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Superheating of Liquid Alkali Metals

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The maximum attainable temperature of superheating and the critical temperature of cesium, rubidium, and potassium are correlated using the generalized van der Waals equation of state. This study shows that the maximum attainable temperatures of superheating for liquid cesium, rubidium, and potassium are 1722, 1802, and 2039 K, respectively. The results of the determination of the maximum attainable temperatures of superheating of liquid cesium, rubidium, and potassium are in agreement with experimental data. The given study establishes that liquid cesium, rubidium, and potassium can be superheated up to temperatures of about 200 K below their critical temperatures of 1924, 2017, and 2280 K, respectively. Moreover, cesium, rubidium, and potassium have been found to obey the single-parameter law of corresponding states, with the maximum attainable reduced temperature of superheating as the thermodynamic similarity parameter.

KEY WORDS: alkali metals; critical point; equation of state; metastable state; spinodal; superheating; thermodynamic similarity.

1. INTRODUCTION

A first-order phase transition is characterized by the presence of not only stable phases, but also metastable phases. At a given temperature and pressure, the free energy of the metastable phase is greater than that of the stable phase. Superheated metastable states are formed when a substance is subjected to a high rate of heating. Metallic liquids, under slow heating, are superheated to temperatures much less than their critical temperatures. However, pulse heating techniques employed for metallic specimens have indicated [1–7] the possibility of significant superheating of the liquid

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phase. Under such conditions of heating, the liquid phase can be superheated up to the maximum attainable temperature of superheating marked by the spinodal.

Technological developments such as cooling systems for fast neutron nuclear reactors, magnetohydrodynamic energy conversion, etc., have focused attention on alkali metals. These applications require the knowledge of high-temperature properties such as spinodal and superheating of liquid alkali metals. However, the studies on these 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 the three-parameter generalized van der Waals equation of state, deals with the determination of the maximum attainable temperature of superheating of liquid alkali metals. Considering the difficulties in obtaining reliable experimental data on the spinodal and superheating of liquid alkali metals, this work is important.

2. GENERALIZED VAN DER WAALS EQUATION OF STATE

An improvement of the known van der Waals equation of state was proposed earlier [8] by modifying the attractive term. Such a generalized van der Waals equation of state for one mole of substance is

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

where P is the pressure, V is the molar volume, and R is the universal gas constant; a, b, and n are constants for the given substance, calculated using experimental data. The substance-specific parameter n is a measure of molecular pressure and, hence, of intermolecular attractive forces of the substance.

Applying the conditions for the critical point, Eq. (1) may be rewritten in the reduced variables $P^* = P/P_c$, $V^* = V/V_c$, $T^* = T/T_c$ as

$$P^* = \frac{1}{(n-1)}\left(\frac{4nT^*}{(n+1)V^* - (n-1)} - \frac{n+1}{V^{*n}}\right), \tag{2}$$

where P_c is the critical pressure, V_c is the critical volume, and T_c is the critical temperature.

For fluids obeying the generalized van der Waals equation of state, the compressibility factor is given by

$$Z = \frac{n+1}{4n}\left(\frac{4nV^*}{(n+1)\,V^* - (n-1)} - \frac{n+1}{T^* V^{*n-1}}\right) \tag{3}$$

That is, we have

$$Z = Z(V^*, T^*, n) \tag{4}$$

Thus, it follows that Eq. (2) is a manifestation of the single-parameter law of corresponding states with the thermodynamic similarity parameter n. That is, substances with the same values of the parameter n are thermodynamically similar.

3. SPINODAL AND SUPERHEATING OF LIQUID

The knowledge of the spinodal, a characteristic 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 of 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,

$$-\left(\frac{\partial P}{\partial V}\right)_T = 0 \tag{5}$$

Application of the condition given by Eq. (5) to Eq. (2) produces one equation for the spinodal in V^*, T^* coordinates as

$$T^* = \frac{[(n+1)V^* - (n-1)]^2}{4V^{*n+1}} \tag{6}$$

Substitution of Eq. (6) into Eq. (2) gives another equation for the spinodal in P^*, V^* coordinates as

$$P^* = \frac{(n+1)V^* - n}{V^{*n+1}} \tag{7}$$

From Eqs. (6) and (7), under zero pressure, the maximum attainable reduced temperature of superheating of the liquid phase is

$$T^*_{\mathrm{so}} \equiv \frac{T_{\mathrm{so}}}{T_{\mathrm{c}}} = \frac{1}{4}\left(\frac{n+1}{n}\right)^{n+1} \tag{8}$$

As a characteristic parameter, the reduced temperature of superheating $T_{\mathrm{so}}{}^*$ is a useful quantity in the study of fluid metals as it represents the

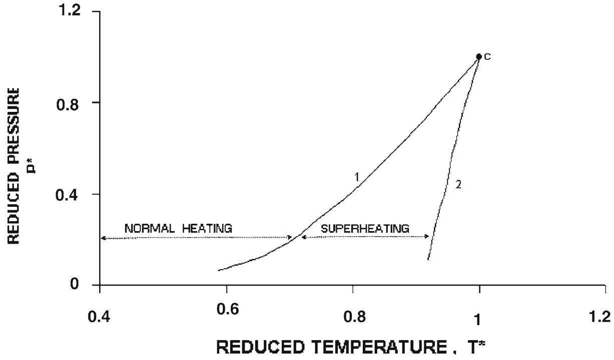

Fig. 1. Phase diagram of a metal [9]: 1—binodal ; 2—spinodal ; and C—critical point.

largest possible difference between the maximum attainable temperature of superheating and the boiling temperature marked by the binodal. This fact is illustrated by the schematic $P^* - T^*$ phase diagram of a typical metal [9] depicted in Fig. 1.

Taking into account Eq. (8), we get the maximum attainable temperature of superheating related to the critical temperature as

$$T_{\mathrm{so}} = \frac{1}{4}\left(\frac{n+1}{n}\right)^{n+1} T_{\mathrm{c}}. \tag{9}$$

4. RESULTS AND DISCUSSION

As the generalized van der Waals equation of state given by Eq. (1) lends itself to the description of high-temperature properties of liquid alkali metals [10], Eqs. (8) and (9) can also be employed in the study of the high-temperature properties of liquid alkali metals.

For the determination of the parameters of the generalized van der Waals equation of state, the following technique was adopted [11]: for fluids obeying the generalized van der Waals equation of state, the heat of evaporation and equation of the binodal at the melting point are given by

$$\Delta H_{\mathrm{v}} = \frac{a}{(n-1)\,V_{\mathrm{m}}^{n-1}} + RT_{\mathrm{m}} \tag{10}$$

$$\frac{RT_{\mathrm{m}}}{V_{\mathrm{m}} - b} - \frac{a}{V_{\mathrm{m}}^{n}} = 0, \tag{11}$$

where T_m is the melting temperature and V_m is the volume of liquid at the melting point.

The critical temperature of the fluids obeying the generalized van der Waals equation of state is given by

$$T_c = \frac{4a}{Rb^{n-1}} \frac{n(n-1)^{n-1}}{(n+1)^{n+1}} \tag{12}$$

Solving Eqs. (10)–(12), the values of the equation of state parameters a, b, and n are determined. The values of the parameter n are presented in Table I. Moreover, the parameter n was determined by various methods [11] using experimental data for fluid alkali metals at different temperatures. And, it was found that the value of the parameter n does not substantially depend on the method of determination.

For liquid cesium, rubidium, and potassium, the maximum attainable temperature of superheating is determined by Eq. (9) with the values of the parameter n and of the critical temperature T_c given in Table I. Our calculations show that liquid cesium, rubidium, and potassium can be superheated up to temperatures of 1722, 1802, and 2039 K, respectively. That is, liquid cesium, rubidium, and potassium can be superheated up to temperatures much greater than their boiling temperatures marked by the binodal. In Table I, the values of the maximum attainable temperature of superheating of liquid cesium, rubidium, and potassium estimated through experimental data for the vapor pressure [12], for the compressibility factor [13, 14] and for the critical compressibility factor [15] are also presented. The results of our calculations agree with the experimental values of the maximum attainable temperature of superheating of liquid cesium, rubidium, and potassium.

Alternatively, T_{so} may also be estimated using vapor–pressure data. This approach requires a vapor–pressure equation employable in the study of fluids on the spinodal. Such an equation is scarce. On the other hand, the experimental difficulties in the study of vapor–pressure on the spinodal

Table I. Maximum Attainable Temperature of Superheating of Liquid Alkali Metals

Metal	n	T_c (K) Experimental [15]	T_{so}(K) Eq. (9)	T_{so}(K) Experimental [12–15]	Percent error in T_{so}
Cesium	1.511	1924	1722	1675 ± 17	2.8
Rubidium	1.523	2017	1802	1758 ± 18	2.5
Potassium	1.515	2280	2039	1988 ± 20	2.6

are severe, resulting from the anomalous behavior of fluids in the vicinity of the spinodal. Considering these facts, this work on the determination of T_{so}, based on the generalized van der Waals equation of state, acquires significance.

It follows from Eq. (8) that the maximum attainable reduced temperature of superheating $T_{\mathrm{so}}{}^*$ can also be used as the thermodynamic similarity parameter instead of the parameter n, as the parameter $T_{\mathrm{so}}{}^*$ is expressed in terms of the parameter n. This means that cesium, rubidium, and potassium with practically the same values of maximum attainable reduced temperature of superheating are thermodynamically similar.

Moreover, it follows from Eq. (9) that the liquid alkali metals can be superheated up to the temperature $[(n+1)/n]^{n+1}T_{\mathrm{c}}/4$. That is, liquid cesium, rubidium, and potassium can be superheated up to temperatures of $0.8950T_{\mathrm{c}}$, $0.8934T_{\mathrm{c}}$, and $0.8945T_{\mathrm{c}}$, respectively, if the values of the similarity parameter n given in Table I are taken into account.

5. CONCLUSION

This work has established a correlation between the maximum attainable temperature of superheating and the critical temperature with the thermodynamic similarity parameter which is a measure of the intermolecular attractive forces in cesium, rubidium, and potassium. The maximum attainable temperatures of superheating of liquid cesium, rubidium, and potassium have been determined, and these values are found to be in good agreement with experimental data. It has also been established that cesium, rubidium, and potassium obey the single-parameter law of corresponding states, with the maximum attainable reduced temperature of superheating as the thermodynamic similarity parameter.

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