

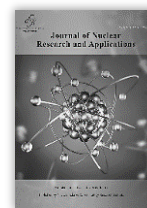


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## Thermophysical Properties of Light and Heavy Water from Second Virial Coefficient; Isotopic Substitution Effect

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### ABSTRACT

In this paper, some thermophysical properties of light and heavy water will be predicted and modeled using the virial equation of state (VEOS), and the effect of isotopic substitution will be studied. In this respect, by fitting the experimental and theoretical data of the second virial coefficient of light and heavy water in the temperature range of 300 to 1800 K, a new equation will be presented, using which the thermodynamic properties of the aforementioned fluids will be predicted  $300 \leq T \leq 1000 \text{ K}$  and  $0.1 \leq P \leq 2 \text{ atm}$ . The results are compared with the experimental data to evaluate the model and the new equation of the second virial coefficient. The results show that this approach has a very good ability to predict the thermophysical properties of light and heavy water. It will also demonstrate that deuterium isotopic substitution reduces the attractive interaction between molecules, especially above the critical temperature, and this causes the difference in the thermodynamic properties of the two fluids. The calculations performed in the above temperatures and pressure range using virial coefficients to determine thermophysical properties of light and heavy water and also the investigation of the effect of isotopic substitution are novelties of this article.

**Keywords:** Light Water, Heavy water, Second virial coefficients, Thermophysical properties

### 1. Introductions

Chemically, water is one of the simplest and most important substances. Both of them are widely used in the industry. For example, heavy water has many applications in industry due to its excellent nuclear and thermal properties. Both will be used as a moderator in nuclear

reactors because they have a small cross-section for neutron capture.

Water is an associating fluid that has a hydrogen bond. Many of the thermodynamic properties of water are dependent on the H-bonds (light and heavy). For instance, As a result of lowering the temperature to below  $4^\circ\text{C}$ ,

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the molar volume increase. A H-bond is responsible for this unusual behavior of water. The important role of H-bonds in the formation of the interesting properties of water is generally accepted. In fact, for the correct interpretation of many facts of the thermophysical behavior of these fluids, it is necessary to discuss the behavior of the average number of H-bonds per molecule. In this regard, Fisenko *et al.* have shown that the temperature dependence of the average number of H-bonds per molecule ( $n_H$ ) on the vapor-liquid coexistence curve is described by the following equation [1].

$$n_H(t) \approx 4 (1 - 0.83 t) \quad (1)$$

in which  $t = T/T_c$ . Therefore, near the melting and critical points take values:  $n_H(T_m) \approx 2.61$  and  $n_H(T_c) \approx 0.68$ . As can be seen, increasing temperature causes a decrease in the average number of H-bonds per molecule. As a fact, this behavior can be seen in all associated fluids. In this manner, Bulavin *et al.* have shown that the qualitative analysis of non-equilibrium water properties, determined by long-living molecular configurations, arises due to H-bonds [2]. In their paper, more definitely, peculiarities of the kinematic shear viscosity of water and its connection with structural parameters of the H-bond network have been carefully investigated. In another paper, Bulavin *et al.* investigated the collective contributions of self-diffusion coefficients of liquids and the effects of H-bond on them, especially for normal and super-cooled water [3].

Lishchuk *et al.*'s analysis has demonstrated that the main thermodynamic properties of light and heavy water in the wide temperature interval are argon-like [4]. Such a similarity takes place for the specific volume and the evaporation heat per molecule at temperatures  $315 \text{ K} < T < 550 \text{ K}$ . It was shown that this

phenomenon is caused by the averaged inter-particle potentials which form due to the rotation of water molecules.

Due to the importance of light and heavy water and the wide range of applications, their thermodynamic properties of them have been studied experimentally and theoretically. The advantage of theoretical research is that it allows the thermophysical behavior of materials to be modeled. Modeling the thermodynamic properties of materials is critical to predict their thermodynamic behavior in different conditions. For light and heavy water, Hill *et al.* developed a fundamental equation for heavy water in the range of up to 100 MPa and 870 K [5]. By using that equation, many of the thermodynamic properties of heavy water have been calculated. In this sense, Kestin *et al.* also presented a fundamental equation in canonical form for the determination and prediction of some thermophysical properties of water and heavy water [6]. In recent years, Herrig *et al.* presented an empirical fundamental model of EOS for heavy water fluids [7]. The equation is explicit in the reduced Helmholtz energy and allows the calculation of all thermodynamic properties over the whole fluid surface.

In the among equations of state, the virial equation of state (VEOS) has an important position. This EOS which is based on statistical mechanics, shows the non-ideal behavior of real fluids.

In this paper, at first, the new equation of the second virial coefficient of light and heavy water will be determined and then using it, some thermodynamic properties of fluids H<sub>2</sub>O and D<sub>2</sub>O are predicted and modeled by the virial equation of state (VEOS). In this respect, the effect of isotopic substitution will be studied. This approach is a novel approach to investigate the thermodynamic properties of light and heavy water and the effects of isotopic substitution on them.

## 2. Virial equation of state (VEOS)

The thermodynamic properties of materials (pure or mixture) and their surfaces and transfer properties can be predicted and modeled by equations of state [8-10]. One of the most widely used equations the virial equation of state (VEOS) which has been used extensively to study the thermodynamic properties of gases and is based on statistical mechanics

$$Z = 1 + \sum_{n=2} B_n^+ P^{n-1}$$

or

$$Z = 1 + \sum_{n=2} B_n \rho^{n-1} \quad (2)$$

in which

$$B_2^+ = B_2 / RT$$

$$B_3^+ = (B_3 - B_2^2) / R^2 T^2 \quad (3)$$

It is better to be considered  $B_2 \equiv B$  and  $B_3 \equiv C$ . In above-mentioned equations,  $Z$  is the compressibility factor ( $Z = PV_m / RT$ ),  $\rho$  is the density ( $\rho = 1/V_m$ ), and  $B_n$  is  $n$ th-virial coefficient related to intermolecular interactions based on statistical mechanics. For example, for the second coefficient  $B$ , we have

$$B = -2\pi \int_0^\infty [e^{-u(r)/RT} - 1] r^2 dr \quad (4)$$

where  $u(r)$  is a function of the intermolecular interaction energy between two molecules. As seen, the second virial coefficient represents the interaction of two molecules in a fluid. Similarly, if the density of a fluid is high enough, the simultaneous interaction of three or even four molecules in the cluster can be imagined. In this case, the third virial  $C$  or fourth virial  $D$  coefficients must be used in the virial equation to calculate the thermodynamic properties of the fluid.

If there is no interaction between the molecules, all the virial coefficients will be zero. In this case, the behavior of the fluid will be like an ideal gas. Because of this, VEOS shows the non-ideal behavior of real fluids. Therefore, virial coefficients and virial equation of state (VEOS) provide a link between microscopic and macroscopic properties, showing their non-ideality, and therefore, can accurately predict and model fluid thermophysical properties.

The virial coefficients can be obtained with various theoretical and experimental methods [11-18]. Experimental methods consist of  $PVT$  measurements, speed of sound measurements, Joule-Thomson measurements, refractive index, and relative permittivity measurements, and vapor pressure and enthalpy of vaporization measurements. Theoretical approaches usually consist of using equations of state and interaction potential functions.

The existence of two-molecule and three-molecule interactions in the fluid and the importance of determining the second and third virial coefficients to study the properties of the fluid have led to many studies by various researchers to determine these coefficients accurately. Some of them have provided exact correlation equations for these coefficients for many molecules [19-28]. As an example, Boushehri et al presented a correlation function of second virial coefficient for linear, near-linear, and near-spherical molecules in 1987 [29]. Zarkova *et al* presented  $B(T)$  for eleven heavy gases [30] and pure small alkanes [31] and Meng *et al* have developed a correlation for  $B(T)$  and  $C(T)$  of pure fluids based on corresponding state principle [32]. We also calculated the second virial coefficient of various fluids using two models, van der Waals and Dieterici equations of state [13, 14, 33].

As shown in Equation 2, the compressibility factor ( $Z$ ) in the virial equation of state can be

written as the expansion by pressure or density in which expansion coefficients are virial coefficients. At low pressure or density, third terms of it onwards can be ignored in the expansion and we have

$$\begin{aligned} Z &= 1 + B\rho \quad \text{or} \\ Z &= 1 + B^*P \end{aligned} \quad (5)$$

Therefore, using equation 5 and having only the exact second virial coefficient ( $B$ ), many thermodynamic properties of fluids at low pressure or density can be predicted and modeled. In the previous papers, many of the thermodynamic properties of fluids like SF<sub>6</sub>, UF<sub>6</sub>, and some refrigerants have been calculated and modeled by this approach [34-36].

In this work, by the fitting experimental and theoretical second virial coefficient of light and heavy water, a new equation of  $B$  will be presented and the effect of isotopic substitution will be studied. Then, by using the new equation, some thermophysical properties of water (light and heavy) at low pressure are calculated and modeled, and compared with experimental data in order to evaluate the new equation presented. In this paper, the following thermophysical properties of light and heavy water at low pressure will be modeled by mentioned approach.

### 2.1 Molar volume

At low pressure, molar volume can be calculated using the second virial coefficient as follows [37]

$$V_m = \frac{RT}{P} + B \quad (6)$$

### 2.2 Thermal expansion

Thermal expansion is one of the properties of materials including solids, liquids and gases. This property indicates the rate at which a substance expands during temperature

changes. The thermal expansion coefficient is given by

$$\alpha = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_p \quad (7)$$

This function depends on virial coefficient. At low pressure we have [36]

$$\alpha = \frac{1}{V_m} \left( \frac{R}{P} + \frac{dB}{dT} \right) \quad (8)$$

### 2.3 Bulk modulus

Bulk modulus is a thermodynamic property of fluids. It is a measure that shows how resistant the material is to pressure. Bulk modulus is defined as the ratio of the infinitesimal pressure increase to the resulting relative volume decrease or density increase as follows

$$\beta_T = \rho \left( \frac{\partial P}{\partial \rho} \right)_T \quad (9)$$

Like the thermal expansion of the fluid, bulk modulus can be written based on the virial coefficients. At low pressure we have

$$\beta_T = RT(\rho + 2B\rho^2) \quad (10)$$

### 3. New equation of second virial coefficient of water

The second virial coefficient of water (light and heavy) is a fundamental quantity. Besides, the study of these coefficients by themselves is useful. In addition, the knowledge of the second virial coefficient of water is required to extract information on the cross-second virial coefficients from the water vapor mixture data. These cross-coefficients are needed for accurate thermodynamic descriptions of a variety of systems, such as combustion gases and

humidity standards [17,38]. As mentioned, experimental and theoretical methods can be used to calculate virial coefficients. The second virial coefficient of a fluid can be derived from accurate *PVT* measurements, which often involve a successive expansion of the fluid. Reliable values of  $B(T)$  at some temperatures may also be obtained from vaporization data. This calculation is done through the Clapeyron equation. The second virial coefficient and its temperature dependence can be obtained from the function  $\phi^\circ (=B - TdB/dT)$ .  $\phi^\circ$  is related to the low-pressure limit of the Joule-Thomson coefficient. If the intermolecular pair potential is accurately known, the second virial coefficient can be obtained from statistical mechanics.

For light water (H<sub>2</sub>O), scholars determined its second virial coefficient using different approaches [17, 38-44]. Also, the second virial coefficient of heavy water (D<sub>2</sub>O) was determined by researchers theoretically and experimentally [46-48]. However, experimentally, it is not possible to find samples of heavy water that are completely and 100% free of light water. These samples are contaminated with different amounts of H<sub>2</sub>O and HDO. But as Herrig *et al* stated, the D<sub>2</sub>O content of the samples reviewed in the relevant references has been considered in order to estimate the experimental uncertainty of the data to fit them

for their modeling and to obtain an equation of state for them [7]. Therefore, their very small amount has not had an impact on modeling and determining the equation of state for them.

This work presents a new equation for the wide range of temperature using experimental and theoretical data of second virial coefficient. To obtain a new equation, numerical analysis was applied to fitting the  $B(T)$  data of Harvey and Lemmon [17], KKHM [39], Keyes [40], Lefevre [41], Abdulagatov [42], Hill and MacMillan [43], and Kell [45]. The final equation is

$$B_r(T_r) = \sum_{n=0}^6 \frac{A_n}{T_r^n} \tag{11}$$

in which  $B_r = B/V_{m,c}$ ,  $T_r = T/T_c$  and  $A_n$  are expansion coefficients of the equation and tabulated in Table 1. In this fit to obtain the final equation, R<sup>2</sup> = 0.9997 and 1.0 for light and heavy water respectively.

Figures 1 and 2 show the deviation plots obtained from equation (12) for the second virial coefficient of light and heavy water respectively. The work differs slightly from the others, as seen. Deviation plot of this work from the others =

$$\left( \frac{B_{this\ work} - B_{others}}{B_{this\ work}} \right) \times 100 \tag{12}$$

**Table 1.** Critical properties of H<sub>2</sub>O and D<sub>2</sub>O and the expansion coefficients of Equation (11).

Molecule	T <sub>c</sub> (K)	V <sub>m,c</sub> (cm <sup>3</sup> /mol)	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>
H <sub>2</sub> O	647.096	55.948	0.9917	-4.1211	4.5991	0.084	-6.614	4.6583	-1.0783
D <sub>2</sub> O	643.89	55.944	-1.4546	14.66	-41.387	51.49	-35.115	12.057	-1.7714

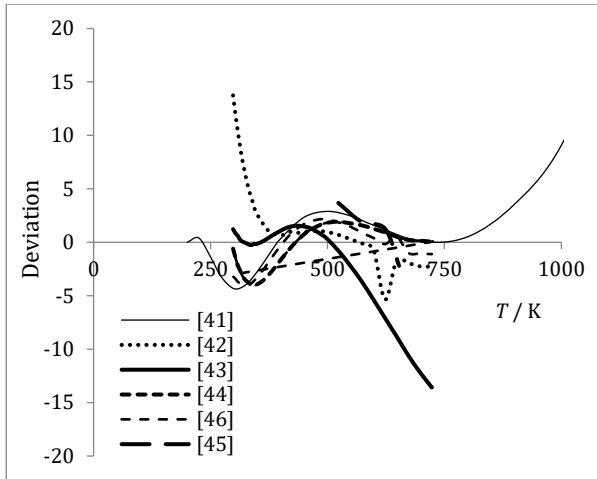


Fig. 1. Deviation plot of this work from the others for heavy water.

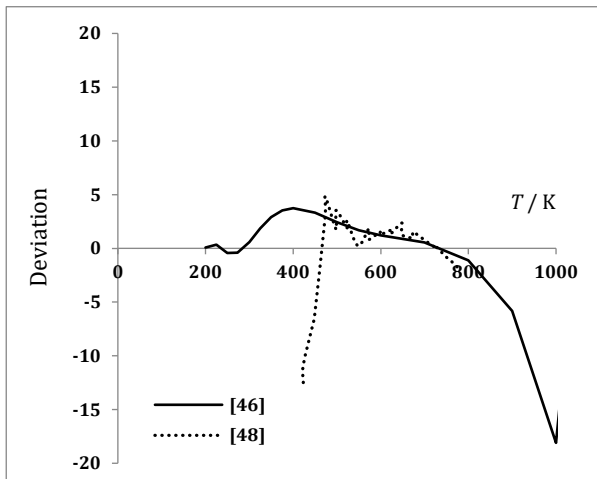


Fig. 2. Deviation plot of this work from the others for light water.

#### 4. Results and discussion

In this paper, a new equation of the second virial coefficient of light and heavy water is presented, some thermophysical properties of them are calculated and modeled and the effect of isotope substitution is determined. It should be noted that the study of thermodynamic properties of water in the so-called place is limited to the low density and pressure. Due to intermolecular interactions in clusters of three or four molecules, it must be used as the third and fourth virial coefficients at high pressure and density.

The Boyle temperature ( $T_B$ ) can be defined as the point in the temperature range where a

real gas begins to behave like an ideal gas over a range of pressures. The temperature at which the second virial coefficient becomes zero is known as Boyle temperature  $B(T_B)=0$ . The volume of the fluid at Boyle temperature is called Boyle volume

$$V_B = T_B \left( \frac{\partial B}{\partial T} \right)_{T=T_B} \tag{13}$$

Boyle Temperature ( $T_B$ ) and Boyle Volume ( $V_B$ ) are sensitive to the equation practically so, in this article, they were determined using the new equation and compared with other sources [17, 43, 46]. The results are shown in Table 2.

Table 2. Calculated Boyle Temperature ( $T_B$ ) and Boyle Volume ( $V_B$ ) of studied molecules.

Molecule	$T_B$			$V_B$
	This work	Source	Error value	
H <sub>2</sub> O	1730.6	1545.5	11.97	33.921
		[17]	4.08	
		1662.6		
D <sub>2</sub> O	1170.7	1239.8	5.57	77.725
		[46]		

The evaluation of the strength of intermolecular interactions and their comparison with each other can be studied by calculating the second virial coefficient. As mentioned,  $B(T)$  depends on intermolecular interaction, so with increasing intermolecular attractive forces, it decreases and  $T_B$  increases.

As seen in Figure 3, at a temperature over critical temperature, the value of  $B(T)$  of studied molecules in comparison with each other is as  $B_{H_2O} < B_{D_2O}$  and Table 2 also shows that the order of  $T_B$  increase is as

$T_B(D_2O) < T_B(H_2O)$  and Boyle volume as  $V_B(D_2O) < V_B(H_2O)$ . This subject has been

demonstrated in Figure 4. As observed, the deviation (calculated by equation 14) rises sharply above the critical temperature of the water.

$$(14)$$

$$\text{Deviation of } B \text{ of the molecules} = \left| \frac{B(H_2O) - B(D_2O)}{B(H_2O)} \right| \times 100$$

So based on what has been said before, at that range of temperature, H<sub>2</sub>O has a stronger interaction than D<sub>2</sub>O and therefore, isotope substitution D decreases attractive interaction between molecules. Like all associating fluids, since the intermolecular interactions in water mainly depend on hydrogen bonding and, as mentioned earlier,

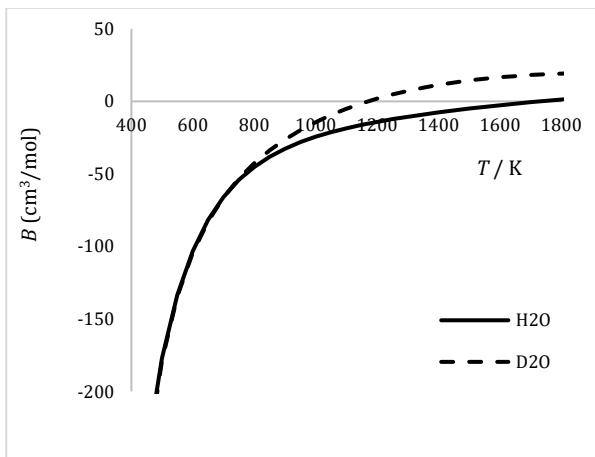


Fig. 3. Second virial coefficients studied molecules as a function of the temperature.

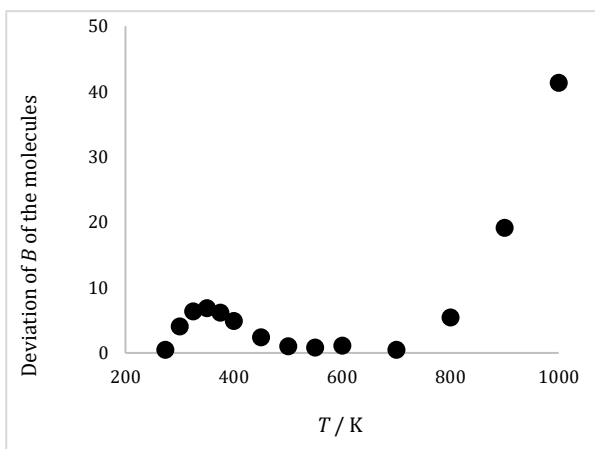


Fig. 4. Deviation of second virial coefficients of studied molecules in terms of temperature.

The average number of H-bonds per molecule ( $n_H$ ) is temperature dependent, so it can be concluded at higher temperatures from the critical temperature,  $n_H$  in light water is more than in heavy water, which reduces the second virial coefficient and the Boyle Volume and increases the Boyle Temperature in the light water compared to the heavy water. From this point of view, the presence of deuterium isotope in water will reduce the hydrogen bond of water at temperatures above the critical temperature.

But, as seen in Figures 4 and 5, at the range  $T_b < T(K) < T_c$ , the second virial coefficient of the two are very close to each other and slightly  $B_{H_2O} > B_{D_2O}$ . This subject was shown by Hill & MacMillan [43] and Kell et al [45] and compared with this work in Figure 5.

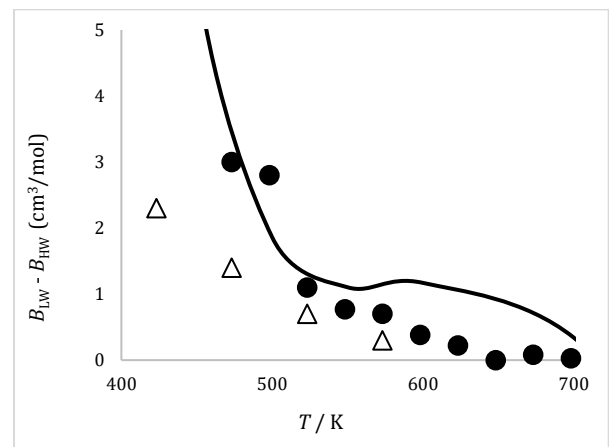
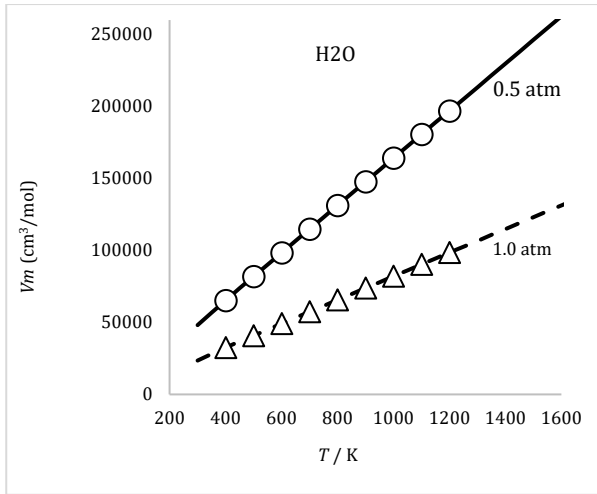
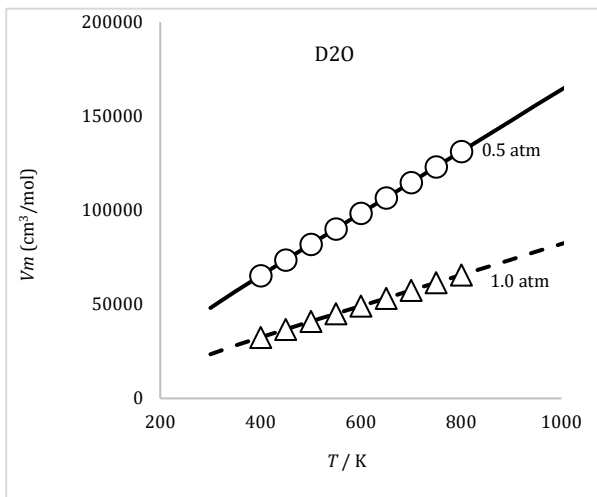


Fig. 5. Differences between Second virial coefficients of studied molecules; line: this work, (●): [45], (Δ): [43].

Figures 6 and 7 show the behavior of the molar volume of the molecules in terms of temperature at two pressures 0.5 and 1.0 atm compared with experimental data [47]. It is known that increasing the temperature beyond 277 K and decreasing the pressure, both increase the molar volume of water (light and heavy). The model presented in this paper has been able to correctly predict the changes in the molar volume of light water and heavy water in a wide range of temperatures.



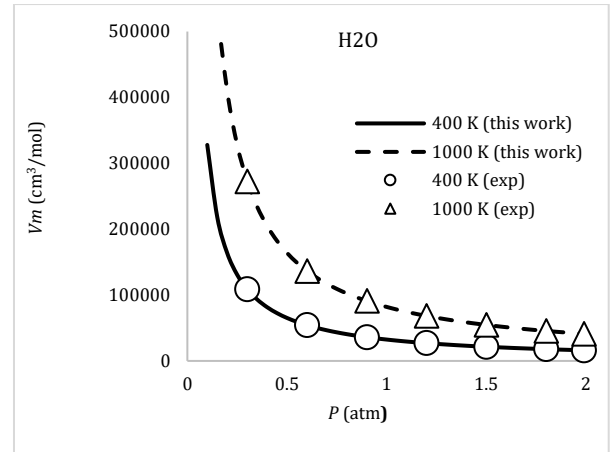
**Fig. 6.** Molar volume of light water as a function of temperature.



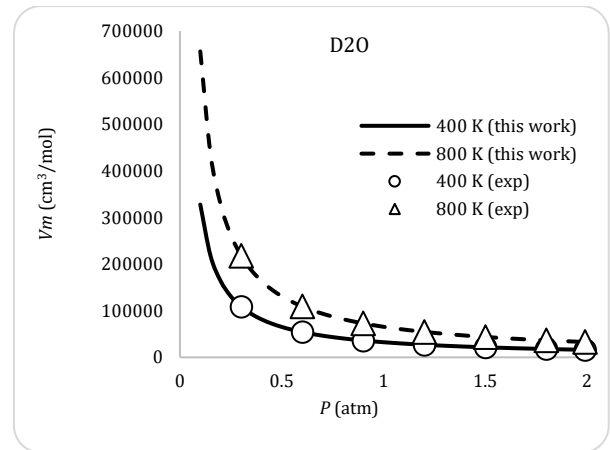
**Fig. 7.** Molar volume of heavy water as a function of the temperature.

Also, Figures 8 and 9 show the variation in the molar volume of the molecules vs pressure at two temperatures. As can be seen, these behaviors are predicted and modeled very well by the new equation and model, qualitatively and quantitatively.

For better consideration, the deviation of molar volume of light and heavy water in terms of temperature at  $P=0.5$  atm in comparison with experimental data [47] is shown in Figure 10. As can be seen, the consistency between the experimental and theoretical data in a wide range of temperatures is very good.



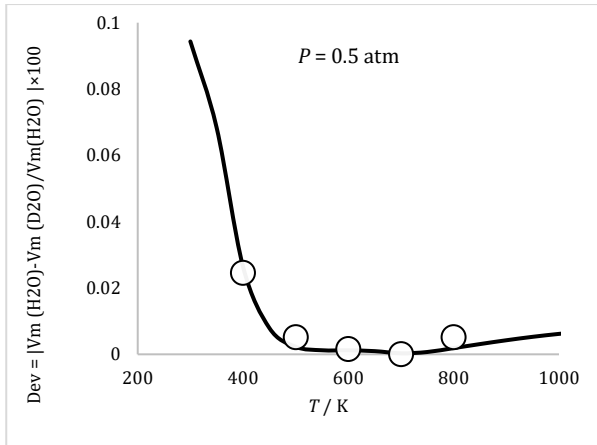
**Fig. 8.** Molar volume of light water as a function of the pressure.



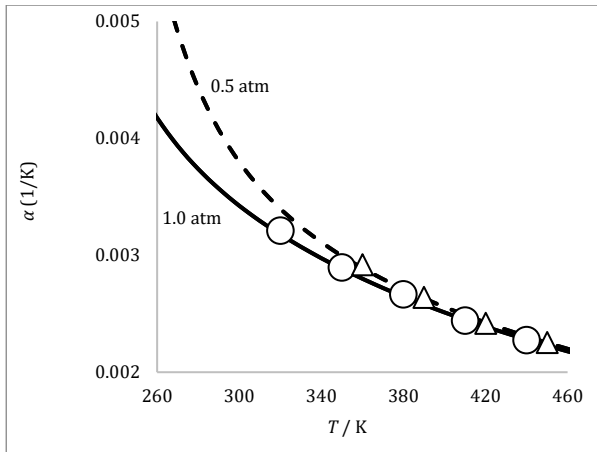
**Fig. 9.** Molar volume of heavy water as a function of the pressure.

It is also clear that, at temperatures below the boiling point, the molar volume of light water with heavy water is different. This fact, which is confirmed by both computational and experimental methods, shows that the average number of H-bonds per molecule ( $n_H$ ) of the two in the mentioned temperature range is different and the reason is the presence of deuterium in the water composition. This is clearly seen in the changes in the coefficient of thermal expansion of these two molecules at temperatures below the boiling point (Figure 13).





**Fig. 10.** Deviation of molar volume of light and heavy water in terms of temperature; line: this work, (O): experimental data [47].

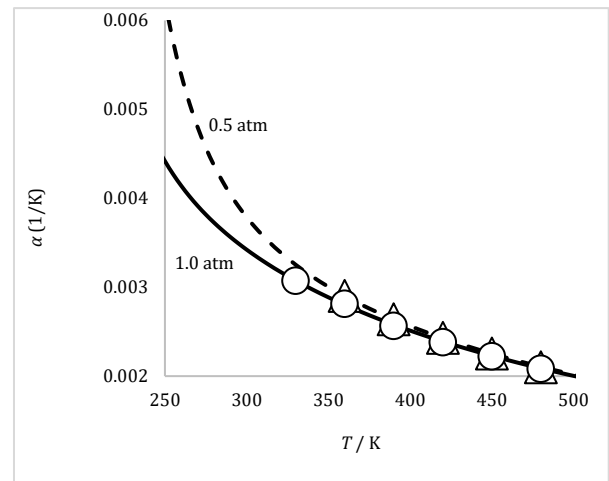


**Fig. 11.** Thermal expansion coefficient of light water vs temperature; line: this work; symbol: experimental data [47].

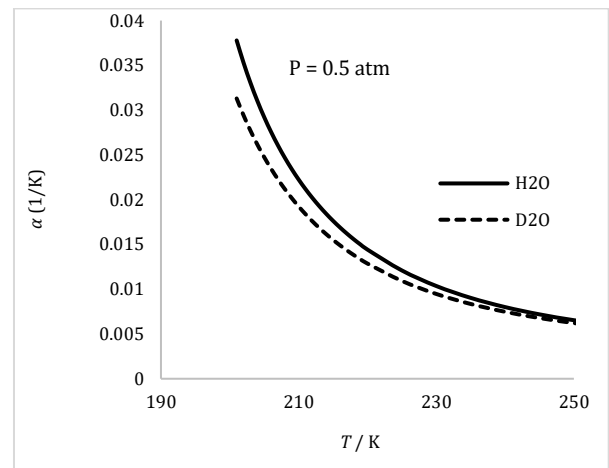
Figures 11 and 12 show the behavior of the thermal expansion coefficient of the molecules in terms of temperatures at two different pressures compared with experimental data [47]. This behavior is predicted and modeled very well by the equation qualitatively and quantitatively. The match of theoretical results from the new equations and experimental data is excellent.

Figure 13 shows the effect of isotopic substitution on thermal expansion. As can be seen, at low temperatures below boiling point, the isotopic substitution reduces thermal expansion but with increasing temperature, the thermal expansion of light and heavy water is the same.

The curve of isothermal bulk modulus for H<sub>2</sub>O and D<sub>2</sub>O as a function of pressure at two temperatures calculated by the equation is shown in Figures 14 and 15 and compared with experimental data [47]. The match of theoretical results from the new equations and experimental data is excellent.



**Fig. 12.** Thermal expansion coefficient of heavy water vs temperature; line: this work; symbol: experimental data [47].



**Fig. 13.** Thermal expansion coefficient of light and heavy water vs temperature at pressure 0.5 atm.

As seen, the curve is completely linear. This linearity is one of the thermodynamic regularities of materials named Tait-Murnaghan regularity. Based on this regularity, the bulk modulus of fluid is nearly linear in pressure for each isotherm [48-49].

$$\beta_T = \beta_{0,T} + \beta'_{0,T}P \tag{15}$$

Where  $\beta_{0,T}$  is  $\beta_T$  in zero pressure and  $\beta'_{0,T}$  is the slope of bulk modulus in zero pressure.  $\beta_{0,T}$  and  $\beta'_{0,T}$  are temperature-dependent parameters. This regularity is predicted very well, qualitatively and quantitatively, by the model. Table 3 shows the value of  $\beta_{0,T}$  and  $\beta'_{0,T}$  at 400 K for light and heavy water.

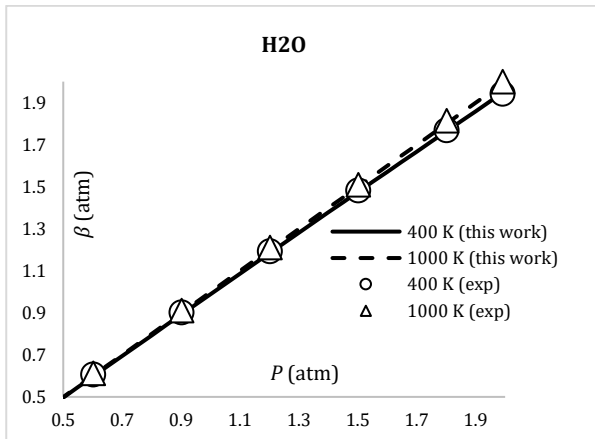


Fig. 14. Bulk modulus of light water as a function of pressure.

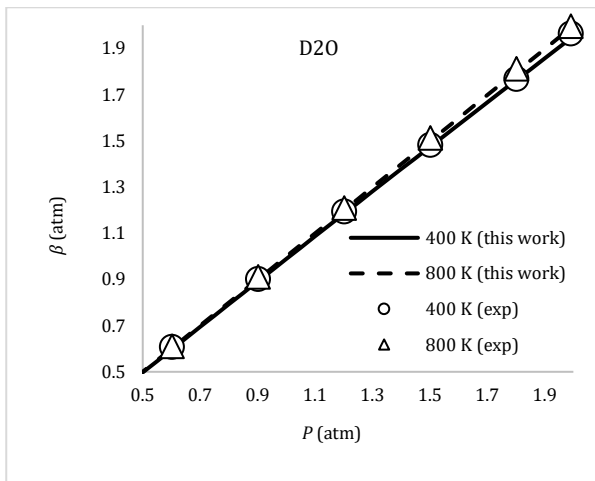


Fig. 15. Bulk modulus of heavy water as a function of pressure.

Table 3. The value of  $\beta_{0,T}$  and  $\beta'_{0,T}$  at 400 K for light and heavy water.

Molecule	$\beta_{0,T}$	$\beta'_{0,T}$
H <sub>2</sub> O	0.9761	0.0091
D <sub>2</sub> O	0.9748	0.0096

### 5. Conclusion

In this paper, a new equation of the second virial coefficient of light and heavy water was presented, some thermophysical properties of them in a wide temperature range were calculated and modeled and the effect of isotopic substitution was determined. A review of the figures, tables and results shows that

- 1) The model and new equation of the second virial coefficient presented have a very good ability to predict and model the thermophysical properties of light and heavy water.
- 2) The presence of deuterium in the water composition causes the change in the average number of H-bonds per molecule  $n_H$ .
- 3) It seems that isotope substitution  $D$  reduces attractive interaction between molecules especially above the critical temperature and affects the thermophysical properties.
- 4) At higher temperatures from the critical temperature,  $n_H$  in light water is more than in heavy water, which reduces the second virial coefficient and the Boyle volume and increases the Boyle temperature in light water compared to heavy water.
- 5) Below the boiling point, the presence of a deuterium isotope reduces the molar volume and the thermal expansion of heavy water compared to light water.
- 6) The model presented is able to predict Tait-Murnaghan's regularity very well.
- 7) The approach presented here, namely the use of precise virial coefficients and virial equation of state (VEOS), is very suitable for modeling many thermophysical properties of fluids and examining and explaining their non-ideal behavior. However, at high densities or pressures due to intermolecular interactions in clusters of three or four molecules, the third and fourth virial coefficients must be used in VEOS.

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