

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

ABSTRACT: In this paper, some thermophysical properties of light and heavy water will be predicted and modeled using virial equation of state (VEOS) and, 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 in $300 \leq T \leq 1000 \text{ K}$ and $0.1 \leq P \leq 2 \text{ atm}$. The obtained results are compared with experimental data to evaluate the model and the new equation of second virial coefficient. The results show that this approach has a very good ability to predict thermophysical properties of light and heavy water. It will also be shown 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. Calculations performed in the above temperatures and pressures range using virial coefficients in order to determine thermophysical properties of light and heavy water and also investigation of the effect of isotopic substitution are novelties of this article.

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

1. Introduction

Light and heavy water is one of the simplest important substances in chemistry. Both of them are widely used in 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. H-bond in water (light and heavy) is very important and many of thermodynamic properties of it depend on these bonds. For instance, as a result of lowering temperature to below 4°C , the molar volume of it increases. This is the unusual behavior of water which is affected by H-bond. The important role of H-bonds in the formation of the interesting properties of water is generally accepted [1]. In fact, for the correct interpretation of many facts of thermophysical behavior of the associating 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 [2]

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

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 decreasing the average number of H-bonds per molecule. As a fact, this behavior can be seen in all associating fluids. In this manner, Bulavin *et al.* have shown that the qualitative analysis of non-equilibrium water properties, determined by long-living molecular configurations, which arise due to H-bonds [3]. 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.* have investigated the collective contributions of self-diffusion coefficients of liquids and effects of H-bond on them, especially for normal and super-cooled water [4].

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 [5]. 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 rotation of water molecules.

Due to importance of light and heavy water and their very wide applications, the thermodynamic properties of them have been studied experimentally and theoretically. Theoretical research has the advantage that it leads to modeling the thermophysical behavior of materials. Modeling the thermodynamic properties of materials is very important 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 up to 100 MPa and 870 K [6]. 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 determination and prediction of some thermophysical properties of water [7] and heavy water [8]. In recent years, Herrig *et al.* presented an empirical fundamental EOS is for heavy water fluid [9]. 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, 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 second virial coefficient of light and heavy water will be determined and then using it, some thermodynamic properties of fluids H_2O and D_2O are predicted and modeled by virial equation of state (VEOS). In this respect, effect of isotopic substitution will be studied. This approach is a novelty one to

investigate the thermodynamic properties of light and heavy water and isotopic substitution effect on them.

2. Virial Equation of State (VEOS)

Thermodynamic properties of materials (pure or mixture) and their surfaces and transfer properties can be predicted and modelled by equations of state [10-12]. One of the oldest ones is the virial equation of state (VEOS) which has been used extensively to study the thermodynamic properties of gases and is based on statistical mechanics

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

in which

$$B_2^+ = B_2 / RT \quad (3)$$

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

It is better to be considered $B_2 \equiv B$ and $B_3 \equiv C$. In above mentioned equations, Z is the compressibility factor ($Z = PV_m / RT$), ρ is the density ($= 1/V_m$) 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

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

where $u(r)$ is the intermolecular interaction energy function of the pair 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 which 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, and 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. So virial coefficients together with virial equation of state (VEOS) are the connection bridge between microscopic and macroscopic properties and show the non-ideality and therefore, can predict and model the thermophysical properties of fluids with good accuracy.

The virial coefficients can be obtained with various theoretical and experimental methods [13-20]. 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, has 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 [21-30]. For example, a correlation function of second virial coefficient for linear, near-linear and near-spherical molecules had been presented by Boushehri *et al* in 1987 [31]. Zarkova *et al* presented $B(T)$ for eleven heavy gases [32] and pure small alkanes [33] and Meng *et al* have developed a correlation for $B(T)$ and $C(T)$ of pure fluids based on corresponding state principle [34]. We also calculated the second virial coefficient of various fluids using two models, van der Waals and Dieterici equations of state [15-16, 35]

As shown in Equation 2, compressibility factor (Z) in 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

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

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_6 , UF_6 and some of the refrigerants have been calculated and modeled by this approach [36-38].

In this work, by fitting of experimental and theoretical second virial coefficient of light and heavy water, new equation of B will be presented and 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 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 second virial coefficient as follows [39]

$$V_m = \frac{RT}{P} + B \tag{6}$$

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 [37]

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

2.3 Bulk modulus

Bulk modulus is a thermodynamic properties 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 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 the fundamental quantity. In addition to the study of these coefficients in themselves are useful, knowledge of the second virial coefficient of water is required to extract the information of the cross second virial coefficients from the water vapor mixture data. These cross-coefficients are important for accurate thermodynamic descriptions in a variety of systems such as combustion gases and humidity standards [40].

As mentioned, experimental and theoretical methods can be used for obtaining virial coefficients of fluids. The second virial coefficient of a fluid can be derived from accurate *PVT* measurements, which often involve successive expansion of the fluid. Reliable values of $B(T)$ at some temperatures may also be obtained from vaporization data. This calculation is through the Clapeyron equation. The second virial coefficient and its temperature dependence can be obtained from the function $\phi^\circ (= B - TdB/dT)$.

ϕ° 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_2O), scholars determined its second virial coefficient using different approaches [40-47]. Also, second virial coefficient of heavy water (D_2O) 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 by a different amount of H₂O and HDO. But as Herrig *et al* stated, the D₂O 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 [9]. Therefore, their very small amount has not had an impact on modeling and determining the equation of state for them.

In this work, experimental and theoretical data of second virial coefficient for light and heavy water has been considered to present a new equation in the wide range temperature. To obtain new equation, it has been used numerical analysis approach for fitting the $B(T)$ data of Harvey and Lemmon [41], KKHM [42], Keyes [43], Lefevre [44], Abdulagatov [45], Hill and MacMillan [46], and Kell [48]. The final equation is

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

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, $R^2 = 0.9997$ and 1.0 for light and heavy water respectively.

Table 1: Critical properties of H₂O and D₂O and the expansion coefficients of Equation (11)

Molecule	T_c (K)	$V_{m,c}$ (cm ³ /mol)	A_0	A_1	A_2	A_3	A_4	A_5	A_6
H ₂ O	647.096	55.948	0.9917	-4.1211	4.5991	0.084	-6.614	4.6583	-1.0783
D ₂ O	643.89	55.944	-1.4546	14.66	-41.387	51.49	-35.115	12.057	-1.7714

Figures 1 and 2 show the deviation plots obtained from equation (12) for second virial coefficient of light and heavy water respectively. As seen, there is a small deviation of this work from the others.

$$\text{Deviation plot of this work from the others} = \left(\frac{B_{\text{thiswork}} - B_{\text{others}}}{B_{\text{thiswork}}} \right) \times 100 \quad (12)$$

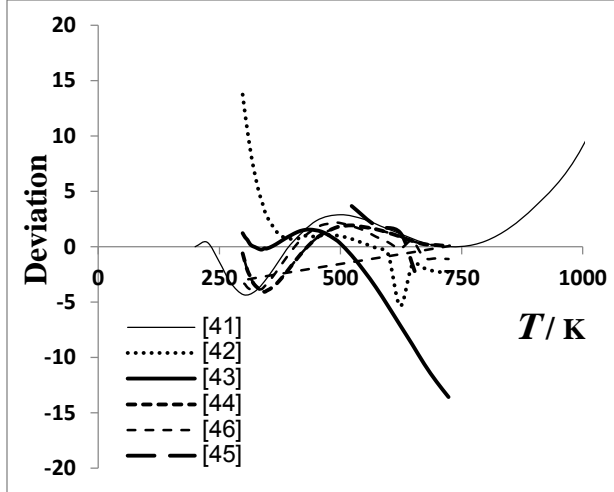


Fig. 1: Deviation plot of this work from the others for light water

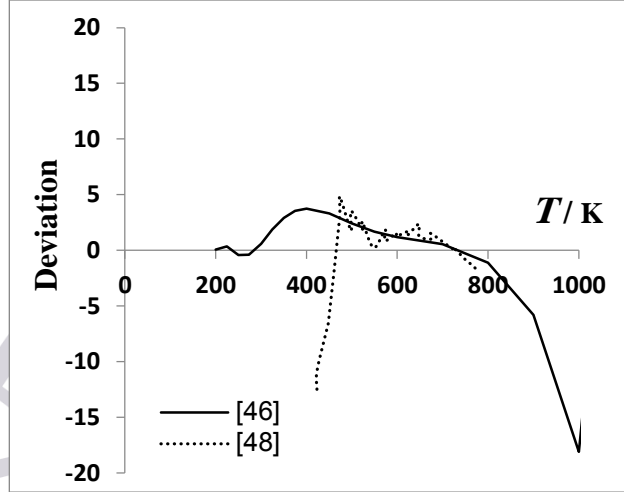


Fig. 2: Deviation plot of this work from the others for heavy water

4. Results and Discussion

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

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

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

Boyle Temperature (T_B) and Boyle Volume (V_B) have been shown to be sensitive to the equation in use, so in this article, they were determined using the new equation and compared with other sources. [41, 46, 49]. The results are shown in Table 2.

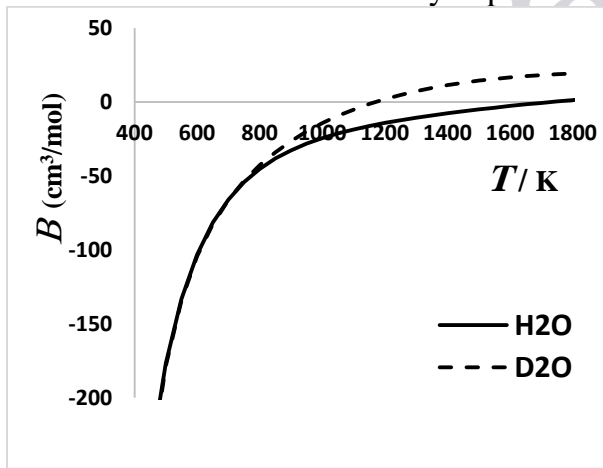
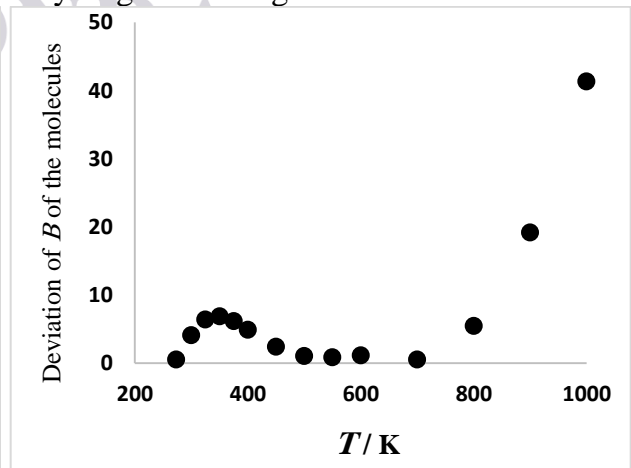
Table 2: Calculated Boyle Temperature (T_B) and Boyle Volume (V_B) of studied molecules

Molecule	T_B			V_B
	This work	Source	Error value	
H ₂ O	1730.6	1545.5 [41]	11.97	33.921
		1662.6 [49]	4.08	
D ₂ O	1170.7	1239.8 [46]	5.57	77.725

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 that with increasing intermolecular attractive forces, it decreases and T_B increases. As can be seen in Figure 3, at a given 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 clearly shown in Figure 4. As observed, the deviation (calculated by equation 14) rises sharply above the critical temperature of water.

$$\text{Deviation of } B \text{ of the molecules} = \left| \frac{B(H_2O) - B(D_2O)}{B(H_2O)} \right| \times 100 \quad (14)$$

So based on what has been said before, at that range of temperature, H₂O has a stronger interaction than D₂O and therefore, isotope substitution D decrease attractive interaction between molecules. In other words, like all associating fluids, since the intermolecular interactions in water are mainly dependent on hydrogen bonding and as mentioned earlier,

**Fig. 3:** Second virial coefficients of studied molecules as a function of temperature**Fig. 4:** Deviation of second virial coefficients of studied molecules in terms of temperature

Average number of H-bonds per molecule (n_H) is temperature dependent, so it can be concluded that 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. 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 $T_b \langle T(K) \langle T_c$, second virial coefficient of the two are very close to each other and slightly $B_{H_2O} \rangle B_{D_2O}$. This subject was shown by Hill & MacMillan [46] and Kell et al [48] and compared with this work in Figure 5.

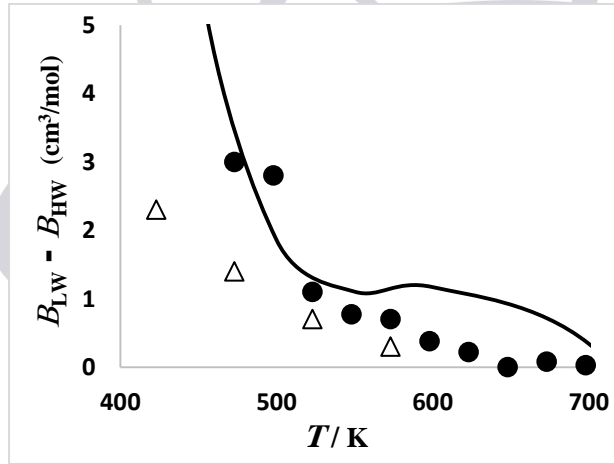


Fig. 5: Differences between Second virial coefficients of studied molecules; line: this work, (●): [48], (Δ): [46]

Figures 6 and 7 show the behavior of molar volume of the molecules in terms of temperature at two pressures 0.5 and 1.0 atm compared with experimental data [50]. 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 temperature.

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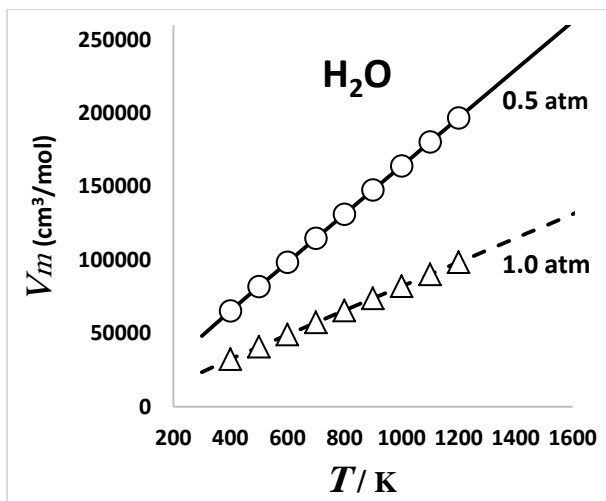


Fig. 6: Molar volume of light water as a function of temperature

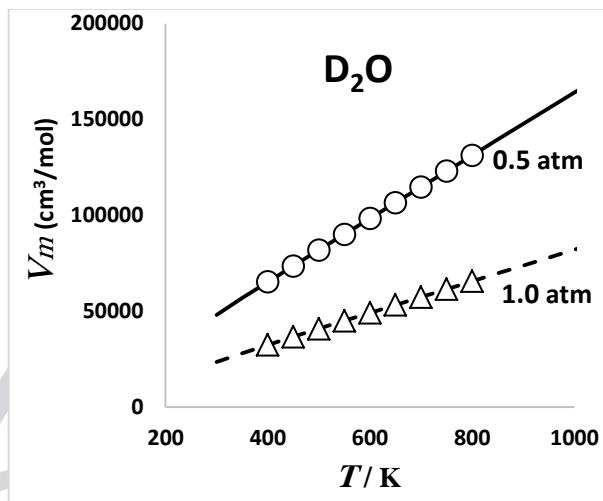


Fig. 7: Molar volume of heavy water as a function of temperature

Also, Figures 8 and 9 show the variation of 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.

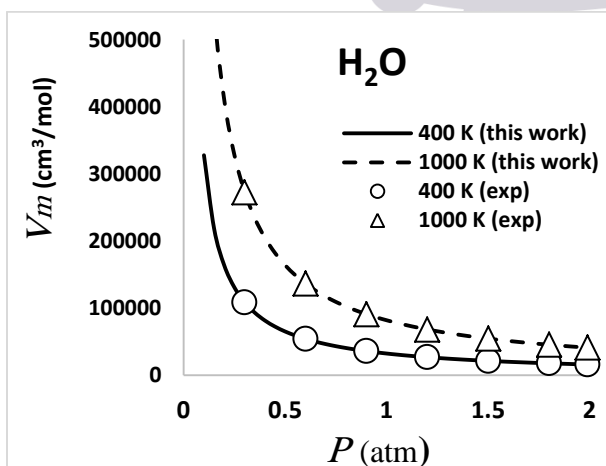


Fig. 8: Molar volume of light water as a function of pressure

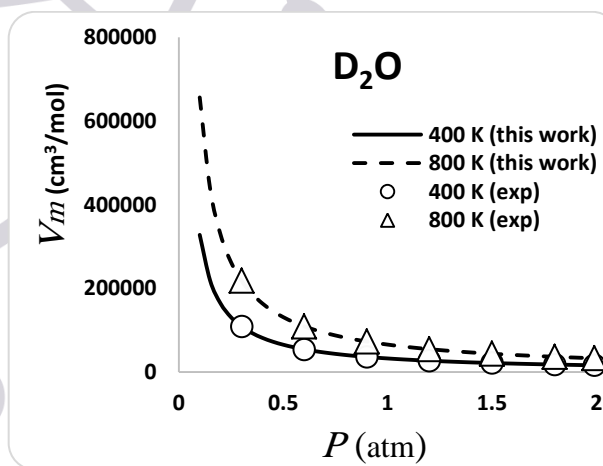


Fig. 9: Molar volume of heavy water as a function of pressure

For better consideration, deviation of molar volume of light and heavy water in terms of temperature at $P=0.5$ atm in comparison with experimental data [50] has shown in Figure 10. As can be seen, the consistency between the experimental and theoretical data in wide range temperature is very good. 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).

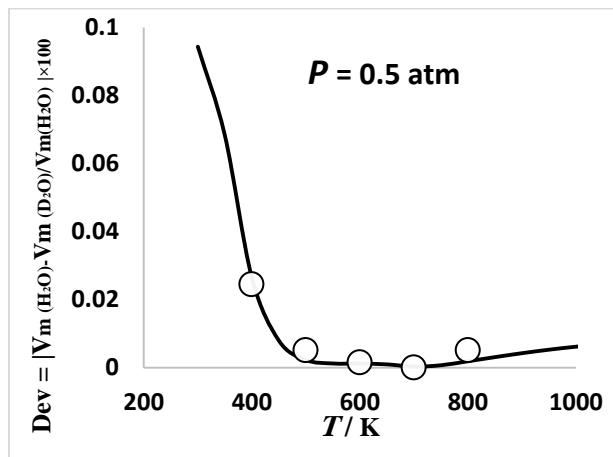


Fig. 10: Deviation of molar volume of light and heavy water in terms of temperature; line: this work, (O): experimental data [50]

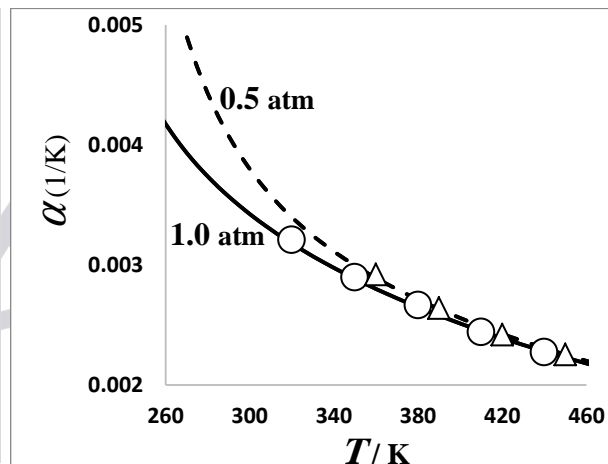


Fig. 11: Thermal expansion coefficient of light water vs temperature; line: this work; symbol: experimental data [50]

Figures 11 and 12 show the behavior of thermal expansion coefficient of the molecules in terms of temperatures at two different pressures compared with experimental data [50]. This behavior are predicted and modeled very well by the equation qualitatively and quantitatively. The match of theoretical results from new equation and experimental data is excellent.

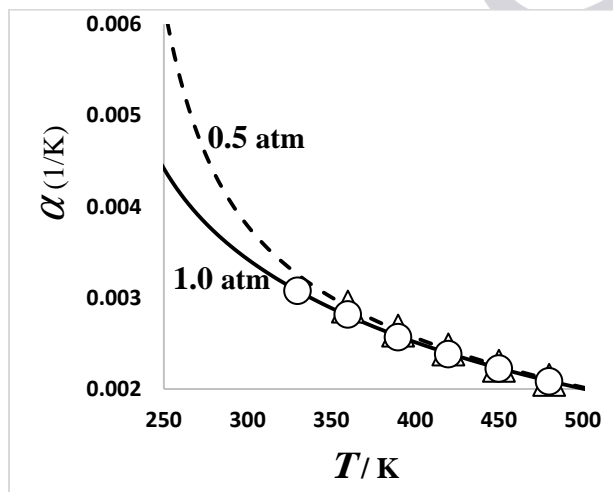


Fig. 12: Thermal expansion coefficient of heavy water vs temperature; line: this work; symbol: experimental data [50]

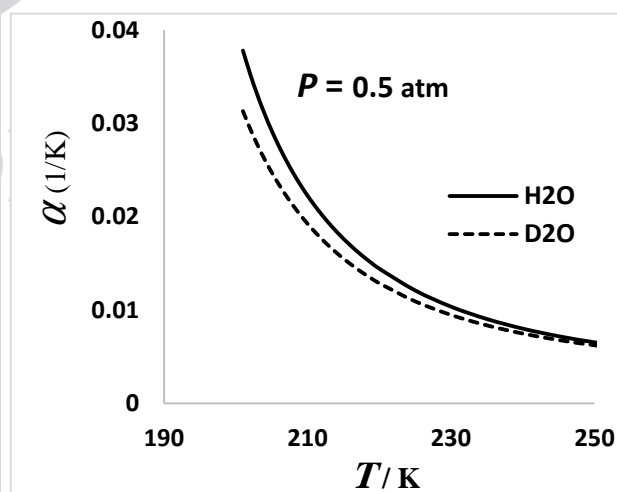


Fig.13: Thermal expansion coefficient of light and heavy water vs temperature at pressure 0.5 atm

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 H₂O and D₂O as a function of pressure at two temperatures calculated by the equation is shown in Figures 14 and 15 and compared with experimental data [50]. The match of theoretical results from new equation and experimental data is excellent.

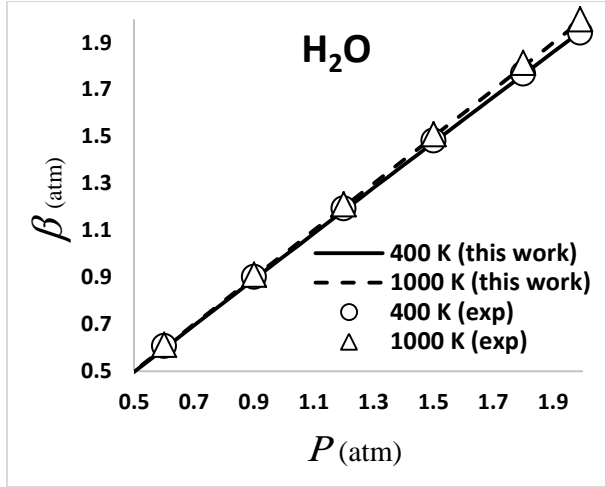


Fig. 14: Bulk modulus of light water as a function of pressure

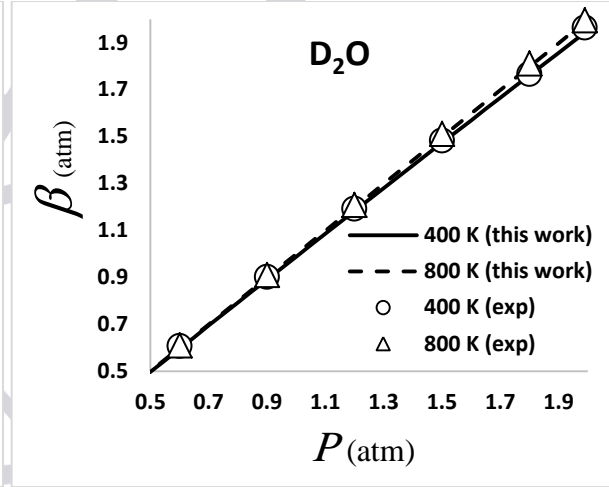


Fig. 15: Bulk modulus of heavy water as a function of pressure

As seen, the curve is completely linear. This linearity is one of the thermodynamic regularity of materials named Tait-Murnaghan regularity. Based on this regularity, the bulk modulus of fluid is nearly linear in pressure for each isotherm [51-52]

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

where $\beta_{0,T}$ is β_T in zero pressure and $\beta'_{0,T}$ is slope of bulk modulus in zero pressure. $\beta_{0,T}$ and $\beta'_{0,T}$ are temperature-dependent parameters. This regularity are 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.

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 ₂ O	0.9761	0.0091
D ₂ O	0.9748	0.0096

5- Conclusion

In this paper, new equation of second virial coefficient of light and heavy water was presented, some thermophysical properties of them in wide temperature range was calculated and modeled and 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 has 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 average number of H-bonds per molecule n_H .
- 3- it seems that isotope substitution D reduces attractive interaction between molecules especially above critical temperature and affects on 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 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 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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References

- [1] Franks F., (Ed.), *Water, A Comprehensive Treatise*, Plenum, New York, p. 255 (1972)
- [2] Fisenko A. I., Malomuzh N. P. and Oleynik A. V., To what extent are thermodynamic properties of water argon-like?, *Chemical Physics Letters* **450**: 297–301 (2008)
- [3] Bulavin L. A., Fisenko A. I. and Malomuzh N. P., Surprising properties of the kinematic shear viscosity of water, *Chemical Physics Letters* **453**: 183–187 (2008)
- [4] Bulavin L. A., Lokotosh T. V. and Malomuzh N. P., Role of the collective self-diffusion in water and other liquids, *Journal of Molecular Liquids*, **137**: 1-24 (2008)
- [5] Lishchuk S. V., Malomuzh N. P. and Makhlaichuk P. V., Why thermodynamic properties of normal and heavy water are similar to those of argon-like liquids?, *Physics Letters A*, **374**: 2084-2088(2010)
- [6] Hill P. G., Chris MacMillan R. D. and Lee V., A fundamental equation of state for heavy water, *J. Phys. Chem. Ref. Data*, **11**(1): 15 (1982)
- [7] Kestin J., Sengers J. V., Kamgar Parsi B. and Levelt Sengers J. M. H., Thermophysical properties of fluid D₂O, *J. Phys. Chem. Ref. Data*, **13**(1): 175 (1984)

- [8] Kestin J., Sengers J. V., Kamgar Parsi B. and Levelt Sengers J. M. H., Thermophysical properties of fluid D₂O, *J. Phys. Chem. Ref. Data*, **13**(2): 601-609 (1984)
- [9] Herrig S., Thol M., Harvey A. H. and Lemmon E. W., A Reference Equation of State for Heavy Water, *J. Phys. Chem. Ref. Data*, **47**(4): 043102 (2018)
- [10] Wei Y.S. and Sadus R. J., Equations of state for the calculation of fluid-phase equilibria, *AIChE J.*, **46**(1): 169-196 (2000)
- [11] Valderrama J.O., The State of the Cubic Equations of State, *Ind. Eng. Chem. Res.*, **42**: 1603-1618 (2003)
- [12] Guevara-Rodriguez F de J., A methodology to define the Cubic Equation of State of a simple fluid, *Fluid Phase Equilibria*, **307**(2): 190-196 (2011)
- [13] Assael M. J., Trusler J. P. M. and Tsolakis T. F., *An introduction to their prediction thermophysical properties of fluids*, Imperial College Press, London, UK, 1996
- [14] Meng L. and Duan Y-Y, Prediction of the second cross virial coefficients of nonpolar binary mixtures, *Fluid Phase Equilibria*, **238**(2): 229 (2005)
- [15] Najafi M. and Marzbanpour E., Determination of the Second Virial Coefficient for Binary Mixtures of Ar with CH₄ and CO using Van der Waals and Dieterici Models, *Journal of Sciences, Islamic Republic of Iran*, **30**: 325 (2019)
- [16] Najafi M. and Marzbanpour E., On the Calculation of the Second Virial Coefficient of Pure Polar and Non-Polar Gases Using van der Waals and Dieterici Models; Temperature-Dependence Covolume Parameter, *Russian Journal of physical Chemistry A*. **94**(2): 287 (2020)
- [17] Vetere A., An improved method to predict the second virial coefficients of pure compounds, *Fluid Phase Equilibria*, **164**(1): 49-59 (1999)
- [18] Ramos-Estrada M., Iglesias-Silva G. A., Hall K. R. and Kohler F., Estimation of third virial coefficients at low reduced temperatures, *Fluid Phase Equilibria*, **240**(2): 179-185 (2006)
- [19] Harvey A. H. and Lemmon E. W., Correlation for the Second Virial Coefficient of Water, *J. Phys. Chem. Ref. Data*, **33**(1): 369-376 (2004)
- [20] Tian J., Gui Y. and Mulero A., New Closed Virial Equation of State for Hard-Sphere Fluids, *J. Phys. Chem. B*, **114**(42): 13399-13402 (2010)
- [21] Pitzer K. S. and Curl R. F., The Volumetric and Thermodynamic Properties of Fluids. III. Empirical Equation for the Second Virial Coefficient, *J. Am. Chem. Soc.*, **79**: 2369 (1957)
- [22] O'Connell J. P., Prausnitz J. M., Empirical correlation of second virial coefficient for vapor-liquid equilibrium calculations, *Ind. Eng. Chem. Process Des.*, **6**: 245-250 (1967)
- [23] Tsonopoulos C., An empirical correlation of second virial coefficients, *AIChE J.* **20**: 263-272 (1974)
- [24] Tsonopoulos C., Second virial coefficients of polar haloalkanes, *AIChE J.* **21**: 827-829 (1975)
- [25] Ramanathan R., Tarakad R. R., Danner R. P., An improved corresponding states method for polar fluids: Correlation of second virial coefficients, *AIChE J.*, **23**: 685 (1977)
- [26] Orbey H. A., A four parameter Pitzer-Curl type correlation of second virial coefficients, *Chem. Eng. Commun.*, **65**(1): 1-19 (1988)

- [27] Weber L.A., Estimating the virial coefficients of small polar molecules, *Int. J. Thermophys.*, **15**(3): 461–482 (1994)
- [28] Hou H., Holste J. C., Hall K. R., Marsh K. N., and Gammon B. E., Second and Third Virial Coefficients for Methane + Ethane and Methane + Ethane + Carbon Dioxide at (300 and 320) K, *J. Chem. Eng. Data*, **41**(2): 344-353 (1996)
- [29] Esper G., Beckermann W., and Kohler F., Acoustic determination of ideal gas heat capacity and second virial coefficient of small hydrocarbons, *Fluid Phase Equilib.*, **105**(2): 173-192 (1995)
- [30] H. Eslami, M. Mozaffari and A. Boushehri, Calculation of the second virial coefficient of nonspherical molecules: Revisited, *Int. J. Therm. Sci.*, **40**: 999–1010 (2001)
- [31] Boushehri A., Bzowski J., Kestin J. and Mason E. A., Equilibrium and Transport Properties of Eleven Polyatomic Gases At Low Density, *J. Phys. Chem. Ref. Data*, **16**: 445 (1987)
- [32] Zarkova L. and Hohm U., pVT–Second Virial Coefficients $B(T)$, Viscosity $\eta(T)$, and Self-Diffusion $\rho D(T)$ of the Gases: BF_3 , CF_4 , SiF_4 , CCl_4 , SiCl_4 , SF_6 , MoF_6 , WF_6 , UF_6 , $\text{C}(\text{CH}_3)_4$, and $\text{Si}(\text{CH}_3)_4$ Determined by Means of an Isotropic Temperature-Dependent Potential, *J. Phys. Chem. Ref. Data*, **31**: 183 (2002)
- [33] Zarkova L. and Hohm U. and Damyanova M., Viscosity, Second pVT-Virial Coefficient, and Diffusion of Pure and Mixed Small Alkanes CH_4 , C_2H_6 , C_3H_8 , n- C_4H_{10} , i- C_4H_{10} , n- C_5H_{12} , i- C_5H_{12} , and $\text{C}(\text{CH}_3)_4$ Calculated by Means of an Isotropic Temperature-Dependent Potential. I. Pure Alkanes, *J. Phys. Chem. Ref. Data*, **35**: 1331 (2006)
- [34] Meng L., Duan Y-Y and Li L., Correlations for second and third virial coefficients of pure fluids, *Fluid Phase Equilibria*, **226**: 109 (2004)
- [35] Najafi M. and Sadat Ghafelehbashi N., Calculation of the Virial Coefficients for Refrigerant Fluids Using Two Models of Equations of State, *Iranian Journal of Chem. and Chem. Eng.*, **41**(1): 242-252 (2022)
- [36] Najafi M., Prediction of Joule-Thomson and Deviation Functions at Low Pressure for Refrigerants Using Correlation Function, *Russian J of Physical Chemistry A*, **95**: S140-S148 (2021)
- [37] Najafi M., Calculation of Some Thermophysical Properties of SF_6 at Low Pressure, *PRAMANA, Journal of Physics*, **95**: 139 (2021)
- [38] Najafi M., Modeling of Some Thermodynamic Properties of UF_6 at Low Pressure Using Correlation Function, *Journal of Nuclear Research and Applications*, **1**: 18-27 (2021)
- [39] Levine I., “*Physical Chemistry*”, 5th Edition, McGraw-Hill International Editions, 2002
- [40] Eubank P. T., Joffrion L. L., Patel M. R. and Warowny W., Experimental densities and virial coefficients for steam from 348 to 498 K with correction for adsorption effects, *J. Chem. Thermodynamics*, **20**(9): 1009-1034 (1988)
- [41] Harvey A. H. and Lemmon E. W., Correlation for the Second Virial Coefficient of Water, *J. Phys. Chem. Ref. Data.*, **33**(1): 369-376 (2004)
- [42] Keenan J. H., Keyes F. G., Hill P. G. and Moore J. G., Steam Tables: Thermodynamic Properties of Water Including Vapor, Liquid, and Solid Phases, (Wiley: New York. 1969)

- [43] Keyes F. G., The second virial coefficient for steam, *Int. J. Heat Mass Transfer*, **5**(3-4): 137-142 (1962)
- [44] LeFevre E. J., Nightingale M. R., Rose J. W. J., The Second Virial Coefficient of Ordinary Water Substance: A New Correlation, *Mech. Eng. Sci.*, **17**: 243-251 (1975)
- [45] Abdulagatov M., Bazaev A. R., Gasanov R. K. and Ramazanova A. E., Measurements of the (p, ρ, T) properties and virial coefficients of pure water, methane, *n*-hexane, *n*-octane, benzene, and of their aqueous mixtures in the supercritical region, *J. Chem. Thermodynamics*, **28**(9): 1037-1057 (1996)
- [46] Hill P. G. and MacMillan R. D. C., Virial equations for light and heavy water, *Ind. Eng. Chem. Res.*, **27**(5): 874-882 (1988)
- [47] Garberoglio G., Jankowski P., Szalewicz K. and Harvey A. H., Fully quantum calculation of the second and third virial coefficients of water and its isotopologues from *ab initio* potentials, *Faraday Discussions*, **212**: 467 (2018)
- [48] Kell G. S., McLaurin G. E. and Whalley E., PVT Properties of Water. III. Virial Coefficients of D₂O in the Range 150°–500°C, *J. Chem. Phys.*, **49**: 2839 (1968)
- [49] Estrada-Torres R., Iglesias-Silva G. A., Ramos-Estrada M. and Hall K. R., Boyle temperatures for pure substances, *Fluid Phase Equilibria.*, **258**(2): 148-154 (2007)
- [50] NIST Chemistry WebBook, www.nist.gov.
- [51] Maghari A. and Shahri L. H., Evaluation of the performance of cubic equations of state in predicting the regularities in dense fluids, *Fluid Phase Equilibria.*, **206**(1-2): 287-311 (2003)
- [52] Maghari A. and Tahmasbi N., Prediction of Some Important Regularities Using a Statistical Mechanical Equation of State, *Int. J. Thermophys.*, **25**: 205-219 (2004)

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