Equation of State for Fluid Alkali Metals: Binodal[1]

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The three-parameter generalized van der Waals equation of state for liquids and gases is analyzed. This equation contains the generalized expression $a V^{-m}$ for the molecular pressure; here the parameter n takes into account the specificity of intermolecular attractive forces for various substances. The equation is presented in the reduced form, from which follows the single-parameter law of corresponding states with the thermodynamic similarity parameter n. It is established that for alkali metals the value of the parameter n is the same and does not depend on temperature substantially. From the given generalized equation, the expressions for the binodal (equilibrium curve of the liquid and vapor phases) are obtained. For cesium, rubidium, and potassium, the temperature dependence of density is calculated over the temperature range from their melting point to the critical point; the results of the calculations agree with experimental data. It is established that for alkali metals, the law of rectilinear diameter breaks down in the vicinity of the critical point.

KEY WORDS: alkali metals; binodal; corresponding states; equation of state; fluid metals; rectilinear diameter; thermodynamic similarity.

1. INTRODUCTION

Alkali metals are typical metals. Hence the investigation of their thermodynamic properties is of great scientific interest. Owing to their high thermal conductivity, some of these metals are used as coolants of the active zone in fast neutron nuclear reactors. This fact suggests the great practical value of these investigations.

In recent years, the thermodynamic properties of cesium, rubidium, and potassium in the fluid state have been experimentally investigated over the temperature range from their melting point to the critical point. The critical point parameters of these metals have also been measured. The accuracy of these high-temperature measurements is not good. This can be illustrated by the following fact: according to a review [1], the mean value of cesium's critical temperature by numerous experimental data is 2043 K, whereas recent results [2] show that this value is 1924 K. This fact indicates the acute necessity for constructing the high-temperature equation of state for alkali metals.

Numerous equations of state for liquids and gases are known [3]. Most of them consist of many parameters, which are calculated by experimental data. Due to the deficiency of the experimental data, these equations of state are not suitable for the description of high-temperature thermodynamic properties of metals.

The well-known two-parameter van der Waals equation is one of the simple equations of state. However, this equation is not suitable for the quantitative description of the thermodynamic properties of fluid metals. This can easily be seen from the following example: according to this equation, for any substance, the liquid phase's reduced density in the low-temperature region is around three, whereas the experimental data [2] show that this value is greater than five.

It is therefore necessary to have a simple as well as sufficiently precise equation of state for liquids and gases. The present work is dedicated to the analysis of the application of the three-parameter generalized van der Waals equation of state [4] for the description of thermodynamic properties of fluid alkali metals and to the construction of the equations of the binodal (equilibrium curve of the liquid and vapor phases).

2. GENERALIZED VAN DER WAALS EQUATION OF STATE AND SINGLE-PARAMETER LAW OF CORRESPONDING STATES

The known two-parameter van der Waals equation of state is modified [4] into a three-parameter equation by introducing the third parameter n in the expression for molecular pressure. In this way, the three-parameter equation of state for 1 mol of substance has the form

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

here P is the pressure; V is the molar volume; R is the universal gas constant; and a, b, and n are constants calculated from experimental data.

The parameter n takes into account the specificity of intermolecular attractive forces of various substances.

At the critical point we have

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

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

$$V_c = \frac{n+1}{n-1} b \tag{3}$$

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

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

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

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

The critical compressibility ratio is then given by

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

By taking into account Eqs. (3)–(5), we may write Eq. (1) in terms of reduced variables $\pi = P/P_c$, $\varphi = V/V_c$, $\tau = T/T_c$:

$$\pi = \frac{1}{n-1} \left[\frac{4n\tau}{(n+1)\,\varphi - (n-1)} - \frac{n+1}{\varphi^n} \right] \tag{7}$$

The reduced equation of state, Eq. (7), expresses the single-parameter law of corresponding states with the thermodynamic similarity parameter n. In this way, the substances with the same value of the parameter n are thermodynamically similar. It follows from Eqs. (3) and (6) that the parameter b/V_c or Z_c can also be used as the thermodynamic similarity parameter instead of parameter n, because these parameters are expressed through the parameter n.

3. BINODAL

The binodal is defined by the equalities of the Gibbs free energy, the pressure, and the temperature of the liquid and vapor phases:

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

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

For the fluids whose properties are described by Eq. (7), we have the following expression for the Gibbs free energy:

$$G^* = \frac{G}{RT_c} = \tau \left\{ \frac{(n+1)\,\varphi}{(n+1)\,\varphi - (n-1)} - \ln \left[\frac{(n+1)\,\varphi - (n-1)}{n+1} \right] \right.$$
$$\left. + \frac{C_v}{R}(1 - \ln \tau) - \frac{C}{R} \right\} - \frac{(n+1)^2}{4(n-1)\,\varphi^{n-1}} \tag{9}$$

where C_v is the isochoric heat capacity and C is the constant of integration in the expression for the entropy.

Taking into account the expression for the Gibbs free energy, Eq. (9), and also assuing that $C_{v1} = C_{v2} = C_v$ and $\tau_1 = \tau_2 = \tau$, we obtain, presuming the equality of the Gibbs free energy for the liquid and vapor phases, the equation of the binodal in δ, τ coordinates ($\delta = 1/\varphi$ is the reduced density):

$$\tau \left\{ \frac{(n+1)(n-1)(\delta_1 - \delta_2)}{[n+1-(n-1)\delta_1][n+1-(n-1)\delta_2]} + \ln \left[\frac{\delta_1(n+1-(n-1)\delta_2)}{\delta_2(n+1-(n-1)\delta_1)} \right] \right\}$$
$$- \frac{(n+1)^2}{4(n-1)}(\delta_1^{n-1} - \delta_2^{n-1}) = 0 \tag{10}$$

Equation (7) along with the assumption that $\tau_1 = \tau_2 = \tau$ yields, assuming the equality of the pressure for the liquid and vapor phases, the equation of the binodal in another form:

$$\frac{4n(\delta_1 - \delta_2)\,\tau}{[n+1-(n-1)\delta_1][n+1-(n-1)\delta_2]} - (\delta_1^n - \delta_2^n) = 0 \tag{11}$$

In the low-temperature region, the vapor-phase density can be neglected in comparison to the liquid-phase density ($\delta_2 = 0$). In this region, the equation of the binodal, Eq. (11), takes the form

$$\frac{4n\tau}{(n+1)[n+1-(n-1)\delta_1]} - \delta_1^{n-1} = 0 \tag{12}$$

The equation of the binodal, Eq. (10), obtained from the equality of the Gibbs free energy for the liquid and vapor phases can be rewritten in ω, ϑ coordinates ($\omega = \delta - 1$, $\vartheta = 1 - \tau$). In the vicinity of the critical point we have

$$\omega_1 < 1, \qquad \omega_2 < 1 \tag{13}$$

Taking account of these conditions, expanding Eq. (10) into a Taylor's series, and limiting ourselves to the third-order terms, we obtain the approximate equation of the binodal in the vicinity of the critical point:

$$\{(n+1)(n-1) - \vartheta[(n+1)^2 - 2(3-n)(n-1)]\}(\omega_1^2 + \omega_1\omega_2 + \omega_2^2)$$
$$+ 6(2-n)\,\vartheta(\omega_1 + \omega_2) - 12\vartheta = 0 \tag{14}$$

In a similar way, from Eq. (11), which was obtained from the equality of the pressure for the liquid and vapor phases, we obtain another approximate equation of the binodal in the vicinity of the critical point:

$$[6 + 3(n-1)(\omega_1 + \omega_2) + (n-1)(n-2)(\omega_1^2 + \omega_1\omega_2 + \omega_2^2)]$$
$$\times [2 - (n-1)\,\omega_1][2 - (n-1)\,\omega_1] - 24(1-\vartheta) = 0 \tag{15}$$

4. CALCULATION OF EQUATION'S PARAMETERS

The parameters a, b, and n in Eq. (1) were calculated by us through various methods. The formulas used in these calculations are given below.

It follows from Eq. (1) with $T = 0$, $P = 0$ that the parameter b is equal to

$$b = V_0 = \frac{\mu}{D_0} \tag{16}$$

Here D_0 is the density of the condensed phase at absolute zero; μ is the molar mass of the substance.

According to Eq. (1), the heat of sublimation of the condensed phase at absolute zero is equal to

$$A_0 = \int_{V_0}^{\infty} \frac{a}{V^n}\, dV = \frac{a}{(n-1)\, V_0^{n-1}} \tag{17}$$

The parameter n may be calculated through the critical parameters of the substances. From Eq. (3) we have

$$n = \frac{V_c + b}{V_c - b} \tag{18}$$

The parameter n can also be calculated through the critical temperature T_c. Taking into account the expressions for the parameters a [Eq. (17)] and b [Eq. (16)], from Eq. (4) we have

$$T_c = \frac{4.1_0}{R} \frac{n(n-1)^n}{(n+1)^{n+1}} \tag{19}$$

The equation of the binodal may also be used for the calculation of the parameters a, b, and n. According to Eq. (1), and equating the pressure for the liquid and vapor phases, we obtain the equation of the binodal:

$$RT\left(\frac{1}{V_1-b} - \frac{1}{V_2-b}\right) - a\left(\frac{1}{V_1^n} - \frac{1}{V_2^n}\right) = 0 \tag{20}$$

Furthermore, according to Eq. (1), the heat of evaporation of the condensed phase at the given point of the binodal is represented by

$$\Delta H_v = (U_2 - U_1) + P(V_2 - V_1) = \int_{V_1}^{V_2} \frac{a}{V^n} dV + P(V_2 - V_1) \tag{21}$$

where U is the internal energy and P is the saturated vapor pressure at the given point of the binodal.

From Eq. (21) we have

$$\Delta H_v = \left(\frac{a}{n-1}\right)\left(\frac{1}{V_1^{n-1}} - \frac{1}{V_2^{n-1}}\right) + P(V_2 - V_1) \tag{22}$$

Now we will consider various methods of calculating the parameters a, b, and n.

Method J. The parameter b is calculated by Eq. (16) through V_0 [5]. The parameter n is calculated by Eq. (18) through V_c [2]. Finally, the parameter a is calculated by Eq. (17) through V_0 [5] and A_0 [6].

Method K. The parameter b is calculated by Eq. (16) through V_0 [5]. The parameter n is calculated by Eq. (19) through T_c [2] and A_0 [6]. The parameter a is calculated by Eq. (17) through V_0 [5] and A_0 [6].

Method L. At the melting point, the volume of the vapor phase is much higher than that of the liquid phase ($V_2 \gg V_1$). Hence Eq. (22) takes the form

$$\Delta H_v = \frac{a}{(n-1)V_1^{n-1}} + PV_2 \tag{23}$$

Assuming the vapor at the melting point as an ideal gas, we can rewrite Eq. (23) as

$$\Delta H_v = \frac{a}{(n-1) V_1^{n-1}} + RT \tag{24}$$

In the low-temperature region ($V_2 \gg V_1$) including the melting point, the equation of the binodal. Eq. (20), takes the form

$$\frac{RT}{V_1 - b} - \frac{a}{V_1^n} = 0 \tag{25}$$

We write Eqs. (24) and (25) for the melting point. Then solving the system of these equations together with the equation for T_c, Eq. (4), we obtain the values of the parameters a, b, and n. In these calculations we use the experimental data [7, 8] for the melting point and the experimental data [2] for T_c of alkali metals.

Method M. The parameter b is calculated by Eq. (16) through V_0 [5]. We write the equation of the binodal, Eq. (20), and the equation for ΔH_v, Eq. (22), for the normal boiling point. Then, solving the system of these equations, we obtain the values of the parameters a and n. In these calculations we use the experimental data [7, 8] for ΔH_v, V_1 at the normal boiling point, and also the values for V_1 calculated from the equation of state for an ideal gas.

Method N. The substitution of V_c in the first equality of Eq. (2) by Eq. (3) gives the expression for the parameter a:

$$a = \frac{RT_c V_c^{n+1}}{V_c^2 - b^2} \tag{26}$$

Finally, substitution of Eq. (26) in Eq. (1) gives the quadratic equation

$$P_c b^2 + RT_c b - P_c V_c^2 = 0 \tag{27}$$

Due to physical considerations ($b > 0$), one of the solutions of this equation gives the expression for the parameter b:

$$b = \frac{V_c}{2Z_c} [(1 + 4Z_c^2)^{1/2} - 1] \tag{28}$$

Here $Z_c = P_c V_c / RT_c$ is the critical compressibility ratio.

In this way, the parameter b is calculated by Eq. (28) through P_c, V_c, and T_c [2]. Then the parameter n is calculated by Eq. (18) through V_c [2]. Finally, the parameter a is calculated by Eq. (26).

Metal	Parameter n for given method of calculation				
	J	K	L	M	N
Cesium	1.464	1.464	1.511	1.436	1.483
Rubidium	1.439	1.455	1.523	1.455	1.529
Potassium	1.535	1.481	1.515	1.428	1.409
Mean value	1.479	1.467	1.516	1.440	1.474

The results of the calculations of the thermodynamic similarity parameter n for alkali metals are presented in Table I. The calculations show that for the given method the value of n for cesium, rubidium, and potassium is the same if one confines oneself to the accuracy of the used experimental data. This fact gives the basis for considering the parameter n as a thermodynamic similarity parameter for alkali metals and for these metals the single-parameter law of corresponding states is satisfied. Moreover, the value of n practically does not depend on the method of its calculation. In various methods, experimental data at different temperatures are used. So, it can be considered that the value of n for alkali metals does not depend on temperature substantially. From here, it can be concluded that the generalized van der Waals equation of state given by Eqs. (1) and (7) is suitable for the calculation of the thermodynamic properties of alkali metals in the liquid and vapor phases over a temperature range from their melting point to the critical point.
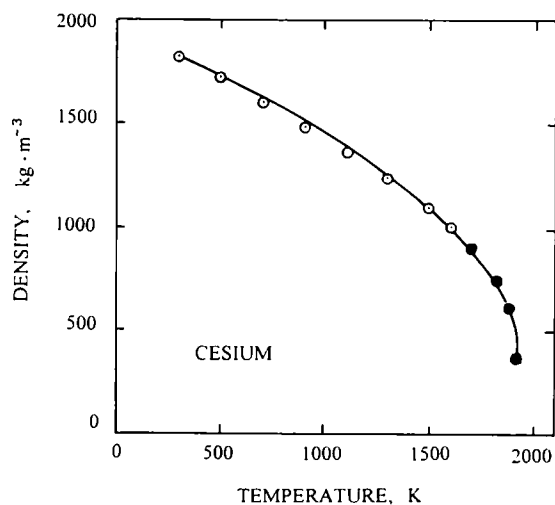
5. CALCULATION OF BINODAL

For cesium, rubidium, and potassium, we carried out the calculations of the binodal in δ, τ coordinates, followed by a change to D, T coordinates. In these calculations we used the experimental data for T_c and V_c from Hensel and Uchtmann [2].
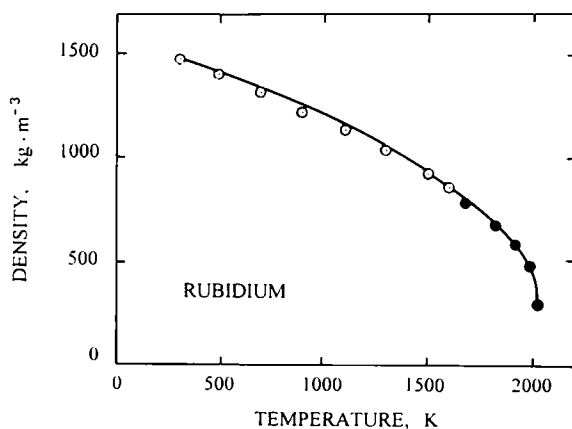
In the low-temperature region, we calculated the temperature dependence of the density of alkali metals by Eq. (12). In the vicinity of the critical point, we calculated the temperature dependence of the densities δ_1 and δ_2 by solving the system of approximate equations (14) and (15). In these calculations we used the value of the parameter n obtained by method L (Table I).

For cesium and rubidium, the temperature dependence of the density of the liquid phase in the saturation curve is presented in Figs. 1 and 2.

Fig. 1. Teperature dependence of the density of liquid cesium on the binodal. Continuous line, calculation; ⊙, experimental data [7]; ●, experimental data [9].

Fig. 2. Temperature dependence of the density of liquid rubidium on the binodal. Continuous line, calculation; ⊙, experimental data [7]; ●, experimental data [9].

The results of our calculations satisfactorily agree with experimental data reported by other authors [7, 9, 10].

In the vicinity of the critical point, we represented [11] the temperature dependence of the density of the liquid phase δ_1 by the formula

$$\delta_1 - 1 = A(1 - \tau)^{\beta_1} \tag{29}$$

In the vicinity of the critical point, the difference of the density of the liquid phase δ_1 and the density of the vapor phase δ_2 was represented by Goldhammer's formula:

$$\delta_1 - \delta_2 = B(1 - \tau)^{\beta} \tag{30}$$

By the least square method, we calculated the parameters A, B, β_1, and β of Eqs. (29) and (30) using the density data from Eqs. (14) and (15). For cesium, rubidium, and potassium, the mean values of the critical amplitudes are equal to $A = 3.690$, $B = 3.499$ and those of the critical indices are equal to $\beta_1 = 0.5122$, $\beta = 0.4065$.

The results of our calculations for alkali metals show that the law of rectilinear diameter does not hold in the vicinity of the critical point. In this region, the temperature dependence of the mean value of the density $\delta_d = (\delta_1 + \delta_2)/2$ is a nonlinear function and it can be expressed by the formula

$$\delta_d - 1 = E(1 - \tau)^{\gamma} \tag{31}$$

According to our calculations for cesium, rubidium, and potassium, the mean values of these parameters are equal to $E = 3.031$, $\gamma = 0.7941$. For cesium and rubidium, the violation of the law of rectilinear diameter was experimentally established earlier by Jungst et al. [9].

6. CONCLUSION

This work shows that the three-parameter generalized van der Waals equation of state [4] is suitable for describing the thermodynamic properties of fluid alkali metals over the temperature range from their melting point to the critical point.

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