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A Study on the Thermodynamic Limit of Superheat of Refractory Metals

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Abstract: ***The thermodynamic limit of superheat of titanium, zirconium, hafnium, vnadium, niobium, tantalum, chromium, molybdenum, and tungsten is determined using a new three-parameter generalized Berthelot equation of state. The results of the determination of the thermodynamic limit of superheat of liquid titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten are in agreement with experimental data. The given study establishes that liquid titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten can be superheated up to temperatures of 10736K, 13430K, 11263K, 11404K, 8685K, 8049K, 8787K, 10394K, 12748K, respectively. Moreover, titanium, zirconium, hafnium. vanadium, niobium, tantalum, chromium, molybdenum and tungsten have been found to obey the single-parameter law of corresponding states, with the thermodynamic limit of superheat as the thermodynamic similarity parameter. It is shown that the substances obeying the generalized Berthelot equation of state exhibit considerable uniformity when their thermodynamic properties are expressed in a suitable reduced form.***

Keywords: Equation of state, Law of corresponding states, Refractory metals, Spindol, Superheating

1. Introduction

One of the fundamental tasks of thermodynamic and statistical physics is to find the equations of state of substances. Having accurate equations of state for the substances is important in the design of several industrial processes and for precise calculations describing a variety of thermodynamic phenomena. Many modifications of the known equations of the known equation of state have been proposed [1-3] to improve the accuracy. These modifications result in the generalization of the known equations of state. There is a need for the generalized equations of state with numerical stability and ability to describe the thermodynamic properties of a wide range of technically important substances used in industries. To improve the accuracy of an equation of state usually its attractive term and/or the repulsive term is modified. In some cases, the equation-of-state parameter's dependence on temperature is assumed.

Refractory metals are used by the metallurgy industry in the internal linings of furnaces, kilns, reactors and other vessels for holding, transporting metal and slag. These applications require the knowledge of high-temperature properties such as spinodol and superheating of liquid refractory metals. However, the studies on the high-temperature properties are seldom easy, as a result of the anomalous behavior of liquid metals in the vicinity of the spinodal.

The present work, based on a new three-parameter generalized Berthelot equation of state, deals with the determination of the thermodynamic limit of superheat of refractory metals. Considering the difficulties in obtaining reliable experimental data on the spinodal and superheating of refractory metals, this work acquires scientific and technological significance.

2. Generalized Berthelot Equation of State

To improve the accuracy of the known two-parameter Berthelot equation of state, an improvement of this equation is proposed by introducing a third parameter n in the attractive term. Such a generalized Berthelot equation of state for one mole of substance has the form:

$$P=\frac{RT}{V-b}-\frac{a}{\sqrt{T}V^{n}} \tag{1}$$

Where a, b and n are constants for a given substances, calculated from experimental data. The substance-specific parameter n is a measure of intermolecular attractive forces of the substances.

Application of the critical-point conditions to the equation of state given by Eq.(1) produces two equations in V_c and T_c. eliminating T_c between them gives the critical volume as

$$V_c=\left(\frac{n+1}{n-1}\right)b \tag{2}$$

Back substitution in the two equations then gives the critical temperature as

$$T_c=\left[\frac{4na}{R(n+1)^2}\left(\frac{n-1}{(n+1)b}\right)^{(n-1)}\right]^{2/3} \tag{3}$$

Finally, substitution of V_c and T_c in Eq(1) gives the critical pressure as

$$P_c=\left[\frac{Ra^2(n+1)^2}{4nb^{2n+1}}\left(\frac{n-1}{n+1}\right)^{2(n+2)}\right]^{1/3} \tag{4}$$

The critical compressibility factor is then given by

$$Z_c=\frac{P_cV_c}{RT_c}=\frac{n^2-1}{4n} \tag{5}$$

Taking into account Eqs (2)-(5), Eq. (1) may be rewritten in terms of the reduced variables $P^*=P/P_c$, $V^*=V/V_c$, $T^*=T/T_c$ as

$$P^* = \frac{1}{(n-1)}\left[\frac{4nT^*}{(n+1)V^* - (n-1)} - \frac{n+1}{\sqrt{T^*}V^{*n}}\right] \quad (6)$$

The reduced equation of state given by Eq.(6) represents the single-parameter law of corresponding states with the thermodynamic similarity parameter *n*. That is, substances obeying the generalized Berthelot equation of state given by Eq.(1), with the same value of parameter *n*, are thermodynamically similar. Such substances have similar intermolecular force characteristics. It follows from Eqs.(2) and (5) that the parameter b/V_c or Z_c can also be used as the thermodynamic similarity parameter instead of the parameter *n*, as these parameters are expressed in terms of the parameter *n*.

3. Spinodal and Superheating of Liquid

The knowledge of the spinodal, a characteristics curve on the phase diagram, is essential in describing the high-temperature properties of a substance in the critical and in the metastable states with decreased thermodynamic stability. The spinodal defines the thermodynamic stability boundary on the phase envelope. The thermodynamic stability of the phase is defined by values of the second derivatives of the Gibbs free energy, one of which is the isothermal elasticity, $-(\partial P/\partial V)_T$. The spinodal encloses the region of unstable states for which the isothermal elasticity is negative. For the stable states, the isothermal elasticity is positive.

The spinodal is, therefore, defined by the condition,

$$-\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad (7)$$

Application of the condition given byEq(7) to Eq (6) gives the spinodal in V^*, T^* coordinates as

$$T^*_s = \frac{(n+1)^2\left[V^* - \left(\frac{n-1}{n+1}\right)\right]^2}{4V^{*n+1}} \quad (8)$$

Liquids remaining in the liquid state above the boiling temperature in the ambient pressure are said to be superheated. These liquids are in metastable state in a thermodynamic sense. A liquid cannot be superheated up to its critical temperature, There is a limit to the Thermodynamic limit of superheat for any liquid without boiling. This heating limit is called thermodynamic limit of superheat. It represents the deepest possible penetration of a liquid in the domain of metastable state. The practical significance of the thermodynamic limit of superheat lies in the consequences of phase transitions such as explosive boiling that eventually occurs when this limit is reached. Hence, it is important to accurately predit the conditions, under which liquids may undergo explosive boiling.

The thermodynamic limit of superheat is given by the conditions.

$$\left(\frac{\partial P^*}{\partial V^*}\right)_{T^*} = 0 \quad P^*=0 \quad (9)$$

,

Eqs (6) and (8) along with the condition of zero pressure gives the parmetersof thermodynamic limit of superheat as

$$V^*_{s,0} = \frac{n}{n+1} \quad (10)$$

$$T^*_{s,0} = \left[\frac{1}{4}\left(\frac{n+1}{n}\right)^{n+1}\right]^{2/3} \quad (11)$$

4. Calculations and Analysis

Using the experimental data [4-6] on the critical-point parameters for refractory metals, the values of *a, b* and *n* are determined through Eqs.(2)-(5). The results presented in Table.1

Table 1: Parameters of the generalized Berthelot-equation of state

Refractory metal	a $Jkg^{-1}K^{-1}m^3mol^{-1}$ 10^{-7}	b m^3mol^{-1} 10^{-6}	n
Titanium	48.4216	9.809	1.7262
Zirconium	0.00093	13.799	1.5373
Hafnium	2.8801	12.954	1.4874
Vanadium	48.0948	6.975	1.7032
Niobium	317.7902	19.718	2.5173
Tantalum	251.1626	18.799	2.5867
Chromium	20.0752	5.789	1.6884
Molybdenum	58.9662	7.00141	1.475
Tungsten	118.2485	5.444	1.2918

By substituting the values of thermodynamic similarity parameter *n*the reduced volume of liquid refractory metals at the thermodynamic limit of superheat under zero pressure and thermodynamic limit of superheat at zero pressure are estimated through Eqs(10) and (11). The obtained results are presented in Table 2.

Table 2: Thermodynamic limit of superheat of refractory metals

Metals	T_c K [4-6]	$T^*_{s,0}$	$T_{s,0}$ K	$V^*_{s,0}$	$V_{s,0}$ m^3 / mol 10^{-6}
Ti	11790	0.911	10736	0.634	23.315
Zr	14500	0.927	13430	0.606	39.479
Hf	12100	0.931	11263	0.598	16.894
V	12500	0.913	11404	0.631	0.0169
Nb	9989	0.869	8685	0.716	32.712
Ta	9284	0.868	8049	0.722	30.647
Cr	9620	0.914	8787	0.629	14.198
Mo	1150	0.933	10394	0.596	21.722
W	13400	0.952	12748	0.564	24.099

5. Conclusion

This work has established a correlation between the thermodynamic limit of superheat and the critical

temperature with the thermodynamic similarity parameter which is a measure of the intermolecular attractive forces in titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten. The thermodynamic limit of superheat of liquid titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten have been determined, And these values are found to be in good agreement with experimental data. It has also been established that titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten obey the single-parameter law of corresponding states, with the thermodynamic limit of superheat as thermodynamic similarity parameter.

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