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Acentric Factor of Alkali Metals

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The acentric factors of cesium, rubidium and potassium are determined on the basis of the generalized van der Waals equation of state. This generalized equation differs from the known van der Waals equation of state by the third parameter n in the expression for molecular pressure. The results of the determination of the acentric factors of cesium, rubidium and potassium are in good agreement with experimental data.

KEY WORDS: acentric factor; alkali metals; binodal; corresponding states; critical point; equation of state; thermodynamic similarity.

1. INTRODUCTION

The acentric factor [1, 2] is one of the common pure component constants. As originally proposed, the acentric factor represented the acentricity or nonsphericity of a molecule. However, at present, the acentric factor is widely used in determining the thermodynamic properties of substances, such as the compressibility factor [3–8], fluid phase equilibrium [9, 10], virial coefficients [11, 12], vapor pressure [13, 14] and enthalpy of vaporization [2, 15]. Hence, knowledge of the acentric factor of substances acquires significance.

In general, the values of the acentric factor are determined from experimental data on vapor pressure and critical point parameters. For the determination of the acentric factor, therefore, the study of substances in the critical state is needed. In recent years, the behavior of various substances, particularly, of fluid alkali metals near the critical state, has been intensively studied. Alkali metals are typical metals. Hence, the study of their thermodynamic properties is of scientific interest. Owing to their high

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thermal conductivity, some of these metals are used as coolants in fast-neutron nuclear reactors. This fact underscores the practical value of these investigations.

Static heating methods are usually employed [16] to investigate the fluid alkali metals near the critical state. The critical parameters of fluid alkali metals have been studied [17, 18] considering the long-range Coulomb interactions in the alkali metals. The critical point parameters of alkali metals have also been measured [19–26]. But the accuracy of these high-temperature measurements is not good. This can be illustrated by the following fact: according to a review [23], the mean values of cesium's critical temperature and critical pressure by numerous experimental data are 2043 K and 11.70 MPa respectively, whereas more recent results [25] give these values as 1924 K and 9.25 MPa, respectively. This fact shows that, over the years, the accepted values of the acentric factor of alkali metals may change due to new data on critical point parameters. Hence arises the necessity for a more accurate determination of the acentric factor of alkali metals.

The present work is dedicated to the determination of acentric factors of cesium, rubidium, and potassium on the basis of the generalized van der Waals equation of state.

2. GENERALIZED VAN DER WAALS EQUATION OF STATE

The known two-parameter van der Waals equation of state is not suitable for precise description of the thermodynamic properties of liquids and gases. An improvement of this equation was proposed [27] 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 is

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

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 the given substance, calculated through experimental data. The parameter n takes into account the specificity of intermolecular attractive forces of various substances.

At the critical point, we have

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \tag{2}$$

Application of these conditions to the equation of state given by Eq. (1) produces two equations in V_c and T_c, where V_c is the critical volume and T_c is the critical temperature. Eliminating T_c between them gives the critical volume as

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

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

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

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

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

The critical compressibility factor is then given by

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{n^2-1}{4n} \tag{6}$$

Taking into account Eqs. (3)–(6), we may write Eq. (1) in terms of reduced variables $P^* = P/P_c$, $V^* = V/V_c$, $T^* = T/T_c$ as

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

The reduced equation of state given by Eq. (7) expresses the single-parametric law of corresponding states with the thermodynamic similarity parameter *n*. That is, substances with the same value of parameter *n* are thermodynamically similar.

3. BINODAL

The binodal (in fluid phase equilibrium) is defined by the equalities of the Gibbs free energy, the pressure, and the temperature of liquid and vapor phases:

$$G_1 = G_2, \qquad P_1 = P_2, \qquad T_1 = T_2 \tag{8}$$

where indices 1 and 2 refer to liquid and vapor phases, respectively.

Application of the conditions given by Eq. (8) to Eq. (7) produces two equations for the binodal in V^*, T^* coordinates and one equation for the binodal in P^*, V^* coordinates:

$$T^* \left\{ \frac{(n^2-1)(V_2^*-V_1^*)}{[(n+1)V_1^*-(n-1)][(n+1)V_2^*-(n-1)]} + \ln\left(\frac{(n+1)V_2^*-(n-1)}{(n+1)V_1^*-(n-1)}\right) \right\} - \frac{(n+1)^2}{4(n-1)}\left(\frac{1}{V_1^{*n-1}} - \frac{1}{V_2^{*n-1}}\right) = 0 \tag{9}$$

$$\frac{4n(V_2^*-V_1^*)T^*}{[(n+1)V_1^*-(n-1)][(n+1)V_2^*-(n-1)]} - \left(\frac{1}{V_1^{*n}} - \frac{1}{V_2^{*n}}\right) = 0 \tag{10}$$

$$(V_2^*-V_1^*)P^* - \frac{(n+1)}{(n-1)}\left(\frac{1}{V_1^{*n-1}} - \frac{1}{V_2^{*n-1}}\right) + \left(\frac{1}{V_1^{*n}} - \frac{1}{V_2^{*n}}\right) = 0 \tag{11}$$

It was established [28, 29] that the generalized van der Waals equation of state can be used for studying the high-temperature properties of fluid alkali metals. Hence, Eqs. (9)–(11) can be considered to be valid for fluid alkali metals.

4. ACENTRIC FACTOR

The acentric factor of a substance is defined [30] as

$$\omega = -\log P_{\mathrm{vp}}^* \quad (\text{at } T^* = 0.7) - 1 \tag{12}$$

To obtain the values of ω, therefore, the reduced vapor pressure P_{vp}^* at $T^* = 0.7$ is required.

5. CALCULATIONS AND ANALYSIS

The parameter n of the generalized van der Waals equation of state was determined [31] through experimental data [23, 25, 32, 33] for the fluid alkali metals. The values of the parameter n are presented in Table I. As can be seen, the values of the thermodynamic similarity parameter n for cesium, rubidium, and potassium are only slightly different, which may reflect the accuracy of the experimental data used.

Table I. Thermodynamic Similarity Parameter and Acentric Factor of Alkali Metals

Metal	n	ω Eqs. (9)–(12)	ω Experimental
Cesium	1.511	−0.1934	−0.1951
Rubidium	1.523	−0.2006	−0.1978
Potassium	1.515	−0.1847	−0.1836

For cesium, rubidium, and potassium, the reduced vapor pressures at $T^* = 0.7$ are estimated by solving Eqs. (9)–(11) with the values of the parameter n presented in Table I. The acentric factors of cesium, rubidium and potassium are then determined by Eq. (12) with the values of the reduced vapor pressures determined by the generalized van der Waals equation of state. The results are presented in Table I. The values of the acentric factor of cesium, rubidium, and potassium estimated through experimental data on vapor pressure [34] and critical point parameters [25] are also presented in Table I. As can be seen, the results of our calculations satisfactorily agree with the experimental values of the acentric factor of cesium, rubidium, and potassium.

6. CONCLUSION

The acentric factors of cesium, rubidium and potassium have been determined on the basis of a generalized van der Waals equation of state, and these values are found to be in good agreement with the experimental data.

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