Regularities of liquid potassium at different temperatures

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ABSTRACT

Several new regularities in liquid potassium have been found from the existing experimental data and calculated thermodynamic properties along the isothermal lines with the equation of state (EoS) of a power law form. The quantity \((Z - 1)V^2\) is nearly linear with \(V^2\) for thirteen fluids where \(Z\) = \(\frac{P}{RT}\) is the compressibility factor, \(V\) is the molar volume, \(P\) is the pressure, \(R\) is the gas constant and \(T\) is the temperature. There is a common intersection point for all isotherms at high temperature and \(PV\) versus \(V^2\) is nearly linear, where \(Z\) and \(P\) are compressibility factor, molar volume and internal pressure. Both the isothermal bulk modulus and internal pressure are nearly a linear function of pressure at constant temperature. There is a linear relationship existing between the calculated reduced isothermal bulk modulus and \(V^2\). Based on the linear isotherm regularity EoS, analytical expression of thermodynamic properties of liquid potassium can be obtained. Furthermore, we found crossing points existing in the isobaric thermal expansion coefficient and Anderson-Grüneisen parameter.

Potassium is one of the alkali metals which are among the most well-studied materials at ambient conditions and extensively used in technology due to their unique physical and chemical properties. Also, as a basic scientific research goal, an accurate knowledge of the physical properties of liquid alkali metals has become essential important which depend on the information from the atomic scale. And very recently, liquid sodium-potassium (Na-K) alloy, with the relatively low melting temperature and highly negative redox potential, was explored to be used as the electrolyte under pressure in flow batteries. For these applications, liquid K is usually under very high pressure and naturally, and it has been a focus to investigate the pressure effects on the melting curve and other thermodynamic properties. X-ray diffraction of K up to pressures of 22 GPa has been used to obtain a maximum melting temperature around 530K at 5.8 GPa in a body centered cubic phase of K and a following minimum existing around 390K at 19GPa. Such unexpected behavior of liquid K under high pressure certainly brings new challenge to describe various thermodynamic properties important for technological interest and basic understanding. Since liquid K is a simple dense liquid thermodynamically, without enough direct experimental information...
under high pressure and high temperature, ab initio methods and molecular-dynamics simulations are alternatively adopted to investigate superconductivity and transport properties. Since scaling laws and transport properties have been investigated in liquid K at ambient pressure, much more thermodynamic data is still needed to study the above behaviors in liquid K under high pressure.

In our recent work, an EoS in the power law form has been applied to liquid Indium and liquid sodium to obtain their thermodynamic properties in a certain range of temperature and pressure. The EoS was originally proposed on the pseudospinodal hypothesis and successfully used for a variety of solids and liquids such as mercury. It holds very well for materials over a wider range of temperature and density. Several measurements of liquid K at various temperature and pressure were made, such as the volume measured by Makarenkov, et al. and sound-velocity measured as a function of pressure along different isothermal paths.

The purpose of this work is to find new regularities from predicted properties by the power law form of EoS for liquids, such as isobaric thermal expansion coefficient, adiabatic bulk modulus, isochoric heat capacity, the isobaric heat capacity, heat capacity ratio, and Grüneisen parameter. The calculated isothermal bulk modulus and volume as function of pressure agree very well with existing experimental values; and other properties predicted from the theory without experimental support need to be tested in the future. We find new linear isotherm regularities from the available thermodynamic data and several other regularities are reported.

II. THEORETICAL BACKGROUND

The isothermal bulk modulus $B(T, P) = B_T(P)$ at the fixed temperature $T$ can be expressed in a power law form as

$$B_T(P) = \frac{1}{\kappa^*(T)} (P - P_\nu(T))^\beta,$$  
(1)

where $\beta$ is a constant, $B_T$ and $P$ are isothermal bulk modulus and pressure, respectively, and $\kappa^*$ and $P_\nu$ are constants along the isothermal line, $\beta = 0.85$ is used.

The molar volume as a function of pressure is derived by integration of Eq. (1)

$$V(T, P) = V_\nu(T) \exp\left(-\frac{\kappa^*(T)}{1 - \beta} (P - P_\nu(T))^{1 - \beta}\right),$$  
(2)

in terms of zero pressure quantities, $V_0$, the molar volume and $B_{T0}$, the isothermal bulk modulus, and $B'_{T0}$, its isothermal pressure derivative. $P_\nu$, $\kappa^*$ and $V_\nu$ are the characteristic parameters in terms of the zero-pressure quantities defined as

$$P_\nu(T) = P_0 - \frac{\beta B_{T0}(T)}{B'_{T0}(T)} \left(\frac{\kappa^*(T)}{B'_{T0}(T)} \right)^\beta,$$

$$V_\nu(T) = V_0(T) \exp\left(\frac{1}{(1 - \beta) B_{T0}(T)} \right),$$

at temperature $T$.

The speed of sound $C_{\nu0}$, density $\rho_0$ and heat capacity $C_{\nu0}$ of liquid potassium at ambient pressure condition have been obtained to calculate the required input parameters listed in Table I. The least-square fitting of Eq. (1) is used to obtain the appropriate values of $B_{T0}$ from the derived isothermal bulk modulus with the variation of pressure at constant temperature, and we choose an exponential fitting function to express $B_{T0}$ as

$$B'_{T0}(T) = 4.29555 \times 27.39047 \exp\left(-\frac{T}{86.96121}\right),$$

in the considered temperature region $373.15 \, K \leq T \leq 473.15 \, K$.

Once the sound velocity and density are obtained, we can get the adiabatic bulk modulus $B_S$ by

$$B_S(T, P) = \rho(T, P) C_S^2(T, P),$$

and the isothermal bulk modulus $B_T$ by

$$B_T(T, P) = \frac{B_S(T, P)}{\gamma(T, P)},$$

where heat capacity ratio is calculated as

$$\gamma(T, P) = \frac{C_P(T, P)}{C_V(T, P)} = 1 + \frac{T \alpha(T, P) C_S^2(T, P)}{C_P(T, P)},$$

with the substitution of heat capacity $C_P$ and the isobaric thermal expansion coefficient $\alpha_P$ defined as

$$\alpha_P(T, P) = \frac{1}{V(T, P)} \left(\frac{\partial V(T, P)}{\partial T}\right)_P.$$

Table I. Summary of the input parameters of Eq. (1) and other calculated thermodynamic properties of liquid K at zero pressure. $T$ is temperature, $V_0$ volume (Ref. 23), $\alpha_{p0}$ thermal expansion coefficient, $B_{T0}$ isothermal bulk modulus, $C_{\nu0}$ sound velocity (Ref. 22), $C_{\nu0}$ heat capacity at constant pressure (Ref. 24), $\left(\frac{\partial B_T}{\partial P}\right)_{T0}$ isothermal pressure derivative of isothermal bulk modulus, $P_{\text{iso0}}$ internal pressure, $\gamma_0$ heat capacity ratio, and $\gamma_{\nu0}$ Grüneisen parameter.

| $T$ (K) | $V_0$ (cm$^3$ mol$^{-1}$) | $\alpha_{p0}$ ($10^4$ K$^{-1}$) | $B_{T0}$ (GPa) | $C_{\nu0}$ (m$^2$ s$^{-1}$) | $C_{\nu0}$ (J mol$^{-1}$ K$^{-1}$) | $\left(\frac{\partial B_T}{\partial P}\right)_{T0}$ | $P_{\text{iso0}}$ (GPa) | $\gamma_0$ |
|---------|--------------------------|-------------------------------|---------------|--------------------------|---------------------------------|-------------------------------|----------------------|---------|
| 373.15  | 47.644                   | 2.896                         | 2.511         | 1863.2                   | 31.531                          | -0.271                        | 1.135                |
| 413.15  | 47.921                   | 2.923                         | 2.393         | 1843.1                   | 31.107                          | -0.290                        | 1.151                |
| 453.15  | 48.771                   | 2.946                         | 2.284         | 1823.2                   | 30.753                          | -0.305                        | 1.167                |
| 473.15  | 49.059                   | 2.956                         | 2.234         | 1813.7                   | 30.606                          | -0.312                        | 1.174                |
III. RESULTS

A. Linear isotherm regularities: Bulk modulus, compressibility factor, and internal pressure

In Fig. 1(a), the calculated isothermal bulk modulus $B_T$ is near linearly as a function pressure $P$ and shows good agreement with the experimental data. Isothermal bulk modulus $B_T$ increases with pressure at constant temperature and decreases with rising temperature at constant pressure. The calculated volume $V$ as a function pressure $P$ is used to investigate the linearity of the new regularities. In Fig. 1(b), for the compressibility factor $Z = \frac{V}{PV}$, the linearity $(Z - 1)V^2$ versus $V^2$ is indicated and all these isotherms at high temperature of $T = 413.15K$, $T = 453.15K$ and $T = 473.15K$ intersect at a common point. And the EoS of Eq. (2)

\[ a(T) = \exp\left(a_3\frac{T_m0}{T}\right)^3 + a_2\left(\frac{T_m0}{T}\right)^2 + a_1\frac{T_m0}{T} + a_0, \] (10)

\[ b(T) = -\exp\left(b_3\left(\frac{T_m0}{T}\right)^3 + b_2\left(\frac{T_m0}{T}\right)^2 + b_1\frac{T_m0}{T} + b_0\right), \] (11)

with the melting point $T_m0 = 336.7 K$ at zero pressure, $a_0 = 1.82195$, $a_1 = -4.95565$, $a_2 = 5.68506$, $a_3 = 1.34197$ and $b_0 = 1.93585$, $b_1 = -5.45561$, $b_2 = 6.47717$, $b_3 = 0.18153$. Fig. 2(a) shows that thermal expansion coefficient $\alpha_T$ decreases with increasing pressure along each isothermal line and crossing points exist among different isothermal lines. The thermal expansion coefficient $\alpha_T$ increases with the rising temperature at low pressure and the tendency is reversed under larger pressure once beyond the certain crossing points. The temperature derivative of thermal expansion coefficient at constant pressure $\left(\frac{\partial \alpha_T}{\partial T}\right)_p$ also decreases with increasing pressure along the isothermal lines and crossing points exist at different temperatures in Fig. 2(b). The sign of $\left(\frac{\partial \alpha_T}{\partial T}\right)_p$ changes from positive to negative at $T = 306.25$ GPa at $T = 373.15 K$, $P = 0.117$ GPa at $T = 413.15 K$, $P = 0.106$ GPa at $T = 453.15 K$ and $P = 0.101$ GPa at $T = 473.15 K$.

The internal pressure of liquids is defined as the negative value of the partial derivative of the internal energy $\frac{\partial E}{\partial V}$ of the system with respect to the volume,

\[ \left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial (U + E_k)}{\partial V}\right)_T = P - T \left(\frac{\partial P}{\partial T}\right)_V. \] (12)

FIG. 1. Calculated (a) bulk modulus $B_T$ (black square at $T=373.15K$, red circle at $T=413.15K$, and blue triangle at $T=453.15K$ and green start $T=473.15K$ for experimental data) of liquid potassium as a function of pressure $P$, (b) isotherms of $(Z - 1)V^2$ versus $V^2$ with the compressibility factor $Z = \frac{V}{PV}$ and molar volume $V$ (the same notation for experimental data) as in (a) at $T=373.15K$ (black solid line), $T=413.15K$ (red solid line), $T=453.15K$ (blue solid line), and $T=473.15K$ (green solid line); (c) and (d) fitting coefficients $a(T)$ and $b(T)$ of Eq. (10) and Eq. (11) of liquid potassium as a function of temperature $T/V_m0$, molar volume at melting point under zero pressure).

FIG. 2. Calculated (a) thermal expansion $\alpha_T$, (b) temperature derivative of thermal expansion at constant pressure $\left(\frac{\partial \alpha_T}{\partial T}\right)_p$, and (c) internal pressure $P_{int}$ of liquid potassium as a function of pressure $P$ along the isotherms. The symbols are the same as in Fig. 1(b).
where $U$ is the potential energy and $E_k$ is the kinetic energy. And from Eq. (15), we have

$$P_{int} = P - T a v B_T. \quad (13)$$

As shown in Fig. 2(c), the internal pressure $P_{int}$ increases with rising external pressure along the isothermal lines. And there is a crossing point existing at $P = 0.75$ GPa between two isothermal lines of $T = 453.15$ K and $T = 473.15$ K. Along all the isotherms, the internal pressure $P_{int}$ is linearly proportional to pressure as

$$P_{int} \approx P_{int0} + b_{int} P,$$  

where $P_{int0}$ is the internal pressure at zero pressure and the parameter $b_{int} = \left( \frac{\partial P_{int0}}{\partial P} \right)_V$ at zero pressure. For the considered pressure region in Fig. 2(c), the values of $P_{int0}$ are listed in Table I and the values of $b_{int}$ are 0.949 for $T = 373.15$ K, 0.915 for $T = 413.15$ K, 0.914 for $T = 453.15$ K and 0.921 for $T = 493.15$ K. Also, from the linear isotherm regularity of EoS of Eq. (9), we have the following approximations as:

$$P = \frac{RT}{V} \left( 1 + b(T) + a(T) \frac{1}{V^2} \right), \quad (15)$$

and

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{V} \left( 1 + b(T) + T \frac{da(T)}{dT} + \left( a(T) + T \frac{da(T)}{dT} \right) \frac{1}{V^2} \right). \quad (16)$$

After substituting Eq. (15) and Eq. (16) into Eq. (12), we obtain:

$$P_{int} = -\frac{RT^2}{V} \left( \frac{db(T)}{dT} + a(T) \frac{1}{V^2} \right) \quad (17)$$

And Eq. (17) can rearranged into

$$Z_{int} = \frac{P_{int} V}{RT} = -T \left( \frac{db(T)}{dT} + a(T) \frac{1}{V^2} \right),$$

which predicts $P_{int} V$ versus $V^{-2}$ is nearly linear for a liquid with along the isothermal lines as shown in Fig. 3(a).

In general the potential energy $U$ can be divided into two parts, $U = U^r + U^a$, where $U^r$ and $U^a$ are the energy from repulsive and attractive atomic interaction. Substituting $U$ into Eq. (12),\textsuperscript{13} we have

$$P_{int} = -\left( \frac{\partial (U + E_k)}{\partial V} \right)_T = -\left( \frac{\partial U}{\partial V} \right)_T = P_{int}^r + P_{int}^a, \quad (18)$$

where the repulsive internal pressure, $P_{int}^r$, is positive in sign while for attractive internal pressure, $P_{int}^a$ is negative. Comparing the approximation of Eq. (18) with Eq. (17), we get:

$$P_{int}^r = -RT \frac{da(T)}{dT}, \quad P_{int}^a = -RT \frac{db(T)}{dT} \frac{1}{V^2}, \quad (19)$$

since $\frac{da(T)}{dT} < 0$ and $\frac{db(T)}{dT} > 0$ by Eq. (10) and Eq. (11). So that we can approximate the potential energy as the following:

$$U(T, V) = K_0 \ln V + K_1 \frac{V}{V^*}.$$

where

$$K_0 = RT^2 \frac{db(T)}{dT}, \quad K_1 = -\frac{1}{2} RT^2 \frac{da(T)}{dT}. \quad (21a)$$

By using Eq. (15), the isothermal bulk modulus can be approximated as:

$$B_T = -V \left( \frac{\partial P}{\partial T} \right)_V = \frac{RT}{V} \left( 1 + b(T) + \frac{3a(T)}{V^2} \right). \quad (22)$$

So the reduced isothermal bulk modulus can be written as

$$B^* = \frac{B_T V}{RT} = 1 + b(T) + \frac{3a(T)}{V^2}, \quad (23)$$

And the linearity of $B^*$ versus $V^{-2}$ is shown in Fig. 3(b).

**B. Entropy, internal energy and enthalpy by linear isotherm regularity of EoS**

The entropy change with pressure from $P_0$ to $P$ at constant temperature is defined by\textsuperscript{13}

$$\Delta S(T, P) = S(T, P) - S(T, P_0) = -\int_{P_0}^{P} \left( \frac{\partial V}{\partial T} \right)_P dP. \quad (24)$$

The internal energy change with pressure from $P_0$ to $P$ at constant temperature is defined by\textsuperscript{17}

$$E(T, P) - E(T, P_0) = \int_{P_0}^{P} \left( T \left( \frac{\partial V}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial P} \right)_T \right) dP. \quad (25)$$

With Eq. (24), the internal energy change of Eq. (25) can rewritten as

$$\Delta E(T, P) = E(T, P) - E(T, P_0) = T \Delta S(T, P) + E^m(T, P), \quad (26)$$

with the defined internal energy contribution from the mechanical work $E^m(T, P) = -\int_{P_0}^{P} P \left( \frac{\partial V}{\partial T} \right)_P dP$. The enthalpy change with pressure from $P_0$ to $P$ at constant temperature is defined by\textsuperscript{13}

$$H(T, P) - H(T, P_0) = \int_{P_0}^{P} \left( V - T \left( \frac{\partial V}{\partial T} \right)_P \right) dP, \quad (27)$$

![FIG. 3. Calculated (a) $Z_{int} = \frac{P_{int} V}{RT}$ and (b) reduced isothermal bulk modulus $B^*$ of Eq. (28) (the same notation for experimental data as in Fig. 1(a)) in liquid potassium as a function of $(\frac{V}{V_m})^2$ along the isotherms ($R$: gas constant; $V_m$: molar volume at melting point under zero pressure). The symbols are the same as in Fig. 1(b).](image-url)
and with Eq. (24), it can rewritten as

\[ \Delta H(T, P) = H(T, P) - H(T, P_0) = T \Delta S(T, P) + H^m(T, P), \]  

(28)

with the given enthalpy change related to the mechanical work

\[ H^m(T, P) = \int_{P_0}^P V dP. \]

The Gibbs free energy change with pressure from \( P_0 \) to \( P \) at constant temperature is defined by

\[ G(T, P) - G(T, P_0) = \int_{P_0}^P V dP, \]

(29)

and

\[ \Delta G(T, P) = G(T, P) - G(T, P_0) = H^m(T, P), \]

(30)

In Fig. 4(a), the Gibbs free energy of liquid \( \text{K} \), after subtracting the total Gibbs free energy at \( 0 \) K, increases with rising pressure along the isothermal line and also increases with rising temperature at constant pressure. The Gibbs free energy change \( \Delta G(T, P) \) is positive and increases with increasing pressure at constant temperatures.

With the linear isotherm regularity EoS of Eq. (15), Eq. (16) and the basic relation \( \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial H}{\partial T} \right)_V \), the entropy \( S(T, V) \) can be approximated as

\[ S(T, V) = S_0(T) + S_1(T, V) + S_a(T, V), \]

(31)

with

\[ S_1(T, V) = \frac{R}{2} \left( 1 + b(T) + T \frac{db(T)}{dT} \right) \ln V - \frac{1}{2} \left( a(T) + T \frac{da(T)}{dT} \right) \frac{1}{V^2} \].

(32)

After substituting the calculated \( S(T, V) \) of Eq. (24) and Eq. (10), Eq. (11) into Eq. (31), we obtain the calculated \( S_0(T) \) as a decreasing function of temperature \( T \) in Fig. 4(b). \( S_0(T, V) \) is negligible comparing with the other two terms in Eq. (31) since \( |S_0(T, V)| \leq 0.020 \text{ J mol}^{-1} \text{ K}^{-1} \) and caused by the adapted approximation of Eq. (10) and Eq. (11). From the definition of internal pressure of Eq. (12), Eq. (17) and Eq. (20), we can obtain the approximation of internal energy \( E(T, V) \) as

\[ E(T, V) = E_0(T) + U(T, V) + E_a(T, V), \]

(33)

with

\[ U(T, V) = RT^2 \left( \frac{db(T)}{dT} \ln V - \frac{1}{2} \left( \frac{da(T)}{dT} \right) \frac{1}{V^2} \right). \]

(34)

By using the calculated \( E(T, V) \) of Eq. (25) and substituting Eq. (10), Eq. (11) into Eq. (33), we obtain the calculated \( E_0(T) \) as a decreasing function of temperature \( T \) in Fig. 4(c) and \( E_a(T, V) \) is negligible comparing with the other two terms in Eq. (33) with \( |E_a(T, V)| \leq 50.0 \text{ J mol}^{-1} \). The reason of the relatively smallness and dependence of temperature and volume of \( E_a(T, V) \) might be caused by the adapted approximation of Eq. (10) and Eq. (11).

Based on Eq. (15) and Eq. (33), the enthalpy \( H(T, V) = E(T, V) + PV \) of liquid \( \text{K} \) can be expressed as

\[ H(T, V) = RT \left( 1 + b(T) + T \frac{db(T)}{dT} \ln V + \left( a(T) - \frac{1}{2} \frac{da(T)}{dT} \right) \frac{1}{V^2} \right) + E_0(T) + E_a(T, V). \]

(35)

By substituting Eq. (31), Eq. (32), and Eq. (35) into the Gibbs free energy \( G(T, V) = H(T, V) - TS(T, V) \), we have

\[ G(T, V) = RT \left( (1 + b(T))(1 - \ln V) + \frac{3}{2} a(T) \frac{1}{V^2} \right) + G_0(T) + G_a(T, V), \]

(36)

with

\[ G_0(T) = E_0(T) - TS_0(T), \]

(37)

and

\[ G_a(T, V) = E_a(T, V) - TS_a(T, V), \]

(38)

In Fig. 4(d), the calculated \( G_0(T) \) is decreasing with the increasing temperature.

C. Heat capacity by linear isotherm regularity of EoS

With the numerical integration of the following equation\(^13\)

\[ \left( \frac{\partial S(T, P)}{\partial P} \right)_T = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_{pp}, \]

(39)

the heat capacity at constant pressure \( C_P(T, P) \) at constant temperature is defined by

\[ C_P(T, P) - C_P(T, P_0) = - \int_{P_0}^P T \left( \frac{\partial^2 V}{\partial T^2} \right)_{pp} dP, \]

(40)

which is related to the behavior of volume along the isothermal paths since it is convex if \( \left( \frac{\partial^2 V}{\partial T^2} \right)_{pp} > 0 \) and concave if \( \left( \frac{\partial^2 V}{\partial T^2} \right)_{pp} < 0 \). With Eq. 2, in Fig. 5(a), the calculated isobaric specific heat capacity \( C_P \)
of liquid K is the convex function of pressure at constant temperature. From Fig. 5(a), the corresponding minimum values of $C_P$ are estimated at $P_{\text{min}} = 0.197$ GPa at $T = 373.15$ K, $P_{\text{min}} = 0.206$ GPa at $T = 413.15$ K, $P_{\text{min}} = 0.21$ GPa at $T = 453.15$ K and at $P_{\text{min}} = 0.214$ GPa at $T = 473.15$ K, respectively. With rising pressure, the volume along the isothermal lines is convex for $P < P_{\text{min}}$ and concave for $P > P_{\text{min}}$. By using the above calculated heat capacity at constant pressure, we can get the corresponding heat capacity at constant volume along the isothermal line (Fig. 5(b)) with the defined difference between the heat capacity at constant pressure and constant volume,

$$C_V = C_P - TVB_T \alpha T^2. \quad (41)$$

With rising pressure, the heat capacity at constant volume increases monotonically along the isothermal lines while decreases with increasing temperature at constant pressure.

After substituting Eq. (31) and Eq. (33) into the definition of heat capacity at constant volume $C_V = \left( \frac{\partial E}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V$, we have

$$C_V = RT \left( \frac{\partial b(T)}{\partial T} + T \frac{\partial^2 b(T)}{\partial T^2} \right) \ln V - \left( \frac{\partial a(T)}{\partial T} + \frac{T}{2} \frac{\partial^2 a(T)}{\partial T^2} \right) \frac{1}{V^2} + \left( \frac{\partial E_a}{\partial T} \right)_V + \frac{dE_a(T)}{dT}, \quad (42)$$

and

$$\left( \frac{\partial E_a}{\partial T} \right)_V + \frac{dE_a(T)}{dT} = T \left( \frac{\partial S_a}{\partial T} \right)_V + T \frac{dS_a(T)}{dT}, \quad (43)$$

where both $\left( \frac{\partial E_a}{\partial T} \right)_V$ and $\left( \frac{\partial S_a}{\partial T} \right)_V$ are negligible and undetermined.

D. Common intersection points: Heat capacity ratio and Grüneisen parameter

The calculated heat capacity ratio values $\gamma$ in Eq. (9) decrease with rising pressure at constant temperature and these isotherms at high temperature intersect at a common point as seen in Fig. 6(a).

With the obtained isothermal bulk modulus (Fig. 1(a)), volume (Fig. 1(b)), and heat capacity ratio (Fig. 6(a)), we can calculate the adiabatic modulus and speed of sound at constant temperature by Eq. (8) and Eq. (7).

From the definition of the Grüneisen parameter as

$$\gamma_0 = \frac{\alpha_T B_V}{C_P} = \frac{\alpha_T B_V}{C_V}, \quad (44)$$

the Grüneisen parameter $\gamma_0$ is decreasing with the rising pressure along the isothermal lines from zero pressure. After the Grüneisen parameter $\gamma_0$ reaches a minimum and it slightly increases with the rising pressure as shown in Fig. 6(b) at $T = 413.15$ K. At high temperature, the Grüneisen parameter $\gamma_0$ is decreasing with pressure as shown in Fig. 6(b) at $T = 453.15$ K and $T = 473.15$ K.

In Fig. 6(c), the calculated Anderson-Grüneisen parameter is defined as

$$\delta_T = \frac{1}{\alpha_T B_T} \left( \frac{\partial B_T}{\partial T} \right)_V, \quad (45)$$

and decreasing monotonically with the rising pressure at constant temperature with a common intersection point for all isotherms. By using the definition of Helmholtz free energy, $F(T, P) = E(T, P) - TS(T, P)$, and pressure $P = \left( \frac{\partial F}{\partial T} \right)_P$, we can rewrite the following expressions for the isothermal bulk modulus as

$$B_T = V \left( \frac{\partial^2 F}{\partial V^2} \right)_T = B_E + B_{ES}, \quad (46)$$

with internal energy contribution $B_E = V \left( \frac{\partial E}{\partial T} \right)_T$ and entropy contribution $B_{ES} = -VT \left( \frac{\partial S}{\partial T} \right)_T$. Since $\left( \frac{\partial S}{\partial T} \right)_T = \left( \frac{\partial E}{\partial T} \right)_V = \alpha_T B_V$, we
obtain

$$B_{ES} = -VT\left(\frac{\partial (a_N B_T)}{\partial V}\right)_T = B_T T\left(\frac{\partial (a_N B_T)}{\partial P}\right)_T.$$  \tag{47}

By using the linear regularity approximation of Eq. (31) and (33), we can have

$$B_E(T, V) = V \left(\frac{\partial^2 (U + E_a)}{\partial V^2}\right)_T = -\frac{RT^2}{V} \left(\frac{d_b(T)}{dT} + 3 \frac{d a(T)}{dT} \frac{1}{V^2}\right) + V \left(\frac{\partial^2 E_a}{\partial V^2}\right)_T, \tag{48}

$$B_E = -VT\left(\frac{\partial^2 S_a}{\partial V^2}\right)_T,$$  \tag{49}

And we have

$$\left(\frac{\partial^2 E_a}{\partial V^2}\right)_T - T\left(\frac{\partial^2 S_a}{\partial V^2}\right)_T = 0.$$  \tag{50}

With Eq. (45) and the help of the relation

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{B_T}\left(\frac{\partial B_T}{\partial T}\right)_V,$$  \tag{51}

we can rewrite Eq. (47) as

$$\frac{B_{ES}}{B_T} = T\left(\frac{\partial B_T}{\partial P}\right)_T - \delta_T.$$  \tag{52}

By substituting Eq. (22) and Eq. (49) into Eq. (52), we obtain the corresponding linear regularity approximation as

$$\frac{B_{ES}}{B_T} = \frac{RT}{V} \left(1 + b(T) + \frac{T \frac{d b(T)}{dT}}{\delta_T} V^2 + 3 \left(\frac{a(T)}{\delta_T} + \frac{T \frac{d a(T)}{dT}}{\delta_T}\right) \frac{1}{V^2}\right) + V \left(\frac{\partial^2 E_a}{\partial V^2}\right)_T.$$  \tag{53}

$\frac{B_{ES}}{B_T}$ increases with the rising pressure at constant temperature and all isotherms intersect at a common point in Fig. 6(d). And we have $B_{ES} > 0$, and then $\left(\frac{\partial B_T}{\partial P}\right)_T > \delta_T$.

**IV. DISCUSSION AND CONCLUSION**

It is always a difficult task to obtain reliable thermodynamic data in liquid metals at high pressure and temperature experimentally and numerically. In this paper, with an EOS of the power law form, we studied the thermodynamic properties of liquid potassium under high temperature and high pressure. The calculated isothermal bulk modulus, the specific volume, and internal energy for liquid potassium with the variation of pressure are in good agreement with the available data from experiments. In particular, we found that the calculated entropy decreases and both enthalpy and Gibbs free energy increase with the rising pressure at constant temperatures. At constant pressure, both entropy and enthalpy increase with temperature and the calculated Gibbs free energy decreases with temperature.

Simple regularities have been proposed for years in pure liquids and liquid mixtures although there is no theoretical basis to explain them.\cite{1,2,3} By using the power law EOS of Eq. (1) and (2), the calculated isothermal bulk modulus and internal pressure of liquid K can be approximated as a linear of pressure as shown in Fig. 1(a) and Fig. 2(c), and the first is named as the Tait-Murnaghan relation.\cite{4} A crossing point may exist in internal pressure along the isotherms at high temperature. Based on Eq. (2), the new linear isothermal regularity is that the quantity $(Z - 1)V^2$ is linear in $V^2$ in Fig. 1(b), which is in good agreement with experimental results, and a common intersection point is observed for isotherms at high temperature. From that linear regularity, the predicted relation of $P_{int}V$ versus $V^{-2}$ which is nearly linear if liquid K is obtained in Fig. 3(a). Also, the calculated reduced isothermal bulk modulus from Eq. (1) is found to be linearly proportional to $V^{-2}$ and the result is very close to that obtained from the experimental data in Fig. 3(b). And that linearity could be derived from the linear isothermal regularity of Eq. (10) as indicated by Eq. (26). Based on the linear isotherm regularity EOS, analytical expression of thermodynamic properties of liquid potassium can be written out.

And the existing crossing point in isobaric thermal expansion coefficients along the isothermal lines are observed in liquid Na\textsuperscript{+} and liquid K. We observed a crossing point existing for the calculated heat capacity ratio which decreases with pressure along the isothermal paths. For the calculated Grüneisen parameter, we had the crossing points and the minimum at relatively low temperature along certain isothermal path. The calculated Anderson-Grüneisen parameter is found to decrease with pressure at constant temperature and a common intersection point is observed for all isotherms. Much more work is necessary to explore the explanation on the atomic scale for regularities in dense liquids. It would benefit the development of equation of states to acquire thermophysical properties in liquids.

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