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RESEARCH ARTICLE

Parameters of the UNIQUAC model for describing the vapor–liquid phase equilibrium of D_2–T_2, D_2–DT, DT–T_2 hydrogen isotope mixtures

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Abstract

Objectives. *Determination of the parameters of the binary energy interaction of the (UNIversal QUAsiChemical) UNIQUAC model on the basis of mathematical processing of experimental literature data on the phase equilibrium of hydrogen isotopic mixtures D_2–T_2, D_2–DT, DT–T_2 to calculate the activity coefficients of the components D_2, DT, and T_2.*
Methods. *The method of successive approximations was used in junction with the "from stage to stage" method, which consists in calculating a single evaporation process on a theoretical plate.*
Results. *Equations were written for calculating the activity coefficients of hydrogen isotopes on the basis of the Sherwood theory as applied to binary D_2–T_2, D_2–DT, DT–T_2 and ternary D_2–DT–T_2 hydrogen isotope mixtures. The graphical dependences of the activity coefficients and separation coefficients of mixtures D_2–T_2, D_2–DT, and DT–T_2 are compared in the range of the concentration of a highly volatile component from 0 to 100 mol % at atmospheric pressure for three options: ideal mixtures; non-ideal mixtures using the Sherwood theory; non-ideal mixtures on the basis of the UNIQUAC model. The dependences of the separation coefficients α were found to be similar for all binary isotopic mixtures. However, when considering mixtures as ideal, α increases. According to Sherwood's theory, α remains a practically constant value, which is independent of the composition of the mixture. The UNIQUAC model predicts a decrease in α with an increase in the concentration of a less volatile component in the mixture. The profile of the distribution of hydrogen isotopes D_2, DT, and T_2 of a three-component mixture D_2–DT–T_2 along the*

height of a distillation column operating in a closed mode was calculated for three variants. It was accepted that: pressure along the height of the column is constant and equal to atmospheric 760 mm Hg. Art.; number of theoretical plates 21; concentration of components in the liquid phase on the first plate (stage), in mol %: $x_{D_2} = 65$; $x_{DT} = 10$; $x_{T_2} = 25$; *the accuracy of calculating the composition of the vapor phase is* 10^{-10}.

Conclusions. *The parameters of the binary energy interaction of the UNIQUAC model of hydrogen isotopic mixtures* D_2–T_2, D_2–DT, *and* DT–T_2 *are determined. The UNIQUAC model is adequate in relation to experimental data on the coefficient of separation. Due to systematic deviations in the theoretical Sherwood and ideal models, they are not suitable for further calculations of phase equilibrium of isotopic mixtures of hydrogen* D_2–T_2, D_2–DT, DT–T_2, *and* D_2–DT–T_2.

Keywords: *UNIQUAC model, hydrogen isotopic mixtures* D_2–T_2, D_2–DT, DT–T_2, D_2–DT–T_2, *vapor–liquid phase equilibrium*

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НАУЧНАЯ СТАТЬЯ

Параметры модели UNIQUAC для описания фазового равновесия пар – жидкость изотопных смесей водорода D_2–T_2, D_2–DT, DT–T_2

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Аннотация

Цели. *Определение параметров бинарного энергетического взаимодействия модели UNIversal QUAsiChemical (UNIQUAC) на основе математической обработки литературных экспериментальных данных по фазовому равновесию изотопных смесей водорода* D_2–T_2, D_2–DT, DT–T_2 *для расчета коэффициентов активности компонентов* D_2, DT *и* T_2.

Методы. *Применены метод последовательных приближений и метод «от ступени к ступени», заключающийся в расчете процесса однократного испарения на теоретической тарелке.*

Результаты. *Записаны уравнения для расчета коэффициентов активности изотопов водорода на основе теории Шервуда применительно к бинарным* D_2–T_2, D_2–DT, DT–T_2 *и тройной* D_2–DT–T_2 *изотопным смесям водорода. Приведено сравнение графических зависимостей коэффициентов активности и коэффициентов разделения смесей* D_2–T_2, D_2–DT, DT–T_2 *в диапазоне изменения концентрации легколетучего компонента от 0 до 100 мол. % при атмосферном давлении для трех вариантов: идеальных смесей; неидеальных с использованием теории Шервуда и неидеальных на основе модели UNIQUAC. Выявлено, что характер поведения зависимостей коэффициентов разделения* α *аналогичен для всех бинарных изотопных смесей. При рассмотрении смесей в качестве идеальных* α *возрастает. По теории Шервуда* α *остается* *практически постоянной величиной, не зависящей от состава смеси. Модель UNIQUAC прогнозирует снижение α с ростом концентрации легколетучего компонента в смеси. Для трех вариантов вычислен профиль распределения изотопов водорода D_2, DT и T_2 трехкомпонентной смеси D_2–DT–T_2 по высоте ректификационной колонны, работающей в замкнутом режиме. Принято: давление по высоте колонны постоянно и равно атмосферному 760 мм рт. ст.; число теоретических тарелок 21; концентрации компонентов в жидкой фазе на первой тарелке (ступени), в мол. %: $x_{D_2} = 65$; $x_{DT} = 10$; $x_{T_2} = 25$; точность расчета состава паровой фазы 10^{-10}.*

Выводы. *Определены параметры бинарного энергетического взаимодействия модели UNIQUAC изотопных смесей водорода D_2–T_2, D_2–DT, DT–T_2. Модель UNIQUAC адекватна по отношению к экспериментальным данным по коэффициентам разделения. Теоретическая модель Шервуда и идеальная модель дают систематические отклонения и не пригодны для дальнейших расчетов фазового равновесия изотопных смесей водорода D_2–T_2, D_2–DT, DT–T_2 и D_2–DT–T_2.*

Ключевые слова: *модель UNIQUAC, изотопные смеси водорода D_2–T_2, D_2–DT, DT–T_2, D_2–DT–T_2, фазовое равновесие пар – жидкость*

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INTRODUCTION

When calculating the low-temperature distillation of liquid mixtures of hydrogen isotopes, the separation factor α^{o} is determined as the ratio of the vapor pressures of the pure components of the highly volatile P_1^{o} to the hardly volatile P_2^{o}, calculated at a certain temperature [1], while the phase equilibrium constant of the *i*th component K_i is given as the ratio of the vapor pressure of the pure component to the total pressure P [2]. This approach involves classifying isotopic mixtures of hydrogen as ideal, obeying Raoult's law.

$$\alpha_{\text{ideal}} = \alpha^{\text{o}} = \frac{P_1^{\text{o}}}{P_2^{\text{o}}}, \tag{1}$$

$$K_i = \frac{P_i^{\text{o}}}{P}. \tag{2}$$

It is known from experimental studies that mixtures D_2–T_2, D_2–DT, and DT–T_2 deviate from ideal ones [3, 4]. Note that isotopic mixtures of hydrogen are not azeotropic. In such binary mixtures, the low-boiling component is highly volatile, while the high-boiling component is hardly volatile. The non-ideality of the mixture in the liquid phase is taken into account by the activity coefficient of the component, the calculation of which presents a certain difficulty, since the identification of empirical or thermodynamically justified equations should be based on experimental data on vapor–liquid equilibrium.

The theory of multicomponent liquid hydrogen solutions presented in Sherwood and Souers in 1984 takes into account non-ideal vapor–liquid equilibrium [5]. Activity coefficient of the *i*th component γ_i is related to the molar excess Gibbs free energy of mixing $\Delta\bar{G}_i^E$ according to the following expression:

$$\gamma_i = \exp\left(\frac{\Delta\bar{G}_i^E}{RT}\right), \tag{3}$$

$$\Delta\bar{G}_i^E = \sum_j x_j A_{i,j} - G^E, \tag{4}$$

$$G^E = \frac{1}{2}\sum_i\sum_j x_i x_j A_{i,j}\left(A_{i,j} = 0,\ i = j\right), \tag{5}$$

where T is temperature, K; R is the universal gas constant, R = 8.314 J/(mol K); x is the mole fraction of the component in the liquid; $A_{i,j}$ is the parameter of the binary interaction of hydrogen isotopes, J/mol; indices *i* and *j* are component numbers.

Based on the virial equation of state, an equation was obtained for calculating the total pressure P (Pa) as the sum of the partial pressures of the components in which the second virial coefficient of the gas mixture B_i (m^3/mol) takes into account the imperfection of the gas phase, while the binary interaction parameter $A_{i,j}$ (J/mol) represents the imperfection of the liquid phase. In the case of a binary mixture, the equation is represented as:

$$P = x_1 P_1^{\mathrm{o}} \exp\left(\frac{B_1 P_1^{\mathrm{o}} - B_1 P + x_2^2 A_{12}}{RT}\right) + \\ + x_2 P_2^{\mathrm{o}} \exp\left(\frac{B_2 P_2^{\mathrm{o}} - B_2 P + x_1^2 A_{12}}{RT}\right), \tag{6}$$

where

$$B = B_0 \left(\frac{T}{20}\right)^{-b}, \tag{7}$$

$$A_{12} = 12.1\left(\lambda_1^2 - \lambda_2^2\right)^{1.6} \exp\left[\left(\frac{14.74}{T}\right)^6\right]. \tag{8}$$

Here, P_1^{o} and P_2^{o} are vapor pressure values of pure components, Pa; x_1 and x_2 are mole fractions of components in the liquid, mole fractions; index 1 denotes the highly volatile component, while index 2 is the hardly volatile component.

Coefficients for calculating partial pressures of hydrogen isotopes D_2, DT, and T_2 are presented in Table 1 [5].

For a ternary mixture, Eq. (5) is given as:

$$G^E = x_1 x_2 A_{12} + x_1 x_3 A_{13} + x_2 x_3 A_{23}. \tag{9}$$

For the first component of the ternary mixture

$$\Delta \bar{G}_1^E = \left(1 - x_1\right) x_2 A_{12} + \left(1 - x_1\right) x_3 A_{13} - x_2 x_3 A_{23}. \tag{10}$$

In the present article, the parameters of the binary energy interaction of the UNIQUAC model for calculating the activity coefficients γ of components D_2, DT, and T_2 for isotopic mixtures of hydrogen are obtained by analyzing the known experimental data [3, 4]. We compared the calculated data obtained for ideal mixtures and non-ideal mixtures for binary D_2–T_2, D_2–DT, DT–T_2 and ternary mixtures D_2–DT–T_2 according to the UNIQUAC method and informed by the theory of multicomponent liquid hydrogen solutions [5] presented above and referred to as the Sherwood theory in further presentation.

Based on the calculation of the vapor–liquid phase equilibrium, the separation coefficients α are calculated for mixtures D_2–T_2, D_2–DT, DT–T_2 at different boiling temperatures depending on pressure and composition. The calculations were performed in the Pascal programming language. To calculate the separation factor α, the Raoult–Dalton law is applied for non-ideal mixtures

$$\alpha = \frac{P_1^{\mathrm{o}} \gamma_1}{P_2^{\mathrm{o}} \gamma_2}. \tag{11}$$

METHODS

To determine the energy binary interaction parameters Δu_{12} and Δu_{21} of the UNIQUAC model, the method of successive approximations was used until the minimum deviation of the calculated values of the separation coefficients from the experimental ones was reached.

For the calculation of closed rectification, the "stage to stage" method was used, which consists in calculating the process of single evaporation on a theoretical plate. When calculating from bottom to top for a steady process on each overlying tray, the composition of the liquid is equal to the composition of the vapor rising from the underlying tray.

Table 1. Coefficients for calculating partial pressures of hydrogen isotopes

Isotope	B_0 (10^6 m^3/mol)	b	λ
D_2	−184	1.64	1.224
DT	−190	1.70	1.111
T_2	−197	1.77	1.000

RESULTS AND DISCUSSION

Vapor pressure of pure components D_2, DT, T_2

The value of the separation factor α depends to a great extent on the vapor pressure of pure components, whose calculation is carried out according to empirical equations.

Vapor pressure D_2. The results of measurements on the vapor pressure $P^o_{D_2}$ of normal deuterium D_2 are given in [6–10]. Equations have been proposed by a number of authors [7, 10–13]. In this work, the following equation was used [7]:

$$\lg P^o_{D_2} = 8.58549 - \frac{74.2894}{T} - 0.029345 \cdot T + \\ + 0.00047507 \cdot T^2, \tag{12}$$

where $P^o_{D_2}$ is the vapor pressure of deuterium, Pa; T is the temperature, K.

Vapor pressure DT. Equations [14, 15] were proposed to calculate the deuterotritium vapor pressure DT P^o_{DT}. The Sherwood equation is adopted [15]:

$$\ln P^o_{DT} = 11.3802 - \frac{167.989}{T} + \\ + 4.5193 \cdot 10^{-3} \cdot T + 7.6369 \cdot 10^{-5} \cdot T^2, \tag{13}$$

where P^o_{DT} is the vapor pressure of deuterotritium, kPa; T is the temperature, K.

Vapor pressure T_2. The vapor pressure $P^o_{T_2}$ of normal tritium T_2 was measured by Grilly. The measurement results and the calculation equation $P^o_{T_2}$ are given in [10]. There is also data of $P^o_{T_2}$ in the work [9]. Other equations [14, 16] were proposed to calculate $P^o_{T_2}$. In this work, the Grilly equation is adopted.

$$\lg P^o_{T_2} = 6.0334 - \frac{78.925}{T} + 2 \cdot 10^{-4} \left(T - 25\right)^2, \tag{14}$$

where $P^o_{T_2}$ is the vapor pressure, mm Hg; T is the temperature, K.

Equations (12)–(14) used in this work are selected based on a comparison of calculated and experimental data. It is of note that, on the whole, the analyzed equations adequately describe the experimental data.

There is no experimental data on the vapor pressure of DT in the literature. Preference is given to the Sherwood equation [15] rather than the Frost–Kalkwarf equation [14] due to the fact that Sherwood performed an analysis of the available *P–T–x–y* data in dilute solutions, where the heteronuclear isotope is present as stable trace particles. Here, the vapor pressure of trace components was calculated on the basis of a phase equilibrium model using the Chueh–Prausnitz modification of the Redlich–Kwong equation. This model better describes the parameter $A_{i,j}$ to take into account the imperfection of hydrogen isotopic mixtures.

A small deviation between the calculated vapor pressure curves, which are constructed according to the Sherwood and Frost–Kalkwarf equations, increases with increasing temperature. In the Frost–Kalkwarf equation, the deuterotritium vapor pressure P^o_{DT} is defined as the geometric mean, i.e., as the square root of the product of the vapor pressures of the pure components D_2 and T_2: $P^o_{DT} = \sqrt[2]{P^o_{D_2} P^o_{T_2}}$.

Equations for calculating the activity coefficients of hydrogen isotopes based on the theory of multicomponent liquid hydrogen solutions for isotopic mixtures D_2–T_2, D_2–DT, DT–T_2 and D_2–DT–T_2

Based on the Sherwood theory [5], the activity coefficients of the components in binary mixtures γ_{D_2} and γ_{T_2} ; γ_{D_2} and γ_{DT} ; γ_{DT} and γ_{T_2} can be determined from Eq. (6), writing it in the form of

$$P - x_1 P^o_1 \gamma_1 \exp\left(\frac{B_1 P^o_1 - B_1 P}{RT}\right) - \\ - x_2 P^o_2 \gamma_2 \exp\left(\frac{B_2 P^o_2 - B_2 P}{RT}\right) = 0, \tag{15}$$

where

$$\gamma_1 = \exp\left(\frac{x_2^2 A_{12}}{RT}\right), \tag{16}$$

$$\gamma_2 = \exp\left(\frac{x_1^2 A_{12}}{RT}\right). \tag{17}$$

Here, index 1 is the highly volatile component, while index 2 is the hardly volatile component.

The temperature T of the vapor–liquid phase equilibrium for a given mixture composition and external pressure P is the root of the function of Eq. (15), which can be obtained with some accuracy using one of the well-known numerical methods, for example, the method of successive approximations. Here, the values of B_1, B_2, γ_1, γ_2, and A_{12} are recalculated during the iterative search for temperature.

Let us apply Sherwood's theory to a three-component mixture D_2–DT–T_2. We introduce the notation: D_2 – 1; DT – 2; T_2 – 3, where the numbers indicate the number of the component in accordance with their volatility. The highly volatile component is D_2, the hardly volatile component is T_2, and DT is an intermediate component, which behaves as a hardly volatile component with respect to D_2, and as a highly volatile component with respect to T_2 over the entire range of concentrations. Then Eq. (15) takes the form of

$$P - x_1 P_1^{o} \gamma_1 \exp\left(\frac{B_1 P_1^{o} - B_1 P}{RT}\right) - \\ - x_2 P_2^{o} \gamma_2 \exp\left(\frac{B_2 P_2^{o} - B_2 P}{RT}\right) - \\ - x_3 P_3^{o} \gamma_3 \exp\left(\frac{B_3 P_3^{o} - B_3 P}{RT}\right) = 0, \tag{18}$$

where by expanding Eqs. (3)–(5), we have

$$\gamma_1 = \exp\left(\frac{\Delta \bar{G}_1^E}{RT}\right) = \\ = \exp\left(\frac{(1-x_1)x_2 A_{12} + (1-x_1)x_3 A_{13} - x_2 x_3 A_{23}}{RT}\right), \tag{19}$$

$$\gamma_2 = \exp\left(\frac{\Delta \bar{G}_2^E}{RT}\right) = \\ = \exp\left(\frac{(1-x_2)x_1 A_{12} + (1-x_2)x_3 A_{23} - x_1 x_3 A_{13}}{RT}\right), \tag{20}$$

$$\gamma_3 = \exp\left(\frac{\Delta \bar{G}_3^E}{RT}\right) = \\ = \exp\left(\frac{(1-x_3)x_1 A_{13} + (1-x_3)x_2 A_{23} - x_1 x_2 A_{12}}{RT}\right). \tag{21}$$

The above equations are subsequently used in the calculation of the phase equilibrium of the single evaporation process in the vapor–liquid system.

Separation factor of D_2–T_2

The results of an experimental study of the separation factor α of the D_2–T_2 isotope mixture were obtained by Sherman *et al*. [3] for three temperatures at a D_2:T_2 molar ratio of 0.991:0.009. The experimental value of the separation factor was calculated from the expression, where the index 1 is the highly volatile component, index 2 is the hardly volatile component

$$\alpha = \frac{y_1 x_2}{y_2 x_1} \tag{22}$$

The averaged experimental values of the separation coefficient of the D_2–T_2 isotope mixture are given in Table 2.

Analyzing the obtained α values for the D_2–T_2 binary mixture and those obtained for other molar ratios of the D_2–DT–T_2 ternary mixture [3], Sherman noted that the values of the separation factor $\alpha_{D_2-T_2}$ are approximately 5–6% lower than the ideal α° values.

In this work, the mathematical processing of experimental data [3] is carried out as follows. Molar ratio 0.991:0.009 converted to mole fractions: $x_{D_2} = 0.994$; $x_{T_2} = 0.006$. Molar mass D_2 = 4.028204 g/mol; T_2 = 6.032100 g/mol [17]. For the obtained molar composition of the liquid isotope mixture D_2–T_2, the phase equilibrium *y*–*x* was calculated in the temperature range from 20 to 30 K. The activity coefficients γ_{D_2} and γ_{T_2} were calculated using the UNIQUAC equation [18]. The volume parameters *r* and area *q* are taken to be the same as for the hydrogen isotope H_2, which are given in the Hysys modeling software (*Aspen Technology*, USA): *r* = 0.4092; *q* = 0.47549 and are taken here and below to be the same for all hydrogen isotopes. This assumption is acceptable, since the approximately

Table 2. Experimental values of the separation factor of the D_2–T_2 isotopic mixture

Temperature, K	Separation factor α
23	1.455 ± 0.048
25	1.382 ± 0.056
27	1.318 ± 0.077

similar radius of hydrogen isotopes is: $r_{H_2} = 0.7414 \cdot 10^{-10}$ m, $r_{D_2} = 0.7417 \cdot 10^{-10}$ m, $r_{T_2} = 0.7414 \cdot 10^{-10}$ m, $r_{DT} = 0.7417 \cdot 10^{-10}$ m [17].

The identification of the parameters of the binary energy interaction Δu_{12} and Δu_{21} between the molecules of the D_2 and T_2 components of the UNIQUAC group composition model was carried out according to the experimental data (Table 2) in the following sequence. Arbitrarily set parameters Δu_{12}, Δu_{21}, whose values are in the range from $-\infty$ to $+\infty$. For a given molar composition of the mixture ($x_{D_2} = 0.994$ mol fract.; $x_{T_2} = 0.006$ mol fract.) the activity coefficients were calculated according to the UNIQUAC equation, and the pressure was iteratively determined by the method of successive approximations for each given boiling point of the mixture in the range from 20 to 30 K until the sum of the molar concentrations of the components in the vapor phase was equal to unity.

$$\sum_i y_i = \sum_i \frac{P_i^{o}}{P} x_i \gamma_i = 1. \qquad (23)$$

The calculation accuracy was 10^{-10}. The separation factor was calculated according to Eq. (11). Based on the obtained values (α, *t*), a graph was built and the deviation of the calculated values of α from the experimental values for three temperatures was determined (Table 2). Restriction: the *y*–*x* phase equilibrium curve with the found parameters Δu_{12} and Δu_{21} should not have an azeotrope point. The discovered parameters Δu_{12} and Δu_{21} are presented in Table 3.

A similar calculation was carried out with the activity coefficients calculated according to Eqs. (16) and (17) based on the Sherwood theory, where the separation coefficient was calculated according to Eq. (22).

Figure 1 shows the experimental values of the separation factor [3] along with the calculated curves constructed when considering the mixture as ideal ($\alpha^{o}(1)$), based on the theory of multicomponent liquid hydrogen solutions (α(2)), as well as when calculating the activity coefficients according to the UNIQUAC equation (α(3)), where the relative the deviation between the experimental and calculated data according to the UNIQUAC equation does not exceed 0.5%.

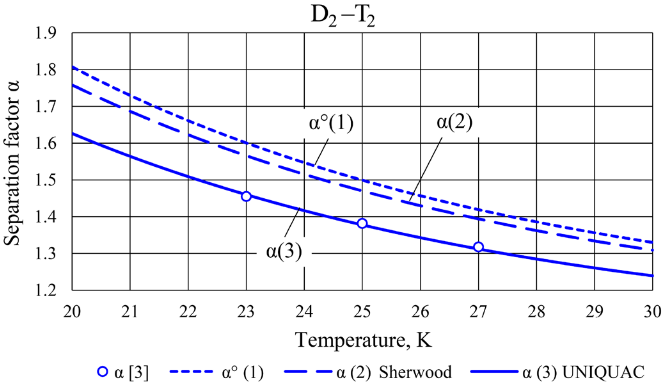


Fig. 1. D_2–T_2 separation factor dependence from temperature with liquid phase composition $x_{D_2} = 0.994$ mol fract.; $x_{T_2} = 0.006$ mol fract.

The discovered parameters Δu_{12} and Δu_{21} are used to calculate the phase equilibrium *y*–*x* at a pressure of 760 mm Hg and concentration change x_{D_2} from 0 to 100 mol %. The boiling point was calculated according to the algorithm described and presented in the form of a block diagram in [19].

Figure 2 shows the calculated curves of the dependence of activity coefficients γ_{D_2} and γ_{T_2} on concentration x_{D_2} in the liquid phase, both as obtained according to the Sherwood theory and using the UNIQUAC model.

Table 3. UNIQUAC model parameters Δu_{12} и Δu_{21} for mixtures D_2–T_2, D_2–DT, DT–T_2

Mixture	Δu_{12}, cal/mol	Δu_{21}, cal/mol
D_2 (1) – T_2 (2)	11.23	−2.21
D_2 (1) – DT (2)	31.2	−21.43
DT (1) – T_2 (2)	2.91	−1.93

Note: The energy binary interaction parameters Δu_{12} и Δu_{21} are given at the universal gas constant *R* = 1.98721 cal/(mol·K); *r* = 0.4092; *q* = 0.47549.

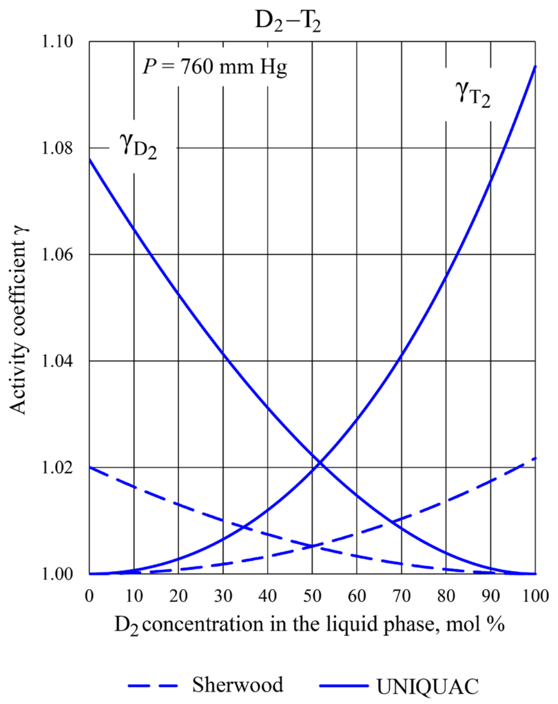


Fig. 2. Calculated curves of activity coefficients γ_{D_2} and γ_{T_2} of D_2–T_2 mixture components versus D_2 concentration in the liquid phase at atmospheric pressure.

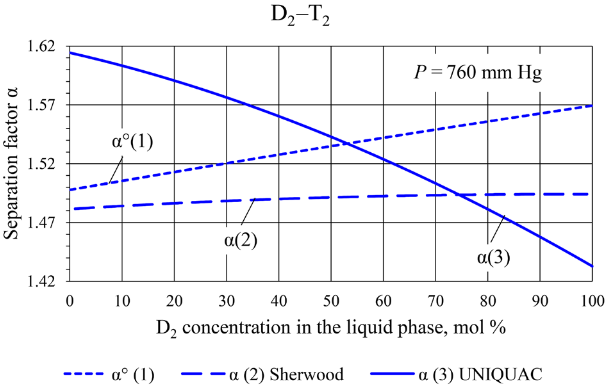


Fig. 3. Dependence of the separation factor α of the D_2–T_2 mixture on the concentration of D_2 in the liquid phase at atmospheric pressure.

Figure 3 shows the calculated dependences of the separation coefficient α of the D_2–T_2 mixture on the concentration x_{D_2} in the liquid phase at a pressure of 760 mm Hg. An analysis of the curves shows that, with increasing concentration x_{D_2}, the separation factor $\alpha^{\circ}(1)$ calculated from Eq. (1) increases; meanwhile, α(2) calculated according to the Sherwood theory changes insignificantly, and α(3) calculated according to the UNIQUAC equation decreases. Moreover, for smaller values of x_{D_2}, the value of α(3) is greater than $\alpha^{\circ}(1)$ and α(2), while for larger values of x_{D_2} the value of α(3) is smaller. This means that the UNIQUAC calculation predicts that the separation between D_2 and T_2 will deteriorate as the concentration x_{D_2} in the mixture increases.

Note that the separation factor α(2) calculated using the Sherwood theory is practically independent of the concentrations of the components in the mixture. As will be shown below for D_2–DT and DT–T_2 mixtures, this is a feature of the theory of multicomponent liquid hydrogen solutions.

Vapor–liquid phase equilibrium and separation factor D_2–DT

Experimental studies of the separation factor α of the D_2–DT isotope mixture at various temperatures were carried out by Bigeleisen and Kerr in [4]. The concentration x_{DT} was $1\cdot10^{-8}$ mole fractions. Here the separation factor is defined as the ratio of the concentration of DT in the liquid phase x_{DT} to the concentration of DT in the vapor phase y_{DT}.

$$\alpha_{D_2-DT} = \frac{x_{DT}}{y_{DT}}. \qquad (24)$$

Such a calculation of the separation factor is legitimate, since, at a concentration of $x_{DT} = 1\cdot10^{-8}$ mole fractions the concentrations D_2 both in the liquid and vapor phases tend to 1, and, being in the numerator and denominator of Eq. (24), are reduced. From Eq. (24), one can determine the value of the concentration DT in the vapor phase y_{DT}.

Binary energy interaction parameters Δu_{12} and Δu_{21} between the molecules of the D_2 and DT components of the UNIQUAC group composition model were identified as with the D_2–T_2 mixture. The results are shown in Table 3 and in Fig. 4.

The maximum relative deviation of the experimental value of the separation factor from the calculated one according to UNIQUAC is 1.6%. Figure 4 demonstrated plotted in the form of squares the separation factors α_{D_2-DT}, obtained by Sherman in [3] in the study of the phase equilibrium of a three-component mixture D_2–DT–T_2 at molar ratios D_2 : DT : T_2 in the liquid phase of 0.931 : 0.062 : 0.0011 and 0.879 : 0.117 : 0.0041.

At the next stage, taking γ_{D_2} equal to 1 from Eq. (11), the experimental values of the activity coefficient γ_{DT} were calculated. Vapor pressures were calculated from experimental temperatures using Eqs. (12) and (13). The calculation results are given in Table 4.

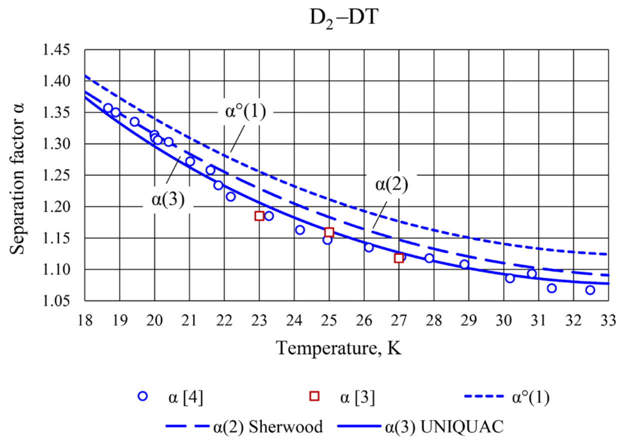


Fig. 4. Temperature dependence of the D_2–DT separation factor at concentration $x_{DT} = 10^{-8}$ mol fract.

The values of the activity coefficient γ_{DT} given in Table 4 are in the range from 1.017 to 1.057 demonstrating their slight deviation from unity. Nevertheless, the application of the Sherwood theory is widely practiced in the calculation of columns for the separation of nonideal mixtures of hydrogen isotopes [1].

Figure 5 compares the behavior of the deuterotritium activity coefficient DT with temperature. The data of Table 4 are plotted as experimental points. The calculated curves were obtained from the Sherwood and UNIQUAC models. The position of the experimental points shows an increase in the activity coefficient γ_{DT} with increasing temperature; thus, according to the Sherwood model γ_{DT}, it decreases. The application of the discovered parameters of the

Table 4. Experimental and calculated data D_2–DT

Experimental data [4]			**Calculated data**			
x_{DT}, **mol fract.**	***T*, K**	α_{D_2-DT}	y_{DT}, **mol fract.**	$P^o_{D_2}$, **kPa**	P^o_{DT}, **kPa**	γ_{DT}
$1\cdot10^{-8}$	18.669	1.357	$7.369\cdot10^{-9}$	16.746	12.096	1.02018
$1\cdot10^{-8}$	18.882	1.350	$7.407\cdot10^{-9}$	18.465	13.410	1.01998
$1\cdot10^{-8}$	19.428	1.335	$7.491\cdot10^{-9}$	23.487	17.289	1.01760
$1\cdot10^{-8}$	19.997	1.314	$7.610\cdot10^{-9}$	29.757	22.207	1.01979
$1\cdot10^{-8}$	20.015	1.309	$7.639\cdot10^{-9}$	29.974	22.378	1.02325
$1\cdot10^{-8}$	20.093	1.306	$7.657\cdot10^{-9}$	30.928	23.133	1.02371
$1\cdot10^{-8}$	20.402	1.303	$7.675\cdot10^{-9}$	34.932	26.318	1.01867
$1\cdot10^{-8}$	21.015	1.272	$7.862\cdot10^{-9}$	44.006	33.620	1.02902
$1\cdot10^{-8}$	21.601	1.258	$7.949\cdot10^{-9}$	54.210	41.953	1.02716
$1\cdot10^{-8}$	21.828	1.234	$8.104\cdot10^{-9}$	58.596	45.568	1.04206
$1\cdot10^{-8}$	22.181	1.216	$8.224\cdot10^{-9}$	65.925	51.649	1.04969
$1\cdot10^{-8}$	23.272	1.185	$8.439\cdot10^{-9}$	92.812	74.309	1.05401
$1\cdot10^{-8}$	24.163	1.163	$8.598\cdot10^{-9}$	120.018	97.677	1.05651
$1\cdot10^{-8}$	24.952	1.147	$8.718\cdot10^{-9}$	148.497	122.490	1.05695
$1\cdot10^{-8}$	26.137	1.135	$8.811\cdot10^{-9}$	199.841	167.879	1.04880
$1\cdot10^{-8}$	27.069	1.120	$8.929\cdot10^{-9}$	248.171	211.143	1.04944
$1\cdot10^{-8}$	27.872	1.118	$8.945\cdot10^{-9}$	295.945	254.253	1.04113
$1\cdot10^{-8}$	28.871	1.108	$9.025\cdot10^{-9}$	363.957	315.995	1.03951
$1\cdot10^{-8}$	30.177	1.086	$9.208\cdot10^{-9}$	468.507	411.305	1.04887
$1\cdot10^{-8}$	30.807	1.093	$9.149\cdot10^{-9}$	525.802	463.570	1.03774
$1\cdot10^{-8}$	31.378	1.070	$9.346\cdot10^{-9}$	581.854	514.646	1.05663
$1\cdot10^{-8}$	32.479	1.067	$9.372\cdot10^{-9}$	701.712	623.475	1.05481

binary energy interaction of the UNIQUAC model (Table 3) of the D_2–DT mixture to calculate the activity coefficient γ_{DT} demonstrated qualitative agreement. The scatter of the experimental points indicates the complexity of carrying out experimental studies on the phase equilibrium of hydrogen isotope mixtures.

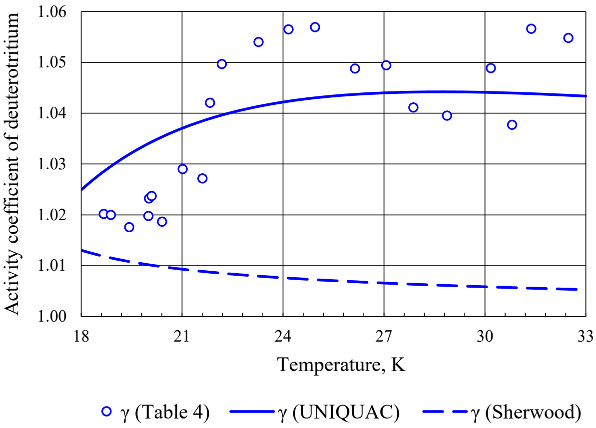


Fig. 5. Temperature dependence of activity coefficient DT.

Figure 6 shows the calculated curves of dependence of activity coefficients γ_{D_2} and γ_{DT} on concentration x_{D_2} in the liquid phase; these were obtained according to the Sherwood theory and using the UNIQUAC method. The behavior of the curve γ_{D_2} is non-standard. If we take into account a small deviation of values from unity, we can conclude that this will not greatly affect the separation of isotopes in a distillation column or cascades of columns.

Figure 7 shows the calculated dependences of the separation factor α_{D_2-DT} oon the D_2 concentration in the liquid phase at atmospheric pressure. The character of the curves is similar to that of the D_2–T_2 mixture. The difference here is that the curve constructed according to Sherwood's theory decreases slightly with growth x_{D_2}, and does not increase.

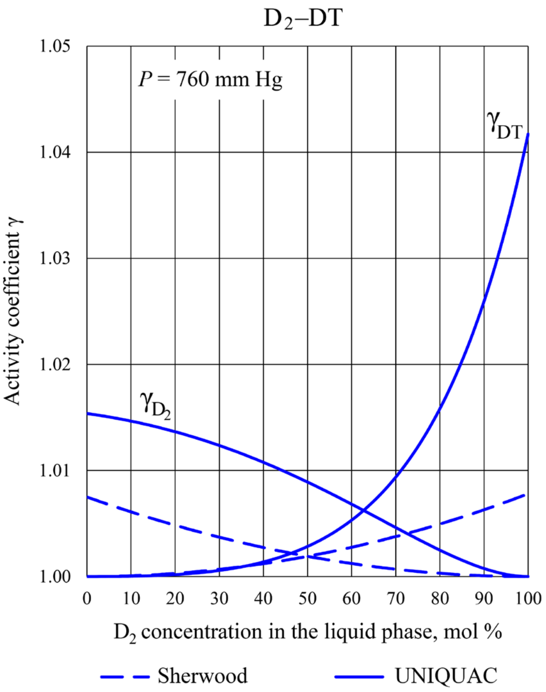


Fig. 6. Calculated curves of the activity coefficients γ_{D_2} and γ_{DT} of the components of the D_2–DT mixture versus the concentration D_2 in the liquid phase at atmospheric pressure.

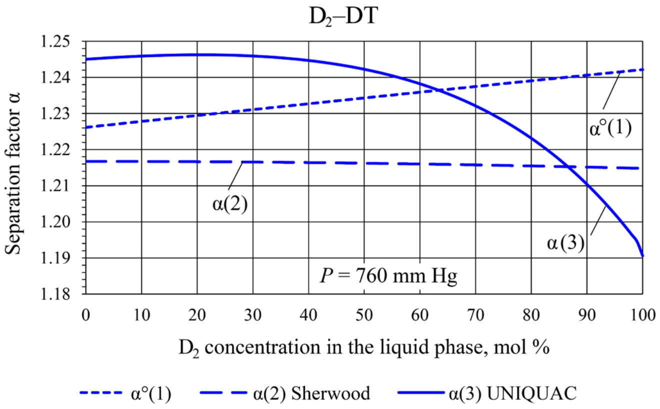


Fig. 7. Dependence of the separation coefficient α of a D_2–DT mixture on the D_2 concentration in the liquid phase at atmospheric pressure.

Vapor–liquid phase equilibrium and separation factor DT–T_2

While Sherman [3] does not provide experimental data on the separation factor $\alpha_{D_2-T_2}$ in his experimental study of the separation factor α_{DT-T_2}, he reports that α_{DT-T_2} is below $\alpha^\circ_{DT-T_2}$, as obtained for ideal mixtures by approximately 1%. Taking into account the experience of the experimenter, a temperature dependence curve $\alpha^\circ_{DT-T_2}$ was constructed and the parameters of the binary energy interaction Δu_{12} and Δu_{21} of the UNIQUAC model for the DT–T_2 mixture were selected (Table 3), which made it possible to reduce α_{DT-T_2} by about 1%. Restriction: the y–x phase equilibrium curve with the found parameters Δu_{12} and Δu_{21} should not have an azeotrope point. A comparison of the curves of the dependence of the separation factor $\alpha_{D_2-T_2}$, α_{D_2-DT}, α_{DT-T_2}, and $\alpha^\circ_{DT-T_2}$ on the temperature is shown in Fig. 8. As consistent with the data of other researchers, the curve of dependence of the separation factor of the DT–T_2 mixture is located between the curves $\alpha_{D_2-T_2}$ and α_{DT-T_2}.

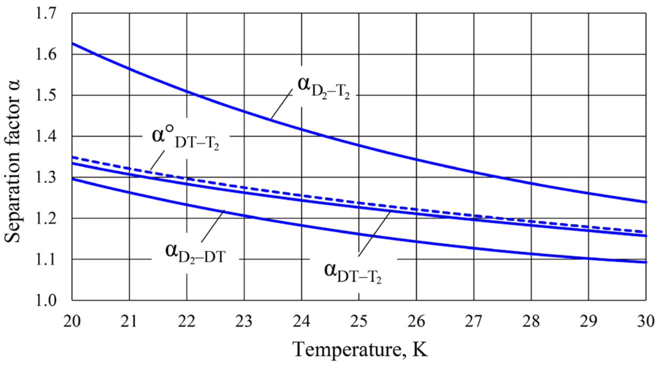


Fig. 8. Dependence of separation factor $\alpha_{D_2-T_2}$, α_{D_2-DT}, α_{DT-T_2}, and $\alpha^{\circ}_{DT-T_2}$ on temperature.

Figure 9 shows the dependence of the activity coefficients γ_{DT} и γ_{T_2} of the DT–T_2 mixture components on the concentration of DT in the liquid phase at atmospheric pressure. The curves calculated by the UNIQUAC equation are located above the curves obtained by the Sherwood theory. This is typical for all three considered binary mixtures D_2–T_2, D_2–DT, DT–T_2.

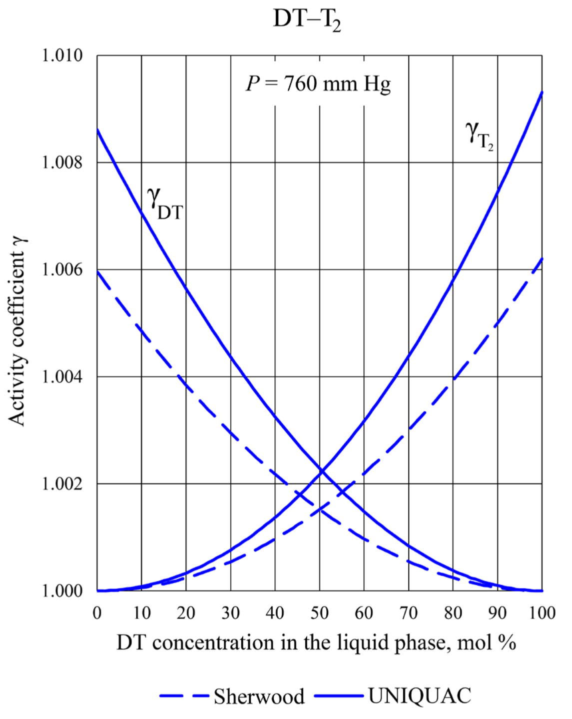


Fig. 9. Curves of the activity coefficients γ_{DT} and γ_{T_2} of the components of the DT–T_2 mixture versus the concentration of DT in the liquid phase at atmospheric pressure.

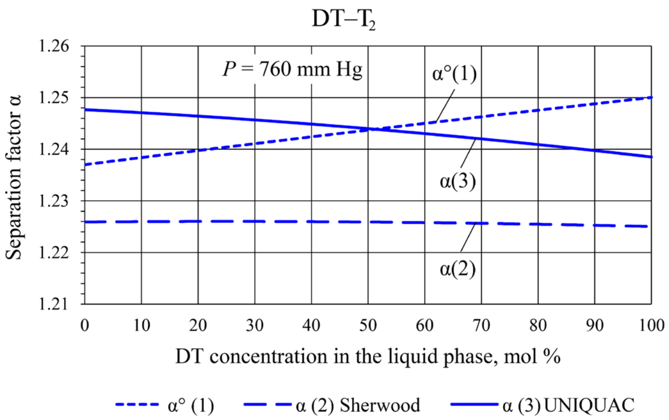


Fig. 10. Dependence of the separation factor α of a DT–T_2 mixture on the concentration of DT in the liquid phase at atmospheric pressure.

Figure 10 shows the dependence of the separation factor α of a DT–T_2 mixture on the concentration of DT in the liquid phase at atmospheric pressure. The behavior of the curves is similar to those shown in Figs. 3 and 7 for mixtures D_2–T_2 and D_2–DT: α° (1) increases, α(2) remains practically constant, while α(3) decreases with increasing concentration of the volatile component in the mixture.

Analyzing graphic dependences in Figs. 3, 7, and 10, it can be concluded that, based on Sherwood's theory, the separation factor is not affected by the composition of the liquid phase.

Distribution profile of components D_2, DT, and T_2 along the height of the distillation column of a three-component mixture D_2–DT–T_2 with closed rectification

Under actual production conditions, the pressure, boiling point, and composition of the liquid on the plate changes along the height of the distillation column. Consequently, the vapor pressures of pure components and the separation factor change. Due to the small deviation from ideality of hydrogen isotope mixtures, obtaining a reliable description of the boiling points of pure components at various pressures, which correspond to the vapor pressures of pure components, is of great importance. Table 5 shows the values of the boiling points D_2, DT, T_2 at various pressures calculated from Eqs. (12), (13) and (14) alongside literature data at atmospheric pressure [7, 20].

Let us consider the distribution profile of hydrogen isotopes of a three-component mixture D_2–DT–T_2 along the height of a distillation column operating in a closed mode for three options: for an ideal mixture at $\gamma_i = 1$, both when calculating the activity coefficients according to the Sherwood theory using Eqs. (19)–(21) and according to the UNIQUAC equation using the parameters of the binary energy interaction (Table 3). Let us use the "stage to stage" method. Let us assume that the

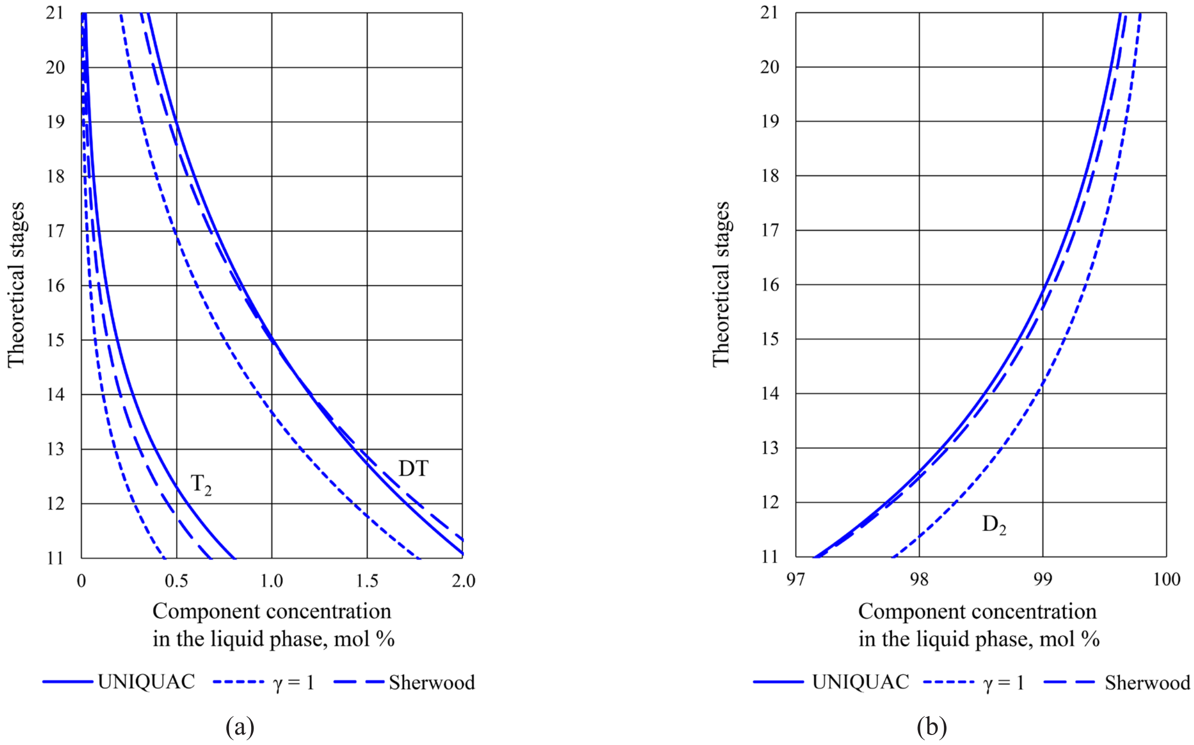
Tabl 5. Boiling point of hydrogen isotope at various pressures

Isotope	Isotope boiling point, K							
	Pressure, mm Hg							
	600	700	760		800	900	1000	1100
D_2	22.785	23.290	23.569	23.56 [7]	23.746	24.162	24.546	24.904
DT	23.506	24.010	24.288	24.38 [20]	24.464	24.878	25.260	25.616
T_2	24.245	24.754	25.035	25.04 [20]	25.213	25.631	26.017	26.375

pressure along the height of the column is constant and equal to atmospheric 760 mm Hg Art.; number of theoretical plates 21; concentration of components in the liquid phase on the first plate (stage), in mol %: $x_{D_2} = 65$; $x_{DT} = 10$; $x_{T_2} = 25$; the accuracy of vapor phase composition calculation is 10^{-10}.

Figure 11 shows the distribution profile of the concentrations of the components D_2, DT, and T_2 in the liquid phase on the plates of the column from the 11th to the 21st. Along the abscissa, the concentration of the component varies from 0 to 2 mol % for DT and T_2 isotopes (Fig. 11a) and from 97 to 100 mol % for D_2 (Fig. 11b) in order to better represent the profile of the curves. The calculation according to the UNIQUAC model showed that the separation of the three-component mixture D_2–DT–T_2 proceeds somewhat worse than according to the Sherwood theory and when the mixture is considered as ideal.

In future studies, it will be of interest to calculate the cascades of continuous distillation columns when feeding is introduced into the middle part of the column using modern simulation environments. Such calculations for the separation of the H_2–HD–HT–D_2–DT–T_2 isotope mixture, which includes six hydrogen isotopes, are currently being carried out in the Aspen Hysys medium [21, 22]. In [21], researchers use the Peng–Robinson equation of state. However, the authors note that, in order to improve the description of the vapor–liquid equilibrium using the Peng–Robinson equation of state, it is necessary to tune the parameters of the binary interaction.



(a) (b)

Fig. 11. The distribution profile of the concentrations of the components D_2, DT, and T_2 along the height of the column with closed distillation for a pressure of 760 mm Hg: (a) DT and T_2; (b) D_2.

CONCLUSIONS

The parameters of the binary energy interaction of the UNIQUAC model are determined on the basis of mathematical processing of literary experimental data on the phase equilibrium of hydrogen isotopic mixtures D_2–T_2, D_2–DT, DT–T_2.

Equations are given for calculating the activity coefficients of hydrogen isotopes based on the Sherwood theory as applied to binary D_2–T_2, D_2–DT, DT–T_2, as well as ternary D_2–DT–T_2 hydrogen isotope mixtures.

A comparison is made of the graphical dependences of the activity coefficients and mixture separation coefficients of D_2–T_2, D_2–DT, DT–T_2 in the range of the concentration of a highly volatile component from 0 to 100 mol % at atmospheric pressure for three options: ideal mixtures; non-ideal using the Sherwood theory and non-ideal based on the UNIQUAC model. It was found that the behavior of the curves of separation coefficients α is similar for all binary isotopic mixtures. However, when considering mixtures as ideal, α increases. Sherwood's theory showed that at P = const α remains practically constant, independent of the composition of the mixture. The UNIQUAC model predicts a decrease in α with an increase in the concentration of a highly volatile component in the mixture.

The profile of distribution of hydrogen isotopes of a three-component mixture D_2–DT–T_2 along the height of a distillation column operating in a closed mode is calculated for three variants. The "stage to stage" method was applied, which consists in calculating the process of single evaporation on a theoretical plate. The pressure along the height of the column is assumed constant at atmospheric 760 mm Hg Art.; number of theoretical plates is 21; concentration of components in the liquid phase on the first plate (stage), in mol %: $x_{D_2} = 65$; $x_{DT} = 10$; $x_{T_2} = 25$; accuracy of vapor phase composition calculation is 10^{-10}. The calculation according to the UNIQUAC model showed that the separation of a three-component mixture D_2–DT–T_2 proceeds somewhat less optimally than according to the Sherwood theory and when considering the mixture as ideal.

On the basis of the conducted studies, the UNIQUAC model is shown to adequately reflect experimental data on separation factors. However, due to the presence of systematic deviations, the theoretical Sherwood and ideal models are not suitable for further calculations of the phase equilibrium of hydrogen isotopic mixtures D_2–T_2, D_2–DT, DT–T_2, and D_2–DT–T_2.

The author declares no conflicts of interest.

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