Equations of state for two alkali metals at high temperatures

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Abstract. Thermodynamic models of equation of state for lithium and sodium with taking into account the melting and vaporization effects are proposed. Calculated parameters of phase diagrams of these two alkali metals are compared with available experimental data at high temperatures.

1. Introduction
The adequacy of description of the thermodynamic properties and phase transformations of metals is very important for numerical simulation of processes of intense pulsed influences on condensed media [1–4].

In the present work new equations of state (EOSs) for lithium and sodium are presented. These EOSs allow for the melting and vaporization effects. As distinct from the previously obtained multi-phase EOSs for these metals [5, 6], new forms of expressions of the individual terms of the thermodynamic potential are proposed. It enables one to take into account more adequately the thermal contribution of heavy particles (atoms, ions, nuclei) in the solid and liquid phases as well as the solid–liquid phase transition. A comparison of calculated results with available high-temperature experimental data is made.

2. EOS model
The specific free energy of the metals is considered as a sum of three components [1],

\[ F(V, T) = F_c(V) + F_a(V, T) + F_e(V, T), \]  

(1)

describing the cold part of interparticle interaction at \( T = 0 \) K \((F_c)\) and the thermal contributions by heavy particles \((F_a)\) and electrons \((F_e)\). The first and second components of equation (1) have different forms for the solid and liquid phases, but the third is defined identically as in the EOS model [2, 5].

The cold interaction energy for the solid phase is given by the relation [7]. The thermal lattice component of the free energy is defined as follows,

\[ F_a(V, T) = RT \left( 3 \ln \left(1 - e^{-\theta_a/T}\right) - D(\theta_a/T) \right), \]

(2)
where \( R = k_B (Am_u)^{-1} \), \( k_B \) is the Boltzmann constant, \( m_u \) is the atomic mass unit (amu), \( A \) is the atomic mass (in amu), \( D \) is the Debye function [8], \( \theta_u = \theta_u (V) \) is the characteristic temperature of phonon spectrum [2, 5],

\[
\theta_u (V) = \theta_{u0} \sigma^{2/3} \exp \left( \frac{(\gamma_{u0} - 2/3)}{B_s^{2/3} + D_s} \frac{B_s \ln \sigma}{B_s^{2} + D_s (\ln \sigma + D_s)} \right),
\]

(3)

where \( \sigma = V_0/V \), \( V_0 \) and \( \gamma_{u0} \) are the values of the specific volume and Grüneisen coefficient of the solid phase under normal conditions (\( P = 0.1 \) MPa, \( T = 298 \) K).

Thus the developed multi-phase EOSs provide a consistent description of thermodynamic properties of two alkali metals and can be used in numerical simulation of processes at high temperatures.

3. Calculation results

Under the normal conditions, the body-centered-cubic (bcc) modifications of lithium and sodium are stable. The transformation of bcc to the face-centered-cubic (fcc) structure occurs in Li and Na under compression at \( T = 298 \) K up to pressure of \( P = 7.5 \) [9] and 65 GPa [10], respectively. In the present work, EOSs for bcc–liquid–vapor systems of the metals are constructed.

Calculated phase diagrams for lithium and sodium are shown in figures 1–4. The melting curves resulting from the present EOSs are in a good agreement with data of measurements [11–13,16] (see figures 1 and 3). The melting occurs on the obtained Hugoniot of Li and Na in the pressure range of \( P = 7.6 \div 11.5 \) and \( 3.9 \div 5.1 \) GPa, correspondingly.

As one can see in figures 2 and 4, calculated values of density of the liquid phase on the boundary of liquid–vapor equilibrium region agree with experimental data for both metals under consideration [14,15]. Obtained parameters of the critical point on the liquid–vapor saturation curve are as follows: \( P_{cr} = 95.4 \) MPa, \( T_{cr} = 3940 \) K, \( \rho_{cr} = 0.097 \) g cm\(^{-3} \), \( S_{cr} = 16.84 \) J (g K\(^{-1} \)) for lithium; \( P_{cr} = 46.73 \) MPa, \( T_{cr} = 2489 \) K, \( \rho_{cr} = 0.24 \) g cm\(^{-3} \), \( S_{cr} = 5.614 \) J (g K\(^{-1} \)) for sodium. These are close to previous evaluations [5,6].

Thus the developed multi-phase EOSs provide a consistent description of thermodynamic properties of two alkali metals and can be used in numerical simulation of processes at high temperatures.
Figure 1. Phase diagram of lithium in $T$–$P$ plane. Solid line is the calculated Hugoniot. Dashed line is the calculated melting curve. Experimental data on melting: ○, [11]; △, [12]; □, [13].

Figure 2. Phase diagram of lithium in $T$–$\rho$ plane. Lines result from present EOS: $M$, melting boundaries; $Sb$, sublimation boundary; $B$, the liquid–vapor binodals with the critical point, $CP$. Experimental data on the liquid density: □, [14]; ○, [15].

Figure 3. Phase diagram of sodium in $T$–$P$ plane. Notation is analogous to figure 1, excepting for data: ○, [16].

Figure 4. Phase diagram of sodium in $T$–$\rho$ plane. Notation is the same as in figure 2.

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