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TEMPERATURE AND PRESSURE EFFECT ON THE THERMODYNAMIC COEFFICIENT $(\partial V/\partial T)_P$ OF WATER

On the basis of literature data, the temperature and pressure dependences of the thermodynamic coefficient $(\partial V/\partial T)_P$ for liquid water have been calculated and analyzed. The obtained results are compared with the relevant data for argon. Taking the principle of corresponding states into account, the existence of a region, where the thermodynamic similarity between water and argon takes place, is confirmed. At the same time, there is a region, where the indicated similarity is not observed, and the thermodynamic properties of water demonstrate a peculiar behavior. In particular, an inflection point at a temperature of $(91.0 \pm 0.2)\,^\circ$C is observed in the temperature dependence of the curve $(\partial V/\partial T)_P$ for water, but not for argon, along the liquid-vapor equilibrium curve. The existence of inflection point in the dependence $(\partial V/\partial T)_P$ for water leads to the presence of negative values of $(\partial V/\partial T)_P$ at temperatures below 3.98 °C, as well as to the intersection of the temperature dependences of isobars $(\partial V/\partial T)_P$ in water at a temperature of $(42.0 \pm 0.2)\,^\circ$C. On the contrary, the temperature dependences of the curves $(\partial V/\partial T)_P$ for argon along the liquid-vapor equilibrium curve do not have a corresponding inflection point.

Keywords: water, argon, isobaric expansion coefficient, liquid-vapor coexistence curve, liquid-solid coexistence curve, hydrogen bonds.

1. Introduction

Among the liquids that exist in nature, liquid water is probably the most complicated one, which demonstrates a number of anomalous properties [1, 2]. The physical origins of the latter were discussed in works [3–5]. Water possesses unique properties of its behavior as a solvent [6–8]. On the other hand, the atomic liquid argon can be considered as a liquid with the simplest structure and possessing the physical properties that are most typical of many liquids [9, 10].

In this work, in order to analyze the anomalous properties of water in the liquid state, we compare the behavior of the thermodynamic coefficient $(\partial V/\partial T)_P = \alpha_P V$ for water and argon. This parameter is associated with the isobaric expansion coefficient $\alpha_P = V^{-1} (\partial V/\partial T)_P$. The latter, for water, was studied in work [11].

Water in the liquid state is characterized by anomalies of both mechanical and caloric quantities [12, 13]. Therefore, the examined parameter $(\partial V/\partial T)_P$ is important, because it determines the transient "combined" mechanical–caloric response of the thermodynamic system to an external action [13],

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T, \tag{1}$$

and is related to the pair correlator of thermal fluctuations "specific entropy S–specific volume V" [14]

$$\langle \Delta V\ \Delta S\rangle = \frac{1}{k_\mathrm{B}T}\left(\frac{\partial V}{\partial T}\right)_P = \frac{\alpha_P V}{k_\mathrm{B}T}. \tag{2}$$

The aim of this work is to calculate and analyze the temperature and pressure dependences of the thermodynamic coefficient $(\partial V/\partial T)_P$ for water in the

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liquid state 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 for water and argon.

2. Calculation Technique for the Thermodynamic Coefficient $(\partial V/\partial T)_P$ for Water and Argon

The calculations of the quantity $(\partial V/\partial T)_P$ were performed on the basis of the most reliable experimental data for the thermodynamic properties of water and argon, which are available in modern reference books [15, 16] and physical databases [17–22]. The existing methods of processing experimental data [16] were supplemented by calculating the thermodynamic derivatives following the method described below. The proposed approach may be of independent interest, and it can be used in the future to analyze the thermodynamic properties of other liquids for which high-quality experimental data are absent. Therefore, let us firstly describe the basic general algorithm for the calculation of the derivative $(\partial V/\partial T)_P$.

In the minimum variant, to obtain data on the derivative $(\partial V/\partial T)_P$, data are required concerning the temperature dependence of the density, $\rho(T) = 1/V(T)$, for the liquid branch of the liquid-vapor coexistence curve for the corresponding substance, as well the temperature dependence of the pressure, $P(T)$, along the equilibrium curve.

In the absence of primary experimental data, the temperature dependence of the density ρ along the coexistence curve can be predicted using the Rackett and Gunn–Yamada methods [16, 23], whereas the temperature dependence of the pressure P along the coexistence curve can be predicted using the Riedel method [16, 23]. In addition, the required data can be obtained using the simulation method and neural networks, on the basis of the most reliable experimental data and quantum mechanical calculations of molecular parameters, namely, the Mol-instincts simulation [23] or the ChemRTP one [24]. The Mol-instincts simulation makes it possible to obtain temperature dependences for a set of thermodynamic quantities, whereas the ChemRTP simulation provides reference values of physical quantities that should be used in combination with the application of modern methods of thermodynamic similarity [25, 26]. It should be noted that, in recent years, simulation methods based on neural networks have made significant progress, which allows physical quantities to be calculated with an error close to their determination errors in modern experimental studies [23, 24].

If the experimental or predicted data for the temperature dependences of the density ρ and the pressure P of the liquid phase along the coexistence curve are available and the temperature dependence of the second virial coefficient B_2 along the isobar $P = 1$ atm is known, the temperature and pressure dependences of the derivative $(\partial V/\partial T)_P$ for the liquid phase can be obtained by applying the following method.

At the first stage, the derivative $(\partial V/\partial T)_P$ is determined at various temperatures by directly differentiating the temperature dependence of the specific volume $V = 1/\rho$ along the liquid-vapor coexistence curve. Far from the critical point, this derivative practically does not differ from that at a constant pressure, $(\partial V/\partial T)_{cxc} \approx (\partial V/\partial T)_P$, where the subscript *cxc* denotes the liquid-vapor coexistence curve. The discrepancy between those quantities is determined by the formula

$$\left(\frac{\partial V}{\partial T}\right)_{cxc} = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{cxc}. \qquad (3)$$

The calculations showed that,far from the critical point, i.e., at $T/T_c \leqslant 0.7$, the second term in Eq. (3) is much smaller than the first one.

The temperature dependences of the derivative $(\partial V/\partial T)_P$ along the isobars can be obtained, for example, as follows. First, using the Tait equation [27], the pressure dependences of the liquid phase density ρ along a successive equidistant set of isotherms with an endpoint on the liquid-vapor equilibrium curve are calculated. Afterward, a transition from isotherms to isobars is carried out in the $T - P$ plane. For this purpose, the temperature dependences of the density ρ are determined on the isobars that equidistantly intersect the obtained pressure dependences of the density on the isotherms. Thus, for the density ρ, the isotherms and isobars form a grid in the $T - P$ plane, with the grid nodes containing the calculated values of the density ρ.

At the next stage, the derivative $(\partial V/\partial T)_P$ is determined in all grid nodes by differentiating the temperature dependences of the specific volume $V = 1/\rho$ along the isobars, i.e., at a constant pressure. As a result, the pressure and temperature dependences for the derivative $(\partial V/\partial T)_P$ are determined in the $T-P$ plane.

Besides the Tait equation [27], one can also use the Kesselman equation [28], the Benedict–Webb–Rubin (BWR) equation [29], its modifications by Starling (BWRS) or Jacobson and Stewart (mBWR), and others [29, 30].

The parameters of the equations of state for the liquid phase beyond the critical region are determined from the available experimental data or from the predicted values for the liquid density ρ and the pressure P along the coexistence curve, as well as for the second virial coefficient B_2 for the vapor along the isobar $P = 1$ atm. In so doing, the values of the virial coefficient B_2 can be calculated using reference experimental data [31, 32] or other prediction methods [31]. In the absence of experimental data for the third virial coefficient B_3, its value can be found by applying the Aubey formula [31] or by solving cubic equations of state using the known values for ρ, P, and B_2 [32].

In modern thermodynamic databases (e.g., Minirefprop [17], Refprop [18], SRD69 [19], Coolprop [20], ThermodataEngine [21], and WTT [22]), the temperature and pressure dependences of the main thermodynamic quantities – in particular, the density ρ – are presented in the form of certain mathematical functions, with each analytical function used for a reliable representation of every physical quantity in the indicated databases being described in detail.

The indicated reference functions for a particular substance are determined on the basis of a statistical analysis of most reliable experimental data available for this physical quantity. As a result, it becomes possible to analytically calculate thermodynamic derivatives of various orders for those dependences. The corresponding calculation error is not larger than the error of the primary experimental data. Therefore, it is the error of the initial experimental data forming the basis for the calculations that is mainly responsible for the error of calculated physical quantities. Our analysis showed that the error of temperatures peculiar for water which are determined by us is the sum of the errors of values experimentally obtained and presented in the literature, and this error equals ±0.2 K for the temperature at which the isothermal compressibility of water is minimum.

When calculating the derivative $(\partial V/\partial T)_P$ for water and argon in the temperature interval from their melting points to temperatures $T/T_c < 0.7$ and for the pressures from $P/P_c > 0.02$ to the liquid-solid coexistence curve, the examined temperature intervals were represented by 10^3 equidistant points. Provided such a representation, the results of numerical calculations of thermodynamic derivatives and the results of analytical calculations carried out by differentiating the corresponding analytical functions differed from each other by less than 1%.

When calculating the pressure dependences, the examined pressure intervals were represented by at least 200 equidistant points. However, the pressure derivatives were not calculated in this article. Therefore, when constructing the grid of orthogonal isotherms and isobars in the $T-P$ plane for the temperature-pressure dependences, the selected pressure interval was represented by 20 equidistant points.

3. Comparison of Specific Features in the Behavior of $(\partial V/\partial T)_P$ for Water and Argon

3.1. Temperature dependences of $(\partial V/\partial T)_P$

Figures 1 and 2 illustrate the temperature dependences of the derivative $(\partial V/\partial T)_P$ for water and argon, respectively, which were calculated using the method described above along the coexistence curve and certain isobars. Let us compare the temperature dependences of the derivative $(\partial V/\partial T)_P$ obtained for water and argon along the liquid-vapor equilibrium curve. As we can see from Fig. 1, the temperature dependence of the derivative $(\partial V/\partial T)_P$ for water along the liquid-vapor coexistence curve has an inflection point at the temperature $T = (364.0 \pm 0.2)$ K. The inset demonstrates the temperature dependence of the derivative $\left(\partial^2 V/\partial T^2\right)_P$ along the liquid-vapor coexistence curve. It has a minimum – i.e., here $\left(\partial^3 V/\partial T^3\right)_P = 0$ – at the temperature $T = 364$ K, which coincides with the inflection temperature in the temperature dependence of the derivative $(\partial V/\partial T)_P$ along the liquid-vapor coexistence curve.

For temperatures higher than the inflection temperature $T = 364$ K, the derivative $(\partial^2 V/\partial T^2)_P$ decreases, as the temperature grows, along the liquid-vapor coexistence curve. The derivative $(\partial^3 V/\partial T^3)_P$ remains positive at that. At temperatures lower than $T = 364$ K, the derivative $(\partial^2 V/\partial T^2)_P$ increases, and the derivative $(\partial^3V/\partial T^3)_P$ becomes negative (see the inset in Fig. 1). Therefore, the existence of the inflection temperature $T = 364$ K gives rise to a more rapid variation of the derivative $(\partial V/\partial T)_P$ and, as a result, even to its negative values. This occurs at temperatures below the specific temperature $T = 277.133$ K [33], which corresponds to the minimum – here, $(\partial V/\partial T)_P = 0$ – in the temperature dependence of the specific volume $V = V_m + \int(\partial V/\partial T)_P\,dT$ along the liquid-vapor coexistence curve. In the last formula, V_m is the specific volume at the melting point, and the integral is calculated along the coexistence curve.

In contrast to the case of water, the derivative $(\partial^2V/\partial T^2)_P$ for argon decreases monotonically, as the temperature decreases along the liquid-vapor equilibrium curve, with the derivative $(\partial^3V/\partial T^3)_P$ remaining positive within the entire temperature interval (see the inset in Fig. 2). As a result, the thermodynamic coefficient $(\partial V/\partial T)_P$ for argon also remains positive within the whole temperature interval.

A comparison of the temperature dependences of the derivative $(\partial V/\partial T)_P$ for water and argon along the corresponding coexistence curves on the basis of the principle of corresponding states showed that the relative inflection temperature of the derivative $(\partial V/\partial T)_P$ equals $T/T_c = 0.562$ for water, which is close to the relative freezing point for argon, $T/T_c = 0.556$ (the difference is 1%). In other words, below the temperature $T = 315 \pm 0.2$ K, water has an essentially different behavior of its thermodynamic coefficient $(\partial V/\partial T)_P$ in comparison with that for argon.

In particular, in the case of water, the curves describing the temperature dependences of the derivative $(\partial V/\partial T)_P$ at various pressures approach each other, as the temperature decreases, and mutually intersect at the temperature $T = 315 \pm 0.2$ K (see Fig. 1). Owing to the intersection of those isobars, the temperature dependence of the derivative $(\partial V/\partial T)_P$ along the liquid-vapor coexistence curve at $T < 315$ K lies below the isobars of this quantity (see Fig. 1), which is also an example of the anomalous physical behavior of water.

On the contrary, the temperature dependences of the derivative $(\partial V/\partial T)_P$ for argon along various isobars do not intersect each other at any temperature (see Fig. 2). The interval of relative temperatures $T/T_c < 0.056$, where the water anomalies manifest themselves – in particular, it occurs

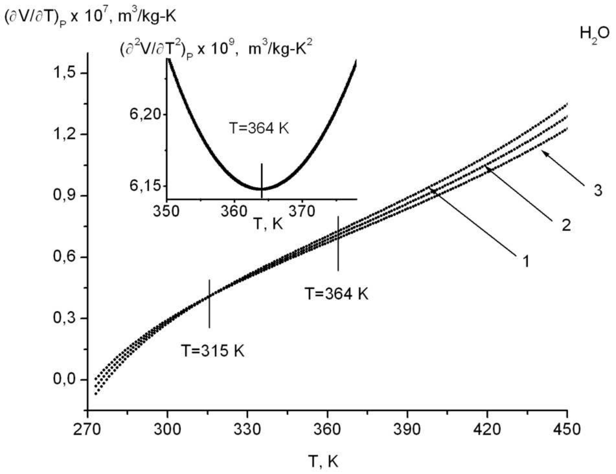

Fig. 1. Temperature dependences of the derivative $(\partial V/\partial T)_P$ for water in the liquid state in the temperature interval 273.15 K $\leqslant T \leqslant$ 450 K, which contains the inflection temperature $T = 364$ K and the intersection temperature of isobars $T = 315$ K: liquid-vapor coexistence curve (*1*), 1×10^4-kPa isobar (*2*), and 2×10^4-kPa isobar (*3*). The temperature dependence of the derivative $\left(\partial^2V/\partial T^2\right)_P$ for water along the liquid-vapor coexistence curve is shown in the inset; its minimum at $T = 364$ K determines the inflection temperature, where $\left(\partial^3V/\partial T^3\right)_P = 0$, of the temperature dependence of the derivative $(\partial V/\partial T)_P$ along the liquid-vapor coexistence curve

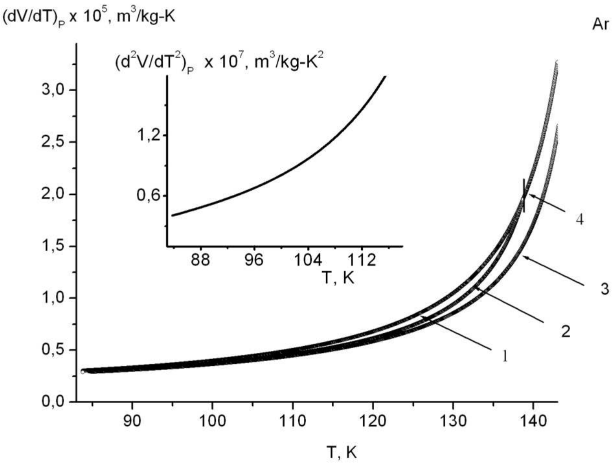

Fig. 2. Temperature dependences of the derivative $(\partial V/\partial T)_P$ for argon in the liquid state in the temperature interval 83.81 K $\leqslant T \leqslant$ 145 K: liquid-vapor coexistence curve (*1*), 3×10^3-kPa isobar (*2*), 4×10^5-kPa isobar (*3*), and boiling point for the 3×10^3-kPa isobar(*4*). The temperature dependence of the derivative $\left(\partial^2V/\partial T^2\right)_P$ for argon along the liquid-vapor coexistence curve in the temperature interval 83.81 K $\leqslant T \leqslant$ 120 K is shown in the inset. The thermodynamic coefficient $(\partial V/\partial T)_P$ is positive within the whole temperature interval

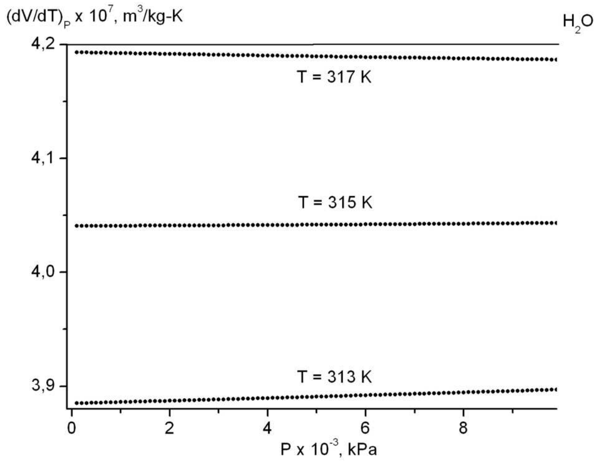

Fig. 3. Pressure dependences of the derivative $(\partial V/\partial T)_P$ for water in the liquid state along the isotherms when moving away from the liquid-vapor coexistence curve. At the temperature $T = 315$ K, the condition $\partial^2 V/\partial T\partial P = 0$ is satisfied

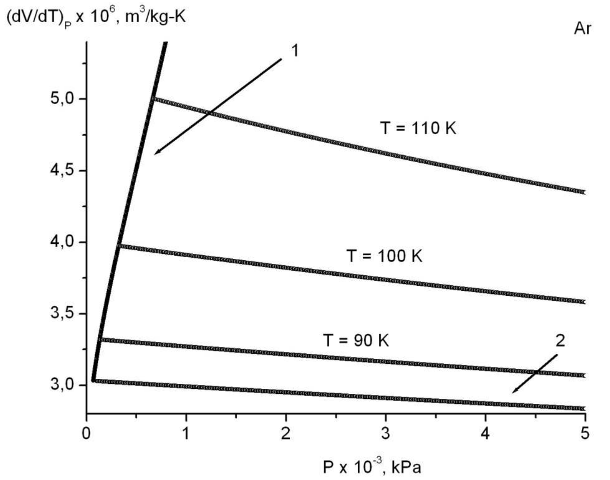

Fig. 4. Pressure dependences of the derivative $(\partial V/\partial T)_P$ for argon in the liquid state along the isotherms when moving away from the liquid-vapor coexistence curve: (*1*) liquid-vapor coexistence curve with the end freezing point at $T_m = 83.81$ K, and (*2*) liquid-solid coexistence curve

at $T = (315 \pm 0.2)$ K and $T = 277.133$ K [33] – is unattainable for argon in the liquid state, because it is located below the freezing point of argon ($T = 83.8058$ K, $T/T_c = 0.056$ [15]).

The graphical analysis of Fig. 1 allows a conclusion to be drawn that all three temperatures $T = 277$, 315, and 364 K that are peculiar in the temperature dependences of the derivative $(\partial V/\partial T)_P$ along the coexistence curve for water and for isobars in a vicinity of the coexistence curve are interrelated. In accordance with the conclusions made in works [3, 34–37], those anomalies can be explained in the framework of the two-structure model of water.

3.2. Pressure dependences of $(\partial V/\partial T)_P$

For water, the presence of the temperature of intersection of the temperature dependences of the derivative $(\partial V/\partial T)_P$ along various isobars in a vicinity of the liquid-vapor coexistence curve means the following: for isotherms above the temperature $T = 315$ K, the derivative $(\partial V/\partial T)_P$ decreases, as the pressure increases; at the temperature $T = 315$ K, the derivative $(\partial V/\partial T)_P$ is constant; and, below the temperature $T = 315$ K, the derivative $(\partial V/\partial T)_P$ increases together with the pressure. For argon, on the contrary, the absence of an analogous temperature with the intersection of the temperature dependences of the derivative $(\partial V/\partial T)_P$ along various isobars means that the derivative $(\partial V/\partial T)_P$ does not change its sign, as the pressure increases, and the derivative $(\partial^2 V/\partial T^2)_P$ remains positive within the whole temperature interval.

In Figs. 3 and 4, the temperature dependences of the derivative $(\partial V/\partial T)_P$ are shown for water and argon, respectively (see Figs. 1 and 2). The data on the pressure dependences for water, which are presented in Fig. 3, allow a conclusion to be made that the derivative

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T = \frac{\partial^2 V}{\partial T\partial P} = -\left(\frac{\partial^2 S}{\partial P^2}\right)_T$$

is negative for the isotherms above the temperature $T = 315$ K. At the temperature $T = 315$ K, the derivative $\partial^2 V/\partial T\partial P$ equals zero, and, below this temperature, the derivative $\partial^2 V/\partial T\partial P$ is positive in the indicated pressure interval. On the contrary, the analysis of experimental data for argon [16] demonstrates that the derivative $\partial^2 V/\partial T\partial P$ is negative along the isotherms at all temperatures.

The analysis of the data presented in Figs. 1 to 4 makes it possible to conclude that the temperature $T = 315$ K should be considered as a peculiar one for water.

3.3. Temperature-pressure dependences of $(\partial V/\partial T)_P$

The pressure-temperature dependences of the derivative $(\partial V/\partial T)_P$ for water and argon were analyzed with regard for the principle of corresponding states [26]. Note that, according to works [38–40], despite a substantial difference between the properties of water and argon, there exists a temperature interval, at $T \ll T_c$, where the principle of corresponding states can be applied.

Since the relative freezing point for argon, $T/T_c = 0.556$ ($T = 83.81$ K), is substantially higher than that for water, $T/T_c = 0.422$ ($T = 273.15$ K), in order to make a comparative analysis of those liquids, we selected the temperature interval $0.556 < T/T_c < 0.7$, where the influence of the critical fluctuations of the order parameter can be neglected. In this temperature interval, the pressure dependences of thermodynamic quantities for argon are limited from the higher-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).

Let us plot three-dimensional surfaces of the $P - T$ dependences for water (Fig. 5) and argon (Fig. 6) in the same intervals of relative temperature, $0.556 < T/T_c < 0.7$, and pressure, $0.02 < P/P_c < 20.56$. The corresponding absolute parameter intervals are $359.87\text{ K} < T < 452.97$ K and $441.28\text{ kPa} < P < 4.54 \times 10^5$ kPa for water, and $83.81\text{ K} < T < 105.48$ K and $97.26\text{ kPa} < P < 1 \times 10^5$ kPa for argon. It should be noted that, unlike the case with argon, the indicated intervals of relative temperatures and pressures for water does not contain the liquid-solid coexistence curve.

The analysis of the data presented in Figs. 5 and 6 showed that the surfaces of the pressure-temperature dependences of the derivative $(\partial V/\partial T)_P$ for water and argon are qualitatively similar in the intervals of relative temperatures $0.56 < T/T_c < 0.7$ and pressures $0.02 < P/P_c < 20$. This fact confirms the validity of the principle of corresponding states for water and argon and is consistent with the conclusions of works [38–40].

By comparing Figs. 6 and 7, a conclusion can also be drawn that the regions of thermodynamic anomalies in the derivative $(\partial V/\partial T)_P$ are qualitatively different for water and argon. In particular, the pressure dependences of the derivative $(\partial V/\partial T)_P$ for water are non-monotonic along the isotherms in a vicinity of the temperature $T = 315$ K. Really, a line of extremes in the derivative $(\partial V/\partial T)_P$ – i.e., where $(\partial(\partial V/\partial T)_P/\partial P)_T = (\partial^2 V/\partial T \partial P) = 0$ – can be observed in Fig. 7 in the region, where the temperatures are lower than $T = 320$ K, and the pressures are larger than $P = 1.5 \times 10^5$ kPa. The presence of such a line of maxima in the derivative $(\partial V/\partial T)_P$ means that, at temperatures below $T = 315$ K, the derivative $(\partial V/\partial T)_P$ increases along the isotherms, as the pressure grows (see Fig. 3), but only in the region

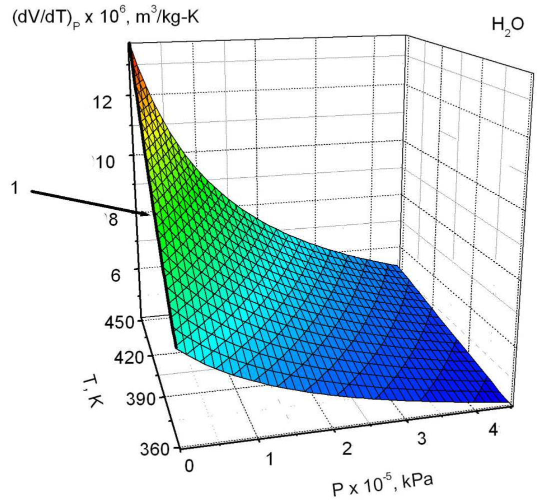

Fig. 5. Surface of $P - T$ dependences of the derivative $(\partial V/\partial T)_P$ for water in the liquid state in the intervals of relative temperatures $0.556 < T/T_c < 0.7$ and relative pressures $0.02 < P/P_c < 20.56$: liquid-vapor coexistence curve (*1*)

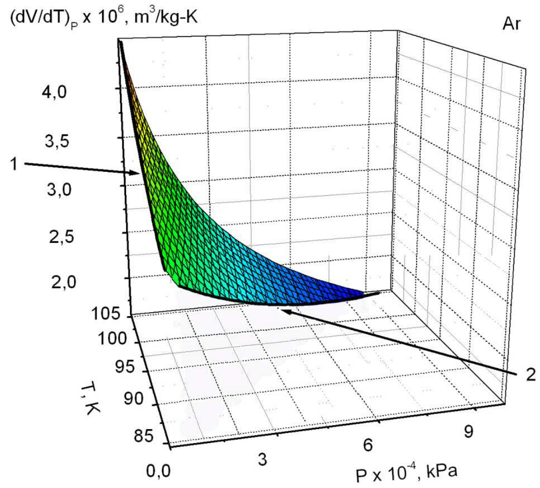

Fig. 6. Surface of $P - T$ dependences of the derivative $(\partial V/\partial T)_P$ for argon in the liquid state in the intervals of relative temperatures $0.556 < T/T_c < 0.7$ and relative pressures $0.02 < P/P_c < 20.56$: liquid-vapor coexistence curve (*1*), and liquid-solid coexistence curve (*2*)

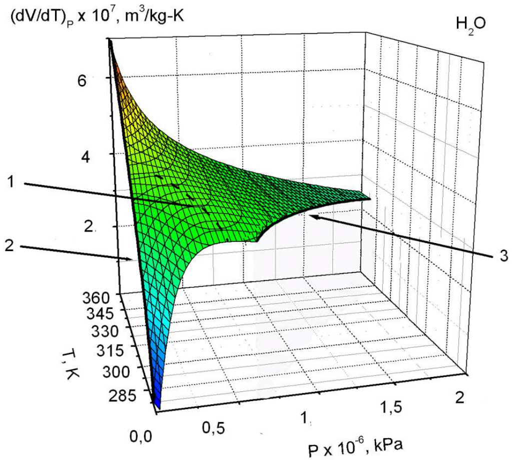

Fig. 7. The surface of the $P - T$ dependences of the derivative $(\partial V/\partial T)_P$ for water in the liquid state in the interval of relative temperatures $0.422 < T/T_c < 0.556$, i.e., from the freezing point for water, $T = 273.15$ K, to the temperature $T = 359.87$ K, which, according to the principle of corresponding states, corresponds to the freezing point for argon, $T = 83.81$ K: line of maxima of the derivative $(\partial V/\partial T)_P$, where $\partial^2 V/\partial T\partial P = 0$ (*1*); liquid-vapor coexistence curve (*2*); and liquid-solid coexistence curve (*3*)

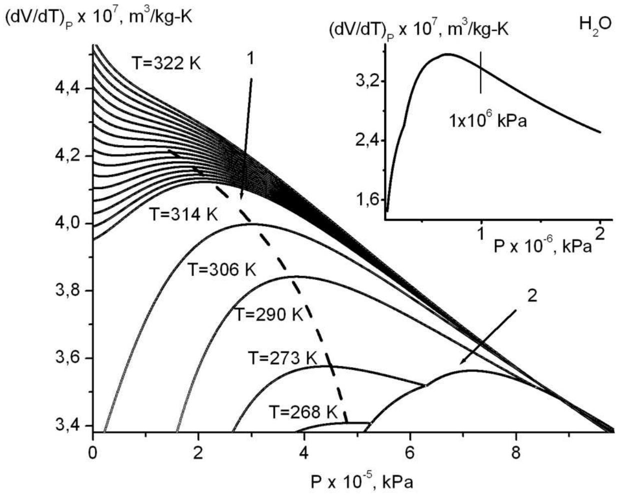

Fig. 8. Pressure dependences of the derivative $(\partial V/\partial T)_P$ for water along the isotherms: line of maxima of the derivative $(\partial V/\partial T)_P$, where $\partial^2 V/\partial T\partial P = 0$ (*1*); and liquid-solid coexistence curve (*2*). The non-monotonic pressure dependence of the derivative $(\partial V/\partial T)_P$ along the liquid-solid coexistence curve with the inflection point, where $\partial^3 V/\partial T\partial P^2 = 0$, at $P = 1 \times 10^6$ kPa is shown in the inset

extending from the liquid-vapor coexistence curve to the line of maxima in the derivative $(\partial V/\partial T)_P$ (see Fig. 8).

The analysis of Fig. 8 showed that, in the case of water, if the pressure grows further beyond the line of maxima, the derivative $(\partial V/\partial T)_P$ decreases and, when the liquid-solid equilibrium curve is reached, has lower values than it would have in the absence of the line of maxima. In the case of water, such a behavior leads to the growth of the derivative $(\partial V/\partial T)_P$ along the liquid-solid equilibrium curve at pressures lower than $P = 7.2\times10^5$ kPa. If the pressure increases further, the derivative $(\partial V/\partial T)_P$ decreases.

Furthermore, the curve $(\partial V/\partial T)_P$ has an inflection point, where $(\partial^2(\partial V/\partial T)_P/\partial P^2)_T = \partial^3 V/\partial T\partial P^2 = 0$, along the liquid-solid equilibrium curve at $P = 1 \times 10^6$ kPa (see the inset in Fig. 8). Its presence means that the derivative $(\partial(\partial V/\partial T)_P/\partial P)_T = \partial^2 V/\partial T\partial P$ decreases along the liquid-solid equilibrium curve at pressures less than $P = 1 \times 10^6$ kPa. As the pressure grows further above the inflection point, the derivative $\partial^2 V/\partial T\partial P$ increases.

Hence, the above-described behavior of the derivative $(\partial V/\partial T)_P$ for water along the liquid-solid equilibrium curve is associated with the presence of the line of extremes, where $\partial^2 V/\partial T\partial P = 0$, for the family of isotherms (Figs. 7 and 8) and with the presence of the intersection point for the family of isobars, for which $\partial^2 V/\partial T\partial P = 0$ too at the peculiar temperature $T = 315$ K for water (Figs. 1 and 3). At the same time, contrary to the case of water, the derivative $(\partial V/\partial T)_P$ for argon decreases with the increasing pressure along the liquid-solid equilibrium curve (see Fig. 6), and the derivative $\partial^2 V/\partial T\partial P$ increases at all temperatures.

At the same time, from the analysis of the results presented above, it follows that, for argon, there is no intersection point of isobars, no line of extremes of the derivative $(\partial V/\partial T)_P$, and no non-monotonic dependence of this quantity along the liquid-solid equilibrium curve. All those facts testify that the temperature $T = 315$ K is peculiar for water, and the thermodynamic features of the latter are associated with this temperature.

This conclusion is consistent with the results of other studies. For instance, in a vicinity of the temperature $T = 315$ K, the specific behavior is observed for such quantities as the Raman depolarization ratio [41], thermodynamic coefficients [13], the second peak in the oxygen-oxygen pair correlation function [42], pH [43], the interaction of solvents in water [44], the dielectric permittivity [45], the pressure derivative of the refractive index [46], the viscosity [47, 48], and the self-diffusion coefficient [13]. The data obtained using neutron methods [49] show that if the temperature grows and reaches a value of 315 K, the residence time of water molecules tends to zero in the framework of the Frenkel model; in other words, water loses its quasicrystalline character at this temperature. In a vicinity of the temperature $T = 315$ K, the pH relaxation time in water is minimum [50, 51]. Thus, the conclusion of this work about the peculiar temperature $T = 315$ K for water is consistent with the results of studies of other water properties presented in the scientific literature.

4. Conclusions

On the basis of existing physical databases, a comparative analysis of the temperature and pressure dependences of the thermodynamic coefficient $(\partial V/\partial T)_P$ has been carried out for water and argon in the liquid state.

1. The existence of a region of thermodynamic similarity between water and argon is confirmed. The indicated similarity is observed in the relative-temperature interval $0.56 < T/T_c < 0.7$ and the relative-pressure interval $0.02 < P/P_c < 20$. At the same time, there is a region of thermodynamic parameters, where the properties of water and argon are substantially different.

2. It is shown that, in the case of water, the curve of the temperature dependence of the thermodynamic coefficient $(\partial V/\partial T)_P$ along the liquid-vapor equilibrium line has an inflection point, where $(\partial^3 V/\partial T^3)_P = 0$, at a temperature of (91.0 ± 0.2) °C. This temperature corresponds to the lower boundary of the water and argon similarity region.

3. The presence of the inflection point on the curve for the thermodynamic coefficient $(\partial V/\partial T)_P$ leads to negative values of this quantity at temperatures below 3.98 °C. The specific volume of water V_m reaches a minimum at the indicated temperature.

4. It is shown that there exists a peculiar temperature of (42.0 ± 0.2) °C for water, which is the intersection temperature for the curves of the isobar family $(\partial V/\partial T)_P$, and where the thermodynamic coefficient $-(\partial V/\partial P)_T$ is minimum.

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ВПЛИВ ТЕМПЕРАТУРИ ТА ТИСКУ НА ТЕРМОДИНАМІЧНИЙ КОЕФІЦІЄНТ $(\partial V/\partial T)_P$ ВОДИ

На основі літературних даних проведено розрахунки та аналіз температурних і баричних залежностей термодинамічного коефіцієнта $(\partial V/\partial T)_P$ для води у стані рідини. Проведено порівняння вказаного коефіцієнта для води та аргону. З урахуванням принципу відповідних станів підтверджено існування області термодинамічної подібності між водою та аргоном. При цьому існує область, в якій зазначена подібність між водою та аргоном не спостерігається і наявна особлива поведінка термодинамічних властивостей води. Так, у води крива температурної залежності $(\partial V/\partial T)_P$ уздовж лінії рівноваги рідина–пара має точку перегину за температури (91,0 ± 0,2) °C, чого не спостерігається в аргоні. Існування для води точки перегину кривої $(\partial V/\partial T)_P$ приводить до від'ємних значень $(\partial V/\partial T)_P$ при температурах, нижчих 3,98 °C. Крім того, наявність точки перегину на вказаній температурній залежності приводить до перетину температурних залежностей сімейства ізобар $(\partial V/\partial T)_P$ у воді при температурі $(42,0 \pm 0,2)$ °C. На відміну від цього, криві температурної залежності $(\partial V/\partial T)_P$ аргону уздовж лінії рівноваги рідина–пара не мають відповідної точки перегину.

Ключові слова: вода, аргон, коефіцієнт об'ємного розширення, крива співіснування рідина–пара, крива співіснування рідина–тверде тіло, водневі зв'язки.