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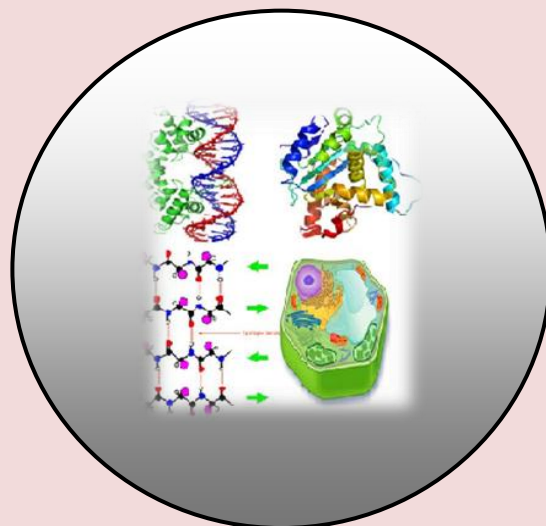
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RESEARCH PAPER

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Computation of Thermodynamic, Thermophysical and Thermoacoustical Properties of Liquid Metals Using Sonic Speed and Density Data

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ABSTRACT

Density and ultrasonic velocity measurements of high-purity liquid metals sodium, potassium, rubidium, cesium, lead and tin at temperatures from their melting point to 250°C have been used to estimate the values of thermal expansion coefficient (α), isothermal compressibility (β_T), internal pressure (P_{int}), surface tension (σ), specific heat ratio (γ) and pseudo-Grüneisen parameter (Γ) using empirical relations at different temperatures. The non-linearity parameter (B/A) and internal pressure (P_{int}) as evaluated by Hartmann and Ballou relation at different temperatures are the key focus of the work.

Keywords: Empirical relations, Sonic speed, Density, Thermodynamic properties, Thermophysical properties and Thermoacoustical properties, Liquid metals.

INTRODUCTION

Density (ρ) and sonic speed (u) have been found to be a versatile tool for estimating a number of useful and important properties of liquids and solution. Since the experimental techniques involved in the measurements of density and sonic speed are very simple, precise, accurate and economical.

Density and sonic speed data are available in literature for pure liquids, binary and higher order mixtures, it is worthwhile to obtain various thermodynamic, thermophysical and thermoacoustical properties of such systems. For fulfilling such problem, a number of empirical relations, based on dimensional analysis, have been deduced. These relations (Pandey *et al.*, 2013; Pandey *et al.*, 1997; Pandey *et al.*, 2006; Pandey *et al.*, 2000) have been successfully applied for the calculations of some important and useful thermodynamic properties of liquid systems. Recently, Marcus (2013) has also given emphasis on these relations. An exhaustive literature survey reveals that the aforesaid correlations between p - u -thermodynamic properties have, so far, not been applied to liquid metals. In the present work we are presenting the results of calculation of a number of important and useful thermodynamic, thermophysical and thermoacoustical properties of liquid metals mainly Na, K, Rb, Cs, Pb, and Sn for which the experimental data of density and sonic speed have been taken from the paper of Letcher *et al.* (1970). The data for Pb and Sn were taken from the literature (Konyudnenb, 1972; Pandey *et al.*, 1984; Shukla *et al.*, 2007; Pandey *et al.*, 2004; Blairs, 2006) reported the experimental values of p and u for several liquid metals at their melting points. Contrast to the experimental work on liquid metals considerable work has been done on the theoretical aspects of liquid metals (Sharma, 1979; Khanna, *et al.*, 1981; Khanna *et al.*, 1982). It is not possible here to give references of all such papers. However, we are referring some important contributions. Eslami *et al.*, (1998) calculated density and virial coefficients of alkali

metals and alloys Cs-K, Na-K, and Na-K-Cs on the basis of equation of state. Eyring *et al.*, (1972) applied significant structure theory on the several metals and calculated a number of equilibrium and transport properties. Hard sphere equation of state has been employed to compute various thermodynamic properties (Pandey *et al.*, 1981) of metallic liquids. Flory's statistical theory has been successfully applied by Pandey *et al.*, (1981) and Chaturvedi *et al.*, (1982) to calculate various thermodynamic properties of liquid metals. In the present work we are presenting the results of calculation of a number of thermodynamic, thermophysical and thermoacoustical properties of six liquid metals on the basis of recently obtained p-u- thermodynamic properties correlations mentioned earlier. The metals undertaken for the present study are Na, K, Rb, Cs, Pb, and Sn.

FORMULATION

Based on the dimensional analysis (Pandey *et al.*, 2013; Pandey *et al.*, 1997; Pandey *et al.*, 2006; Pandey *et al.*, 2000), following correlations between p-u-thermodynamic properties are used:

Thermal expansion coefficient

$$\alpha = \frac{75.6 \times 10^{-3}}{T^{1/9} u^{1/2} \rho^{1/3}} \quad (1)$$

Isothermal compressibility

$$\beta_T = \frac{1.71 \times 10^{-3}}{T^{4/9} \rho^{4/3} u^2} \quad (2)$$

Internal pressure

$$P_{\text{int}} = \alpha T / \beta_T = 44.2 \times 10^{4/3} u^{3/2} \rho T^{4/3} \quad (3)$$

Surface tension

$$\sigma = u^{3/2} \rho T^{4/3} \times 10^{-4} \quad (4)$$

Specific heat ratio

$$\gamma = \frac{17.1}{T^{4/9} \rho^{1/3}} \quad (5)$$

Pseudo-Grüneisen parameter

$$\Gamma = \frac{\gamma - 1}{\alpha T} \quad (6)$$

where α , β_T , P_{int} , σ , γ and Γ are respectively the thermal expansion coefficient, isothermal compressibility, internal pressure, surface tension, specific heat ratio and pseudo-Grüneisen parameter.

The thermoacoustic non-linearity parameter, B/A, is related to p-u by the following equations:

Hartmann-Balizer (Hartmann *et al.*, 1987)

$$\frac{B}{A} = 2 + \left[\frac{0.98 \times 10^4}{u} \right] \quad (7)$$

Ballou²⁰

$$\frac{B}{A} = -0.5 + \left[\frac{1.2 \times 10^4}{u} \right] \quad (8)$$

Internal pressure

$$P_{\text{int}} = \frac{\rho u^2}{1 + B/A} \quad (9)$$

RESULTS AND DISCUSSION

The density (ρ) and sonic speed (u) data of liquid alkali metals Na, K, Rb and Cs have been taken from the paper of Kim et al., 1970, as measured by Kim et al over a temperature range from the sample melting point to 250°C has been taken from literature (Pandey *et al.*, 1981). The experimental value of ρ and u for liquid metals Pb and Sn were taken from the literature (Konyudnenb 1972; Pandey *et al.*, 1984; Shukla *et al.*, 2007). The calculated values of thermal expansion coefficient (α), isothermal compressibility (β_T), internal pressure (P_{int}), surface tension (σ), specific heat ratio (γ) and pseudo- Grüneisen parameter (Γ) of Na, K, Rb, Cs, Pb and Sn using empirical relations (1-6) are reported in Table 1 at different temperatures.

Table 2 focuses on the thermoacoustic non-linearity parameter (B/A) and internal pressure (P_{int}) of high purity liquid alkali metals (Na, K, Rb, Cs, Pb and Sn) as calculated from formulation (7) and (8) consecutively at the different temperature. The values of α , β_T and Γ show marked decrease with rise in temperature in each metal indicating that the inter atomic distances is reduced with a simultaneous increase of 3-5% in the specific volume (1% per 100°C) in narrow temperature range. Calculated values of internal Pressure (P_{int}) and surface tension (σ) decrease sharply with temperature showing that the metallic bonding or cohesive force decreases with an increase of molecular thermal activity or kinetic energy. There is evidence from the data trend in Table1 that α , β_T values are maximum in case of cesium and minimum in sodium, the order being (Cs > Rb > K > Na) as shown in Figure 1 which indicates that as the size of the liquid alkali metal increases the tendency to release electron increases, electron affinity decreases, making it less dense. Similar is the case of Pb and Sn as shown in Figure 2.

Table 2 indicates the calculated values of nonlinearity parameter B/A and P_{int} from equations (7-9). The values are in increasing order with rising temperature, in each liquid alkali metal. As sonic speed decreases the B/A increases for each metal indicates strong interaction between molecules. Amongst all the metals (Na, K, Rb, and Cs) B/A is highest in case of Cesium (Cs) as its sonic speed is lowest followed by Rb, K and Na. The values are in excellent agreement with experimental data which indicates that the molecular structure of the fluid have strong intermolecular or interatomic potential.

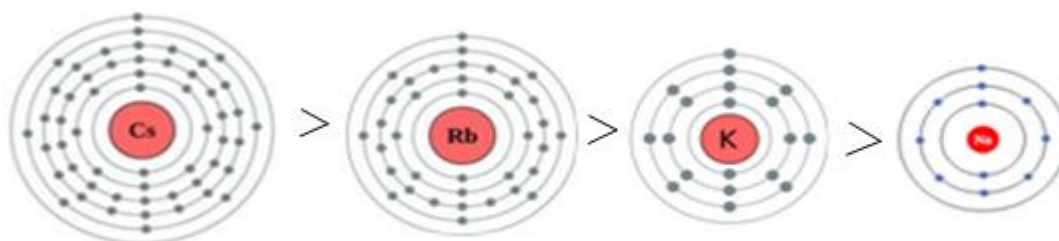


Figure 1.

The order is reverse in case of P_{int} , γ and Γ with slight decrease in value in case of sodium (Na) as the thermodynamic parameter are inversely proportional to α , β_T .

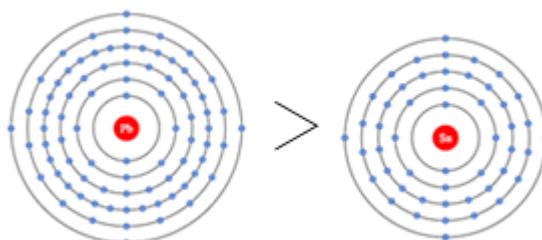


Figure 2.

Table 1. Estimated values of thermal expansivities(α), isothermal compressibility(β_T), internal pressure(P_{int}), surface tension(σ), specific heat ratio(γ), pseudo-Grüneisen parameter(Γ), for high purity liquid alkali metals(viz. Na, K, Rb & Cs) at various temperatures by empirical equations

T	$\alpha \times 10^{-4}$	$\beta_T \times 10^{-5}$	$P_{int} \times 10^3$	σ	γ	Γ
K	K ⁻¹	atm ⁻¹	atm	Nm ⁻¹		
Sodium (Na)						
373.15	8.01	2.18	295.26	31.42	1.26	0.88
423.15	7.96	2.13	340.86	36.27	1.20	0.59
473.15	7.94	2.11	383.61	40.82	1.14	0.39
494.15	7.93	2.10	401.81	42.75	1.12	0.31
518.15	7.92	2.09	423.72	45.09	1.10	0.25
Potassium (K)						
343.15	9.73	4.76	151.18	16.09	1.36	1.08
386.15	9.71	4.71	171.34	18.23	1.30	0.79
436.15	9.68	4.66	195.06	20.76	1.23	0.55
464.15	9.68	4.66	207.84	22.11	1.20	0.45
502.15	9.69	4.68	223.83	23.82	1.17	0.34
536.15	9.71	4.71	238.13	25.34	1.14	0.26
Rubidium (Ru)						
316.15	9.91	5.11	132.02	14.05	1.16	0.52
357.15	9.89	5.06	150.14	15.98	1.11	0.30
393.15	9.85	5.00	166.98	17.77	1.06	0.16
452.15	9.85	5.00	192.01	20.43	1.00	0.01
481.15	9.86	5.01	203.90	21.70	0.98	-0.04
518.15	9.88	5.05	218.41	23.24	0.95	-0.09
Cesium (Cs)						
308.15	10.43	6.27	110.31	11.74	1.09	0.29
349.15	10.40	6.20	126.11	13.42	1.04	0.11
395.15	10.37	6.13	143.98	15.32	0.99	-0.03
442.65	10.37	6.13	161.27	17.16	0.94	-0.12
480.65	10.38	6.15	174.58	18.58	0.91	-0.17
520.15	10.41	6.24	186.98	19.90	0.89	-0.21
Lead (Pb)						
673	6.29	0.83	1095.86	116.60	0.43	-1.34
873	6.00	0.69	1640.44	174.55	0.39	-1.17
973	5.89	0.64	1933.82	205.77	0.37	-1.10
Tin (Sn)						
673	10.71	6.99	222.22	23.64	0.50	-0.70
873	10.34	6.06	320.65	34.12	0.45	-0.61
973	10.13	5.59	380.00	40.43	0.43	-0.58

Table 2. Calculated values of B/A and P_{int} by using Hartmann & Ballou relations for high purity liquid alkali metals (viz. Na, K, Rb & Cs) at different temperatures.

metals (viz. Na, K, Rb & Cs) at different temperatures.				
T	B/A	P _{int}	B/A	P _{int}
K		Atm		atm
	Hartmann		Ballou	
Sodium (Na)				
373.15	5.89	0.840	4.27	1.099
423.15	5.92	0.813	4.31	1.061
473.15	5.97	0.778	4.37	1.011
494.15	6.00	0.763	4.40	0.990
518.15	6.01	0.753	4.42	0.976
Potassium (K)				
343.15	7.23	0.347	5.91	0.414
386.15	7.31	0.331	6.00	0.393
436.15	7.37	0.316	6.08	0.374
464.15	7.42	0.307	6.13	0.362
502.15	7.48	0.293	6.22	0.345
536.15	7.54	0.283	6.28	0.331
Rubidium (Ru)				
316.15	9.84	0.210	9.10	0.225
357.15	9.96	0.199	9.25	0.213
393.15	10.02	0.193	9.32	0.206
452.15	10.18	0.180	9.52	0.191
481.15	10.26	0.174	9.61	0.184
518.15	10.37	0.166	9.75	0.176
Cesium (Cs)				
308.15	11.99	0.134	11.73	0.137
349.15	12.13	0.128	11.91	0.130
395.15	12.26	0.122	12.06	0.123
442.65	12.43	0.115	12.27	0.116
480.65	12.56	0.109	12.43	0.110
520.15	12.73	0.103	12.64	0.104
Lead (Pb)				
673	15.84	0.308	16.44	0.298
873	15.15	0.349	15.60	0.340
973	14.86	0.367	15.25	0.358

CONCLUSIONS

The above studies conclude that the use of empirical relations to liquid alkali metals, using density and sonic speed data are in excellent agreement with the experimental values, indicating the validity of the applied equations. The non-linearity parameter (B/A) and internal pressure (P_{int}) calculated are in 100% agreement with the pre-established relations.

The above holds good, to serve our purpose to establish that metals in liquid state behave as perfect liquid. They show similar trend in properties and validate all the thermodynamic and interaction parameters to its completeness. It is thus helpful in predicting their behaviour about the interactions occurring in the liquid metals. These calculations can further help, in its use, in nuclear power station and industry where mixing of liquid metals to form alloys are in progress.

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NOMENCLATURE

u – sonic speed
T – temperature
 P_{int} – internal pressure
B/A – non-linearity parameter
V – molar volume
 V^E – excess molar volume
R – Rao number
W – Wada constant
 L_f – intermolecular free length

ABBREVIATION

Na – sodium
K – potassium
Rb – rubidium
Cs – cesium
Pb – lead
Sn – tin

GREEK LETTER

ρ – density
 α – thermal expansion coefficient
 β – isothermal compressibility
 σ – surface tension
 γ – specific heat ratio
 Γ – pseudo-Grüneisen parameter

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