A New Three-Parameter Generalized van der Waals Equation of State for Water, Heavy Water, Tritium Oxide and Silica

R. Balasubramanian[1], K. Sugumar[3]

[1, 2]Department of Physics, Arignar Anna Govt. Arts College, Namakkal 637 002, Tamilnadu, India

Abstract: ***A new three- parameter generalized van der Waals equation of state has been proposed and employed to calculate the spinodal and thermodynamic limit of superheat of water, heavy water, tritium oxide and silica. It is established that water, heavy water, tritium oxide and silica obey the single parameter law of corresponding states. It is established that the newly introduced parameter n is a thermodynamic similarity parameter. It has been established that water, heavy water, tritium oxide and silica can be superheated, under rapid heating, up to temperatures $0.877T_c$, $0.876T_c$, $0.875T_c$ and $0.860T_c$,respectively. This fact is to be taken into account when water, heavy water, tritium oxide and silica are subjected to rapid heating.***

Keywords: Equation of state, Heavy water, Law of corresponding states, Silica, Spindol, Superheating, Tritium oxide, Water.

1. Introduction

The knowledge of thermophysical properties of substances is of scientific and technological significance. Reliable data on the thermophysical properties of substances are required also for designing various technological processes and understanding the nature of substances. The experimental studies on the thermo physical properties of substances, particularly in the high – temperature region, encounter severe difficulties. This is due to the anomalous behavior of substances in the high – temperature region. Thus, arises a necessity for theoretical studies on the thermo physical properties of substances, particularly of water, heavy water, tritium oxide and silica. Considering the scientific and technological significance, in recent years, numerous studies have made[1-15] on the thermophysical properties of water, heavy water, tritium oxide and silica. Statistical mechanics and thermodynamics provide several approaches for the theoretical studies on the thermo physical properties of substances. One of such commonly employed [16-27] approach is the development of equation of state for substances.

This work is aimed at developing a new equation of state for water, heavy water, tritium oxide, silica in the metastable state. In this work, the known two – parameter van der Waals equation of state is generalized by modifying the attractive term. The performance characteristics of the new generalized van der Waals equation of state in describing the high- temperature properties of water, heavy water, tritium oxide, silica are investigated.

2. Generalization of van der waals equation of state

The known two – parameter van der Waals equation of state does not lend itself to precise description of the thermodynamic properties of liquids and gases. Hence, in this work, an improvement of this equation is proposed by introducing the parameters b and n in the attractive term. Such a generalized van der Waals equation of state for one mole of substance has the form :

$$P = \frac{RT}{V-b} - \frac{a}{(V+b)^n} \quad (1)$$

where P – Pressure, V - Molar volume, T - Temperature, R - Universal gas constant, and a ,b are substance-specific constants.

The vapor-liquid critical point conditions are

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \quad ; \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \quad (2)$$

From Eqs.(1)-(2),we get the critical volume ,critical temperature and critical pressure as

$$V_c = \left(\frac{n+3}{n-1}\right) b \quad (3)$$

$$T_c = \frac{4na}{R(n+1)^2}\left(\frac{n-1}{2b(n+1)}\right)^{n-1} \quad (4)$$

$$P_c = \frac{a}{2^n b^n}\left(\frac{n-1}{n+1}\right)^{n+1} \quad (5)$$

When Eqs.(3)-(5) are taken into account, we get the critical compressibility factor as

$$Z_c = \frac{(n-1)(n+3)}{8n} \quad (6)$$

The generalized van der Waals equation of state may be rewritten in terms of the reduced variables $P^* = P/P_c$, $V^* = V/V_c$, $T^* = T/T_c$ as

$$P^* = \frac{8nT^*}{(n-1)(n+3)V^* - (n-1)} - \frac{2^n(n+1)^{n+1}}{(n-1)[(n+3)V^* + (n-1)]^n} \quad (7)$$

The reduced equation of state given by Eq. (7) represents the single- parameter law of corresponding states with the thermodynamic similarity parameter n. That is, substances obeying the generalized van der Waals equation of state , with the same values of parameter n are thermodynamically similar.

3. Determination of equation–of–State Parameters

The parameters a, b and n of the generalized van der Waals equation of state may be determined through the critical – point parameters.

Eq.(6) is a quadratic equation with respect to the parameter n. The physically meaningful solution of Eq.(6) is

$$n = 4Z_C - 1 + \sqrt{(1-4Z_C)^2 + 3} \tag{8}$$

Eq.(4) gives the parameter a of the generalized van der Waals equation of state as

$$a = \left[\frac{2(n+1)b}{n-1}\right]^{n-1} \frac{R(n+1)^2 T_c}{4n} \tag{9}$$

Eq.(5) gives the parameter a of the generalized van der Waals equation of state as

$$a = 2^n b^n P_c \left(\frac{n+1}{n-1}\right)^{n+1} \tag{10}$$

Eqs.(3) gives the parameter b of the generalized van der Waals equation of state as

$$b = \left(\frac{n-1}{n+3}\right) V_c \tag{11}$$

Using Eqs.(8)-(11), the parameters the generalized van der Waals equation of state can be determined.

4. Spinodal by Generalized van der Waals Equation of State

The knowledge of the spinodal, a characteristic curve on the phase diagram, is essential[28-32] in describing the high-temperature properties of a substance in the critical and in the metastable states. The spinodal defines the thermodynamic stability boundary of the phase envelope. The spinodal encloses the rigion of unstable states for which the isothermal is negattve. For stable states, the isothermal elastically is positive. The spinodal is therefore, defined by the condition:

$$-\left(\frac{\partial P}{\partial V}\right)_T = 0 \tag{12}$$

Applying the condition given by Eq.(12) to Eq.(7), we get the equation of spinodal in T^*, V^* coordinates :

$$T^*_s = \frac{2^n n(n+1)^{n+1}\left[(n+3)V^* - (n-1)\right]^2}{8n\left[(n+3)V^* + (n-1)\right]^{n+1}} \tag{13}$$

Substituting Eq. (13) into Eq. (7), we get the equation of spinodal in P^*, V^* coordinates

$$P^*_s = \frac{8nT^*}{(n-1)\left[(n+3)V^* - (n-1)\right]} - \frac{2^n (n+1)^{n+1}}{(n-1)\left[(n+3)V^* + (n-1)\right]^n} \tag{14}$$

4.1 Thermodynamic limit of superheat of fluids

With decrease in pressure, the superheat of substances increases. The thermodynamic limit of superheat is attained at

$$P = 0 \tag{15}$$

Applying the condition given by Eq.(15) to Eq.(7) and using Eq.(13),we get the reduced volume of the fluid at the thermodynamic limit of superheat and the thermodynamic limit of superheat as

$$V^*_{s,p=0} = \left(\frac{n-1}{n+3}\right) \tag{16}$$

$$T^*_{s,p=0} = \frac{1}{4}\left(\frac{n+1}{n}\right)^{n+1} \tag{17}$$

That is, thermodynamic limit of superheat of substances depends only on the parameter n but not on the parameters a,b of the generalized of van der Waals equation of state.

5. Determination of Equation-of State Parameters

The parameters of the equation of state can be determined using any characteristic point on the phase diagram. However, the use of the critical-point parameters in determining the equation-of –state parameters will improve the accuracy of the equation of state in describing the high-temperature properties of substances. The parameter n for water, heavy water, tritium oxide and silica is determined through the Eq.(8) using experimental data[33-36] on the critical compressibility factor. The obtained values of n are presented in Table1. The parameter a for water, heavy water, tritium oxide and silica is determined through the Eqs. (9) and (10) using experimental data on critical-point parameters along with the values of n. The parameter b for water, heavy water, tritium oxide and silica is determined through the Eq.(11) using experimental data on critical-point parameters along with the values of n. The obtained values of a are presented.

Table 1: Equation-of–state parameters

Substance	a JKg^{-1}K^{-1}m^3 mol^{-1} Eq.(9)	Eq.(10)	b 10^{-5} m^3/mol Eq.(11)	n Eq.(8)
H_2O	854281.601	85299.209	7.822	1.650
D_2O	880308.659	88125.778	7.950	1.658
T_2O	95430.803	95414.403	8.397	1.671
SiO_2	199089.6	199016.178	14.875	1.810

6. Determination of Spinodal

Considering the values of *n* (Table1) for water, heavy water, tritium oxide and silica, the spinodal is determined by Eqs.(13)-(14).The obtained spinodal-parameters are presented in Tables2-5. These spinodal-parameters define the stability boundary of water heavy water, tritium oxide and silica in the phase diagram.

Table 2: Spinodal of water

V^*	T_s^*	P_s^*
0.1	0.133	- 68.008
0.2	0.115	-21.622
0.3	0.432	-7.826
0.4	0.663	-2.863
0.5	0.809	-0.752
0.6	0.899	0.220
0.7	0.952	0.679
0.8	0.982	0.891
0.9	0.996	0.978
1.0	0.999	0.999

Table 3: Spinodal of heavy water

V^*	T_s^*	P_s^*
0.1	0.143	-68.183
0.2	0.116	-21.368
0.3	0.427	-7.877
0.4	0.660	-2.886
0.5	0.808	-0.761
0.6	0.899	0.215
0.7	0.952	0.678
0.8	0.982	0.891
0.9	0.996	0.979
1.0	0.999	0.999

Table 4: Spinodal of tritium oxide

V^*	T_s^*	P_s^*
0.1	0.161	-68.519
0.2	0.107	-21.549
0.3	0.418	-7.959
0.4	0.653	-2.924
0.5	0.804	-0.778
0.6	0.896	0.208
0.7	0.951	0.674
0.8	0.981	0.890
0.9	0.996	0.978
1.0	1.000	1.000

Table 5: Spinodal of silica

V^*	T_s^*	P_s^*
0.1	0.422	-72.642
0.2	0.037	-23.679
0.3	0.326	-8.919
0.4	0.587	-3.357
0.5	0.763	-0.973
0.6	0.874	0.123
0.7	0.940	0.640
0.8	0.977	0.879
0.9	0.995	0.976
1.0	1.000	1.000

7. Determination of Thermodynamic Limit of Superheat

The volume at the thermodynamic limit of superheat for water, heavy water, tritium oxide and silica are determined through the Eq.(16) using the values of the parameters *n* (Table1). The obtained values are presented in Table 6. The thermodynamic limit of superheat for water, heavy water, tritium oxide and silica is determined through Eq.(17) using the values of the parameters *n* (Table1). The obtained values are presented in Table 6.Below the thermodynamic limit of superheat, heterogeneous nucleation will prevail. And, above the thermodynamic limit of superheat, homogeneous nucleation will prevail resulting in the explosive boiling of fluids.

Table 6: Thermodynamic limit of superheat

Substance	$V^*_{s,0}$	$T^*_{s,0}$	$V_{s,0}$ 10^{-5} m^3/mol	$T_{s,0}$ K
H_2O	0.569	0.877	31.886	567.792
D_2O	0.570	0.876	32.124	564.369
T_2O	0.571	0.875	33.438	561.450
SiO_2	0.584	0.860	51.596	4413.852

8. Results and Discussion

The three- parameter generalized van der Waals equation of state has been employed to calculate the spinodal, and thermodynamic limit of superheat of water, heavy water tritium oxide and silica. water, heavy Moreover, the performance characteristics of the generalized van der Waals equation of state in evaluating the spinodal, and the thermodynamic limit of superheat of water, heavy water, tritium oxide and silica have been studied.The parameters of the generalized van der Waals equation of state are expressed in terms of the critical pressure, the critical volume, and the critical temperature. Thus, is has been established that the three characteristic properties of the fluids viz., the critical pressure, the critical volume and the critical temperature characterize the generalized van der Waals equation of state. It has been established that water, heavy water, tritium oxide and silica can be superheated, under rapid heating, up to temperatures $0.877T_c$, $0.876T_c$, $0.875T_c$ and $0.860T_c$,respectively. This fact is to be taken into account when water, heavy water, tritium oxide and silica are subjected to rapid heating.

9. Conclusion

A new three-parameter generalized van der Waals equation of state is proposed for describing the high-temperature properties of water, heavy water, tritium oxide, silica in the metastable state. It is established that water, heavy water, tritium oxide and silica obey the single parameter law of corresponding states. It is established that the newly introduced parameter *n* is a thermodynamic similarity parameter. The spinodal (stability boundary on the phase diagram) of water, heavy water, tritium oxide, and silica has been determined. The thermodynamic limit of superheat of water, heavy water, tritium oxide and silica has been determined.

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Author Profile

Dr. R. Balasubramanian is an Assistant Professor of Physics at the Arignar Anna Government Arts College, Namakkal, India. He has 24 years of post-doctoral research and teaching experience. He did his Doctorate at the Russian Peoples" Friendship University, Moscow, Russia under the supervision of renowned Professor M.M.Martynyuk who conceptualized the phenomenon of Explosive Boiling of liquids. His research interests include Phase transitions, Critical phenomena and Equations of state.

K.Sugumar is a graduate student in the Department of Physics at the Arignar Anna Government Arts College, Namakkal, India. He is pursuing his graduate research project under the supervision of Dr.R.Balasubramanian.