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Prediction of H$_2$O $PVT$ relations at high temperatures by VHL equation of state

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ABSTRACT

Based on the VHL equation of state (EOS) described by the L-J potential function, the water in the high-temperature situation is depicted by medium-high pressure thermodynamic states. The L-J potential function parameters of water adopt a temperature-dependent function form, and by using complex configuration optimization method, the specific value is obtained from the data in NIST during the range of 800K-1275K and 0.1GPa-1.0GPa. In order to test the suitability of VHL equation of state in high-temperature and medium-high pressure state, the theoretical and experimental data of higher temperature and pressure range are investigated. What’s more, the theoretical calculation results of VLW, DMW, BS and TIP4P equations of state are compared. The results show that, during the high-temperature and medium-high pressure section, the volumetric error of water calculated by VHL equation of state is less than 7%. Considering the uncertainty of the experimental data, it can be thought that the VHL equation of state and the temperature-dependent potential function form proposed in this paper can describe the state of water in high temperature, medium-high pressure better.

I. INTRODUCTION

In nature, water is considered as an important part of many fluids and participates in a variety of natural activities, such as mineral deposits, volcanic eruptions, magmatic activities, metamorphism, hydrothermal venting, geothermal evolution, petroleum and natural gas formation and migration, and waste disposal. Therefore, understanding the thermodynamic properties of water is important for explaining the physical and chemical processes in the earth’s crust and mantle. At the same time, since water is one of the important components of explosive detonation products, understanding the $PVT$ relationship of water in high temperature and high-pressure situation is conducive to evaluate the performance of detonation accurately. However, due to the hydrogen bond between water molecules, the phase diagram of water is extremely rich and presents many different properties. Because of this, most of EOS describing water are limited to a certain temperature and pressure range due to the lack of experimental data in a relevant region. And the equation of state in this region mainly depends on an analog computation of the extended part of low pressure or molecular dynamics. Although these results are commonly used, there still exist some differences among the consequences given by various equations of state, at hence more experimental data in the high-pressure and high-temperature state are needed to describe the equation of state of water.

In the last century, a large number of $PVT$ experimental data on water has been accumulated, but they usually limited by the temperature range below 1273.15K and pressures range below 1.0Gpa. The newly developed technology makes it possible to enlarge the range to the temperature of 1873.15K and pressure of 5.0Gpa. At the same time, as temperature and pressure are increasing, experiments become more and more difficult and have significant uncertainties. Proceed with the experimental work, various EOS of water were proposed. By accurately calibrating the parameters in these equations, some mature EOS can be used to precisely reproduce
experimental data. However, extrapolation is limited for data outside the experimental range.\(^\text{13-16}\)

The results of research on literature show that the potential function of water molecules changes with temperature in the high-temperature environment.\(^\text{17}\) In this paper, by using complex configuration optimization method and NIST database,\(^\text{18}\) the optimal potential parameters of water are obtained with a pressure range of 0.1GPa-1.0GPa and temperatures of 800K, 900K, 1000K, 1100K, 1150K, 1200K, and 1275K. And by the least squares method, the variation of the potential function of water with temperature is fitted. At the same time, the calculated value of the volume in characteristic pressure point at different temperatures is counted by the VHL equation of state,\(^\text{19}\) and is compared with the calculated value of VLW. In order to test the suitability between the VHL equation of state and potential function parameters of water proposed later in the high-temperature and high-pressure section, the theoretical calculation of thermodynamic properties of water in that situation is carried out, and comparison of the VLW, DMW, BS, TIP4P equations of state are made.

**II. VHL EQUATIONS OF STATE**

Through the nonlinear optimization method, based on the results of Barker's theory,\(^\text{20}\) the third-order and fourth-order dimensionless virial coefficients are expressed in the form of analytic functions, and the higher-order virial coefficients are expressed by the simplified combination function. Specifically, in Eq. (1),\(^\text{19}\) the coefficient value of the combination function is obtained by optimizing the high-temperature experimental data and molecular dynamics data of methane.\(^\text{21}\) The specific coefficient values are shown in Table I. Compared with other equations of state, the VHL equation of state is closer to the theoretical value in the third-order and fourth-order virial coefficients. And thus, the form of the equation of state should be more physically meaningful. For nonpolar molecules or weakly polar molecules, the thermodynamic state parameters can be obtained using methane gas as a reference. For the strong polar molecules in this paper, according to the references, a temperature-dependent functional relationship is introduced to the potential parameters.

The specific form of the VHL equation of state is:

\[
\frac{pV}{RT} = 1 + \omega T^* + \omega^2 C^* + \omega^3 D^* + \omega^4 E^* + (a + b T^*) \omega^4
\]

\[C^* = c_1 T^{e_1} + c_3 T^{e_3} + c_5 T^{e_5} + c_7 T^{e_7} + c_9 T^{e_9}\]

\[D^* = d_1 T^{e_1} + d_3 T^{e_3} + d_5 T^{e_5} + d_7 T^{e_7} + d_9 T^{e_9}\]

\[E^* = e_1 T^{e_1} + e_3 T^{e_3}\]

\[T^* = \frac{T}{\varepsilon}\]

\[\omega = \frac{b_0^2}{b_{CH} V}\]

\[b_0 = 2mN\sigma^2/3\]

\[\varepsilon_T = \varepsilon_0 (1 + j/T)\]

\[b_T = b_0 + k \exp(-T/c)\]

\(P, V, T\) are the actual pressure, volume, and temperature of the gas, \(b_{CH}=67.21, R\) is the molar gas constant \(8.3144 \times 10^{-5}\), \(C^*, D^*, E^*\) are the third-order and fourth-order dimensionless virial coefficients respectively, \(T^*\) is dimensionless temperatures, \(N\) is the Avogadro constant \(6.022045 \times 10^{23}\text{mol}^{-1}\), \(\varepsilon, d\) is the L-I potential parameters. The specific values of \(c_1\sim c_{10}, d_1\sim d_{10}, e_1\sim e_4, a, b, f\) are shown in Table I.

By using complex configuration optimization method and the NIST database from Table II, the optimized potential parameters of water are acquired with a pressure range of 0.1GPa-1.0GPa and temperatures of 800K, 900K, 1000K, 1100K, 1150K, 1200K, and 1275K. And the least squares method is used to fit the law of how the water potential energy function is changed by temperature according to Eq. (2) and Eq. (3).

**Table I.** Constants for the fitting formula of dimensionless virial coefficients of each order.

| coefficients | value   |
|--------------|---------|
| \(C_1\)      | -0.96665|
| \(C_2\)      | -4.51039|
| \(C_3\)      | -2.58733|
| \(C_4\)      | -0.85487|
| \(C_5\)      | 2.08033 |
| \(C_6\)      | -0.51631|
| \(C_7\)      | 2.02825 |
| \(C_8\)      | -2.15543|
| \(C_9\)      | -0.12489|
| \(C_{10}\)   | -7.65161|
| \(d_1\)      | -2.31154|
| \(d_2\)      | -7.49608|
| \(d_3\)      | -2.56864|
| \(d_4\)      | -1.14947|
| \(d_5\)      | 2.09543 |
| \(d_6\)      | -0.84757|
| \(d_7\)      | 2.81486 |
| \(d_8\)      | -4.4448 |
| \(d_9\)      | -0.30669|
| \(d_{10}\)   | -11.36945|
| \(e_1\)      | 2.15701 |
| \(e_2\)      | -2.52736|
| \(e_3\)      | 0.2708  |
| \(e_4\)      | -1.0019 |
| \(a\)        | -0.00243|
| \(b\)        | 0.0001776|
| \(f\)        | 3.608   |

**Table I.** Constants for the fitting formula of dimensionless virial coefficients of each order.

By fitting it’s obtained that \(\varepsilon_0=229.61778, j=1188.7, b_0=45.0936, k=-70.86645, c=352.4585\). Here \(\varepsilon_T, b_T\) stands for \(\varepsilon, b_0\) in Eq. (1). The volumetric values of the characteristic pressure point at different temperatures calculated by Eqs. (1), (2), and (3) are compared with the NIST database and the calculated values of VLW equation of state, as shown in Table II.
### TABLE II. The high-temperature $PVT$ relationship of water calculated by VHL equation of state.

| No. | T/K | $p$/GPa | $V_{\text{NIST}}$ (cm$^3$/mol) | $V_{\text{VLW}}$ | $V_{\text{VHL}}$ | $(V_{\text{VHL}} - V_{\text{VLW}})/V_{\text{NIST}} \times 100$ |
|-----|-----|---------|-------------------------------|-----------------|----------------|---------------------------------------------------|
| 1   | 800 | 0.1     | 37.36                         | 37.55           | 37.36          | 0.509                                             |
| 2   | 800 | 0.2     | 31.98                         | 32.03           | 31.98          | 0.221                                             |
| 3   | 800 | 0.3     | 26.87                         | 26.83           | 26.87          | 0.125                                             |
| 4   | 800 | 0.4     | 22.72                         | 22.70           | 22.72          | 0.000                                             |
| 5   | 800 | 0.5     | 27.15                         | 27.06           | 27.15          | −0.047                                            |
| 6   | 800 | 0.6     | 20.23                         | 20.21           | 20.23          | −0.090                                            |
| 7   | 800 | 0.7     | 19.53                         | 19.51           | 19.53          | −0.148                                            |
| 8   | 800 | 0.8     | 18.96                         | 18.94           | 18.96          | −0.216                                            |
| 9   | 800 | 0.9     | 18.48                         | 18.47           | 18.48          | −0.221                                            |
| 10  | 800 | 1       | 18.02                         | 18.00           | 18.02          | −0.221                                            |
| 11  | 900 | 0.1     | 67.87                         | 67.83           | 67.87          | 0.221                                             |
| 12  | 900 | 0.2     | 37.74                         | 37.69           | 37.74          | 0.221                                             |
| 13  | 900 | 0.3     | 26.65                         | 26.61           | 26.65          | 0.221                                             |
| 14  | 900 | 0.4     | 24.5                          | 24.48           | 24.5           | 0.221                                             |
| 15  | 900 | 0.5     | 23.02                         | 23.00           | 23.02          | 0.221                                             |
| 16  | 900 | 0.6     | 21.93                         | 21.91           | 21.93          | 0.221                                             |
| 17  | 900 | 0.7     | 20.16                         | 20.10           | 20.16          | 0.221                                             |
| 18  | 900 | 0.8     | 19.39                         | 19.36           | 19.39          | 0.221                                             |
| 19  | 900 | 0.9     | 18.75                         | 18.73           | 18.75          | 0.221                                             |
| 20  | 900 | 1       | 18.02                         | 18.00           | 18.02          | 0.221                                             |
| 21  | 1000| 0.1    | 67.87                         | 67.83           | 67.87          | 0.221                                            |
| 22  | 1000| 0.2    | 37.74                         | 37.69           | 37.74          | 0.221                                            |
| 23  | 1000| 0.3    | 26.65                         | 26.61           | 26.65          | 0.221                                            |
| 24  | 1000| 0.4    | 24.5                          | 24.48           | 24.5           | 0.221                                            |
| 25  | 1000| 0.5    | 23.02                         | 23.00           | 23.02          | 0.221                                            |
| 26  | 1000| 0.6    | 21.93                         | 21.91           | 21.93          | 0.221                                            |
| 27  | 1000| 0.7    | 20.16                         | 20.10           | 20.16          | 0.221                                            |
| 28  | 1000| 0.8    | 19.39                         | 19.36           | 19.39          | 0.221                                            |
| 29  | 1000| 0.9    | 18.75                         | 18.73           | 18.75          | 0.221                                            |
| 30  | 1000| 1      | 18.02                         | 18.00           | 18.02          | 0.221                                            |
| 31  | 1100| 0.1    | 81.66                         | 81.62           | 81.66          | 0.221                                            |
| 32  | 1100| 0.2    | 43.88                         | 43.82           | 43.88          | 0.221                                            |
| 33  | 1100| 0.3    | 33.82                         | 33.76           | 33.82          | 0.221                                            |
| 34  | 1100| 0.4    | 29.18                         | 29.12           | 29.18          | 0.221                                            |
| 35  | 1100| 0.5    | 26.43                         | 26.38           | 26.43          | 0.221                                            |
| 36  | 1100| 0.6    | 24.58                         | 24.53           | 24.58          | 0.221                                            |
| 37  | 1100| 0.7    | 23.23                         | 23.18           | 23.23          | 0.221                                            |
| 38  | 1100| 0.8    | 22.19                         | 22.14           | 22.19          | 0.221                                            |
| 39  | 1100| 0.9    | 21.26                         | 21.21           | 21.26          | 0.221                                            |
| 40  | 1100| 1      | 20.66                         | 20.61           | 20.66          | 0.221                                            |
| 41  | 1150| 0.1    | 88                            | 88.95           | 88             | 0.221                                            |
| 42  | 1150| 0.2    | 46.95                         | 47.18           | 46.95          | 0.221                                            |
| 43  | 1150| 0.3    | 35.69                         | 35.5            | 35.69          | 0.221                                            |
| 44  | 1150| 0.4    | 30.5                          | 30.31           | 30.5           | 0.221                                            |
| 45  | 1150| 0.5    | 27.44                         | 27.33           | 27.44          | 0.221                                            |
| 46  | 1150| 0.6    | 25.39                         | 25.34           | 25.39          | 0.221                                            |
| 47  | 1150| 0.7    | 23.91                         | 23.89           | 23.91          | 0.221                                            |
| 48  | 1150| 0.8    | 22.77                         | 22.78           | 22.77          | 0.221                                            |
| 49  | 1150| 0.9    | 21.86                         | 21.88           | 21.86          | 0.221                                            |
| 50  | 1150| 1      | 21.11                         | 21.14           | 21.11          | 0.221                                            |
| 51  | 1200| 0.1    | 94.06                         | 95.96           | 94.06          | 0.221                                            |


### III. RESULTS AND DISCUSSION

Comparing with the VLW equation of state, where the expression of VLW is as follows:\(^{22}\)

\[
\frac{p V_m}{RT} = 1 + B m \left( \frac{b m}{V_m} \right) + B m^2 \left( \sum_{n=5}^{\infty} \frac{b m}{V_m} \right)^{n-1} \quad \text{when } n \geq 3, \ T^* \geq 20
\]

(4)

From Table II, the average relative deviation calculated by the VHL equation of state is 0.471%, and the maximum deviation is 3.662%, which is much lower than the average relative deviation calculated by the VLW equation of state of 14.738% and the maximum deviation of 95.396%. The VLW equation of state is used to calculate the explosive detonation performance and propellant combustion performance. The potential parameter values are not directly described in the basic experiments of the gas components in detonation product (static pressure data, Molecular dynamics data or shock Hugoniot data). They are obtained according to the literature, or adjusted according to the experimental value of explosive detonation performance, so it is insufficient to describe the thermodynamic state of water. It can be seen in the scope of the NIST database (800-1275K, 0.1-1GPa), VHL can describe the PVT state of water well.

Since the referenced data source is mainly in the range of fitted potential parameters in the NIST database, in order to test the suitability of the VHL equation of state and the parameters of Eqs. (2) and (3) for other high-temperature and medium-high pressure sections. This paper deals with the high-temperature and medium-high pressure thermodynamic properties of water theoretically. The comparison result of the VLW and BS equations shows in Table III:

At the same time, in order to describe the accuracy of the thermodynamic equation of state of water more clearly, Fig. 1–5 lists their area chart of error.

The BS equation of state\(^{2}\) uses the exp-6 intermolecular potential to simulate the PVT relationship of water from 0.5GPa to 100GPa and 700k-4000k. The equation of state is based on the fitted result of experimental values and molecular dynamics simulations. The formula is as follows:

\[
P = a/V + b/V^2 + c/V^4.586
\]

\[
a = 1.40203 \times 10^5 - 41.23367T
\]

\[
b = -7.72779 \times 10^3 + 6.70124 \times 10^3T
\]

\[
c = 6.52012 \times 10^9 - 0.45580 \times 10^8T
\]

(5)

From Table III, It can be seen that the average relative deviation calculated by the VHL equation of state is 2.216%, and the maximum deviation is -5.017%, which is lower than the average relative deviation calculated by the BS equation of state of 4.684% and the maximum deviation of -7.131% and much lower than the average relative deviation calculated by the VLW equation of state of 16.108% and the maximum deviation of -27.99%. It can be figured out that in the high-temperature and medium-high pressure range,
TABLE III. The PVT relationship of water in high temperature and medium-high pressure calculated by VHL equation of state.

| NO | T/K   | p/Ga | VHL        | VLW   | BS   | Exp.   | Ref.          |
|----|-------|------|------------|-------|------|--------|---------------|
| 1  | 1293.15 | 1.75 | 18.68      | 16.26 | 18.19| 19.15  | Brodholt and wood⁹ |
| 2  | 1393.15 | 1.75 | 19.24      | 17.10 | 18.76| 19.54  | Brodholt and wood⁹ |
| 3  | 1493.15 | 1.75 | 19.82      | 17.89 | 19.35| 20.49  | Brodholt and wood⁹ |
| 4  | 1593.15 | 1.75 | 20.39      | 18.65 | 19.94| 21.47  | Brodholt and wood⁹ |
| 5  | 1693.15 | 1.75 | 20.97      | 19.37 | 20.54| 21.79  | Brodholt and wood⁹ |
| 6  | 1273.15 | 3    | 15.92      | 12.50 | 15.45| 16.22  | Withers et al.¹² |
| 7  | 1273.15 | 2.95 | 15.99      | 12.6  | 15.52| 16.27  | Withers et al.¹² |
| 8  | 1273.15 | 2.45 | 16.83      | 13.7  | 16.36| 16.69  | Withers et al.¹² |
| 9  | 1273.15 | 1.45 | 19.69      | 17.69 | 19.19| 20.03  | Frost and Wood¹⁰ |
| 10 | 1373.15 | 1.45 | 20.37      | 18.65 | 19.87| 20.83  | Frost and Wood¹⁰ |
| 11 | 1473.15 | 1.45 | 21.06      | 19.56 | 20.56| 21.6   | Frost and Wood¹⁰ |
| 12 | 1573.15 | 1.45 | 21.77      | 20.43 | 21.26| 22.3   | Frost and Wood¹⁰ |
| 13 | 1673.15 | 1.45 | 22.47      | 21.26 | 21.97| 23.15  | Frost and Wood¹⁰ |
| 14 | 1373.15 | 3    | 16.24      | 13.11 | 15.79| 16.51  | Withers et al.¹² |
| 15 | 1373.15 | 4    | 14.99      | 11.56 | 14.56| 15.25  | Withers et al.¹² |
| 16 | 1373.15 | 2.5  | 17.13      | 14.26 | 16.67| 17.31  | Withers et al.¹² |
| 17 | 1373.15 | 3.5  | 15.55      | 12.25 | 15.11| 15.65  | Withers et al.¹² |
| 18 | 1173.15 | 0.85 | 22.57      | 22.22 | 22.12| 23.54  | Larrieu and Ayers¹¹ |
| 19 | 1173.15 | 2    | 17.37      | 14.23 | 16.88| 17.65  | Larrieu and Ayers¹¹ |
| 20 | 1173.15 | 3    | 15.6       | 11.84 | 15.12| 15.79  | Withers et al.¹² |
| 21 | 1173.15 | 3.5  | 15.01      | 11.08 | 14.52| 15.38  | Withers et al.¹² |

*Values from experiment or molecular dynamics.

the VHL equation of state can describe the PVT relationship of water more accurately than the VLW and BS equations.

In order to test the suitability of describing the EOS of water by using potential parameters in Equations (1), (2), and (3) in higher pressure state (to simulate detonation state). This paper selects the specific data points with pressure up to tens of GPa to calculate and uses them to compare with the calculation results of BS, TIP4P, DMW, VLW, as shown in Table IV:²³,²⁴

The DMW equation of state¹ is obtained by Duan et al. based on molecular dynamics simulation and liquid experiments with temperatures above 273.15K and pressures above 100 MPa. The formula is as follows:
FIG. 3. $T = 1173.15K$, using various equations of state to describe the deviation of water volume at different pressures.

$Z = \frac{PV}{RT} = 1 + \frac{B}{V_r^2} + \frac{C}{V_r^4} + \frac{D}{V_r^6} + \frac{E}{V_r^8} + \left( \frac{F}{V_r^2} + \frac{G}{V_r^4} \right) \exp \left( -\frac{y}{V_r^2} \right)$

$B = a_1 + \frac{a_2}{T_r} + \frac{a_3}{T_r^2}$

$C = a_4 + \frac{a_5}{T_r} + \frac{a_6}{T_r^2}$

$D = a_7 + \frac{a_8}{T_r} + \frac{a_9}{T_r^2}$

$E = a_{10} + \frac{a_{11}}{T_r} + \frac{a_{12}}{T_r^2}$

$F = \frac{a_{13}}{T_r}$

$G = a_{14} T_r$

$T_r = \frac{T}{T_c}$

FIG. 4. $T = 1273.15K$, using various equations of state to describe the deviation of water volume at different pressures.

FIG. 5. $T = 1373.15K$, using various equations of state to describe the deviation of water volume at different pressures.

TIP4P\textsuperscript{5} combines the virial coefficient and is based on molecular dynamics simulations with pressures above 1 GPa, following the equation of state of the MRK type. The formula is as follows:

$$P = \frac{RT}{V} - b - a\frac{1}{\sqrt{TV(V + b)}} + c\frac{1}{V} + d\frac{1}{V^2} + e\frac{1}{V^3} + f\frac{1}{V^4}$$

$a = -582468 - 3038.79 T - 9.24574 \times 10^{-3} T^2 + 3.02674 \times 10^9 T^2$

$b = -3.90463 \times 10^{-2} - 0.991078 V$

$c = 3.64905 \times 10^4$

$d = -1.02451 \times 10^7$

$e = -1.79681 \times 10^8$

$f = 2.18437 \times 10^9$

From Table IV, the average relative errors of VHL, DMW, TIP4P, VLW and BS are 4.475%, 8.424%, 23.473%, 19.951%, and 5.411%, respectively. It can be seen that when the temperature and pressure are higher ($T > 2000K$, $P > 30GPa$), the VHL keeps precisely calculation results compared to other equations, the error within the range of 2%-7%.

For detonation environment, the thermodynamic state of gas products ranges from high pressure (about tens GPa) to medium pressure (about hundreds MPa) at high temperature ($>1000K$). As for the DMW, TIP4P equations, they mainly describe the medium pressure state of the gas, and the description is inaccurate for the high-temperature and high-pressure states. For the VLW equation, it cannot accurately describe the thermodynamic state of a single gas. And the BS equation, it mainly describes the high-temperature and high-pressure state of the gas, but the description is inaccurate for the high-temperature and medium-pressure states. In view of the uncertainty of experimental data,\textsuperscript{25,26} it can be considered that
TABLE IV. The PVT relationship of water in high temperature and high pressure calculated by VHL equation of state.

| NO | T/K | p/Gpa | VHL | DMW | TIP4P | VLW | BS | Exp. | Ref. |
|----|-----|-------|-----|-----|------|-----|----|-----|------|
| 1  | 2037| 30    | 9.263 (5.086) | 8.496 (-3.614) | 6.600 (-25.126) | 6.434 (-27.011) | 9.11 (3.340) | 8.815 | Rice et al. 25 |
| 2  | 2407| 35    | 8.964 (5.845) | 8.776 (3.625) | 6.265 (-26.025) | 6.480 (-23.485) | 8.90 (5.145) | 8.469 | Rice et al. 25 |
| 3  | 2777| 40    | 8.717 (6.903) | 8.870 (8.783) | 6.552 (-19.646) | 6.495 (-20.351) | 8.73 (7.048) | 8.154 | Rice et al. 25 |
| 4  | 3208| 48.9  | 8.338 (4.059) | 8.562 (11.129) | 6.148 (-19.524) | 6.293 (-18.319) | 8.42 (5.509) | 7.978 | Lyzenga et al. 24 |
| 5  | 3830| 58.5  | 8.018 (4.059) | 8.562 (11.129) | 6.148 (-19.524) | 6.293 (-18.319) | 8.42 (5.509) | 7.978 | Lyzenga et al. 24 |
| 6  | 4090| 61.9  | 7.930 (3.795) | 8.492 (11.148) | 5.693 (-23.898) | 6.293 (-17.635) | 8.15 (5.738) | 7.705 | Lyzenga et al. 24 |
| 7  | 4480| 71.0  | 7.678 (2.629) | 8.246 (10.225) | 5.473 (-25.030) | 6.160 (-17.659) | 7.85 (4.876) | 7.481 | Lyzenga et al. 24 |
| 8  | 5270| 80.0  | 7.517 (2.969) | 7.964 (9.101) | 6.600 (-25.126) | 6.188 (-15.228) | 7.73 (5.872) | 7.300 | Lyzenga et al. 24 |

1Values calculated using the VHL equation of state. The values inside brackets is relative errors between the calculated values and the experimental values.
2Values calculated using the DMW equation of state. The values inside brackets is the same as above.
3Values calculated using the TIP4P equation of state. The values inside brackets is the same as above.
4Values calculated using the VLW equation of state. The values inside brackets is the same as above.
5Values calculated using the BS equation of state. The values inside brackets is the same as above.
6Values from experiment or molecular dynamics.

the VHL equation of state with the temperature-dependent potential energy function form proposed in this paper can accurately describe the thermodynamic state of water in detonation environment.

IV. CONCLUSIONS

For the highly polar detonation product gas H2O, this paper uses the temperature-dependent L-J potential function. The relevant parameters are based on the thermodynamic data of water in the NIST database (the pressure range is 0.1GPa-1.0GPa, the temperature range is 800K-1275K), which obtained through the complex configuration optimization method. Based on the L-J potential energy function and the VHL equation of state, the average relative deviation calculated using the VHL equation of state is 0.471% and the maximum deviation is 3.662% in the NIST database, which is much lower than the value of average relative deviation 14.738% and the maximum deviation is 95.396% calculated by the VLW equation. In the high-temperature and medium-high pressure data sections, like in the detonation environment, the VHL equation of state with temperature-dependent potential function form can describe the thermodynamic state of water more accurately than other equations.

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