

# Scientific and technical journal «Technogenic and Ecological Safety»

RESEARCH ARTICLE  
OPEN ACCESS

## DEVELOPMENT AND GENERALIZATION OF THE METHOD FOR CALCULATING THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIUM IN HYDROCARBON MIXTURES AS FUELS FOR RECIPROCATING ICE WITH THE PURPOSE OF THEIR ECOLOGIZATION

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UDC 504.064.4 : 355.695.1 : 621.039.542.4 : 621.039.542.5 : 544-971 : 544.01

DOI: 10.52363/2522-1892.2023.2.1

Received: 24 September 2023

Accepted: 29 November 2023

**Cite as:** Kondratenko O., Umerenkova K., Koloskov V., Koloskova H., Strokov O., Lytvynenko O. (2023). Development and generalization of the method for calculating thermodynamic properties and phase equilibrium in hydrocarbon mixtures as fuels for reciprocating ICE with the purpose of their ecologization. *Technogenic and ecological safety*, 14(2/2023), 3–15. doi: 10.52363/2522-1892.2023.2.1

### Abstract

In the article, which shows the results of the authors' own research, the purpose of which was the development of a mathematical apparatus built on the basis of a modified perturbation theory, and its application to describe the thermophysical characteristics of alternative motor fuels of arbitrary aggregate state, which are characterized by a spherical configuration of interacting structural elements, the following tasks regarding the improvement of the mathematical apparatus developed earlier, presented in the open press and tested at a number of scientific and technical conferences of the international level were consistently solved, namely: the analysis and development of the modified disturbance theory scheme for multi-component alternative fuels has been performed; analytical expressions for the parameters of heterogeneous interaction potentials have been obtained; construction of a complex of thermodynamic values of mixtures and working expressions of its mathematical description has been completed; construction and analysis of phase diagrams of binary mixtures of components of hydrocarbon systems have been performed; the construction and description of the system of equations for phase equilibria have been completed; the analysis and description of the results of the calculation study of the thermodynamic characteristics of alternative types of motor fuel have been carried out. The object of research is the thermophysical properties of alternative motor fuels in a liquid or gaseous aggregate state with a spherical configuration of interacting structural elements. The subject of the research is a mathematical apparatus based on a modified perturbation theory for describing the thermophysical characteristics of motor fuels in a liquid or gaseous aggregate state with a spherical configuration of interacting structural elements. The scientific novelty of the research results is that the approach to the construction of a mathematical apparatus based on the modified perturbation theory for a comprehensive description of all thermophysical properties of alternative and traditional motor fuels, which are in an arbitrary aggregate state, has been further developed, which made it possible to reduce determination errors and reduce calculation time thermophysical properties compared to experimental or reference data. The practical significance of the research results is that the mathematical apparatus transformed and supplemented in the research is marketable for providing accurate information to the list of initial data in research on the full life cycle of motor fuel of any genesis (ie traditional, alternative and mixed) – production, storage, transportation, distribution, use, which at the same time is in both a liquid and a gaseous aggregate state, as well as for forecasting the course and consequences of atmospheric pollution processes with gaseous products of complete and incomplete combustion of fuel components in the combustion chambers of various types of heat engines.

**Key words:** thermophysical properties, traditional motor fuels, alternative motor fuels, mathematical model, environmental protection technologies, ecological safety, power plants, reciprocating internal combustion engines.

### Statement of the problem and analysis of the sources

In all developed civilized countries of the world, there are several environmental problems caused by the operation of various types of power plants (PP), equipped with the internal combustion piston engines (RICE). Among such problems, the depletion of raw materials for the production of motor fuels as natural resources is especially relevant, taking into account the development trends of the main sectors of the energy market [1]. Such a problem causes the active development of alternative energy sources, primarily the production of renewable types of motor fuel [2], which leads to the need to solve a coordinated set of related scientific and technical problems, namely, the implementation of a complex criterion evaluation of the fuel and environmental efficiency of transferring RICE to consuming alternative fuel or mixed motor fuel [3–6], adapting RICE – improvement of the design, organization of the work process, settings and adjustments, as well as the study of performance

indicators of RICE on such fuels [7] etc. At the same time, it should be noted that a separate and integral independent direction of the specified research works is the calculation or experimental obtaining of numerical values of physical quantities that characterize the properties of various types of motor fuels, namely thermophysical [8]. Such results are also suitable to be used in the research, the purpose of which is to ensure environmental, fire and explosion safety of processing raw materials into motor fuel and its storage [9–11]. The indicated direction of research allows some postponement of the planned transition in the European Union countries to the complete replacement of PP with RICE to motor vehicles with a hybrid engine drive or electric vehicles [12]. The disposal of solid combustion products of various types of fuel becomes a separate issue [13,14].

In the previous parts of the study, the team of authors suggested a mathematical model based on a modified thermodynamic theory of disturbances to describe the main thermodynamic properties of different

types of motor fuels [15], it was improved and applied to a number of traditional and alternative types of motor fuels [16–18]. The model, changes to it, and the application of its results were widely tested [19–22].

The above considered, it can be confidently stated that the chosen research subject, the results of which have been presented in the article, is relevant, especially considering the prospects of solving the problems of post-war economic recovery of our country and the participation of the personnel and equipment of the units of the State Emergency Service of Ukraine.

**The aim of the study.** The development of a mathematical apparatus built on the basis of a modified perturbation theory and its application to describe the thermophysical characteristics of alternative motor fuels of arbitrary aggregate state, which are characterized by a spherical configuration of interacting structural elements.

**The problem of the research** is to provide a basis for increasing the accuracy and reducing the time of recognition of the values of motor fuels thermophysical characteristics, in particular – alternative fuels, in comparison with experimental or reference data.

**Object of study.** Thermophysical properties of alternative motor fuels in a liquid or gaseous aggregate state with a spherical configuration of interacting structural elements.

**Subject of study.** A mathematical apparatus based on a modified perturbation theory for describing the thermophysical characteristics of motor fuels in a liquid or gaseous aggregate state with a spherical configuration of interacting structural elements.

**The research objectives** are as follows.

1. Analysis and development of the MPT (modified perturbation theory) scheme for multi-component fuel.
2. Obtaining analytical expressions for the parameters of heterogeneous interaction potentials.
3. Construction of a complex of thermodynamic quantities of mixtures and working expressions of its mathematical description.
4. Construction and analysis of phase diagrams of binary mixtures of components of hydrocarbon systems.
5. Construction and description of the system of equations for phase equilibria.
6. Analysis and description of the results of a computational study of the thermodynamic characteristics of fuel.

During the implementation of this scientific research, the following **research methods** have been used: the analysis of scientific and technical, reference, normative, and patent literature, the modified scheme of the thermodynamic theory of disturbances, the analysis of experimental data, least squares method.

Analysis of the results of the conducted research allows us to highlight the following aspects of their **scientific novelty**. The approach to building a mathematical apparatus based on a modified perturbation theory for a comprehensive description of all thermophysical properties of alternative and traditional motor fuels in an arbitrary aggregate state *has been further developed*, which allows to reduce determination errors and reduce the time of calculating

thermophysical properties compared to experimental or reference data.

The results of the performed research can be of the following **practical use**. The mathematical apparatus transformed and supplemented in the study is *suitable* for providing accurate information to the list of initial data in the studies regarding the full life cycle of motor fuel of any genesis (ie, traditional, alternative and mixed) – production, storage, transportation, distribution, use, which at the same time is in both a liquid and a gaseous aggregate state, just as it is for predicting the course and consequences of atmospheric pollution processes with gaseous products of complete and incomplete combustion of fuel components in the combustion chambers of various types of heat engines.

### 1 Analysis and development of the MPT scheme for multi-component AF

Thermodynamic properties of multi-component AF are required in a wide range of states – from combustion parameters (or pyrolysis of components) to liquefied gas, taking into account the huge spectrum of energy carrier compositions. For this reason, fragmentary experimental data on the properties of AF and their components are unable to provide the information necessary to solve a specific technical task. In addition, such information should be suitable for operational use in practical calculations.

Therefore, the prediction of AP properties becomes important, that is, the calculation of the necessary characteristics in the absence of experimental information or on the basis of a minimum amount of easily available initial data. Analytical expressions for thermodynamic properties have been obtained within the framework of the above perturbation theory (MPT) scheme. The properties calculations have been carried out on the basis of statistical-mechanical methods, on the basis of data on the potentials of interactions and do not contain any empirical correlations. A comparison with the available experimental data for fuel components (individual substances) have shown the high efficiency of the method (errors in determining the properties are at the level of experimental ones). This is an advantage of the suggested method of calculation, since the MPT scheme simultaneously meets such requirements as universality, accuracy, and the possibility of application in a wide range of states (temperatures, pressures, and compositions). In this section, the MPT scheme is generalized for the case of multicomponent fuel.

When generalizing the MPT scheme outlined above for the mixtures with conformal interaction potentials of the LD type and a list of parameters  $\{\varepsilon_{\alpha\beta}\}$ ,  $\{\sigma_{\alpha\beta}\}$  a mixture of fluids is used as a zero approximation. The disturbing parts  $u_{\alpha\beta}^{(1)}$  in the mixture have been chosen in a similar form (1), with breakpoints  $a_{\alpha\beta}(T_{\alpha\beta}^*)$ , where

$$T_{\alpha\beta}^* = kT/\varepsilon_{\alpha\beta} \cdot$$

$$u_1(r) = \varphi_1(r) = \begin{cases} 0, & r < a(T^*); \\ u(r), & r > a(T^*), \end{cases} \quad (1)$$

Free energy  $F_m = Nf_m$  of the  $n$ -component mixture at the temperature  $T$  and particle number densities  $\rho = N_A/v_m$  (where  $v_m$  – molar volume of the mixture) in the first order has the form (2):

$$\beta f_m = \beta f_m^{(0)} - 4\pi\rho \sum_{\alpha < \beta} x_\alpha x_\beta d_{\alpha\beta}^2 (d_{\alpha\beta} - h_{\alpha\beta}) g_{\alpha\beta}^{(0)}(d_{\alpha\beta}) + \sum_{\alpha, \beta} x_\alpha x_\beta (\rho_{\alpha\beta}^*/T_{\alpha\beta}^*) I_{\alpha\beta}^{(1)}(\rho_{\alpha\beta}^*, T_{\alpha\beta}^*). \quad (2)$$

B (2)  $f_m^{(0)}$  – free energy of the  $n$ -component mixture fluids with the diameters  $d_{\alpha\alpha}$ ,  $x_\alpha = N_\alpha/N$  – molar concentration of  $\alpha$ -component  $\left(\sum_\alpha N_\alpha = N\right)$ ,  $g_{\alpha\beta}^{(0)}(r)$ ,  $\rho_{\alpha\beta}^* = \rho \sigma_{\alpha\beta}^3$  – radial distribution functions of the fluids-mixture.

Here and further, there is the summary of  $\alpha$  and  $\beta$  from 1 to  $n$ .

The values  $h_{\alpha\beta}$  have been defined according to (3)

$$h_{\alpha\beta} = \xi \sigma_{\alpha\beta} = \int_0^{a\alpha\beta} \left[ 1 - \exp\left[-\phi(r/\sigma_{\alpha\beta})/T_{\alpha\beta}^*\right] \right] dr, \quad (3)$$

and in the MPT scheme for conformal induced potentials  $\phi(r)$  the dependence  $a_{\alpha\beta}^* = a_{\alpha\beta}/\sigma_{\alpha\beta}$  on the temperature  $T_{\alpha\beta}^*$ , is obviously identical to the the dependence  $a(T^*)$ , defined according to (4).

$$d = \xi \sigma = \int_0^{a(T^*)} \left[ 1 - e^{-\phi(r)/T^*} \right] dr, \quad (4)$$

Free energy  $f_m^{(0)}$  can be obtained in the same approximations as equation (5), by generalizing it to the case of a multicomponent mixture. The corresponding Mansouri equation can be as follows (6)

$$\beta f_0 = (4 - 3\eta)\eta(1 - \eta)^{-2} + \beta f^{id}, \quad (5)$$

$$\beta f_m^{(0)} = \beta f_m^{(id)} + \eta_m(4 - 3\eta_m)(1 - \eta_m)^{-2} + \beta(\Delta f_m^{(0)}), \quad (6)$$

where  $\eta_m = 0,4177\rho_m^* = \sum_\alpha x_\alpha \eta_{\alpha\alpha}$ ,  $\rho_m^* = \sum_\alpha x_\alpha \rho_{\alpha\alpha}^*$  – the average specified density of the mixture;  $\eta_{\alpha\alpha} = (\pi/6)\rho_{\alpha\alpha}^3 d_{\alpha\alpha}^3 = (\pi/6)\xi^3 \rho_{\alpha\alpha}^*$ ,  $\Delta f_m^{(0)}$  – correction, quadratic by  $\delta_{\alpha\beta}^-$  – relative differences in particle sizes  $\left(\delta_{\alpha\beta}^\pm = (d_{\alpha\alpha} \pm d_{\beta\beta})/\sqrt{d_{\alpha\alpha}d_{\beta\beta}}\right)$ . The compact form of this amendment is given in the research [19].

The ideal-gas part of (6) equal to (7)

$$\beta f_m^{(id)} = \sum_\alpha x_\alpha \left[ \psi_\alpha + \ln(x_\alpha \rho_{\alpha\alpha}^*) \right] = \sum_\alpha x_\alpha (\psi_\alpha + \ln \rho_{\alpha\alpha}^*) + \sum_\alpha x_\alpha \ln x_\alpha \quad (7)$$

and the first order integrals  $I_{\alpha\beta}^{(1)}$ , contained in (2), are the generalization of expressions (8) in case of mixtures:

$$I_1 = (1/2) \int \phi_1(x) g_0(x) dx = 2\pi \int_{a^*}^{\infty} \phi(x) g_0(x) x^2 dx, \quad x = r/\sigma. \quad (8)$$

Identity of functions  $a_{\alpha\beta}^*(T_{\alpha\beta}^*)$  and  $a^*(T^*)$  in the MPT scheme allows us to construct the integrals (8) to the expressions  $I_{\alpha\beta}^{(1)}$  and consequently (9), to obtain (10):

$$I_1 = I_1(\rho^*, T^*) = \sum_{i=0}^3 \sum_{k=0}^3 a_{ik} \rho^{*i}/T^*. \quad (9)$$

$$I_{\alpha\beta}^{(1)}(\rho_{\alpha\beta}^*, T_{\alpha\beta}^*) \approx I_1(\rho_m^*, T_{\alpha\beta}^*) = \sum_{i,k=0}^3 a_{ik} \left( \sum_\alpha x_\alpha \rho_{\alpha\alpha}^* \right)^i / (T_{\alpha\beta}^*)^k, \quad (10)$$

where the coefficients  $a_{ik}$  are presented in table 1.

Table 1 – The value of the coefficients  $a_{ik}$  in the expression (9) [15]

$T^*$	$i$	$a_{ik}$			
		$k=0$	$k=1$	$k=2$	$k=3$
0,3...0,696	0	-0.8498	-9.2400	3.5832	-0.4612
	1	2.1493	3.5820	1.1501	0.1560
	2	-8.5320	-0.4782	-1.0255	0.0972
	3	6.5743	-0.2250	0.7208	-0.0659
0,696...5	0	-5.5896	-0.2681	-1.4458	0.2115
	1	-2.7573	8.9226	-6.2375	2.7819
	2	0.8321	-7.5416	2.1787	-1.3682
	3	1.5895	3.0889	-0.2246	0.2152

Based on the expressions (2)–(10) the free energy of a multicomponent mixture in the MPT-1 scheme can be represented as (11)

$$\beta f_m = \beta(f_m^{(0)} + f_m^{(1)}) = \sum_\alpha x_\alpha (\psi_\alpha + \ln \rho_{\alpha\alpha}^*) + \sum_\alpha x_\alpha \ln x_\alpha + \eta_m(4 - 3\eta_m)/(1 - \eta_m)^2 + \beta(\Delta f_m^{(0)}) + \sum_{\alpha, \beta} x_\alpha x_\beta (\rho_{\alpha\beta}^*/T_{\alpha\beta}^*) \sum_{k=0}^3 \rho_m^k A_{\alpha\beta}^{(k)}, \quad (11)$$

where  $A_i(T^*) = a_{i0} + a_{i1}/T^* + a_{i2}/T^{*2} + a_{i3}/T^{*3}$ .

The ratio between the given values included in (11), and the temperature  $T$ , molar volume  $v_m$ , mass density  $D_m$  of the mixture of components with molar masses  $M_\alpha$  and interaction potential parameters  $\varepsilon_{\alpha\beta}$ ,  $\sigma_{\alpha\beta}$ , are of the appearance (12):

$$\begin{cases} T_{\alpha\beta} = T/E_{\alpha\beta} \quad (E_{\alpha\beta} = \varepsilon_{\alpha\beta}/k); \\ \rho_{\alpha\beta}^* = N_A \sigma_{\alpha\beta}^3 / v_m; \\ D_m = M_m / v_m \quad (M_m = \sum_\alpha x_\alpha M_\alpha). \end{cases} \quad (12)$$

## 2 Obtaining analytical expressions for the parameters of heterogeneous interaction potentials

Usually, in the models of mixtures of spherical non-polar molecules, as well as for individual substances, the additivity of intermolecular forces is assumed, that is, the potential energy of interaction is equal to the sum

of pair potentials. Moreover, each pair interaction is described by a two-parameter type potential (13) –  $u_{\alpha\beta}(r) = \varepsilon_{\alpha\beta} \varphi(r/\sigma_{\alpha\beta})$ . These limitations of models are not fundamental, including the schemes of perturbation theory [15–17].

$$u_{\alpha\beta}(r) = \varepsilon_{\alpha\beta} \varphi(r/\sigma_{\alpha\beta}) = 4\varepsilon_{\alpha\beta} \left[ \left( \sigma_{\alpha\beta}/r \right)^{12} - \left( \sigma_{\alpha\beta}/r \right)^6 \right], \quad (13)$$

With this approach, the main task comes down to estimating the parameters of the interaction of heterogeneous particles, that is, quantities  $\sigma_{\alpha\beta}$  and  $\varepsilon_{\alpha\beta}$  при  $\alpha \neq \beta$ . There are two possibilities here. The first one is to introduce phenomenological parameters that characterize  $\sigma_{\alpha\beta}$  and  $\varepsilon_{\alpha\beta}$  regarding their values for components. This method is used, for example, in the quasi-chemical approximation of the theory of solutions. Divergence  $\varepsilon_{\alpha\beta}$  and  $\varepsilon_{\alpha\alpha}$ ,  $\varepsilon_{\beta\beta}$  can be specified as a value  $u_0 = \varepsilon_{\alpha\beta} - 1/2(\varepsilon_{\alpha\alpha} + \varepsilon_{\beta\beta})$  [15–17]. The second possibility is to use various semi-empirical rules based on both qualitative theoretical estimates and experimental regularities. Expressions connecting the parameters of mixed and homogeneous interactions are called combinational rules. Fair dependencies in the form of a geometric mean are approximated (14) and (15)

$$\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha}\sigma_{\beta\beta})^{1/2}, \quad (14)$$

$$\varepsilon_{\alpha\beta} = (\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta})^{1/2}. \quad (15)$$

More often, however, the value  $\sigma_{\alpha\beta}$  is determined by the rule of the arithmetic mean (16)

$$\sigma_{\alpha\beta} = 1/2 (\sigma_{\alpha\alpha} + \sigma_{\beta\beta}). \quad (16)$$

The combination (15) i (16) are called Lorenz-Bertello combination rules. On the one hand, the rule (15) is based on the London theory of dispersion forces, resulting from the formulas (17)–(19), and on the other hand, it is confirmed by experimental data.

$$u_{\alpha\beta} = -\frac{3}{2} \cdot \frac{h\nu_{\alpha}\nu_{\beta}}{\nu_{\alpha} + \nu_{\beta}} \cdot \frac{\alpha_{\alpha}\alpha_{\beta}}{r_{\alpha\beta}^6}, \quad (17)$$

$$u = -\frac{3}{4} \cdot h\nu_{\alpha} \cdot \frac{\alpha^2}{r^6}, \quad (18)$$

$$u_{\alpha\beta} = -\frac{3}{2} \cdot \frac{E_{\alpha}E_{\beta}}{E_{\alpha} + E_{\beta}} \cdot \frac{\alpha_{\alpha}\alpha_{\beta}}{r_{\alpha\beta}^6}. \quad (19)$$

The parameters  $\varepsilon_{\alpha\beta}$ ,  $\sigma_{\alpha\beta}$  of pair potentials for pure components and heterogeneous interactions are connected with each other using combinational rules (20)

$$\begin{cases} \varepsilon_{\alpha\beta} = \zeta_{\alpha\beta} \sqrt{\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}}; \\ \sigma_{\alpha\beta} = 0,5(\sigma_{\alpha\alpha} + \sigma_{\beta\beta}), \end{cases} \quad (20)$$

where the parameters  $\zeta_{\alpha\beta}$  describe deviations from Bertello's rule ( $\zeta_{\alpha\beta} = 1$ ). Often they are considered as the main parameters – to the same extent as the parameters  $\varepsilon_{\alpha\alpha}$ ,  $\sigma_{\alpha\alpha}$  of individual components and are determined by experimental data – mainly about redundant properties. At the same time, the description excludes mixtures where the components are substances for which there is no experimental information on the properties of binary combinations. This significantly narrows the class of studied mixtures. Secondly, the introduction of custom parameters  $\zeta_{\alpha\beta}$  means

introducing additional artificial elements into the calculation scheme in addition to the model assumptions used. Applying the simplest Bertello rule or some empirical rules [23,24] for the parameters  $\varepsilon_{\alpha\beta}$  often gives unsatisfactory results.

Thus, it is necessary to find and use explicit analytical expressions for the parameters  $\zeta_{\alpha\beta}$ . It is quite simple to obtain such expressions in the assumption  $c^{(6)} = b$ , where  $-c^{(6)}$  and  $-b$  are the coefficients in members  $\sim r^{-6}$  in the dispersion interaction energy formula and in the LD potential. Indeed, according to London's formula (21)

$$c_{\alpha\beta}^{(6)} = (3/2)\alpha_{\alpha}\alpha_{\beta}I_{\alpha}I_{\beta}/(I_{\alpha} + I_{\beta}) \quad (21)$$

The coefficients  $c_{\alpha\beta}$  for heterogeneous and homogeneous ( $c_{\beta\beta}^{(6)} = 3\alpha_{\beta}^2 I_{\beta}/4$ ) interactions are interconnected ( $\alpha_{\beta}$ ,  $I_{\beta}$  – polarization and ionization potential of molecules of  $\beta$ -th component). Next, the minima of the LD curves  $-\varepsilon_{\alpha\beta}$  are reached in points

$R_{\alpha\beta} = 2^{1/6}\sigma_{\alpha\beta}$ , so that for  $R_{\alpha\beta}$  the ratio is fair, analogous to the second rule in (20). Given the fact that these minima in the dipole approximation for the dispersion energy are equal  $\varepsilon_{\alpha\beta} = c_{\alpha\beta}^{(6)}/2R_{\alpha\beta}^6$ , it is possible to obtain the connection between the parameters  $\varepsilon_{\alpha\beta}$  and  $\varepsilon_{\alpha\alpha}$ , that is value  $\zeta_{\alpha\beta}$ . Excluding the potentials from the expressions  $I_{\beta}$ , we obtain  $\zeta_{\alpha\beta} = \zeta'_{\alpha\beta}$ , де (22)

$$\zeta'_{\alpha\beta} = (\delta_{\alpha\beta}^+/2)^6 2\sqrt{\omega_{\alpha}\omega_{\beta}}/(\omega_{\alpha} + \omega_{\beta}), \quad (22)$$

where  $\omega_{\beta} = \varepsilon_{\beta\beta}\sigma_{\beta\beta}^6/\alpha_{\beta}^2$ ,

and  $\delta_{\alpha\beta}^+ = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/\sqrt{\sigma_{\alpha\alpha}\sigma_{\beta\beta}}$  coincides with the similar parameter given above based on  $\xi = \text{const}$  in MPT scheme [15–17]. Excluding polarization gives an alternative form (23)

$$\zeta'_{\alpha\beta} = (\delta_{\alpha\beta}^+/2)^6 2\sqrt{I_{\alpha}I_{\beta}}/(I_{\alpha} + I_{\beta}). \quad (23)$$

The values  $I$  and  $\alpha$  substances when determining the parameters  $\zeta_{\alpha\beta}$  according to (20) have been borrowed from the research works [15–17]. The values of these parameters determine the degree of imperfection of real mixtures and the associated peculiarities of thermodynamic behavior, in particular, when modeling phase equilibria.

In table 2 [15] the values of the ionization potential of molecules are given ( $I$ ) as well as the values of the principal semi-axes of the molecular polarization ellipsoids ( $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ ). The effective value of polarizations is calculated according to the formula (24) [15–17]

$$\alpha_{\text{eff}} = \frac{\alpha_1 + 2\alpha_2}{3}. \quad (24)$$

In table 3 [15] the parameter values are given  $\zeta_{\alpha\beta}$  for the main fuel components.

According to the experimental data available in the literature on the parafluid equilibrium of basic mixtures [15–17] comparisons and refinements of the calculated parameter values have been performed  $\zeta_{\alpha\beta}$ .

Table 2 – Value of ionization potentials and polarizability of fuel component molecules [15]

Substance	Ionization potential of molecules I, eV	References	Polarizability of molecules		References
			$\alpha_1, \text{ \AA}^3$	$\alpha_2 (\alpha_3), \text{ \AA}^3$	
CH <sub>4</sub>	12.98±0.05	[23]	2.60		[23]
	13.00±0.05	[24]	2.61	2.61	[24]
C <sub>2</sub> H <sub>6</sub>	11.65±0.05	[23]		4.52	[23]
	11.50±0.05	[24]	5.60	4.00	[24]
			5.50	4.05	[24]
			5.11	4.23	[23]
C <sub>3</sub> H <sub>8</sub>	11.07±0.03	[23]	6.35		[23]
	11.00±0.03	[24]			
n-C <sub>4</sub> H <sub>10</sub>	10.63±0.05	[23]	8.19		[23]
	10.67±0.05	[23]			
	10.66±0.05	[24]			
i-C <sub>4</sub> H <sub>10</sub>	10.69±0.05	[23]			
	10.98±0.05	[24]			
n-C <sub>5</sub> H <sub>12</sub>	8.60	[24]	10.02		[23]
i-C <sub>5</sub> H <sub>12</sub>	8.60	[24]			
C <sub>6</sub> H <sub>14</sub>	10.17±0.05	[24]	11.85		[23]
	10.18±0.05	[23]			
	10.27±0.05	[23]			
C <sub>7</sub> H <sub>16</sub>	10.06±0.05	[24]			
C <sub>8</sub> H <sub>18</sub>	10.03±0.05	[24]			
C <sub>9</sub> H <sub>20</sub>	10.02±0.05	[24]			
C <sub>10</sub> H <sub>22</sub>	9.95±0.05	[24]			
O <sub>2</sub>	12.075±0.01	[24]	2.34	1.23	[23]
			2.35	1.21	[23]
			2.43	1.19	[24]
H <sub>2</sub>	15.427±0.001	[23]	0.99	0.69	[23]
	15.4261±0.0001	[24]			
H <sub>2</sub> O	12.61±0.02	[24]	1.496	1.670(1.250)	[23]
H <sub>2</sub> S	10.47±0.01	[24]	3.93	4.21(3.21)	[24]
N <sub>2</sub>	15.58±0.001	[24]	2.38	1.45	[23]
			2.43	1.43	[24]
			2.24	1.52	[23]
CO	14.014±0.004	[23]	2.60	1.625	[23]
			2.33	1.80	[24]
CO <sub>2</sub>	13.79±0.02	[23]	4.10	1.93	[23]
			4.03	1.93	[24]
			4.01-4.10	1.97-1.93	[24]

### 3 Construction of a complex of thermodynamic quantities of mixtures and working expressions of its mathematical description

The relationship between the given parameters included in the equation (2)–(11), and the state parameters of a specific mixture are given by the ratio (12), where the values  $E_{\alpha\beta}$ ,  $\sigma_{\alpha\beta}$  for the individual components are presented in table 4 [15], and for heterogeneous ( $\alpha \neq \beta$ ) interaction those have been obtained according to the combinational rules (20).

The initial stage of calculations of thermodynamic properties of a  $n$ -component mixture is the determination of its density  $D_m$  (molar volume  $v_m$ ). at given temperature  $T$ , pressure  $p$  and a certain number of selected concentrations  $\{x_\alpha\}$ ,  $\alpha = 1, 2, \dots, n-1$  the values of  $v_m$  are determined in the single-phase field with (25)

$$p_m(v_m, T, \{x_\alpha\}) - p = 0, \quad (25)$$

and in the field of two-phase, for example, parafluids ( $L$ - $V$ ) equilibrium – from the solution of the system of equations at a fixed temperature (26)

$$\begin{cases} p_m(v_m^L, T, \{x_i^L\}) - p = 0, \\ p_m(v_m^V, T, \{x_i^V\}) - p = 0, \\ \mu_1(v_m^L, T, \{x_i^L\}) - \mu_1(v_m^V, T, \{x_i^V\}) = 0, \\ \dots \\ \mu_n(v_m^L, T, \{x_i^L\}) - \mu_n(v_m^V, T, \{x_i^V\}) = 0, \end{cases} \quad (26)$$

where  $p_m$  – pressure,  $\mu_\gamma = 1, 2, \dots, n$  – chemical potentials of components.

The system (26) is the main one for solving the problem of phase equilibria of the mixture. For a two-phase  $n$ -component closed system at constant temperature, the molar volumes of coexisting phases and their equilibrium compositions ( $n-1$  concentration for  $L$ - and  $V$ -phases) according to the rule of phases are uniquely determined by pressure and  $n-2$  concentrations of components in any of the phases. In particular, for the binary system, syllables are completely determined by the values  $T, p$ .

Table 3 – Values of parameters of heterogeneous interaction potentials ( $\zeta_{\alpha\beta} \cdot 1000$ ) [15]

Substance	Parameters of heterogeneous interaction potentials $\zeta_{\alpha\beta} \cdot 1000$																		
	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	n-C <sub>4</sub> H <sub>10</sub>	i-C <sub>4</sub> H <sub>10</sub>	n-C <sub>5</sub> H <sub>12</sub>	i-C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>14</sub>	C <sub>7</sub> H <sub>16</sub>	C <sub>8</sub> H <sub>18</sub>	C <sub>9</sub> H <sub>20</sub>	C <sub>10</sub> H <sub>22</sub>	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> S	O <sub>2</sub>	CO	H <sub>2</sub>	H <sub>2</sub> O
CH <sub>4</sub>	1000	996	966	980	961	974	978	876	851	828	806	785	926	997	995	992	921	951	991
C <sub>2</sub> H <sub>6</sub>	996	1000	996	995	990	986	988	937	918	899	881	862	904	974	989	963	978	895	959
C <sub>3</sub> H <sub>8</sub>	966	996	1000	996	992	989	990	972	958	944	929	914	885	942	965	925	947	840	919
n-C <sub>4</sub> H <sub>10</sub>	980	995	996	1000	993	992	992	990	980	970	959	947	867	908	939	887	915	791	881
i-C <sub>4</sub> H <sub>10</sub>	961	990	992	993	1000	997	998	990	982	972	961	949	865	905	937	885	912	788	878
n-C <sub>5</sub> H <sub>12</sub>	974	986	989	992	997	1000	1000	998	993	986	978	969	855	875	911	852	883	749	845
i-C <sub>5</sub> H <sub>12</sub>	978	988	990	992	998	1000	1000	998	993	986	977	968	855	875	911	853	883	750	846
C <sub>6</sub> H <sub>14</sub>	876	937	972	990	990	998	998	1000	999	995	989	983	840	844	883	819	853	712	811
C <sub>7</sub> H <sub>16</sub>	851	918	959	980	982	993	993	999	1000	999	996	991	814	817	859	790	826	680	782
C <sub>8</sub> H <sub>18</sub>	828	899	944	970	972	986	986	995	999	1000	999	996	790	793	836	765	803	654	757
C <sub>9</sub> H <sub>20</sub>	806	881	929	959	961	978	977	989	996	999	1000	999	768	770	814	741	780	629	733
C <sub>10</sub> H <sub>22</sub>	785	862	914	947	949	969	968	983	991	996	999	1000	746	748	793	718	759	605	710
N <sub>2</sub>	926	904	885	867	865	855	855	840	814	790	768	746	1000	983	979	991	986	969	991
CO <sub>2</sub>	997	974	942	908	905	875	875	844	817	793	770	748	983	1000	989	996	987	970	996
H <sub>2</sub> S	995	989	965	939	937	911	911	883	859	836	814	793	979	989	1000	989	989	937	986
O <sub>2</sub>	992	963	925	887	885	852	853	819	790	765	741	718	991	996	989	1000	994	977	990
CO	921	978	947	915	912	883	883	853	826	803	780	759	986	987	989	994	1000	965	994
H <sub>2</sub>	951	895	840	791	788	749	750	712	680	654	629	605	969	970	937	977	965	1000	982
H <sub>2</sub> O	991	959	919	881	878	845	846	811	782	757	733	710	991	996	986	990	994	982	1000

Table 4 – Fuel component parameters [15]

Substance	$M$ , kg/kmol	$E=\varepsilon/k$ , K	$\sigma \cdot 10^{10}$ , m	$\tilde{D}$ , kg/m <sup>3</sup>	$\tilde{P}$ , MPa
CH <sub>4</sub>	16.0430	150.86	3.7424	508.27	39.739
C <sub>2</sub> H <sub>6</sub>	30.0701	244.32	4.2263	661.47	44.685
C <sub>3</sub> H <sub>8</sub>	44.0972	288.35	4.6623	722.55	39.283
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	58.1243	327.98	5.0281	759.28	35.622
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	58.1243	318.84	5.0538	747.76	34.104
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	72.151	362.01	5.3535	780.88	32.576
<i>i</i> -C <sub>5</sub> H <sub>12</sub>	72.151	347.12	5.3457	784.30	31.373
C <sub>6</sub> H <sub>14</sub>	86.172	398.23	5.6503	793.24	30.479
C <sub>7</sub> H <sub>16</sub>	100.198	416.85	5.9059	807.72	27.939
C <sub>8</sub> H <sub>18</sub>	114.224	433.61	6.1407	819.14	25.854
C <sub>9</sub> H <sub>20</sub>	128.25	449.34	6.3642	826.20	24.068
C <sub>10</sub> H <sub>22</sub>	142.276	465.52	6.5749	831.22	22.613
N <sub>2</sub>	28.0134	97.55	3.5996	997.38	28.877
CO <sub>2</sub>	44.011	228.36	3.5641	1614.24	69.640
H <sub>2</sub> S	34.08	318.62	3.7581	1066.20	82.878
O <sub>2</sub>	31.9988	120.84	3.3806	1375.33	43.183
H <sub>2</sub>	2.016	37.00	2.9280	133.36	20.351
H <sub>2</sub> O	18.015	547.62	3.3467	798.07	201.705
C <sub>6</sub> H <sub>6</sub>	78.114	426.26	4.9963	1040.39	47.203

Let us give equations for the main thermodynamic properties of mixtures as functions  $v_m$ ,  $T$  and  $\{x_\alpha\}$  in MPT scheme, which takes into account members of the second order (MPT-2), which are based on the expression  $f_m = f_m^{(0)} + f_m^{(1)} + f_m^{(2)}$ , in the same approximations as for equations (27)–(42) [15–17] – those are the formulas (43)–(57).

Pressure  $p = \tilde{P} T^* \rho^* z$ . (27)

Compressibility factor  $z = 10^3 p / RTD$ , (28)

$$z = 1 + 2\eta \frac{2 - \eta}{(1 - \eta)^3} + \kappa_1 [i + 1].$$
 (29)

Free energy  $F = RT(\beta f)$ , (30)

$$\beta f = \beta h_0 - s_0 - 1 - \ln z_N + \eta \frac{4 - 3\eta}{(1 - \eta)^2} + \kappa_1 [1] + \kappa_2 [1].$$
 (31)

Entropy  $S = R s (s = \beta u - \beta f)$ , (32)

$$s = s_0 + \ln z_N - \eta \frac{4 - 3\eta}{(1 - \eta)^2}$$
 (33)

$$+ \kappa_1 [k] + \kappa_2 [j].$$

Enthalpy  $H = RT(\beta h)(\beta h = \beta u + z)$ , (34)

$$\beta h = \beta h_0 + 2\eta \frac{2 - \eta}{(1 - \eta)^3} + \kappa_1 [i + k + 2] + \kappa_2 [j + 1].$$
 (35)

Gibbs energy  $G = RT(\beta \mu)$ , (36)

where chemical potential is

$$\mu = f + z/\beta,$$
 (37)

$$\beta \mu = \beta h_0 - s_0 - \ln z_N + \eta \frac{8 - 9\eta + 3\eta^2}{(1 - \eta)^3} +$$
 (38)

$$+ \kappa_1 [i + 2] + \kappa_2 [1].$$

Isochoric heat capacity  $C_v = R c_v$ , (39)

$$c_v = c_{p_0} - 1 - \kappa_1 [k(k + 1)] - \kappa_2 [j(j + 1)]$$
 (40)

Isohar heat capacity  $C_p = R c_p$ , (41)

$$c_p = c_v + \rho^* T^* \beta_T^* \left\{ 1 + 2\eta \frac{2 - \eta}{(1 - \eta)^2} - \chi_1 [(i + 1)k] \right\}^2,$$
 (42)

Pressure  $p_m = \tilde{P}_\alpha T_{\alpha\alpha}^* \rho_{\alpha\alpha}^* z_m$ . (43)

Compressibility factor  $z_m = p_m v_m / R_0 T$ , (44)

$$z_m = 1 + 2\eta_m \frac{2 - \eta_m}{(1 - \eta_m)^3} + \Delta z_m^{(0)} + \sum_{\alpha, \beta} x_\alpha x_\beta \rho_{\alpha\beta}^* \kappa'_{1\alpha\beta} [i + 1].$$
 (45)

Free energy  $F_m = R_m T(\beta f_m)$ , (46)

$$\beta f_m = \sum_\alpha x_\alpha (\beta h_{0\alpha} - s_{0\alpha}) - 1 + \sum_\alpha x_\alpha \ln x_\alpha - \ln z_{Nm} + \eta_m \frac{4 - 3\eta_m}{(1 - \eta_m)^2} + \beta (\Delta f_m^{(0)}) + \sum_{\alpha, \beta} x_\alpha x_\beta \rho_{\alpha\beta}^* \left\{ \kappa'_{1\alpha\beta} [1] + \kappa'_{2\alpha\beta} [1] \right\}$$
 (47)

Entropy  $S_m = R_m s_m (s_m = \beta u_m - \beta f_m)$ , (48)

$$s_m = \sum_\alpha x_\alpha s_{0\alpha} - \sum_\alpha x_\alpha \ln x_\alpha + \ln z_{Nm} - \eta_m \frac{4 - 3\eta_m}{(1 - \eta_m)^2} - \beta (\Delta f_m^{(0)}) + \sum_\alpha x_\alpha x_\beta \rho_{\alpha\beta}^* \left\{ \kappa'_{1\alpha\beta} [k] + \kappa'_{2\alpha\beta} [j] \right\}$$
 (49)

Enthalpy  $H_m = R_m T(\beta h_m) (\beta h_m = \beta u_m + z_m)$ , (50)

$$\beta h_m = \sum_\alpha x_\alpha \beta h_{0\alpha} + 2\eta_m \frac{2 - \eta_m}{(1 - \eta_m)^3} + \Delta z_m^{(0)} + \sum_\alpha x_\alpha x_\beta \rho_{\alpha\beta}^* \left\{ \kappa'_{1\alpha\beta} [i + k + 2] + \kappa'_{2\alpha\beta} [j + 1] \right\}$$
 (51)

Gibbs energy

$$G_m = R_m T(\beta \mu_m) (\beta \mu_m = \beta f_m + z_m),$$
 (52)

$$\beta \mu_m = \sum_\alpha x_\alpha (\beta h_{0\alpha} - s_{0\alpha}) + \sum_\alpha x_\alpha \ln x_\alpha - \ln z_{Nm} + \eta_m \frac{8 - 9\eta_m + 3\eta_m^2}{(1 - \eta_m)^3} + \beta (\Delta f_m^{(0)}) + \Delta z_m^{(0)} + \sum_{\alpha, \beta} x_\alpha x_\beta \rho_{\alpha\beta}^* \left\{ \kappa'_{1\alpha\beta} [i + 2] + \kappa'_{2\alpha\beta} [1] \right\},$$
 (53)

Isochoric heat capacity  $C_{vm} = R_m c_{vm}$ , (54)

$$c_{vm} = \sum_\alpha x_\alpha c_{p0\alpha} - 1 - \sum_{\alpha, \beta} x_\alpha x_\beta \rho_{\alpha\beta}^* \left\{ \kappa'_{1\alpha\beta} [k(k + 1)] + \kappa'_{2\alpha\beta} [j(j + 1)] \right\}.$$
 (55)

Isohar heat capacity  $C_{pm} = R_m c_{pm}$ , (56)

$$c_{pm} = c_{vm} + T_{\alpha\alpha}^* \alpha_m^* / P_{\alpha\alpha}^* \beta_{Tm}^*.$$
 (57)

In (43)–(57)  $h_{0\alpha}, s_{0\alpha}, c_{p0\alpha}$  – ideal gas functions of  $\alpha$ -th component,

$$z_{Nm} = p_{st} v_m / R_0 T$$
 (58)

$$R_m = R_0 / M_m,$$
 (59)

$\Delta f_m^{(0)}$  i  $\Delta z_m^{(0)}$  are minor corrections in the zero order of MPT.

Forms  $\kappa'_{1\alpha\beta} [n]$ ,  $\kappa'_{2\alpha\beta} [n]$  for the mixtures are defined according to (60) and (61)

$$\kappa'_{1\alpha\beta}[n] = \sum_{i,k=0}^3 n a_{ik} (\rho_m^*)^i / (T_{\alpha\beta}^*)^{k+1}, \quad (60)$$

$$\kappa'_{2\alpha\beta}[n] = \sum_{i=0}^3 b_i (\rho_m^*)^{i+1} \sum_{j=0}^3 n c_j / (T_{\alpha\beta}^*)^{j+1}. \quad (61)$$

#### 4 Construction and analysis of phase diagrams of binary mixtures of components of hydrocarbon systems

The solution of practically important questions, such as the processes of separation and processing of mixtures of organic substances, the design of chemical technology devices is determined by the availability and quality of known equilibrium data. Experimental methods for determining phase equilibrium parameters are quite diverse, but in most cases very complicated. Publications on parafluid equilibrium, despite their seeming sufficiency, provide only part of the necessary amount of information.

The data on the equilibrium of binary mixtures are of particular importance, since on their basis it is possible to predict the behavior of a multicomponent mixture. The analysis of literature data showed that the share of binary mixtures accounted for 83% of the total number of studied mixtures, ternary – 14%, and the share of all other complex mixtures – only 3 % [25].

Although binary mixtures are rarely encountered in practice, quantification of their behavior is important, since methods describing the behavior of multicomponent systems are usually based on data obtained for individual binary systems.

In addition, the published data on the equilibrium of the studied base mixtures can be used to check the equilibrium data obtained by calculation during the mathematical modeling of parafluid equilibrium.

Graphical interpretation of phase equilibria in the form of state diagrams has important practical significance. The construction of diagrams for binary basic systems helps in the study of issues of thermodynamics of mixtures and allows to visually compare the correspondence of calculated and experimental data and thereby draw conclusions about the adequacy of the proposed model for the description of PE (phase equilibrium).

When modeling PE, numerous results were obtained for the construction of phase diagrams of mixtures, typical for working bodies of the hydrocarbon type, in particular, of various basic binary mixtures. Thermodynamic properties for them are determined from the solution of the system of equations (25).

Fig. 1–3 show phase diagrams of mixtures of methane with ethane, propane and nitrogen for a set of isotherms. Comparison with experimental data [25–27] allows to estimate the errors in the description of the compositions of the liquid and vapor phases 4–5 mole %. These systems are characterized by positive deviations from the properties of ideal solutions, which increase with increasing differences in the effective sizes of molecules ( $\sigma_{\alpha\alpha}$ ) and potential pit depth values ( $\varepsilon_{\alpha\alpha}$ ). These deviations, however, do not lead to limited mutual solubility of the components, and liquid phase

separation is observed only for mixtures CH<sub>4</sub> with C<sub>6</sub>H<sub>14</sub> and with heavier marginal hydrocarbons.

At temperatures higher than the critical temperature of the low-boiling component ( $T_c = 190,8$  K for methane – fig. 1, fig. 2 and  $T_c = 126,2$  K for nitrogen – fig. 3) the phase diagram has the characteristic appearance of a closed loop moving away from the vertical  $x = 1$  when the temperature rises. As a rule, there are no experimental data at the pressures higher than 4–6 MPa, so the obtained data predict the phase behavior of mixtures when approaching critical points. The location of the critical curve connecting these points [15], is an extremely important characteristic of mixtures that allows identification of the phase states of hydrocarbon working bodies of heat engineering devices. Thus, the modeling of phase diagrams based on the calculation method testifies to the adequacy of the physical model for describing the properties of hydrocarbons and the proposed calculation procedure.

#### 5 Construction and description of the system of equations for phase equilibria

Let us consider the  $N$ -component mixture at the given temperature  $T$ , pressure  $p$  and the original composition  $\{x_i^0\}$  (set of initial molar concentrations). For the initial mixture, obviously, (62)

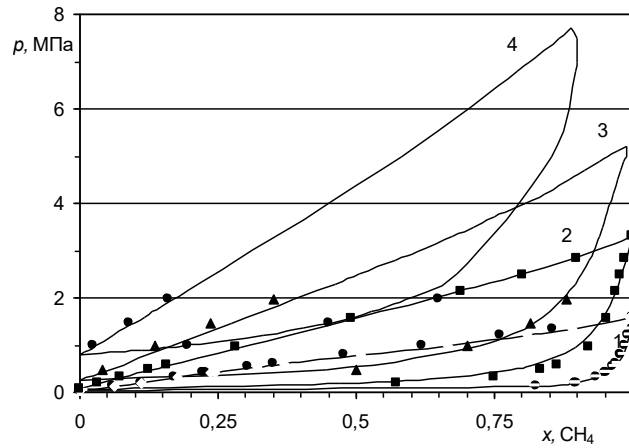
$$\sum_{i=1}^N x_i^0 = 1. \quad (62)$$

The task consists in determining given conditions  $T$ ,  $p$  and  $\{x_i^0\}$  of the phase state (liquid, gas or two-phase system liquid + steam), compositions and thermodynamic properties of coexisting phases that were formed from the original mixture. In the single-phase region (liquid, gas, fluid state), the thermodynamic properties of the mixture of the initial composition are determined.

The initial stage of calculating the thermodynamic properties of a mixture within the framework of the MPT method is the determination of its density (molar volume). In the single-phase region, the density is determined from the equality of the expression for pressure (42) to the given pressure. In the two-phase region of liquid-vapor equilibrium ( $L$ - $V$ ) necessary together with the densities  $L$ - and  $V$ -phases to determine the compositions  $\{x_i^L\}, \{x_i^V\}$  of these phases and gas content  $n^V$  (mole fraction of the vapor phase in a two-phase mixture), that is  $2N + 3$  parameters.

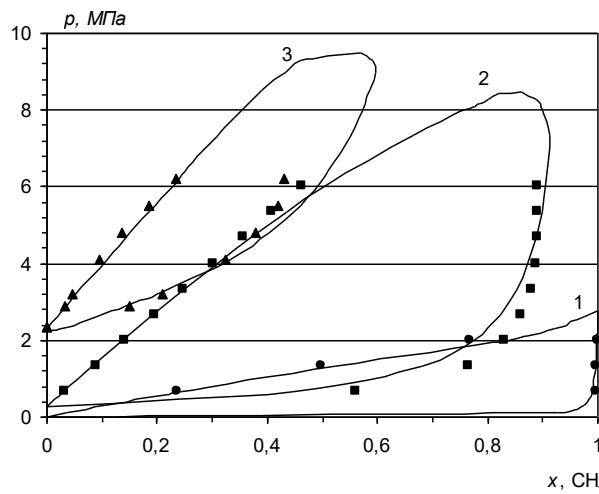
Thus, the system of equations describing the equilibrium of phases, in addition to the obvious conditions of equality of pressures in phases at a given pressure, equality of chemical potentials  $\mu_i$  of all  $N$  components  $L$ - and  $V$ -phases and similar equations (62), for the sets  $\{x_i^L\}$  and  $\{x_i^V\}$ , should also contain  $N-1$  material balance equation [15–17], which connect  $n^V$  and concentrations (in phases and in the original mixture) (63)

$$n^V (x_i^V - x_i^L) = x_i^0 - x_i^L, i = 1, \dots, N. \quad (63)$$



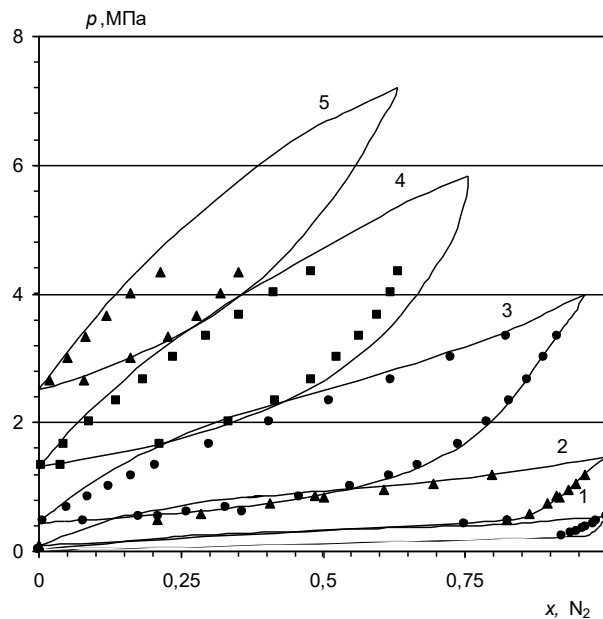
1 – calculation,  $T = 160$  K; 2 – calculation,  $T = 180$  K; 3 – calculation,  $T = 203,15$  K; 4 – calculation,  $T = 233,15$  K; marks are the experimental data [25–26]

Figure 1 – Diagrams of PE of liquid-vapor mixtures of methane-ethane at the indicated temperatures



1 – calculation,  $T = 174,85$  K; 2 – calculation,  $T = 256,45$  K; 3 – calculation,  $T = 338,15$  K; marks are the experimental data [26]

Figure 2 – Diagrams of PE liquid-vapor mixtures of methane-propane at the indicated temperatures



1 – calculation,  $T = 95$  K; 2 – calculation,  $T = 110$  K; 3 – calculation,  $T = 133,15$  K; 4 – calculation,  $T = 155,35$  K; 5 – calculation,  $T = 172,05$  K; marks are the experimental data [26–27]

Figure 3 – Diagrams of PE liquid-vapor mixtures of nitrogen-methane at the indicated temperatures



Supplementing the system with such equations (25), we obtain a formal system  $2N+3$  of equations for the above parameters. Existence of permanent connections (63) with additional conditions (62) allows to reduce the number of unknown parameters by substitution (64)

$$x_i^V = [x_i^0 - (1 - n^V)x_i^L] / n^V, i = 1, \dots, N. \quad (64)$$

After converting the system of  $2N+3$  equations determination of phase equilibria and thermodynamic properties of coexistence  $L$ - and  $V$ -phases is carried out by solving a system of  $N+3$  equations (65)

$$\begin{cases} p(T, \rho^L, \{x_i^L\}) - p = 0, \\ p(T, \rho^V, \{x_i^V\}) - p = 0, \\ \mu_i(T, \rho^L, \{x_i^L\}) - \mu_i(T, \rho^V, \{x_i^V\}) = 0, i = 1, \dots, n, \\ \sum_{i=1}^n x_i^L = \sum_{i=1}^n x_i^V \end{cases} \quad (65)$$

for  $N+3$  parameters  $(\rho^L, \rho^V, \{x_i^L\}, n^V)$  with an additional condition (61). Here  $\rho^L, \rho^V$  are the densities of  $L$ - and  $V$ -phases. In the system (64) the symbol  $x_i^V$  shows not additional unknowns, but auxiliary expressions accordingly (64). The concentrations are determined from these expressions (after solving the working system)  $\{x_i^V\}$ , complementing the defined set of  $N + 3$  parameters to the full  $(2N + 3)$ -set.

When solving practical problems, parameters of phase equilibria and thermodynamic properties of single- and multi-component fuels are required in a wide range of states – from combustion parameters (or pyrolysis of components) to liquefied gas, taking into account a wide range of mixture compositions. Fragmentary experimental data on the fuel properties and their components are unable to provide the information necessary to solve a specific technical task. Therefore, the prediction of phase equilibria of fuels, that is, the calculation of the necessary characteristics in the absence of experimental information or in the sufficiency of the minimum amount of available initial data, becomes important.

Methods of calculating thermodynamic properties used in practice are based mainly on reliable data used to construct empirical equations with many parameters. The disadvantages of such methods are limited areas of applicability in terms of state parameters, the need to have a significant amount of experimental information on the thermodynamic behavior of components and their binary mixtures, significant distortions of concentration dependences, etc.

The developed mathematical model describes the thermodynamics of multicomponent molecular systems in different phase states. The resulting analytical expressions have a simple structure and are easily translated into computer language. Calculations of PE parameters are performed within the framework of statistical-mechanical methods (MPT scheme), based on data on interaction potentials and do not contain any empirical correlations. Comparison with available experimental data for fuel components revealed the high efficiency of the technique (errors in determining properties are at the level of experimental ones).

The numerical implementation of the developed mathematical model is carried out with the help of a computer program for determining phase equilibria and thermodynamic properties of the liquid and vapor phases of multicomponent fuels, which also includes a subroutine for calculating properties in the single-phase region (homogeneous state).

The software has been created to solve a working system of nonlinear equations (65) by modified Newton's method. At the same time, a set of initial data is used: a list of mixture components, concentrations of mixture components, temperatures, pressures.

The developed complex of computer modules is designed in the form of a software suit "Thermodynamic properties and phase equilibria in multicomponent liquid and gas mixtures".

This software is intended for operational calculations of phase equilibria and thermodynamic properties of individual substances and multicomponent mixtures in liquid and gaseous states.

Calculation procedures for all programs of the package are based on the MPT scheme with fast series convergence. Features of the complex of computer programs are: sufficient limitation of the amount of source information; high accuracy; applicability to a wide class of substances in any practically important range of states.

The properties of the following components and their mixtures are determined:

Boundary hydrocarbons ( $\text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, n\text{-C}_4\text{H}_{10}, i\text{-C}_4\text{H}_{10}, n\text{-C}_5\text{H}_{12}, i\text{-C}_5\text{H}_{12}, \text{C}_6\text{H}_{14}, \text{C}_7\text{H}_{16}, \text{C}_8\text{H}_{18}, \text{C}_9\text{H}_{20}, \text{C}_{10}\text{H}_{22}$ ); inert gases ( $\text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$ ); nitrogen  $\text{N}_2$ ; carbon dioxide  $\text{CO}_2$ ; carbon monoxide  $\text{CO}$ ; hydrogen  $\text{H}_2$ ; oxygen  $\text{O}_2$ ; water  $\text{H}_2\text{O}$ ; hydrogen sulfide  $\text{H}_2\text{S}$ ; benzene  $\text{C}_6\text{H}_6$  etc.

These sets provide, in particular, a description of natural gas, gas condensate, mine gas, energy carriers based on hydrogen, nitrogen, working bodies of fuel cells of electrochemical generators (ECG) and other mixtures.

Properties to be determined: equation of state ( $p, V, T$  – ratio, density); coefficients of thermal expansion and isothermal compression; liquid-vapor phase equilibria; energy (Gibbs, internal, free); enthalpy; entropy; heat capacity ( $C_p, C_v$ ).

State ranges:

– liquid state: pressure – from the lines of paraliq equilibrium to 1000 MPa (or to the lines of crystallization); temperature – from the triple point to the critical point;

– gaseous (fluid) state: pressure – from 0 to 1000 MPa; temperature – up to 5000 K (or pyrolysis temperatures).

Calculations of properties in this software package do not contain fitted parameters and empirical correlations and are based only on the obtained data on the interaction potentials of substances. Average calculation errors are at the level of conventional experimental ones (for modern experimental methods). This eliminates the need for time-consuming and expensive experimental research, which gives a significant economic effect.

**6 Analysis and description of the results of a computational study of the thermodynamic characteristics of the fuel**

The abilities of the developed method for calculating phase equilibria and thermodynamic properties are demonstrated by the results for binary and multicomponent mixtures. A large set of results for phase diagrams and sets of thermodynamic properties were obtained, which agree well with the experiment in overlapping ranges of states and predict the specified properties within the working limits of the method:

– liquid state – pressure from the lines of paraliqid equilibrium to 1000 MPa, or to the lines of crystallization, temperature from the triple point to the critical point;

– gaseous (fluid) state – pressure from 0 to 1000 MPa, temperature up to 5000 K or up to temperatures of thermal decomposition (pyrolysis) of components.

The area of the liquid state of mixtures, which has received special attention, is the most difficult to describe and relatively little studied experimentally.

The calculated values of the densities of the liquid components are given in the table 2, are compared with experimental data available in the literature [28], and determined by other calculation methods [29]. Application of the equations with a larger number of coefficients [29] allows to describe a wider range of states, but only experimentally studied. When the empirical equations of state are extrapolated even slightly into experimentally unexplored ranges, the calculation error increases dramatically.

It can be seen that MPT provides an average of 3 times fewer errors in the description of properties compared to other methods.

Table 5 shows (at  $T = 112$  K) the values of thermodynamic properties of liquid multicomponent mixtures, close in composition to natural gas. The compositions of the mixtures are given in the table 6. The density of the mixture in the single-phase area and on the equilibrium lines with the vapor phase (at equilibrium pressure  $p = p_s$ ) has been obtained from the solution of the equation (23) and the system (64) respectively. Here  $D_m$  – density,  $H_m$  - enthalpy,  $S_m$  – entropy,  $C_{pm}$  – isobaric heat capacity,  $\alpha_m$  – coefficient of thermal expansion,  $\beta_m$  – coefficient of isothermal compression. Results for the isotherm  $T = 112$  K correspond to a temperature close to the normal boiling point of methane ( $CH_4$ ) and real PG - with small impurities of other components to  $CH_4$ . It should be noted that the average error of the description of the density is, as well as for individual components, equal to approx 0,1 %. Similar results (calculation errors at the level of conventional experimental ones) have been obtained for a set of basic thermodynamic properties.

Calculations of the thermodynamic properties of a number of multicomponent mixtures: natural gas, gas condensate, biogas, mine gas, lighting gas, coke gas, etc. were also performed, presented in the research works [15–17].

Table 5 – Thermodynamic properties of natural gas mixtures on the equilibrium line at  $T = 112$  K [15]

N of the mixture	$D_m$ , kg/m <sup>3</sup>	$-v^E$ , cm <sup>3</sup> /mole	$-H_m$ , kJ/mol	$H^E$ , J/mol	$S_m$ , kJ/(kg·K)	$C_{pm}$ , kJ/(kg·K)	$\alpha_m \cdot 10^3$ , 1/K	$\beta_{Tm} \cdot 10^3$ , 1/MPa
0	422.07	–	285.46	–	4.942	3.368	3.344	2.236
1	424.97	0.062	280.30	10.31	4.950	3.359	3.374	2.264
2	427.79	0.123	275.33	20.43	4.951	3.351	3.406	2.298
3	431.45	0.144	293.68	6.47	4.905	3.256	3.235	2.089
4	434.49	0.187	296.34	8.66	4.888	3.221	3.200	2.046
5	434.34	0.211	288.64	17.04	4.913	3.248	3.263	2.118
6	438.71	0.288	288.05	26.51	4.891	3.215	3.251	2.098
7	436.97	0.242	289.71	20.32	4.898	3.219	3.239	2.090
8	441.32	0.258	289.11	29.78	4.876	3.187	3.228	2.071
9	437.19	0.277	283.72	27.43	4.914	3.240	3.292	2.148
10	437.38	0.255	291.32	19.32	4.895	3.213	3.228	2.074
11	441.57	0.295	283.18	36.90	4.892	3.207	3.280	2.128
12	439.82	0.309	284.82	30.72	4.899	3.212	3.268	2.119
13	441.74	0.271	290.72	28.75	4.873	3.181	3.217	2.055
14	439.98	0.284	292.36	22.56	4.881	3.186	3.205	2.047
15	444.19	0.326	284.27	40.19	4.877	3.179	3.256	2.099
16	444.32	0.299	291.75	32.00	4.859	3.154	3.194	2.09
17	440.25	0.322	286.42	29.80	4.896	3.206	3.256	2.102
18	444.61	0.339	285.86	39.24	4.875	3.174	3.245	2.083
19	442.84	0.352	287.49	33.05	4.882	3.178	3.233	2.075
20	447.20	0.368	286.92	42.50	4.860	3.147	3.222	2.056

Table 6 – Composition of natural gas mixtures [15]

N of the mixture	Mole fractions of components, %				
	$C_1$	$C_2$	$C_3$	$N_2$	$CO_2$
0	100	–	–	1	–
1	99	–	–	–	–
2	98	–	–	2	–
3	97	3	–	–	–
4	96	4	–	–	–
5	96	3	–	1	–
6	95.5	3	–	1	0.5
7	95.5	3	0.5	1	–
8	95	3	0.5	1	0.5
9	95	3	–	2	–
10	95	4	–	1	–
11	94.5	3	–	2	0.5
12	94.5	3	0.5	2	–
13	94.5	4	–	1	0.5
14	94.5	4	0.5	1	–
15	94	3	0.5	2	0.5
16	94	4	0.5	1	0.5
17	94	4	–	2	–
18	93.5	4	–	2	0.5
19	93.5	4	0.5	2	–
20	93	4	0.5	2	0.5

**Conclusion**

Thus, based on the results of the research, reflected in the sections of this work, the following general conclusions can be drawn.

The analysis of the given results confirms the expediency of using the developed mathematical model for determining the parameters of the PE and thermophysical properties of the hydrocarbon-type fuel. According to the entire set of calculated properties, this method has significant advantages over existing model and empirical methods.

The main advantages of the calculation method based on the MPT scheme are:

- the minimum number of initial data necessary and sufficient for calculations;
- lack of need for fitted parameters and empirical correlations;
- adequacy of the statistical-mechanical model underlying the method;
- applicability to a large class of substances and their mixtures;

- suitability for use in a wide range of conditions;
- calculation errors do not exceed experimental errors.

The application of the developed method provides the possibility of current determination of thermophysical properties and phase equilibria of multicomponent mixtures in many technological processes, allows limiting or eliminating time-consuming and lengthy experimental studies, which contributes to increasing their cost-effectiveness.

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**Кондратенко О.М., Умеренкова К.Р., Колосков В.Ю., Колоскова Г.М., Строков О.П., Литвиненко О.О.  
РОЗВИТОК І УЗАГАЛЬНЕННЯ МЕТОДИКИ РОЗРАХУНКУ ТЕРМОДИНАМІЧНИХ ВЛАСТИВОСТЕЙ І ФАЗОВИХ  
РІВНОВАГ У ВУГЛЕВОДНЕВИХ СУМІШАХ ЯК ПАЛИВ ДЛЯ ПОРШНЕВИХ ДВЗ З МЕТОЮ ЇХ ЕКОЛОГІЗАЦІЇ**

У статті, яка відображає результати власного дослідження колективу авторів, метою якого було розвиток математичного апарату, побудованого на базі модифікованої теорії збурень, та застосування його для описання теплофізичних характеристик альтернативних моторних палив довольного агрегатного стану, для яких характерною є сферична конфігурація взаємодіючих структурних елементів, послідовно вирішено наступні задачі щодо вдосконалення розробленого раніше, наведеного у відкритому друку та апробованого на низці науково-технічних конференцій міжнародного рівня математичного апарату, а саме: виконано аналіз та розвиток схеми модифікованої теорії збурень для багатокомпонентних альтернативних палив; одержано аналітичні вирази для параметрів різнорідних потенціалів взаємодії; виконано побудову комплексу термодинамічних величин сумішей та робочих виразів його математичного описання; виконано побудову та аналіз фазових діаграм бінарних сумішей компонентів вуглеводневих систем; виконано побудову і описання системи рівнянь для фазових рівноваг; здійснено аналіз та описання результатів розрахункового дослідження термодинамічних характеристик альтернативних видів моторного палива. Об'єктом дослідження є теплофізичні властивості альтернативних моторних палив, що перебувають у рідинному чи газоподібному агрегатному стані, зі сферичною конфігурацією взаємодіючих структурних елементів. Предметом дослідження є математичний апарат на основі модифікованої теорії збурень для описання теплофізичних характеристик моторних палив, що перебувають у рідинному чи газоподібному агрегатному стані, зі сферичною конфігурацією взаємодіючих структурних елементів. Наукова новизна результатів дослідження полягає в тому, що набув подальшого розвитку підхід до побудови математичного апарату на основі модифікованої теорії збурень для вичерпного описання усіх теплофізичних властивостей альтернативних і традиційних моторних палив, які перебувають у довольному агрегатному стані, що дозволило знизити похибки визначення та зменшити час розрахунку теплофізичних властивостей порівняно з експериментальними чи довідниковими даними. Практичне значення результатів дослідження, полягає у тому, що перетворений і доповнений у дослідженні математичний апарат придатний для надання точної інформації до переліку вихідних даних у дослідженнях щодо повного життєвого циклу моторного палива будь-якого генезису (тобто традиційних, альтернативних та сумішевих) – виробництва, зберігання, перевезення, дистрибуції, використання, яке при цьому перебуває як у рідинному, так і у газоподібному агрегатному стані, рівно як і для прогнозування перебігу та наслідків процесів забруднення атмосфери газоподібними продуктами повного і неповного згоряння компонентів палив у камерах згоряння теплових машин різного типу.

**Ключові слова:** теплофізичні властивості, традиційні моторні палива, альтернативні моторні палива, математична модель, технології захисту навколишнього середовища, екологічна безпека, енергоустановки, поршневі двигуни внутрішнього згоряння.

#### ЛІТЕРАТУРА

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