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Thermodynamic modelling as a basis for forecasting phase states of hydrocarbon fluids at great and super-great depths

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Abstract. The possibility of discovering oil and gas occurrences at great (more than 5 km) and super-great (more than 6 km) depths is considered in two aspects. The first one is the preservation conditions of large hydrocarbon accumulations forming at depths to 4 km and caused by different geological and tectonic processes occurring at great and super-great depths with partial oil-to-gas transformation. It was ascertained that among the factors controlling preservation of liquid and gaseous hydrocarbons are the temperature, pressure, subsidence rate (rate of temperature and pressure increase), time spent under ultrahigh thermobaric conditions, and initial composition of organic matter. The possibility of existence of liquid components of oil at great and super-great depths is characteristic of sedimentary basins of China, the Gulf of Mexico, the Santos and Campos basins on the Brazilian shelf, and in the Russian Federation it is most probable for the Caspian Depression, some submontane troughs and zones of intense accumulation of young sediments. Determination of critical temperatures and pressures of phase transitions and the onset of cracking is possible using the approach considered in the article, based on estimation of organic matter transformation degree, kinetic and thermobaric models taking into account the composition of hydrocarbon fluid. The second aspect is the estimation of composition of hydrocarbons associated with rocks forming at great depths or rocks transformed under conditions of critical temperatures and pressures. This aspect of considerable science intensity can hardly be considered as practically significant. The study focuses on the investigation of the possibilities of thermodynamic modelling and the use of alternative methods for studying the transformation degree of liquid formation fluid into components of the associated gas through the example of two areas with identified oil, condensate and gas accumulations.

Keywords: deep oil; thermodynamic modelling; hydrocarbon phase transitions; hydrocarbon preservation; deep occurrences

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Introduction. A large number of oil and gas occurrences recently discovered at great and super-great depths due to the development of drilling technologies and indirect signs of the occurrence of reservoirs in supercritical thermodynamic conditions call for reconsidering the theoretical ideas about the conditions of hydrocarbon (HC) generation and preservation in high pressure and temperature zones as well as developing the methods for prospecting zones of decompression or stability of reservoirs [1, 2].

The following issues are most often discussed and debated:

• arguments for the presence of oil and gas generation signs at great and super-great depths;

• influence of thermobaric conditions on HC generation and breakdown;

• influence of subsidence and upwarping rate and extent determining the time of high temperature impact on HC generation and reformation;

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• identification of criteria (boundary values) of HC phase transitions;

• influence of initial composition and transformation of organic matter, such as kerogen, on phase composition of the generated HC;

• influence of lithological composition, sedimentation conditions and diagenesis of kerogen-bearing strata on their hydrocarbon potential, migration and accumulation conditions;

• influence of overlying salt-bearing strata and deep conductive faults significantly changing the distribution of temperature and pressure gradients and determining the character and maximum occurrence depth of oil and gas accumulations;

• influence and contribution of deep methane to generation of HC accumulations including high-molecular compounds.

Although the elaboration of these issues influences the development of theoretical concepts to varying degrees, only their joint consideration allows to hope for a possibility of obtaining practical results and specific technologies of prospecting for hydrocarbon accumulations at great and super-great depths.

A bright example of the influence of theoretical developments on the implementation of practical achievements is the discussion that took place in the 50-60s of the last century on the origin and migration of oil, which made it possible to conduct mass experiments, arrange the knowledge and ideas into well-organized theories, identify the research methods, patterns and dependencies fit for practical use that were later implemented as highly efficient technologies for prospecting and exploration of oil and gas accumulations. The basis for these prospecting technologies were experimentally proved balance equations that do not contradict the laws of physics and chemistry and allow calculating volume ratios of the products of organic matter components transformation into hydrocarbon compounds [3-5], and later to develop the tools for numerical basin modelling and successfully use them in forecasting and estimating of oil and gas presence potential.

Decreasing efficiency of geological exploration caused by exhaustion of large anticlinal traps of oil and gas led to the need for a comprehensive analysis of all processes of oil and gas ontogenesis, starting from identification of possible sources, burial conditions of sediments enriched in organic matter, the subsidence history (influence of temperatures and pressures), migration routes, distribution of accumulation, and preservation zones of the generated hydrocarbons. The developed basin modelling technology was efficiently integrated into the process of geological exploration and estimation of hydrocarbon potential, therefore, the theory of adherents of deep origin of oil and gas, which at that time had no obvious practical solution [6, 7], turned out to be unclaimed.

The challenge of the new millennium associated with a fundamentally new raw material base confined to low-permeability shale and carbonate strata, forced to reconsider the notions not so much of oil and gas generation, but of one of the processes of ontogenesis – migration (emigration from generation strata) as well as the efficiency of use and technological build-up of porosity and permeability space. At the same time, the theory of oil generation was further developed due to a detailed study of oil-producing strata enclosing mobile hydrocarbons that did not emigrate from them.

Analysis of the influence of a set of the above factors on the prospects of deep-seated complexes taking into account new investigations and achievements mainly in the sedimentary basins of China (Tarim, Dzungar, Ordos, Sichuan), the Gulf of Mexico and the shelf of Brazil (Santos) allowed typifying the sedimentary basins and large depressions in the RF with distinguishing of potential areas for the study of HC at great and super-great depths.

Thermobaric and historical geological criteria were elaborated, and a methodology for a detailed study of potential areas was proposed including geochemical studies of hydrocarbons and their extracts (pyrolytic, chromatographic), lithological and petrophysical studies of core aimed at estimating the prospects of oil and gas presence in deep-seated complexes in the sedimentary basins of the RF and subsequent localization of the most promising areas for deep drilling.

Thermodynamic modelling is widely used to estimate phase composition and thermodynamic parameters of generation and transformation of hydrocarbon occurrences at great and super-great

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depths, along with experimental studies that partially reproduce the environment at great depths. It is based on the assumption of a local equilibrium in the system, which allows making calculations using the mathematical methods of equilibrium thermodynamics. As shown by numerous investigations, the assumption of achieving the equilibrium can be considered justified if the processes occur at a high temperature (>1,500 K), or the time available to establish the equilibrium is sufficient [8].

Theoretical foundations of thermodynamic analysis were formulated by Gibbs in his work [9]. It was found that all known methods for calculating the composition and parameters of the equilibrium state of real thermodynamic systems can be divided into combined and direct. Combined-type algorithms are applicable not only to slightly nonideal, but also to strongly nonideal thermodynamic systems. Direct algorithms, unlike the combined ones, presume a direct calculation of the equilibrium composition and parameters of real systems. The equilibrium state is characterized by preset values of temperature and pressure or temperature and volume, therefore, the algorithm for calculating the equilibrium composition under isobaric isothermal conditions deserves consideration first.

Experimental studies of water-oil fluids showed that to 320 °C phase composition and state of oil remained unchanged. However, at higher temperatures, especially in the 350-380 °C range, and pressures close to saturated steam pressures and higher (to 150 MPa), oil begins to actively change with generation of methane, butane, propane, and carbon dioxide. At the same time, the proportion of light fractions in the fluid increases, they occur in the gas phase as condensate or the so-called invisible oil. Solid bitumen also appears. At 550-600 °C, oil is completely transformed into methane and anthraxolite, up to graphite [10]. Research data confirm an extremely high influence of the ratio of reservoir temperatures and pressures on the temperature of the onset of oil cracking in the reservoir, i.e. a significant increase in the cracking onset temperature at abnormally high formation pressure.

In previous studies, the method of thermodynamic potentials [11, 12] was adopted as the main tool for thermodynamic modelling allowing to investigate the system of geochemical organomineral facies (areas of thermodynamic stability) [13, 14].

The interpretation of equilibrium processes described in the work of H.Helgeson [15] was taken as a prototype. Helgeson's model allows presuming a sequence of biomass transformation processes with a stagewise generation of bitumen and kerogen as well as liquid oil and the accompanying gas, which also form in areas of high pressures, temperatures and great depths. The model is based on the assumption that all transformations occur in accordance with basic postulates of Hess's law, Kirchhoff's law and the second law of thermodynamics. At the same time, it is possible to present oil, gas and solid kerogen as chemical compounds of an assigned stoichiometry, and, thus, to reduce their thermodynamic functions of state for further calculations. For example, light oils can be represented as compounds of $C_{10}H_{22}$ type, solid kerogens – $C_{128}H_{68}O_7$, $C_{292}H_{288}O_{12}$, gases (alkanes) – C_nH_{2n+2} [15]. Such an assumption simplifies the set of possibilities of HC transformation but allows judging about a possible existence of individual components of liquid oil, gaseous reservoir fluid and solid mass of kerogen under different thermobaric conditions.

By resolving a system of equations for different temperatures and pressures, it is possible to obtain the dependences of quantitative ratio of the described components on the occurrence depth, which, in turn, will allow predicting the areas of oil occurrence in atypical geological environments.

Modern basin analysis also uses models to predict the degree of kerogen transformation and the extent of oil generation in potential source rocks. Such models assign kinetic parameters on the basis of a general depositional environment and stratigraphic age, which is useful in areas for which no sufficient geochemical data are available including the exploration boundaries. Five kinetic organofacies of kerogen are distinguished, each characterized by a certain contribution of organic matter and an early diagenetic imprint; sensu lato they can be assigned to the sedimentary facies/age associations, even when using only seismic sequence stratigraphy:

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- A – aquatic, marine, siliceous, or carbonate/evaporite of any age;
- B – aquatic, marine, siliciclastic of any age;
- C – aquatic, non-marine, lacustrine, Phanerozoic;
- D/E – terrigenous, non-marine, perennially wet, coastal, Mesozoic and younger;
- F – terrigenous, non-marine, coastal, Late Paleozoic and younger [16].

It is possible to divide organic carbon in immature source rock based on pyrolytic analysis into four initial components: oil, oil-bearing, gas-generating and inert. This yields kinetic parameters for oil- and gas-generating fractions allowing to calculate the evolving concentration and composition of products.

Thermal transformation of organic matter of rocks. The most common viewpoint on the processes leading to generation of oil and gas accumulations is the idea that oil and gas are products of temperature transformation of organic matter (sedimentary migration theory) accumulated in sedimentary strata and later subjected to subsidence into an area of high pressure and temperature. According to this theory based on numerous experiments on the effect of temperature on physicochemical transformations of the main components of organic matter (OM), the identified dependencies of the initial composition of OM and hydrocarbon products, the developed balance calculations and equations [5, 17, 18], it is possible to determine HC evolution stages as a function of pressure and temperature for each type of organic matter identified. Back in the 60s of the last century, even with relatively limited possibilities of laboratory studies of OM and its transformation kinetics, boundary temperature values were proposed determining the component and phase composition of the generated hydrocarbons [5]. Further development of the theory led to understanding that when estimating the conditions for OM transformation into HC, actual phase transformations of HC and their destruction, it is necessary to take into account not only the influence of temperature, but also the time of its impact, the rate of its increase, the combination of "temperature – pressure" factors and a cyclical temperature increase-decrease caused by a set of geological factors characteristic of the study objects.

Arguments of adherents of abiogenic origin of oil are reduced to contradictions that are difficult to explain at first glance, such as identification of hydrocarbon compounds in meteorites, volcanic and metamorphic strata that were exposed to temperatures much higher than the limit values determined by experimental data on the transformation of hydrocarbons from OM. Though there are relatively few such cases in the world (less than 0.5 % of all identified economic HC accumulations according to S.G.Neruchev [5]), upon a detailed study, additional facts are disclosed that allow an easy explanation of the arising contradictions, such as the case of a group of well-known fields on the shelf of Vietnam or a large Hassi-Massaoud field in Algeria (forming due to OM potential of oil and gas source strata, partially eroded in the area of the identified fields and overlying the pays). These contradictions initiate numerous investigations based on the notions of a deep inorganic origin of hydrocarbons, and recently the experiments were conducted for proving the evolution of hydrocarbon transformation which differs significantly from that accepted in the sedimentary migration theory (presented as inorganic sources of kerogen carbon – oil and gaseous hydrocarbons (HC) → natural gas → oil → kerogen), i.e. when deep HC_s fluids rise to the surface as a result of a drop in hydrogen fugacity, oil reservoirs form. Thus, most incomprehensible from the viewpoint of possible physicochemical transformations is the discussion of phase transitions (freezing) of liquid oil into solid kerogens caused by a decreasing hydrogen pressure and temperature. Dehydrogenation of oil in the processes of high-temperature CO_2 fixation and low-temperature HC_s hydration, which are the main geochemical pathways for oil transformation into kerogen, is proposed as a mechanism [14].

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OM transformation under the influence of increasing temperature and pressure is contrasted with generation of carbon matter as a result of regressive metamorphism of deep HC_s fluids. This formulation of the question is not new. Numerous discussions about the origin of oil in the 60-70s of the last century ended with the impossibility of a practical use of mainly speculative results of the adherents of deep origin of oil headed by N.A.Kudryavtsev, due to the lack of evidence for physicochemical transformations of "radicals" and conditions for their transformation into hydrocarbons [19].

When the sediment containing OM leaves the diagenesis zone, the bacterial activity ceases, the processes of OM transformation under the action of bacteria stop, and a new stage of changes in sedimentary rocks and their OM begins under the influence of temperature and pressure in the subsurface – the stage of catagenesis.

Catagenesis begins at the end of diagenesis and continues until the start of metagenesis. In this case, the formation temperature (to 250-300 °C) and pressure (to 130-150 MPa) increase significantly. Chemical processes depend on temperature, which increases with subsidence depth. Changes in physical properties of rocks are determined by pressure. A significant compaction of clay rocks occurs. By the end of catagenesis, the porosity of clay rocks decreases to 1-2 %. Clay rocks at corresponding depths in ancient basins have a slightly higher density than in young basins, i.e. the time of exposure to pressure has a certain effect, but the difference is negligible. In sandstones, the porosity also decreases 2-3-fold, from 25 to 10 % or less. Chemical changes also occur in polymictic sandstones, and mineralogical changes are recorded n clays. Montmorillonite, a swelling mineral, gradually transforms into hydromica minerals. The composition of organic matter of rocks changes significantly from the initial stage of protocatagenesis to the high stages of catagenesis at MC_1-MC_2 gradations, when the breakdown of polymer-lipid OM components occurs. Breakdown of polymer-lipid components leads to formation of liquid and, to a lesser extent, gaseous HC. At higher stages of catagenesis, other processes occur: sapropelic OM losing most of polymer-lipid components during breakdown, approaches humus OM in composition, and further gas generation processes predominate – mainly methane generation, but carbon dioxide, NH_3 and H_2S [17, 18] also form. The prevailing viewpoint is that the main factor of catagenesis is temperature, when it reaches the limits of activation of certain reactions [17].

The most sensitive component of catagenesis intensity is organic matter of sedimentary rocks. The main indicator that can be measured is vitrinite reflectance which can be used by compiling the corresponding scale of catagenetic transformations of sedimentary rocks and organic matter on the catagenesis scale constructed by N.B.Vassoevich and his outstanding disciples N.V.Lopatin and S.G.Neruchev (Table 1) [13, 17, 18]. Depths at which certain changes in OM occur and critical values of vitrinite reflectance index are recorded are shown.

The catagenesis scale is related to I.I.Ammosov's scale of coal metamorphism [20]. Protocatagenesis corresponds to the brown coal stage, mesocatagenesis and its gradations correspond to a series of coal grades: MC_1 – long-flame, MC_2 – gas, MC_3 – fat, MC_4 – coke, MC_5 – residually caking. In apocatagenesis, AC_1 gradation corresponds to lean coals, AC_2 – to initial stages of anthracite, and AC_4 – to the highest degree of carbonization of anthracites, when they contain 95-98 % carbon.

Both coals and vitrinite are used to estimate catagenesis, but since coals as well as terrestrial paleovegetation and, thus, vitrinite, were extremely rare prior to the Carboniferous, diagnostics can be accomplished using phytoplankton remains, the colloidal forms of which were used to substantiate the catagenesis scale of G.M.Parparova [5]. Such catagenesis scale for dispersed organic matter after colloalginite compares well with refractive indices in air and allows judging about the stages of rock and OM catagenesis in sediments without vitrinite and terrestrial vegetation remains. Modern analytics, in particular pyrolytic studies, allow getting an idea of OM transformation degree based on T_{max} index.

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Table 1

Scale of catagenesis (compiled by G.S.Kalmykov with supplements by G.M.Parparova) [5])

R°, %	Unified scale of VNIGRI MGU and VNIIYAGG (S.G.Neruchev et al., 1975)				Scale of IGiRGI (I.I.Ammosov et al., 1967, 1971)			Coal rank and R° comparison scale	
	Approximate depth, km	Lithogenesis stage	Gradation	Rº, %	Stage	Stage (coal rank)	Rº, %	Catagenesis gradation (coal rank)	Rº, %
0-0.5	1-3	Diagenesis	D	0.25	Brown coal	0_1-B_1	0.26	B-PC	0.45
		Procatage-nesis	PC_1	0.3		0_2-(B_2)	0.41		
			PC_2	0.4					
			PC_3	0.5		0_3-(B_3)			
0.5-0.8		Mesocata-genesis	MC_1	0.65	Hard coal	I (LF)	0.50	LF-MC_1	0.60
			MC_2	0.85		II (G)	0.64	G-MC_2	0.85
0.8-1.5	2-6		MC_3	1.15		III (F)	0.90	F-MC_3	1.15
			MC_4	1.55		IV (C)	1.12	C-MC_4	1.55
1.5-2.0			MC_5	2.0		V (LC)	1.61	LC-MC_5	2.00
2.0-2.5		Apocata-genesis	AC_1	2.5	Anthracite	VI (L)	2.04	L-AC_1	2.50
3.0 3.5 4.0 4.5 5.0 5.5 6.0 … 11.0	3-9		AC_2	3.4		VII (A_1) VIII (A_2)	2.45 3.04	A-AC_2	3.50
	4-12		AC_3	11		IX (A_3)	3.85	A-AC_3	5.00
	5-15		AC_4			X (A_4)	5.2 6.2	A-AC_4	6.00

The established deep zonation of catagenesis of dispersed organic matter in the Paleozoic and Mesozoic deposits in some oil and gas regions of Russia, for example, in the Caspian Depression, ends with MC_3 zone at a depth of 8.5 km, and MC_4 zone extends, according to the forecasts, to 10 km [21-23], AC_3 stage – to 12 km. All researchers agree that the main reason for such deep zonation is a low heat flow or the absence of a heat-insulating cap, therefore, the time of exposure to thermal energy is significantly reduced, and temperatures are much lower at great depths, and high gradations of catagenesis are achieved at very low depths. Other causes are also possible. For example, in the southern Siberian Platform, large oil and gas fields were discovered at great depths with extremely low bottomhole temperatures, which is due to occurrence of a salt layer.

In the Paleozoic deposits of the Caspian Depression, an additional factor is high thermal conductivity of the overlying salt-bearing rocks, the effect of which extends not only to organic matter, but also to the host rocks. Since clay rocks were overlain by salts, there was no efficient outflow of water, and the rocks are characterized by a much higher porosity than in normal sections. The intensity of organic matter transformation depends not so much on depth as on the temperature regime at the corresponding gradations of catagenesis. Based on deep zonation of catagenesis in a certain

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basin under investigation, it is possible to presume what transformation stages dispersed organic matter of rocks attained, what happened to it, and at what depths oil and gaseous hydrocarbons were generated.

Based on the data on organic matter transformation, it is possible to determine at what stages of catagenesis, at what subsidence depths, in what deposits of the sedimentary basin the processes of oil and gas generation occur, i.e. it is possible to identify the sources of generation and emigration of oil and gaseous HC and use these data when considering oil and gas potential of the basin under study.

Examples of applying thermodynamic modelling. Thermodynamic modelling is one of the most efficient approaches to estimating the phase state of hydrocarbons at great depths.

The analysis accomplished at the previous stage of work on a group of sedimentary basins in Inland China (Tarim, Dzungar and Sichuan) showed that, along with such important indicators for the preservation of hydrocarbons at great depths as pressure, temperature, subsidence rate, cooling effect – salts and/or sea water column, initial composition of OM plays a significant role [24, 25].

Similar conclusions were made by researchers [26] when testing the generation, migration and cracking modelling of petroleum fluids using a 2D compositional basin simulator with kinetic models based on chemical classes of compounds in the Elgin field area (North Sea) characterized by both high pressure (110 MPa) and high temperature (190 °C). The study focused on kinetic modelling of secondary cracking, since paraffinic condensates containing almost 50 % C_{6+} alkanes were found in this zone, while, given the high temperature conditions, only gas (C_{5-}) was expected. Detailed hydrocarbon composition of the Fulmar Sands Formation in the Elgin field was compared with results of several simulations aimed at testing the influence of the Jurassic source rocks, kinetic parameters and temperature variations on the predicted fluid composition. The influence of pressure in modelling was neglected based on the results published in [26]. The results show that in the North Sea region primary cracking of kerogen with generation of oil was completed regardless of the source rock under consideration. At the same time, secondary cracking of the accumulated petroleum hydrocarbons was recorded. The presence of a single-phase paraffinic liquid (alkanes), despite a high temperature, is accounted for by its very recent increase from 160 to more than 180 °C over the last million years, i.e., a high subsidence rate. The results of using the compositional kinetic scheme of F.Behar et al. [26] for secondary cracking showed a fairly good agreement between the calculated and observed detailed fluid composition, with the exception of methylated aromatic compounds, which are overestimated, and methane, which is underestimated [27]. Comparison of kinetic parameters obtained from pyrolysis experiments on model compounds showed that it was erroneous to presume, as was done previously, that there is the same frequency coefficient for all chemical classes of compounds. A higher stability of methylated aromatic compounds compared to the saturated ones observed under laboratory conditions can also apply to geological conditions. A series of simulations using frequency coefficients and activation energies obtained on these model compounds corresponded better to methylated aromatic compounds. However, methane is still much underestimated, which requires a special discussion.

Physicochemical modelling of complex heterogeneous man-made and natural systems is possible applying the principle of determining the equilibrium composition of components included in the system.

Thermodynamic modelling as a basis for predicting phase states of HC at great and super-great depths. The main modern approach to solving the problem of thermodynamic modelling of the equilibrium composition of HC in formation fluid is the method based on compilation of all possible reactions between the formation fluid components, calculation of equilibrium constants

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for these reactions and further solution of a system of equations using the initial composition, temperature and pressure at which the transformations will occur as data for modelling. This methodology is described in detail in [28],], the approach was acknowledged in modelling of sorption processes [27], developing a methodology for increasing the efficiency of quarry water purification [29], studying secondary mineral formation [30], hypergene ore formation processes [31], sedimentation in the Baltic Sea [32], calculation of physicochemical properties of technogenic systems [33, 34], modelling the equilibrium ionic composition of solutions [35].

The main objective of the work was the development, theoretical substantiation and practical implementation of thermodynamic modelling method that allows predicting the stability of hydrocarbons in the Earth's crust under different thermobaric conditions.

Modelling methodology. Thermodynamic modelling of a possible existence of liquid hydrocarbons contained in oil is based on fundamental postulates of physical chemistry and chemical thermodynamics [36] as well as the patterns of thermobaric characteristics influence on formation fluids [37, 38]. Thermodynamic calculations were performed using the Mathcad software package. The main thermodynamic characteristics of the components of formation fluid were obtained using publicly available databases*. Fluids from the Russian hydrocarbon fields were selected as the objects of modelling.

Oils from these fields are dominated by aliphatic hydrocarbons, which made it possible to test the proposed simplified thermodynamic model on them, taking into account the interaction between liquid and gaseous linear alkanes up to C_7 in length with components of the associated petroleum gas taking into account hydrogen, carbon dioxide, carbon monoxide, and water vapour. Alkanes with a longer hydrocarbon radical are not taken into account in the model, since they have a higher thermal stability compared to shorter representatives of the homologous series.

Modelling of reservoir conditions at the Urmanskoye field (West Siberian sedimentary basin). One of the tasks set in this work was modelling the generation of liquid components of reservoir fluid from gas fractions comprised into the associated petroleum gas. The Nyurol'skaya Depression with the Archinskoye and Urmanskoye fields lying within it in the southeastern West Siberian Basin was selected as the main study area.

Based on statistical data on localization of hydrocarbon occurrences, their areal distribution and confinement to tectonic and geological structures, it is possible to determine the main potential trends and areas that are of scientific interest from the viewpoint of studying actual oil and gas presence at great depths and the presumed phase composition of hydrocarbons.

Hydrocarbon occurrences in the Paleozoic sediments are mainly localized within M Bed (weathering crust) composed of aluminosilicates (bauxite-like deposits) and sideritized carbonate varieties from limestones to dolomites. The results of quantitative analysis of oil, gas condensates and the associated gases from several deep wells were used as source data for modelling (Table 2).

Yu-14-15 reservoir was characterized by formation temperature of 100 °C at a depth 3,050 m and formation pressure 29.6 MPa (Fig.1); $M + M_1$ reservoir was characterized by formation temperature 104 °C and reservoir pressure 32.7 MPa, occurrence depth 3,129 m (Fig.2).

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Table 2

Characteristic of fluids in the Urmanskoe field

Parameter	Yu-14-15 reservoir					M + M_1 reservoir				
	At single degassing of reservoir oil under standard conditions		At differential degassing of reservoir oil under operating conditions		Reservoir oil	At single degassing of reservoir oil under standard conditions		At differential degassing of reservoir oil under operating conditions		Reservoir oil
	Released gas	Oil	Released gas	Oil		Released gas	Oil	Released gas	Oil	
Carbon dioxide	3.02	0.00	3.14	0.00	1.56	2.10	0.03	2.12	0.03	1.42
Nitrogen	0.24	0.00	0.25	0.00	0.13	0.64	0.00	0.64	0.00	0.43
Helium	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methane	51.22	0.23	53.19	0.07	26.58	79.68	0.35	80.40	0.10	53.28
Ethane	9.03	0.28	9.36	0.25	4.80	7.14	0.23	7.15	0.30	4.84
Propane	14.76	1.75	14.69	2.27	8.48	5.78	0.69	5.59	1.14	4.09
Isobutane	6.30	1.83	5.84	2.45	4.14	1.21	0.41	1.10	0.63	0.95
n-butane	8.37	3.70	7.48	4.76	6.11	2.12	1.05	1.88	1.54	1.77
Isopentane	3.15	3.62	2.62	4.13	3.37	0.53	0.68	0.44	0.85	0.58
n-pentane	3.10	4.88	2.57	5.34	3.96	0.47	0.82	0.39	0.97	0.59
Hexanes	0.68	10.62	0.66	10.29	5.48	0.33	1.64	0.28	1.72	0.77
Higher heptanes	0	73.08	0.2	70.45	35.38	0.00	94.10	0.0	92.71	31.32

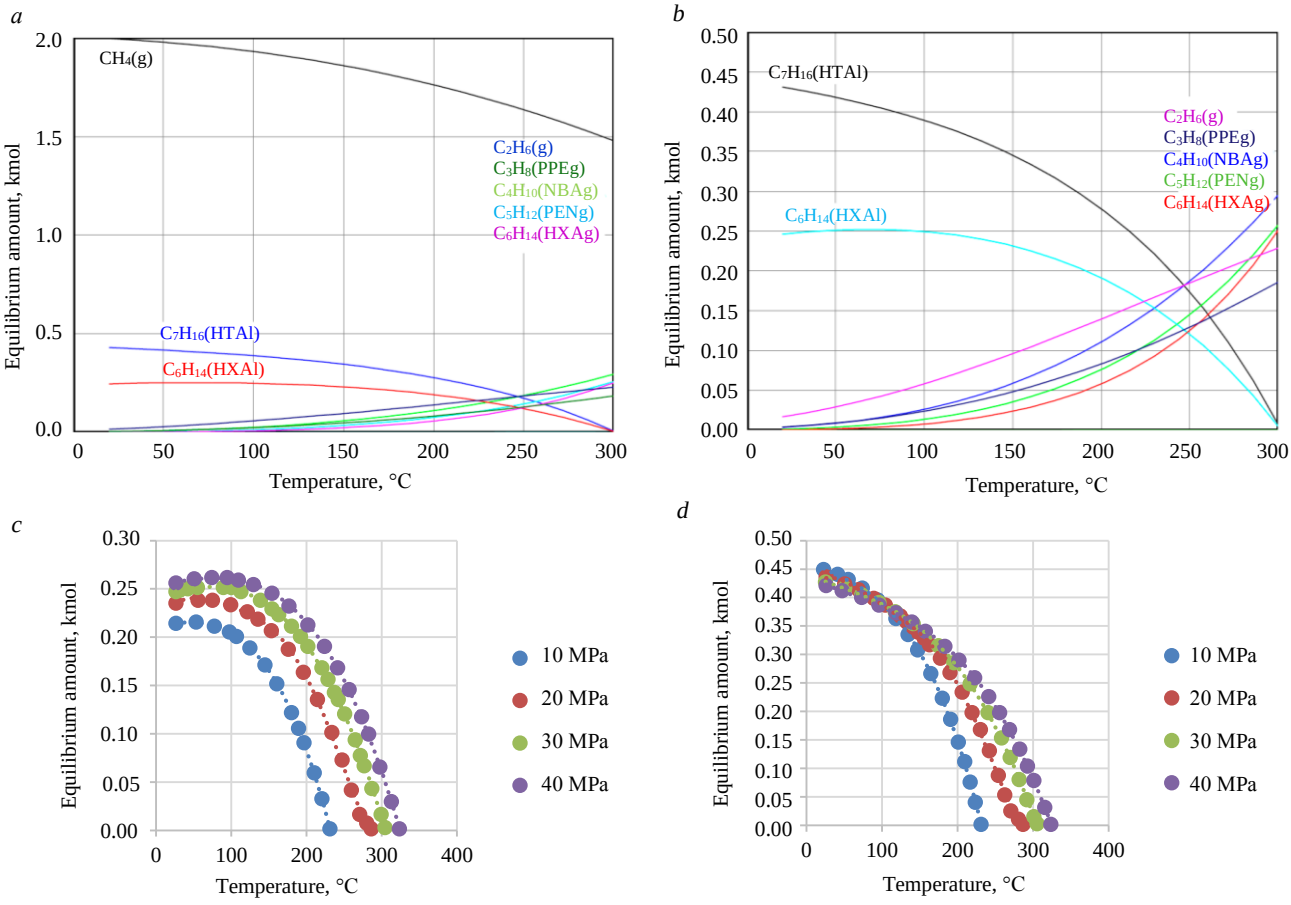


Fig.1. Equilibrium composition of formation fluid in Yu-14-15 reservoir (temperatures 20-300 °C, pressure 29.6 MPa) (*a*), excluding methane (*b*) and equilibrium amount in formation fluid of Yu-14-15 reservoir under different formation conditions (simulation results) of liquid hexane (*c*), liquid heptane (*d*)

C_6H_{14}(HXAl) – hexane (liquid); C_7H_{16}(HTAl) – heptane (liquid); CH_4(g) – methane (gaseous); C_2H_6(g) – ethane (gaseous); C_3H_8(PPEg) – propane (gaseous); C_4H_{10}(NBAg) – butane (gaseous); C_5H_{12}(PENg) – pentane (gaseous); C_6H_{14}(HXAg) – hexane (gaseous)

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Based on modelling data for Yu-14-15 reservoir (Fig.1), the existence of liquid hydrocarbons at pressure 29.6 MPa is possible in the entire modelled temperature range from 20 to 300 °C, while with increasing temperature (or lower pressure) the liquid phase mainly decomposes to methane with formation of shorter gaseous alkanes. To confirm the positive effect of reservoir pressure on the stability of liquid hydrocarbons, the equilibrium compositions of components of reservoir fluid were calculated at different pressures (Fig.1, *c*, *d*).

From Fig.1, *d* it follows that for Yu-14-15 reservoir the existence of liquid hydrocarbons at pressure 29.6 MPa is possible in the entire temperature range from 20 to 300 °C, with a significant proportion of them remaining to 220-230 °C. With increasing temperature, the liquid phase also decomposes with generation of shorter gaseous alkanes. Pressure increases the proportion of preserved liquid hydrocarbons, and vice versa.

For M + M_1 reservoir, the equilibrium compositions of formation fluid components were calculated at different pressures (Fig.2). Proceeding from modelling data, the existence of liquid hydrocarbons at pressure 32.7 MPa is possible in a narrower temperature range – from 20 to 220 °C, while with increasing temperature (or at lower pressure) the liquid phase decomposes with generation of shorter gaseous alkanes, mainly to methane.

For M + M_1 reservoir, the existence of liquid hydrocarbons at pressure 32.7 MPa is maintained at much lower temperatures 180-210 °C than for Yu-14-15 reservoir, which corresponds to the lower boundary of oil generation zone of MC_3-MC_4 catagenesis stages. With increasing temperature, the liquid phase also decomposes.

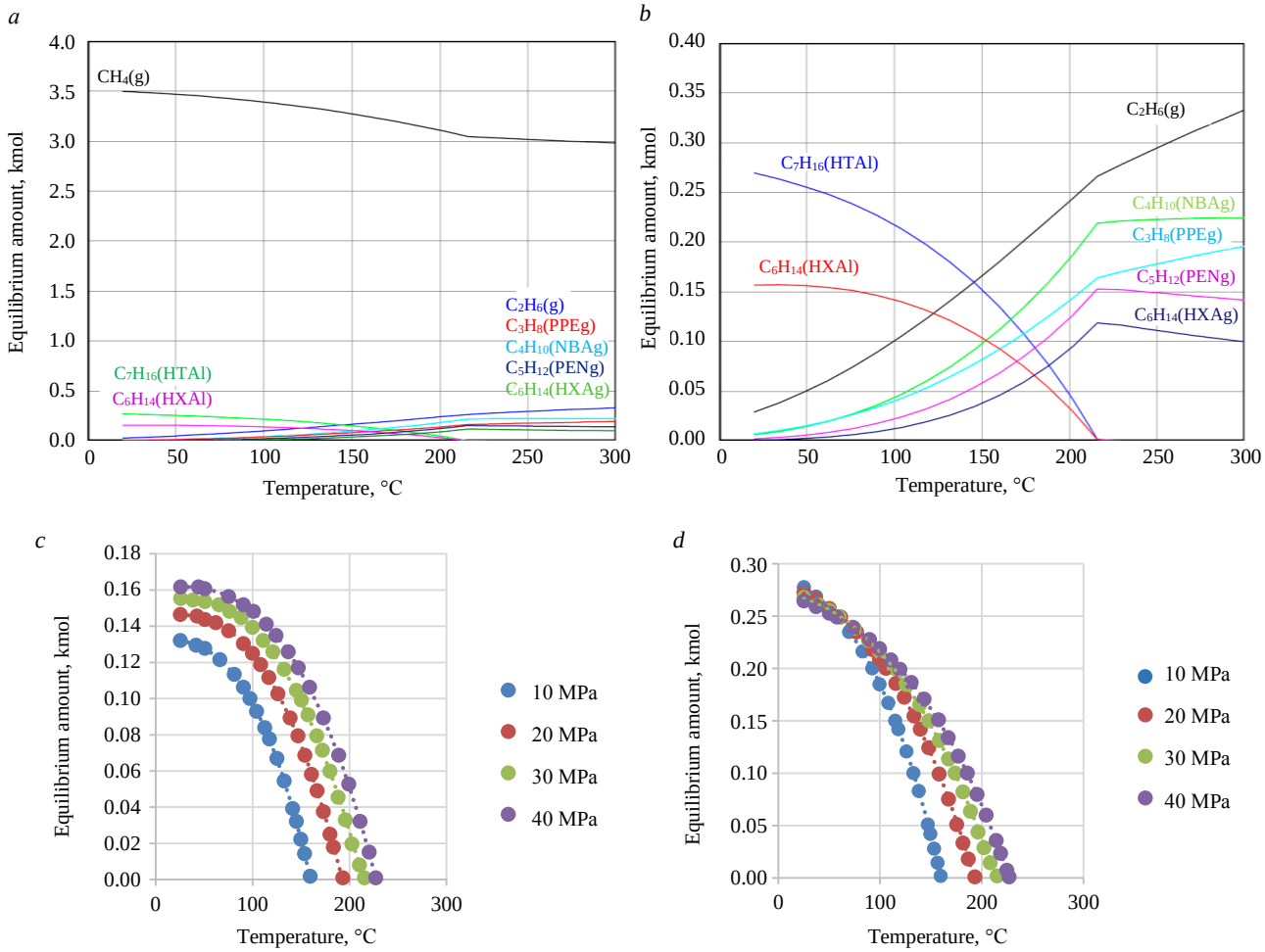


Fig.2. Equilibrium composition of formation fluid of M + M_1 reservoir (temperatures 20-300 °C, pressure 32.7 MPa) (*a*), excluding methane (*b*) and equilibrium amount in formation fluid of M + M_1 reservoir under different formation conditions (simulation results) of liquid hexane (*c*), liquid heptane (*d*)

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Data obtained as a result of modelling confirm a possibility of existence of liquid hydrocarbons in the Urmanskoye field at depths below 3,000 m.

Modelling of reservoir conditions in the junction zone of the Sol'-Iletsk Arch in the Volga-Ural OGP and the Bazyrovskaya zone of the Caspian OGP (drilling site of Well 501 Vershinovskaya). One of the objectives of this work was to estimate the possibilities of modelling the generation of liquid components of reservoir fluid from gas fractions in the associated petroleum gas.

Initial data for modelling were the chemical composition of the associated gases obtained during sampling of parametric Well 501 Vershinovskaya, which is within the Sol'-Iletsk Arch in the junction zone of the Sol'-Iletsk oil and gas area of the Orenburg oil and gas region in the Volga-Ural oil and gas province, the Sakmaro-Ilek oil and gas area in the South-Pre-Ural oil and gas region of the Volga-Ural oil and gas province, and the Bazyrovskaya oil and gas accumulation zone in the Caspian oil and gas province (OGP).

The most deep-seated Eifelian-Lower Frasnian complex was penetrated by a well at a depth of 6,288 m and is represented by the Middle Devonian limestones. The rocks are dense, fine-medium-grained, fractured with rare caverns to 2 cm and porosity 0.3-4.2 % without signs of oil and gas. As a result of sampling in the interval 6,267-7,005 m, the influx of formation water was attained.

According to laboratory studies, the porosity coefficient of core samples taken in the depth interval 6,188-6,288 m varies from 0.4 to 6.5 %; gas permeability, from 0.02 to 0.1 mD; bulk density – from 2.72 to 2.83 g/cm^3. In the interval 6,199-6,220 m (Tournasian (Lower Carboniferous)) an inflow test was performed. Influx of formation fluid was not recorded.

Up the section, the Oka-Bashkirian oil and gas complex (OGC) was penetrated in the interval 5,357-6,124 m; according to GIS data, the Bashkirian deposits in the interval 5,370-5,398 m are interpreted as oil and gas saturated with porosity 6-10 %.

Lower Permian carbonate OGC is estimated as having the highest potential within the Sakmaro-Ileksky, Sol'-Iletsk oil and gas geological regions. The Orenburg oil and gas condensate field, which is in commercial development, was discovered there. At the Nagumanovskoe field, gas of the Artinskian gas condensate field has the following composition: methane 72-81, ethane 4.6-7.4, propane 2.9-5.9, hydrogen sulfide 2.9-8.0, carbon dioxide 2.3-3.9 %. Gas density is 0.735-0.740 g/cm^3, mass concentration of condensate is 140 g/m^3.

In the section of well 501 Vershinovskaya, the Lower Permian OGC was penetrated in the interval 4,883-5,353 m and is represented by the Asselian (Lower Permian) reefogenic and organogenic clastic limestones. In the interval 4,951-4,963 m, according to GIS interpretation results, a pay with porosity 5-12 %, oil and gas saturation 60-80 %, permeable, judging by micromethods, was identified.

As a result of inflow testing (interval 5,359-5,369 m of the Bashkirian and interval 5,285-5,345 m of the Asselian), inflows of formation water were recorded. In the perforation interval 4,875-4,940 m, an inflow of formation water with an oil film was recorded.

In 4,810-5,174 m interval, an inflow of gas interrupted by black liquid with a condensate film was noted. In the interval 4,825-5,301 m, an inflow of HC gas was observed after 58 min of exposure, reservoir pressure was 53.2 MPa. Gas is of methane composition (81-85 %), density 0.772-0.840 g/cm^3. In the interval 5,040-5,141 m, no inflow from the reservoir was obtained.

Chemical composition of natural gas from the Vershinovskaya area determined from a sample taken at a depth 4,991.3 m, reservoir temperature 114 °C, pressure 55.9 MPa: methane 81.3, ethane 6.26, propane 3.28, isobutane 0.52, *n*-butane 1.16, isopentane 0.47, *n*-pentane 0.45, hexane 0.49, heptane 0.25 vol.%.

The results of modelling the equilibrium composition of gas are shown in Fig. 3. From the obtained data it can be concluded that the liquid phase under reservoir conditions at pressure 55.9 MPa can condense at temperatures not exceeding 102 °C. According to the data on well N 501 Vershinovskaya, formation temperature at the depth 4,991.3 m is 114 °C, which corresponds to the zone where only the gas phase exists.

During gas migration to the surface, intra-formation pressure will decrease, and to confirm a possibility of condensation of liquid components of gas as a result of migration, the equilibrium composition of fluid components was determined at pressure 10 MPa (Fig.4).

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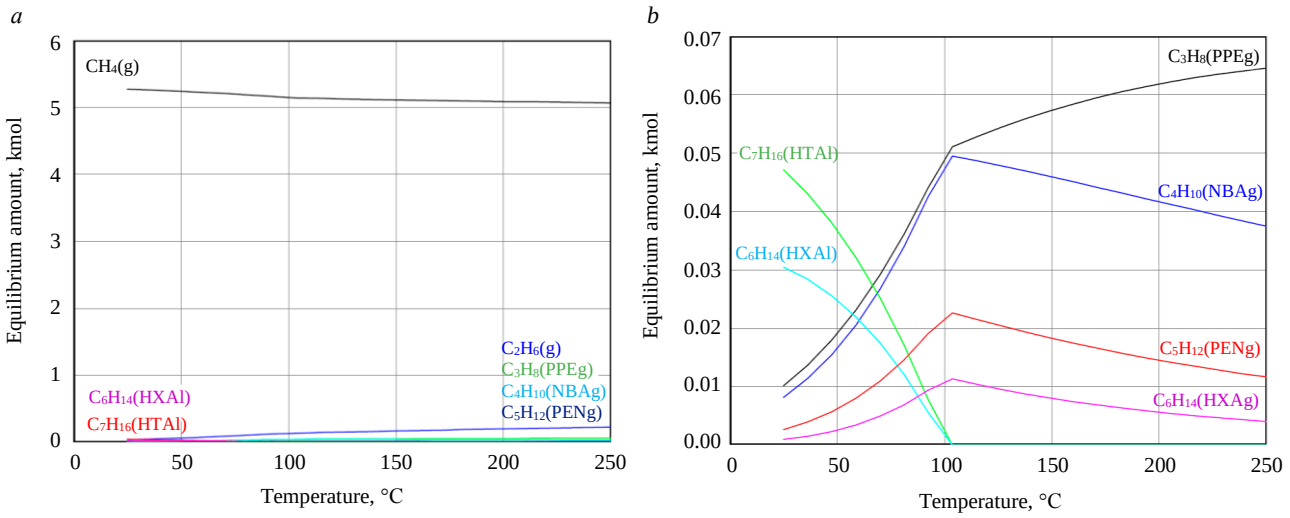


Fig.3. Equilibrium composition of formation fluid in Vershinovskaya area (temperature 20-300 °C, pressure 55.9 MPa) (*a*), excluding methane and ethane (*b*)

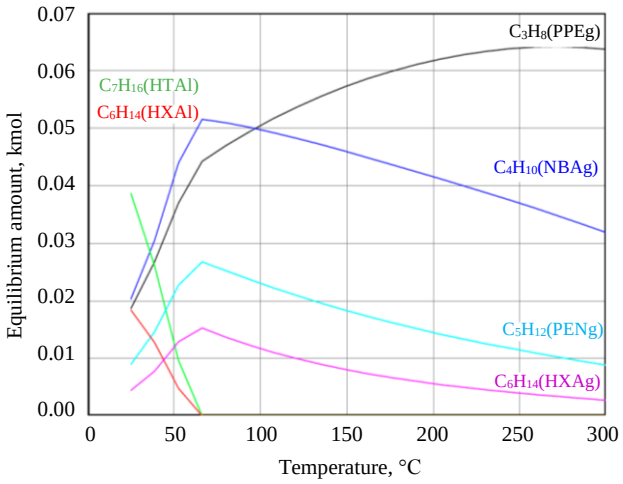


Fig.4. Equilibrium composition of formation fluid in Vershinovskaya area (temperature 20-300 °C, pressure 10 MPa) excluding methane and ethane

From modelling data, it is evident that at pressure 10 MPa the existence of a liquid phase is possible at temperatures not exceeding 62 °C. Thus, it can be concluded that thermal stability of liquid hydrocarbons increases with increasing reservoir pressure.

Modelling the equilibrium composition of fluid containing aliphatic, naphthenic and aromatic hydrocarbons. The main simplification of the earlier proposed model [24] was the impossibility of taking into account the aromatic and naphthenic compounds comprised into the formation fluid. At this stage, an attempt was made to make changes to the model that would remove these limitations. A system consisting of an equimolar amount of methylcyclohexane (representative of naphthenes), methylbenzene (representative of aromatic compounds), and 2-methylhexane (representative of aliphatic compounds) was adopted as the initial composition for modelling. The dependence of the equilibrium composition on temperature at pressure 10 MPa is shown in Fig.5.

It follows from modelling results that with increasing temperature the amount of naphthenic hydrocarbons (methylcyclohexane) decreases due to dehydrogenation and thermal cracking, and, in turn, an increase of liquid aliphatic (2-methylhexane) and aromatic (methylbenzene) hydrocarbons is recorded until the temperature reaches 170-190 °C, after which their amount also starts decreasing due to transition to a gaseous state. Modelling results show that at pressure 10 MPa, liquid components of the investigated system can exist at temperatures below 375 °C. Based on the model, it can be noted that with increasing formation temperature of reservoir fluid, the aliphatic and aromatic components will dominate in it.

The results of thermodynamic modelling for estimating a possibility of existence of individual components of liquid oil, gaseous reservoir fluid and solid mass of kerogen under different thermobaric conditions should be supplemented by analytical data of pyrolytic studies of hydrocarbons,

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bitumoid extracts from the core and the study of their kinetic characteristics. Such investigations are widely used to estimate phase states in sedimentary basins of China [39].

Alternative approaches to determination of boundary values of hydrocarbon phase transitions. Thermal cracking is the process of long-chain hydrocarbons splitting with formation of shorter ones. At atmospheric pressure, this process proceeds at temperatures above 300 °C. Under such conditions, phase transition of the majority of liquid oil components into a gaseous form will be observed as well as cracking of solid asphaltenes, resins and paraffins to form simpler hydrocarbons. Similar to the processes of oil generation from solid kerogen, these processes will occur via free-radical and carbonium-ion mechanisms [40, 41]. As a rule, the main factors influencing the degree of thermal decomposition of high-molecular hydrocarbons are thermobaric characteristics, exposure time under given conditions and composition of the source organic material.

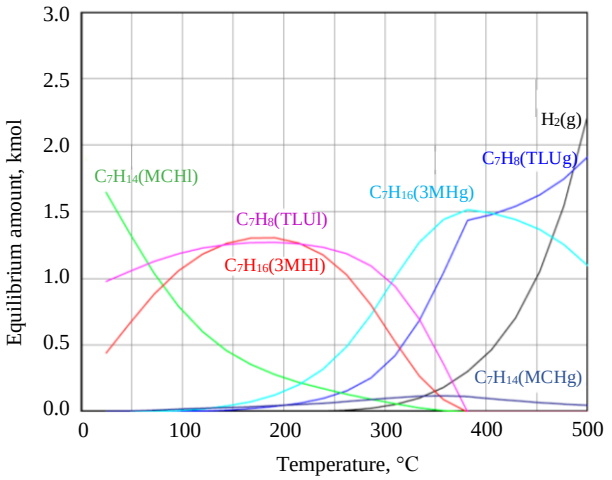


Fig.5. Effect of temperature on equilibrium composition of the system (methylcyclohexane, methylbenzene, 2-methylhexane) at pressure 10 MPa

C_7H_{14}(MCHl) – methylcyclohexane (liquid);
C_7H_{14}(MCHg) – methylcyclohexane (gas);
C_7H_{16}(3MHl) – 2-methylhexane (liquid);
C_7H_{16}(3MHg) – 2-methylhexane (gas3);
C_7H_8(TLUl) – methylbenzene (liquid);
C_7H_8(TLUg) – methylbenzene (gas); H_2(g) – hydrogen (gas)

The degree of thermal cracking of liquid petroleum hydrocarbons increases with occurrence depth and reaches the maximum in the zone lying below the so-called oil window (or "main zone of oil generation" according to N.B.Vassoevich [17]), which is commonly limited by the depth of about 4-5 km and temperature 150-180 °C [17, 18, 42].

The study of physicochemical equilibria between liquid, solid and gaseous components of oil allowed drawing conclusions about the patterns of relationship between the composition and the range of thermobaric conditions of its generation. Thus, according to S.N.Obryadchikov [43], two types of oil can be distinguished:

• oils generated in the temperature range 250-300 °C – the composition is dominated by methane hydrocarbons of normal structure with minor admixtures of naphthenic hydrocarbons;

• oils generated at low temperatures (less than 150 °C) – the composition is dominated by six-membered naphthenes, and methane HC are represented mainly by isomeric forms.

Proceeding from this classification and the ratio of cyclohexane to methylcyclopentane amounts [44], theoretical temperature range of oil generation was determined from 150 °C (Grozny Region, USSR) to 250 °C (Midway, California, USA), 290 °C (East Texas, USA), 310 °C (Maikop, North Caucasus, USSR), and 340 °C (Winkler, Texas, USA). This points to a clear correlation between the composition of the investigated oils and thermobaric conditions of their generation, which can be used in modelling in the research. This fact was confirmed by numerous studies around the world. For example, in deep-seated reservoirs in the central North Sea (Great Britain), oil was obtained from the formation with temperature 174-195 °C; the investigation of samples showed the minimal degree of its thermal cracking [45]. In addition, in the Jizhong Depression of the Bohai Gulf Basin (China), liquid hydrocarbon inflows were recorded from reservoir with formation temperature 190-201 °C [46]. Similarly, light oil was obtained from Longtan-1 (LT1) Well on the Tabei Rise at a depth to 8,260 m and at temperature to 171 °C [47]. Thus, we can talk not only about great depths of preservation of liquid hydrocarbons (in areas with abnormally low temperatures), but also about significant differences in limiting temperatures of existence of liquid hydrocarbons in different basins, which can be associated with a number of different factors affecting the stability of liquid fractions of oil.

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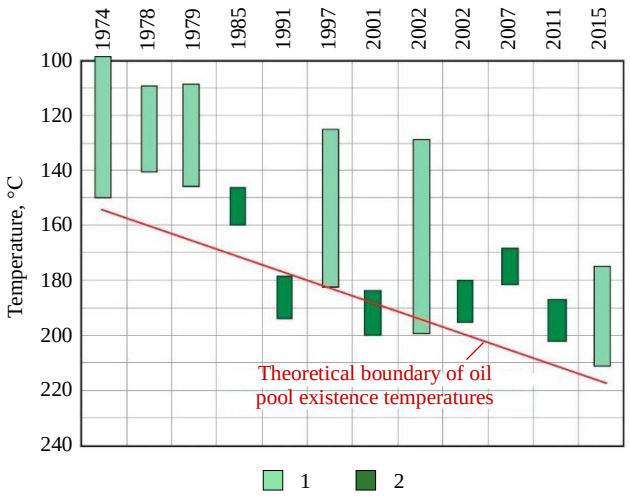


Fig.6. Theoretical boundary of the possibility of oil pool existence [21, 52]

1 – theoretical assumptions; 2 – discovered fields

Factors potentially influencing oil stability include high pressure, rapid heating as well as short-term exposure to high temperatures [24, 48, 49]. It should be noted that the presence of clay minerals in the reservoir is, on the contrary, an unfavourable factor influencing thermal stability of liquid hydrocarbons [50, 51].

Excessive pressure slows down maturation of organic matter and oil generation by increasing the activation energy of thermal cracking [48]. Stability of oil composition varies greatly in different sedimentary basins depending on thermobaric conditions. Thus, due to development of modern geological exploration technologies, the possibility of existence of hydrocarbons at great depths was established (Fig.6) [24, 25].

In the most general case, both temperature and pressure are a function of the occurrence depth, and, accordingly, at great and super-great depths high temperatures should correspond to high pressures.

Since pressure can suppress thermal transformation of hydrocarbons, the possibility of preserving liquid and gaseous hydrocarbons under high pressure conditions will be realized at great depths. Abnormally high pressure can also slow down compaction of the overlying sediments, which contributes to formation and preservation of deep and super-deep zones with high residual porosity [22, 25, 53]; typical examples are the Keshen gas fields in the Tarim Basin, Kelasu and Dabei in the Kukai Depression of the Jungar Basin [54].

In the articles describing thermobaric conditions of deep-seated hydrocarbon accumulations [24-26, 55] the following types of basins are distinguished:

- sedimentary basins of high pressures and high temperatures;
- sedimentary basins of high pressures and low temperatures;
- sedimentary basins of low pressures and high temperatures.

Recent studies proposed new indicators for determining the degree of oil-to-gas transformation, which make it possible to judge about the stability of oil and to predict phase distribution of hydrocarbons in deep reservoirs [23]. One of indicators could be the amount of diamondoids, a class of petroleum compounds whose unique thermal stability leads to their gradual concentration in the process of cracking [56]. The degree of oil-to-gas transformation can also be estimated in a more traditional way by gas/oil ratio, assuming that the reservoir is considered as a closed system and the hydrocarbons it contains are regarded as reagents and products [57, 58]. An indicator of the transformation degree was proposed in the study of China's unique sedimentary basin, Tarim, where it was possible to investigate the composition of occurrences in a wide range of depths and temperatures, and to investigate the factors influencing oil stability (using the adjusted method for determining diamondoids by Dahl et al. with an estimation of the effect of sulfur reduction degree). The main objective of the study was to identify the correlation between the factors determining the stability of oil and its composition by comparing the mechanisms of oil and gas genesis in different reservoirs.

Works in the Tarim Basin, where about 90 oils from the Cambrian and Ordovician deposits at great depths were inestigated, showed a possibility of determining the boundary conditions of oil transformation [39]. Oils were analysed for the presence of biomarkers, diamondoids and thiadiamondoids, and gas/oil ratios were determined from them.

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For three areas in the Tarim sedimentary basin (Tazhong, Tabei, and Shunbei), where hydrocarbons were discovered at great depths, the maximum depths of light oil inflows are 8,260 m, temperature at bottomhole is quite low –171 °C, using the transformation indicator – the amount of diamondoids (EOGC) – the maximum temperature at which liquid hydrocarbons can be preserved was determined [39]. It was also noted that sulfur reduction indicator had a significant effect on oil transformation. Thus, in the Tazhong area, oils were identified that were not affected by sulfur reduction (TSR). In the Tazhong area, higher EOGC values (28.0-49.2 %) are noted than for the other two (areas Tabei 0-9.7 %) and (Shunbei 0-32.7 %). It was concluded that a long heating duration (< 5 Ma) at high temperatures (> 150 °C) could be the reason for the lower EOGC values in the Tabei and Shunbei areas.

Oil can be completely transformed to methane-dominated gas if exposed to high temperatures for a longer period, as exemplified by the Lower Cambrian gas reservoirs in the Sichuan Basin. In this case, oil was heated at a rate of 1 °C/Ma after its generation and accumulation in the reservoir and survived temperatures > 200 °C for 50 Ma. Thermochemical reduction of sulfates found in oil increased oil-to-gas transformation resulting in EOGC values growing from 30 % for non-affected TSR to 98 % for the exposed ones. A similar case of elevated EOGC due to TSR is known from the Smackover Formation in the Gulf of Mexico.

According to the conclusions, liquid hydrocarbons in the Tabei and Shunbei areas can be preserved at temperature > 200 °C and depth > 9,500 m (geothermal gradient 19 °C/km). The exact temperature and depth threshold at which liquid oil is transformed to gas can also be estimated by kinetic modelling.

Presumably, the process of oil cracking with gas generation can be described using a set of parallel first-order reactions [49], i.e. using a constant frequency coefficient $1.78 \times 1{,}014\ s^{-1}$ and activation energy distributed according to Gauss [$\sigma = 2.5\ \%\ E_o$], which can be applied to model oil cracking.

Thus, in the Tarim Basin, by recording current EOGC values by kinetic modelling, it can be determined that the maximum temperature and depth at which oil is preserved in a separate liquid phase (EOGC < 51 %) reaches 9,800 m and temperatures 205 °C in the Tabei area, 7,000 m and 170 °C in the Tazhong area where the impact of TSR is not recorded (Fig.7), and only about 6,100 m and 150 °C where such impact is significant.

Thus, there are several ways to estimate the depth and temperature of oil-to-gas transformation, allowing to judge about the stability of oil and predict the phase distribution of hydrocarbons at great and super-great depths. The most important condition for obtaining objective notions both in case of thermodynamic modelling, and when using the amount of diamondoids as an indicator, characterized by thermal stability in the cracking process, is reliable information on the composition of hydrocarbons.

Conclusion. Sedimentary basins with extensively developed HC occurrences at great and super-great depths are confidently typified by their prospects determined by temperature to formation pressure ratio, geothermal gradient, occurrence (or forecast) and occurrence of strata containing specific organic matter and belonging to a certain geodynamic (tectonic) environment determining the rate of temperature increase during subsidence and the time of its impact.

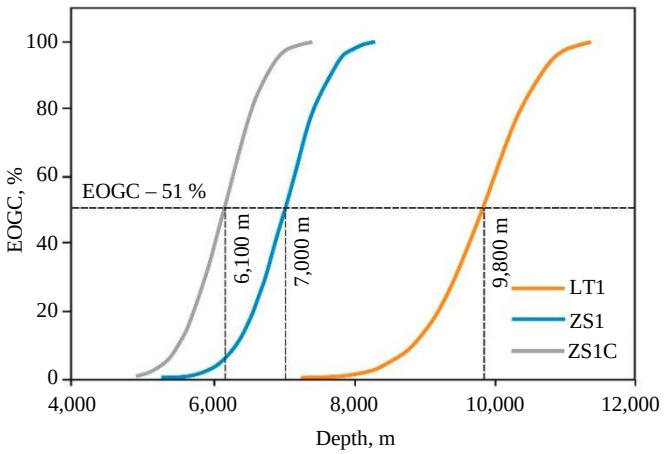


Fig.7. EOGC dependence on burial depth obtained by kinetic modelling [57]

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One of strongly underestimated factors for great depths, not included in the technology of basin modelling, is the time factor (which relates both to the subsidence rate and to the time of exposure to high temperatures). Effective heating time strongly affects the phase composition of hydrocarbon accumulations forming earlier, but moved to ultra-great depths,

The possibility of preserving oil and gas condensate reserves of significant size at great and super-great depths of 8-10 km is determined by both a low geothermal gradient, abnormally high pressures, and a high heating rate. Revealing of gas fields under conditions of progressing cracking of oil or at comparatively low temperatures is not limited by super-high pressures, possibly, to a depth 10-12 km.

In general, thermodynamic modelling points to a possibility of HC preservation at much higher temperatures than in standard balance equations in case of intense subsidence of oil and gas condensate accumulations earlier formed under conditions of "classical" temperatures and catagenesis. The increasing proportion of gases and methane with depth is a consequence of thermal cracking of high-molecular compounds, including liquids, the formation of which is not directly related to the exhaustion of oil and gas source strata potential at great depths.

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