin and its products were measured by combustion calorimetry method. It was shown, that solid residue produced from lignin decomposition has larger HHV than other species. Simultaneous thermogravimetry and differential scanning calorimetry technique with mass-spectrometric gas detection was used for studies of heat effects of pyrolysis and its kinetics. It was shown that pyrolysis of lignin and its products is a complicated process which consists of several stages. Start temperatures of pyrolysis process for all three samples were similar, about 320°C. Mass loss of samples increases in the series: solid residue < lignin < liquid fraction. Kinetic parameters of lignin pyrolysis based on the measurements at four heating rates were determined using different model-free methods.

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### MODELING AND ANALYSIS OF MEMBRANE PROCESSES USING NON-EQUILIBRIUM THERMODYNAMICS APPROACH: CASE OF PERVAPORATION

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Pervaporation is a separation process which is based on the selective transport through a membrane. Low down-stream pressure in vacuum mode of pervaporation causes the permeation of substances through membrane material with different rates that leads to the separation of initial liquid mixture. The well-known applications of pervaporation include a dehydration of organic solvents, a recovery of organic substances from water and waste water treatment.

There are various models to describe the mass transport performance in the pervaporation such as Maxwell-Stephan equations, free volume theories, Flory-Huggins and Fick's law. It should be mentioned that various approaches related to the solution – diffusion model usually neglect the coupling fluxes or have a significantly increasing complexity.

Contrary to these models the nonequilibrium thermodynamics approach combines a minimum of complexity with the opportunity to give a clear description of the pervaporation process including the coupling fluxes effect. A calculation model is based on the relationships of linear nonequilibrium thermodynamics (phenomenological equations).

The calculation model, which aligns nonequilibrium thermodynamic, pervaporation data and vapor–liquid equilibrium data, is developed. The approximation of vapor–liquid equilibrium data for feed mixtures was performed by Wilson and NRTL equations. Approbation of proposed approach with the use of different polymeric membranes was carried out for some binary alcohol – water systems. The procedure of kinetic coefficients determination for the equations of nonequilibrium thermodynamics requires several experimental points on pervaporation and relevant VLE data. The compatibility between the experimental pervaporation data and the results of estimation are discussed.

The workability range of concentration for the discussed calculation procedure is depends on the quantity and quality experimental data. In case of wide range concentration systems it was shown that the procedure maintain a good fit ( $R^2 > 0.9$ ) to the experimental data is mainly located in range from 0.01 to 0.8 mol fr.

The results of approximations are discussed in comparison with other calculation methods. We also consider the theoretical base of our method and other models in comparison.

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### THERMODYNAMIC EXERGY ANALYSIS FOR DESIGNING OPTIMAL WATER-USE CHEMICAL PROCESSES

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The **objective** of this work was the development of science-based optimal **resource-saving** chemical processes of **water management system** for industrial enterprise of various manufacturing branches. This system should provide the reduction of specific flowrates of fresh water consumption and wastewater disposal, reducing the mass of pollutants in sewage discharge into natural water basins, high-performance technology of local wastewater treatment aimed at water reuse. In order to reach the objective it was needed to solve the following **tasks**: **1)** to execute comprehensive **environmental and technological analysis** of the main production processes; **2)** to develop and to apply the **thermodynamic exergy analysis method**, allowing to solve the problem of separation - mixing of technological water streams; **3)** to apply **thermodynamic water pinch method** in order to re-organize the traditional straight-flow system of water-use processes to repeatedly-serial one, providing the significant reduction of specific flowrates of fresh water consumption and wastewater disposal; **4)** to study and to implement in practice the high effective methods of **wastewater treatment**; **5)** to assess the **environmental and economic benefits** of proposed innovative technical solutions.

The **thermodynamic approach** to designing of resource-saving water management system had been developed. This methodology is based on simultaneous consideration of the following principles: the foundation of **chemical thermodynamics**; the basic environmental protection principles (system analysis, integrated approach, recycling, rational architecture, environmental safety demands); real technical and organizational capabilities of industrial plants. As one of the main component of this **thermodynamic approach** - the **thermodynamic exergy analysis method** for designing of water-use chemical processes had been carried out. Also the application of **thermodynamic water pinch method** was fruitful for designing of water-supply and water-disposal systems. The efficiency investigation of various **wastewater treatment** methods aimed at possibility of treated water re-use had been fulfilled. It was proved, that the most effective are physicochemical **advanced oxidation processes**: electrocatalytic destruction, catalytic destruction with strong oxidizing agents presence, catalytic destruction oxidation combined with coagulation. Transition and other metals compounds as catalysts have been used in our research. Hydrogen peroxide and some other chemical compounds were examined as strong oxidizing agents. Particular sorts of criterion toxic contaminants in water medium have been examined as the objects for destruction aimed in waste water purification. The advantages of proposed sewage treatment technology are high efficiency, relative economy, small amount of reagents demand and the absence of sludge formation.

The project's design procedure was approved by designing of optimal water-use chemical processes for large-scale textile, chemical, food, machinery construction, glass-production, motor-transport and some other industrial enterprises of Central, Volga, Southern Federal Districts of **Russia** and for major textile factories of **China**.

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## THERMODYNAMIC AND KINETIC CHARACTERISTICS OF COMBINED PROCESS OF CRYSTALLIZATION–MELTING OF TUNGSTATE–TELLURITE GLASS USING DSC-DATA

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The new approach to differential scanning calorimetry study of stable to crystallization glass together with novel model for data processing in the case of combined crystallization-melting are presented. Both high purity  $\text{TeO}_2\text{-WO}_3\text{-La}_2\text{O}_3$  glass bulk specimens and powder of different dispersity were investigated. While the bulk material showed the extremely high stability against crystallization under all heating rates used, the successive thermal effects of non-full crystallization and melting have been observed for the powder. The new model for analysis of combined crystallization-melting DSC data is proposed. The model processing results finely agree with experimental DSC curves. The three-dimensional dependencies of crystallization degree on time-temperature obtained by parameterization of DSC data allow to predict the optimum conditions for thermal treatment of the glass. The suggested technique can be useful for other glass-forming systems DSC studies.

The bulk high-purity  $(\text{TeO}_2)_{0.72}(\text{WO}_3)_{0.24}(\text{La}_2\text{O}_3)_{0.04}$  glass in the form of cut pieces and drops represented extremely high stability against crystallization. There were no any thermal effects of crystallization and melting at DSC-thermograms of the bulk material at heating rates of 2.5, 5, 10 K/min., that confirms the high applicability of the composition for fiber optics but makes difficulties for study of crystallization behavior.

Surface, core-cladding interface and the cladding-protective layer interface defects can lead to the appearance of crystallization, especially in the cases of non-optimal procedures of preforms and optical fibers fabrication.

The original approach to DSC study of stable against crystallization glasses for fiber optics was proposed. It is based on three components:

1. Fractionated by granules sizes powders of glass are applied for DSC studies.
2. Thermal effects of crystallization-melting are processed according to the new model, fully considering the non-isothermal conditions of the experiment and including the determination of regression dependencies of crystallization parameters on the fractional granules size.
3. Time-temperature dependences of the degree of crystallization  $\alpha(t, T)$  are calculated by model parameters, including parameters extrapolated to the real particle size distribution of the material.

Due to prediction of suitable time-temperature procedures of preforms and optical fibers production, the crystallization degree dependences  $\alpha(t, T)$ , obtained through model processing, result in possibility to calculate and minimize the effect of crystallization in glasses.

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### PC-SAFT PREDICTION OF LIMITING ACTIVITY COEFFICIENTS OF VARIOUS SOLUTES IN DEEP EUTECTIC SOLVENTS, IONIC LIQUIDS, AND ORGANIC COMPONENTS

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Limiting activity coefficient ( $\gamma_i^\infty$ ) is a fundamental thermodynamic measure for the non-ideality of a solution, and it governs dilute range fluid phase equilibria. The values  $\gamma_i^\infty$  closely reflect solute - solvent interactions, and, thus, play an important role for separation applications. Moreover,  $\gamma_i^\infty$  values are useful for the parameter estimation of thermodynamic models (e.g.  $G^E$  models or equations of state) for describing non-ideal systems.

In this work, the classical PC-SAFT model [1] was applied to predict the activity coefficients of bulk chemicals of different classes (alkanes, aromatics, polar components, alcohols) at infinite dilution in various solvents such as deep eutectic solvents (DES), ionic liquids (ILs), and common organic solvents. The solvent class of DES is especially green and an inexpensive alternative to classical ILs. The PC-SAFT predictions were based on pure-component parameters, and binary parameters were not applied. Necessary pure-component PC-SAFT parameters for all substances were available. For most of the considered systems, PC-SAFT predicted  $\gamma_i^\infty$  values agreed qualitatively with experimentally measured limiting activity coefficients. According to experimental  $\gamma_i^\infty$  data for a series of DES, the predicted  $\gamma_i^\infty$  values decreased with increasing temperature in a broad range of temperature. The general dependency of the predicted  $\gamma_i^\infty$  values on hydrophobicity was reflected correctly: with increasing carbon chain (increasing hydrophobicity) the experimental values of  $\gamma_i^\infty$  increased.

For the systems with DES, real ternary solute + glycerol + choline chloride systems with fixed glycerol : choline chloride molar ratios (1:1 and 1:2) were considered. Two strategies were applied to predict  $\gamma_i^\infty$  values in DES. In the first strategy, the PC-SAFT parameters for pure glycerol and choline chloride (which are constituents of DES) were used, in the second strategy the DES was treated as a pseudo-pure component (glyceline). Predicted  $\gamma_i^\infty$  values obtained from both approaches were very similar. The predictions using the real-component approach was slightly more accurate for polar solutes (ethyl acetate, tetrahydrofuran, methyl isobutyl ketone, pyridine, acetone) whereas the pseudo-component approach showed advantages for apolar components (alkanes). Both approaches yielded poor predictions for  $\gamma_{\text{methanol}}^\infty$  in DES.

On the basis of  $\gamma_i^\infty$  the selectivities  $S_{12}^\infty$  at infinite dilution in ILs, DES and choline chloride were predicted. Extremely accurate selectivity predictions were obtained for systems containing ILs. In accordance with experiment, PC-SAFT-screened selectivity nicely showed that DES (1:1) is the best agent for the separation of alkane and alcohol mixtures. Predicted PC-SAFT results obtained manifest suitable predictive abilities of the PC-SAFT model for  $\gamma_i^\infty$  estimations in the complex systems with various molecular cross-interactions in the liquid phase.

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## APPLIED ASPECTS OF P-V-T DEPENDENCES IN THE FLUID OF THE CO<sub>2</sub>

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The aim of the present work is in research of P-V-T dependences near critical point of carbon dioxide and calculation of the critical parameters of the state in the oil fractions. For research experiments were hold at P-V-T aggregate of “UGK-4” model equipped with the inspection window making it possible to observe disequilibrium effects in researched region. Scaling of carbon dioxide processing status at the apparatus was carried out at subcritical and overcritical values:  $T = 298\text{--}305$  K and  $P = 1\text{--}10$  MPa. Hysteresis is observed on isotherms carbon dioxide CO<sub>2</sub> i.e. the variation of  $P$ - $V$  under conditions of increase and decrease of pressure did not coincide. As it is known, a hysteresis is typical to nonlinear processes the state of which is determined by not only current external conditions, but its prehistory as well. For change of system state, definite time is always required, in consequence of which a system reaction falls behind reasons causing it. Hysteresis processes differ by that a lag while deceleration of external conditions change does not decrease. Nonlinear dependences of hysteresis type occurred both at subcritical and overcritical values of state while research of dependence P-V for carbon dioxide.

From these isotherms P-V it follows that quantity of fluid phase at subcritical parameters is much more than at overcritical parameters of CO<sub>2</sub>. That is found parameters of state made it possible to change stability of system under subcritical conditions and realize fluid solubility.

Thus, it is determined that at a definite speed of CO<sub>2</sub> pressure increase ensuring process non-equilibrium and its further decrease at temperatures which are lower than critical temperature ( $< 304.2$  K), the quantity of CO<sub>2</sub> fluid phase in system grows many-fold, what is important for effective use of CO<sub>2</sub> as a dissolvent. Under the same conditions, but at experiment temperatures, which are higher than critical  $T (> 304.2$  K), the quantity of fluid phase considerably decreases, what causes “drying” of gas.

Experimentally studied P-V-T dependences of carbon dioxide near the critical point are needed to determine the quantitative ratio of phases. Based on the experimental and theoretical data we have developed modified equations for calculation of critical properties of systems containing oil components. These modified equations to estimate physical-chemical properties can be used for calculation of critical properties and for other natural hydrocarbons.

## Section 5. Applied aspects of chemical thermodynamics

### AU AND AG NANOPARTICLES INFLUENCE ON TEMPERATURE TRANSITIONS IN POLY(TITANIUM OXIDE - HYDROXYETHYLMETHACRYLATE) COPOLYMERS

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Nowadays Au and Ag nanoparticles are the subject of numerous investigations due to the prospects of their application in photonics, biotechnology, pharmacy and other fields of science [1]. Furthermore, they have identified the unique catalytic properties which are not detected for these metals in the block state. It was found that the doping of known photocatalyst - anatase TiO<sub>2</sub> - by Au or Ag nanoparticles leads to the multiple photoactivity increase of TiO<sub>2</sub> [2]. In these applications powders, films or surfaces containing Au/TiO<sub>2</sub> nanoparticles exhibit high photocatalytic activity under visible light irradiation in waste in water purification and highly selective catalytic oxidation of benzene to phenol [1]. The important performance property of such catalytic materials is their thermophysical properties, which are practically unexplored.

The aim of this research is obtaining new polymeric composite materials containing poly(titanium oxide) in a highly dispersed state, doped by Au or Ag nanoparticles, in the organic polymer matrix in one pot reaction and the study of their thermophysical properties for creation high catalytic systems. Thermophysical properties of obtained polymeric nanocomposites were studied by differential-scanning calorimetry method (DSC), the materials structure - by atomic force microscopy, mass spectrometry on the secondary ions and X-ray analysis. It was shown that poly(titanium oxide) forms nanoparticles with average size 6 - 8 nm in the organic polymer matrix and have structure near to anatase. The doping of poly(titanium oxide) by Au or Ag nanoparticles took place in one pot reaction by UV-irradiation of the polymer composition containing the dopant (HAuCl<sub>4</sub> or AgNO<sub>3</sub>). It was found the significant influence of metal nanoparticles on the thermophysical properties of the composites (Table).

**Table.** The influence silver nanoparticles concentration to the glass transition temperature of the polymeric composites.

$\phi$ (Ag), wt. %	T <sub>glass transition</sub> of polymeric material, °C
0.000	143
0.008	88.5
0.016	76
0.040	70
0.080	69
0.160	65
0.480	66

It was experimentally found that even small amounts of nanoparticles (up to 0.08 wt.%) in both cases leads to decreasing of the glass transition temperature of polymeric materials by 60–70°C and inessential changing of the materials decomposition temperature (within 10–20°C). The absence of the melting point on DSC curves confirms the three-dimensional structure of polymeric nanocomposites.

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### THERMODYNAMIC DESCRIPTION OF THE Cu–Zr–O AND Cu–Al–O SYSTEMS

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Thermodynamic description of the Cu–Zr–O and Cu–Al–O systems was done using Surfaces of Component Solubility in Metal Melts (SCSM) under the temperature ranging from 1100 °C to 1300 °C.

SCSM allowed to relate the microchanges in compositions of the metal melt to changes in compositions of the equilibrium nonmetallic compounds (which are formed in the metal melt).

Equilibrium constants of the chemical reactions (that occur in the metal melt), Wagner first-order interaction parameters and energy parameters of the subregular ionic solution theory were used for construction of the SCSM in this work. Subregular ionic solution theory described properties of oxide melt which exists in equilibrium with the metal melt.

Isotherms of oxygen solubility in liquid copper were important components of the constructed SCSM for Cu–Zr–O and Cu–Al–O systems. SCSM showed that zirconium and aluminum are strong reducing agents for copper. Thermodynamic modeling showed that in presence of zirconium and aluminum in copper melt with dissolved oxygen the formation of the copper oxide in the metal melt was unlikely. Addition of zirconium to the copper melt with dissolved oxygen permits to decrease the percent of oxygen in copper melt to  $10^{-9}$  weight %. Deoxidation product in this case is only  $ZrO_2$ . Addition of aluminum to the copper melt with dissolved oxygen also permits to decrease oxygen content in copper melt to  $10^{-9}$  weight %. Deoxidation products in this case may be  $CuAlO_2$  (for aluminum concentration in copper melt of  $10^{-12}$  weight %) or  $Al_2O_3$  (for a wide range of aluminum concentration in copper melt up to  $10^{-1}$  weight %).

Results of this work may be used for analyzing technological processes of production of copper and copper alloys.

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## Section 5. Applied aspects of chemical thermodynamics

### DEEP EUTECTIC SOLVENTS: DO THEY HAVE CAPACITY IN SEPARATION PROCESSES?

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Separation units are high energy consuming parts of chemical plants and they are contributing to atmosphere contamination due to the loss of solvents. Solvents are broadly used in many separation processes, most commonly extraction and extractive distillation operational units. Use of heavy volatile organics in separation process, such as DMSO, ethylene glycol, sulfolane, glycerol etc. is intended to reduce solvent losses [1].

About fifteen years ago ionic liquids (ILs) were considered for large scale separations. ILs are non-volatile, thermally stable, but very expensive neoteric solvents. Recently, another type of heavy volatile solvents, so called deep eutectic solvents (DESs), have been regarded as promising cost-effective and environmentally benign alternatives to conventional volatile organic solvents. Questions that have only rarely been investigated are: Do DESs have capacity in separation processes? Could they work as effective entrainers? The answers to these questions are addressed in this work.

The screening and selection of suitable solvents for separations is an important part of the process design. Limiting activity coefficients provide a useful precursor for the optimal choice of the selective solvent. For the first time activity coefficients at infinite dilution have been measured in DESs as a solvent for 23 most common solutes (aliphatic and aromatic hydrocarbons, alcohols, ketones, ethers, and esters). The DESs were constituted from choline chloride and glycerol in molar ratios 1:1 and 1:2. The measurements were carried out with the help of gas-liquid chromatography in the temperature range 298-358 K. Using experimental results, selectivity of different separation systems like alcohols – acetates, alcohols – alkanes, cyclohexane – benzene was assessed.

To verify the efficiency of the separation performance of the DESs the perturbed-chain statistical associating fluid theory (PC-SAFT) was employed. This method appears to be a powerful tool for screening of suitable precursors and evaluation of separation performance at temperatures relevant for practical applications. It has turned out, that the separation performance of DESs is comparable to that of ionic liquids, but with significantly lower prices and more appropriate for also biological processes, because they are composed of natural and renewable nontoxic bioresources.

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### DOUBTS ON KISSINGER'S METHOD OF KINETIC EVALUATION BASED ON SEVERAL CONCEPTUAL MODELS SHOWING THE DIFFERENCE BETWEEN THE MAXIMUM OF REACTION RATE AND EXTREME OF DTA PEAK

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The famous Kissinger's kinetic evaluation method [1] is examined with respect to the feasible impact of the individual quantities and assumptions involved, namely the model of reaction mechanism,  $f(\alpha)$  (with the iso- and noniso-thermal degrees of conversion,  $\alpha$  and  $\lambda$ ) the rate constant,  $k(T)$  (and associated activation energy,  $E$ ), heating/cooling rate,  $\beta$  (supplementing additional thermodynamic term for the melt undercooling,  $\Delta T$ ), e.g.,  $(3\beta)/[T_m^2(\Delta T)^2] = df(\alpha)/d\alpha (A/B) \exp\{-B/T_m(\Delta T)\}$ , and above all, the association of the characteristic temperature with the DTA peak apex. It is shown that the Kissinger's equation, in contrary to the results of Vold [2], is omitting the term of heat inertia arising from the true balance of heat fluxes, e.g.,  $d^2\alpha/dt^2 = (K/H) (d\theta/dt)$ , (where  $\theta$ , is the difference in temperature of the centers of the two samples) explicitly showing the misfit between,  $T_m$  and broadly implemented value of the DTA apex,  $T_p$ . The absence of this term skews the evaluated values of activation energies. Despite a long lasting history of kinetic evaluation it is clear that such an important part of DTA peak analysis has been overlooked at everyday applications. It is possibly caused by the obvious methods simplicity, which provides easy publishable values of activation energies. It is surprising that anybody who evolved various alternatives of the Kissinger method did not find any reasons for its criticism.

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## Section 5. Applied aspects of chemical thermodynamics

### CENTEM: THERMONANALYTICAL CENTER AT THE CZECH WEST BOHEMIAN UNIVERSITY AND ITS INTERNATIONAL COOPERATIVE PROGRAM

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Specified research in the spheres of polymeric membranes, hydrogels, polysialates and geopolymers, composites (and their profiles drawn by new pultrusion technology), photovoltaic cells and panels, fuel cells, batteries and solid electrolytes, biomaterials and biomedical application, car exhaust catalyses, nanomaterials and noncrystallites, foams heat isolators, etc., is concerned. Instrumentation comprise MTGA – Thermogravimetric analyzer Q500, MDSC – Differential scanning calorimeter Q200, DMA – Dynamical mechanical analyzer Q800, MTMA – thermo mechanical analyzer – Q400, Rotary rheometer – ARES G2, Electrochemical impedance spectrometer – AIS, Dynamic thermogravimetry of vapor sorption – DVS, Inverse gas chromatography – IGS-SEA, Fuel cell testing with polymer membrane – PEMFC-TS, Laser deposition of thin layers, Dispersive fluorescence RTG spectrometer – AXS Bruker S4, Capillary electrophoresis with UV detection, Low angle RTG diffraction – SAXS Anton Paar, 3-D light microscopy, electron microscopy, etc.

The Centre is prepared to serve as an international reference laboratory ready to cooperate on the explication of variety methodical, scientific and industrial problems, providing material analysis and allied data evaluation, eventual explanation of whole problematic including the selection and association of individual types of measurements, analysis and material's option.

Beside international assignments, domestic projects and cooperation with industry, the Centre provides education service in both the material science and a wider range of interdisciplinary learning; recently is subordinating the international program "Excellence of human resources as basis for the competition ability" granting postdoctoral studies. Research includes powerful state of theoretical basis on thermophysical measurements, thermal analysis and calorimetry, material thermodynamics and technology, mechanical dynamics, reaction kinetics, data evaluation, computer data processing and analysis. It encompasses links to various international boards as well as wider publication activities, including special book (now exhibited):

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## ISOPROPYLBENZENES. THEORY AND PRACTICE OF THE ALKYLATION OF BENZENE AND METHYLBENZENE WITH PROPYLENE

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Isopropylbenzene (IPB) is a base raw for phenol and acetone production through the cumylhydroperoxide. At the present time about 95% of worldwide synthetic phenol production are accounted for this method. The main processing technology of MeIPB in the corresponding hydroxyderivate is in many ways similar to phenol and acetone receiving. The question is how to provide extremely high selectivity at every stage of process.

It is known that maximal IPB concentrations consisting in reaction mass of alkylation of benzene with propylene are reached in conditions of thermodynamic control. For MeIPB this question remains open up to the present time. Thermodynamic principles of mono-MeIPB production and other features of the individual compounds receiving process are considered by us in studies [1-3]. For di-MeIPB such information is practically absent and it is investigated by our research. The results are presented on this conference and, regarding to liquid-phase chemical equilibrium, concluded in follows.

- Equilibrium mixture of isopropyl-para-xylenes (IPpX) is presented by 3 compounds: 2-IPpX, 2,5-diIPpX and 2,6-diIPpX. The group of di-IPpX contains 2,5-diIPpX with its 8-10 multiple prevalence over 2,6-diIPpX.
- Equilibrium mixture of isopropyl-meta-xylenes (IPmX) is presented by 6 compounds: 2-IPmX, 4-IPmX, 5-IPmX with prevalence of the last isomer in group and 4,6-diIPmX, 2,5-diIPmX, 2,4-diIPmX in the almost complete absence of the last isomer in group.
- Equilibrium mixture of isopropyl-ortho-xylenes (IPoX) is presented by 5 compounds: 3-IPoX, 4-IPoX in the almost complete prevalence of the last isomer in group and 3,5-diIPoX, 3,6-diIPoX, 4,5-diIPoX with prevalence of 3,5-diIPoX and in the almost complete absence of the last isomer in group.
- The ratio of mono- and di-IPX is regulated by a ratio of initial reagents for the alkylation.

The results of the liquid-phase chemical equilibrium research in local systems (ortho-, meta- or para-)Xylene+correspond IPpX and in system presented by all considered series of compounds (IPX+IPBenzenes+IPToluenes) are received for a wide temperature interval and formed the basis for prediction of the IPX thermodynamic properties in gas and liquid phase. Critical properties of substances were chosen by us according to [4]. Necessary correctives were introduced in existing methods of prediction.

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## Section 5. Applied aspects of chemical thermodynamics

### THERMODYNAMIC FUNDAMENTALS OF BRANCHED ALKENES OLIGOMERIZATION

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Higher branched alkenes (HBA) are extremely important for modern industry. They are used for production of fuel blend components, lubricants, plasticizers, pharmaceuticals, resins, detergents, etc. The main source of their synthesis is oligomerization of lower alkenes. Quality of commodity product directly depends on composition of oligomerization product. Therefore, oligomerization equilibrium study is of immediate interest for selective synthesis of essential components.

So far, oligomerization of olefins is carried out with sulfocationites at 40-150°C, with zeolitic catalysts at temperatures up to 420°C, using solid phosphoric acid, Lewis acids, etc. Selective synthesis means that we can manage the process. Branched olefins are highly reactive and subsequently wide range of oligomers obtained creates technical difficulties in separation, processing, and further application.

In our study we investigate isomerization of branched olefins (C<sub>8</sub>, C<sub>12</sub>) obtained by isobutylene oligomerization in presence of sulfocationites of well-known brands. Temperature range of research is limited by technical capabilities of catalysts.

The study established the following:

- Oligomerization of isobutylene with sulfocationite proceeds with formation of 14 isomeric compounds of C<sub>8</sub>.
- Isomerization of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 proceeds to equilibrium value.
- Oligomerization of isobutylene is accompanied by competing isomerization, destruction and oligomerization conversions.
- Temperature increase leads to increase in depth of oligomerization and oligomers destruction, which results in reduced selectivity of the process.
- Increase of moisture content in the system increases the selectivity and reduces original reagent conversion.

On the basis of experimental data liquid-phase equilibrium constants have been calculated, enthalpy and entropy effects have been determined, equilibrium mixtures compositions as function of temperature calculated. Recommendations have been given as to implement the processes aimed to obtain specific products under the conditions of equilibrium achievement. Recommendations have been given for the temperature conditions of oligomerization process with fresh catalyst.

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### THERMODYNAMIC MODELING OF PHASE EQUILIBRIUM IN SYSTEMS Me-B-C-O (Me=Ti, Fe, V, W) IN VACUUM AND SYNTHESIS OF BORIDES/CARBIDES LAYERS UNDER INFLUENCE INTENSIVE ELECTRON BEAMS

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We have presented results of the thermodynamic calculations simulating the interaction between transition metal oxides with carbon and various boron compounds in the equilibrium conditions. The thermodynamic investigation of equilibrium in systems Ti-B-C-O, Fe-B-C-O and V-B-C-O is carried out with the purpose of formation conditions optimization of functional layers on a surface of iron-carbon and titan alloys as a result of electron beam boriding in vacuum. Originally the boriding component choice and the determination of optimum conditions for the boriding on temperature and pressure are main purposes of thermodynamic consideration. The interaction of oxide with carbon and various boriding components (boron carbide B<sub>4</sub>C, boron B, boron oxide B<sub>2</sub>O<sub>3</sub>) is investigated.

The thermodynamic calculations were executed with the computer systems ASTRA-4/pc or TERRA. The calculations were carried out in a temperature of 673 - 1813 K (melting temperature of pure iron Fe 1812 K) and in pressure range 10<sup>5</sup>-10<sup>-4</sup> Pa.

As a result of thermodynamic modeling is fixed, that at borides synthesis in quality various boriding components the use of a B or a B<sub>4</sub>C, instead of a B<sub>2</sub>O<sub>3</sub> is most much preferable. Greatest power expenditures were observed for compositions with participation of B<sub>2</sub>O<sub>3</sub>, then B<sub>4</sub>C. The difference reached 550-600 kJ/kg (B<sub>2</sub>O<sub>3</sub>) and 2-3 kJ/kg (B<sub>4</sub>C) [Ti-B-C-O].

The sequence of the chemical transformations at borides synthesis, namely, the oxides → the carbides → the lowest borides → the supreme borides is established. First temperature of borides formation depends on total pressure in system. So in system Ti B-C-O at pressure 10<sup>5</sup> Pa the TiO<sub>2</sub> interaction with various boron components (B<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C, B) begins at temperatures 1900-2100 K but at pressure 10<sup>-2</sup>-10<sup>-3</sup> Pa the formation beginning temperature is reduced up to 850-900K. It is established, that in mixes with participation B<sub>4</sub>C and B originally there should be a phase transformation into the condensed condition with formation of liquid phase B<sub>2</sub>O<sub>3</sub>.

It is submitted, that investigated systems MeO<sub>2</sub>-B (B<sub>4</sub>C, B<sub>2</sub>O<sub>3</sub>)-C [Me = Ti, Fe] and V<sub>2</sub>O<sub>3</sub>-B (B<sub>4</sub>C, B<sub>2</sub>O<sub>3</sub>)-C are not ternary. In all investigated ternary systems, at least, two sides of a concentration triangle are not binary sections of systems Me-B-O<sub>2</sub>. The special attention is given to ternary system B-C-O<sub>2</sub> as interaction B<sub>2</sub>O<sub>3</sub>-C determines behavior of all quaternary system as a whole. Thermal properties and character dissociation of B<sub>2</sub>O<sub>3</sub> are shown depending on the common pressure in system. Fields of crystallization of all possible phases, and also influence of temperature and pressure upon their behavior are established.

Preliminary results of electron beam boriding of carbon steels are presented. The thickness of TiB<sub>2</sub> layer was of the order of 80-100 μm, FeB - 100-150 μm, Fe<sub>2</sub>B - 100-500 μm, VB<sub>2</sub> - 150 μm and WC - 200-300 μm. Layers will consist from TiB<sub>2</sub>, ZrB<sub>2</sub>, VB<sub>2</sub> and WC (X-ray analysis (D2 Phaser, Cu K<sub>α</sub>- radiation)). Research by means of a scanning microscope (LEO 1430VP) has shown, that borides layers formation is difficult physical and chemical process. Their formation is difficult physical and chemical process. The structure, phase structure and strength characteristics are investigated.

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## Section 5. Applied aspects of chemical thermodynamics

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### THERMODYNAMIC ASPECTS OF AGING GYPSUM BINDERS

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On the physical and chemical positions processes of aging binders, including gypsum are examined. Aging is presented as a spontaneous thermodynamic process, the result of which is to increase the mass of the material, change of the energy, thermodynamic characteristics and reactivity.

The expediency of attracted funds and apparatus of thermokinetics and thermodynamics to analyze the reactivity and thermodynamic characteristics of gypsum binders are shown. To this end, the methods of isothermal calorimetry and differential scanning calorimetry are attracted.

The experimental studies of the kinetics of heat during hydration of gypsum binders are fulfilled. The indicators of reaction rate, the heat and the degree of hydration are identified. The values of enthalpy, entropy and Gibbs energy of gypsum binders are defined by differential scanning calorimetry

It was stated that aging leads to a decrease of the binders' reactivity and, as a consequence, to a decrease in the rate of heat evolution during hydration. Decrease of the hydration heat during aging is caused by the growth of the Gibbs energy.

It is shown that the established changes are conditioned by specific surface, crystal size and degree of crystallinity and, especially, by reduction in internal energy crystalline.

The possibility of quantitative estimation of changes of thermodynamic characteristics of gypsum binders during aging and improving of the construction and technical properties by stabilizing their phase composition. Investigation of the influence of aging on the reactivity and thermodynamic properties of gypsum binders will allow the design of the rational composition with the desired shelf life.



## V-L-EQUILIBRIA IN THE SYSTEM OF GLYCIDOL SYNTHESIS PRODUCTS

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The synthesis of glycidol by direct epoxidation of allyl alcohol with hydrogen peroxide in methanol with a titanium-containing zeolite as the catalyst involves the problem of glycidol isolation from the reaction mixture, which contains both the main product and a number of by-products, as well as the methanol used as the solvent. In order to see whether glycidol can be isolated from the reaction mixture by conventional distillation, it is necessary to have data concerning phase equilibria in the systems of glycidol synthesis products.

Such problems are being increasingly widely solved by mathematical modeling, which provides means to optimize the solution procedure and to obtain the necessary results in a more rational way. Applying this approach to research practice involves the problem of selecting an adequate model and that of estimating its parameters for obtaining a qualitative and quantitative description of the thermodynamic behavior of binary and, subsequently, multicomponent systems. There have been many recommendations as to what equation should be preferred for describing VLE for a given nature of the components of a binary mixture and for given classes of binary solutions. For the organic system considered here, we used the local composition models NRTL and UNIQUAC. In some cases, one of the equations provides better results in describing VLE. It is necessary to take into account azeotropy data, which impose serious limitations on the separation of the reaction mixture, and to pay great attention to the accuracy of the description of the properties of the azeotropes.

In the epoxidation process, the reaction mixture leaving the reactor unit contains the following components: methanol (M), allyl alcohol (AA), glycidol (Gd), water (W), glycerol (Gl), and 3-methoxy-1,2-propanediol (MPD), which form 15 binary systems. The binary interaction parameters for the AA-W, W-Gl, M-W, and M-Gl systems were estimated from experimental data, which had been reported in the literature in sufficient detail. For the AA-M, AA-Gd, AA-Gl, Gd-M, Gd-Gl, W-Gd, M-MPD, W-MPD, Gd-MPD, Gl-MPD, and AA-MPD binary systems, there are no data in the literature. For this reason, the unknown parameters of these systems were derived from pseudoexperimental data calculated using the UNIFAC model. The vapor phase was described with both ideality and nonideality taken into account. In the latter case, the vapor phase was modeled using the Redlich-Kwong equation, which provides a good description for the gas phase at moderate pressures and all temperatures. The properties of solutions were described using symmetric normalization of activity coefficients. The saturation vapor pressures of individual compounds were determined via the Antoine equation.

In order to choose the best VLE model, we estimated the parameters of the NRTL and UNIQUAC equations, assuming that the vapor phase is either ideal or nonideal, and, using these parameters, we simulated phase equilibria in binary systems described in the literature.

The analysis of the goodness of fit to different experimental and pseudoexperimental (UNIFAC) data arrays demonstrated that, for most of the systems, the most appropriate binary interaction model is the NRTL equation taking into account the nonideality of the vapor phase. The parameters of this equation for various binary systems were identified.

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### POWER AND LIMITATION OF CHANGING THE ELECTROPHORETIC MOBILITIES OF ANALYTES BY MEANS OF COMPLEXATION IN CAPILLARY ELECTROPHORESIS

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Changing the electrophoretic mobilities of analytes by means of complexation is the one of most widespread way of separation optimization in capillary electrophoresis (CE). Any analytes seems may be separated. However, it is not true, this way has the limitations. In several cases, it is not proper to use in practice the successful system in theory. The aim of present study is to reveal the power and limitation of changing the electrophoretic mobilities of analytes due to complexation. The study was made by experimentally using as example the complexes of iron (III) and copper (II) with a number of organic acids. The study was carried out using capillary electrophoresis system with a diode-array detector Agilent <sup>3D</sup>CE G1600A (Agilent Technologies, Waldbronn, Germany) of the Center for Collective Use of the Siberian Branch of the Russian Academy of Sciences.

For labile systems, the effective electrophoretic mobility is calculated as follows [1]:

$$\mu_{\text{eff}} = \sum_i^N \mu_i \cdot \alpha_i, \quad \alpha_i = \frac{[ML_i]}{C_M} = \frac{\beta_i [L]^i}{1 + \sum_i^n \beta_i [L]^i},$$

where  $\mu_i$  is the electrophoretic mobility of the  $i$ -th species,  $\alpha_i$  is the mole fraction,  $[L]$  is the ligand concentration in background electrolyte,  $\beta_i$  is the stability constants. Migration time is calculated using equations

$$t = \frac{l_{\text{eff}}}{U(\mu_{\text{eff}} + \mu_{\text{EOF+P}})}, \quad \mu_{\text{EOF+P}} = \mu_{\text{EOF}} - v_P \cdot \frac{l}{U},$$

where  $l$  and  $l_{\text{eff}}$  are the total and effective capillary lengths,  $U$  is voltage,  $\mu_{\text{EOF+P}}$  is the electroosmotic mobility reduced by applying hydrodynamic pressure,  $\mu_{\text{EOF}}$  is the electroosmotic mobility,  $v_P$  is the hydrodynamic flow velocity [2-4].

It is found that the most considerable factors specified the success of complexation usage are the effective charge and stability of complex species, the electroosmotic flow velocity and the side interactions of analytes with capillary walls. The conditions for using complexation reactions and separation are stated. The obtained results allow selecting the optimal conditions of analyte separation by CE.

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**THERMODYNAMICS OF COMPONENTS INTERACTION IN CRYSTALLIZING  
LOW-ALLOY BORON STEEL MELT**

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The interaction of metal melt components depends on a large number of factors, therefore direct studies of these processes, which are, in addition, high-temperature, is complicated to a marked degree. At the same time the thermodynamic analysis of proceeding interaction reactions allows defining the pattern of phase equilibria realized in the system and also tracing the transformation of non-metallic phases formed during cooling and crystallization of a metal melt. In this research a thermodynamic analysis of the phase equilibria in the Fe–Mn–Cr–Si–Al–Ti–Ni–V–Mo–B–S–P–C–N–O system at the temperatures of molten metal existence and within the crystallization temperatures was performed. The concentrations of some elements were fixed ([Mn]=0.7; [Cr]=0.9; [Si]=0.3; [Al]=0.03; [Ti]=0.04; [Ni]=0.15; [Mo]=0.4; [V]=0.0075; [B]=0.003; [S]=0.025; [P]=0.01; [C]=0.38; [N]=0.008 wt %).

The nonmetallic phases formation upon cooling and crystallization of various composition liquid metal solutions was studied. It was established how the aluminum and titanium content in the liquid metal solution affects the composition and amount of the separated excess phases.

Calculations have indicated that corundum can be in equilibrium with the molten metal at T=1848 K. Cooling the molten metal is also accompanied by release of corundum inclusions (Al<sub>2</sub>O<sub>3</sub>). After the crystallization starts formation of these inclusions continues till the moment when solidified metal fraction reaches 40 %. Further metal crystallization is accompanied by alternate release of corundum and titanium oxycarbonitride inclusions [TiO, TiC, TiN] of variable composition. Potential composition of equilibrium titanium oxycarbonitrides vary within 9.96 mol. % TiO; 2.60 mol. % TiC and 87.44 mol. % TiN up to practically pure titanium carbonitride (at the end of crystallization titanium oxide content makes 2.52; titanium carbide – 31.10; and titanium nitride 66.28 mol %).

Calculations indicate that in the case of decreasing titanium concentration in the liquid metal, titanium oxycarbonitrides are formed later, and their weight is substantially less. It leads to increase of unbound nitrogen in solidified metal (0.005 wt % vs. 0.0024 wt % in the base version).

Decrease of aluminum concentration also leads to a slight increase of unbound nitrogen in solidified metal (0.0026 wt % vs. 0.0024 wt % in the base version) by means of TiN proportion decreasing in the equilibrium titanium oxycarbonitride solution due to TiO content increase.

Calculations demonstrated that boron nitride and carbonitride in the liquid metal and during crystallization not are formed.

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## Section 5. Applied aspects of chemical thermodynamics

### THERMODYNAMIC MODELING OF THE Li–Ga–N AND Li–Na–Ga–N SYSTEMS

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In recent years, vigorously develop various options technique for growing single crystals of gallium nitride in solutions of low pressure (LPSG method). Gallium nitride is widely used for creation of blue light-emitting diodes, semiconductor lasers, super-high-frequency transistors and ect. Different methods of the gallium nitride single-crystals growth in solutions of low pressure (LPSG method) intensively develop last years. LPSG is one of the most interesting method. One of perspective LPSG varieties is the GaN crystals growth in the metal melts that include lithium and sodium. Presence of lithium that forms fusible ionic nitride ( $\text{Li}_3\text{N}$ ), as well as forms with gallium nitride relatively fusible double nitride ( $\text{Li}_3\text{GaN}_2$ ), allows significantly to increase nitrogen solubility in such melt and to conduct the process at relatively low temperatures (800–900 °C) and pressures (less than 20 bar).

At the same time experimenters working in this direction, there is no important information needed for the development of high-grade technology. There are no data are available about influence of different parameters (temperature, pressure, composition of the melt) on composition of the interaction products, and also about their influence on properties of the gallium nitride single-crystals of grown from melt. Information is practically absent about the phase diagrams of the Li–Ga–(...)-N systems. Critical analysis and synthesis of the available capacity of disparate data on these systems, charting status in an easy to use form – works with obvious relevance to the development of modern innovative technology.

This research deals with the analysis of thermodynamic systems Li–Ga–N and Li–Na–Ga–N. The study explored the possibility of using these systems to describe the various model approximations theory of the structure of solutions (different model variants regular subregular solution, as well as associated solutions model and Redlich–Kister model. Based on separate literature experimental data the required values of models parameters were determined. Phase diagrams of the Li–Ga, Li–Na, Li–N, Na–Ga, Na–N, Ga–N and  $\text{Li}_3\text{N}$ –GaN double systems were calculated in the process of parameters selection. Possibilities of programmatic complex "FactSage" (version 6.4), developed by "Thermfact" (Canada) and "GTT Technologies" (Germany), we used to carry out some of the calculations.

Isothermal and isoeconcentration sections of phase diagrams (including the surfaces of liquidus) for the studied systems were calculated. The conditions (concentration limits, borders of temperature ranges and pressure) of liquid metal existence in the equilibrium with gallium nitride were determined.

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## COMPLEX STUDY OF HYDRATION AND PROTONATION PROCESSES OF LAYERED TITANATES $A_2Ln_2Ti_3O_{10}$ BY METHODS OF THERMAL ANALYSIS

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Layered perovskite-like oxides  $A_2Ln_2Ti_3O_{10}$  belong to Ruddlesden-Popper phases. There are crystalline compounds in which three-dimensional perovskite blocks are interleaved with layers of rock salt structure. These materials attract the attention of scientists because they demonstrate high ionic conductivity and photocatalytic activity, particularly in the reaction of water splitting with hydrogen production. Therefore, from a practical point of view, the study of oxides in aqueous solutions and humid atmosphere where the processes of hydration and ion exchange (protonation) are possible is relevant.

Alkaline forms of layered perovskite oxides are able to undergo protonation (substitution of alkali cations to protons) and hydration (sorption of the water molecules on the surface of the oxide and introduction of water molecules into the interlayer space) when exposed to an aqueous solution or humid atmosphere [1]. These processes can significantly influence the physico-chemical properties of oxides and their investigation should not be neglected.

Complex oxides  $A_2Ln_2Ti_3O_{10}$  (A = Li, Na, K; Ln = La, Nd) were prepared by the ceramic method in the temperature range of 1100 – 1200°C in air at the atmospheric pressure:



Suspensions of obtained compounds were prepared by adding the powdered samples to distilled water. These suspensions were kept under constant stirring for certain periods of time, then the samples were centrifuged and dried. The summary protonation/hydration process occurring under contact with aqueous medium can be described as:



The phase composition and structural parameters of the raw materials and the obtained samples were monitored by XRD analysis. To determine the degree of protonation and the number of intercalated water thermogravimetric analysis (Netzsch TG 209 F1 Iris) was used. The thermal effects of dehydration processes were determined by the DSC 204 F1 Phoenix.

As a result, the complex study of hydration and protonation processes was conducted. The composition of the hydrated and protonated forms was calculated [2]. The thermal desorption and deintercalation effects were determined. It was found that the protonation is typical for all forms of layered oxides  $A_2Ln_2Ti_3O_{10}$ . In addition to the protonation process the intercalation of water molecules into the interlayer space was observed for  $K_2Ln_2Ti_3O_{10}$ . Thus, these materials exist in aqueous solution in the form of compounds with the general formula  $H_xK_{2-x}Ln_2Ti_3O_{10} \cdot yH_2O$  or  $H_xA_{2-x}Ln_2Ti_3O_{10}$  (A = Li, Na).

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## Section 5. Applied aspects of chemical thermodynamics

### THERMAL ANALYSIS AND CALORIMETRY STUDY ON COMBUSTION AND PYROLYSIS OF TATARSTAN CRUDE OILS

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*In-situ* combustion (ISC) is one of the promising thermal methods of heavy oil recovery. Combustion process is caused by the injection of air into the well. Preliminary tests have shown that the use of *in-situ* combustion technology can achieve the greatest performance of recovery rates compared with other methods of enhanced oil recovery. Heat generated directly inside the oil reservoir significantly reduces the heat loss and reduces power consumption compared with other thermal techniques. However, the practical application of *in-situ* combustion technology has a number of problems. The main problems are weak scientific study of the technology and the lack of general guidelines for its application. In this work we decided to make first step to solve these problems using thermal analysis and calorimetry techniques.

Thermal analysis techniques used in crude oil characterization was directed towards correlation between thermal behavior of the samples and kinetic studies. Crude oil is a complex mixture of different chemical species consisting mostly of hydrocarbons and combustion process involves variety of chemical reactions in the presence of air. One of the major difficulties in handling crude oils is processing since its thermal behavior is not well understood. Up to the present, there have been many studies dealing with the characterization of crude oils by various thermal analysis techniques.

This research focused on the thermal characterization and kinetics of three Tatarstan crude oils by combustion calorimetry, thermogravimetry (TG-DTG) and DSC techniques. The present study was carried out to investigate the non-isothermal thermal behavior of high-molecular hydrocarbons in the absence of rock matrix. A detailed kinetic study was conducted to understand the mechanism of crude oils and determine the main reaction parameters by different mathematical approaches. This research also intended to reveal the heating rate effect on combustion properties and kinetics of crude oils for a possible *in-situ* combustion process.

Calorimetric experiments show that crude oil with higher saturates content and low resins fraction has higher heating value. TG-DTG curves indicates that the crude oils undergoes two major transitions when subjected to an oxidizing and constant rate environment known as low (LTO) and high temperature oxidation (HTO) at each heating rate studied. Kinetic analysis in the low and high temperature oxidation regions were performed using different well-established kinetic methods. According to the kinetic results, apparent activation energies in HTO region were considerably higher than those in LTO. Heavier oil with higher asphaltene amount had higher activation energy values in HTO region.

## KINETIC UNIT FOR TESTING CONSTRUCTION MATERIALS BIOPROOFNESS IN MODEL MEDIUMS

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In the literature are described many test methods for the bioproofness of construction materials. However, these methods require special conditions, they are intensive and expensive. Also they may be conducted in a narrow range of temperatures and at a certain pH value of the medium. For studying the biological corrosion of construction materials we have proposed the indirect evaluation method for the bioproofness of mineral materials in solutions of mono-, di- and tribasic carboxylic acids, simulating metabolic products of microorganisms [1, 2]. For this purpose designed a kinetic unit that allows to test construction materials on the biological stability in a wide range of temperatures and pH value of the medium. The unit includes a test tank, in which test samples are located and immersed in model medium, make-up and drain tank, the temperature and pH value control unit of the medium (Figure 1, 2).

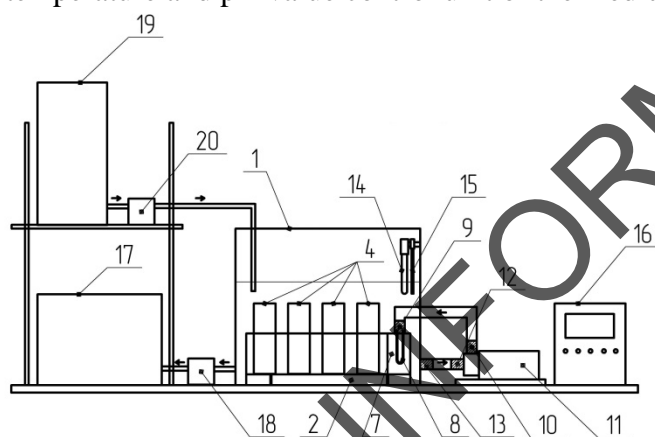


Figure 1: The composition of the kinetic unit.

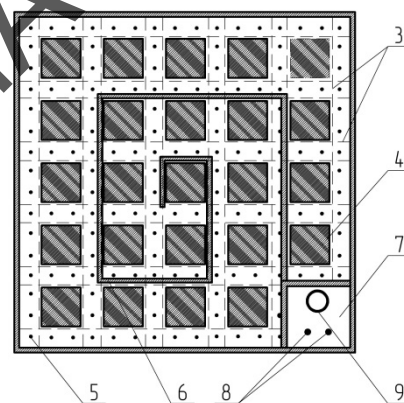


Figure 2: Cartridge for the samples.

1 – testing tank; 2 – cartridge for the test samples; 3 – polymer network for the fixing the samples of the materials in the cartridge; 4 – samples of cement-sand mortar; 5 – holes in the upper double bottom of the cartridge; 6 – strips of plexiglas, forming a spiral duct of the cartridge; 7 – in-line heater of model medium in the cartridge; 8 – electric heater of the medium in the cartridge; 9 – inlet fitting of on-line heater for the inflow the model medium; 10 – injection pipe of the pump; 11 – centrifugal pump; 12 – pump suction; 13 – test tank pipe; 14 – pH-electrode; 15 – temperature sensor of model medium; 16 – electronic control unit; 17 – drain tank; 18 – solenoid valve in the bottom of the test tank; 19 – make-up tank; 20 – solenoid valve

The bioproofness of the construction materials is defined by their chemical resistance ratio, characterizing change of strength characteristics of samples of cement-sand mortar on compression and cross-breaking before and after an exposition in the model medium.

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## Section 5. Applied aspects of chemical thermodynamics

### THERMODYNAMIC ANALYSIS OF CATALYST INFLUENCE ON THE 1,2,4,5-TETRAMETHYLBENZENE OXIDATION PROCESS

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At the present time 2,4,5-trimethylbenzoic acid is used for obtaining polycarboxylic acids and their dianhydrides, as well as plasticizers and other valuable specialty chemicals.

Among all existing ways of 2,4,5-trimethylbenzoic acid synthesis, the most promising from our point of view, is oxidation of 1,2,4,5-tetramethylbenzene (durol) using nitric acid (50-58%) at temperature 30÷50°C, which gives high yield and quality of obtained product [1]. Based on a number of factors (higher selectivity, mild conditions of the oxidation process, fire and explosion safety of the oxidizer, ease and completeness of target product purification) the approach, proposed by us, significantly surpasses processes, based on catalytic oxidation of durol by oxygen [2, 3].

This paper represents the investigation of process improvement of 2,4,5-trimethylbenzoic acid synthesis using nitric acid as oxidizer in order to completely exclude durol nitration reaction. For that reason catalytic influence of metal salts with mixed valence on the reaction behavior of 2,4,5-trimethylbenzoic acid formation was investigated. Metal nitrates content in reaction mass was kept within the interval from 0 to 13.6 mass %; mole ratio of durol : nitric acid – 1 : 11÷54. Concentration of nitric acid was within 37-56 mass %.

Since the reaction we are interested in is exothermic, application of thermochemical analytical procedures is possible for its investigation. We carried out calorimetric analysis by means of micro calorimeter DSC III (Setaram) with leak-proof cells, made of inert material and working under pressure up to 2MPa. The result of this research is the set of calorimetric curves, showing the temperature of investigated system at which the maximum oxidation reaction rate is occurred in the mode of linear heating.

As a conclusion of this analysis the catalytic activity of metal nitrates, decreasing in the following range: Fe>Cu>Co>Ni>Cr>Mn is established. It is observed, that iron and copper nitrates additions lead to the maximum effect on temperature decrease, corresponding to the maximum rate of reaction. When converting, 1 mass % of this additives conforms to about 4,7°C.

Therefore, applying salt additives of stated above metals in different amounts, the temperature of a durol oxidation process can be adjusted, reaching almost entire excluding of its nitration and other side reactions.

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### THERMODYNAMIC MODELING OF THE STEEL SLAGS RECOVERY PROCESS

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Development of rational techniques recycling of steel-smelting production slags (including slags of slagheaps) is the task remaining actual to present tense. One of the methods of deep processing of high-temperature slag is contained in the recovery of valuable metals with carbon. Thermodynamic modeling allows us to evaluate the possibility of such an approach.

For thermodynamic modeling high-temperature recovery slag of Zlatoust metallurgical factory's slagheaps were used programmatic complex "FactSage" (version 6.4), developed by "Thermfact" (Canada) and "GTT Technologies" (Germany) as well as databases (FSstel, FToxid, FactPS) compatible with it.

Data on the composition of the slag, which were used in the modeling process, obtained in the course of averaging the results of the quantitative analysis slag samples of Zlatoust metallurgical factory's slagheaps.

During modeling were assumed the existence of the gas phase (ideal gas under pressure of 1 atmosphere), which includes all the gaseous substances (91 substances) that contained in the FactPS database for a given set elements. In the course of calculation allows the existence in the system of almost all (with a few exceptions) the individual solids from used bases (346 substances). Selection of solutions of their total amount is carried out during a preliminary simulation.

In the simulation it is assumed that in an excessive amount introduced deliberately reducing agent (carbon).

The calculation was executed for the interval of temperatures 700-1700 °C with the step in 5 °C. The 201 set of numeral values was got. The basic results of modeling are presented as dependences of the components masses or the phases compositions on the temperature.

The modeling has made the following main practically relevant conclusions:

- 1) The metal mass that can be obtained by the recovery can be 18-20% by weight of the recycled slag.
- 2) The using of reducing agent (carbon) mass about the 10 % by masses of recyclable slag must be enough for realization of the procedure.
- 3) The liquid-phase recovery of slag it is expedient to conduct at temperatures about 1500 °C and higher with the purpose of metals more complete recovery and formation of the consolidated metallic phase.
- 4) At planning of aggregates for the technology realization is necessary to envisage measures on utilization of the large volume carbon monoxide and metals steams that present in the gas phase.
- 5) Implementation of the recovery process will require a significant investment of thermal energy.

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### POROUS SILICON SUPPORTED NANOCOMPOSITES FOR ELECTROCHEMICAL ENERGY CONVERTERS

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The development of fuel cells (FC) is considered as one of the main breakthrough technologies in the energetics of the 21st century [1-4]. The efficiency of the direct transformation of the chemical energy to the electric energy in the cells achieves 50-70%. The unique properties of the porous silicon (PS) offer the possibility for developing electrocatalytic composites with high surface area and for preparing specific catalysts in the structure directing porous matrix with the desirable size and shape [1-3]. Silicon micro fuel cells are promising power supplies for microelectronic applications, however their development is still at early stages compared to the conventional PEMFC (proton exchange membrane fuel cells). The fuel in the PS based FC is hydrogen, methanol, ethanol or formic acid, whereas the oxidant is the oxygen of the air. The reaction products are either H<sub>2</sub>O or H<sub>2</sub>O with CO<sub>2</sub>. In our previous works we have investigated the functional nanocomposite catalysts on porous silicon of n- and p-type with monometallic nanoparticles of Pt and Pd [2,3].

During the past several years, a few research groups have investigated another type of novel carbon nanostructures – graphene, which as a catalyst support have demonstrated the improved the electrocatalytic activity of Pt nanoparticles for methanol and ethanol oxidation compared to Vulcan XC-72R [1]. Bimetallic systems like Pt-Ru and Pt-Pd on different kinds of supports have attracted serious attention in recent years. Such catalysts had demonstrated high activity in respect to electrooxidation of hydrogen-containing fuel compared to the monometallic nanocatalysts on carbon substrates mainly due to the influence of the second metal [4].

Thus the objective of this work is to enhance the performance of micro fuel cells with novel platinum metal catalyst on porous silicon support (n- and p-type) in order to evaluate the influence of electrode structure and fuel cell architecture on the activity and long-term durability. For this purpose bimetallic Pt-Ru and Pt-Pd nanoparticles were synthesized by chemical reduction of platinum metal ions in water-organic solutions with ultrasonic treatment using NaBH<sub>4</sub> as reducing agent. By varying the synthesis conditions one can control the nanoparticles size, content and emerging properties. By means of the electron microscopy, phase analysis, cyclic voltammetry methods it was performed the investigation of nanocomposite functional properties. It was found that the highest electrocatalytic activity have composites which was obtained from reverse micelle solutions on silicon sheets with a porosity degree of 72%. According to the electron microscopy data, the nanoparticles are fixed not only on the surface but also in the porous silicon volume. The average size of the nanoparticles was about 3 nm. The obtained nanocomposites on porous silicon containing platinum metal nanoparticles of different composition, size and shape, can be used as functional membrane-electrode materials for micro-power energy converters.

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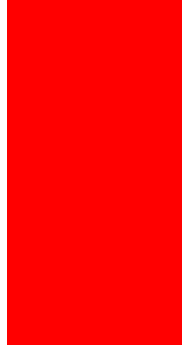
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