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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**DEVELOPMENT OF VANADATE AND
TITANATE FRACTIONS OF ACINOHUR
TITANMAGNETITE CONCENTRATES, SYNTHESIS
AND THERMODYNAMICS STUDY OF LITHIUM
POLYTITANATES AND POLYVANADATES**

Speciality: 2303.01 – Inorganic chemistry

Field of science: Chemistry

Applicant: **Ulviyya Novruz Sharifova**

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Dissertation work carried out in the laboratory "Processing of iron and titanium ore raw materials" at the Institute of Catalysis and Inorganic Chemistry named after academician Murtuza Nagiyev of Ministry of Science and Education of Azerbaijan.

Scientific supervisor: D. Chem. Sc., Professor
Asif Nasib Mammadov

Official opponents: D. Chem. Sc., Professor
Imir Ilyas Aliyev

D. Chem. Sc., Associate Professor
Yasin Isa Jafarov

PhD in Chem. Sc., Associate Professor
Ali Adil Ibrahimov

Dissertation council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Catalysis and Inorganic Chemistry named after academician Murtuza Nagiyev of Ministry of Science and Education of Azerbaijan.



Chairman of the Dissertation council:

D. Chem. Sc., Academician
Dilgam Babir Tagiyev

Scientific secretary of the Dissertation council:

PhD in Chem., Associate Prof.
Ulviyya Ahmad Mammadova

Chair of the Scientific Seminar:

D. Chem. Sc., Professor
Akif Shikhan Aliyev

GENERAL CHARACTERISTIC OF WORK

Relevance and degree of study of the topic. As a result of the systematic exploitation of titanium and vanadium-rich ore deposits, their reserves have significantly decreased. Many countries, including Azerbaijan, use such ores as titanium-based ilmenite, rutile, leucocoxene and vanadium-based vanadinite, decaussite, etc. it is deprived. Therefore, the development of the scientific foundations for the extraction of titanium and vanadium from titanomagnetite concentrates is one of the urgent issues. Titanomagnetite sand and sandstones, which belong to complex ore raw materials, are widely distributed in most regions of the Earth's crust, including Azerbaijan. Titanomagnetites consist mainly of solid solutions containing iron 2-titanate FeTiO_3 , magnetite Fe_3O_4 and $(\text{Fe}_3\text{O}_4)_{1-x}(\text{TiO}_2)_x$. Titanomagnetite sandstones contain 13-15 mass % Fe, 3-3.5% TiO_2 , 0.5% v. The concentrates obtained after enrichment contain target components – Fe – 45-54% by mass, TiO_2 – 5-7%, V – 0.7-1%. There are a number of pyrometallurgical and hydrometallurgical methods of extracting titanium and vanadium from titanomagnetite concentrates. These methods are based on high-temperature melting of concentrates to obtain vanadate cast iron and titanium slag, and then separation of cast iron-steel and vanadate slag. The resulting slags are processed by various chemical methods to remove titanium and vanadium. In the laboratory "Processing of iron and titanium ore raw materials" of the academician M.Nagiev Institute of Catalysis and Inorganic Chemistry, technological schemes of complex processing processes for obtaining iron ore, titanium and vanadium compounds by direct reduction of magnetite and titanomagnetite concentrates of the south-west coast of the Caspian Sea (Lankaran, Astara) shelf titanomagnetite sprinkles and Ajinohur sandstones with natural gas.

Until this research work, the issue of extracting vanadium from Acinohur titanomagnetite sandstones concentrates has not been studied. Although oxidation-reduction reactions, which form the basis of technological processes, proceed under gas flow conditions, the nonequilibrium thermodynamics approach was not used in thermodynamic modeling. The thermodynamic properties of the polytitanates of alkali metals, obtained in the process of extracting vanadates and titanates and which

are promising substances for ion batteries, have not been sufficiently studied. The process of obtaining titanium from the titanate phase by means of organic reducers has been little studied.

Object of research. Concentrates obtained from Acinohur titanomagnetite deposit ores of Azerbaijan were used in the research work.

The aim and tasks of the research. The purpose of the research work is the extraction and processing of vanadate, titanates from non-magnetic fractions, synthesis and thermodynamic research of substances with important application areas in the process of complex processing of adjinohur sandstone titanomagnetite concentrates. To achieve the purpose of the study, the following tasks were set and solved:

- Obtaining concentrates by enrichment of titanomagnetite powders by magnetic separation. Flustering and granulation of concentrates.
- Modeling of the temperature composition dependence of Gibbs energy of vanadium and titanium-containing concentrates, oxidation-reduction processes with natural gas with hydrogen and carbon-monoxide additive.
- Determination of the optimal mode of processes using the thermodynamic function of the nonequilibrium process, taking into account the fact that oxidation-reduction reactions take place in the reactor under gas flow conditions.
- Development and implementation of technological schemes of titanate and vanadate fraction processing processes.
- Synthesis and determination of thermodynamic properties of lithium polytitanates and vanadates of great practical importance using titanium dioxide and vanadium pentaoxide.

Research methods. DSC (brand NETZSCH STA 449f3 STA449F3A-0836-m), DTA (Netzsch 404 F1 Pegasus system) and XRF (dust diffractometer D8 Advance of Bruker, $\text{CuK}\alpha$ radiation), Thermo Scientific XRF spectrometer were used in the studies. As theoretical research methods, an analytical version of the mathematical apparatus of phenomenological thermodynamics, an asymmetric model of regular solutions, and the concepts of the theory of Fuzzy Logic were used. Origin-Lab, for calculations and analytical modelling Grafikus.ru, www.matematika.ru was conducted through computer programs.

The following are submitted for defense:

- The scheme and implementation of the processing of titanate and vanadate fractions of Acinohur titanomagnetite concentrates of Azerbaijan.

- Analytical and mathematical models of temperature dependence of Gibbs energy of vanadium and titanium concentrates, oxidation-reduction processes with natural gas with hydrogen and carbon-monoxide additives

- Obtaining of 99.5% purity Ti, TiO₂, V₂O₅ from titanomagnetite concentrates

- Experimentally determined values of Gibbs energy, enthalpy and entropy of lithium polytitanates and vanadates

Scientific novelty *Scientific novelty of the research is included in the list of important scientific results in the field of inorganic chemistry of ICIC for 2022.*¹

- The process of processing vanadate fraction of Acinohur titanomagnetite concentrates of Azerbaijan has been developed.

- In determining the conditions of oxidation-reduction processes, a fuzzy logic approach was used based on the differences of Gibbs energies of equilibrium and Nonequilibrium States.

- For the first time, it was established that the endothermic reaction $\text{Li}_2\text{CO}_3 + \text{TiO}_2 \rightarrow \text{Li}_2\text{TiO}_3 + n\text{CO}_2\uparrow$ consists of two combined reactions: 1) the decomposition of the starting substance lithium carbonate (endothermic) and 2) the reaction of titanium dioxide obtained from this reaction with lithium oxide, the decomposition product of lithium carbonate (exothermic). The exothermic reaction provides a complete synthesis of lithium titanate by stimulating the endothermic reaction.

- for the first time lithium titanates Li₄Ti₅O₁₂, Li_{1.92}Ti_{1.04}O_{3.04}, Li₂TiO₃, Li_{2.12}Ti_{0.94}O_{2.92}, Li₄TiO₄ and the Gibbs energy and entropy of lithium vanadates Li_{2+x}V₆O₁₆ (x=0.26-0.66) have been determined.

Scientific and practical significance.

Mathematical models of granulation of titanomagnetite concentrate powders in drum type apparatus and analytical 3D model of

¹ <https://kqkiamea.az/az/content/26>

temperature-pressure dependence of Gibbs energy can be used in ores processing processes. The thermodynamic parameters of the compound $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$, Li_2TiO_3 , $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$, Li_4TiO_4 və $\text{Li}_{2+x}\text{V}_6\text{O}_{16}$ ($x=0.26-0.66$) indicate the thermodynamic stability of these phases and the prospect of their use in lithium-ion batteries. The method of thermodynamic modeling of chemical reactions based on the fuzzy logic approach is included in the textbook written for Masters and is used in teaching; Dilqəm Tağıyev, Asif Məmmədov. *Gələcəyin kimyası / Chemistry of the future/*. 2019, səh.249-252

Approbation of work.

The results of the dissertation were included in the program of the following conferences and discussed: V Межд. Конф. Российского Химического Общества им. Д.И. Менделеева / Ресурсо- и энергосберегающие технологии в химической и нефтехимической промышленности. Москва, 2013; VI Межд. Конф. РХО им. Д.И.Менделеева / Химическая технология и биотехнология новых материалов и продуктов. Москва, 2014;

Materials of the conference dedicated to the 80th anniversary of the Institute of Catalysis and Inorganic Chemistry named after Nagiyev. Baku, 2016; Actual problems of modern chemistry and biology. International scientific conference. Ganja 12-13 may 2016, 5-6 may 2023; IX Всерос. Науч. конф. / Керамика и композиционные материалы. Сыктывкар, 2016; 22nd Intern. Conf. on Chem. Therm. in Russia - RCCT 2019. Saint Petersburg, Russia. June 19-23, 2019; 21st ICS Inter. Chem. Congress (ICC 2022), 26-28 July 2022, Tabriz, Iran; 15th Inter. Conf. on Appl. of Fuzzy Systems (ICAFS-2022), Budva, Montenegro, August 25-26, 2022. Международная конференция по естественным наукам и технологиям.

Personal contribution of the author.

He is the main shareholder in the implementation of the dissertation work, in the publication and approval of its results in the scientific press.

Publications on the topic of the dissertation. 19 scientific works related to the dissertation topic, including 1 patent, 8 articles (2 WoS, 3 in journals included in Scopus databases), 10 conference materials were published.

Structure and scope of work. The dissertation consists of introduction, 4 chapters, 17 tables, 4 schemes, 39 pictures, conclusions, list of used literature in 195 titles and has a volume of 133 pages. Chapter 1, table of Contents and introduction from 55000 conditional signs (30 pp.); Chapter 2, from 33500 conventional signs (24 pp.); Chapter 3, from 58500 conventional signs (42 pp.); Chapter 4 and the main conclusions from 22500 conventional signs (16 pp.), which consists of a total of 169 500 conventional signs, excluding the list of literature.

MAIN CONTENT OF THE WORK

In the introduction the relevance of the topic, its purpose, the issues solved are substantiated, the provisions put in defense, scientific innovations, the scientific and practical significance of the work are presented.

(kütlə %): 55-64% Fe, 2,5-17% TiO₂, 0,5-1,3% V₂O₅(V₂O₃), 0,5-3% SiO₂, 0,5-4% Al₂O₃, 0,1-1,05% Cr₂O₃, 0,5-3% MgO, 0,1-1,7% MnO). The technological scheme of the complex processing of granules of fluxed titanium magnetite concentrate was selected for the study.

The first chapter (literature review) is devoted to the composition of vanadium-containing titanomagnetite ore, its distribution in the ground, physico-chemical bases of processing methods, including thermodynamic modeling-testing. Titanomagnetites are mainly composed of ilmenite FeTiO₃, magnetite Fe₃O₄ and the solid solutions formed by them. Since their composition includes V⁺³ cations, which are isomorphic substitutes for the Fe⁺³ cations of magnetite, their composition also includes V₂O₃ oxides. Since the main part of them is oxidized to V⁺⁵ cation, they consist of vanadium pentoxide V₂O₅. Depending on the source, the composition of enriched titanomagnetite concentrates, including Titanomagnetite concentrates of Acinohur sandstones, is as follows (mass %): 55-64% Fe, 2,5-17% TiO₂, 0,5-1,3% V₂O₅(V₂O₃), 0,5-3% SiO₂, 0,5-4% Al₂O₃, 0,1-1,05% Cr₂O₃, 0,5-3% MgO, 0,1-1,7% MnO). For the study, a technological scheme of complex processing of granules of fluxed titanomagnetite concentrate was chosen. For the study, a technological scheme of complex processing of granules of fluxed titanomagnetite concentrate was chosen.

The topic of the second chapter is the complex processing of

titanomagnetite concentrates of Ajinohur sandstone, the separation of vanadate and titanate fractions. For obtaining concentrates of sandstones by enrichment and granulation, it was separated into fractions consisting of easy grinding particles with a size of 0.67 mm and difficult grinding with a size of 0.075 mm. In the composition of these fractions, target elements are found in the amount of Fe – 13-15%; TiO₂ – 2.3-3.0%; V – 0.6% and Mn – 0.7%. Taking into account the composition and size of the sandstones, water decontamination was carried out, and then wet magnetic separation was carried out on the basis (in 7800 erstets) and cleaning (in 500 erstets) by controlling the magnetic field tension. As a result, the content of target elements in the composition of titanomagnetite concentrates reached Fe_{um} - 45-52%; TiO₂ - 5-7%; V - 0.7-1% and Mn - 0.8%. Since the preparation of fractions with dimensions of 0,075 mm requires a lot of energy, less energy-intensive titanomagnetite concentrates with dimensions of 0,1 mm are fluffed with soda. Fluting was carried out by adding 25% anhydrous sodium carbonate to titanomagnetite concentrates, and the fluted concentrates were granulated with water in a drum-type granulator

The formation of granules in the drum apparatus: the processes of sequential accumulation and compaction of layers are modeled by the following equation proposed by Gudrat Kalbaliyev ².

$$a(t) = (a_0 + \gamma t)^{1/2} + a_0 \exp(-b_0 t) \sin\left(\frac{\nu t}{2}\right) \quad (1)$$

Here $\gamma = \frac{2R\omega\lambda}{\pi}$; a - current diameter of granule; a_0 - the average value of the diameter for the initial state of powder; b_0 - parameter regarding the density of particles of powder substance; t -granule formation time; R - radius of the drum assembly; λ - layer thickness; ω - drum unit rotation frequency; ν - dynamic is a parameter related to viscosity.

Experimental and theoretical studies have made it possible to determine the distribution and distribution of granules in the size and length of the apparatus (Fig. 1).

² Г.И.Келбалиев, Ф.М.Садыхов, Г.М.Самедзаде, А.Н.Мамедов, Д.Б.Тагиев. "Теория и практика гранулирования порошкообразных материалов". Баку: ЭЛМ. 2016. 330 с.

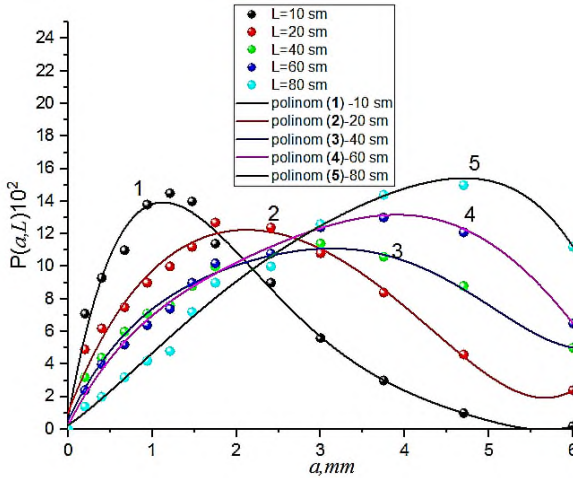


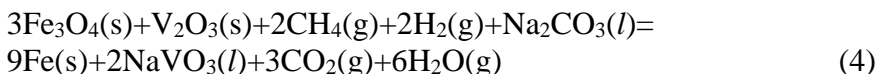
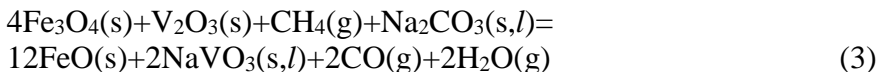
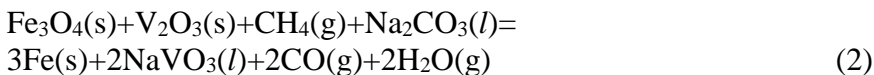
Fig. 1. Variation of the distribution function along the length of the drum granulator. The curves in the figure are modeled with polynomials of the 5th degree using the OriginLab computer program: $P(a,L) = B_0 + B_1 a + B_1 a^2 + B_1 a^3 + B_1 a^4 + B_1 a^5$

Coefficients of the distribution function: $P(a,L) = B_0 + B_1 a + B_1 a^2 + B_1 a^3 + B_1 a^4 + B_1 a^5$.

		Standard Error	t-Value	Prob> t	
10	Intercept	0,67974	0,78817	0,86243	0,41702
	B1	29,14574	3,50729	8,31004	7,14449E-5
	B2	-21,29035	4,40571	-4,83245	0,00189
	B3	6,08772	2,10023	2,8986	0,02303
	B4	-0,80333	0,41646	-1,92896	0,09507
	B5	0,0408	0,0289	1,41162	0,20093
20	Intercept	0,99946	0,72891	1,37117	0,21266
	B1	14,12013	3,24357	4,35328	0,00334
	B2	-6,8652	4,07443	-1,68495	0,13587
	B3	1,81787	1,94231	0,93594	0,38046
	B4	-0,3076	0,38514	-0,79867	0,45073
	B5	0,02184	0,02673	0,81711	0,44079
40	Intercept	0,48597	0,39395	1,2336	0,25716
	B1	11,67366	1,75304	6,6591	2,8809E-4
	B2	-6,624	2,20209	-3,00805	0,01972
	B3	2,31662	1,04975	2,20683	0,06309
	B4	-0,41925	0,20816	-2,0141	0,08386
	B5	0,02777	0,01445	1,92199	0,09605
60	Intercept	0,26741	0,36265	0,73739	0,48486
	B1	10,05656	1,61376	6,23177	4,31715E-4
	B2	-4,50293	2,02713	-2,22133	0,06176
	B3	1,36966	0,96635	1,41736	0,19932
	B4	-0,21534	0,19162	-1,12378	0,29816
	B5	0,01173	0,0133	0,88221	0,40694
80	Intercept	0,23774	0,51279	0,46362	0,65699
	B1	3,84797	2,28185	1,68633	0,13559
	B2	1,04472	2,86637	0,36447	0,72626
	B3	-0,53535	1,36642	-0,39179	0,70687
	B4	0,09258	0,27095	0,34168	0,74262
	B5	-0,00696	0,0188	-0,36988	0,72241

Standard Error was scaled with square root of reduced Chi-Sqr.

The reactions of direct reduction of magnetite to iron 2 oxide, free iron, oxidation of V^{+3} to V^{+5} in granules of sodium-vanadium-titanomagnetite concentrates fluted with sodium soda are as follows:



Titanium dioxide, which does not participate in the oxidation-reduction process, is not included in the TiO_2 reaction equation. The temperature dependencies of the Gibbs free energy of reactions in the 900-1200K temperature range (2-4) are determined by the Temkin-Schwarsman equation version, developed by A.N.Məmmədov³ was used

$$\begin{aligned} \Delta G_T = & \Delta H_{298}^0 - \Delta S_{298}^0 T - T \left(\Delta a \left(\ln \left(\frac{T}{298} \right) - \frac{298}{T} - 1 \right) + \right. \\ & \Delta b \left(\frac{T}{2} + \frac{298^2}{2T} - 298 \right) + \Delta c^* \left(\frac{T^2}{6} + \frac{298^3}{3T} - \frac{298^2}{2} \right) + \\ & \Delta c \left(\frac{T^{-2}}{2} + \frac{298^{-1}}{-T} + \frac{298^{-2}}{2} \right) - nRT [x \ln f(x) + (1-x) \ln f(1-x)] + \\ & RT \sum v_i \ln P_i \end{aligned} \quad (5)$$

$\Delta G_T, \Delta H_{298}^0, \Delta S_{298}^0$ - are the values of the standard Gibbs energy, enthalpy and entropy formation of substances in (2-4) reactions.

v_i - stoichiometric coefficients;

P_i - partial pressures of components in a nonequilibrium state (the reaction goes in the reactor in the gas mixture flow mode).

$RT [x \ln f(x) + (1-x) \ln(1-x)]$ - Gibbs free energy of solid solutions $x\text{Fe}_3\text{O}_4 + (1-x)\text{V}_2\text{O}_3 \rightarrow \text{Fe}_{3x}\text{V}_{2(1-x)}\text{O}_{3+x}$;

formed by replacing Fe^{3+} ions with V^{3+} ions Fe_3O_4 in the crystal lattice: n is the number of non-identical cations in the crystal lattice;

³ А.Мамедов. «Термодинамика систем с немOLEкулярными соединениями». LAP LAMBERT Academic Publishing. 2015.115 с.

the last member of eq. (5) takes into account the deviation of the process from the equilibrium state in the gas flow regime.

Fig. 2 shows the results of the calculations carried out using the equation (5) to determine the nature of the outflow from the equilibrium state, three-dimensional modeling of the dependence of the reduction of iron and vanadium with a mixture of methane and hydrogen on the ratio of partial pressures in the flow mode was carried out (Fig. 3).

Fig. 2 and 3 show that (2-4) reactions occur when gas reaction products are removed, and the reactions proceed under non-equilibrium thermodynamic conditions, at lower temperatures. At the lowest temperature, at 950 k, the reaction (4) begins. This is due to the fact that in the phase of the reducing gas, in addition to methane, there is also hydrogen.

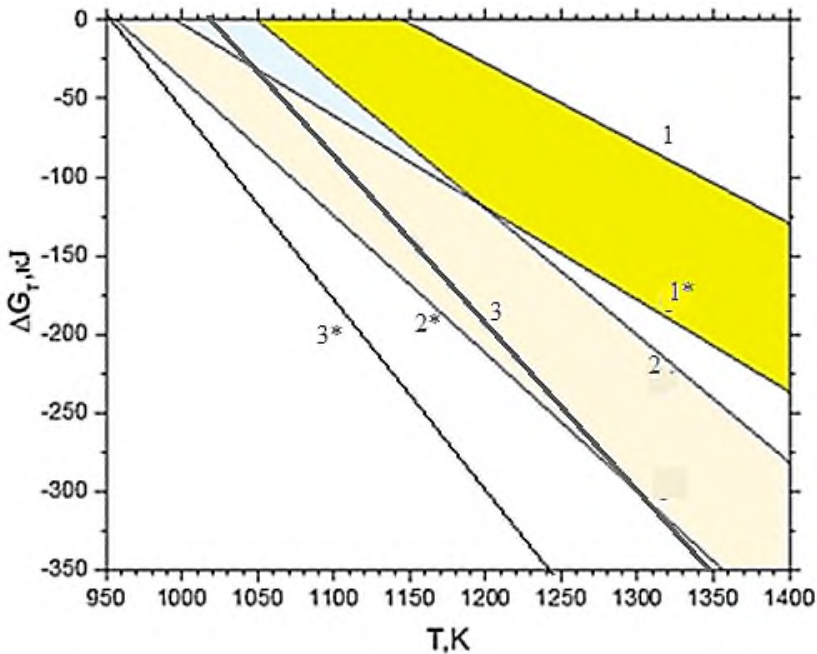


Fig 2. Dependencies of the Gibbs energies of the reactions (2-4) on temperature in the equilibrium state (line 1, 2, 3) and in the non-equilibrium state (line 1*, 2*, 3*).

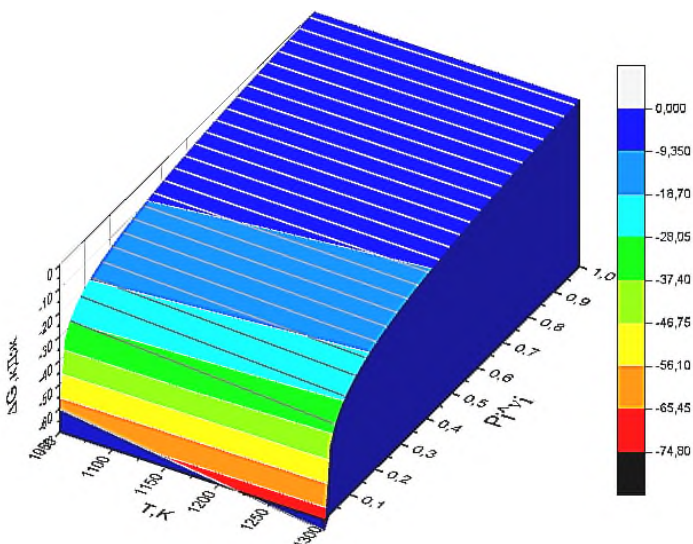
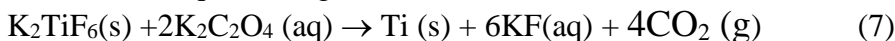
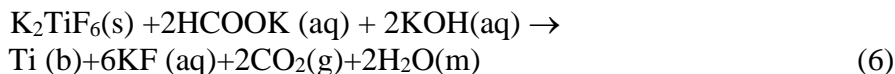


Fig. 3. Three-dimensional model of the dependence of Gibbs energy on the ratio of partial pressures in the gas flow mode of a mixture of methane and hydrogen in the reaction of reduction and vanadium oxidation of iron.

3D analytical model of the difference between free Gibbs energies of reactions under equilibrium and nonequilibrium conditions (Fig. 3) shows that a sharp decrease in the temperature of oxidation-reduction reactions is observed in the region of low pressure values of the reaction products ($\sum_1^n P_i^{Y_i} < 0.01 \text{ atm}$). As a result of thermodynamic analysis, a temperature range of 950-980 K was selected to obtain metallic iron and sodium vanadate.

As a result of the non-magnetic fraction processing of titanomagnetite concentrates, titanium dioxide (rutile modification) of technical purity was obtained (Fig. 4).

Titanium metal was obtained at 80-100°C using organic reducers (Fig. 5):



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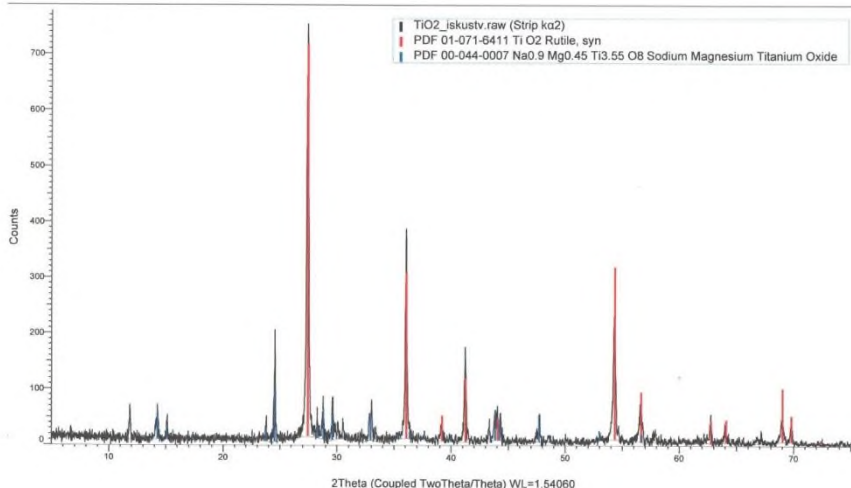


Fig. 4. Diffractogram of rutile (99%TiO₂) obtained from incandescent of polytitanate nTiO₂·mH₂O acids

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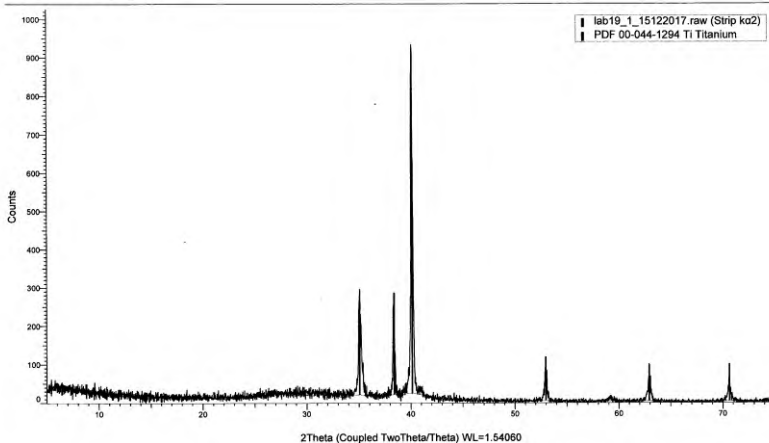
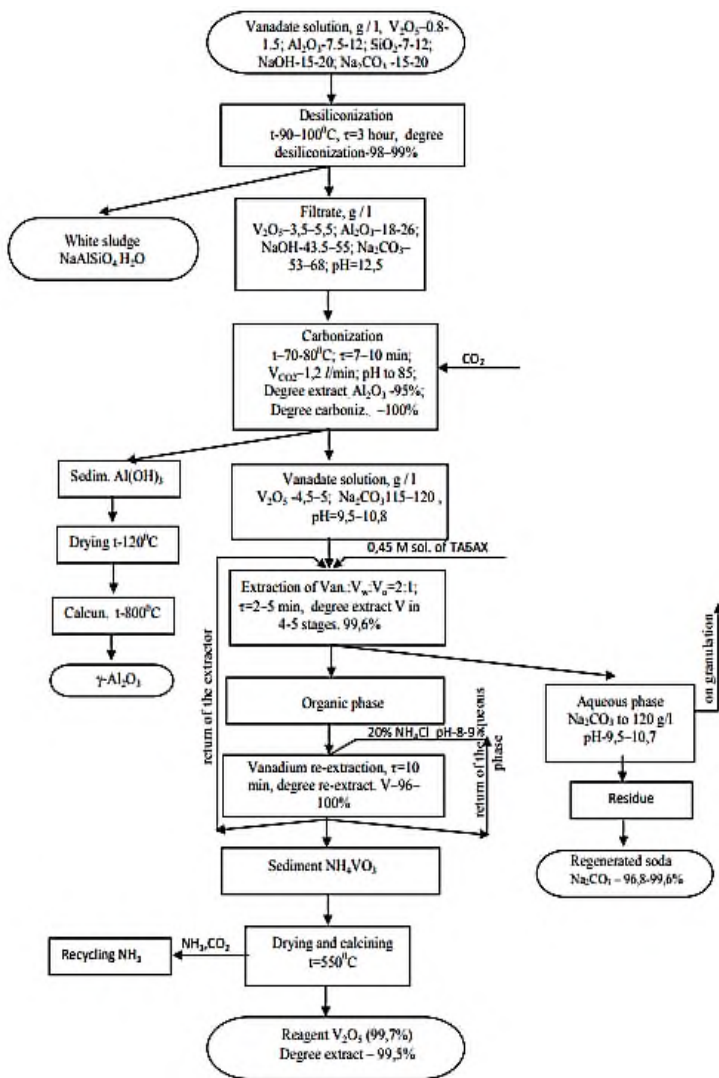


Fig. 5. Diffractogram of Ti (99%) powder obtained by means of reactions (6 and 7)

The topic of the third chapter is the study of carbonization purification and recycling conditions of carbonate-vanadate solutions in

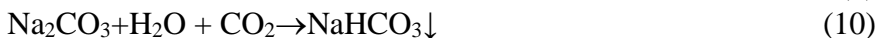
complex processing of titanomagnetite concentrates. The processing of carbonate – vanadate solutions by the carbonization phase method and the obtaining of vanadium pentoxide are summarized in Scheme 1.



Scheme 1. Technological scheme of vanadate fraction processing [List of published 15]

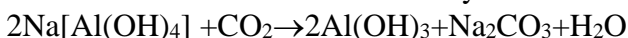
The scheme for processing vanadate solution by carbonization consists of these stages: the stage of silicification of the solution with the separation of white slurry - sodium hydroaluminosilicate (degree of silicification 98-99%); phased carbonization by carbon dioxide, consisting of aluminum hydroxide deposition and carbonization stage by aluminum oxide extraction (aluminum oxide removal rate 95%), sodium bicarbonate deposition and regeneration of soda used (soda removal rate 95%, purity 96.7-99.5%), and to obtain technical V₂O₅ (deposition rate V₂O₅-97%, total actual extraction of vanadium 99.5%, purity 93.8%) deposition stage. The developed technological scheme is efficient, does not require expensive reagents, is waste-free and closed.

During carbonization, the precipitation of sodium aluminosilicate, the conversion of caustic alkali into sodium carbonate, and the precipitation of sodium bicarbonate are carried out step by step.:



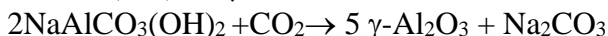
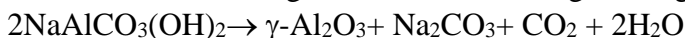
To study the conditions of carbonization of vanadate solutions by separation of aluminum compounds, after silicification (reaction 8), a vanadate solution of the following composition was studied, g/l: V₂O₅ - 3.5; Al₂O₃ - 22; Na₂O(total)- 68.5; Na₂O(caustic)- 37.5; Na₂O(carbonate) - 3.1; (NaOH - 46.4; Na₂CO₃ - 53) pH = 12.5.

Deposition reaction of aluminum orthohydroxide:



The solution also contains a partially sodium aluminum carbonate base salt $\text{Al}(\text{OH})_3 + \text{Na}_2\text{CO}_3 \rightarrow \text{NaAlCO}_3(\text{OH})_2 + \text{NaOH}$

During roasting (incandescent) of the precipitate at 1000⁰C, dauzonite and sodium aluminate decompose with the formation of Al₂O₃ and Na₂CO₃, since the following reactions occur during roasting:

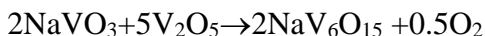


These reactions are confirmed by the diffraction pattern of X-rays of incandescent aluminum hydroxide compounds at 1000⁰C. It should be emphasized here that one of the undesirable phenomena in the production of γ - aluminum oxide is the passivation of aluminum oxide into

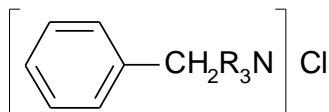
the α -form, since γ -oxide is more valuable, has chemical activity and better catalytic properties. The change in the modification of the crystal grid of aluminum oxide during the burning of Gibbsite and other aluminum compounds is carried out by the active action of high temperatures and water vapor.

After soda regeneration from a solution of vanadate purified from mixtures of silica and aluminum, by phased carbonization of the solution with carbon dioxide and precipitation of the main soda mass (96%) in the form of sodium bicarbonate, the purified vanadate solution contains 68.5-60 g/l V_2O_5 and 70 g/l Na_2CO_3 . The pH of the solution is 1,8-2. One of the accepted methods for removing vanadium from such solutions is hydrolytic deposition of vanadium pentoxide

As a result of solidification and heating of vanadate solutions, sodium metavanadate is obtained from the reaction of vanadium pentoxide with soda. Metavanadate, on the other hand, reacts with vanadium pentoxide in excess to form polyvanadates (Figure 6), including NaV_6O_{15} :



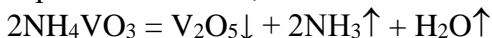
Extraction of vanadium pentoxide by extraction method. Technical TABACH (trialkylbenzylammonium chloride) solution was used for extraction [20]:



Where R is the alkyl radical: $C_7 - C_9$.

A 0.45 M TABAKH solution allows you to remove vanadium directly from carbonate solutions. When removing vanadium in a carbonate environment (V_2O_5 - 4.5 g/l, Na_2CO_3 - up to 120 g / l), the degree of removal of vanadium even when carbonate ions are 20 times higher (t-2-5 min, $V_{H_2O} : V_{org} = 2 : 1$, pH-10.8-11) is quite high for one stage -60%, and in 5-6. When extracting vanadium from carbonate-vanadate solutions, the saturation of the TABAKH solution with vanadium was from 21 to 28.8 g/l. A number of compounds were tested to study the conditions for the re-extraction of vanadium from the extractant. The most effective re-

gents were solutions of NH_4Cl and $(\text{MH}_4)_2\text{CO}_3$ salts. Studies have shown that in $V_{\text{H}_2\text{O}}: V_{\text{org}} = 2:1$ and reextraction with ammonium chloride at a time of 10 minutes, the maximum removal of vanadium occurs at a concentration of NH_4Cl 20%, while when using a solution of 40% $(\text{NH}_4)_2\text{CO}_3$, the separation rate already at one stage reaches 90%. When the separated nh_4vo_3 ammonium metavanadate is dried to a constant weight and heated to a temperature of 550°C , vanadium 5-oxide is obtained:



The aqueous phase with residual vanadium is returned to the retraction process again. After the decomposition of NH_4VO_3 , vanadium pentoxide with a reactive purity of 99.7% is obtained in accordance with the qualitative analytical degree (Fig. 7).

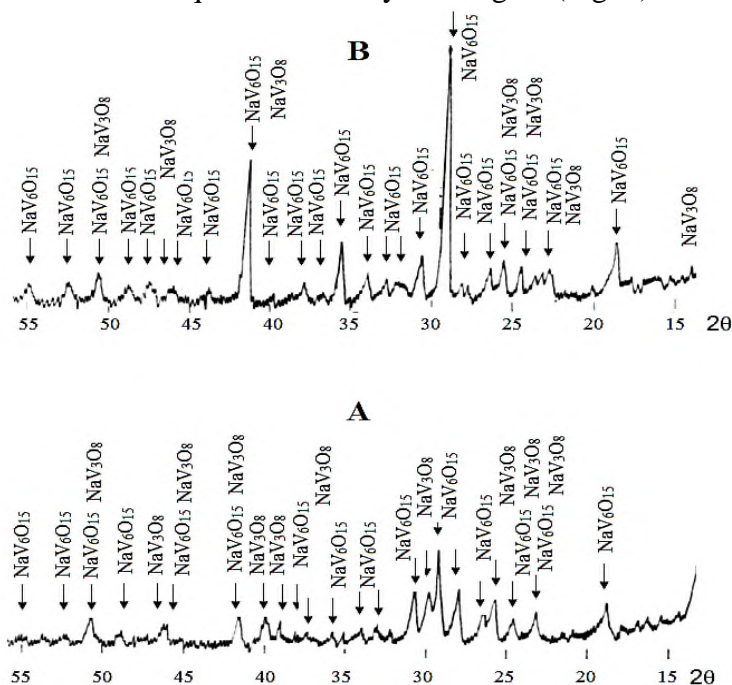


Fig. 6. A-diffractogram of the sample of sodium polyvanadates precipitated from artificial solutions of sodium vanadate at 500°C ; B-diffractogram of the sample of sodium polyvanadates precipitated from concentrated vanadate solutions obtained from the processing of Acinohur sandstone titanomagnetite concentrates at 600°C

Obtaining vanadium pentoxide from metavanadate and polyvanadates occurs by the following reaction:

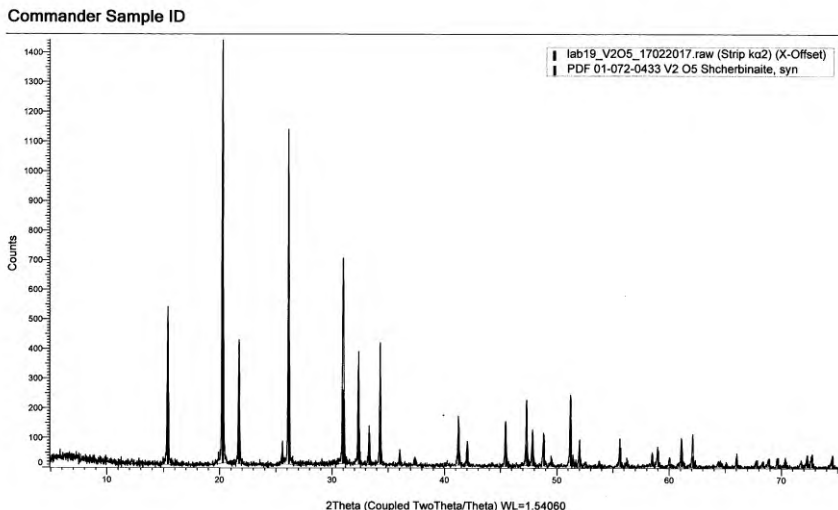
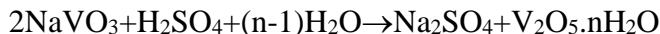
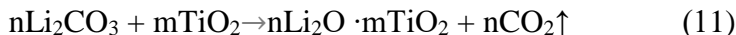


Fig. 7. Diffractogram of vanadium pentoxide powders from vanadate solutions

The fourth chapter is devoted to the synthesis and thermodynamic research of lithium titanates and vanadates using titanium dioxide and vanadium oxides obtained from the processing of titanomagnetite concentrates.

Lithium titanates are obtained by melting a mixture of lithium carbonate and titanium dioxide in stoichiometric proportions according to the reaction:



For the synthesis Li_2CO_3 with a purity of 99,9%, marked 2-2-3 and TiO_2 with a purity of 99.8%, marked 6-09-01-629-83 were used. The results of derivatographic analysis of the reaction of lithium carbonate and titanium dioxide in the equimolar ratio (12) are shown in Fig. 8.

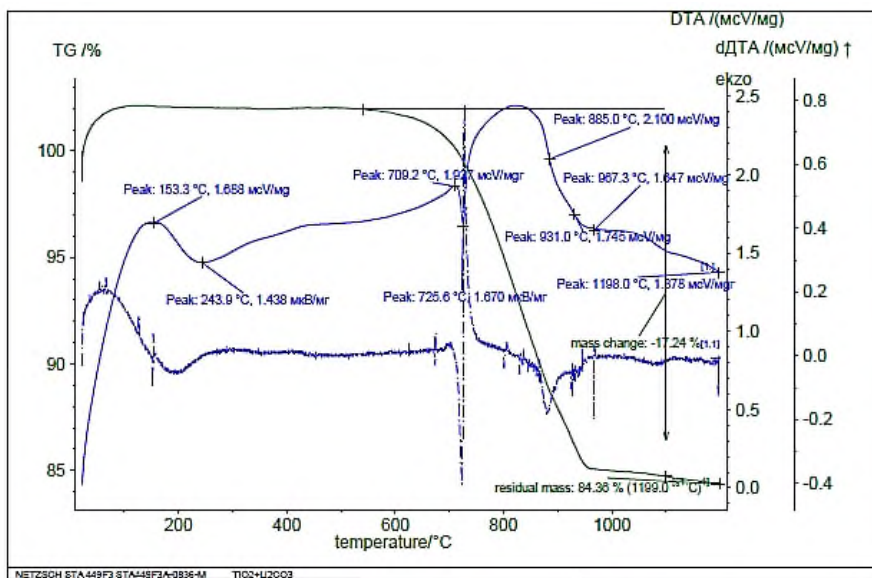
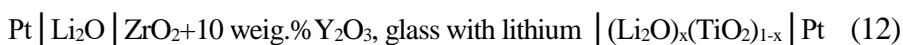


Fig. 8. Results of derivatographic analysis of the reaction of lithium carbonate and titanium dioxide in the equimolar ratio Li₂CO₃:TiO₂= 1: 1.

From the TA and DTA curves in Fig. 8 it follows that at 153 C an endothermic process occurs, associated with the dehydration of the moisture present in the mixture of reagents. The exothermic minimum is due to the reaction between TiO₂ and Li₂O, which is achieved by the decomposition of Li₂CO₃. Thermodynamic calculation of the enthalpy of the Li₂O + TiO₂→Li₂TiO₃ reaction shows that this reaction is exothermic. The temperature of this exothermic reaction (11) makes the endothermic reaction complete at 726⁰C.

To determine the thermodynamic parameters of lithium titanates, the EMF of the following concentration circuits was measured:



The thermodynamic parameters calculated based on the values of the electrical force of action of the element (12) are presented in Table 1.

Table 1

Thermodynamic functions and values of standard entropy of the formation of lithium titanates from simple substances and compounds Li₂O, TiO₂ (denoted*)

Compound	$-\Delta G_{1200K}^{0,*}$	$-\Delta H_{1200K}^{0,*}$	$-\Delta S_{1200K}^{0,*}$	$-\Delta G_{298}^0$	$-\Delta H_{298}^0$	S_{298}^0
	kJ/mol		J/mol. K	kJ·/mol		J/mol. K
Li ₄ Ti ₅ O ₁₂	356.1±4	371.1±5	12.51±0.2	5923±30	6287±40	315.7±4
Li ₂ TiO ₃	115.2±1	120.2±2	4.16±0.2	1565±10 1571±10	1662±20 *1668±20	84.0±2 *91.8±2
Li ₄ TiO ₄	137,9±1	146.1±3	8.82±0.2	2149±10	2286±15	119.1±3

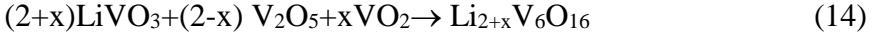
* *The database. Thermal constants of substances./orish V.S., Jungman V.S. //Institute of Thermophysics of Extreme States of the Russian Academy of Sciences. Faculty of Chemistry. Moscow State University. -2006.*

Comparison of the free energies of the formation of compounds Li₄Ti₅O₁₂, Li_{1.92}Ti_{1.04}O_{3.04}, Li₂TiO₃, Li_{2.12}Ti_{0.94}O_{2.92}, Li₄TiO₄ from compounds Li₂O and TiO₂ (Table 1) shows that Li₂TiO₃ has the highest stability. At the same time, the compounds Li₄Ti₅O₁₂, Li_{1.92}Ti_{1.04}O_{3.04}, and Li_{2.12}Ti_{0.94}O_{2.92} have relative stability compared with neighboring phases. The components Li₄Ti₅O₁₂, Li_{1.92}Ti_{1.04}O_{3.04}, and Li_{2.12}Ti_{0.94}O_{2.92} are boundary phases for the region of homogeneity of Li₂TiO₃.

Vanadium oxide bronzes of alkali metals have such areas of application as OVB (vanadates), including lithium vanadates, catalyst, comparison electrodes, anticorrosion materials, electronic appliances. The general formulas of lithium vanadates are as follows: Li_{2+x}V₆O₁₆ (x=0.26-0.66) the formula contains vanadium atoms in V⁺⁵, as well as V⁺⁴, which is the reason for the outflow from stoichiometry. To determine the thermodynamic parameters of lithium vanadates the EMF of following concentration circuits were measured at a temperature range of 900-1200K:



The potentiating reaction of the element (13) is as follows:



The dependence of the standard thermodynamic parameters of lithium vanadates on the composition is presented in Fig. 9

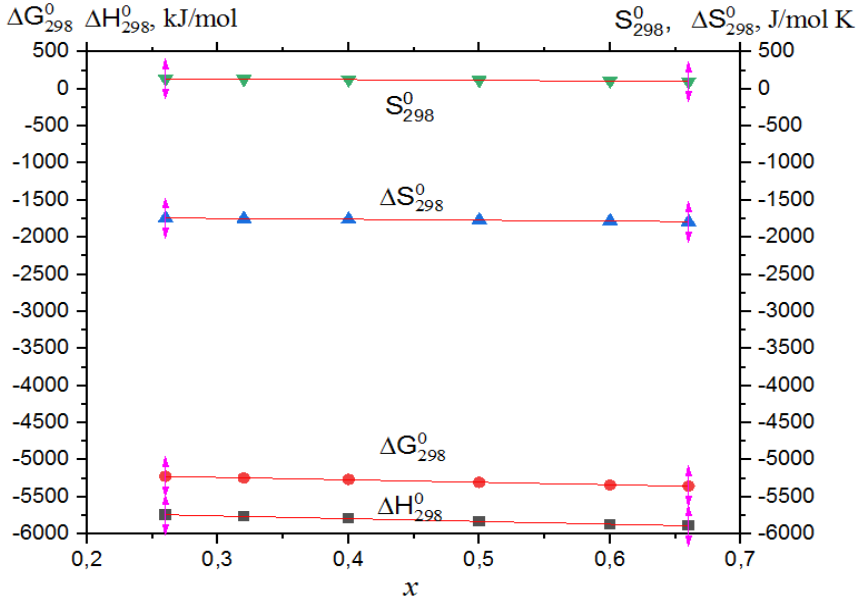


Fig. 9. Composition dependence of entropy, enthalpy, Gibbs energy and standard entropy of $\text{Li}_{2+x}\text{V}_6\text{O}_{16}$ lithium vanadates:

$$S_{298}^0 \left(\frac{\text{C}}{\text{mol.K}} \right) = 163.1 - 92.17x; \quad \Delta S_{298}^0 \left(\frac{\text{C}}{\text{mol.K}} \right) = -1708 - 121.7x;$$

$$\left(\Delta G \left(\frac{\text{kJ}}{\text{mol}} \right) = -5134 - 334.4x; \quad \Delta H_{298}^0 \left(\frac{\text{C}}{\text{mol.K}} \right) = -5643 - 372.7x;$$

Fig. 9 on the basis of analytical dependencies, the following equations for the temperature-composition dependence of Gibbs energy were obtained.

$$\Delta G \left(\frac{\text{kJ}}{\text{mol}} \right) = -5643 - 372.7x + (1,708 + 0,1217x)T \quad (15)$$

Here $y=x$; $x=T$. The 3D image of the equation (3) by means of the “analyze” function of the OriginLab program is presented in Fig. 10.

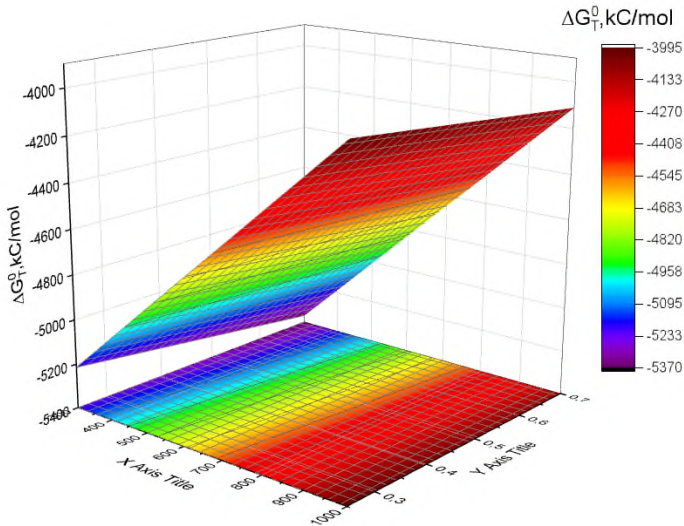


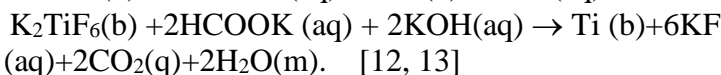
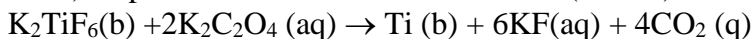
Fig. 10. 3D image of the dependence of the Gibbs energy of formation of $\text{Li}_{2+x}\text{V}_6\text{O}_{16}$ lithium vanadates on temperature and composition

The composition-temperature dependencies of the entropy, enthalpy, Gibbs energy and standard entropy of $\text{Li}_{2+x}\text{V}_6\text{O}_{16}$ lithium vanadates indicate the stability of these substances over a wide temperature range. Relatively small values of absolute entropy S_{298}^0 are a sharp decrease in entropy of a three-component compound when it is formed from two-component compounds. This shows that $\text{Li}_{2+x}\text{V}_6\text{O}_{16}$ crystals have high regularity.

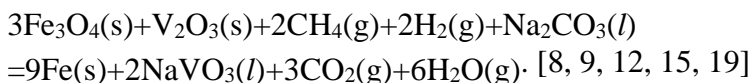
MAIN RESULT

1. Taking into account the composition and size of the Acinohur sandstones, water decontamination was carried out, magnetic separation of the main (7800 ersted) and purifying (500 ersted) was carried out by controlling the magnetic field voltage, and the content of target elements in titanomagnetite concentrates was increased to Fe - 45-52%; TiO_2 - 5-7%; V - 0.7-1%. The process of obtaining soda fluted granules from titanomagnetite concentrate powders in drum type apparatus and the temperature and pressure dependencies of Gibbs energy of oxidation-reduction reactions are modeled [1, 7, 6, 8, 13-15].

2. High purity titanium (99.5% Ti) was obtained from the treatment of titanomagnetite concentrates, including ilmenite, with hexafluorsilicate acid and potassium chloride with organic reducers (HCOOK, $K_2C_2O_4$) of potassium hexafluorite titanium salt (K_2TiF_6):



3. Using a fuzzy logic approach based on the differences in Gibbs energies of equilibrium and nonequilibrium states of the reaction of direct reduction of magnetite to free iron and oxidation of V^{+3} to V^{+5} under gas flow conditions with hydrogen added natural gas the temperature range of 950-980 K was selected to obtain metallic iron and sodium vanadate on the reaction



4. The block scheme of the complex processing of titanomagnetite concentrates by carbonization of carbonate-alkaline vanadate solutions fraction has been developed and implemented. The scheme for processing vanadate solution by carbonization consists of these stages: the stage of silicification of the solution with the separation of white slurry - sodium hydroalumin-osilicate (degree of silicification 98-99%); phase of carbonization with aluminum hydroxide deposition and carbonization stage with aluminum oxide extraction, phase of carbonization with carbon dioxide consisting of sodium bicarbonate deposition and regeneration of soda used (soda removal rate 95%, purity 96.7-99.5%) and hydrolytic deposition stage of hydrated vanadium pentoxide to obtain technical V_2O_5 (deposition rate V_2O_5 -97%, total actual extraction of vanadium 99.5%, purity 93.8%) [12.15].

5. The Gibbs energy, enthalpy and entropy of the compounds $Li_4Ti_5O_{12}$, $Li_{1.92}Ti_{1.04}O_{3.04}$, Li_2TiO_3 , $Li_{2.12}Ti_{0.94}O_{2.92}$, Li_4TiO_4 were determined by the method of electric force of action. The thermodynamic functions of formation of other compounds other than Li_2TiO_3 have been determined for the first time. Comparison of the free energies of the formation of compounds $Li_4Ti_5O_{12}$, $Li_{1.92}Ti_{1.04}O_{3.04}$, Li_2TiO_3 , $Li_{2.12}Ti_{0.94}O_{2.92}$, Li_4TiO_4 from compounds Li_2O and TiO_2 shows that

Li_2TiO_3 has the highest stability. At the same time, the compounds $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{1.92}\text{Ti}_{1.04}\text{O}_{3.04}$ and $\text{Li}_{2.12}\text{Ti}_{0.94}\text{O}_{2.92}$ have relative stability compared with neighboring phases and can be used to make lithium-ion batteries [10, 14, 16, 17].

6. Using V_2O_5 from vanadate phase, $\text{Li}_{2+x}\text{V}_6\text{O}_{16}$ ($x=0.26-0.66$) lithium vanadates were synthesized and thermodynamic parameters were determined by EFM method. The composition-temperature dependencies of entropy, enthalpy, Gibbs energy and standard entropy of lithium vanadates indicate the stability of these substances over a wide temperature range. Relatively small values of absolute entropy S_{298}^0 are a sharp decrease in entropy of a three-component compound when it is formed from two-component compounds. This shows that $\text{Li}_{2+x}\text{V}_6\text{O}_{16}$ crystals have high regularity [15].

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