DENSITY AND ENTHALPY OF LIQUID ALKALI METALS AT PRESSURES TO 1500 BARS

V. G. Stepanov and V. F. Kozhevnikov

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The similarity principle is used to find the density and enthalpy of the fused alkali metals lithium, sodium, and potassium at pressures to 1500 bars, and cesium to 1000 bars.

Information on the thermodynamic properties of liquid alkali metals in the present-day literature refers only to the saturation line. This fact is explained by the absence of reliable experimental data at pressures exceeding the saturation pressure P_S [29, 31]. In current technology alkali metals are widely used as heat-exchange and working substances, and thus it is of interest to determine their thermodynamic properties at pressures significantly exceeding P_S. The present study is dedicated to a prediction of thermodynamic properties of alkali metals on the basis of the similarity principle developed theoretically in [22, 23, 25, 30].

At the present time the electronic and atomic properties of metals can be analyzed most systematically with the aid of the pseudopotential theory [1-3]. The basic principles of this theory may be stated briefly as follows.

1. All valence electrons in the metal are collectivized. The remaining ions occupy a small part of the atomic volume (~10%). do not overlap, and interact in a Coulomb manner.
2. Interaction between conduction electrons and ions is always of a Coulomb nature except within the volume occupied by the ion core, within which the electron wave function oscillates strongly. This is the reason for the sharp decrease in ion–electron interaction within the ion core, which, in turn, leads to the appearance of a small parameter in the metal theory $\omega(k)/\varepsilon_F$, where $\omega(k)$ is the Fourier component of the pseudopotential ($k \sim k_F$) and ε_F is the Fermi energy.
3. In liquid metals it can be assumed that the ion subsystem follows classical mechanics, which is analogous to the Born–Oppenheimer approximation.

Based upon these considerations the Hamiltonian of the liquid–metal system may be written in the form

$$H = \sum_{i=1}^{N} \frac{P_i^2}{2M} + \frac{1}{2} \sum_{i=i'} \frac{z^2 e^2}{\vec{R}_i - \vec{R}_{i'}} + \sum_{j=1}^{zN} \frac{P_j^2}{2m} + \frac{1}{2} \sum_{j=j'} \frac{e^2}{\vec{r}_j - \vec{r}_{j'}} + \sum_{i,j} \omega(\vec{R}_i - \vec{r}_j).$$

We can then obtain the following expression for the free energy [4, 5]:

$$F = E_e + \Delta E + F_I, \tag{1}$$

where E_e is the energy of the electron system; F_I is the free energy of the classical ion subsystem; and ΔE is a function dependent on density.

The basic difficulties in the quantitative description of the atomic properties of liquid-metal systems develop in selecting expressions for the terms on the right side of Eq. (1). The first of these is the electron subsystem energy E_e, for which the Noziere–Pines approximation is usually employed [6], providing only a qualitatively true description of an electron liquid in metals [7].

Other approximate expressions appearing in Eq. (1) are the electron gas dielectric function under conditions of mean density, the radial ion distribution function in the metal $g(R)$, and the ion–electron interaction pseudopotential $\omega(\vec{R})$, which, generally speaking, is a nonlocal operator.

The function $g(R)$ is usually taken from experimental data on neutron and x-ray scattering (see, for example [8]), from computer experiments [9], or from the Percus–Yevich or hypergrid approximations [10].

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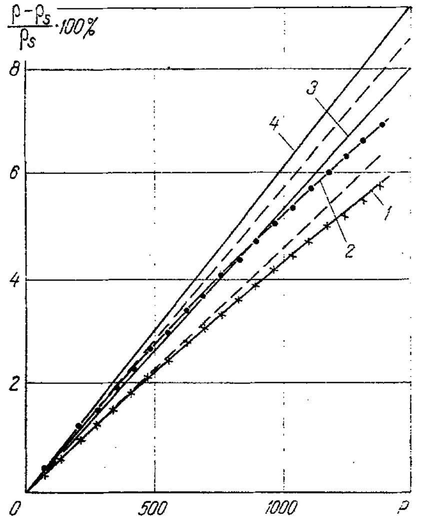

Fig. 1

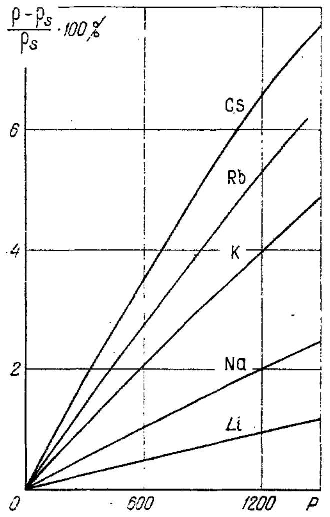

Fig. 2

Fig. 1. PV-isotherms obtained in [20] and [14]. Dashed lines) linear approximations of experimental curves: 1, 2) experiment [20] (1, T = 313°K; 2, 473°K); 3, 4) calculated from equation of [14] (3, T = 325°K; 4, 475°K); P, bars.

Fig. 2. Isothermal density change of liquid alkali metals at $T \approx T_m$. P, bars.

Because of difficulties in model description of a liquid, the form and parameters of the pseudopotential $\omega(\vec{R})$ are usually taken from studies of metals in the solid phase [5, 8], which obviously becomes less justifiable with removal from the melting point. In the vicinity of the melting point, studies [8, 9, 11, 12] have calculated various thermodynamic properties of nontransition liquid metals and obtained good agreement with experimental data.

Studies [5, 13, 14] calculated the thermodynamic properties of liquid alkali metals in the one-phase region by the pseudopotential method, with recourse to perturbation theory for simple liquids. Results for free energy F, entropy S, density ρ, and isothermal compressibility β_T are comparable with experimental data on the saturation line [15]. Good agreement between theory and experiment was noted for the temperature dependence of free energy.

A characteristic result of these calculations is linearity of PV-isotherms at temperatures to $4.4T_m$. This fact was the basis for the selection in [14] of a linear form for the dependence of density on pressure, with a slope obtained from the compressibility on the saturation line, as taken from experiments on measurement of the velocity of sound [16-19]. In [20] the velocity of sound u in Rb at pressures to 1400 bars and temperatures to 200°C,

$$u = A_1 + A_2T + A_3P + A_4TP + A_5P^2 + A_6TP^2 \text{ (cm/sec)}$$

was obtained, where $A_1 = 0.126954\cdot 10^6$; $A_2 = -0.391247\cdot 10^2$; $A_3 = 0.537494$; $A_4 = 0.805498\cdot 10^{-3}$; $A_5 = -0.233758\cdot 10^{-5}$; $A_6 = -0.145987\cdot 10^{-7}$.

From the velocity of sound the PVT surface and other thermophysical properties of rubidium were calculated by the iteration method [20].

Figure 1 shows two experimental PV-isotherms obtained in [20], with corresponding isotherms calculated from the equation of [14]. It is evident from the figure that the experimental isotherms are straight lines at moderate pressure (dashed lines), which agrees with conclusions made from theoretical consideration of the PVT-surface of liquid alkali metals. However, even at temperatures close to the melting point the curvature of the experimental curve becomes noticeable at pressures above 500 bars.

The difference in absolute density values may be explained by the differences in experimental data on velocity of sound in [18] and [20], and also by the fact that the data on the saturation line used as a reference here were taken from different studies (in [20] from [21] and in [14] from [15]) and thus differ.

TABLE 1. Density and Enthalpy of Liquid Rubidium, Obtained from Experimental Measurements of Velocity of Sound [20]

P, bars	ρ, kg/m^3					$H_T - H_0$, 10^3 J/kg	
	40°C	80°C	120°C	160°C	200°C	120°C	200°C
P_S	1477,0	1460,9	1444,6	1428,2	1411,6	145	179
100	1483,9	1468,0	1452,0	1435,9	1419,6	155	185
200	1490,7	1475,0	1459,4	1443,5	1427,6	161	191
300	1497,4	1482,0	1466,6	1451,0	1435,4	167	197
400	1504,0	1488,9	1473,6	1458,3	1443,0	174	203
500	1510,5	1495,7	1480,5	1465,5	1450,4	180	209
600	1516,9	1502,3	1487,4	1472,5	1457,6	186	215
700	1523,2	1508,8	1494,1	1479,5	1464,7	192	221
800	1529,4	1515,2	1500,8	1486,3	1471,8	198	227
900	1535,5	1521,4	1507,3	1493,1	1478,8	204	233
1000	1541,5	1527,6	1513,8	1499,8	1485,8	210	239
1100	1547,4	1533,8	1520,2	1506,4	1492,6	216	245
1200	1553,2	1539,9	1526,5	1513,0	1499,3	222	251
1300	1559,9	1546,0	1532,7	1519,4	1505,9	227	257
1400	1565,5	1552,0	1538,8	1525,6	1512,3	233	263

It is known [22, 23] that the alkali metals Na, K, Rb, and Cs are thermodynamically similar. Consequently, it is possible to use data obtained for rubidium to calculate the thermodynamic characteristics of the remaining alkali metals. However, the absence of sufficiently accurate values for critical parameters of the alkali metals makes it impossible to employ the law of corresponding states in its classical form [24]. Since according to the law of corresponding states the molecular interaction potentials should be similar, for a two parameter potential of the Lennard–Jones type for the correction parameters we may use the energy and distance parameters of the potential curve [25]. Calculation of corrected isothermal compressibility of liquid Na, K, Rb, and Cs [26], where the depth ε and position R_e of the minimum of the potential curve were used for correction parameters, supports the existence of thermodynamic similarity among these metals.

In [27-29] analysis of experimental data on density, compressibility, and other properties demonstrated that the parameters of any corresponding states, such as the triple point and the normal boiling point, may be used as correction parameters for liquid alkali metals.

The generalized expressions obtained in [26-29] refer only to the saturation line, since here there is a sufficient quantity of experimental material. There is insufficient experimental data to obtain generalized empirical relationships for the liquid alkali metals.

In [30] it was demonstrated by analysis of effective interion interaction $\Phi(R)$ for alkali metals in the liquid phase that $\Phi(R)$ can be described with satisfactory accuracy (2-5%) by the expression

$$\Phi(R) = \varepsilon\varphi\left(\frac{R}{R_e}\right),$$

where ε is the depth, and R_e, the position, of the minimum of the potential curve, both of these being functions of density. Hence, according to [25] it is concluded that the ionic subsystems of the liquid alkali metals are thermodynamically similar. Since the major contribution to the thermodynamic parameters of the liquid-metal system is made by the ionic subsystem, we may expect that the liquid-metal systems, as a whole, are similar.

Onishchenko [14] calculated the free energy F, density ρ, and other thermodynamic characteristics of liquid Na, K, Rb, and Cs with the use of pseudopotentials taken from various works, with recalculation of F values for the remaining alkali metals (including Li) from the value obtained for Na by the similarity method.

The similarity principle which then becomes applicable consists of the following. For a mole of material the corrected free energy value F/RT is identical for all liquid alkali metals at equal values of corrected density $\rho^* = \rho/\rho_m$ and temperature $T^* = T/T_m$.

The free energy values obtained by the both methods agree well with each other, and comparison of values obtained for Li with data on the saturation line [15] allows inclusion of Li in the group of thermodynamically similar substances.

This similarity principle may be used to obtain generalized expressions for recomputation of thermodynamic values from one metal to another.

We denote by the index 0 the values referring to a metal whose thermodynamic properties are known, while the prime refers to the metal whose properties must be defined. Then at

$$T' = aT^0 \text{ and } \rho' = b\rho^0 \tag{2}$$

TABLE 2. Density and Enthalpy of Liquid Li, Na, K, and Cs

P, bars	ρ·kg/m^3				H_T-H_0, 10^{3}J/kg	
	510K	570K	630K	690K	570K	690K
Lithium						
P_S	512,6	506,4	500,5	494,3	2210	2716
100	513,0	506,8	500,9	494,7	2224	2731
200	513,4	507,2	501,3	495,2	2238	2745
300	513,8	507,7	501,7	495,6	2253	2760
400	514,1	508,1	502,2	496,1	2267	2775
500	514,5	508,5	502,6	496,5	2281	2789
600	514,9	508,9	503,0	496,9	2295	2804
700	515,3	509,3	502,4	497,4	2310	2819
800	515,7	509,7	503,8	498,8	2324	2833
900	516,1	510,1	504,2	498,3	2338	2848
1000	516,5	510,5	504,7	498,7	2352	2862
1100	516,8	510,9	505,1	499,1	2367	2877
1200	517,2	511,4	505,5	499,5	2381	2892
1300	517,6	511,8	506,0	500,0	2395	2906
1400	518,0	512,2	506,4	500,4	2409	2921
1500	518,4	512,6	506,8	500,8	2424	2935

P, bars	ρ, kg/m^3				H_T-H_0. 10^3 J/kg	
	420K	470K	520K	570K	470K	560K
Sodium						
P_S	916,1	904,2	892,3	880,4	622	744
100	917,7	905,9	894,1	882,2	631	753
200	919,3	907,6	895,9	884,0	640	763
300	920,9	909,3	897,6	885,8	649	772
400	922,5	911,0	899,3	887,7	659	781
500	924,1	912,7	901,0	889,5	668	790
600	925,7	914,3	902,7	891,2	677	799
700	927,3	915,9	904,4	892,9	686	808
800	928,9	917,5	906,1	894,6	695	817
900	930,5	919,1	907,8	896,4	704	826
1000	932,0	920,7	909,5	898,1	714	835
1100	933,5	922,3	911,1	899,8	723	844
1200	935,0	923,9	912,7	901,5	732	853
1300	936,5	925,5	914,3	903,3	741	862
1400	938,0	927,1	915,9	904,9	750	871
1500	939,4	928,7	917,5	906,5	759	880

P, bars	ρ, kg/m^3				H_T-H_0. 10^3 J/kg	
	380K	420K	460K	510K	420K	510K
Potassium						
P_S	818,4	809,0	799,5	788,1	339	411
100	821,4	812,1	802,7	791,5	350	422
200	824,4	815,2	805,9	794,9	361	433
300	827,4	818,3	809,1	798,3	372	443
400	830,4	821,4	812,3	801,6	382	453
500	833,3	824,5	815,4	804,9	393	464
600	836,2	827,5	818,5	808,1	404	474
700	839,0	830,5	821,6	811,3	414	485
800	841,8	833,4	824,6	814,4	425	495
900	844,6	836,3	827,6	817,4	436	506
1000	847,3	839,1	830,4	820,3	446	516
1100	850,0	841,9	833,3	823,2	456	527
1200	852,7	844,7	836,2	826,3	467	538
1300	855,4	847,4	839,0	829,1	478	548
1400	858,0	850,1	841,8	831,9	488	559
1500	860,6	852,7	844,5	834,7	499	569

P, bars	ρ, kg/m^3				H_T-H_0, 10^3 J/kg	
	340K	380K	420K	460K	380K	460K
Cesium						
P_S	1814,8	1792,0	1769,2	1746,4	94	113
100	1826,3	1804,0	1781,5	1759,4	99	118
200	1837,5	1815,6	1793,8	1771,0	104	123
300	1848,6	1827,0	1805,8	1783,2	109	128
400	1859,3	1838,3	1817,3	1796,5	114	133
500	1870,0	1849,4	1828,7	1808,2	119	138
600	1880,5	1860,2	1839,7	1819,7	124	142
700	1890,7	1870,7	1850,7	1831,0	129	147
800	1900,8	1881,0	1861,4	1842,0	133	152
900	1909,1	1891,2	1872,0	1852,3	138	157
1000	1918,2	1900,1	1882,4	1863,2	143	162

we have

$$P' = \frac{ab}{c} P^0, \quad H' = \frac{a}{c} H^0; \quad \beta'_T = \frac{c}{ab} \beta^0_T, \tag{3), (4}$$

where $a = T'_m / T^0_m$; $b = \rho'_m / \rho^0_m$; $c = M'/M^0$; M is the molecular weight of the metal; and H is the enthalpy.

As was shown in [14], Eq. (4) may be rewritten in the form

$$\beta^*_T = \frac{T_m \rho_m}{M} \beta_T.$$

Using Eqs. (2), (3) the PVT-surfaces and enthalpies of liquid Li, Na, K, and Cs were calculated from data on Rb [20]. Results are presented in Table 1. Comparison of the calculated density and enthalpy values with data on the saturation line [31] shows some divergence (3-5%), which can be explained by the approximate character of the similarity principle employed. We therefore consider it reasonable to preserve the dependence of density and enthalpy on pressure and correct the values on the saturation line to the experimental ones.

Table 2 presents values of density ρ and enthalpy $H_T - H_0$, corrected to the values of [31] on the saturation line with the following formulas:

$$\rho = \rho' \frac{\rho_S}{\rho'_S}, \quad H = H' \frac{H_S}{H'_S},$$

where ρ_S and H_S are tabular values of ρ and H on the saturation line [31]; ρ'_S and H'_S, corresponding values obtained from Eqs. (2)-(4).

Figure 2 shows the isothermal change of density $(\rho - \rho_S)/\rho_S$ as a function of pressure for all liquid metals at the melting point. It is evident from the figure that the most compressible substance is Cs and the least compressible, Li, while the compressibilities of the remaining metals are of intermediate values. This fact agrees completely with the experimental data of [16-19] and can be explained qualitatively by the difference in atomic concentration in the various liquid alkali metals.

NOTATION

H, Hamiltonian function and enthalpy; P_i, M, $\vec{R}_i$, z, N, momentum, mass, radius vector, valence, and number of ions; P_j, m, e, $\vec{r}_j$, momentum, mass, charge, and radius vector of electrons; ω, local pseudopotential; F, free energy; u, velocity of sound; T, temperature; R, universal gas constant; ρ, density; β_T, isothermal compressibility; P, pressure; V, volume; ρ_S, P_S, H_S, density, pressure, and enthalpy on saturation line.

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THERMAL CONDUCTIVITY OF GASEOUS NEON AND KRYPTON AT REDUCED TEMPERATURES AND ATMOSPHERIC PRESSURE

N. A. Nesterov and V. M. Sudnik

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The results of an experimental and theoretical investigation of the thermal conductivity of neon and krypton at reduced temperature and atmospheric pressure are presented and discussed.

The thermal conductivities (λ) of krypton [1, 2, 15] and neon [1, 3-5, 15] have been investigated fairly completely at temperatures of 273°K and below and an atmospheric pressure, and preliminary values of the thermal conductivity of neon measured as a function of the temperature and pressure have been given in [6]. In view of the fact that existing methods of calculating the thermal conductivity do not describe the experimental data sufficiently accurately over a wide temperature range, the latter are of particular value both for the further development of molecular-kinetic theory and for use in calculations of heat-exchange apparatus and heat-transfer processes.

In this paper we present the results of experimental investigations of the thermal conductivities of neon and krypton at atmospheric pressure in the temperature range of 90-273°K and 120-273°K, respectively. The investigations were made using experimental equipment based on the use of the absolute heated-filament method described in [7].

For the investigation we used neon of high purity containing up to 0.11% of impurity, of which 0.1% was helium, and pure krypton with a krypton content of 99.97%.

Figure 1 compares the experimental values obtained for the thermal conductivities of neon and krypton as a function of temperatures with existing experimental and theoretical values calculated using the Lennard-Jones [8-10], Morse [11], and exp-6 [9-12] potentials.

Our experimental data on neon are in good agreement with the results obtained by other authors and with the preliminary values of the thermal conductivity given in [6], which indicates that they are reliable and independent of the pressure in the limits from 0.7 atm to 1 atm.

Calculation shows that for neon the values calculated for the Lennard-Jones potential with intermolecular interaction parameters $\varepsilon/k = 35.7$°K, $\sigma = 2.789$ Å [8]; $\varepsilon/k = 43$°K, $\sigma = 2.73$ Å [9]; $\varepsilon/k = 45.58$°K, $\sigma = 2.707$ Å agree best of all with the experimental data. The maximum disagreement between the data is 0.8, 1.5, and 1.6%, respectively.

A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 30, No. 5, pp. 863-867, May, 1976. Original article submitted August 1, 1975.