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A New Four-Parameter Modified Berthelot Equation of State: Stability Boundary of Isomers and Isotopes of Hydrogen

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Abstract: *A new four- parameter modified Berthelot equation of state has been proposed and employed to calculate the spinodal (stability boundary) and the thermodynamic limit of superheat of normal hydrogen, of the isomers of hydrogen i.e. orthohydrogen, parahydrogen and of the isotopes of hydrogen i.e. deuterium and tritium. It is established that normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium obey 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 normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium can be superheated, under rapid heating, up to temperatures 30.916K,30.705K, 30.619K, 35.574K, and 37.536Krespectively. Above these temperatures, normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium undergo explosive boiling by virtue of homogeneous nucleation. This fact is to be taken into account when normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium are subjected to rapid heating.*

Keywords: Deuterium, Equation of state, Law of corresponding states, Orthohydrogen, Normal Hydrogen, Parahydrogen, Spinodal, Superheating, Tritium

1. Introduction

The study of the thermodynamic properties of the isomers and isotopes of hydrogen is of scientific and technological significance. The experimental studies on the thermodynamic properties of the isomers and isotopes of hydrogenin 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 [1-11] on the thermodynamic properties of normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium. This fact manifests the relevance of the study of the thermodynamic properties of the isomers and isotopes of hydrogen. One of the Statistico-mechanical and thermodynamical 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 [12-22] by modifying the repulsive and attractive terms.

This work is aimed at developing a new equation of state for normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium in the metastable state. In this work, the known two–parameter Berthelot equation of state is by modifying its repulsive and attractive terms. The performance characteristics of modified Berthelot equation of state in describing the properties of normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium in the metastable state are investigated.

2. Modification of Berthelot equation of state

The known two – parameter Berthelot 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 Berthelot 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. such a modified Berthelot equation of state for one mole of substance has the form:

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

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

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

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

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

Where,

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

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

$$P_c = \frac{(n-1)}{2}\left[\frac{aR}{nN^{n+1}(b-c)^{n+1}}\right]^{\frac{1}{2}} \quad (5)$$

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

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

The modified Berthelot equation of state may be rewritten in terms of the reduced variables as

$$P^* = N\left[\frac{4nT^*}{(n^2-1)(NV^*-1)} - \frac{1}{T^* V^{*n}}\right] \quad (7)$$

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 Berthelot 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 Berthelot 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

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

Eq. (4) gives the parameter a of the modified Berthelot equation of state as

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

Eqs. (3) gives the parameter b of the modified Berthelot equation of state as

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

Using Eqs.(8)-(10), the parameters of the modified Berthelot 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 schematically depicts [23] the vapour-liquid equilibrium curve (bimodal) and the stability boundary curve (spinodal) of substances.

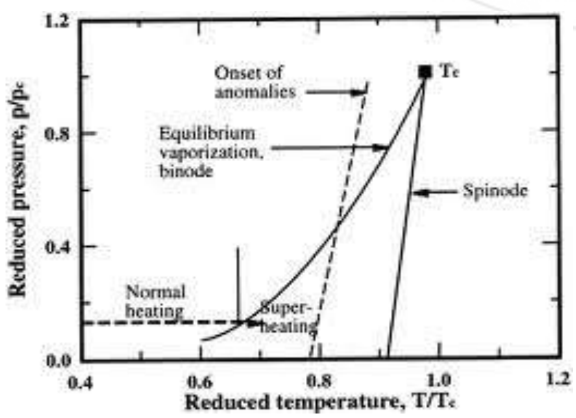

Figure 1

The spinodal defines the thermodynamic stability boundary of the phase envelope. The spinodal encloses 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 [24-34] 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 spinodal in T^*, V^* coordinates as

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

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

$$P_s^* = \left(\frac{2}{n-1}\right) \frac{1}{V_s^{*\frac{n-1}{2}}} \left[\frac{n}{V_s^*} - \frac{1}{\left(V_s^* - \frac{1}{N}\right)}\right] \tag{13}$$

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) and using 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

$$T_{s,0}^* = \frac{1}{2}\left(\frac{n}{n+1}\right)^{\frac{n+1}{2}} \tag{16}$$

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 Berthelot equation of state.

5. Determination of Equation-of- State Parameters

The parameters of the modified Berthelot 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 normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritiumis determined through the Eq. (8) using experimental data [35-37] on the critical compressibility factor. The obtained values of n are presented in Table1. The parameter a for normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium is determined through the Eqs (9) using experimental data on critical-point parameters along with the values of n. The parameter b-c for normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium is 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: Equation-of-state parameters

Substance	a NKm^{3n-2}/mol^n	b-c $10^{-5} m^3/mol$	n
Hydrogen	5.901	23.100	1.769
Orthohydrogen	4.481	22.824	1.792
Parahydrogen	5.634	23.089	1.773
Deutrium	7.268	20.894	1.769
Tritium	5.950	19.785	1.799

6. Determination of Spinodal

Considering the values of n (Table1) for normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium, the spinodal is determined by Eqs.(12) and (13).The obtained spinodal-parameters are presented in Tables 2-6.These spinodal-parameters define the stability boundary of normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium in the phase diagram.

Table 2: Spinodal of normal hydrogen

V_s^*	T_s^*	P_s^*
0.3	0.162	-162.512
0.4	0.602	-13.920
0.5	0.804	-3.227
0.6	0.819	-0.621
0.7	0.958	0.475
0.8	0.985	0.841
0.9	0.997	0.971
1	1	1

Table 3: Spinodal of orthohydrogen

V_s^*	T_s^*	P_s^*
0.3	0.122	-225.249
0.4	0.584	-14.947
0.5	0.795	-3.453
0.6	0.901	-0.541
0.7	0.956	0.459
0.8	0.984	0.836
0.9	0.997	0.970
1	1	0.999

Table 4: Spinodal of parahydrogen

V_s^*	T_s^*	P_s^*
0.3	0.157	-169.121
0.4	0.592	-14.054
0.5	0.802	-3.291
0.6	0.904	-0.497
0.7	0.958	0.473
0.8	0.985	0.840
0.9	0.997	0.971
1	1	1

Table 5: Spinodal of deterium

V_s^*	T_s^*	P_s^*
0.3	0.163	-161.721
0.4	0.602	-13.909
0.5	0.803	-3.266
0.6	0.905	-0.491
0.7	0.958	0.474
0.8	0.985	0.840
0.9	0.997	0.971
1	1	1

Table 6: Spinodal of tritium

V_s^*	T_s^*	P_s^*
0.3	0.109	-256.852
0.4	0.183	-15.311
0.5	0.792	-3.517
0.6	0.899	-0.558
0.7	0.956	0.454
0.8	0.984	0.835
0.9	0.997	0.969
1	1	1

7. Determination of thermodynamic limit of superheat

The volume at the thermodynamic limit of superheat for normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritiumare 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 normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium 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 the thermodynamic limit of superheat, homogeneous nucleation will prevail resulting in the explosive boiling of fluids.

Table 7: Thermodynamic limit of superheat

Substance	$T^*_{s,0}$	$V^*_{s,0}$	$T_{s,0}$ K	$V_{s,0}$ $10^{-5} m^3/mol$
Hydrogen	0.929	0.639	30.916	4.102
Ortho hydrogen	0.929	0.642	30.705	4.155
Para hydrogen	0.929	0.639	30.619	4.115
Deuterium	0.929	0.639	35.574	3.708
Tritium	0.929	0.634	37.536	3.632

8. Results and Discussion

The four- parameter modified Berthelot equation of state has been employed to calculate the spinodal, and thermodynamic limit of superheat of normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium. The performance characteristics of the Berthelot type equation of state in evaluating the spinodal, and the thermodynamic limit of superheat of normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium have been studied. The parameters of the modified Berthelot equation of state are expressed in terms of the critical-point parameters of normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium. 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 modified Berthelot equation of state. It has been established that normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritiumcan be superheated, under rapid heating, up to temperatures 30.916*K*,30.705*K*,30.619K, 35.574K and 37.536*K*respectively. That is, normal hydrogen orthohydrogen and parahydrogen, can be superheated to above 11 K above their normal boiling temperatures, deuterium and tritium,can be superheated to above 12 K above their normal boiling temperatures. This fact is to be taken into account when normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritiumare subjected to rapid heating.

9. Conclusion

A new four-parameter modified Berthelot equation of state is proposed for describing the high-temperature properties of normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium. It is established that normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritiumobey 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 normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritium has been determined. The thermodynamic limit of superheat of normal hydrogen, orthohydrogen, parahydrogen, deuterium and tritiumhas been determined.

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