A New Four-Parameter Generalized Van der Waals Equation of State: Metastable State of Group III Elements

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Abstract: *A new four- parameter modified van der Waals equation of state has been proposed and employed to calculate the spinodal (metastable state) and the thermodynamic limit of superheat of aluminum, gallium, and indium. It is established that aluminum, gallium, and indiumobey the single parameter law of corresponding states. It is established that the new parameter introduced in the attractive term of the equation of state is a thermodynamic similarity parameter. It has been established that aluminum, gallium, and indiumcan be superheated, under rapid heating, up to temperatures 6961K, 6286K, and 5604Krespectively. Above these temperatures, aluminum, gallium, and indium undergo explosive boiling by virtue of homogeneous nucleation. This fact is to be taken into account when aluminum, gallium, and indium are subjected to rapid heating.*

Keywords: Equation of state, Law of corresponding states. Aluminum, Gallium, Indium Spinodal, Superheating

1. Introduction

The study of the thermodynamic properties of aluminum, gallium, and indium of scientific and technological significance. The experimental studies on the thermodynamic properties of the aluminum, gallium, and indium in the metastable region, encounter severe difficulties. Thus, arises a need for theoretical studies on their thermodynamic properties. In recent years, several studies have been made [1-7] on the thermodynamic properties of aluminum, gallium, and indium. This fact manifests the relevance of the study of the thermodynamic properties of the aluminum, gallium and indium of the Statistico-mechanical and thermodynamically approaches to study the thermodynamic properties of substance is the development of equations of state for substances. To improve the accuracy, the known equations of state are generalized [8-20] by modifying the repulsive and attractive terms.

This work is aimed at developing a new equation of state for aluminum, gallium, and indium in the meta stable state. In this work, the known two–parameter van derWaals equation of state is by modifying its repulsive and attractive terms. The performance characteristics of modified van der Waals equation of state in describing the properties of aluminum, gallium and indium in the metastable stateare investigated.

2. Modification of van der Waals equation of state

The known two – parameter van der Waals equation of state does not precisely describe the thermodynamic properties of fluid. This may be attributed to the inaccurate repulsive and attractive terms in the van der Waals equation of state of state. Hence, in this work, this equation is proposed by introducing a parameters c in the repulsive term and n in the attractive term. Sucha modified van der Waals equation of state for one mole of substance has the form :

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

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

The vapor-liquid critical point conditions are

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

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

$$V_c = N(b - c) \qquad (3)$$

Where,

$$N \equiv \frac{n+1}{n-1}$$

$$T_c = \frac{n(N-1)^2 a}{RN^{n+1}(b-c)^{n-1}} \qquad (4)$$

$$P_c = \frac{a}{N^{n+1}(b-c)^n} \qquad (5)$$

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

$$Z_c \equiv \frac{P_c V_c}{RT_c} = \frac{n^2 - 1}{4n} \qquad (6)$$

The modified van der Waals equation of state may be rewritten in terms of the reduced variables as

$$P_c = \frac{N}{V^{*n}} \left[\frac{n\left(V^* - \frac{1}{N}\right)}{V^*} - 1 \right] \qquad (7)$$

Where

$$P^* = P/P_c \ , \ V^* = V/V_c, \ T^* = T/T_c$$

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 modified van der Waals equation of state, with the same values of parameter n are thermodynamically similar. That is, such substances, have similar intermolecular force characteristics

3. Equation-of-state parameters

The parameters a, b, c and n of the modified van der Waals equation of state are determined through the critical–point parameters. Eq. (6) is quadratic equation with respect to the parameter n. the physically meaningful solution (i.e. n>0) of Eq. (6) is

$$n = 2Z_c + \sqrt{4Z_c^2 + 1} \tag{8}$$

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

$$a = \frac{(n+1)^2 \, RT_c^2 V_c^{n-1}}{4n} \tag{9}$$

Eq. (3) gives the parameter b of the modified van der Waals equation of state as

$$b - c = \left(\frac{n-1}{n+1}\right) V_c \tag{10}$$

Using Eqs.(8)-(10), the parameters of themodified van der Waals equation of state can be determined. Moreover using the Riedel's parameter along with the critical volume, the values of the parameter b and c can be determined.

4. Spinodal

The knowledge of the spinodal, a characteristic curve on the phase diagram, is essential in describing the properties of a substance in the critical and in the metastable states. Fig 1 schemtically depicts [21] the vapour-liquid equilibrium curve (bimodal) and the stability boundary curve (spinodal) of substances.
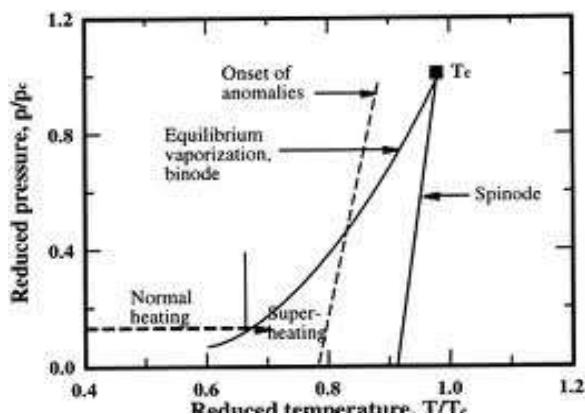

Figure 1

The spinodal defines the thermodynamic stability boundary of the phase envelope. The spinodalencloses the region of unstable states for which the isothermal elasticity is negative. For stable states, the isothermal elasticity is positive. In the region between the binodal and the spinodal on the phase diagram, the liquid is in the metastable state. Considering the scientific and technological significance, in recent years, several studies have been made [22-32] on the behavior of the superheated metastable fluids. The spinodal is therefore, defined by the condition:

$$-\left(\frac{\partial P}{\partial V}\right)_T = 0 \tag{11}$$

Applying the condition given by Eq.(11) to Eq.(7), we get the equation of spinodalin T^*, V^* coordinates as

$$T_s^* = \left[\frac{(n^2 - 1)(NV^* - 1)^2}{4NV^{*n+1}}\right] \tag{12}$$

Substituting Eq. (12) into Eq. (7), we get the equation of spinodal in P^*, V^* coordinates as

$$P_s^* = \frac{N}{V^{*n}} \left[\frac{n\left(V^* - \frac{1}{N}\right)}{V^*} - 1\right] \tag{13}$$

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

$$P=0 \tag{14}$$

Applying the condition given by Eq.(14) to Eq.(7) andusing Eq.(12),we get

$$V_{s,0}^* = \frac{n}{n+1} \tag{15}$$

Where,

$V_{s,0}^*$ - The reduced volume of the fluid at the thermodynamic limit of superheat

$$T_{s,0}^* = \frac{1}{4}\left(\frac{n+1}{n}\right)^{n+1} \tag{16}$$

Where,

$T_{s,0}^*$ - The thermodynamic limit of superheat

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

5. Determination of equation-of- state parameters

The parameters of the modified van der Waals 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 aluminum, gallium, and indiumis determined through the Eq. (8) using experimental data [33] on the critical compressibility factor. The obtained values of n are presented in Table1. The parameter $a$for

aluminum, gallium and indium is determined through the Eq. (9) using experimental data on critical-point parameters along with the values of n. The parameter b-c for aluminum, gallium and, indiumis determined through the Eq.(10) using experimental data on critical-point parameters along with the values of n. The obtained values of$a$and$b$-$c$are presented in Table 1.

**Table 1:** Eqution-of-state parameters

| Element	a Pa$(m^3.mol^{-1})^n$	b-c $10^{-6}(m^3.mol^{-1})$	n
Aluminum	5.2775	11.102	1.7160
Gallium	5.1595	10.059	1.7016
Indium	6.9405	15.520	1.6912

6. Determination of spinodal

Considering the values of n (Table1) foraluminum, gallium, and indium the spinodal is determined by Eq.(12) and (13).The obtained spinodal-parameters are presented in Tables2-6.These spinodal-parameters define the stability boundary of aluminum, gallium, and indiumin the phase diagram.

Table 2: Spinodal of Aluminum

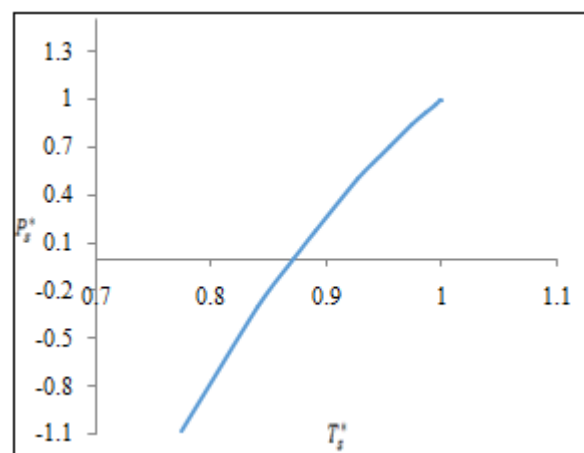| V_s^*	T_s^*	P_s^*
0.55	0.7679	-1.1166
0.6	0.8367	-0.3393
0.6318	0.8701	0
0.65	0.8885	0.1652
0.7	0.9266	0.4927
0.75	0.9543	0.7057
0.8	0.9737	0.8360
0.85	0.9881	0.9248
0.9	0.9951	0.9728
0.95	0.9996	0.9964
1	1.0008	1.0027
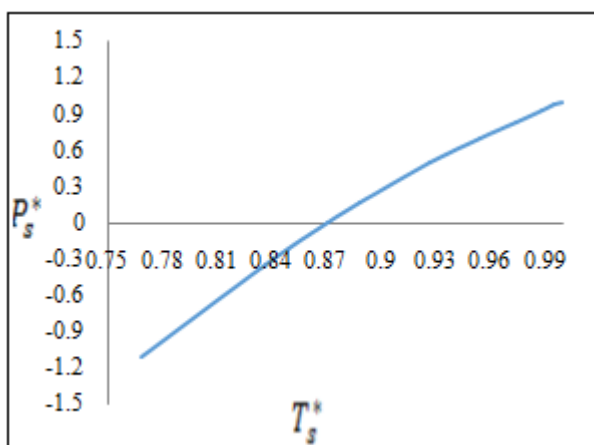
Plot 1.1: Spinodal of aluminum in *P-T* Coordinates
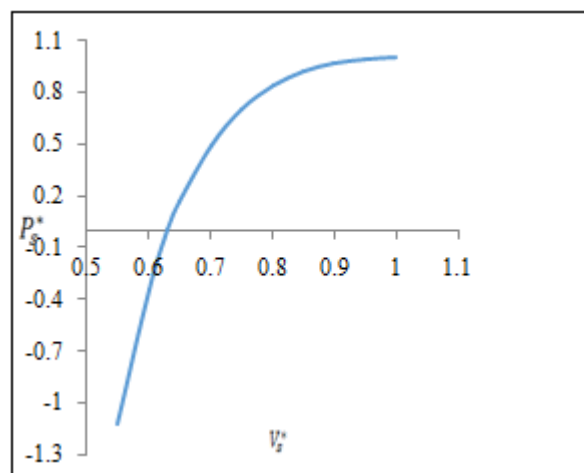
Plot 1.2: Spinodal of aluminum in *P-V* Coordinates

Table 3: Spinodal of Gallium

| V_s^*	T_s^*	P_s^*
0.55	0.7735	-1.0832
0.6	0.8405	-0.3067
0.6298	0.8718	0
0.65	0.8906	0.1763
0.7	0.9273	0.4981
0.75	0.9544	0.7067
0.8	0.9736	0.8449
0.85	0.9864	0.9230
0.9	0.9948	0.9706
0.95	0.9989	0.9943
1	1.0000	1.0003

Plot 2.1: Spinodal of gallium in *P-T* Coordinates
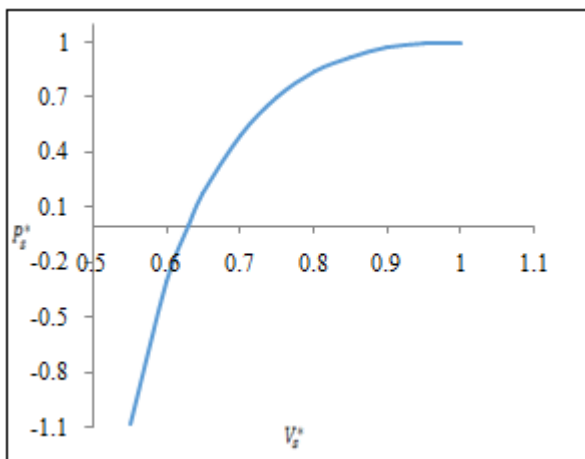
Plot 2.2: Spinodal of gallium in *P-V* Coordinates

Table 4: Spinodal of Indium

V_s^*	T_s^*	P_s^*
0.55	0.7772	-1.0552
0.6	0.8426	-0.3020
0.6284	0.8728	0
0.65	0.8926	0.1847
0.7	0.9287	0.5032
0.75	0.9550	0.7100
0.8	0.9743	0.8416
0.85	0.9864	0.9238
0.9	0.9946	0.9702
0.95	0.9988	0.9936
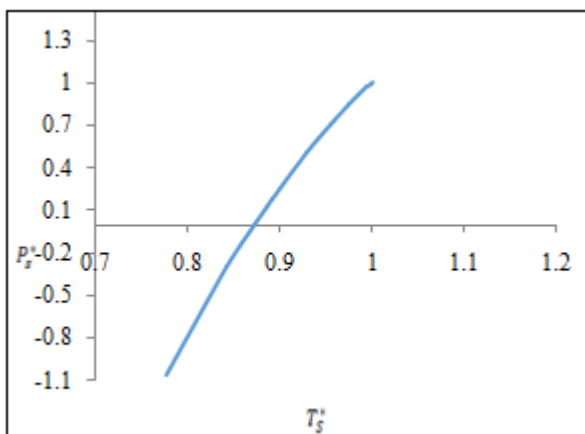
Plot 3.1: Spinodal of Indium in *P-T* Coordinates
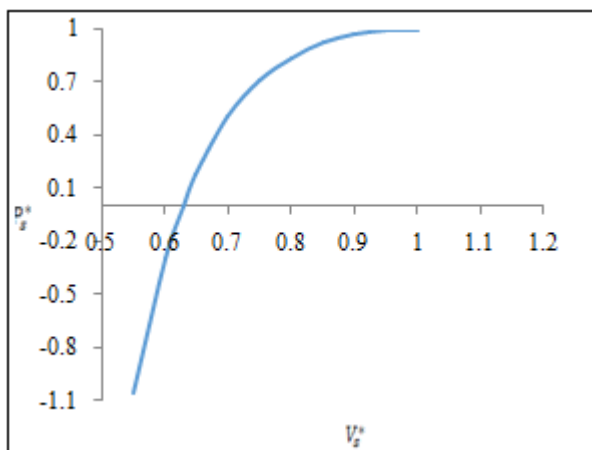
Plot 3.2: Spinodal of Indium in *P-V* Coordinates

7. Determination of thermodynamic limit of Superheat

The volume at the thermodynamic limit of superheat for aluminum, gallium, and indium are determined through Eq (15) using the values of the parameters *n* (Table1). The obtained values are presented in Table7. The thermodynamic limit of superheat for aluminum, gallium, and indium is determined through Eq (16) using the values of the parameters *n* (Table1). The obtained values are presented in Table7.Below the thermodynamic limit of superheat, heterogeneous nucleation prevails. And, above thermodynamic limit of superheat, homogeneous nucleation will prevail resulting in the explosive boiling of fluids.

Table 5: Thermodynamic limit of superheat

Substance	$T_{s,0}^*$	$V_{s,0}^*$	$T_{s,0}$ K	$V_{s,0}$ 10^{-5}m^3/mol
Aluminum	0.8701	0.6318	6961	2.6635
Gallium	0.8718	0.6298	6286	2.4395
Indium	0.8728	0.6284	5604	3.7974

8. Results and Discussion

The four- parameter van der Waals equation of state has been employed to calculate the spinodal, and thermodynamic limit of superheat of aluminum, gallium, and indium. The performance characteristics of the van der Waal type equation of state in evaluating the spinodal, and the thermodynamic limit of superheat of aluminum, gallium and indium have been studied The parameters of the van der Waals equation of state are expressed in terms of the critical-point parameters of aluminum gallium, and indium. 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 van der Waals equation of state .It has been established that aluminum, gallium, and indium can be superheated, under rapid heating, up to temperatures 6961K, 6286K and 5604K respectively. That is aluminium, can be superheated to above 4442 K above their normal boiling temperatures, That is gallium can be superheated to above 4057 K above their normal boiling temperatures. That is indium can be superheated to above 3577Kabove their normol boiling temperature. This fact is to be taken into account when aluminum, gallium, and indum are subjected to rapid heating.

9. Conclusion

A new four-parameter van der Waals equation of state is proposed for describing the high-temperature properties of aluminum, gallium and indium. It is established that aluminum gallium, and indium obey the single parameter law of corresponding states. It is established that the newly introduced parameter *n* is a thermodynamic similarity parameter. The spinodal (Metastable State on the phase diagram) of aluminum, gallium and indium has been determined. The thermodynamic limit of superheat of aluminum gallium and indium has been determined.

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