ГЕОЛОГІЯ

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THERMODYNAMIC AND HYDROGEOLOGICAL CONDITIONS OF FORMING THE HYDROCARBON DEPOSITS OF THE PRE-BLACK SEA AQUIFEROUS BASIN

Purpose. Finding the connection between the thermodynamic conditions of hydrocarbon mixtures synthesis and zones of oil and gas accumulation. **Methodology**. The thermodynamic eguilibrium depths of gas and gas-condensate deposits were fixed by the method of eguilibrium constants of independent reactions based on the chemical composition of hydrocarbons re-counted on chemical elements. The investigations of formation waters, natural gases and water-dissolved gases were based on the methods of chemical, elementary spectral, atomic absorption and gas chromatographic analysis. **Results**. Received data point to essential differences in depths of a thermodynamic equilibrium for the deposits of Eocene, Maikopian, and Neogene on the one hand, and Lower Paleocene and Cretaceous sediments on the other. The first ones are characterized by values of depths in boundaries from 30 to 50 km while the second ones show a similar parameters in the boundaries from 120 to150 km. The analysis of the geological, hydrogeological and geochemical circumstances of the Pre-Black Sea aquiferous basin (PBSAB) testified to that the gas-vapour mixtures that are the sources of the Upper Cretaceous, Paleocene and Maikopian gas deposits are formed in high-temperature zone (about 300 °C) of depth origin. We consider the Lower Paleocene fields as primary formed only if gases rapidly migrated vertically (in free phase) from high-temperature places of their generation. The ways of possible migration were sublatitudinal faults and zones of decompression. The hydrocarbon fields in Maikopian and even Miocene sediments show the further way of vertical migration of gas and its accumulation in the traps throughout the whole way. Based on the analysis of the hydrogeological, hydro-and gas-geochemical investigations and thermodynamic calculations the model of gas fields forming in PBSAB was carried out. **Originality**. Hydrogeological data and thermodynamic calculations indicate the depth of origin of hydrocarbons. We suppose that differences in equilibrium depths between the fields of various deposits are coherent with peculiarities of processes of their filling with fluids. The maximum localization of gas-condensate fields at depths of 1900-3000 m testifies not to hydrocarbons formation in this range of depths, but to optimum geology-hydrogeological conditions of forming and of preservation deposits. The migration and preservation of hydrocarbons demand essentially various geology-physical and hydrogeological circumstances: the first is favoured by dynamics of the hydrostatic pressure systems, active tectogenesis, high temperatures, low mineralization of waters; guasistagnat environment, moderate temperatures, presence of the reservoirs that overlapped by reliable seals are favourable for the other. The zone of oil and gas accumulation is related to elisional systems; and zone of through migration to thermohydrodynamic water drive systems. **Practical significance**. The received data allow forecasting composition of a hydrocarbonaceous component of a field proceeding from its proximity to a decompressions zone and depth of occurrence. We guess that with depth the amount of heavy alkanes will be incremented. The gas condensate fields, on depths more than 1900 m, have a plutonic genesisis.

Keywords: Pre-Black Sea aquiferous basin, thermodynamic equilibrium, equation of state, formation waters, water-dissolved gases, hydrocarbons.

Introduction

The hypothesis, based on the supposition that the deep fluids [Ryuichi Sugisaki, Koichi Mimura, 1994, Chekaliuk E. B., 1971] which are degassed from bowels of the Earth and are the complex multicomponent mixture of compounds and elements situated mainly in the supercritical state can serve as the material for forming hydrocarbons, is actively discussed in oil and gas geology over the last decades. The thermodynamic calculations [C. Zhang, Z. Duan, 2009, Chekaliuk E. B., 1971, Huizenga J. M., 2001, Zubkov V. S., 1998] have shown that the favourable conditions for the synthesis of hydrocarbon compounds are at the depths with a lower limit approx -1000 km. It is determined (Lyubchak O., 2008) that the peak concentrations of alkanes in the synthesis correspond to a depth of approx -430 km. The upper limit of favourable temperature and pressure conditions for increasing of the hydrocarbon skeleton reaches -20 km. The hydrocarbon synthesis is impossible at depths less than -20 km. The latter does not deny the possibility of destruction of high-molecular compounds (dispersed organic matter) in the sedimentary formation with forming saturated hydrocarbons.

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Hydrocarbons of various homologous series can be synthesized in the presence of compounds containing hydrogen and carbon in suitable temperature and pressure conditions. Having based on a series of investigations the depth of –1000 km was adopted as the beginning of the "synthesis zone", where the maximum concentration of hydrocarbons falls on –430 km.

The equilibrium hydrocarbons mixtures are formed at a depth ranging from –20 to – 220 km. This interval is called the "zone of equilibrium".

The site that was called "zone of stability of methane" is situated over the zone of equilibrium. The "zone of equilibrium" is supposed to be a kind of reactor, where the hydrocarbon mixtures are formed and then come into the traps in the presence of nearby sublatitudinal faults or zone of decompression. Methane is the only stable component of the hydrocarbon mixtures, presented at the depths from -20 km to the surface. It should be noted, that in the zone of stable methane the chemical processes are characterized by low values of the equilibrium constants. With a certain degree of approximation it can be argued that the systems like natural gas and gas condensate are "preserved" in these circumstances keeping the information about the primary temperature and pressure conditions of their forming.

Purpose

The establishment of lateral and vertical patterns for the depths of natural hydrocarbons mixtures formation in the "zone of equilibrium" is the main task of this work.

Methodology

The estimation of depths of thermodynamic equilibrium for hydrocarbon deposits was carried out, proceeding from the following. In the literature two basic thermodynamic methods of calculation of composition of equilibrium systems with known values of temperature and pressure are given: equilibrium constants of independent reactions and minimization of Gibbs energy (or entropy maximizations). Restriction of the first method is extreme complexity and even impossibility of composing an adequate set of the equations for systems with many components from different groups and homologous series. The second method, thanks its flexibility and possibility to determine equilibrium composition of heterogeneous systems, has gained wide popularity last years. Now the majority of the scientific software is based on minimization of Gibbs energy (SELECTOR-C, UNITHERM, SUPCRT92, HCh, etc.).

We suppose that the common objective problem of the above-mentioned methods consists in imperfection of methods of definition of activity of individual chemical compounds under high and ultrahigh pressures and temperatures.

The modern software for calculation of activity use equations of heat capacity with various corrections for unionized compounds. Engineering software's apply equations of state on the basis of expansion of Van der Waals classical equation. The error problem at calculation of coefficients of activity was considered in details in works by Karpov et.al. [Karpov I. K., 1981]. Based on the results of testing it is ascertained that, depending on the used equation of state and model of mixture imperfect, the value of an error of a fugacity logarithm increases with increasing pressure and reaches 30 % at pressures exceeding 3000 MPa. Certainly, it is not enough for calculation of an equilibrium state of systems in the conditions of an astenosphere of the Earth. Therefore the task of working out a semiempirical equation of state which would give information about parameters of substance in the conditions of high pressures and temperatures was set by us.

Analyzing character of isochors $(\partial P/\partial T)_V$ on P-T-diagram's it is not hard to note that except a narrow zone round lines of phase changes, they are straight lines, at least, in boundaries of accuracy of experiment. On these direct sites of isochors the values of partial derivatives $(\partial P/\partial T)_V$ and $(\partial U/\partial V)_V$ do not depend neither on temperature, nor on pressure, and only on molar volume V:

$$P_R = \frac{T_R}{\alpha_R} - \left(\frac{T_{SR}}{\alpha_R} - P_{SR} \right), \qquad (1)$$

where lower index R corresponds to the reduced (to value in a critical point) value of parameter, S – to value on a saturation line and $\alpha_R = (\partial T_R/\partial P_R)_V$. Equation (1) should satisfy the conditions of a critical point, and also to requirements of a maximum of saturation lines T_{SR} and P_{SR}, as functions from volume.

For all substances in a critical point function T_{SR} from V_{SR} envelops function P_{SR} from both sides, therefore for individual substance $0<\alpha_C<1$. In 1962 L. Riedel has introduced similarity criterion **Ri**, which in a critical point is equal α^{-1}. On T-P-diagramme α_C is angular coefficient of isochore V_C.

For simplification in the equation (1) expression in parenthesis is replaced by following:

$$\left(\frac{T_{SR}}{\alpha_R} - P_{SR} \right) = F_R, \qquad (2)$$

which F_R was calculated as the absolute term of linear equation of the isochore in T-P co-ordinates and was compared with F_R constructed according to experimental data of lines of saturation P_{SR} and T_{SR}. Outcomes of comparison have shown an adequate accuracy of calculation on all space of volumes including a critical point.

Establishing depending α_R and F_R (as coefficients of the linear equation) on molar volume V_R the observed P-V-T data of 16 substances have been used.

Fig. 1 shows schematically the character of dependence α_R upon V_R :
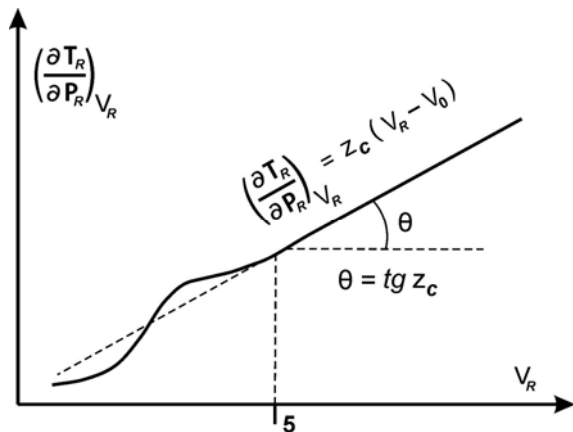
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Fig. 1. The basic character of depending
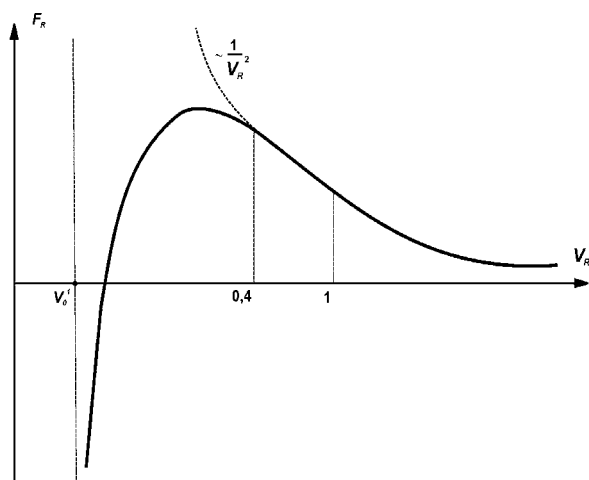$(\partial T/\partial P)_V$ on V_R

Fig. 2. The basic character of dependence
of function F_R on V_R

The carried out analysis points out that for great values of volume ($V_R > 5$) function have linear character, and the angular coefficient is equal to value of a compressibility factor.

Beginning from $V_R < 5$, dependence α_R on V_R starts to lose linear, but preserves the monotonous character to $V_R \approx 0.4$. Substances which by their properties come nearer to ideal, show the linear character of dependence α_R on V_R to values $V_R \approx 1$, however with reduction of volume it gains the above described character.

In Fig. 1 dash line corresponds to α_R from the equation of Van der Waals. It cuts point V_0 on axis V_R which corresponds to volume of one mole of compound in maximum packing. However, it has been shown by experiments that value V_0 for all substances usually is several times less than calculated on the Van der Waals equation

For dependence description α_{R1} on V_R in a range of values V_R from 0.5 and more the functions is offered. This function in detail was described in [Khokha Yu., 2014].

In the equation of state the dependence of temperature and pressure on volume for points of a

line of saturation was not determined separately, and reduced to one function F_R. The basic character of dependence F_R from V_R:

Physical meaning F_R is the additional pressure of intermolecular forces presented as a derivative on volume at constant temperature from an internal energy of intermolecular interactions. The range of values F_R is divided (conditionally) into two parts: before and after $V_R \approx 0.5$. The part with $V_R \geq 0.5$ is proportional to volume raised to the second power, as well as it is in the equation of Van der Waals.

For exposition of dependence F_{R1} on V_R in the space of values $V_R \geq 0.5$ special function is offered. By analogy with previous functional dependence, this function was described in [Khokha Yu., 2014].

Finally the equation of state will be noted:

$$P_R = \frac{T_R}{\alpha_{R1} \cdot \beta} - F_{R1} \cdot \gamma. \qquad (3)$$

For all explored substances constants of the equation (8) are fixed. For some of them factors β and γ remained not fixed. It is related to an insufficient amount of experimental data for these substances.

For calculations of equilibrium compositions of natural gas and gas condensate, taking into account simplicity of system, the method of equilibrium constants of independent reactions has been used. Calculation of activity has been made using an equation of state (4) which has shown an adequate accuracy [Khokha Yu., 2005]. Comparison with experimental data for individual substances shows that the error for the pressures calculating exceeding 100 MPa (for water comparison was made to 25000 MPa, methane – 900 MPa) did not exceed 18 %.

Natural gas, on the whole, contains methane homologues, and also nitrogen, carbon dioxide and in negligible amounts of hydrogen sulphide and helium. Calculation of the thermobaric conditions of formation of natural gases is reduced to a solution of an algebraic equation of the fifth power:

$$\left[\frac{N_{CO_2} + N_{N_2} + N_{He} + N_{H_2S}}{N_{H_2} - N_{H_2S}} \right] \times$$

$$\times \sum_{i=1}^{5} k_i (i+1) \nu_{C_iH_{2i+2}} + \sum_{i=1}^{5} k_i \nu_{C_iH_{2i+2}} - 1 = 0$$

Calculation of a mole portion of homologues of methane is grounded on the supposition that system components compose a regular solution.

We have selected the Pre-Black Sea aquiferous basin (PBSAB) as a model region (Fig. 3), for which the equilibrium depths of the gas and condensate fields were determined and analyzed.

The water area of the PBSAB belongs to regions promising for the search of hydrocarbon accumulations . There are more than a hundred structures, within its boundaries, that can serve as traps for hydrocarbons, that allows us to hope for new discoveries with the full determination of characteristics of gas accumulation based on objective material sheding light on the pressure and temperature conditions of the genesis and migration of hydrocarbons.
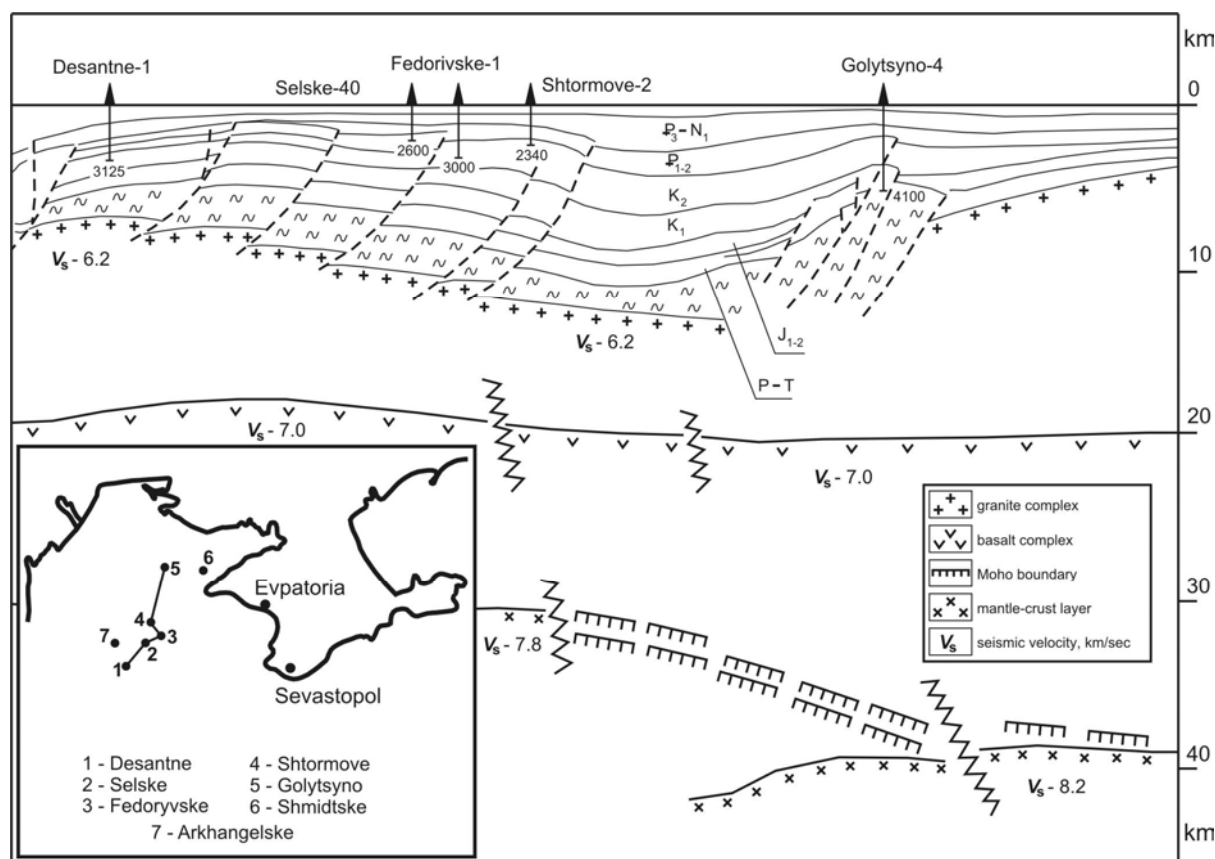
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Fig. 3. Seismic-geological cross section of the model region along line Desantne-Golitsyno

There have been discovered 17gas and 5 gas – condensate reservoirs in the water area of the PBSAB. The gas deposits have been recorded at depths from – 500 to -1600 meters in Neogene, Oligocene–Lower Miocene (Maykopian), Paleocene and Eocene sediments. Four of 5- condensate deposits occur in the Lower Paleocene reservoir (horizon P-XI), and one in the Maastrichtian of Upper Cretaceous. Till now the industrial gas accumulations have not been discovered in the Lower Cretaceous and older formations in the water area of the PBSAB. The small deposits of oil and gas condensate are known in Tarkhankut peninsula.

It is an important thing in the analysis of forming gas deposits in the water area of the PBSAB that the gas deposits irrespective of the age of collectors do not occur at the depths less than -500 for gas, and -1900 m for gas-condensate. The most deep-seated reservoir among exposed ones is Arkhangelske gas field in the horizon P– XI ,in which influx of gas was obtained at an interval of 2973 to 3117 m

All deposits in Low-Paleocene sediments at the depths of 1900 to 3000 m belong are gas- condensate with the condensate factor 39-194 cm^3/m^3. As the exception the Odesa deposit is (interval of 1570 to 1594 m), gases of which do not differ from gases of other Maykopian deposits, which lie hypsometrically considerably higher.

It was also estatablished that the gas-condensate reservoirs are arched, massive-formational, tecto-

nically screened with covers which lie discordantly on the reservoir beds [Atlas..., 1998, etc.]. Emptiness of Paleocene and Cretaceous carbonate rocks is of tectonic or hypergenous origin. Owing to this, after overlapping by fluid impermeable rocks Lower Paleocene reservoires of future gas- condensate fields were formed.

Many researchers believe that commercial oil and gas presence of the basins is associated with the rifts and overrift structures, in particular with near-fault zones that delineate them. Such a connection is considered as genetic. The supporters of the sedimentary- migration hypothesis perceive it in the effect of high heat flow in the rift on the transformation of dispersed organic matter (DOM) into hydrocarbons [V.O. Sokolov, V.Yu. Hain, etc.]. Supporters of mineral mantle origin connect the hydrocarbons with the processes in the mantle. [E.B.Chekalyuk, G.N.Dolenko, G.Yu.Boyko, etc.]. Both of them consider the zone of deep faults of rifts as migration paths of oil and gas. Taking this into account, confinement of gas condensate fields to the side, complicated fracture areas of Odesa- Dzhankoy riftogen is considered to be eloquent [Sollogub V. B., Sologub N. V., 1982].

The essential characteristic of the method of forming gas fields is the degree of gas saturation of formation waters, or its (gas) deficit (inverse value), i. e., the ratio of real gas saturation to the maximum possible under present temperature-pressure condi-

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tions. Maximum saturation of waters with gas while decreasing pressure in a drive water system (e.g.as a result of rising of tectonic movements), in researchers' opinion, promotes degassing waters and formation of gas accumulations [Cortsenshtein V.N., 1984].

The water area of the PBSAB is characterized by the deficiency of gas saturation of formation waters, which is on average 54.2% in all areas. In the productive structures the value of coefficient of elasticity $C_{el} = P_{gas}/P_{bed(blanket)}$ over 0.70 amounts 26.0% of all definitions, and unproductive ones only 6.0%. The value of C_{el} more than 0.75 takes place only in the industrial gas-bearing structures, which accounted 21% of the definitions. In the most productive structures the coefficient of elasticity is from 0.5 to 0.7 (36.8% determinations), and in unproductive ones 0.3–0.5 (35.3 %).

Average values of the coefficient of elasticity of water-dissolved gases (WDG) of aquiferous complexes increase from Miocene to Maykopian and Paleocene from 0.35 to 0.54 and 0.55, and decrease in the Upper Cretaceous and Jurassic to 0.34 and 0.22, respectively, that is well agreed with the industrial content of gas of Maykopian and Paleocene. Nevertheless, there were fixed significant ranges of values C_{el} laterally for different depth intervals: 400 – 1000 m –0.03 to 0.85, 1400-2000 m – 0.02 to 0.92, 2000-2500 m – 0.05 to 0.73 , 2500 -3000 m – 0.02 to 0.92 , and 3000 – 3800 m – 0.05 to 0.80. No changes of- C_{el} in the area of distribution of aquiferous complexes have been observed in the water area. In the Miocene they increase from the North to the South and from Golytsyno and Pradniprovsk structures to Selske, and in Maykopian – from Golytsyno and Pradniprovsk to Flangova and Odesa structures . However, in the Paleocene and Upper Cretaceous complexes C_{el} WDG decreases in this direction. Both of these features suggest that the field of elasticity of WDG is caused by local rather than regional factors .

The most gas saturation is characteristic for calcium chloride (Cl.Ca) (after Sulin) (to $3.148 \cdot 10^{-3}$ m^3/m^3, the average $0.628 \cdot 10^{-3}$ m^3/m^3), and hydrocarbonate natrium (Hyd.Car.Na) ($0.670 \cdot 10^{-3}$–$4.760 \cdot 10^{-3}$ m^3/m^3, average $1.207 \cdot 10^{-3}$ m^3/m^3) waters. Such gas saturation belons to the overcontour waters of gas and undunderlying waters of gas- condensate deposits.

The most absolute gas-saturated waters are characteristic of the Paleocene deposits, but however, they do not reach the maximum possible values established on schedule of O. L. Culberson and I. I. Mc-Ketta [Cortsenshtein V.N,.1977]. Since the solubility of methane in water depends on the temperature and pressure conditions that vary widely in different parts of the basin, we have counted the most theoretically possible gas-saturated water for different ratios P_{pl} and T_{pl}. Only in 4 cases of 44

definitions actual gas saturation comes close to the maximum theoretically possible.

Established by us gas-geochemical zoning is represented by change from down to up the section of fat gases (C_1/C_{2+} <50), medium (C_1/C_{2+} 50-400), dry (C_1/C_{2+} 400-10000) and super dry (C_1/C_{2+} > 10000) due to differentiation composition of hydrocarbon gases, accompanying its migration.

Based on the composition of gases there were distinguished four gas-geochemical zones in the section of sedimentary complex of the water area of the PBSAB. They are: superdry gases of the Neogene sediments , industrial gas content of which is determined in Arkhangelske field at around -601 m; dry and medium gases of the Maykopian and Eocene horizons of Odesa field in the range of marks – 571 to -908 m and fat condensate gases of the Paleocene and the Upper Cretaceous of Shtormove, Golytsyno and Shmidt fields. The gases, similar in composition to the gases of the second zone, occur in the the Paleocene deposits of Odesa deposit, but much deeper: -1595 m -1675 m. Fat gases of Paleocene horizon of Shtormove gas-condensate deposit lie at approximately the same elevation. Thus, gas-bearing horizons of Odesa deposit by the composition of gases, are different from other deposits in the water area of PBSAB that completely is agreed with their special structural- tectonic position.

Subvertical migration of gas-vapour systems was accompanied by changes of their composition and forming in relatively deep-seated horizons the gas-condensate, and at shallow depths – the dry gas fields. Tension strength was manifested on the background of regional contraction the ways of the possible migration were the sublatitudinal faulting and decompression zones in the areas where, for example, at the crossing of faults of different directions.

Edge waters of Maykopian and Eocene and undunderlying waters of Lower Paleocene and Upper Cretaceous industrial gas-bearing reservoires of GD and GCD belong to different genetic types after B. Sulin: – Cl.Ca with salinity of 29-72 g/l and Hyd.Car.Na with salinity of 21-31 g/l, respectively.

Both types of water are enriched with trace elements (TE) –J, Br, B, NH$_4$, some components of water -soluble organic matter (WSOM), what together with high values of hydrostatic coeficient (P_{pl}/ $P_{cond.g}$) testify to hydrogeological isolating gas-bearing reservoirs and, as a consequence, to favourable conditions for preserving deposits in them. In the producing horizons at the base of gas condensate deposits mixtures of "secondary" waters condensed while cooling of gas-vapour mixtures, with the primary formation ones were formed. This is shown by their low salinity of waters (0.5-10 g/l) and their composition (high, sometimes up to 45% eq., content of HCO$_3$, more usual Hyd.Car.Na type, the relative enrichment with some TE and TC).
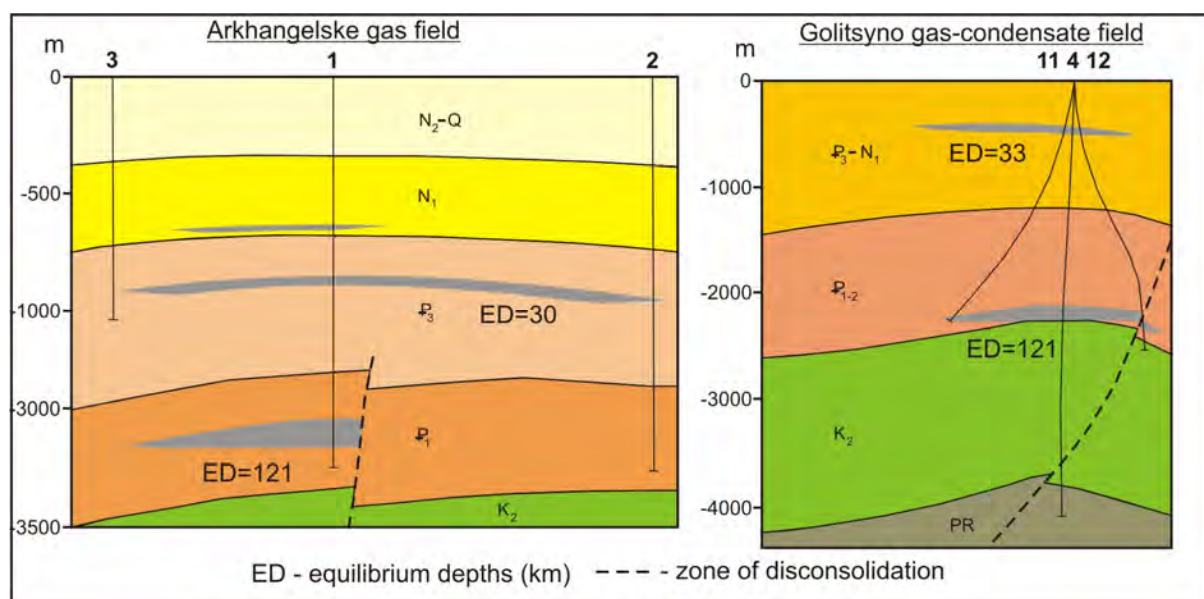
Fig. 4. Schema showing equilibrium depths, stratigrafic and zone
of disconsolidation for Arkhangelske and Golytsyno fields

So, the condensate waters are the hydrogeological criterion of grounding the different aspects of the formation of the hydrocarbons accumulations. They can preserve in the depths only if gases rapidly migrated vertically from high-temperature places of their generation to the traps with significantly lower values of temperature. Bordering the low-salinity waters under the influence of more mineralized hydrogeochemical background is vanished for a relatively short period of time , not exceeding 10^7 years [Kolodiy V. V., Kolodiy I. V. 2002], that is why their presence indicates geologically recent formation of the deposit.

Geological and hydrogeological criteria indicate the time of deposits formation, e.g. screening the Paleocene fields by seals, which stratigraphically diskordantly overlap gas-bearing beds of the Arkhangelske, Shtormove and Schmidt deposits. As it was mentioned above, the indication of geological "youth" of deposits is the presence of poorly mineralized condensate waters, the chemical composition and mineralization of which differ substantially from hydrogeochemical background. The presence of the fields itself in the Miocene sediments indicates Pliocene- Quaternary time of their forming .

The morphology of the traps of gas fields in Paleocene sediments is very characteristic. and indicator, viz. the absence of tectonic screening from deep part of Mikhailivka depression its presence on the opposite side (Odesa, Golitsyno, Schmidt, Arkhangelske deposits). In our opinion, this is due to the important role of Odesa-Dzhankoy rift zone in the formation of hydrocarbon accumulations and subvertical (stepped) gas migration from plunged to risen portions of riftogen sides . Hereby the traps of Golitsyno and Southern Golytsyno fields were filled

from the faults of the northern side and those of Shtormove and Arkhangelske –from southeastern and southern (Fig. 4).

The presence of two or three gas-bearing formations over the massive-formational Paleocene reservoirs in favourable lithological and structural conditions is natural. It reflects the further way of vertical migration of gas and its accumulation in the traps: in the sediments of Maykopian and even Miocene (Arkhangelske deposit). During the migration of gases, especially through the Maykopian clay rocks the sorption of heavy hydrocarbons took place. It caused a decrease of content of heavy hydrocarbon gases. Since the gases in the Maykopian deposits are of different composition –from superdry to fat, we consider them migrational. If the Maykopian gases had been syngenetic to sediments, they would have been approximately of the same type [Kolodiy I.V., 2003).

Results

Calculations have shown that depths, in which equilibrium mixtures of the chemical composition similar to natural gases of known deposits are formed, do not correspond to depths of their bedding in a section of sedimental succession.

Received data (Table) point to essential differences in depths of a thermodynamic equilibrium for the deposits of Eocene, Maikopian, and Neogene on one hand, and Lower Paleocene and Cretaceous sediments on the other. The first are characterized by values of depths in boundaries from 30 to 50 km while the second show a similar parameters in the boundaries 120–150 km.

Table

Chemical composition and equilibrium depths of the Pre–Black Sea aquiferous basin fields

Field	Horizon's index	Gas composition, vol. %											Bedding depths of the producing horizon's top, km	Equilibrium depths, km
		CH_4	C_2H_6	C_3H_8	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$n\text{-}C_5H_{12}$	$i\text{-}C_5H_{12}$	H_2S	CO_2	N_2	He		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Southern Golytsyno	M-III	99.20	0.11	0.05	0	0	0	0	0	0.20	0.34	0	0.575	23
	M-IV	98.89	0.12	0.04	0	0	0	0	0	0.20	0.57	0	0.657	30
Golytsyno	M-3	99.14	0.30	0.10	0	0	0	0	0	0.36	0	0	0.480	33
	M-4	99.70	0.10	0.002	0	0	0	0	0	0.19	0.96	0.007	0.555	21
	M-5	99.72	0.15	0.009	0.005	0	0	0	0	0.12	0.40	0.001	0.565	26
	P-XI	92.31	4.26	1.37	0.66	0.10	0	0.41	0	0	0.86	0	2.123	121
Shtormove	P-XI	85.70	6.49	2.90	0.77	0.65	0.31	0.39	0	0.31	2.20	0	1.800	148
	N₁	98.76	0.005	0	0	0	0	0	0	0.29	0.95	0	0.614	>20
	M-III	98.96	0.271	0.06	0.006	0	0	0	0	0.081	0.627	0	0.806	30
Arkhangelke	M-V	99.14	0.249	0.049	0.008	0	0	0	0	0.07	0.45	0	0.853	30
	P-XI	92.31	4.26	1.37	0.66	0.10	0	0.41	0	0	0.86	0	2.973	121
Shmidt	M-III	98.74	0.30	0.10	0	0	0	0	0	0.10	0.76	0	0.650	36
	M-IV	98.67	0.30	0.05	0	0	0	0	0	0.55	0.43	0	0.690	33
	M-V	98.70	0.39	0.04	0.02	0	0	0	0	0.10	0.52	0	0.700	40
	P-XI	90.03	5.00	1.28	0.70	0	0.33	0	0	1.98	0.68	0	2.710	132
	K₂	86.26	4.78	1.70	0.68	0	0.28	0	0	5.50	0.75	0	2.910	128

We suppose that differences in equilibrium depths between the fields of various deposits are coherent with peculiarities of processes of their filling with fluids. The maximum localization of gas-condensate fields at depths of 1900–3000 m testifies not to hydrocarbons formation in this range of depths, but to optimum geology-hydrogeological conditions of forming and of preservation deposits.

Originality

The migration and preservation of hydrocarbons demand essentially various geology-physical and hydrogeological circumstances: the first is favoured by dynamics of the hydrostatic pressure systems, active tectogenesis, high temperatures, low mineralization of waters; guasistagnat environment, moderate temperatures, presence of the reservoirs that overlapped by reliable seals are favourable for the other. The zone of oil and gas accumulation is related to elisional systems; and zone of through migration to thermohydrodynamic water drive systems [Kolodiy V.V., Kolodiy I.V., 2007, Kolodiy I.V., 2014]. We suppose that migration of hydrocarbons just before filling traps took place in the free hydrocarbons phase, not in water solution. Is sewered in zone of the tectonic deformations connecting the deep bowels with zone of forming deposits in traps. The subvertical migration is predominant though the role of lateral migration is not denied also at small distances.

The essential moment that we wanted to pay attention to is the following: for calculation of depths of an equilibrium we have used exclusively chemical composition of hydrocarbons of the discovered fields, recounted on chemical elements. As a matter of fact, we have supposed that the relationship between chemical elements in a zone of formation of this mixture corresponds to relation fixed in a trap.

Hydrogeological data and thermodynamic calculations indicate the deep character of genesis of hydrocarbons. In our opinion, gases of different composition (from superdry to fat), distributed in Maikopian, are migrational.

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ТЕРМОДИНАМИЧЕСКИЕ И ГИДРОГЕОЛОГИЧЕСКИЕ УСЛОВИЯ ФОРМИРОВАНИЯ УГЛЕВОДОРОДНЫХ МЕСТОРОЖДЕНИЙ ПРИЧЕРНОМОРСКОГО ВОДОНАПОРНОГО БАССЕЙНА

Цель. Установление взаимосвязи между термодинамическими условиями образования углеводородных смесей и зонами аккумуляции залежей углеводородов. **Методика**. Для расчета глубин равновесия нами использовался исключительно химический состав газов месторождений углеводородов, пересчитанный на элементы. В исследованиях подземных вод, свободных и растворенных в воде газов использовались методы химического, количественного спектрального и атомно-абсорбционного анализов, а также газовая хроматография. **Результаты.** Полученные результаты указывают на существенные отличия в глубинах термодинамического равновесия для месторождений в эоценовых, майкопских, и неогеновых отложениях с одной стороны и нижнепалеоценовых, меловых – с другой. Первые характеризуются значениями равновесных глубин в границах от 30 до 50 км, в то время как вторые показывают аналогичные параметры в границах от 120 до 150 км. Анализ геологических, гидрогеологических и геохимических условий Причерноморского водонапорного бассейна (ПВНБ) свидетельствует, что источники газопаровых систем, из которых образовались залежи газа в верхнемеловых, палеоценовых и майкопских отложениях, находились в высокотемпературной (около 300 °C) зоне глубоких впадин бассейна. Мы считаем, что нижнепалеоценовые залежи сформированы первично, вследствие быстротечной субвертикальной миграции гомогенной газопаровой смеси из высокотемпературных зон генерации. Путями возможной миграции были тектонические нарушения и зоны повышенной трещиноватости пород. Залежи в майкопских и миоценовых отложениях отражают дальнейший путь вертикальной миграции газа и его аккумуляции в ловушках. Гидрогеологические, гидро и газогеохимические исследования и термодинамические расчеты дали возможность обоснования модели формирования газовых месторождений ПВНБ. **Научная новизна**. Гидрогеологические исследования и термодинамические расчеты, проведенные нами согласуются с представлениями о высокотемпературном генезисе углеводородов. Мы полагаем, что отличия в равновесных глубинах между месторождениями различных отложений связаны с особенностями процессов их заполнения флюидом. Максимум локализации залежей в интервалах глубин 1900-3000 м свидетельствует не об образовании углеводородов в этом диапазоне глубин, а о наиболее благоприятных геолого-гидрогеологических условиях формирования и сохранения залежей. Миграция и консервация углеводородов требует различных геолого-физических и гидрогеологических обстановок: миграции благоприятствует динамичность водонапорных систем, активный тектогенез, высокие температуры, невысокая минерализация вод; аккумуляции (консервации) углеводородов благоприятствует квазизастойная обстановка, умеренные температуры, наличие резервуаров, перекрытых надежными покрышками. Зона нефтегазонакопления связана с элизионными, а сквозной миграции – с термодинамическими водонапорными системами. **Практическая значимость**. Результаты позволяют прогнозировать состав углеводородной составляющей месторождения исходя из его местоположения, а именно – соседства с зоной разуплотнения пород (повышеной трещиноватости) и глубиной залегания. Мы полагаем, что с глубиной количество тяжёлых алканов будет увеличиваться. Газоконденсатные месторождения, находящиеся на глубинах более 1900 м, имеют глубинное происхождение. Гидрогеологические и термодинамические критерии газонефтеносности Причерноморского ВНБ могут использоваться для прогнозирования залежей в других нефтегазоносных регионах Украины.

Ключевые слова: Причерноморский водонапорный бассейн, термодинамическое равновесие, уравнение состояния, подземные воды, водорастворённые газы, углеводороды.

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ТЕРМОДИНАМІЧНІ І ГІДРОГЕОЛОГІЧНІ УМОВИ ФОРМУВАННЯ ВУГЛЕВОДНЕВИХ РОДОВИЩ ПРИЧОРНОМОРСЬКОГО ВОДОНАПІРНОГО БАСЕЙНА

Мета. Встановлення зв'язку між термодинамічними умовами утворення вуглеводневих сумішей з зонами аккумуляції вуглеводневих відкладів. **Методика.** Для розрахунку рівноважних глибин ми використовували виключно хімічний склад газів родовищ вуглеводнів, перерахованих на елементи. В дослідженнях підземних вод, вільних і водорозчинених газів використовувались методи хімічного, кількісного спектрального і атомно-абсорбційного аналізів, а також газова хроматографія. **Результати.** Одержані результати вказують на існування суттєвої відмінності в глибинах термодинамічної рівноваги для родовищ в еоценових, майкопських і неогенових відкладах з одного боку та нижньопалеоценових, крейдових – з іншого. Перші характеризуються значеннями рівноважних глибин в межах від 30 до 50 км, в той час як інші характеризуються аналогічними параметрами в межах від 120 дор 150 км. Аналіз геологічних, гідрогеологічних і геохімічних умов Причорноморського водонапірного басейна (ПВНБ) свідчить, що джерела газопарових систем, з яких утворились поклади газу в верхньокрейдових, палеоценових та майкопських відкладах, знаходились у високотемпературній (біля 300 °C) зоні глибоких западин басейна. Ми вважаємо, що нижньопалеоценові поклади первинно сформувались внаслідок швидкоплинної субвертикальної міграції гомогенної газопарової суміші з високотемпературних джерел генерації. Шляхами можливої міграції були тектонічні порушення і зони підвищеної тріщинуватості порід. Поклади в майкопських і міоценових відкладах відображають подальший шлях вертикальної міграції газу і його акумуляції в пастках. Гідрогеологічні, гідро і газогеохімічні дослідження і термодинамічні розрахунки дали змогу обґрунтувати модель формування газових родовищ ПВНБ. **Наукова новизна.** Гідрогеологічні дослідження і термодинамічні розрахунки, проведені нами, узгоджуються з уявленнями про високотемпературну генезу вуглеводнів. Ми вважаємо, що відмінності в рівноважних глибинах між родовищами різних відкладів пов'язані з особливостями процесів їх заповнення флюїдом. Максимум локалізації покладів в інтервалах глибин 1900–3000 м свідчить не про утворення вуглеводнів в цьому діапазоні глибин, а про найбільш сприятливі геолого-гідрогеологічні умови формування і збереження покладів. Міграція і консервація вуглеводнів потребує різних геолого-фізичних і гідрогеологічних обстановок: міграції сприяє динамічність водонапірних систем, активний тектогенез, високі температури, невисока мінералізація вод; акумуляції (консервації) вуглеводнів сприяє квазізастійна обстановка, помірні температури, наявність резервуарів, перекритих надійними покришками. Зона нафтогазонагромадження пов'язана з елізійними, а наскрізної міграції – з термодинамічними водонапірними системами. **Практична значущість.** Результати дозволяють прогнозувати склад вуглеводневої складової родовищ, виходячи з їх місцеположення, а саме – близькості до зон розущільнення порід (підвищеної тріщинуватості) та глибини залягання. Ми вважаємо , що з глибиною кількість тяжких алканів буде збільшуватись. Газоконденсатні родовища на глибинах понад 1900 м мають глибинне походження. Гідрогеологічні та термодинамічні критерії газонафтоносності Причорноморського ВНБ можуть застосовуватись для інших нафтогазоносних регіонів України.

Ключові слова: Причорноморський водонапірний басейн, термодинамічна рівновага, рівняння стану, підземні води, водорозчинені гази, вуглеводні.