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Correlations of attainable superheat of fluid alkali metals

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Abstract

The maximum attainable temperature of superheating, the Boyle temperature and the critical compressibility coefficient of cesium, rubidium and potassium are correlated through the generalized van der Waals equation of state. This three-parameter equation differs from the known van der Waals equation of state by the modified attractive term. For cesium, rubidium and potassium, the ratios of the maximum attainable temperature of superheating to the Boyle temperature are estimated. The results of estimation are in agreement with experimental data. It has been established that cesium, rubidium and potassium obey the single-parameter law of corresponding states with the ratio of the maximum attainable temperature of superheating to the Boyle temperature as the thermodynamic similarity parameter.

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1. Introduction

Technological applications such as cooling systems for fast-neutron nuclear reactors, magneto-hydrodynamic energy conversion, etc., employ liquid alkali metals and their alloys. These applications need the knowledge of high-temperature properties of alkali metals because these metals are heated to high-temperatures in these applications. The fact that alkali metals are typical metals underscores the scientific significance of the study of alkali metals. Moreover, the fact that alkali metals are used as coolants in nuclear reactors underscores the practical significance of the study of alkali metals. Considering these facts, a number of experimental and theoretical studies on the properties of alkali metals have been made [1–44].

The experimental difficulties in the study of alkali metals in the high-temperature region are severe. It is attributed to the fact that alkali metals are reactive at high-temperatures. It leads to a poor accuracy in the experimental studies at high-temperatures. Hence, the theoretical studies of alkali metals at high-temperatures are of significance. However, a theoretical study, obviously, cannot replace an experimental study. A theoretical study can be another pathway for exploring the high-temperature properties of alkali metals. This fact indicates the necessity for further theoretical and experimental studies on the high-temperature properties of alkali metals.

The present work deals with a theoretical study of superheated liquid alkali metals. This is based

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on the generalized van der Waals equation of state. The given work establishes the correlations between the maximum attainable temperature of superheating, the Boyle temperature and the critical compressibility coefficient of liquid cesium, rubidium and potassium. Such correlations are significant as the maximum attainable temperature of superheating, the Boyle temperature and the critical compressibility coefficient are determined by intermolecular forces.

2. Generalized van der Waals equation of state

Because 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, an improvement of this equation was proposed [45] by introducing a third parameter, n, in the expression for molecular pressure. Such a generalized van der Waals equation of state for one mole of substance has the form:

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

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

Now, the critical point parameters of fluids obeying the generalized van der Waals equation of state may be determined. The knowledge of the expressions for critical point parameters enables one to correlate the maximum attainable temperature of superheating of the liquid to the critical temperature. Moreover, using the expressions for critical point parameters, the equation of state may be rewritten for the reduced variables from which the law of corresponding states will follow.

It is known that at the critical point, the following equations are fulfilled:

$$\left(\frac{\partial P}{\partial V}\right)_{\mathrm{T}} = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{\mathrm{T}} = 0. \tag{2}$$

Applying the equation of state (Eq. (1)) for the calculation of derivatives (Eq. (2)), one can express the critical values of the molar volume V_c, the temperature T_c, the pressure P_c and the compressibility coefficient Z_c by the a, b and n parameters of Eq. (1). First, eliminating T_c from Eq. (2), one may express the critical molar volume V_c in the form of the following equation:

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

Next, substituting V_c (Eq. (3)) to Eq. (2), the critical temperature T_c can be obtained:

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

And using relations (3) and (4) in Eq. (1), the critical pressure P_c can be presented in the form of the following equation:

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

Finally, applying the equations for V_c (Eq. (3)), T_c (Eq. (4)) and P_c (Eq. (5)), the critical compressibility coefficient Z_c is expressed by the equation

$$Z_c \equiv \frac{P_c V_c}{R T_c} = \frac{n^2-1}{4n}. \tag{6}$$

Taking into consideration Eqs. (3)–(6), one may write Eq. (1) for the reduced variables $P^* = P/P_c$, $V^* = V/V_c$, $T^* = T/T_c$ as follows:

$$P^* = \frac{1}{(n-1)}\left(\frac{4nT^*}{(n+1)V^* - (n-1)} - \frac{n+1}{V^{*n}}\right), \tag{7}$$

The reduced equation of state (Eq. (7)) represents the single-parameter law of corresponding states with the thermodynamic similarity parameter n. That is, substances with the same value of parameter n are thermodynamically similar. It means that such substances have similar intermolecular attractive force characteristics.

3. Spinodal and attainable superheat of liquid

The spinodal, a characteristic curve on the phase diagram, gives the limit of superheating of liquid. Hence, the parameters of superheating of liquid can be determined by the equations for spinodal. The knowledge of the spinodal is essential in describing the high-temperature properties of a substance in the critical and in the metastable states with decreased thermodynamic stability. Because it defines the thermodynamic stability boundary of the phase envelope. Thermodynamic stability of the liquid phase is defined by the values of the second derivatives of the Gibbs free energy and one of which is the isothermal elasticity, $-(\partial P/\partial V)_{\mathrm{T}}$. The spinodal encloses the region of unstable states for which the isothermal elasticity is negative, the region of the stable states, where the isothermal elasticity is positive and it is defined by the following constraint:

$$-\left(\frac{\partial P}{\partial V}\right)_{\mathrm{T}} = 0. \tag{8}$$

Application of the condition (Eq. (8)) to Eq. (7) produces one equation for the spinodal in V^*, T^* reduced coordinates as follows:

$$T^* = \frac{[(n+1)V^* - (n-1)]^2}{4V^{*^{n+1}}}. \tag{9}$$

Replacing T^* in Eq. (7) by the expression (9), one obtaines the equation for the spinodal in P^*, V^* reduced coordinates as follows:

$$P^* = \frac{(n+1)V^* - n}{V^{*^{n+1}}}. \tag{10}$$

At $P^* = 0$, Eq. (10) gives the volume of the superheated liquid under zero pressure as follows:

$$V^*_{\mathrm{so}} \equiv \frac{V_{\mathrm{so}}}{V_{\mathrm{c}}} = \frac{n}{n+1}. \tag{11}$$

Using relation (11) in Eq. (9), one obtains the maximum attainable reduced temperature of superheating of liquid under zero pressure as follows:

$$T^*_{\mathrm{so}} \equiv \frac{T_{\mathrm{so}}}{T_{\mathrm{c}}} = \frac{1}{4}\left(\frac{n+1}{n}\right)^{n+1}. \tag{12}$$

The reduced temperature of superheating T^*_{so} is a useful quantity in the study of liquid metals and it can be considered as a characteristic parameter because it represents the largest possible difference between the maximum attainable temperature of superheating and the boiling temperature marked by the liquid–vapor equilibrium curve.

4. Boyle temperature

Boyle temperature is a characteristic parameter of a substance. Hence, its correlation to the maximum attainable temperature of superheating, another characteristic parameter of a substance, is of significance. For an ideal gas, the compressibility coefficient $Z \equiv PV/RT = 1$ at all temperatures and pressures. In the case of real gases the compressibility coefficient varies with both of these variables. Hence, deviation of the compressibility coefficient from a value of unity is a measure of deviation of the gases from ideal behaviour.

However, there is one temperature at which Z remains close to unity over an appreciable range of pressure. This temperature, at which a real gas obeys the ideal-gas law over an appreciable pressure range, is called the Boyle temperature.

The compressibility coefficient of fluids obeying the generalized van der Waals equation of state is given by the following relation:

$$Z \equiv \frac{PV}{RT} = \frac{1}{1-b/V} - \frac{a}{RTV^{n-1}}. \tag{13}$$

The binomial expansion of term $(1-b/V)^{-1}$ for $b/V < 1$ modifies Eq. (13) to

$$Z = 1 + \left(b - \frac{a}{RTV^{n-2}}\right)\frac{1}{V} + \frac{b^2}{V^2} + \cdots \tag{14}$$

In fact, in the binomial expansion of $(1-b/V)^{-1}$, the higher order terms are not neglected. The terms are so rearranged to have Eq. (14) comparable with the viral equation of state. Comparison of Eq. (14) with the virial equation of state shows that the generalized van der Waals equation expresses the second virial coefficient B as follows:

$$B = b - \frac{a}{RTV^{n-2}}. \tag{15}$$

Because B is inversely proportional to the temperature (Eq. (15)), at high-temperatures it approaches a constant value equal to that of b. At lower temperatures $a/(RTV^{n-2})$ dominates over b and for small T values B reaches negative values.

The temperature at which the second virial coefficient $B = 0$ is the Boyle temperature and it is related to the parameters of the generalized van der Waals equation of state as follows:

$$T_{\mathrm{B}} = \frac{a}{RbV^{n-2}}. \tag{16}$$

Considering Eqs. (3)–(6), the reduced Boyle temperature can be expressed by the following equation:

$$T^*_{\mathrm{B}} \equiv \frac{T_{\mathrm{B}}}{T_{\mathrm{c}}} = \frac{(n+1)^3}{4n(n-1)}. \tag{17}$$

5. Attainable superheat – Boyle temperature correlations

Comparing Eqs. (12) and (17), one obtains the relation describing the dependence of the maximum attainable temperature of superheating on the Boyle temperature and the parameter n in the following

Table 1
Ratio of the maximum attainable temperature of superheating to the Boyle temperature of fluid alkali metals

Metal	n	T_{so}/T_B Eq. (18)	T_{so}/T_B Experimental	Percent error in T_{so}/T_B
Cesium	1.511 ± 0.0325	0.1746 ± 0.0247	0.1681 ± 0.0034	−8.9860
Rubidium	1.523 ± 0.0328	0.1772 ± 0.0250	0.1713 ± 0.0034	−9.3508
Potassium	1.515 ± 0.0326	0.1755 ± 0.0248	0.1691 ± 0.0034	−9.0525

form defining the parameter of thermodynamic similarity T_{so}/T_B as well:

$$\frac{T_{so}}{T_B} = \frac{n-1}{n^n(n+1)^{2-n}}. \tag{18}$$

As follows from Eq. (18), T_{so}/T_B depends only on the parameter n of the generalized van der Waals equation of state. It can be attributed to the fact that T_{so}/T_B is determined by the intermolecular attractive forces, of which parameter n is a measure.

On the other hand, Eq. (6) is a quadratic equation in terms of n. That is,

$$n^2 - 4Z_c n - 1 = 0. \tag{19}$$

One of the solutions of Eq. (19), with the physical consideration i.e. $n > 0$ taken into account, gives

$$n = 2Z_c + \sqrt{4Z_c^2 + 1}. \tag{20}$$

Taking into consideration Eqs. (18) and (20), one gets the ratio of the maximum attainable temperature of superheating to the Boyle temperature related to the critical compressibility coefficient as follows:

$$\frac{T_{so}}{T_B} = \frac{\sqrt{4Z_c^2+1} + 2Z_c - 1}{\left(2Z_c + \sqrt{4Z_c^2+1}\right)^{2Z_c+\sqrt{4Z_c^2+1}} \cdot \left(\sqrt{4Z_c^2+1} + 2Z_c + 1\right)^{2(1-Z_c)-\sqrt{4Z_c^2+1}}} \tag{21}$$

Eq. (21) correlates the maximum attainable temperature of superheating, the Boyle temperature and the critical compressibility coefficient. It represents the fact that the knowledge of critical point parameters makes it possible to predict the high-temperature properties of liquids.

It has been established [46–52] that the generalized van der Waals equation of state can be used for studying the high-temperature properties of liquid alkali metals. Hence, Eqs. (18) and (21) can be considered to be valid for alkali metals.

6. Results and analysis

The parameter n of the generalized van der Waals equation of state was determined by the author of this work [47] for the liquid alkali metals (Cs, Rb, K) based on the experimental data [1,6,53,54]. Their values are presented in Table 1. The relative errors in the estimation of the parameter n for Cs, Rb and K are 2.151%, 2.154% and 2.152%, respectively. As seen, the relative errors in the parameter n for Cs, Rb and K are only slightly different.

In Table 1, the values of the ratio of the maximum attainable temperature of superheating to the Boyle temperature determined by Eq. (18) are also presented. The errors in the estimation of n lead T_{so}/T_B for Cs, Rb and K to have the relative errors of 14.147%, 14.108% and 14.131 %, respectively. The magnitudes of T_{so}/T_B with the lower errors better characterize the studied properties than those with higher errors.

In Table 1, the values of T_{so}/T_B calculated using the experimental data on the vapour pressure [55] and the compressibility coefficient [56] are also presented. The results of our calculations are found to agree, with an accuracy of about −9%, with the experimental values of T_{so}/T_B.

Moreover, it follows from Eq. (18) that the ratio of the maximum attainable temperature of superheating to the Boyle temperature T_{so}/T_B can also be used as the thermodynamic similarity parameter instead of the parameter n, as the parameter T_{so}/T_B is expressed in terms of the parameter n . This means that the substances obeying the generalized van der Waals equation of state, with practically the same values of the ratio of the maximum attainable temperature of superheating to the Boyle temperature, are thermodynamically similar. That is, such substances have similar intermolecular attractive force characteristics.

7. Conclusion

The given work has established correlations of the maximum attainable temperature of superheating, the Boyle temperature of cesium, rubidium and potassium to the thermodynamic similarity parameter and to the critical compressibility coefficient which are measures of the intermolecular forces. For the mentioned alkali metals, the ratios of the maximum attainable temperature of superheating to the Boyle temperature have been determined and they are found to be in agreement with those calculated using the experimental data. It has also been established that cesium, rubidium and potassium obey the single-parameter law of corresponding states. This parameter is defined in this work as the ratio of the maximum attainable temperature of superheating to the Boyle temperature and it can be considered as the new parameter of the thermodynamic similarity.

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