https://doi.org/10.15407/ujpe68.6.390

L.A. BULAVIN,[1] YE.G. RUDNIKOV [1, 2]

[1] Taras Shevchenko National University of Kyiv
(64/13, Volodymyrs'ka Str., Kyiv 01601, Ukraine; e-mail: erudni67@gmail.com)
[2] National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"
(37, Beresteiskyi Ave., Kyiv 03056, Ukraine; e-mail: erudni67@gmail.com)

INFLUENCE OF THE TEMPERATURE AND CHEMICAL POTENTIAL ON THE THERMODYNAMIC COEFFICIENT $-(\partial V/\partial P)_T$ OF WATER

On the basis of available literature data, the temperature, T, and chemical potential, μ, dependences of the thermodynamic coefficient $-(\partial V/\partial P)_T$ for water in the liquid state are calculated and analyzed. The coefficient found for water is compared with that for argon. Taking the principle of corresponding states into account, the existence of a region of thermodynamic similarity between those two substances is confirmed. At the same time, there is a region of thermodynamic parameters, where the indicated similarity is not observed. It is shown that, for water, there is a particular temperature of (42.0 ± 0.2) °C at which the T-dependence of the thermodynamic coefficient $-(\partial V/\partial P)_T$ along the liquid–vapor equilibrium curve has a minimum. This feature leads to a specific behavior of the thermodynamic coefficient $-(\partial V/\partial P)_T$ for water, which is not observed for argon. It is shown that there is a particular μ value for water at which the μ-dependence of the thermodynamic coefficient $-(\partial V/\partial P)_T$ along the liquid-vapor coexistence curve also has a minimum. In addition, at the triple point of water, the thermodynamic coefficient $-(\partial V/\partial P)_T$ as a function of μ reaches a maximum value.

Keywords: water, argon, isothermal compressibility, chemical potential, liquid-vapor coexistence curve, liquid-solid coexistence curve, hydrogen bonds.

1. Introduction

According to its properties, water in the liquid state is, perhaps, the most unique of the liquids existing in nature. It possesses certain anomalous properties [1, 2] and demonstrates certain features as a solvent and under confined-geometry conditions [6, 7]. On the other hand, the atomic liquid argon can be considered the simplest liquid by its structure [8, 9], which prompted us to compare the physical properties of those two substances.

For this purpose, in this work, the temperature, T, and chemical potential, μ, dependences of the thermodynamic coefficient $-(\partial V/\partial P)_T = \beta_T V$ associated with such a mechanical characteristic as the isothermal compressibility $\beta_T = -(\partial V/\partial P)_T/V$ [10], which determines the mechanical response of the thermodynamic system to an external action and is associated with the pair correlator of thermal fluctuations [11]

$$\langle \Delta V \Delta V \rangle = -(\partial V/\partial P)_T/(k_\mathrm{B}T) = \beta_T V/(k_\mathrm{B}T), \quad (1)$$

were compared between water and argon. Here, $V = 1/\rho$ is the specific volume measured in units of m^3/kg, and ρ is the mass density of the substance.

It is known that the T-dependence of the water compressibility measured along the liquid-vapor coexistence curve passes through a minimum at a temperature of about $\theta = 46.4$ °C [12, 13]. The physical origins giving rise to the emergence of this minimum were analyzed in work [14].

The aim of this work was to calculate and analyze the T- and μ-dependences of the thermodynamic co-

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Citation: Bulavin L.A., Rudnikov Ye.G. Influence of the temperature and chemical potential on the thermodynamic coefficient $-(\partial V/\partial P)_T$ of water. *Ukr. J. Phys.* **68**, No. 6, 390 (2023). https://doi.org/10.15407/ujpe68.6.390.

Цитування: Булавін Л.А., Рудніков Є.Г. Вплив температури та хімічного потенціалу на термодинамічний коефіцієнт $-(\partial V/\partial P)_T$ води. *Укр. фіз. журн.* **68**, №6, 390 (2023).

efficient $-(\partial V/\partial P)_T$ for liquid water in the interval of relative temperatures $T/T_c < 0.7$, where T_c is the critical temperature of water, and compare the indicated dependences with their counterparts for argon.

2. Calculation Procedure for the T- and μ-Dependences of the Thermodynamic Coefficient $-(\partial V/\partial P)_T$ for Water and Argon

The calculations of the thermodynamic coefficient $-(\partial V/\partial P)_T$ were performed using the most reliable experimental data for the thermodynamic properties of water and argon, which can be found in modern reference books [15, 16] and physical databases [17–21]. The method of calculation of the T- and μ-dependences of the thermodynamic coefficient $-(\partial V/\partial P)_T$ was as follows.

At the first stage, the T- and baric, P, dependences of the thermodynamic coefficient $-(\partial V/\partial P)_T$ are calculated. In general, in order to obtain the P-dependences of the derivative $-(\partial V/\partial P)_T$ along the isotherms, it is necessary to differentiate, by pressure, the P-dependences of the specific volume of the liquid phase, $V = 1/\rho$, along the isotherms that terminate at the liquid-vapor coexistence curve. Furthermore, the endpoints of the isotherms of the P-dependences of the quantity $-(\partial V/\partial P)_T$ located on the coexistence curve determine the T-dependence of the quantity $-(\partial V/\partial P)_T$ along the coexistence curve. At certain fixed pressure values, the values of the thermodynamic coefficient $-(\partial V/\partial P)_T$ on the isotherms determine the T-dependences of the quantity $-(\partial V/\partial P)_T$ along the isobars.

At the second stage, to determine the reference point and the scale of the chemical potential variations, the reference points selected in a certain way for the entropy and the internal energy of the system are assigned.

Afterward, on the basis of stages 1 and 2, a transition from the (T, P) variables to the (T, μ) ones is carried out.

Consider the indicated calculation stages in more details.

In modern thermodynamic databases (Minirefprop [17], SRD69 [18], Coolprop [19], Refprop [22], WTT [23], and ThermodataEngine [24]), the T- and P-dependences of the main thermodynamic quantities, in particular, the density ρ, are given in the form of analytical functions. Accordingly, the error of the original experimental data determines the error of the physic quantities calculated with the help of those functions. For example, the error for the temperatures determined by us is equal to the total error of the corresponding experimental studies presented in the literature. In particular, the temperature error for the minimum of the thermodynamic coefficient $-(\partial V/\partial P)_T$ determined by us for water equals 0.2 K [25].

As a result of such calculations, the P- and T-dependences of the density ρ, the specific volume V, the compressibility β_T, and the thermodynamic coefficient $-(\partial V/\partial P)_T$ form a mesh in the $T - P$ plane, which is confined from the low-pressure side by the liquid-vapor coexistence curve. The calculations of the corresponding physical quantities were carried out by us at the grid nodes and along the coexistence curve.

In the course of the sequential calculation of the T- and P-dependences of the quantities ρ, V, β_T, and $-(\partial V/\partial P)_T$ for water and argon in the temperature interval from the melting point to temperatures $T/T_c < 0.7$ and the pressure interval from $P/P_c > 0.02$ to the liquid-solid coexistence curve, every isotherm and every isobar were presented by at least 10^3 equidistant points. The corresponding testing showed that, for such a splitting of the temperature interval, the results of direct calculations of the thermodynamic derivative $-(\partial V/\partial P)_T$ and the results of analytic calculations performed by differentiating the analytic functions differed by no more than 1%. Furthermore, the T- and P-dependences of the compressibility β_T and the thermodynamic coefficient $-(\partial V/\partial P)_T$ turned out qualitatively similar.

After obtaining the T- and P-dependences of the derivative $-(\partial V/\partial P)_T$, a transition to the variables (T, μ) was made. When carrying out such calculations, it is necessary to select the reference points for the specific entropy S/m and the specific internal energy E/m (m is the substance mass). We propose to reckon the specific entropy S/m from the absolute zero temperature in accordance with the Nernst theorem, and the specific internal energy E/m from the melting point in the liquid phase on the liquid-vapor coexistence curve. The main argument for this approach consists in the holding of the law of the corresponding states [26, 27]. According to our calculations, if the indicated choice of the reference points for S/m and E/m is made, the law of corresponding

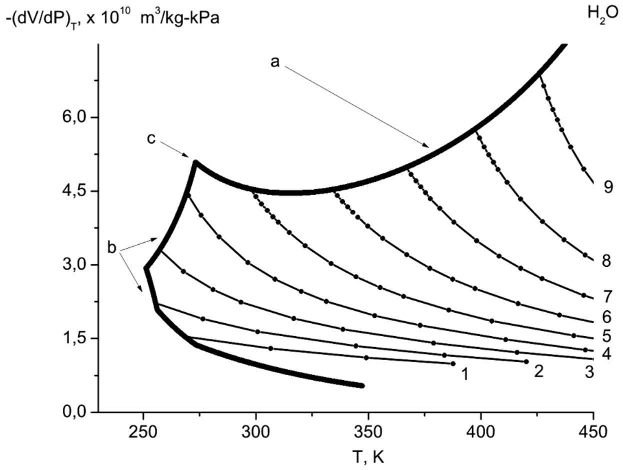

Fig. 1. Temperature dependences of the derivative $-(\partial V/\partial P)_T$ along the family of iso-chemical potential curves with $\mu = -600$ (*1*), -750 (*2*), -900 (*3*), -1050 (*4*), -1200 (*5*), -1350 (*6*), -1500 (*7*), -1650 (*8*), and -1800 kJ/kg (*9*) along the liquid-vapor (*a*) and liquid-solid (*b*) coexistence curves for water in the liquid state in the temperature interval $T \leq 450$ K ($T/T_c < 0.7$). *c* is the triple point

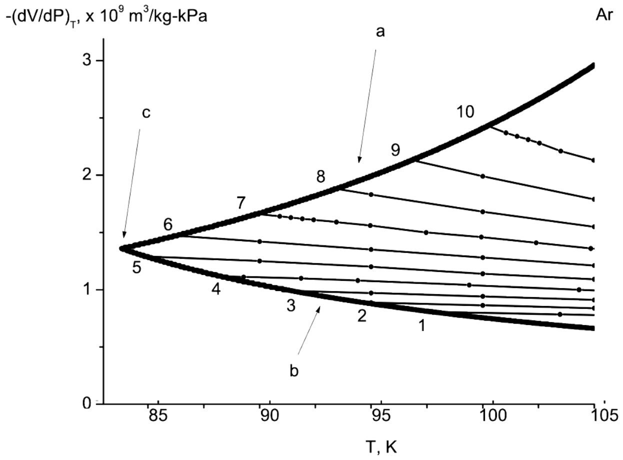

Fig. 2. Temperature dependences of the derivative $-(\partial V/\partial P)_T$ along the family of iso-chemical potential curves with $\mu = -90$ (*1*), -95 (*2*), -100 (*3*), -105 (*4*), -110 (*5*), -115 (*6*), -120 (*7*), -125 (*8*), -130 (*9*), and -135 kJ/kg (*10*) along the liquid-vapor (*a*) and liquid-solid (*b*) coexistence curves for argon in the liquid state in the temperature interval $T \leq 105$ K ($T/T_c < 0.7$). *c* is the triple point

states is obeyed for the critical parameters of some substances, which allows the critical values of the specific entropy S/m, the specific internal energy E/m, and the chemical potential μ to be predicted quantitatively for all molecular liquids.

Afterward, the transition from the (T, P) variables to the (T, μ) ones was carried out as follows. The dependences of the chemical potential μ and the thermodynamic coefficient $-(\partial V/\partial P)_T$ on the pressure P were calculated for every temperature value. Then, with the help of a computer program, equidistant values of the chemical potential and the corresponding values of the thermodynamic coefficient $-(\partial V/\partial P)_T$ were determined on the obtained dependences. As a result, there appears a mesh in the $T - \mu$ plane with equidistant T and μ values, and with already determined values of the thermodynamic coefficient $-(\partial V/\partial P)_T$ at the nodes of this mesh. The described procedure was carried out in the liquid state region corresponding to the temperatures $T/T_c < 0.7$ and confined by the liquid-vapor and liquid-solid coexistence curves.

3. Comparison of the Behavior of the Thermodynamic Coefficient $-(\partial V/\partial P)_T$ for Water and Argon

3.1. T-dependences of $-(\partial V/\partial P)_T$

Figs. 1 and 2 demonstrate the T-dependences of the derivative $-(\partial V/\partial P)_T$ calculated using the above-described method for water and argon, respectively, along certain iso-μ curves for temperatures $T/T_c <$ < 0.7. The iso-μ curves of the quantity $-(\partial V/\partial P)_T$ for water and argon lie between the liquid-vapor and liquid-solid coexistence curves. In Figs. 1 and 2, those curves for water and argon are substantially different by shape. By comparing the T-dependences of the derivative $-(\partial V/\partial P)_T$ exhibited in Figs. 1 and 2, one can see that water has a particular temperature $T = (315.15 \pm 0.2)$ K [or $\theta = (42.0 \pm 0.2)$ °C], at which the T-dependence of the thermodynamic coefficient $-(\partial V/\partial P)_T$ along the liquid-vapor equilibrium curve (curve *1* in Fig. 1) passes through a minimum.

Both for water and argon, the iso-μ curves of the quantity $-(\partial V/\partial P)_T$ are monotonically decreasing functions of the temperature. Note that the quantity $-(\partial^2(\partial V/\partial P)_T/\partial T^2)_\mu$ along the iso-μ curves is positive for water and equals about zero for argon.

3.2. μ-dependences of $-(\partial V/\partial P)_T$

The μ-dependences of the derivative $-(\partial V/\partial P)_T$ calculated along certain isotherms for water and argon are shown in Figs. 3 and 4, respectively. As one can see, the shapes of the liquid-vapor and liquid-solid coexistence curves for water and argon are substantially different. The isotherms of the quantity $-\left(\partial V/\partial P\right)_T$ for water and argon are located under the liquid-vapor and liquid-solid coexistence curves. For argon, the triple point is observed as a weak cusp at the point, where the liquid-vapor and liquid-solid coexistence curves meet. In contrast, for water at the triple point, the thermodynamic coefficient $-\left(\partial V/\partial P\right)_T$, as a function of the chemical potential, has a maximum at this point.

A comparative analysis of the μ-dependences of the derivative $-\left(\partial V/\partial P\right)_T$ presented in Figs. 3 and 4 shows that, for water, in addition to the particular temperature $T = (315.15 \pm 0.2)$ K ($\theta = (42.0 \pm 0.2)$ °C), there exists a particular value of the chemical potential for which the μ-dependence of the thermodynamic coefficient $-\left(\partial V/\partial P\right)_T$ along the curve liquid-vapor coexistence also passes through a minimum. For the selected method of determining μ, its particular value at which the T-dependence of $-\left(\partial V/\partial P\right)_T$ along the liquid-vapor coexistence curve reaches a minimum equals $\mu_{\min} = -(1122 \pm 1)$ kJ/kg.

As one can see, both for water (Fig. 3) and argon (Fig. 4) the isotherms of the quantity $-\left(\partial V/\partial P\right)_T$ are monotonically decreasing functions of the chemical potential. A comparison between Figs. 3 and 4 makes it possible to conclude that the position of the water isotherms, which is different from that of argon isotherms, is associated with an anomalous growth of its compressibility $-\left(\partial V/\partial P\right)_T/V$ and thermodynamic coefficient $-\left(\partial V/\partial P\right)_T$, when the chemical potential increases in the region $\mu > \mu_{\min} = -(1122 \pm 1)$ kJ/kg.

3.3. (T, μ)-dependences of $-\left(\partial V/\partial P\right)_T$

To verify the applicability of the principle of corresponding states [26, 27], we performed a comparative analysis of the (T, μ)-dependences of the derivative $-\left(\partial V/\partial P\right)_T$ for water and argon. It should be noted that, despite a significant difference between the properties of water and argon, nevertheless, according to [28–30], there exists a region at $T < T_c$ (T_c is the critical temperature), where the principle of corresponding states is applicable. A similar conclusion about the existence of the region of thermodynamic similarity was made in work [25] when analyzing the (T, p)-dependences of the thermodynamic coefficient $\left(\partial V/\partial T\right)_P$. In work [25], it was shown that there is a region of thermodynamic similarity between water and argon, as well as another region of thermodynamic parameters, where the water and argon properties differ considerably.

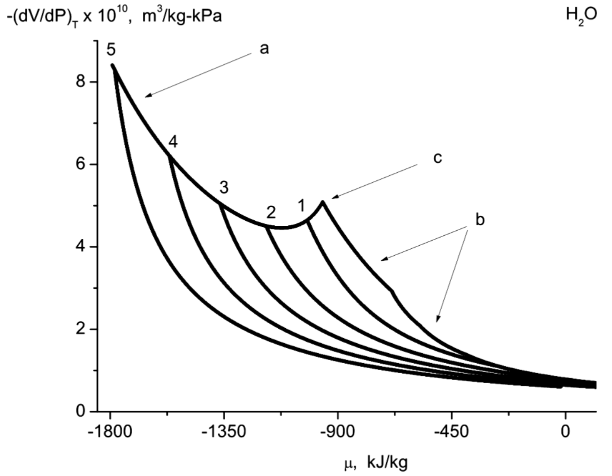

Fig. 3. Chemical potential dependences of the derivative $-\left(\partial V/\partial P\right)_T$ along the family of isotherms with $T = 290$ (*1*), 330 (*2*), 370 (*3*), 410 (*4*), and 450 K (*5*) along the liquid-vapor (*a*) and liquid-solid (*b*) coexistence curves for water in the liquid state in the temperature interval from $T = 273.15$ K to $T = 450$ K ($T/T_c < 0.7$). *c* is the triple point

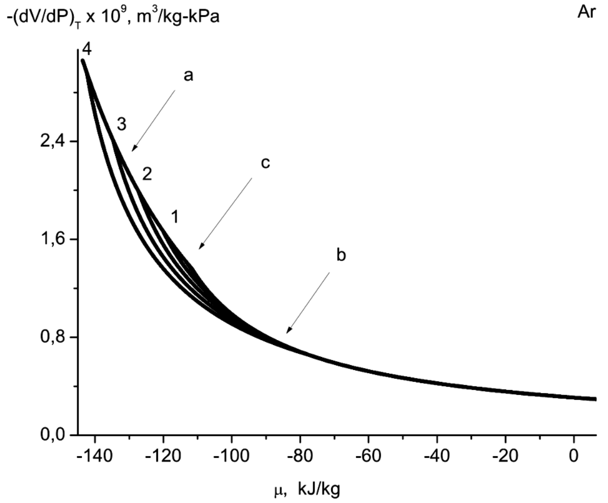

Fig. 4. Chemical potential dependences of the derivative $-\left(\partial V/\partial P\right)_T$ along the family of isotherms with $T = 90$ (*1*), 95 (*2*), 100 (*3*), and 105 K (*4*) along the liquid-vapor (*a*) and liquid-solid (*b*) coexistence curves for argon in the liquid state in the temperature interval from $T = 83.8$ K to $T = 105$ K ($T/T_c < 0.7$). *c* is the triple point

For the comparative analysis of those liquids, consider the temperature interval $0.556 < T/T_c < 0.7$,

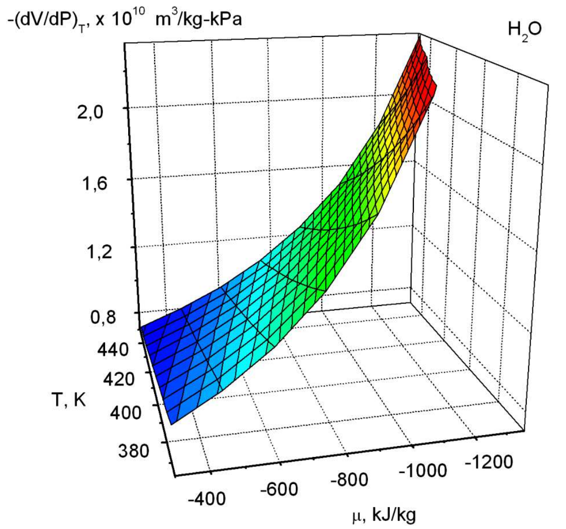

Fig. 5. 3D plot of the temperature-chemical potential dependence of the value $-(\partial V/\partial P)_T$ for water in the liquid state in the relative temperature interval $0.556 < T/T_c < 0.7$

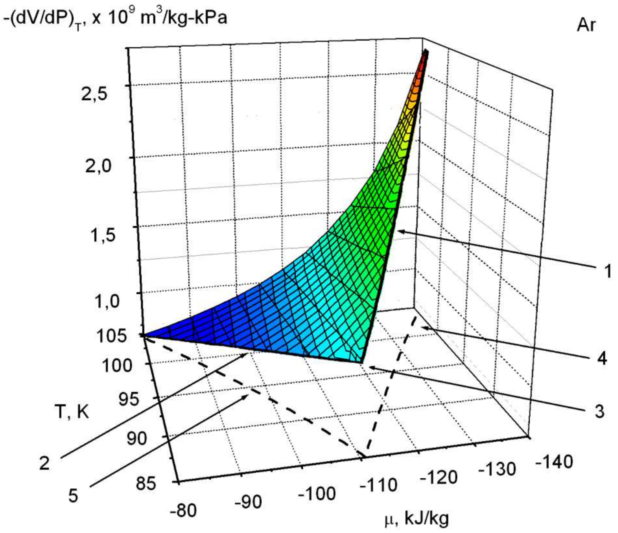

Fig. 6. 3D plot of the temperature-chemical potential dependence of the quantity $-(\partial V/\partial P)_T$ for argon in the liquid state in the relative temperature interval $0.556 < T/T_c < 0.7$. Liquid-vapor coexistence curve (*1*), liquid-solid coexistence curve (*2*), triple point (*3*), projection of the liquid-vapor coexistence curve onto the temperature–chemical potential plane (*4*), projection of the liquid–solid coexistence curve on the temperature–chemical potential plane (*5*)

where the influence of the critical fluctuations of order parameter can be neglected. Note that the relative freezing temperature for argon $T/T_c = 0.556$ ($T = 83.81$ K) is higher than that for water $T/T_c = 0.422$ ($T = 273.15$ K). In the indicated temperature interval, the baric dependences of thermodynamic quantities for argon are confined from the high-pressure side by the liquid-solid coexistence curve. This physical condition determines the maximum pressure value $P/P_c = 20.56$ ($P = 1 \times 10^5$ kPa) at which argon still exists in the liquid state at the temperature $T/T_c = 0.7$ ($T = 105.48$ K).

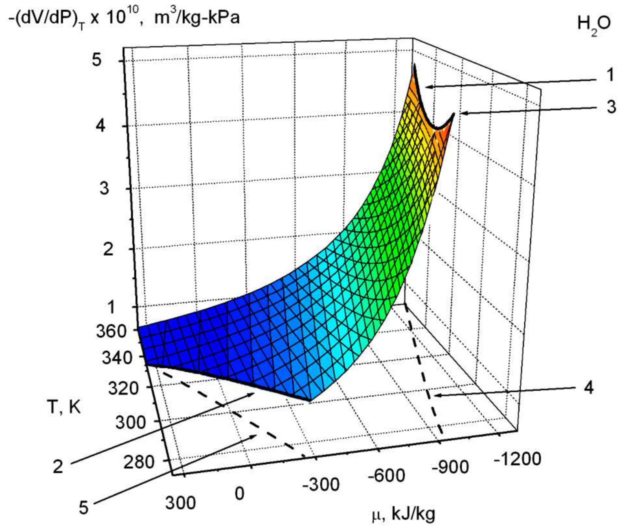

Fig. 7. 3D plot of the temperature-chemical potential dependence of the quantity $-(\partial V/\partial P)_T$ for water in the liquid state in the relative temperature interval $0.422 < T/T_c < 0.556$. Liquid-vapor coexistence curve (*1*), liquid-solid coexistence curve (*2*), triple point (*3*), projection of the liquid-vapor coexistence curve onto the temperature–chemical potential plane (*4*), projection of the liquid–solid coexistence curve on the temperature–chemical potential plane (*5*)

Let us plot and compare the three-dimensional surfaces of the (T, μ)-dependence of the thermodynamic coefficient $-(\partial V/\partial P)_T$ for water (Fig. 5) and argon (Fig. 6) in the same interval of relative temperatures $0.556 < T/T_c < 0.7$. This is the temperature interval 359.87 K $< T <$ 452.97 K for water, and -83.81 K $< T <$ 105.48 K for argon. It should be noted that, unlike the argon case, the selected intervals of relative temperatures and chemical potentials for water do not contain the liquid-vapor and liquid-solid coexistence curves.

As one can see from Figs. 5 and 6, the plotted surfaces are qualitatively similar. This fact confirms the validity of the principle of corresponding states in the indicated temperature and chemical potential intervals for water and argon, and is in agreement with the conclusions of works [25, 28–30].

Let us plot the (T, μ)-dependence of the thermodynamic coefficient $-(\partial V/\partial P)_T$ for water (Fig. 7) in the temperature interval from the water melting temperature $T = 273.15$ K ($T/T_c = 0.442$) to the temperature $T = 358.89$ K ($T/T_c = 0.556$) corresponding to the relative melting temperature of argon, $T = 83.81$ K ($T/T_c = 0.556$). A comparison of Figs. 6 and 7 testifies that there exists a region of thermodynamic parameters where the properties of water and argon differ substantially. It follows from Fig. 7 that, for the thermodynamic coefficient $-(\partial V/\partial P)_T$ of water, the liquid-vapor coexistence curve passes through a minimum located at the coordinates $T_{\min} = (315.15 \pm 0.2)$ K ($\theta_{\min} = (42.0 \pm 0.2)$ °C) and $\mu_{\min} = -(1122 \pm 1)$ kJ/kg.

In contrast to argon, in the case of water, when the temperature decreases in the interval $T < T_{\min} = (315.15 \pm 0.2)$ K and the chemical potential increases in the interval $\mu > \mu_{\min} = -(1122 \pm 1)$ kJ/kg, the thermodynamic coefficient $-(\partial V/\partial P)_T$ along the liquid-vapor coexistence curve abnormally grows and reaches a maximum value at the triple point (see also Figs. 1 and 3).

The results above testify that the temperature $T = 315$ K is particular for water and associated with other specific features in the T- and μ-dependences of its thermodynamic coefficient $-(\partial V/\partial P)_T$. In our opinion, these features can be related to the structures of hydrogen bonds in water according to its two-phase (LDW and HDW) model [31, 32].

4. Conclusions

To summarise, on the basis of available physical databases, the temperature and chemical potential dependences of the thermodynamic coefficient $-(\partial V/\partial P)_T$ for water and argon in the liquid state are calculated, and their comparative analysis is carried out.

1. The existence of a region of thermodynamic similarity between water and argon is confirmed. For the thermodynamic coefficient $-(\partial V/\partial P)_T$, this region is located in the temperature interval $0.56 < T/T_c < 0.7$. At the same time, there is also a region of thermodynamic parameters, where the properties of water and argon differ substantially.

2. It is shown that there is a particular temperature of (42.0 ± 0.2) °C for water, at which the temperature dependence of the thermodynamic coefficient $-(\partial V/\partial P)_T$ along the liquid-vapor equilibrium curve passes through a minimum. This peculiarity is responsible for other features in the behavior of the T- and μ-dependences of the indicated thermodynamic coefficient of water.

3. It is shown that there is a particular value of $-(1122 \pm 1)$ kJ/kg for the chemical potential of water, for which the μ-dependence of the thermodynamic coefficient $-(\partial V/\partial P)_T$ along the liquid-vapor coexistence curve also has a minimum.

4. In contrast to argon, in the case of water, the thermodynamic coefficient $-(\partial V/\partial P)_T$ as a function of chemical potential reaches a maximum value at the triple point (at the meeting point of the liquid-vapor and liquid-solid coexistence curves).

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Received 13.06.23.
Translated from Ukrainian by O.I. Voitenko

Л.А. Булавін, Є.Г. Рудніков

ВПЛИВ ТЕМПЕРАТУРИ ТА ХІМІЧНОГО ПОТЕНЦІАЛУ НА ТЕРМОДИНАМІЧНИЙ КОЕФІЦІЄНТ $-(\partial V/\partial P)_T$ ВОДИ

На основі існуючих літературних даних проведені розрахунки з подальшим аналізом температурних та хімпотенціальних залежностей термодинамічного коефіцієнта $-(\partial V/\partial P)_T$ для води у стані рідини. Проведено порівняння знайденого коефіцієнта для води та аргону. З урахуванням принципу відповідних станів підтверджено існування області термодинамічної подібності між ними. Разом з тим, існує область термодинамічних параметрів, в якій зазначена подібність між водою та аргоном не спостерігається. Показано, що для води існує особлива температура $(42{,}0 \pm 0{,}2)\ {}^\circ C$, за якої крива температурної залежності термодинамічного коефіцієнта $-(\partial V/\partial P)_T$ уздовж лінії рівноваги рідина–пара проходить через мінімум. Вказана особливість приводить до особливості поведінки термодинамічного коефіцієнта $-(\partial V/\partial P)_T$ води, чого не спостерігається для аргону. Показано, що для води існує особливе значення хімічного потенціалу, за якого крива хімпотенціальної залежності термодинамічного коефіцієнта $-(\partial V/\partial P)_T$ уздовж кривої співіснування рідина–пара також має мінімум. Крім того, у потрійній точці води термодинамічний коефіцієнт $-(\partial V/\partial P)_T$ як функція хімічного потенціалу досягає максимального значення.

Ключові слова: вода, аргон, ізотермічна стисливість, хімічний потенціал, крива співіснування рідина–пара, крива співіснування рідина–тверде тіло, водневі зв'язки.