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ENTROPY MAXIMIZATION METHOD IN THERMODYNAMIC MODELLING OF ORGANIC MATTER EVOLUTION AT GEODYNAMIC REGIME CHANGING

Purpose. Our research main purpose is to demonstrate the use of entropy maximization method for calculating the geochemical system composition, which consists of solid and gaseous organic substances. Changing the geodynamic situation is the driving force of elements redistribution between compounds in such systems. According to thermodynamic apparatus, the main factors influencing this redistribution are pressure, temperature and the initial number of elements. **Methods.** Gibbs energy minimizing, maximizing the entropy, independent chemical reactions constants, Lagrange's method of undetermined multipliers, Newton–Raphson iterative method. It is well known that the fossilized organic matter, which is mainly represented by many types of kerogen, is an irregular polymer with structure that cannot be described definitely. To calculate the equilibrium in the kerogen/gas system and obtain reliable results, it is necessary to apply a new model, without using the model structures of kerogen. We have proposed and described in detail a method of applying the Jaynes' formalism and maximizing entropy method to calculate the change in the composition of the kerogen/gas system with geodynamic regimes changing. Software in the Excel macros form and a compiled dynamic library, written in Visual Basic language was created for calculations. **Results.** To verify the reliability of the proposed method and algorithm, we calculated the composition of the geochemical system, consisting of type II kerogen, methane to pentane hydrocarbons (including isomers), carbon dioxide, water and hydrogen sulfide. The calculation result is the molar fractions of hydrocarbon components and additive groups that make up kerogen, for different depths of the earth's crust. The calculations were performed for three heat fluxes: 40, 75 and 100 mW/m^2, taking into account lithostatic pressure. **Scientific novelty.** It is established that the geodynamic situation, changing in a complex way, affects the distribution of elements between gases and kerogen in a closed thermodynamic system; modeling the kerogen/gas system behavior by method of entropy maximization, provides the results that do not contradict study of type II kerogen structure at different stages of maturity; the character of changes in the concentrations of hydrocarbon gases in equilibrium with type II kerogen indicates the inconsistency of the "oil window" hypothesis with the postulates of equilibrium thermodynamics. **Practical significance.** The entropy maximization method can be successfully used to calculate the composition of various geochemical systems consisting of organic compounds. The method is suitable for determining chemical composition of the irregular polymers, such as kerogen, bitumen, humic, in equilibrium with organic and inorganic gases and liquids.

Key words: entropy maximization method; organic matter evolution; kerogen II type; thermodynamic equilibrium; Jaynes' formalism.

Introduction

The permanent matter movement within the sedimentary strata, caused by a number of geodynamic factors, determines chemical transformations in structural-material complexes (SMC). In this paper, SMC is considered as an isolated geochemical system that does not exchange a substance with another SMC. The composition of this system is regulated by many factors that have a different level of influence – it is the gravitational and electromagnetic components, surface tension, pressure, temperature and components initial concentrations. Rate of their absolute values change depends on the specific geodynamic situation inherent in the area of the Earth under consideration.

However, excluding transient phenomena, such as the movement of a high-energy fluid in the decompression zone, the lifetime of the geochemical system under the influence of approximately the same values of the above-mentioned factors is measured in millions of years. Under such initial conditions, it can be assumed that in the evolution process geochemical systems constantly migrate from one zone of thermodynamic equilibrium to another, and have enough time to attain an equilibrium state in each. This means that the equilibrium thermodynamics analytical approach can be used to describe the changes that occur in such systems.

For the sake of simplicity, we will consider the geochemical system to be simple, i.e. in the future only external pressure will be taken into account among the mechanical and non-mechanical forces acting on the system from the outside.

The isolated geochemical system composition naturally changes with temperature and pressure changes in the processes of immersion and uplift, characteristic of both convergent boundaries, where the temperature influence can be the main factor of change, and tectonic depressions, which are gradually filled with sedimentary rocks.

In recent decades, a number of methods have been proposed [Blecic, et al., 2016; Koukkari, 2014; Sanford, & McBride, 1994] that allow calculating the composition of isolated systems consisting of an unlimited number of components in different phase states. Researchers follow two strategies – "stoichiometric", which is based on independent chemical reactions in mutual equilibrium, and "non-stoichiometric", which takes into account the chemical potentials of the system independent components.

"Stoichiometric" strategy applying leads to a solution in the form of a system of nonlinear equations, which dramatically changes when a new component is introduced into the system [Khokha, 2014]. The second method is somewhat easier for systematizing, and the introduction of new components is a comparatively simple operation [Koukkari, 2014]. For both strategies, the system equilibrium conditions are calculated in the same way – either by finding the minimum of the free Gibbs energy or the Helmholtz energy, most often by applying the Lagrange's method of undetermined multipliers. For the "non-stoichiometric" method, nonlinear equations were successfully linearized, which led to its widespread use in scientific and engineering problems solving.

For a system consisting of s pure solids and m ideal gases, the total Gibbs energy G at temperature T and dimensionless pressure P (the ratio of the external pressure acting on the system to the standard pressure of 1×10^5 Pa) can be written (1):

$$G = RT \cdot \sum_{k=1}^{m} n_k^{gas} \left[\left(\frac{\mu}{RT} \right)_k^{gas} + \ln(P) + \ln\left(\frac{n_k^{gas}}{N} \right) \right] + \sum_{k=1}^{s} n_k^{con} \left(\frac{\mu}{RT} \right)_k^{con},$$

where the index "gas" denotes the gaseous components, "con" – the substances in the condensed state (solids and liquids), k – the components number, μ – the pure substance chemical potential, N – the moles number, R – molar gas constant. The chemical elements, which form geochemical system components, represent a set of independent components. As a result, the mass balances needed to solve minimization problem can be presented as:

$$\sum_{k=1}^{m} a_{kj}^{gas} n_k^{gas} + \sum_{k=1}^{s} a_{kj}^{con} n_k^{con} = b_j, \qquad (2)$$

where a is the number of the j-th element atoms in the molecules of the k-th substance, b is the number of the j-th element in the system; $j = 1, 2,..., NC$ (number of components in the system).

The calculation is a minimization of the goal function F from substance amount n_k:

$$F(n) = \sum_{k=1}^{m+s} n_k \cdot \left(\frac{\mu}{RT} \right)_k + \ln(P) \sum_{k=1}^{m} n_k + \sum_{k=1}^{m} n_k \cdot \ln\left(n_k \Big/ \sum_{k=1}^{m} n_k \right). \qquad (3)$$

Mass balance constraint:

$$\vartheta(n) = \left(\sum_{k=1}^{m+s} a_{kj} n_k - b_j \right)_{j=1}^{NC}. \qquad (4)$$

The Gibbs energy minimization is equivalent to the minimization of the function $F(n)$ in equation (3) taking into account constraint (4). When applying the Lagrange's method of undetermined multipliers, the following objective function is minimized from the substance amount n_k:

$$L(n, \lambda) = F - \lambda_j \left(\sum_{k=1}^{m+s} a_{kj} n_k - b_j \right)_{j=1}^{NC}, \qquad (5)$$

$$\lambda = \lambda_1, \lambda_2, ..., \lambda_{NC},$$

where λ are undetermined coefficients. After obtaining derivative of F by the substance amount n_k and further transformations, we obtain for the final solution by iterative methods a set of three equations, of which the first two are linear, and the last (6.3) is nonlinear:

$$\sum_{k=1}^{m+s} a_{kj} n_k - b_j = 0, j = 1, 2, ..., NC; \qquad (6.1)$$

$$\left(\frac{\mu}{RT} \right)_k - \sum_{j=1}^{NC} a_{kj} \lambda_j = 0, k = m+1, .., m+s; \qquad (6.2)$$

$$\left(\frac{\mu}{RT} \right)_k + \ln(P) + \ln\left(\frac{n_k}{N} \right) - \sum_{j=1}^{NC} a_{kj} \lambda_j = 0, \qquad (6.3)$$

$$k = 1, 2, ..., m,$$

To linearize equation (6.3), the Taylor series expansion is used; as a result, the system (6.1)–(6.3) becomes a reliable basis for calculating the composition of systems with an arbitrary number of components. Calculating the composition of geochemical systems composed of real gases will somewhat complicate the above-mentioned simultaneous equations, but will not change the principle of their construction.

To obtain a calculable result, it is necessary to input data about each component of the system in the simultaneous equations (6.1)–(6.3). In chemical technology, where the Gibbs free energy minimization method has become widespread, the engineer has

complete information about the reaction system composition. However, real natural systems consist of three-dimensional polymers of irregular structure, for which only the average mass concentration of elements (C, H, O, N and S) and the proportional content of the main functional groups, characteristic of organic matter are established.

Under such conditions, it is impossible to apply classical minimization methods without introducing a number of assumptions, which necessarily include the exact structure of the irregular polymer (e.g., humin or kerogen) and the value of its thermodynamic functions. Due to the uncertainty of the natural polymer's composition, the model structures themselves can be a source of errors in the final calculations.

Purpose

To determine the composition of a geochemical system consisting of irregular natural polymers in contact with gases, without making assumptions about their structure.

Methods

In the geological publications, the natural polymers structure is traditionally described by models, which are formed to the discretion of the authors, taking into account the accumulated data about polymers elemental composition, molecular weight and information about functional groups obtained by IR-spectroscopy, X-ray diffraction analysis, NMR methods, etc. [Kelemen et al., 2007; Vandenbroucke, & Largeau, 2007; Tissot, & Welte, 1984]. In this paper, we present natural polymers as a set of additive components, each of which makes a defined contribution to the general molecular thermodynamic potentials. Among the additive-group methods used for thermodynamic functions calculation, we chose the van Krevelen method [van Krevelen, & Chermin, 1951], widely used in geochemistry.

Our task in principle cannot be solved by using a deterministic approach. The initial data do not contain enough information for the probabilities determination. By it we mean the molar fractions of the components that make up the system, including additive constituents of irregular natural polymer. To solve such a problem, one should turn to the mathematical apparatus which allows calculating the most consistent distribution of probabilities.

Ten years after the publication of Claude Shannon's papers (1948), in 1957 Edwin Thompson Jaynes concluded that the methods of statistical mechanics, which underlie thermodynamics, are a special case of the error prevention general method [Jaynes, 1957]. In Jaynes' method, as well as in the general method of error prevention, we try to determine the probability function based on given averages.

Myron Tribus proposed the method of Jaynes' formalism applied in thermodynamics [Tribus, 1961]. The task of finding the minimal contradictory probability distribution p_i, is to maximize the unknown function S, which satisfies the equations of connection (7) and (8):

$$\sum_i p_i = 1, \qquad (7)$$

for the task condition (7) is reduced to the sum of molar fractions:

$$\sum_{i=1}^{44} n_i^{add} + \sum_{i=1}^{m} n_i^{gas} = 1, \qquad (7.1)$$

where the index *"add"* corresponds to the 44-th additive parts, which form the natural polymer [van Krevelen, & Chermin, 1951]; *"m"* – the amount of gases in the system, and the set of additive parts and gases will be called "components";

$$\sum_i p_i g_i(X_i) = \{g_r\}; r = 1,2,..., \qquad (8)$$

where $\{g_r\}$ – mathematical expectation function; for the task:

$$\{g_r\} = N_r^{el}; r = C, H, O, N, S, \qquad (8.1)$$

where N^{el} is the number of elements r in 1 mole of system components.

The problem solution by Jaynes: "The least erroneous way to determine probabilities is to maximize the function S (which is called entropy) under the available information". The goal function S is given by the equation:

$$S = -K \sum_i p_i \cdot \ln(p_i), \qquad (9)$$

where K is a constant; for the chosen system, goal function is:

$$S = -R\left[\sum_{i=1}^{44} n_i^{add} \cdot \ln(n_i^{add}) + \sum_{i=1}^{m} n_i^{gas} \cdot \ln(n_i^{gas}) \right], (9.1)$$

Nullification of function (9.1) variation is the equation for determining the system component (both additive part and gas) molar fraction, expressed in terms of the Planck potential:

$$n_i = e^{-\left(\lambda_0 + \lambda_C \cdot N_i^C + \lambda_H \cdot N_i^H + \lambda_O \cdot N_i^O + \lambda_N \cdot N_i^N + \lambda_S \cdot N_i^S\right)},$$

$$\lambda = \lambda / RT, \qquad (10)$$

where N^C, N^H… – the elements number in the component i. For elements λ – indefinite Lagrange multiplier, physical meaning of which is the dimensionless Planck potential, μ – Gibbs potential of component (J/mol); and λ_0 is the zero Lagrange factor, determined from the condition of normalization (7.1):

$$\lambda_0 = \ln\left(\begin{array}{c}\sum\limits_{i=1}^{44+m}\lambda_C N_i^C + \lambda_H N_i^H + \lambda_O N_i^O \\ + \lambda_N N_i^N + \lambda_S N_i^S + \Delta G_i / RT\end{array}\right). \quad (11)$$

The Lagrange factors in equations (10) and (11) are unknown, their values are calculated in the solution process. And the zero Lagrange factor has special properties that determine the entire geochemical system in general:

- its first-order derivative on each of the indefinite factors (λ_C, λ_H...) gives the molar fraction value of the i-th component with the inverse sign;
- the second-order derivative λ_0 on indefinite factors is the variance D of the corresponding element (C, H...) distribution;
- mixed derivative λ_0 on indeterminate factors gives a correlation K between the concentrations of elements.

Accordingly, the correlation coefficient k is derived from the second-order and mixed derivatives λ_0:

$$n_i = -\frac{\partial \lambda_0}{\partial \lambda_r}; D = \frac{\partial^2 \lambda_0}{\partial \lambda_r^2}; K = \frac{\partial \lambda_0}{\partial \lambda_{r1} \cdot \partial \lambda_{r2}};$$
$$k = \frac{K}{\sqrt{D_{r1} \cdot D_{r2}}}; r = C, H, O, N, S, \quad (12)$$

where $r1$ and $r2$ are any two elements. The properties of derivatives play an important role in the analysis of changes in the geochemical system that occur under the influence of dynamic factors, and can be used to compile its multifactor model. In this paper, we used only the first equation from array (12).

All aforementioned methods for calculating the composition of the system in a state of thermodynamic equilibrium require information about the system components chemical potential. To determine this potential when calculating by the method of the Gibbs energy minimizing, maximizing the entropy or independent chemical reactions constants, it is enough to have information about the Gibbs energy of formation of each of the compounds ΔG_f (P, T) that forms the system [Koukkari, 2014]. This potential at standard pressure can be calculated by quantum-chemical methods [Stull, et al., 1969].

The calculation is significantly complicated when the pressure is higher than standard. Such conditions are realized in the bowels of the Earth. The equation of state (EOS) which relates the pressure (P), temperature (T) and volume (V) should be used to determine the Gibbs energy at values greater than the standard. Necessary thermodynamic functions can be determined from EOS parameters. For example, the change in Gibbs energy for an isothermal process (T = const):

$$\Delta G_T = \int\limits_1^2 V dP, \quad (13)$$

where indexes: 1 – standard pressure, 2 – system pressure. It is clear that in order to obtain the full value of the change in Gibbs energy, required for the calculation, it is necessary to add to this integral the standard Gibbs energy of compound formation. To obtain a reliable result, you should choose the EOS that provides the maximal accurate information about the geodynamic system components, as well as choose the thermodynamic constants of compounds, which will be used in quantum-mechanical calculations.

In general, the thermochemical Gibbs energy (G) is obtained in the following way:

$$\sum_k \mu_k n_k = U + \sum_i L_i l_i - TS = H - TS \equiv G, \quad (14)$$

where μ is the chemical potential, n is the amount of matter; U is the system internal energy; L is the force; l is the force vector (the product $L \times l$ is equal to the work W, for simple systems it is reduced to work against external pressure, ie PdV); S – entropy; H – enthalpy; k – system components number; i – work types.

As follows from dependence (14), the absolute values of the Gibbs energy cannot be determined because one of its components is enthalpy. The value of the Gibbs energy can be expressed only as the Gibbs energies difference for two states, one of which should be taken as the standard ΔG_f° (the upper index $^\circ$ indicates the standard pressure). In chemical thermodynamics, it is assumed that $\Delta G_f^\circ(T)$ is the energy of a compound formation in the standard state of an ideal gas, pure liquid or solid phase at a pressure of 0.1 MPa from elements taken in their standard state.

In this paper, the Gibbs energy of individual compounds formation at standard pressure P and temperature T, denoted as $\Delta G_f^\circ(T)$, was selected from the results of quantum mechanical calculations, described in detail in the Stull [Stull, 1969]. The $\Delta G_f^\circ(T)$ calculation was performed after enthalpy $\Delta H_f^\circ(T)$ and entropy $\Delta S_f^\circ(T)$ determination:

$$\Delta H_f^0(T) = \Delta H_f^0(298) + \left(H_T^0 - H_T^0\right)_{com} -$$
$$-\sum\left(H_T^0 - H_T^0\right)_{el};$$
$$\Delta S_f^0(T) = S_T^0(com) - \sum S_T^0(el); \quad (15)$$
$$\Delta G_f^0(T) = \Delta H_f^0(T) - T \cdot \Delta S_f^0(T).$$

In the formula (15), index "com" denotes compound and "el" – element. The enthalpy and entropy changes were calculated from the heat capacity equation (Stall) by integration. At standard pressures within the temperatures realized in all considered heat fluxes, the dependence of the Gibbs energy on the temperature is the equation of the line with minimum standard deviations.

For each gaseous component in the system, a reliable equation of state recommended by NIST was

chosen. If the limits of EOS application are less than the pressure or temperature of the calculation, then we estimated the possibility of EOS data extrapolation.

The calculation of the Gibbs energy of gas components formation $\Delta G_f(P, T)$ at temperatures and pressures of the earth's crust was carried out by the formula:

$$\Delta G_f^P(T) = \Delta G_f^0(T) + \begin{bmatrix} \left(G_T^P - G_T^0\right)_{com} - \\ -\sum\left(G_T^P - G_T^0\right)_{el} \end{bmatrix}, \quad (16)$$

where the Gibbs energies values G_T^P and $G_T^°$ were determined by the EOS using the CoolProp library [Bell, et al., 2014].

Calculations algorithm

For the system described by equations (9.1)–(12) it is practically impossible to use linearization by Taylor series expansion, similar to equation (6.3). Therefore, the maximum entropy value searching was carried out by the Newton–Raphson method in several stages.

At the first stage, the input data (mass fractions of elements in organic matter, %) are reduced to the dimensionless form of molar particles ω_r.

After, the randomizer generates five dimensionless Planck potentials (λ in equation 10) for each element in the system. Limits for potentials generating are set up experimentally: + 100… -100. Next, we establish the correspondence of the generated potentials to the method convergence by a simple procedure. The next step is to start the iterative procedure which consists in compiling a system of equations for four elements from the r series with the exception of sulfur:

$$\frac{\sum\limits_i N_i^r \cdot n_i}{\sum\limits_i n_i} = \omega_r, \quad (17)$$

where ω_r is the element molar fraction, N_i^r is the number of the element r in the additive component or individual compound (component), n_i is the unknown value. The molar fraction of sulfur is taken into account separately after each iteration step. Given the complex topology of the solution space, a limited number of iterations are performed to estimate the convergence in each cycle. In the convergence absence or signs of divergence, the cycle of iterations is interrupted and the calculation returns to the stage of potentials generating. After the last iteration, the following parameters are determined:

- the system totally – Gibbs energy, enthalpy and entropy (in two ways);
- the component – molar fraction;
- the element – variance.

The obtained dataset is one of many quasi-stationary solutions for the selected system. We have found experimentally that when sorting from 10,000 quasi-stationary solutions, we necessarily find the one that characterizes the absolute minimum of Gibbs energy and determines the equilibrium state.

To conduct the calculations, we created software in the Excel macros form and a compiled dynamic library, written in Visual Basic 6.0 language, linked to MS Excel program.

The inverse calculation of mass fractions due to the obtained potentials showed that the error is less than 0.005 mass fractions, which is less than the input data accuracy. The algorithm described above is suitable for calculating the composition of geochemical systems in a wide range of geological conditions. The limitation is the availability of reliable information about the Gibbs energy of the individual substance's formation.

Results

Data about type II kerogen transformations were used to verify the proposed method reliability for calculation of real geochemical systems composition in different geodynamic regimes. It is well-known that this type of kerogen is more common than others in sedimentary rocks, which are considered a source of oil and in oil shale [Tissot, & Welte, 1984], therefore it was chosen for analysis by entropy maximization method. Type II kerogen is characterized by relatively high values of the H/C and relatively small – O/C ratio (Fig. 1). Its primary material is marine sediments, containing residues of microorganisms, phytoplankton and zooplankton, which are transformed in the reducing environment.
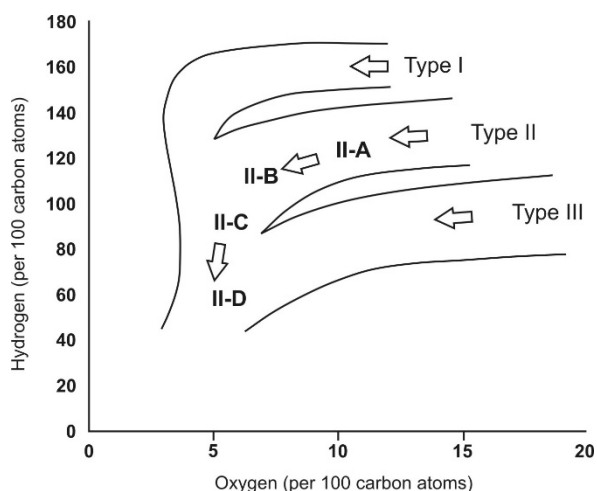

Fig. 1. Van Krevelen diagram and transitional stages of type II kerogen maturity

The arrows in Fig. 1 show the path of type II kerogen transformations from immature (II-A) through the beginning of the "oil window" (II-B) and its end (II-C) to overmature (II-D) [Ungerer, et al., 2015].

The study of type II kerogen structure by chemical and physicochemical methods, such as ^{13}C NMR, X-ray photoelectron spectroscopy and infrared spectroscopy showed that polyaromatic nuclei, which are combined with aliphatic, etheric and esteric groups, play an

important role [Kelemen, et al., 2007]. In addition to these basic structural elements, heteroatomic groups such as hydroxyl, ketones and carboxyl, are observed in smaller quantities. The various type II kerogen models differ slightly, the greatest differences are observed in the interpretation of the length of saturated hydrocarbon chains [Helgeson, et al., 2009; Vandenbroucke, & Largeau, 2007; Ungerer, et al., 2015; Behar, & Vandenbroucke, 1987].

The elemental composition of type II kerogen is obtained by averaging the data given in the following sources: Ungerer, et al., 2015; Helgeson, et al., 2009; Tissot, & Welte, 1984; Behar, & Vandenbroucke, 1987. This paper uses the following type II kerogen composition measured as mass fractions of elements (in %): carbon – 82,5; hydrogen – 6,9; oxygen – 6; nitrogen – 2,6 and sulfur – 2.

The van Krevelen diagram shows (see Fig. 1) that type II kerogen undergoes a series of continuous transformations with increasing maturity, which depends on the transformation time, temperature and pressure.. These transformations are characterized by loss of hydrogen and oxygen in the formation of low molecular weight compounds. The obvious reason of

hydrogen loss is the formation from kerogen, due to destructive processes, low molecular weight saturated and aromatic hydrocarbons, which form the main part of natural gas, gas condensate and oil. For the largest fraction of fossil hydrocarbons – alkanes, the ratio of H/C with increasing molecular weight is about 200 (per 100 carbon atoms), and the aromatic components of oil are characterized by H/C values nearly 100. In addition, the possibility of water formation should be considered, each molecule of which removes two hydrogen atoms from kerogen. Oxygen loss is apparently caused by the formation of water and carbon oxides, mainly CO_2.

A redistribution of elements is also observed during the type II kerogen transformation from stage A to D in structures containing heteroatoms.   . The amount of nitrogen in the pyridine ring and in the amines decreases significantly, while its content in the pyrrole cycle increases. Sulfur is redistributed among additive groups, reducing the amount in aliphatic structures and increasing in cyclic. The information (average data) about changes in the composition of type II kerogen during thermal maturation, obtained from literature sources, are shown in the table:

Composition and structural features for stages of type II kerogen maturity

Parameter	Stage of maturity			
	A	B	C	D
H/C	117	111	89	56
O/C	9.7	5.9	5	4.7
N/C	2.9	2	2.1	2.1
S/C	1.4	1.2	0.6	1
Aromatic carbon, avg., %	40	46.5	54	76
Oxygen in C-O (per 100 C)	6	4.1	4.2	3.3
Pyrrole's N, mol. %	52	59	65	62
Pyridine's N, mol. %	27	19	18	15
Aromatic S, mol. %	46	56	54	80
Aliphatic S, mol. %	54	44	46	20

The calculation of the geochemical system (kerogen/fluid) composition, according to Jaynes' formalism, was reduced to determining the optimal distribution of 5 elements (C, H, O, N, S) among 44 additive components in the solid phase (in this paper – type II kerogen) and individual substances that form system (CO_2, H_2O, H_2S, NH_3, CH_4, C_2H_6, C_3H_8, i-C_4H_{10}, n-C_4H_{10}, i-C_5H_{12}, neo-C_5H_{12}, n-C_5H_{12}). These additive components fully describe any organic substance and are a set of structural units: alkanes, alkenes, alkynes, and various structures containing oxygen, nitrogen and sulfur. We calculated the system composition for three heat fluxes: 40, 75 and 100 mW/m^2 within depths of 1–20 km.

The input data for the calculation are the type II kerogen elemental composition, temperature, pressure

and the Gibbs free energy of formation for the components of the system. Determination of Gibbs free energy of formation of individual substances in thermobaric conditions of sedimentary stratum are describe above in section "Methods". Solutions are sought by maximizing entropy, choosing from a set of quasi-equilibrium intermediate solutions such that is characterized by the minimum of Gibbs free energy.

The results of the calculations are the mole fractions of the system components – kerogen additive groups and gases. By analogy with previous publications [Lyubchak, Khokha and Yakovenko, 2018], to describe the structure of kerogen in a state of thermodynamic equilibrium, we applied a well-known additive-group scheme proposed by van Krevelen. The approximation equations were used to

determine the pressure and temperature within the specified depth limits, for areas with different values of heat flux.. According to the data [Dziewonski, & Anderson, 1981], we deduced the analytical dependence of the geostatic pressure (*P*, MPa) on the depth (*h*, km):

$$P = 0.1 + 604.5 \cdot \left(\frac{h}{24} \right)^{1.64} \cdot e^{-0.02(h-24)}. \quad (18)$$

The temperature distribution for each heat flux was calculated according to the data [Hasterok, & Chapman, 2011]. Based on the results of heat flux

values approximation in the range from 40 to 100 mW/m², we proposed the dependence of temperature (*T*, K) on depth (*h*, km) and heat flux (*q*, mW/m²):

$$T = 291.15 + h \cdot (0.355q - 3.02). \quad (19)$$

The results of the calculation established that main fraction of the solid phase in the state of thermodynamic equilibrium is represented by aromatic carbon, with the exception of heteroatom groups (Fig. 2):
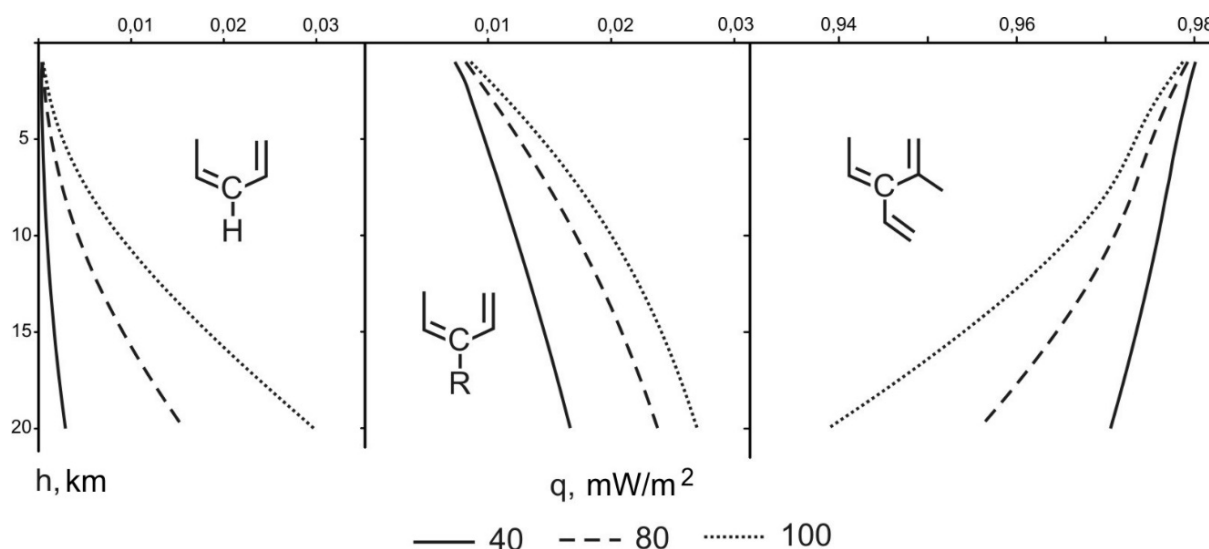

Fig. 2. The content of aromatic additive groups (mole fractions)
of kerogen according to thermodynamic calculation

Generally, all the researchers noted the tendency to type II kerogen aromatization and carbonization during maturation. Extrapolation of this trend to infinity has led to the "methane-graphite death" conception [Planche, 1996]. Data from table 1 show that during the type II kerogen maturation, the percentage of aromatic carbon increases from 40 to almost 80 %. Identical data are given in [Kelemen, et al., 2007], where the content of aromatic carbon in the catagenesis deepest stages exceeds 80 %. Simultaneously with aromatization, we observed an increasing number of carbon atoms in aromatic clusters. In general, the thermodynamic calculation coincides well with the experiments. The deviation can be considered a decreasing of tertiary aromatic carbon content with increasing temperature (at deepening), as shown in Fig. 2.

We have studied the behavior of the sulfur redistribution between the kerogen additive components and hydrogen sulfide in the gas phase. For all heat fluxes, there is a monotonic increase of the hydrogen sulfide amount with a deepening, i.e. increase in pressure and temperature. The results of the calculation

correlate well with experiments on the pyrolysis of high sulfur kerogen. Experiments have shown that the hydrogen sulfide content in the system increases with increasing temperature, along with a decrease in the sulfur content in other pyrolysis products. The increase in the concentration of hydrogen sulfide in equilibrium with type II kerogen is explained by thiol group abstraction and the conversion of sulfide bridges to alkanes bridges.

Contrary to the thiol group and the sulfide bridge, the content of the thiophene group in kerogen depends on the temperature in a complex way. The following pattern is observed with immersion: a significant increase in the content of aromatic sulfur (primarily thiophene sulfur) is replaced by a slowdown and gradual decrease in its content.

The calculation of hydrocarbon gases content from methane to pentane (including isomers) in equilibrium with type II kerogen showed the complex behavior of the changes that occur with rock immersion and heat flux changes (Fig. 3). The distribution of Gibbs energies of the hydrocarbon's formation directly affects their concentration [Khokha, et al., 2019]:
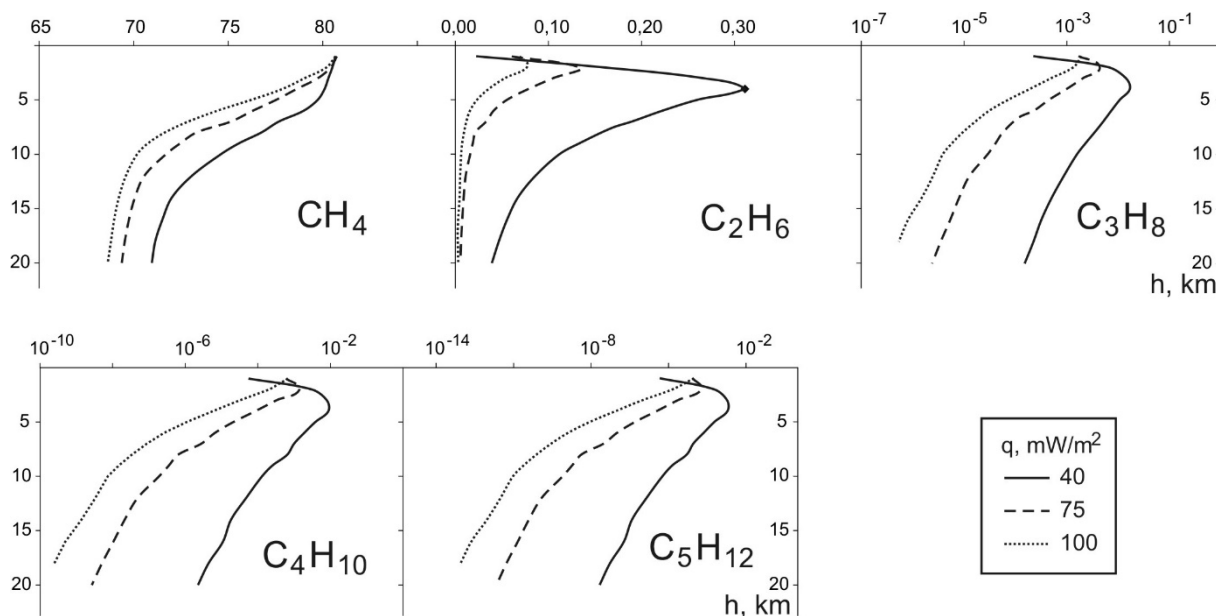
Fig. 3. Change in concentrations of hydrocarbon gases in contact with type II kerogen
(according to the calculation)

Fig. 3 shows the character of carbon redistribution between gases and kerogen with the heat flux changes and sedimentary strata immersion. Methane is the largest gas fraction. Similar results are shown by the experiments on kerogen pyrolysis and calculations by other thermodynamic methods, for example [Khokha, 2014]. This further confirms the reliability of the proposed method of thermodynamic modeling. With the increase of carbon number in a gas molecule, their concentration decreases. A characteristic feature of changes in the hydrocarbons (heavier than methane) concentration is the presence of a maximum, which is observed for all heat fluxes.

This maximum is observed in the depths range from 2 to 4 km, its absolute value increases with decreasing heat flux. As the depth increases, the increase in temperature becomes a basic factor that affects the kerogen/gas system and leads to the destruction of macromolecular components, so the concentration of heavy hydrocarbons decreases. This trend is well correlated with the "oil window" hypothesis, where the zone of heavy oil hydrocarbons generation is in the range of 2–4 km, and methane is the main system component at depths greater than 6 km.

Conclusions

The geodynamic situation changing in a complex way affects the distribution of elements between gases and kerogen in a closed thermodynamic system.

Modeling the kerogen/gas system behavior by method of entropy maximization provides results that do not contradict to study of type II kerogen structure at different stages of maturity.

Calculations show erroneousness of the "methane-graphite death" concept, which assumes the existence in a state of thermodynamic equilibrium of only methane and carbon; the composition of kerogen/gas system always includes heteroatom groups in the solid phase, aromatic structures and a complex of gases.

The character of changes in the concentrations of hydrocarbon gases in equilibrium with type II kerogen indicates the consistency of the "oil window" hypothesis with the postulates of equilibrium thermodynamics.

The flexibility of the proposed method for kerogen transformations modeling allows its improving by introducing new parameters into equations 7–17. Eventually, we will obtain a technique that will allow predicting the scale of oil and gas formation from different organic matter, taking into account changes in geodynamic regimes during catagenesis.

This technique, together with conventionally accepted geological, geophysical and geochemical methods, will improve the accuracy of estimating hydrocarbon reserves in promising oil-and-gas areas.

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МЕТОД МАКСИМІЗАЦІЇ ЕНТРОПІЇ В ТЕРМОДИНАМІЧНОМУ МОДЕЛЮВАННІ ЕВОЛЮЦІЇ ОРГАНІЧНОЇ РЕЧОВИНИ ПРИ ЗМІНІ ГЕОДИНАМІЧНИХ РЕЖИМІВ

Мета. Основна мета нашого дослідження – продемонструвати використання методу максимізації ентропії для розрахунку складу геохімічної системи, що складається із твердих та газоподібних органічних речовин. Зміна геодинамічної обстановки є рушійною силою перерозподілу елементів між сполуками в таких системах. Відповідно до апарату термодинаміки, основними факторами, які впливають на цей перерозподіл, є тиск, температура та початкова кількість елементів. **Методи.** Метод мінімізації енергії Гіббса, метод максимізації ентропії, метод констант незалежних хімічних реакцій, метод невизначених множників Лагранжа, ітераційний метод Ньютона–Рафсона. Відомо, що розсіяна органічна речовина, яка переважно представлена багатьма типами керогену, являє собою нерегулярний полімер, будову якого неможливо описати однозначно. Для розрахунку рівноваги в системі кероген/гази, щоб одержати надійні результати, необхідно застосувати нову модель, яка б не ґрунтувалась на модельних структурах керогену. Ми запропонували і детально описали спосіб застосування формалізму

Джейнса та максимізації ентропії для розрахунку зміни складу системи кероген/газ під час зміни геодинамічних режимів. Для розрахунків створено програмне забезпечення у вигляді макросів Excel та компільованої системної бібліотеки мовою Visual Basic. **Результати.** Для перевірки надійності методу та алгоритму розраховано склад системи, що складається із керогену II типу, вуглеводнів від метану до пентану (з ізомерами), вуглекислого газу, води та сірководню. Результатом розрахунку стали мольні частки вуглеводневих компонентів та адитивних груп, з яких складається кероген, для різних глибин земної кори. Обчислення виконано для трьох теплових потоків: 40, 75 та 100 мВт/м^2, із урахуванням літостатичного тиску. **Новизна.** Встановлено, що зміна геодинамічної обстановки впливає на розподіл елементів між газами та керогеном у замкненій термодинамічній системі; моделювання поведінки системи кероген/газ із застосуванням методу максимізації ентропії дає результати, які не суперечать експериментам з вивчення структури керогену II типу в різних стадіях зрілості; характер змін концентрацій вуглеводневих газів у рівновазі з керогеном II типу свідчить про те, що гіпотеза "нафтового вікна" не суперечить постулатам рівноважної термодинаміки. **Практична значущість.** Метод максимізації ентропії можна успішно використовувати для розрахунку складу різних геохімічних систем із органічних сполук. Метод придатний для визначення хімічного складу нерегулярних полімерів, таких як кероген, бітум, гуміни, у рівновазі з газами та рідинами.

Ключові слова: метод максимізації ентропії; еволюція органічної речовини; керогену II типу; термодинамічна рівновага; формалізм Джейнса.