Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(4):279–292 ISSN 2686-7575 (Online)

UDC 544.012+544.3.032.3
https://doi.org/10.32362/2410-6593-2024-19-4-279-292
EDN WXQZSM

RESEARCH ARTICLE

Comparison of methods for calculating the enthalpy of vaporization of binary azeotropic mixtures

Dmitriy A. Ryzhkin, Valentina M. Raeva✉
MIREA — Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia
✉ *Corresponding author, e-mail: raevalentina1@gmail.com*

Abstract

Objectives. To calculate the molar enthalpy of vaporization of binary homogeneous mixtures based on isothermal and isobaric vapor–liquid equilibrium data, and to compare the results of calculation of molar enthalpy of vaporization by different methods with experimental data.

Methods. Simulation of the vapor–liquid equilibrium of binary systems according to the Non-Random Two Liquid "local compositions" equation and thermodynamic calculations of molar vaporization enthalpies of binary mixtures at different conditions of vapor–liquid equilibrium were used.

Results. Arrays of calculated data were obtained with regard to molar enthalpies of vaporization for 25 compositions of binary azeotropes (isothermal, isobaric conditions of phase equilibrium), and the full range of compositions of the benzene–ethanol system at atmospheric pressure.

Conclusions. The accuracy of thermodynamic methods for calculating the vaporization enthalpy of binary azeotropic mixtures according to vapor–liquid equilibrium data is higher in 85% of cases for isothermal, and in 75% of cases for isobaric conditions. By taking into account the influence of temperature on the activity coefficients of components in the liquid phase, the values of excess molar enthalpy both for azeotrope compositions and for the full concentration range of the benzene–ethanol system under isobaric conditions of liquid–vapor phase equilibrium can be accurately reproduced.

Keywords
molar enthalpy of vaporization, binary azeotropes, vapor–liquid equilibrium

Submitted: 22.08.2023
Revised: 12.12.2023
Accepted: 01.07.2024

For citation
Ryzhkin D.A., Raeva V.M. Comparison of methods for calculating the enthalpy of vaporization of binary azeotropic mixtures. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2024;19(4):279–292. https://doi.org/10.32362/2410-6593-2024-19-4-279-292

НАУЧНАЯ СТАТЬЯ

Сравнение методов расчета энтальпии парообразования бинарных азеотропных смесей

Д.А. Рыжкин, В.М. Раева✉

МИРЭА — Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119571 Россия

✉ *Автор для переписки, e-mail: raevalentina1@gmail.com*

Аннотация

Цели. Расчет молярных энтальпий парообразования бинарных гомогенных смесей по изотермическим и изобарическим данным парожидкостного равновесия; сравнение результатов расчета молярных энтальпий парообразования по разным методам с экспериментальными данными.

Методы. Моделирование парожидкостного равновесия бинарных систем по уравнению «локальных составов» NRTL (Non-Random Two Liquid); термодинамические расчеты молярных энтальпий парообразования смесей в разных условиях парожидкостного равновесия.

Результаты. Получены массивы расчетных данных по молярным энтальпиям парообразования для 25 составов бинарных азеотропов (изотермические, изобарические условия фазового равновесия) и полного диапазона составов системы бензол–этанол при атмосферном давлении.

Выводы. Точность термодинамических методов расчета энтальпий парообразования бинарных азеотропных смесей по данным парожидкостного равновесия выше в 85% случаев для изотермических и в 75% случаев для изобарических условий. Учет влияния температуры на коэффициенты активности компонентов в жидкой фазе позволяет качественно верно воспроизводить значения избыточной молярной энтальпии как для составов азеотропов, так и для полного концентрационного диапазона системы бензол–этанол в изобарических условиях фазового равновесия жидкость–пар.

Ключевые слова

молярная энтальпия парообразования, бинарные азеотропы, парожидкостное равновесие

Поступила: 22.08.2023
Доработана: 12.12.2023
Принята в печать: 01.07.2024

Для цитирования

Рыжкин Д.А., Раева В.М. Сравнение методов расчета энтальпии парообразования бинарных азеотропных смесей. *Тонкие химические технологии*. 2024;19(4):279–292. https://doi.org/10.32362/2410-6593-2024-19-4-279-292

INTRODUCTION

The enthalpy of vaporization is the most important thermophysical property of substances and mixtures [1–4]. The accurate estimation of the enthalpy of vaporization and its dependence on temperature is a requirement for the study of phase transitions [5–7]. In order to calculate the thermal balances of distillation columns, reliable data on molar enthalpies of vaporization of substances H_V^0 and mixtures H_V (designations: V—vaporization, 0—pure substance) in different conditions of phase equilibrium are necessary [8–10].

Direct calorimetric measurements of vaporization enthalpies are difficult and time-consuming [5, 11–15]. Experimentally measured H_V values of mixtures are given in [16–20] for individual compositions. There are few experimental data for the full range of compositions of binary systems $H_V(x)$ [9, 14, 21–23]. $H_V(x)$ binary mixtures can be calculated using different arrays of experimental data: excess enthalpies (heat of mixing) of liquid solution $H^E(x)$ (index E stands for Excess); and enthalpies of vaporization of pure substances at a particular temperature [9, 23, 24]. Thermal calculations of distillation columns require data $H_V(x,T)$ on the isobaric conditions of vapor–liquid equilibrium (VLE).

Data on the enthalpies of vaporization of multicomponent mixtures is much less common. The calorimetric measurements are usually carried out for specific compositions of hydrocarbon fractions [25–27] and fuel mixtures [28–30].

Due to the limited amount of experimental data, including those under different VLE conditions, reliable methods need to be developed to calculate the enthalpies of vaporization of mixtures [9, 15, 20]. Currently, methods for calculating and/or predicting the enthalpies of vaporization of individual substances belonging to certain classes of organic compounds using a limited amount of experimental data have predominantly been developed. The possibilities of calculations using various models and equations of state are considered in [32–35].

Thermodynamic methods for calculations of molar enthalpies of vaporization can be successfully applied to hydrocarbons and their binary mixtures [36–38]. For substances and mixtures, the components of which form hydrogen bonds, special methods for calculating enthalpies of vaporization have been developed [35, 39–41].

CALCULATIONS

A simplified method for calculating the molar enthalpies of vaporization H_{V} of multicomponent systems from $P(T)$ data for the vapor phase under different VLE conditions is presented in [15]. Let us assume that the vapor phase state of a multicomponent system is determined by the equation of state (1) [42, 43]:

$$PV = ZRT, \tag{1}$$

where P—pressure; V—volume of vapor phase; Z—compressibility coefficient; R—universal gas constant; T—temperature, K. According to the Clausius–Clapeyron equation, the H_{V} values are defined as:

$$H_{\mathrm{V}} = -RZ\left[\frac{d\ln P}{d(1/T)}\right]_x. \tag{2}$$

If by correlating the experimental P–T data, the following dependence coefficients can be obtained:

$$\ln P = a + \frac{b}{T}, \tag{3}$$

then we can calculate the values of molar enthalpies of vaporization by using the following formula [15]:

$$H_{\mathrm{V}} = -RZb, \tag{4}$$

where a and b are correlation coefficients. Instead of correlation of experimental data, the following ratio can also be applied:

$$H_{\mathrm{V}} = -\frac{RZ\Delta\ln P}{\Delta\left(\frac{1}{T}\right)}. \tag{5}$$

At phase equilibrium, the pressure P over the liquid phase of composition x_i is defined as:

$$P = \sum_{i=1}^{N} x_i \gamma_i P_i^0, \tag{6}$$

where i—component; γ_i—activity coefficient of the component; P_i^0—saturated vapor pressure of the component. In order to calculate phase equilibria, phase equilibrium models can be used which take into account the dependence of activity coefficients on the mixture composition and model parameters in various ways [43, 44]. For example, for calculations of VLE and molar enthalpies of vaporization from $P(T)$ data of N-component systems, we used the dependence of the activity coefficients of the components on the mixture composition and parameters of the following VLE model: UNIFAC (UNIversal Functional Activity Coefficient) [15] and NRTL (Non-Random Two Liquid) [45].

Tamir [15] obtained a thermodynamic expression which establishes the relationship between the pressure and temperature of the N-component system under VLE conditions:

$$\frac{d\ln P}{dT} = \sum_{i=1}^{N} x_i\left[\left(\frac{x_i\gamma_i P_i^0}{P}\right)\left(\frac{d\ln P_i^0}{dT}\right)\right] + \\ + \sum_{i=1}^{N} x_i\left[\left(\frac{x_i P_i^0}{P}\right)\left(\frac{d\gamma_i}{dT}\right)\right]. \tag{7}$$

For azeotropes (Az), $P_i^0\gamma_i / P = 1.$ After introducing the assumption that the activity coefficients of the components are independent of temperature $(d\gamma_i / dT = 0),$ which is strictly true only for athermal solutions, Eq. (7) can be transformed to the following form:

$$H_{\mathrm{V}}^{\mathrm{Az}} = RT^2 Z\sum_{i=1}^{N} x_i\left[\frac{d\ln P_i^0}{dT}\right]. \tag{8}$$

Tamir [15] used Antoine’s Eq. (9), in order to calculate the dependence of the saturated vapor pressure of the components on temperature, i.e., Eq. (10) is valid for pure substances:

$$\lg P_i^0 = A_i - \frac{B}{(T + C_i)}, \tag{9}$$

$$\frac{dP_i^0}{dT} = P_i^0\frac{B_i}{\left(T + C_i\right)^2}, \tag{10}$$

where A, B, and C are equation coefficients (9).

In order to calculate the enthalpies of vaporization of mixtures of azeotropic composition $H_{\mathrm{V}}^{\mathrm{Az}}$, a simplified expression is proposed [39]:

$$H_{\mathrm{V}}^{\mathrm{Az}} = 2.3026RT^2 Z\sum_{i=1}^{N}\frac{x_i B_i}{(t + C_i)^2},$$

where t is a temperature, °C.

Tamir [15] calculated H_{V}^{Az} for the ideal vapor phase ($Z = 1$):

$$H_{\text{V}}^{\text{Az}} = 2.3026RT^2 \sum_{i=1}^{N} \frac{x_i B_i}{(t + C_i)^2}. \tag{11}$$

In fact, the enthalpy of vaporization of a mixture of azeotropic composition is determined in Eq. (11) by the data $P_i^0(T)$ for individual components.

Earlier we proposed a procedure for calculating the enthalpy of vaporization H_{V} of binary and three-component systems under the assumption of ideal vapor phase behavior, while taking into account the temperature dependence of the activity coefficients of the components for any (zeotropic, azeotropic) compositions [45, 46]:

$$P = \sum_{i=1}^{N} P_i^0(T) x_i \gamma_i(x, T). \tag{12}$$

For binary systems we formulate dP/dT as follows:

$$\begin{aligned} \frac{dP}{dT} &= \sum_{i=1,2} \left(\frac{dP_i^0(T)}{dT} x_i \gamma_i(x,T) + P_i^0(T) x_i \frac{d\gamma_i(x,T)}{dT} \right) = \\ &= \sum_{i=1,2} x_i \left(\frac{dP_i^0(T)}{dT} \gamma_i(x,T) + P_i^0(T) \frac{d\gamma_i(x,T)}{dT} \right). \end{aligned} \tag{13}$$

The values of dP/dT and enthalpy of vaporization of mixtures (14) were determined on the basis of the calculated data of VLE.

$$H_{\text{V}} = \frac{dP}{dT} \frac{RT^2}{P}. \tag{14}$$

A comparison of experimental data arrays $H_{\text{V}}(x)$ with calculated values was previously carried out for the full range of compositions of the benzene–cyclohexane system under isobaric VLE conditions [45], the behavior of the vapor phase of which can be considered ideal [47]. The maximum relative errors for arrays of calculated values of the benzene–cyclohexane system at 50.662, 75.992, and 101.320 kPa do not exceed 5, 5.1, and 6 relative % (rel. %), respectively [45]. A comparison of the results of calculations of molar enthalpies of vaporization, must not only be based on the quantitative indices. The qualitative correspondence of signs of excess values determined from experimental and calculated data was shown to be fundamental.

Molar enthalpies of vaporization can be represented through partial values of

$$H_{\text{V}} = (H_{\text{V1}}^0 + \bar{H}_{\text{V1}}^{\text{E}}) x_1 + (H_{\text{V2}}^0 + \bar{H}_{\text{V2}}^{\text{E}}) x_2. \tag{15}$$

Here $\bar{H}_{\text{V1}}^{\text{E}}$ and $\bar{H}_{\text{V2}}^{\text{E}}$ are partial excess enthalpies of the components, x_i is the composition of the azeotrope ($i = 1; 2$). The partial excess enthalpies for the vapor and liquid phases have opposite signs. The excess value H_{V}^{E} can be determined from experimental or calculated data H_{V} [23, 24, 45]:

$$H_{\text{V}}^{\text{E}} = H_{\text{V}} + H_{\text{V}}^{\text{add}}, \tag{16}$$

where $H_{\text{V}}^{\text{add}}$ is an additive value:

$$H_{\text{V}}^{\text{add}} = H_{\text{V1}}^0 x_1 + H_{\text{V2}}^0 x_2. \tag{17}$$

A comparison of experimental and calculated values $H_{\text{V}}^{\text{E}}(x)$ for the benzene–cyclohexane system shows that the use of Eq. (14) provides a qualitatively correct reproduction of the sign of the excess thermodynamic quantity [45].

The purpose of the present study is to compare experimental and calculated data of molar enthalpies of vaporization for binary homogeneous azeotrope compositions under different VLE conditions.

RESULTS

Binary mixtures of azeotropic compositions $H_{\text{V}}^{\text{exp}}$ for which viable modeling of VLE using the NRTL model is possible, were selected from the array of experimental data [15] (Tables 1 and 2). The parameters of the NRTL equation were taken from the database of the Aspen Plus V.10.0 software package. The azeotropic data description errors do not exceed 5 rel. % for compositions and 0.4 rel. % for temperature. Table 2 additionally summarizes the calculated pressure values P^{calc} (kPa) obtained from the NRTL model.

The molar enthalpies of vaporization of binary mixtures of azeotropic compositions were calculated in different ways according to VLE data.

Method I. VLE and H_{V} were calculated independently using the Aspen Plus V.10.0 platform. Saturated vapor pressures of components P_i^0 in the software package were determined by the following expression:

$$\ln P_i^0 = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i} \ln T + C_{6i} T^{C_{7i}}. \tag{18}$$

C_{1i}–C_{7i} coefficients are given in the Aspen Plus V.10.0 database.

Molar enthalpies of vaporization of substances $H_{\text{V}i}^0$ were calculated by means of the Watson equation in the following form:

$$H_{\text{V}i}^0(T) = H_{\text{V}i}^*(T_1) \left(\frac{1 - \dfrac{T}{T_{\text{c}i}}}{1 - \dfrac{T_1}{T_{\text{c}i}}} \right)^{a_i + b_i \left(1 - \frac{T}{T_{\text{c}i}}\right)}, \tag{19}$$

where T_{ci} is the critical temperature of component *i* (index c stands for critical); T_1 is the temperature for which the experimental value of enthalpy of vaporization H_V^* is known; and *T* is the temperature for which the calculation of H_{Vi}^0 is performed. Parameters a_i, b_i, and critical temperature T_{ci} values are from the NIST database[1].

The enthalpy of vaporization of the mixture H_V was determined as follows:

$$H_V = H^V - H^L, \tag{20}$$

where H^V and H^L are molar enthalpies of vapor (V) and liquid (L) of a mixture of a particular composition.

Method II. The calculations of mixtures H_V were carried out using the VLE data (Eqs. (13) and (14)). The procedure for calculating dP/dT is described in detail in [45]. The molar enthalpies of vaporization of individual substances H_{Vi}^0 (18) were determined using the coefficients of the Antoine equation in the form presented in a previous study [46]:

$$H_{Vi}^0 = \frac{dP_i^0}{dT}\frac{RT^2}{P_i^0}. \tag{21}$$

In all tables, molar enthalpies of vaporization of mixtures H_V are given in kJ/mol, compositions of mixtures—in molar fractions of the component indicated in the name of the mixture first.

Tables 3 and 4 show the data sets for comparison of experimental values H_V^{exp} with the results of calculations H_V^{calc} by methods I and II. Relative errors ΔH_V were determined in the standard way:

$$\Delta H_V = \frac{H_V^{exp} - H_V^{calc}}{H_V^{exp}} \times 100\%. \tag{22}$$

For Eqs. (4) and (11) in [15] only errors (22) are given, by which we determined the calculated values of H_V (Tables 3 and 4).

Table 1. Experimental values of molar vaporization enthalpies for binary mixtures (azeotropic compositions) at atmospheric pressure [15]

No.*	Mixture 1–2	*T*, K	x_1, mol. fr.	H_V^{exp}, kJ/mol
1	*p*-Xylene–hexanol-1	411.49	0.870	42.0
2	Toluene–2-methylpropanol-1	372.64	0.550	39.9
3	Toluene–butanol-1	378.20	0.680	34.2
4	Benzene–methanol	330.62	0.609	33.6

*Experimental point number.

Table 2. Experimental values of molar vaporization enthalpies for binary mixtures (azeotropic compositions) at isothermal VLE [15]

No.	Mixture 1–2	*T*, K	x_1, mol. fr.	H_V^{exp}, kJ/mol	P^{calc}, kPa
5	Chloroform–ethanol	320	0.859	31.7	65
6	Acetone–chloroform	320	0.384	33.6	54
7	Propanol-1–ethyl acetate	330	0.218	34.6	52
8	Ethanol–1,4-dioxane	330	0.871	39.7	42
9	Water–1,4-dioxane	330	0.447	39.7	30

---

[1] Standard Reference Database of National Institute of Standards and Technology. *NIST Chemistry WebBook*. Number 69 (SRD 69). 2022. https://doi.org/10.18434/T4D303

Table 2. Continued

No.	Mixture 1–2	T, K	x_1, mol. fr.	H_V^{exp}, kJ/mol	P^{calc}, kPa
10	Carbon tetrachloride–propanol-1	320	0.876	33.0	39
11	Methanol–benzene	350	0.649	33.2	198
12	Cyclohexane–propanol-2	330	0.647	34.9	64
13	Water–2-chloroethanol	350	0.852	42.8	45
14	Benzene–ethanol	350	0.522	34.9	139
15	Tetrahydrofuran–water	300	0.903	31.0	24
16		320	0.855	32.1	55
17	Water–formic acid	320	0.582	42.4	9
18		360	0.490	41.1	50
19	Water–pyridine	310	0.718	44.7	8
20		350	0.758	41.5	53
21	Ethanol–ethyl acetate	293.8	0.296	36.4	11
22		314.2	0.341	36.0	30
23		320	0.384	35.8	38
24		334	0.417	35.5	67
25		363.2	0.543	34.8	189

Note: Experimental point numbers are given for each temperature condition.

Table 3. Calculated values of molar vaporization enthalpies and relative errors at 101.32 kPa

No.	Eq. (4)		Eq. (11)		Method I		Method II	
	H_V^{calc}, kJ/mol	ΔH_V, %	H_V^{calc}, kJ/mol	ΔH_V, %	H_V^{calc}, kJ/mol	ΔH_V, %	H_V^{calc}, kJ/mol	ΔH_V, %
1	45.2	7.6	43.8	4.4	37.2	−11.5	39.0	−7.1
2	40.7	1.9	46.2	15.7	35.6	−10.8	37.3	−6.5
3	30.5	−10.8	29.8	−12.9	34.7	1.5	36.4	6.3
4	32.6	−3.0	32.7	−2.6	32.3	−3.9	33.9	0.9

Note: the mixture number corresponds to the same number in Table 1.

Table 4. Calculated values of molar vaporization enthalpies and relative errors at isothermal VLE

No.	Eq. (11)		Method I		Method II	
	H_V^{calc}, kJ/mol	ΔH_V, %	H_V^{calc}, kJ/mol	ΔH_V, %	H_V^{calc}, kJ/mol	ΔH_V, %
5	31.5	−0.6	31.4	−1.0	31.8	0.3
6	36.4	8.3	32.0	−4.9	32.8	−2.3
7	32.7	−5.5	34.3	−0.7	34.6	0.1
8	38.7	−2.5	39.7	−0.1	40.4	1.7
9	40.4	1.8	39.2	−1.2	39.7	0.1
10	32.4	−1.8	32.5	−1.5	33.1	0.4
11	31.5	−5.1	31.7	−4.6	33.8	1.8
12	33.6	−3.7	34.5	−1.1	35.1	0.6
13	43.3	1.2	42.4	−1.0	42.7	−0.3
14	35.2	−3.7	33.8	−3.2	35.1	0.7
15	28.5	−8.1	32.9	6.0	33.2	7.1
16	30.9	−3.7	32.4	0.8	32.9	2.5
17	44.5	5.0	36.4	−14.1	40.8	−3.9
18	44.1	7.3	33.7	−17.9	38.8	−5.5
19	33.6	4.5	43.3	−3.1	43.6	−2.5
20	46.7	1.0	41.5	0	41.8	0.7
21	41.9	4.5	36.8	1.1	36.7	0.8
22	38.0	4.3	35.7	−0.8	35.9	−0.4
23	37.5	−4.5	35.5	−0.7	35.8	−0.1
24	34.2	4.6	34.8	−2.0	35.4	−0.3
25	37.1	5.7	33.4	−3.9	35.2	1.3

Note: the mixture number corresponds to the same number in Table 2.

Method II provides a higher level of calculation accuracy when compared to Eqs. (4) and (11), and method I for atmospheric pressure in 75% of cases (Table 3). For isothermal VLE conditions, method II provides a more accurate calculation compared to the results of (11) for 85% of azeotropic compositions (18 out of 21) (Table 4). The accuracy of calculations using method II is lower than by method I only in the systems ethanol–1,4-dioxane, tetrahydrofuran–water, and pyridine–water (Nos. 8, 15, 16, 20, Table 4).

For the benzene–ethanol system, experimental data $H_V^{exp}(x)$ is also available for the full range of compositions at atmospheric pressure, but no temperature values are given [22]. The calculated values obtained by the NRTL model are presented in Table 5.

The calculation of VLE using the NRTL model was performed with the binary interaction parameters (τ_{ij}, τ_{ji}, G_{ij}, G_{ji}, α) in the following form:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T},\ G_{ij} = \exp(-\alpha\tau_{ij}),$$

where i and j are component indices; τ, α, and G are parameters of the NRTL equation. The parameter α determines the ordering of the molecule distribution in the solution and is related to the coordination number of the liquid, τ is the reduced energy parameter, and G is a variable characterizing the interaction energy. The values $i = 1; 2$, $j = 1; 2$. The parameters were estimated on the basis of experimental data of the VLE of the benzene (1)–ethanol (2) system [48, 49]. Where $a_{12} = 0.7596, b_{12} = 309.183, a_{21} = -5.8653, b_{21} = 2314.74$, and $\alpha = 0.604$. The average relative errors of the array descriptions do not exceed 1.01 (maximum 3.55) rel. % for vapor phase compositions and 0.02 (maximum 0.08) rel. % for temperature.

The arrays of calculated data for the benzene (1)–ethanol (2) system at atmospheric pressure are summarized in Table 5. The average relative errors of calculation of molar enthalpies of vaporization of binary mixtures do not exceed 3 rel. %.

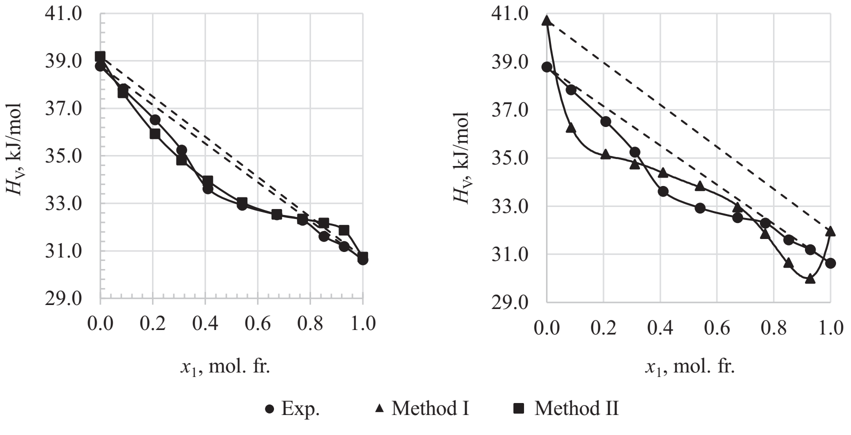
The concentration dependencies $H_V(x)$ are presented in Fig. 1. Quantitative differences are caused, as in the case of the benzene (1)–cyclohexane (2) system [45], by the values of molar enthalpies of vaporization of pure substances calculated differently by Eqs. (16) and (18).

Method II provides a qualitative coincidence of concentration dependence types for experimental and calculated data, namely in the whole range of compositions $H_V < H_V^{add}$ (Fig. 1b). Method I provides qualitatively incorrect results for benzene-enriched mixtures: $H_V > H_V^{add}$, which does not correspond to the experimental data (Fig. 1a).

The excess values H_V^E were calculated using Eqs. (16) and (17). Quantitative agreement of the values of H_V^E, determined on the basis of experimental and calculated values under isobaric VLE conditions was not achieved. However, method II also qualitatively correctly reproduces the sign of the excess component of the molar enthalpy: $H_V^E < 0$ for all compositions of binary mixtures (Fig. 2b).

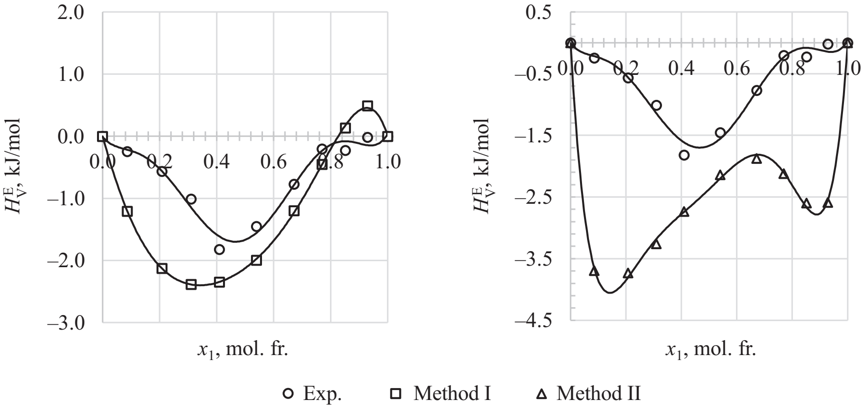
Table 5. Experimental and calculated values of the enthalpy of vaporization and relative errors for the benzene (1)–ethanol (2) system at 101.32 kPa

x_1, mol. fr.	Experiment [22]		Method I			Method II		
	H_V^{exp}, kJ/mol	H_V^E, kJ/mol	H_V^{calc}, kJ/mol	ΔH_V, %	H_V^E, kJ/mol	H_V^{calc}, kJ/mol	ΔH_V, %	H_V^E, kJ/mol
1	30.6	0	30.7	−0.36	0	32.0	−4.35	0
0.929	31.2	−0.02	31.9	−2.18	0.53	30.9	0.81	−1.64
0.852	31.6	−0.23	32.2	−1.80	0.19	31.6	−0.04	−1.63
0.770	32.3	−0.20	32.3	−0.13	−0.34	32.6	−0.99	−1.35
0.672	32.5	−0.77	32.5	−0.01	−0.98	33.6	−3.17	−1.27
0.540	32.9	−1.45	33.0	−0.36	−1.58	34.4	−4.40	−1.61
0.410	33.6	−1.82	33.9	−0.97	−1.78	34.9	−3.78	−2.24
0.310	35.2	−1.01	34.8	1.19	−1.74	35.2	0.11	−2.79
0.208	36.5	−0.57	35.9	1.61	−1.50	35.5	2.65	−3.34
0.086	37.8	−0.25	37.7	0.47	−0.80	36.4	3.71	−3.53
0	38.8	0	39.2	−1.05	0	40.7	−4.98	0



(a) (b)

Fig. 1. Dependencies of molar vaporization enthalpy for benzene (1)–ethanol (2) system on the composition:
(a) method I,
(b) method II



(a) (b)

Fig. 2. Comparison of experimental and calculated values of the excess molar vaporization enthalpy for benzene (1)–ethanol (2) system at 101.32 kPa:
(a) method I,
(b) method II

The results obtained are similar to the conclusions for the benzene–cyclohexane system at 50.663, 75.992, and 101.320 kPa (Table 6). Method II allows qualitatively correct types of concentration dependencies $H_V^E(x) < 0$ to be obtained, while method I familiar-variable ones to be obtained, when in one region of compositions H_V^E are negative and in the other—positive [45].

Thus, the calculation of molar enthalpies of vaporization of binary systems from *dP*/*dT* data under VLE conditions is more correct for isobaric conditions.

The properties of binary systems formed by non-associated liquids are usually linear functions of composition or exhibit insignificant deviations from additive values. However, the enthalpies of vaporization of mixtures H_V are an exception [9]. Therefore, for systems containing substances which form complexes of molecules, the association constants of molecules in the vapor phase must be taken into account [40]. Analysis of experimental calorimetric data for binary systems containing lower carboxylic acids allowed the authors [40] to conclude that simplified methods for estimating enthalpies of vaporization in mixtures with associated components are acceptable, if the excess molar enthalpy (heat of mixing) of the liquid solution does not exceed 5% of the enthalpy of vaporization.

It was established that calculated values H_V^{calc}, obtained from *dP*/*dT* data at VLE are less accurate than calculations based on independent arrays of experimental data in systems formed by components capable of

Table 6. Excess values for benzene (1)–cyclohexane (2) system at isobaric vapor–liquid

x_1, mol. fr.	P^{calc}, kPa								
	101.320			75.992			50.662		
	H_V^{exp}, kJ/mol	Method I	Method II	H_V^{exp}, kJ/mol	Method I	Method II	H_V^{exp}, kJ/mol	Method I	Method II
		H_V^{calc}, kJ/mol			H_V^{calc}, kJ/mol			H_V^{calc}, kJ/mol	
0.143	−0.34	0.03	−0.05	−0.35	0.01	−0.05	−0.41	0.01	−0.04
0.250	−0.42	0.01	−0.08	−0.47	0.00	−0.07	−0.72	−0.01	−0.07
0.397	−0.57	−0.03	−0.11	−0.54	−0.03	−0.10	−0.78	−0.04	−0.09
0.443	−0.59	−0.04	−0.12	−0.55	−0.05	−0.11	−0.66	−0.06	−0.11
0.541	−0.55	−0.06	−0.13	−0.60	−0.07	−0.13	−0.73	−0.08	−0.13
0.700	−0.37	−0.05	−0.15	−0.41	−0.06	−0.14	−0.37	−0.07	−0.14
0.842	−0.12	−0.02	−0.12	−0.47	−0.03	−0.14	−0.34	−0.04	−0.14

forming hydrogen bonds in solutions: tetrahydrofuran–water, water–pyridine, ethanol–1,4-dioxane. The application of method II for calculations of molar enthalpies of vaporization of benzene–cyclohexane system provides more accurate reproduction of experimental data H_V^{exp} in comparison with benzene–ethanol mixtures. This can be explained by the use of the assumption of ideal behavior of the vapor phase containing ethanol.

CONCLUSIONS

Molar enthalpies of vaporization of azeotropic mixtures were calculated for 18 binary systems under different conditions of phase VLE and for the full range of compositions of the benzene–ethanol system at atmospheric pressure.

Rigorous thermodynamic methods of calculating the molar enthalpies of vaporization from VLE data of binary systems, even under the assumption of ideal behavior of the vapor phase, are more accurate than simplified methods of calculation.

The comparison of experimental and calculated data arrays obtained by thermodynamic methods I and II was carried out. The proposed calculation method II provides more accurate results for 85% of the compositions of azeotropic mixtures in isothermal conditions, and for 75% of them in isobaric conditions.

Acknowledgments

The work was financially supported by the grant of the State Assignment No. FSFZ-2023-0003.

Authors' contributions

D.A. Ryzhkin—conducting a calculating research, analysis and presentation of research results, and preparing the work for publication.

V.M. Raeva—formulation of research objectives and aims, analysis of results, preparing the work for publication, and leadership for the research execution.

The authors declare no conflicts of interest.

REFERENCES

1. Karapet'yants M.Kh. *Khimicheskaya termodinamika* (*Chemical Thermodynamics*). Moscow: Khimiya; 1975. 583 p. (in Russ.)
2. Black C. Importance of thermophysical data in process simulation. *Int. J. Thermophys*. 1986;7(4):987–1002. https://doi.org/10.1007/BF00503853
3. Sandler S.I. Thermophysical properties: What have we learned recently, and what do we still need to know? *Int. J. Thermophys*. 1994;15(6):1013–1035. https://doi.org/10.1007/BF01458812
4. Oscarson J.L., Rowley R.L., Wilding W.V., Izatt R.M. Industrial need for accurate thermophysical data and for reliable prediction methods. *J. Therm. Anal. Calorim*. 2008;92(2):465–470. https://doi.org/10.1007/s10973-007-8972-0
5. Solomonov B.N., Varfolomeev M.A., Nagrimanov R.N., Novikov V.B., Zaitsau D.H., Verevkin S.P. Solution calorimetry as a complementary tool for the determination of enthalpies of vaporization and sublimation of low volatile compounds at 298.15 K. *Thermochimica Acta*. 2014;589:164–173. https://doi.org/10.1016/j.tca.2014.05.033
6. Yu D., Chen Z. A theoretical analysis on enthalpy of vaporization: Temperature dependence and singularity at the critical state. *Fluid Phase Equil*. 2020;516:112611. https://doi.org/10.1016/j.fluid.2020.112611
7. Solomonov B.N., Yagofarov M.I. Compensation relationship in thermodynamics of solvation and vaporization: Features and applications. II. Hydrogen-bonded systems. *J. Mol. Liq*. 2023;372(2):121205. https://doi.org/10.1016/j.molliq.2023.121205
8. Tyrer D. CLXXXVI. Latent heats of vaporization of mixed liquids. Part I. *J. Chem. Soc., Trans*. 1911;99:1633–1645. https://doi.org/10.1039/CT9119901633
9. Shivabasappa K.L., Nirguna Babu P., Jagannadha Rao Y. Enthalpy of mixing and heat of vaporization of ethyl acetate with benzene and toluene at 298.15 K and 308.15 K. *Braz. J. Chem. Eng*. 2008;25(1):167–174. https://doi.org/10.1590/S0104-66322008000100017
10. Zakharov M.K., Egorov A.V., Podmetenny A.A. Liquid mixtures separation and heat consumption in the process of distillation. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2021;16(1):7–15 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2021-16-1-7-15
11. Pashchenko L.L., Druzhinina A.I. Enthalpy of vaporization measurements by calorimetric techniques. *J. Therm. Anal. Calorim.* 2018;133(2):1173–1179. https://doi.org/10.1007/s10973-018-7370-0
12. Vicencio L.A., López-Porfiri P., de la Fuente J.C. Vapour pressure and vaporisation enthalpy for two key apple odorants, ethyl butyrate and ethyl hexanoate, at pressures from (15 to 105) kPa. *J. Chem. Thermodyn*. 2020;142:105982. https://doi.org/10.1016/j.jct.2019.105982
13. Abdullah R.S., Solomonov B.N.. Sublimation/vaporization and solvation enthalpies of monosubstituted pyridine derivatives. *Chem. Thermodyn. Therm. Anal.* 2022;8(20):100087. https://doi.org/10.1016/j.ctta.2022.100087
14. Dong J.-Q., Lin R.-S., Yen W.-H. Heats of vaporization and gaseous molar heat capacities of ethanol and the binary mixture of ethanol and benzene. *Can. J. Chem*. 1988;66(4):783–790. https://doi.org/10.1139/v88-136
15. Tamir A. Prediction of latent heat of vaporization of multicomponent mixtures. *Fluid Phase Equil.* 1982;8(2):131–147. https://doi.org/10.1016/0378-3812(82)80031-9
16. Ito T., Yamaguchi T., Akasaka R. Heat of vaporization of mixtures. *Heat Transfer Japanese Res.* 1996;25(1):12–24. https://doi.org/10.1002/(SICI)1520-6556(1996)25:1%3C12::AID-HTJ2%3E3.0.CO;2-1
17. Marchelli G., Ingenmey J., Hollóczki O., Chaumont A., Kirchner B. Hydrogen-bonding and vaporization thermodynamics in hexafluoroisopropanol-acetone and -methanol mixtures. A Joined cluster analysis and molecular dynamic study. *ChemPhysChem*. 2022;23(1):e202100620. https://doi.org/10.1002/cphc.202100620
18. Swietoslawski W., Zielenkiewicz A. Vaporization enthalpy of the homologous series of binary azeotropes. *Rocz. Chem*. 1958;32:913–922.
19. Tamir A. Compilation and correlation of binary azeotropic data. *Fluid Phase Equil*. 1981;5(3–4):199–206. https://doi.org/10.1016/0378-3812(80)80057-4
20. Zherin I.I. Halogen fluorides in nuclear fuel technology. Thermodynamics of phase equilibria in systems containing UF$_6$, BrF$_3$, IF$_5$, and HF. *Izvestiya Tomskogo Politekhnicheskogo Univesiteta = Bulletin of the Tomsk Polytechnic University.* 2003;306(6):8–11(in Russ.).
21. Neilson E.F., White D. The heat of vaporization and solution of a binary mixture of fluorocarbons. *J. Phys. Chem*. 1959;63(9):1363–1365. https://doi.org/10.1021/j150579a005
22. Pandey J.D., Srivastava T., Chandra P., Prashant R., Dwivedi P.K. Estimation of cohesive forces, energy of vaporization, heat of vaporization, cohesive energy density, solubility parameter and Van der Waals constant of binary liquid mixtures using generalized hole theory. *Indian J. Chem*. 2007;46A:1605–1610.
23. Bedretdinov F., Tsvetov N., Raeva V., Chelyuskina T. Research of the properties of binary biazeotropic mixtures. In: *Proc. of the 46th International Conference of the Slovak Society of Chemical Engineering*. Tatranské Matliare, High Tatras, Slovakia May 20–23, 2019. Bratislava; 2019. P. 171.
24. Raeva V.M. Vaporization heat of binary mixtures. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2013;8(1):43–50 (in Russ.).
25. Lenoir J.M., Hipkin H.G. Measured enthalpies of eight hydrocarbon fractions. *J. Chem. Eng. Data*. 1973;18(2):195–202. https://doi.org/10.1021/je60057a026
26. Grigoriev B., Alexandrov I., Gerasimov A. Application of multiparameter fundamental equations of state to predict the thermodynamic properties and phase equilibria of technological oil fractions. *Fuel*. 2018;215:80–89. https://doi.org/10.1016/j.fuel.2017.11.022
27. Tatar A., Barati-Harooni A., Partovi M., Najafi-Marghmaleki A., *et al*. An accurate model for predictions of vaporization enthalpies of hydrocarbons and petroleum fractions. *J. Mol. Liq*. 2016;220:192–199. https://doi.org/10.1016/j.molliq.2016.04.069
28. Balabin R.M., Syunyaev R.Z., Karpov S.A.. Molar enthalpy of vaporization of ethanol–gasoline mixtures and their colloid state. *Fuel*. 2007;86(3):323–327. https://doi.org/10.1016/j.fuel.2006.08.008
29. Gautam A., Kumar A.A.. Determination of important biodiesel properties based on fuel temperature correlations for application in a locomotive engine. *Fuel*. 2015;142:289–302. https://doi.org/10.1016/j.fuel.2014.10.032
30. Abernathy S.M., Brown K.R. Predicting the enthalpy of vaporization and calculating the entropy of vaporization of 87 octane gasoline using vapor pressure. *Open Access Library Journal* (*OALib. Journal*). 2016;3(e2954):1–11. http://doi.org/10.4236/oalib.1102954
31. Akasaka R., Yamaguchi T., Ito T. Practical and direct expressions of the heat of vaporization for mixtures. *Chem. Eng. Science*. 2005;60(16):4369–4376. https://doi.org/10.1016/j.ces.2005.03.005

32. Benkouider A.M., Kessas R., Guella S., Yahiaoui A., Bagui F. Estimation of the enthalpy of vaporization of organic components as a function of temperature using a new group contribution method. *J. Mol. Liq*. 2014;194:48–56. https://doi.org/10.1016/j.molliq.2014.01.006
33. Bolmatenkov D.N., Yagofarov M.I., Notfullin A.A., Solomonov B.N. Calculation of the vaporization enthalpies of alkylaromatic hydrocarbons as a function of temperature from their molecular structure. *Fluid Phase Equil*. 2022;554:113303. https://doi.org/10.1016/j.fluid.2021.113303
34. Bolmatenkov D.N.,Yagofarov M.I., Valiakhmetov T.F., Rodionov N.O., Solomonov B.N. Vaporization enthalpies of benzanthrone, 1-nitropyrene, and 4-methoxy-1-naphthonitrile: Prediction and experiment. *J. Chem. Thermodyn*. 2022;168:106744. https://doi.org/10.1016/j.jct.2022.106744
35. Bolmatenkov D.N., Yagofarov M.I., Sokolov A.A., Solomonov B.N. Vaporization enthalpies of self-associated aromatic compounds at 298.15 K: A review of existing data and the features of heat capacity correction. Part I. Phenols. *Thermochimica Acta*. 2023;721:179455. https://doi.org/10.1016/j.tca.2023.179455
36. Arutionov B.A., Elsadig Y.A. Thermodynamic method of calculation of heat of steam formation for binary mixes. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2010;5(5):36–39 (in Russ.).
37. Arutionov B.A., Elsadig Y.A., Ausheva E.V. Temperature dependence of heat of vaporization of pure hydrocarbons and their binary mixtures. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2010;5(5):40–42 (in Russ.).
38. Arutyunov B.A., Rytova E.V., Raeva V.M., *et. al.* Methods for calculating the evaporation heats of hydrocarbons and their mixtures in a wide temperature range. *Theor. Found. Chem. Eng*. 2017;51(5):742–751. https://doi.org/10.1134/S0040579517050268

    [Original Russian Text: Arutyunov B.A., Rytova E.V., Raeva V.M., Frolkova A.K. Methods for calculating the heat of vaporization of hydrocarbons and their mixtures in a wide temperature range. *Teoreticheskie Osnovy Khimicheskoi Tekhnologii*. 2017;51(5):595–604 (in Russ.). https://doi.org/10.7868/S0040357117050025]
39. Tamir A., Dragoescu C., Apelblat A., Wisniak J. Heats of vaporization and vapor–liquid equilibria in associated solutions containing formic acid, acetic acid, propionic acid and carbon tetrachloride. *Fluid Phase Equil*. 1983;10(1):9–42. https://doi.org/10.1016/0378-3812(83)80002-8
40. Solomonov B.N., Yagofarov M.I., Nagrimanov R.N. Additivity of vaporization enthalpy: Group and molecular contributions exemplified by alkylaromatic compounds and their derivatives. *J. Mol. Liq.* 2021;342:117472. https://doi.org/10.1016/j.molliq.2021.117472
41. Solomonov B.N., Yagofarov M.I. Compensation relationship in thermodynamics of solvation and vaporization: Features and applications. II. Hydrogen-bonded systems. *J. Mol. Liq.* 2023;372:121205. https://doi.org/10.1016/j.molliq.2023.121205
42. Morachevskii A.G., Smirnova N.A., Alekseeva M.V., Balashova I.M., Viktorov A.I., Kuranov G.L., Piotrovskaya E.M., Pukinskii I.B. *Termodinamika ravnovesiya zhidkost'–par* (*Thermodynamics of Liquid–Vapor Equilibrium*). Leningrad: Khimiya; 1989. 344 p. (in Russ.).
43. Reid R.C., Prausnitz J.M., Sherwood T.K. *Svoistva gazov i zhidkostei* (*The Properties of Gases and Liquids*); transl. from Engl. Leningrad: Khimiya; 1982. 592 p. (in Russ.).

    [Reid R.C., Prausnitz J.M., Sherwood T.K. *The Properties of Gases and Liquids*. NY: McGraw-Hill; 1977. 710 p.]
44. Walas S.M. *Fazovye ravnovesiya v khimicheskoi tekhnologii* (*Phase Equilibria in Chemical Engineering*): in 2 v.; transl. from Engl. Moscow: Mir; 1989. V. 1. 304 p. (in Russ.).

    [Walas S.M. *Phase Equilibria in Chemical Engineering*. Oxford: Butterworth-Heinemann Publ., 1985. 671 p.]
45. Raeva V.M., Anisimov A.V., Ryzhkin D.A. Calculation of vaporization enthalpies of a benzene–cyclohexane system. *Russ. Chem. Bull*. 2021;70(4):715–721. https://doi.org/10.1007/s11172-021-3141-3

    [Original Russian Text: Raeva V.M., Anisimov A.V., Ryzhkin D.A. Calculation of vaporization enthalpies of a benzene–cyclohexane system. *Izvestiya Akademii Nauk. Seriya Khimicheskaya.*2021;(4):715–721 (in Russ.).]
46. Ryzhkin D.A., Raeva V.M. Calculation of vaporization enthalpies of methanol–tetrahydrofuran–acetonitrile at atmospheric pressure. In: *Proc. of the 23rd International Conference on Chemical Thermodynamics in Russia.* Russia, Kazan, August 22–27, 2022. P. 298.
47. Carrero-Mantilla J., Llano-Restrepo M. Vapor–phase chemical equilibrium for the hydrogenation of benzene to cyclohexane from reaction-ensemble molecular simulation. *Fluid Phase Equil.* 2004;219(2):181–193. https://doi.org/10.1016/j.fluid.2004.02.009
48. Wang X., Xu W., Li Y., Wang J., He F. Phase equilibria of three binary systems containing 2,5-dimethylthiophene and 2-ethylthiophene in hydrocarbons. *Fluid Phase Equil. 2016*;409:30–36. https://doi.org/10.1016/j.fluid.2015.09.030
49. Chen G., Wang Q., Zhang L.-Z., Bao J., Han S.-J. Study and applications of binary and ternary azeotropes. *Thermochim. Acta*. 1995;253:295–305. https://doi.org/10.1016/0040-6031(94)02078-3

СПИСОК ЛИТЕРАТУРЫ

1. Карапетьянц М.Х. Химическая термодинамика. М.: Химия; 1975. 583 с.
2. Black C. Importance of thermophysical data in process simulation. *Int. J. Thermophys*. 1986;7(4):987–1002. https://doi.org/10.1007/BF00503853
3. Sandler S.I. Thermophysical properties: What have we learned recently, and what do we still need to know? *Int. J. Thermophys*. 1994;15(6):1013–1035. https://doi.org/10.1007/BF01458812
4. Oscarson J.L., Rowley R.L., Wilding W.V., Izatt R.M. Industrial need for accurate thermophysical data and for reliable prediction methods. *J. Therm. Anal. Calorim*. 2008;92(2):465–470. https://doi.org/10.1007/s10973-007-8972-0
5. Solomonov B.N., Varfolomeev M.A., Nagrimanov R.N., Novikov V.B., Zaitsau D.H., Verevkin S.P. Solution calorimetry as a complementary tool for the determination of enthalpies of vaporization and sublimation of low volatile compounds at 298.15 K. *Thermochimica Acta.* 2014;589:164–173. https://doi.org/10.1016/j.tca.2014.05.033

6. Yu D., Chen Z. A theoretical analysis on enthalpy of vaporization: Temperature dependence and singularity at the critical state. *Fluid Phase Equil*. 2020;516:112611. https://doi.org/10.1016/j.fluid.2020.112611
7. Solomonov B.N., Yagofarov M.I. Compensation relationship in thermodynamics of solvation and vaporization: Features and applications. II. Hydrogen-bonded systems. *J. Mol. Liq*. 2023;372(2):121205. https://doi.org/10.1016/j.molliq.2023.121205
8. Tyrer D. CLXXXVI. Latent heats of vaporization of mixed liquids. Part I. *J. Chem. Soc., Trans*. 1911;99:1633–1645. https://doi.org/10.1039/CT9119901633
9. Shivabasappa K.L., Nirguna Babu P., Jagannadha Rao Y. Enthalpy of mixing and heat of vaporization of ethyl acetate with benzene and toluene at 298.15 K and 308.15 K. *Braz. J. Chem. Eng.* 2008;25(1):167–174. https://doi.org/10.1590/S0104-66322008000100017
10. Захаров М.К., Егоров А.В., Подметенный А.А. Разделение жидких смесей и затраты теплоты при ректификации. *Тонкие химические технологии*. 2021;16(1):7–15. https://doi.org/10.32362/2410-6593-2021-16-1-7-15
11. Pashchenko L.L., Druzhinina A.I. Enthalpy of vaporization measurements by calorimetric techniques. *J. Therm. Anal. Calorim.* 2018;133(2):1173–1179. https://doi.org/10.1007/s10973-018-7370-0
12. Vicencio L.A., López-Porfiri P., de la Fuente J.C. Vapour pressure and vaporisation enthalpy for two key apple odorants, ethyl butyrate and ethyl hexanoate, at pressures from (15 to 105) kPa. *J. Chem. Thermodyn*. 2020;142:105982. https://doi.org/10.1016/j.jct.2019.105982
13. Abdullah R.S., Solomonov B.N.. Sublimation/vaporization and solvation enthalpies of monosubstituted pyridine derivatives. *Chem. Thermodyn. Therm. Anal.* 2022;8(20):100087. https://doi.org/10.1016/j.ctta.2022.100087
14. Dong J.-Q., Lin R.-S., Yen W.-H. Heats of vaporization and gaseous molar heat capacities of ethanol and the binary mixture of ethanol and benzene. *Can. J. Chem*. 1988;66(4):783–790. https://doi.org/10.1139/v88-136
15. Tamir A. Prediction of latent heat of vaporization of multicomponent mixtures. *Fluid Phase Equil.* 1982;8(2):131–147. https://doi.org/10.1016/0378-3812(82)80031-9
16. Ito T., Yamaguchi T., Akasaka R. Heat of vaporization of mixtures. *Heat Transfer Japanese Res.* 1996;25(1):12–24. https://doi.org/10.1002/(SICI)1520-6556(1996)25:1%3C12::AID-HTJ2%3E3.0.CO;2-1
17. Marchelli G., Ingenmey J., Hollóczki O., Chaumont A., Kirchner B. Hydrogen-bonding and vaporization thermodynamics in hexafluoroisopropanol-acetone and -methanol mixtures. A Joined cluster analysis and molecular dynamic study. *ChemPhysChem*. 2022;23(1):e202100620. https://doi.org/10.1002/cphc.202100620
18. Swietoslawski W., Zielenkiewicz A. Vaporization enthalpy of the homologous series of binary azeotropes. *Rocz. Chem*. 1958;32:913–922.
19. Tamir A. Compilation and correlation of binary azeotropic data. *Fluid Phase Equil*. 1981;5(3–4):199–206. https://doi.org/10.1016/0378-3812(80)80057-4
20. Жерин И.И. Фториды галогенов в технологии ядерного топлива. Термодинамика фазовых равновесий в системах, содержащих UF_6, BrF_3, IF_5 и HF. *Изв. Томского политехн. ун-та*. 2003;306(6):8–11.
21. Neilson E.F., White D. The heat of vaporization and solution of a binary mixture of fluorocarbons. *J. Phys. Chem*. 1959;63(9):1363–1365. https://doi.org/10.1021/j150579a005
22. Pandey J.D., Srivastava T., Chandra P., Prashant R., Dwivedi P.K. Estimation of cohesive forces, energy of vaporization, heat of vaporization, cohesive energy density, solubility parameter and Van der Waals constant of binary liquid mixtures using generalized hole theory. *Indian J. Chem*. 2007;46A:1605–1610.
23. Bedretdinov F., Tsvetov N., Raeva V., Chelyuskina T. Research of the properties of binary biazeotropic mixtures. In: *Proc. of the 46th International Conference of the Slovak Society of Chemical Engineering*. Tatranské Matliare, High Tatras, Slovakia May 20–23, 2019. Bratislava; 2019. P. 171.
24. Раева В.М. Теплоты испарения бинарных смесей. *Тонкие химические технологии*. 2013;8(1):43–50.
25. Lenoir J.M., Hipkin H.G. Measured enthalpies of eight hydrocarbon fractions. *J. Chem. Eng. Data*. 1973;18(2):195–202. https://doi.org/10.1021/je60057a026
26. Grigoriev B., Alexandrov I., Gerasimov A. Application of multiparameter fundamental equations of state to predict the thermodynamic properties and phase equilibria of technological oil fractions. *Fuel*. 2018;215:80–89. https://doi.org/10.1016/j.fuel.2017.11.022
27. Tatar A., Barati-Harooni A., Partovi M., Najafi-Marghmaleki A., *et al*. An accurate model for predictions of vaporization enthalpies of hydrocarbons and petroleum fractions. *J. Mol. Liq*. 2016;220:192–199. https://doi.org/10.1016/j.molliq.2016.04.069
28. Balabin R.M., Syunyaev R.Z., Karpov S.A.. Molar enthalpy of vaporization of ethanol–gasoline mixtures and their colloid state. *Fuel*. 2007;86(3):323–327. https://doi.org/10.1016/j.fuel.2006.08.008
29. Gautam A., Kumar A.A.. Determination of important biodiesel properties based on fuel temperature correlations for application in a locomotive engine. *Fuel*. 2015;142:289–302. https://doi.org/10.1016/j.fuel.2014.10.032
30. Abernathy S.M., Brown K.R. Predicting the enthalpy of vaporization and calculating the entropy of vaporization of 87 octane gasoline using vapor pressure. *Open Access Library Journal* (*OALib. Journal*). 2016;3(e2954):1–11. http://doi.org/10.4236/oalib.1102954
31. Akasaka R., Yamaguchi T., Ito T. Practical and direct expressions of the heat of vaporization for mixtures. *Chem. Eng. Science*. 2005;60(16):4369–4376. https://doi.org/10.1016/j.ces.2005.03.005
32. Benkouider A.M., Kessas R., Guella S., Yahiaoui A., Bagui F. Estimation of the enthalpy of vaporization of organic components as a function of temperature using a new group contribution method. *J. Mol. Liq*. 2014;194:48–56. https://doi.org/10.1016/j.molliq.2014.01.006
33. Bolmatenkov D.N., Yagofarov M.I., Notfullin A.A., Solomonov B.N. Calculation of the vaporization enthalpies of alkylaromatic hydrocarbons as a function of temperature from their molecular structure. *Fluid Phase Equil*. 2022;554:113303. https://doi.org/10.1016/j.fluid.2021.113303
34. Bolmatenkov D.N.,Yagofarov M.I., Valiakhmetov T.F., Rodionov N.O., Solomonov B.N. Vaporization enthalpies of benzanthrone, 1-nitropyrene, and 4-methoxy-1-naphthonitrile: Prediction and experiment. *J. Chem. Thermodyn*. 2022;168:106744. https://doi.org/10.1016/j.jct.2022.106744
35. Bolmatenkov D.N., Yagofarov M.I., Sokolov A.A., Solomonov B.N. Vaporization enthalpies of self-associated aromatic compounds at 298.15 K: A review of existing data and the features of heat capacity correction. Part I. Phenols. *Thermochimica Acta*. 2023;721:179455. https://doi.org/10.1016/j.tca.2023.179455

36. Арутюнов Б.А., Мохаммед Ю.А. Термодинамический метод расчета теплоты парообразования бинарных смесей. *Тонкие химические технологии*. 2010;5(5):36–39.
37. Арутюнов Б.А., Мохаммед Ю.А., Аушева Е.В. Температурная зависимость теплоты парообразования чистых углеводородов и их бинарных смесей. *Тонкие химические технологии*. 2010;5(5):40–42.
38. Арутюнов Б.А., Рытова Е.В., Раева В.М., Фролкова А.К. Методы расчета теплот парообразования углеводородов и их смесей в широком диапазоне температур. *Теор. основы хим. технологии*. 2017;51(5):595–604. https://doi.org/10.7868/S0040357117050025
39. Tamir A., Dragoescu C., Apelblat A., Wisniak J. Heats of vaporization and vapor–liquid equilibria in associated solutions containing formic acid, acetic acid, propionic acid and carbon tetrachloride. *Fluid Phase Equil*. 1983;10(1):9–42. https://doi.org/10.1016/0378-3812(83)80002-8
40. Solomonov B.N., Yagofarov M.I., Nagrimanov R.N. Additivity of vaporization enthalpy: Group and molecular contributions exemplified by alkylaromatic compounds and their derivatives. *J. Mol. Liq*. 2021;342:117472. https://doi.org/10.1016/j.molliq.2021.117472
41. Solomonov B.N., Yagofarov M.I. Compensation relationship in thermodynamics of solvation and vaporization: Features and applications. II. Hydrogen-bonded systems. *J. Mol. Liq.* 2023;372:121205. https://doi.org/10.1016/j.molliq.2023.121205
42. Морачевский А.Г., Смирнова Н.А., Алексеева М.В., Балашова И.М., Викторов А.И., Куранов Г.Л., Пиотровская Е.М., Пукинский И.Б. *Термодинамика равновесия жидкость-пар*. Л.: Химия; 1989. 344 с.
43. Рид Р., Праусниц Дж., Шервуд Т. *Свойства газов и жидкостей*; пер. с англ. Л.: Химия; 1982. 592 с.
44. Уэйлес С. *Фазовые равновесия в химической технологии*: в 2-х ч.; пер. с англ. М.: Мир; 1989. Ч. 1. 304 с.
45. Раева В.М., Анисимов А.В., Рыжкин Д.А.. Расчет энтальпий парообразования системы бензол–циклогексан. *Изв. АН. Сер. хим*. 2021;(4):715–721. https://doi.org/10.1007/s11172-021-3141-3
46. Ryzhkin D.A., Raeva V.M. Calculation of vaporization enthalpies of methanol–tetrahydrofuran–acetonitrile at atmospheric pressure. In: *Proc. of the 23rd International Conference on Chemical Thermodynamics in Russia.* Russia, Kazan, August 22–27, 2022. P. 298.
47. Carrero-Mantilla J., Llano-Restrepo M. Vapor–phase chemical equilibrium for the hydrogenation of benzene to cyclohexane from reaction-ensemble molecular simulation. *Fluid Phase Equil.* 2004;219(2):181–193. https://doi.org/10.1016/j.fluid.2004.02.009
48. Wang X., Xu W., Li Y., Wang J., He F. Phase equilibria of three binary systems containing 2,5-dimethylthiophene and 2-ethylthiophene in hydrocarbons. *Fluid Phase Equil. 2016*;409:30–36. https://doi.org/10.1016/j.fluid.2015.09.030
49. Chen G., Wang Q., Zhang L.-Z., Bao J., Han S.-J. Study and applications of binary and ternary azeotropes. *Thermochim. Acta.* 1995;253:295–305. https://doi.org/10.1016/0040-6031(94)02078-3

About the authors

Dmitry A. Ryzhkin, Postgraduate Student, Department of Chemistry and Technology of Basic Organic Synthesis, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA — Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: dima-ryzhkin@mail.ru. Scopus Author ID 57223230408, ResearcherID AAU-6583-2021, RSCI SPIN-code 7429-1472, https://orcid.org/0000-0001-6415-8059

Valentina M. Raeva, Cand. Sci. (Eng.), Associate Professor, Department of Chemistry and Technology of Basic Organic Synthesis, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA — Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: raevalentina1@gmail.com. Scopus Author ID 6602836975, ResearcherID C-8812-2014, RSCI SPIN-code 5147-0319, https://orcid.org/0000-0002-5664-4409

Об авторах

Рыжкин Дмитрий Антонович, аспирант кафедры химии и технологии основного органического синтеза, Институт тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА — Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: dima-ryzhkin@mail.ru. Scopus Author ID 57223230408, ResearcherID AAU-6583-2021, RSCI SPIN-code 7429-1472, https://orcid.org/0000-0001-6415-8059

Раева Валентина Михайловна, к.т.н., доцент кафедры химии и технологии основного органического синтеза, Институт тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА — Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: raevalentina1@gmail.com. Scopus Author ID 6602836975, ResearcherID C-8812-2014, RSCI SPIN-code 5147-0319, https://orcid.org/0000-0002-5664-4409

Translated from Russian into English by H. Moshkov
Edited for English language and spelling by Dr. David Mossop