MODIFICATION OF THE VAN DER WAALS EQUATION FOR DESCRIBING THE THERMODYNAMIC PROPERTIES OF LIQUID WATER

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Abstract. In the point of view of liquid water as a real gas, the Van der Waals equation of state is modified for describing isotherms, isochores, and isobars of liquid water in a wide range of pressures and temperatures. The new thermal equation provides a standard transition to thermodynamics with the reproduction of internal energy *U*, free energy *F*, heat capacity C_V and entropy *S*.

Keywords: *liquid water, phase diagram, thermodynamic parameters*

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INTRODUCTION

The van der Waals (VdW) equation of state, written in 1873. [1], is rooted in the courses of molecular physics, physical chemistry, thermodynamics and statistical physics as the basic one for the study of gases and liquids [2-5]. It postulates the relationship between the quantities characterizing a real gas: external and internal pressures P and P_i, volume V and temperature T. The simple equation predicts an important phenomenon - the occurrence of liquid-gas phase transition in matter. The effect arises due to the cubicity of van der Waals isotherms: the cubic parabola $P(V)$ has a loop, the position of which on the phase diagram by pressure P and the sweep by temperature T determine the vaporization curve. The curve breaks at the so-called critical point, beyond which the liquid-gas transition ceases to exist.

The cubic behavior of the $P(V)$ isotherms has been successful for describing the condensation process in a wide variety of substances: from simple gases to complex hydrocarbons. Cubic equations as refinements of the VdV equation form a large class [6-10]. Due to their simplicity, they allow physical analysis of parameters and development of the molecular theory of liquids and gases in the VdV paradigm. Attempts to extend the scope of application of the VdV equation and to improve the accuracy of data description continue for the third century [11]. Tens and hundreds of more complex equations of state: virial, polynomial, multiparametric - with the established designation EoS (equation of state) - have been written on condensation topic, which have their own advantages and disadvantages in specific applications. They are used for large databases and have a wide range of applications related to the balance of matter in the liquid-gas state [11-17]. The topics are diverse, ranging from the viscosity of petroleum products [18] to marine cloud formation [19,20] and shock waves in explosion [21,22]. Some of the applied problems are solved using the relatively simple Tate equation [22,23]. It is purely empirical in nature and is not interpreted at the basic physical level.

The most famous liquid-gas balance is inherent in water. It is the basis of many natural and technological processes and largely determines the picture of the surrounding world. It would seem that, as a vital and simple chemical compound, water could become a favorite object of application of the VdV model and a source of information about the structure of matter. However, this has not happened. Experience shows that the VdV equation does not apply well to water. The VdV parabola passing through the critical point in the liquid phase is very far from reality [24,25]. This fact is a long habitual fact and is not analyzed in detail in the literature. A rare analysis of the topic is carried out in [25]. By inertia, textbooks offer a large number of problems related to applications of the VdV equation to water, but all of them are considered for special cases and limited conditions [26]. A complete and physically clear equation of state for water does not exist [24], its search continues [9].

The lack of a satisfactory description of the thermodynamic properties of liquid water is accompanied by a lack of understanding of its microscopic properties. The molecular mechanism of the liquid-gas phase transition remains controversial. What microscopic mechanisms are behind the critical behavior? Is the liquid a real gas? One has to argue about the same things that at first glance seem simple and commonplace [27,28].

In the present work we actualize the question of applicability of the VdV model to liquid water in connection with an unexpected conclusion following from the analysis of its wide-range dielectric spectra [29,30]. The description of the spectra turns out to be more successful in envisioning water bound by the Coulomb fields of the single-charged ions H_3O^+ and $OH^{(-)}$, than, as [31,32] is commonly believed, by hydrogen bonds. In our ion-molecular model (IM model) molecules and ions are free, make thermal collisional motion and form a medium representing a real HdV gas. We see it possible to describe the properties of such a medium by the simplest possible water-specific equation of state. By the trial method (by comparing the calculation results with reference data) we find a modification of the VdV equation that allows us to calculate the thermodynamic parameters of liquid water with satisfactory accuracy. From the agreement of the calculated data with the reference data, we conclude that the gas approach for liquid water is correct, and the IM model is promising for further study.

THERMAL EQUATION OF STATE

We start from the VdV equation in its original form - for pressure P, temperature T and volume V for one mole of gas molecules:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}, \tag{1}$$

where R = 8.314 J/(mol-K) is the universal gas constant, k_B = 1.38-10$^{(-)\,(23)}$J/K is the Boltzmann constant, b is the excluded volume (inaccessible for molecular motion) and a is the attraction coefficient (of intermolecular forces and forces from the molecules of the boundary layer of the medium). Calculations are performed for mass M= 1000 kg (55.5 kmol) in SI system.

The coefficients a and b are the hallmark of the VdV equation. They are derived from the critical temperature and pressure so that by definition they do not depend on temperature. For water, a = 5.53 bar-(m($^{3)}$/kmol^2) and b = 0.03 m^3/kmol [33], the same in all books and reviews. The calculated VdV isotherms with these parameters are shown in Fig. 1a. They are shown as thin lines on the right and, as can be seen, are far from the reference points on the left, taken from the IAPWS database [12].

We aim to align the model lines with the reference points. For this purpose, we assume that the internal pressure $P_{(i)\ (the}$second summand in formula (1)) depends on temperature. We set the second numerator in binomial form with respect to T and change the denominator degree exponent from 2 to 1.4. This variant of modification is not the only one, but it is the simplest of the tested ones. By the method of successive approximations we approximate the new equation to reference data from the IAPWS database [12] and arrive at the optimal formula

$$P = \frac{RT}{V-b} - \frac{CT - BT^2}{V^{1.4}} \text{ [MPa]}, \tag{2}$$

where b, C and B are the optimal parameters presented in Table 1. The operation of formula (2) for isotherms and isochores is shown in Fig. 1. The dependences of $P(V)$ and $P(T)$ were calculated by the method of successive fixations of T and V in equation (2). As can be seen, the curves lie well on the array of reference points, huge in number and scatter of absolute values. The isobars $V(T)$ are also well transferred by formula (2) (not shown graphically) with the peculiarity that due to the inherent weak compressibility of liquid water at temperatures from the triple to the critical point, they lie on one common curve. For convenience of calculations we set this dependence by a simplified formula

$$V(T) = 73/(700 - T) + 0.82 \ [^{\text{M(3)}}], \tag{3}$$

transmitting isobar behavior with deviations from the reference data within 5% (see Fig. 3a in [34]).

CALORIC EQUATIONS OF STATE

The thermal equation (2), like the original VdV equation (1), admits a textbook transition to thermodynamics, taking into account the first and second laws of thermodynamics [4,5]. It involves a series of differential-integral operations with the thermal equation of state of the form $P(V,T)$ (expression for pressure) to obtain energy (caloric) equations of state of the form $E(V,T)$ (expressions for free F and internal U energies).

We carry out with equation (2) the procedure according to the scheme from textbooks [4,5]:

1) we take the pressure P as the sum of thermal and internal pressures

$$P = T\left(\partial P/\partial T\right)_V - \left(\partial U/\partial V\right)_T \tag{4}$$

and as a partial derivative of the free energy

$$P = -\left(\partial F/\partial V\right)_T; \tag{5}$$

2) we take into account the relation between internal energy U and heat capacity C_V

$$C_V = \left(\partial U/\partial T\right)_V, \tag{6}$$

relation between free energy F and entropy S

$$S = -\left(\partial F/\partial T\right)_P \tag{7}$$

and the relationship between free F and internal U energies:

$$U = F + TS\,. \tag{8}$$

We obtain a system of equations (4)-(8), with respect to which we set the problem to express thermodynamic quantities *U*, *F*, C_V and *S* through the parameters *b*, *B* and *C* found for equation (2).

Transposition of the dependencies *V*(*T*) and *T*(*V*) in equation (3) allows to manipulate equations (4)-(8) (integrate, differentiate and plot) in two variants separately: when the values *U*, *F*, C_V and *S* depend only on pressure *P* and when they depend only on temperature *T*. Under these conditions, the three caloric equations of state for *U*, *F*, and *TS* with integration constants $c_{(U)}$ (V,T) and $c_{(F)}$ (V,T) directly follow from the thermal equation (2):

$$U = -2.5BT^2 / V^{0.4} + c_U, \tag{9}$$

$$F = -RT\ln\left(V-b\right) + 2.5\left(BT^2 - CT\right) / V^{0.4} + c_F, \tag{10}$$

$$TS = RT\ln\left(V-b\right) - 2.5\left(2BT^2 - CT\right) / V^{0.4} + c_U - c_F, \tag{11}$$

as well as expressions for heat capacity C_V and entropy *S*:

$$C_V = -5BT / V^{0.4} + \partial c_U / \partial T, \tag{12}$$

$$S = R\ln\left(V-b\right) - 2.5\left(2BT - C\right) / V^{0.4} + \left(c_U - c_F\right) / T. \tag{13}$$

Fitting equations (9)-(13) to the reference data from the IAPWS database [12] yields the integration constants, which in binomial terms are presented in Tables 2 and 3. Illustrative material of the fitting is presented in Figs. 2 and 3. The calculated dependencies are in good agreement with the reference data.

The presence of the shift parameter *Z* in the integration constants $c_{(U)}$ (V,T) and $c_{(F)}$ (V,T) makes it possible to calculate the energy spectrum of liquid water in absolute terms by distributing the energy curves referenced to the triple point 0 ºC in Fig. 2a vertically with respect to the absolute temperature 0 K in Fig. 2b. We use the fact, discovered by us earlier, that the evaporation energy $E_{\mathrm{ICP}}$is uniquely related to the density ρ [34,36]:

$$E_{\text{исп}} = \frac{qp\rho^{5/3}}{2^{4/3}\pi\varepsilon_0 m^{5/3}}\ [\text{kJ-kg}^{(-1)}], \tag{14}$$

where m = 3.1-10^{-26}kg and p = 6.14-10^{-30}Cl-m are the mass and dipole moment of the $\mathrm{H}_{(2)\,\mathrm{O}}$molecule, q = 1.6-$10^{(-19})$ Cl is the elementary charge, ε_0= 8.85-$10^{(-12)}$F-$\mathrm{m}^{(-)\,(1)}$is the dielectric constant of vacuum. Fig. 2a shows that the dependence $F(T)$, shifted upward by 1250 kJ/kg well, within the error ±5%, lies on the curve $½E_{(\mathrm{ICP})\,(}T)$. On this basis we establish

$$F = E_{\text{исп}}/2, \tag{15}$$

and the energy 1250 kJ/kg is set as the zero level for all energy curves. Accordingly, we recalculate the constants $c_U$and $c_{(F)\ of}$the first column of Table 2, containing the parameter Z, into the constants of the second column. The curves with the new $c_U$and c_F, expressed in absolute units, are shown in Fig. 2b. The recalculated entropy curve $S(T)$ in absolute terms is shown in Fig. 3c.

From equations (10), (14) and (15), an expression for the density ρ of liquid water follows:

$$\rho = 4m\left(\frac{10^6\pi\varepsilon_0 F}{qp}\right)^{3/5}\ [\text{kg-m}^{(-3)}]. \tag{16}$$

In graphical representation, it is shown in Fig. 3a. As can be seen, the calculated curve corresponds to the reference points with high accuracy.

The transformation of equation (1) into equations (2) gives a new analytical expression for the internal pressure $P_{(i)}$ (second summand). A comparison of the new P_i with the generally accepted one [37] is presented in Fig. 4. As can be seen, the curves $P_{(i)}$ (T) are close in the range of intermediate temperatures 400-600 K, but the dependence $P_{(i)}$ (T) of equation (2) goes further to the right beyond the critical point and provides an opportunity to calculate isochores already in the gas phase. The calculated phase diagram is qualitatively close to the reference one and completely coincides with it at low pressures.

DISCUSSION

The central result of the present work is that the gas approach used, simple against the background of other research methods, gives a definitely positive result - the possibility to predict the thermal and caloric characteristics of liquid water by simple algebraic expressions proceeding from one general formula (2). Equation (2) turns out to be simple and comprehensive.

For the first time, the hypothesis (15) based on the virial theorem [38] was applied to describe the properties of liquid water. The reason for the application of this theorem was obtained from the analysis of dielectric spectra of liquid water [30,34]. We found that liquid water can be considered to consist of free particles (molecules and ions) that make thermal collision motion and are pulled together in volume V by electrostatic ion-dipole interaction. The picture meets the requirements of the virial theorem, according to which at internal coupling of particles in a bounded space the average kinetic energy of particles E_{KIN} is related to the average potential energy $E_{(\mathrm{POT})}$ as $E_{\mathrm{KIN}} = n/2 \cdot E_{\mathrm{POT}}$, where n is the degree of potential energy as a homogeneous algebraic function of coordinates [39]. When, for example, $n = 2$, the average kinetic energy is equal to the average potential energy, and each of them is equal to half of the total energy - this is the result for a linear oscillator.

For liquid water, the potential energy of its particles $E_{POT}$is reliably demonstrated by the temperature curve of water evaporation (decomposition)$E_{(ICP)}$ [2]. We established the functional expression $E_{(COI)}(T)$ in the form of equation (14) earlier in [34,36]. Now we take half of the decay energy $E_{(COI)}(T)$ as the energy of mutual attraction of molecules. This energy, competing with the energy of thermal expansion of molecules $\sim k_{(B)\,T}$, provides a steady state of liquid water: the free energy $F(T)$ in the form (10) has the fundamentally required minimum (we do not demonstrate it graphically). In favor of the legitimacy of using the virial theorem in application to water is evidenced by the accurate description (without additional fitting) of the density of liquid water $\rho(T)$ by means of the model curve (16), as shown in Fig. 3a. Equation (16) is particularly valuable in that it relates the density of liquid water $\rho(T)$ to the microscopic parameters of the particles: mass m, charge q, and dipole moment p.

The agreement of the calculated $\rho(T)$ curve in Fig. 3a with the reference data extends over a wide temperature range of 300-630 K, but the famous density anomaly in the region of 4 °C is not conveyed by the model. To this it should be said that although the anomaly is textbook due to its vital importance [40-42], it unfolds in a very narrow temperature range (less than± 1 K) and can be correctly interpreted only when the large-scale course of the entire $\rho(T)$ dependence is understood.

Hypothesis (15) allows us to plot the energy spectrum of liquid water in absolute terms, as shown in Fig. 2b. The model curves naturally behave in the limit of low temperatures: the entropic part of the free energy TS tends to zero, and the values of U and F equalize [4]. A shift of ΔF = 1250 kJ/kg gives two curve crossings, both at 0 °C. The temperature 0 °C turns out to be the point of equality of the two parts of internal energy. The same temperature becomes the point of equality of kinetic and potential energies, as well as the beginning of their change with increasing temperature.

In the modified equation (2), the internal pressure $P_{(i)}$ (second summand) takes a new analytical form compared to P_i in the original equation (1). The value of P_i has an independent important value, because it is directly related to other properties of water: isobaric expandability, isothermal compressibility, and surface tension [4]. In Fig. 4 the found dependence $P_{(i)}(T)$ is compared with the generally accepted dependence [37]. The two dependences are close in the intermediate temperature range of 400-600 K, but the new one passes further to the right beyond the critical point in the phase diagram. This allows us to calculate the isochorus pattern using equation (2), which, as can be seen, is qualitatively similar to the reference one. Interestingly, although the modeling goes beyond the initial assumptions (equation (3) is violated), the predictive ability of equation (2) is preserved.

In Fig. 1b, in the region of high pressures, the curves noticeably deviate from the reference points. The agreement can be improved by increasing the constant R in equation (2), but we do not do it, leaving the first term purely "gas", van der Waals, to escape from the known problem of the difference of the gas constant R for critical and room temperatures [26,43]. The latter for water is one and a half times larger than the former. This is interpreted as follows: since the value of R *is* by definition proportional to the number of "structural units" in a mole of a substance, water molecules are partially bound into complexes in the critical state (in a strongly compressed gas at high temperature). The problem of supramolecular structuring of liquid water - clustering, ice-like, coexistence of phases of high-low density, etc. - is extensive and hotly debated [44-49]. It is independent, and we do not discuss it in this paper.

CONCLUSION

With the present work we continued the discussion on the appropriateness of applying the gas-ion-molecular approach to the study of the properties of liquid water. The central result of the work was the very fact of successful prediction of reference data by a real gas model. The gas approach for liquid water is fundamentally new. It opens a simple algebraic access to thermodynamics, the possibility of fast and systematic handling of myriads of tabular data, the possibility of tracking the parameters encrypted in them. We have proposed algebraic relations that consistently and adequately betray the thermodynamic parameters of liquid water. The formulas are convenient for further modeling and detailed analysis of the revealed regularities.

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Table 1. Parameters of the original VdV equation (1) [26] and the modified version (2).

Parameter	VdV [26]	Modif. ver.
R, J/(kg-K)	460	460 (const)
b, dm^h/kg	1.7	0.74 (const)
a, MPa-m^6/kg^2	1700	-
Degree indicator	2	1.4 (const)
B, J/(kg-K$^{2)}$ -(dm^s/kg)$^{0.4}$	-	2.5 ± 0.3
C, J/(kg-K)-(dm^s/kg$^{)(0.4)}$	-	2500 ± 300

Table 2. Integration constants $c_U$and $c_F$for the dependences $U(T)$ and $F(T)$: 1) referenced to the 0 °C triple point; 2) calibrated by equation (15).

	1. RH. 0 °C	2. abs. from equation (15)
c_U, kJ/kg	$XT^2 + YT - Z$	$XT^2 + YT + 1050$

c_F, kJ/kg	$-3.7XT^2 + YT$	$-3.7XT^2 + YT + 1250$
$c(U) - c(F)$, kJ/kg	$4.7XT^2 - Z$	$4.7XT^2 - 200$

Table 3. Coefficients of the integration constants c_U and c_F, presented in Table 2.

X, kJ/(kg-K^2)	0.0027 ± 0.0002
Y, kJ/(kg-K)	6.5 ± 0.2
Z, kJ/kg	1450 ± 100

FIGURE CAPTIONS

Fig. 1. Isotherms (a) and isochores (b) of liquid water. Thin lines at the top right are calculations using the VdV model (1). Dots - IAPWS reference data [12], lines above the dots - calculation by the modified model (2).

Fig. 2. Temperature dependences of the internal energy of liquid water U, entropic part TS, evaporation energy E_{ICP} and free energy F: a) referenced to the triple point 0 ºC) and b) in absolute terms (distributed in the spectrum vertically). Dots - IAPWS reference data [12], lines - calculation by formulas (9)-(11).

Fig. 3. Temperature dependences of density ρ (a), isochoric heat capacity $C_{(V)\ (b})$ and entropy S (c) of liquid water. Dots are reference data [12,35], lines are calculations using formulas (16), (12) and (13), respectively. For completeness of the picture, the isobaric heat capacity $C_{P)\ (b}$ is also given.

Fig. 4. Phase diagram of water in isochoric representation. Dotted lines - internal pressure $P_{(i)}$ (T)according to formula (2) and from [37]. Solid dark lines - IAPWS reference data [12], light lines - calculation by formula (2).

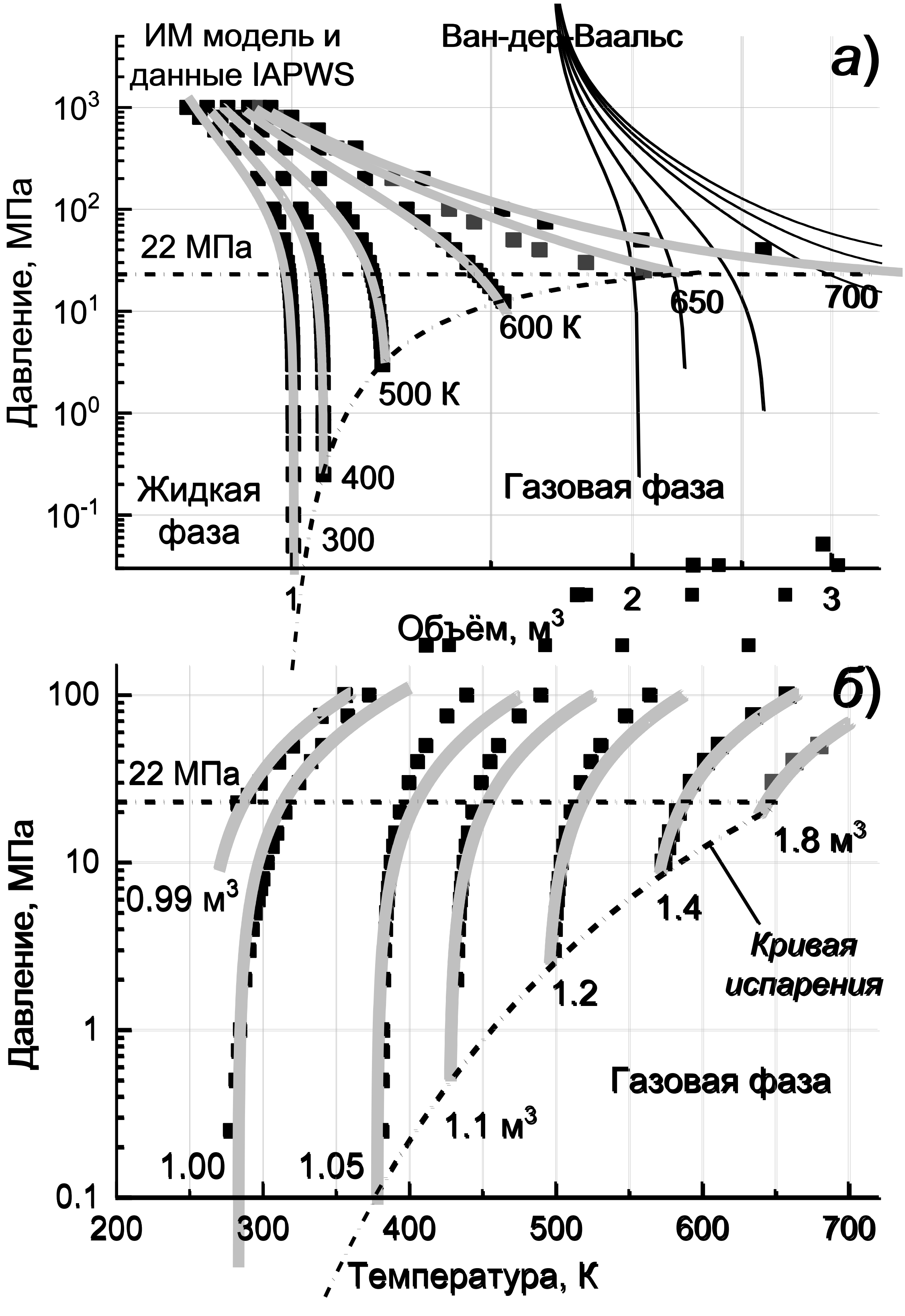
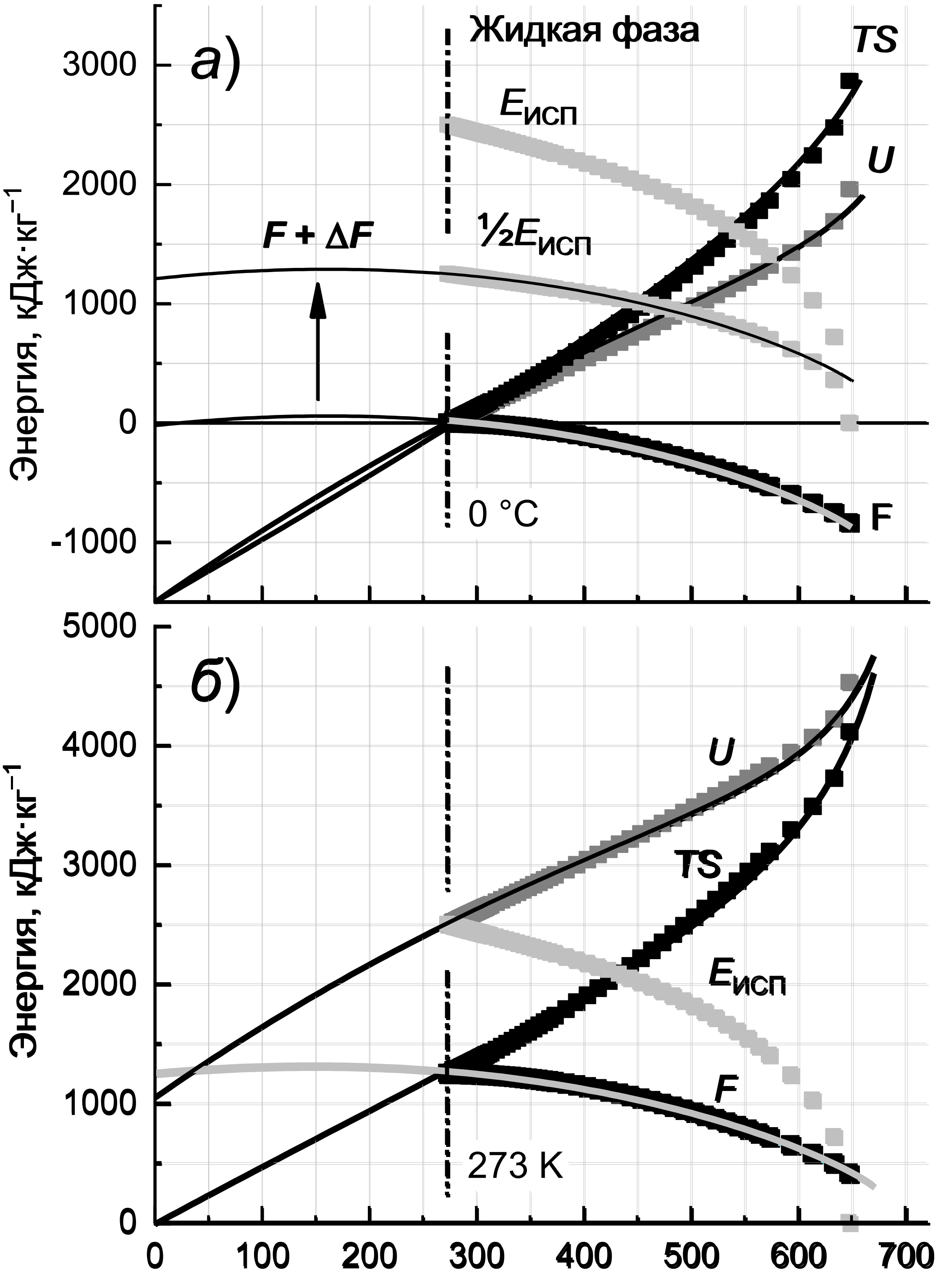

ИМ модель и данные IAPWS
Ван-дер-Ваальс
а)
Давление, МПа
10^3
10^2
10^1
10^0
10^{-1}
22 МПа
600 К
650
700
500 К
400
300
Жидкая фаза
Газовая фаза
1
2
3
Объём, м^3
б)
100
10
1
0.1
0.99 м^3
1.00
1.05
1.1 м^3
1.2
1.4
1.8 м^3
Кривая испарения
200
300
400
500
600
700
Температура, К

Fig. 1.


а)
Жидкая фаза
TS
Eисп
U
F + ΔF
½Eисп
0 °C
F
3000
2000
1000
0
-1000
Энергия, кДж·кг⁻¹
б)
U
TS
Eисп
F
273 K
5000
4000
3000
2000
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Энергия, кДж·кг⁻¹
0
100
200
300
400
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600
700
Температура, К

Fig. 2.

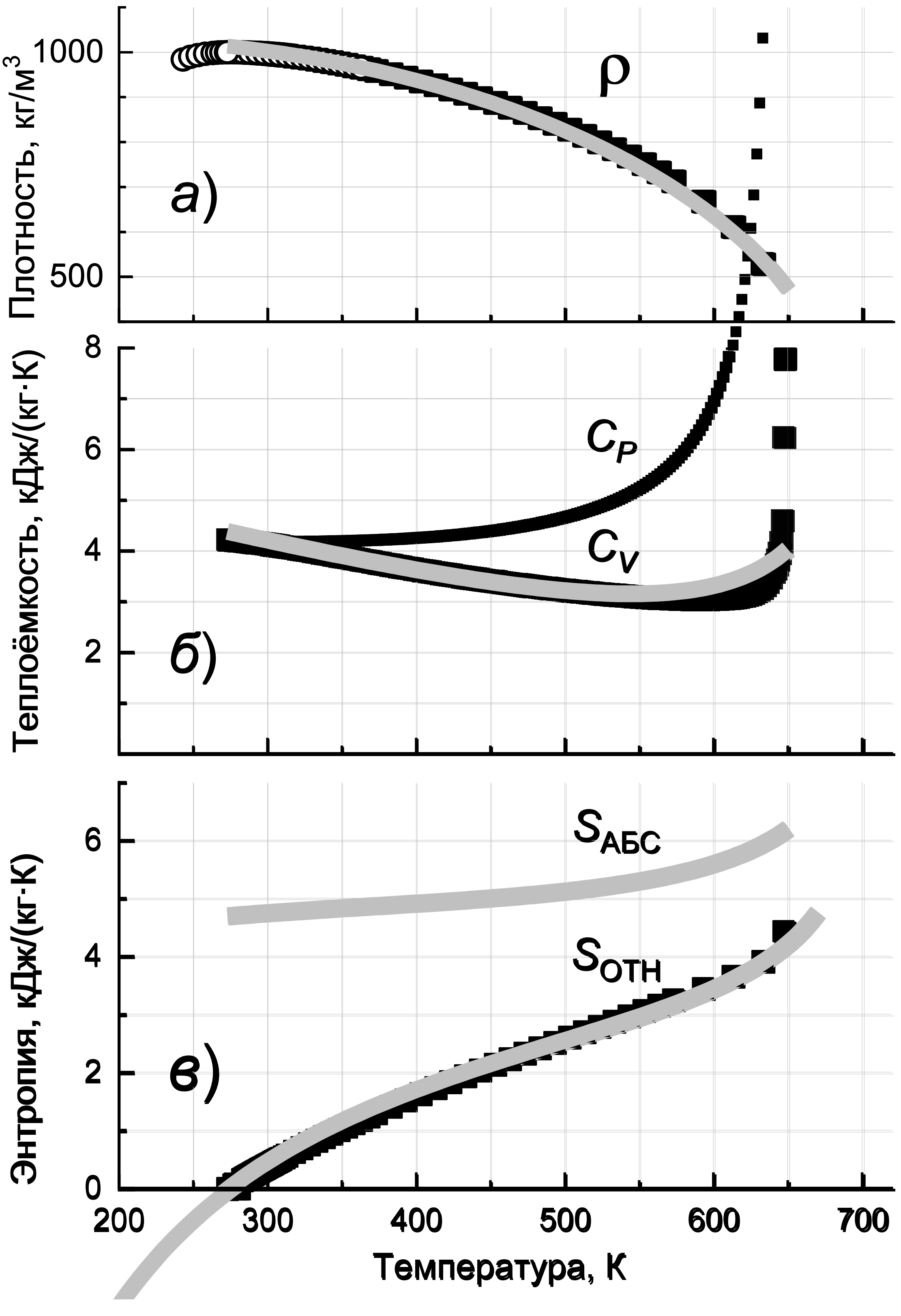
Плотность, кг/м³
1000
500
ρ
а)
Теплоёмкость, кДж/(кг·К)
8
6
4
2
C_P
C_V
б)
Энтропия, кДж/(кг·К)
6
4
2
0
$S_{АБС}$
$S_{ОТН}$
в)
200
300
400
500
600
700
Температура, К

Fig. 3.

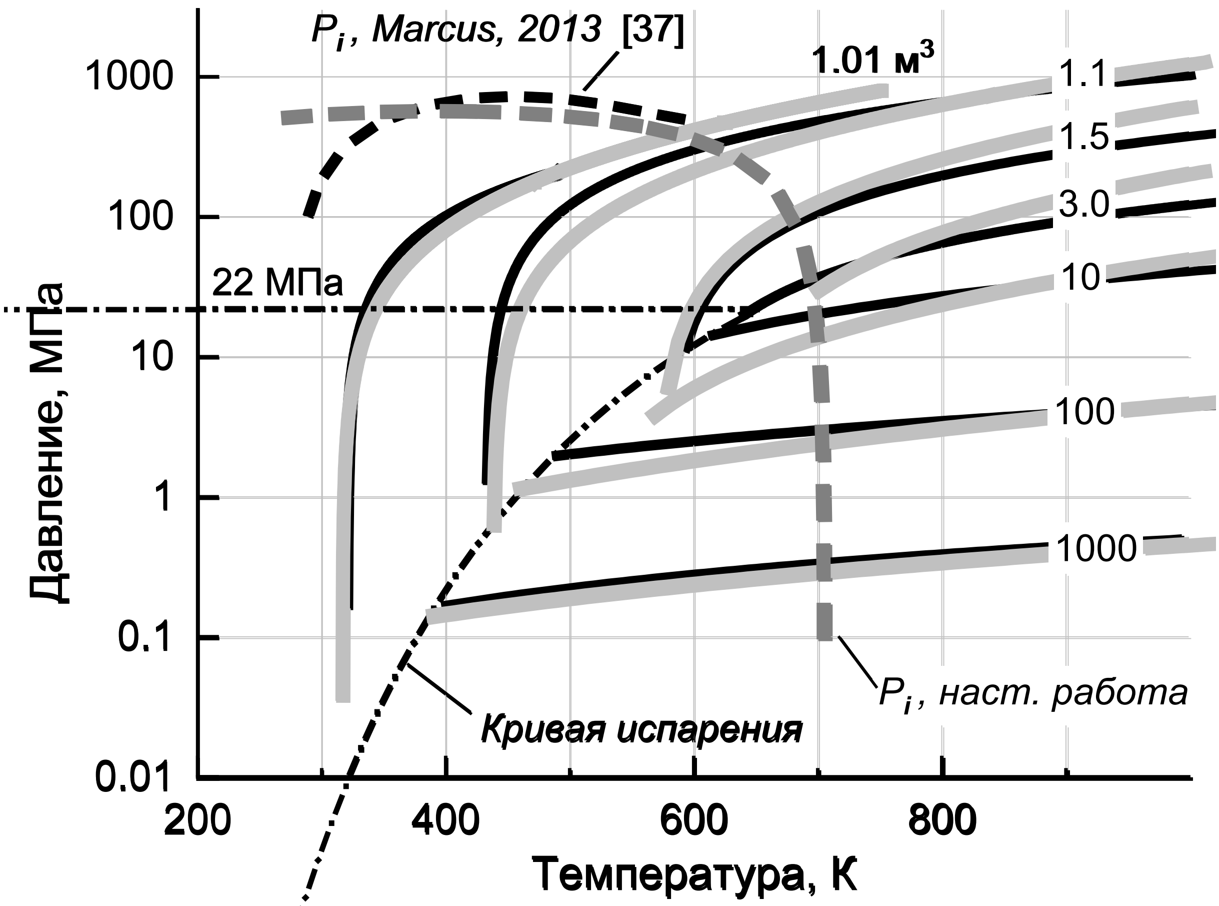
P_i, Marcus, 2013 [37]
1.01 м³
1.1
1.5
3.0
10
100
1000
22 МПа
P_i, наст. работа
Кривая испарения
1000
100
10
1
0.1
0.01
200
400
600
800
Давление, МПа
Температура, К

Fig. 4.