A new equation of state for predicting the thermodynamic properties of liquid alkali metals

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Abstract

The density of liquid alkali metals in the extended ranges of temperature and pressure has been calculated using a new equation of state (EoS). A wide comparison with experimental data was made. The results show that the equation of state reproduces the experimental PVT data of liquid alkali metals within experimental errors throughout the liquid phase. The thermodynamic properties such as isobaric expansion coefficient, isothermal compressibility, and internal pressure have been calculated for these liquids using this EoS and compared with the corresponding experimental results. The generally excellent agreement with experimental data indicates that this EoS can be used to calculate the thermodynamic properties of liquid alkali metals with a high degree of certainty.
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1. Introduction

Alkali metals have a unique combination of physicochemical properties, such as extremely high electrical and thermal conductivities, small densities and viscosities, low melting temperatures and work functions, wide temperature ranges of a liquid state, large heat of evaporation, etc. Therefore, they are widely used in modern science and technology, for example, in nuclear energetic, emission electronics, new power-intensive chemical current sources, medicine, and other fields [1–5]. Liquid alkali metals act as coolant in nuclear power plants. The construction of high energy electrochemical cells as well as thermionic and magneto-hydrodynamic converters is only possible using these metals. They could be also more effectively used in extraction metallurgy, especially in that of some precious metals from their ores and wastes [6].

The reliable and consistent set of thermodynamic data for liquid alkali metals is of essential importance. This importance is based on their growing technical applications, due mainly to their specific advantages for high temperature applications. Although, the thermodynamic properties of liquid alkali metals are widely investigated, there are temperature regions where accurate information does not exist. The measurement of thermophysical properties of liquid alkali metals especially at high temperatures is very difficult since most liquid

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metals are reactive at high temperatures. Prediction of these properties using accurate equations of state appears at present to be the only alternative to the experimental difficulties associated with their measurements.

The purpose of this work is to report the results of simultaneous calculations of volumetric and thermodynamic properties such as isobaric expansion coefficient, α_P, isothermal compressibility, β_T, and internal pressure, p_i, for liquid alkali metals using a new EoS derived by Goharshadi-Morsali-Abbaspour 'GMA EoS' [7]. A wide comparison with experimental data was made. The accuracy of the equation of state in prediction of volumetric properties of liquid alkali metals has been determined by the statistical parameters, namely, the absolute

where A_0 to A_2 and B_0 to B_2 are constants. To use the equation of state for a liquid, the A and B parameters must be known. To find these parameters, we may plot (2Z-1) V_m^3 against ρ_m for different isotherms. The slope and intercept of the straight lines can be fitted to Eqs. (2) and (3) from which A_0 to A_2 and B_0 to B_2 can be found, respectively.

The functions used for calculating density, isobaric expansion coefficient, isothermal compressibility, and internal pressure using Eq. (1) are given as Eqs. (4)–(7), respectively. These equations have been used in calculating the tables of thermodynamic properties of liquid alkali metals. The constants A_0–A_2 and B_0–B_2 can be used to calculate these properties of liquid alkali metals at any temperature and pressure.

$$(B_0RT/2 - B_1 + TB_2 \ln T)\rho_m^5 + (A_0RT/2 - A_1 + A_2T \ln T)\rho_m^4 + \frac{\rho_m RT}{2} - p = 0, \tag{4}$$

$$\alpha_P = \frac{(2B_1 + 2B_2T)\rho_m^5 + (2A_1 + 2A_2T)\rho_m^4 + 2p}{5\rho_m^5(RT^2B_0 - 2B_1T + 2T^2B_2 \ln T) + 4\rho_m^4(A_0RT^2 - 2A_1T + 2A_2T^2 \ln T) + RT^2\rho_m}, \tag{5}$$

$$\beta_T = \frac{2}{\rho_m RT + 4\rho_m^4(RTA_0 - 2A_1 + 2TA_2 \ln T) + 5\rho_m^5(B_0RT - 2B_1 + 2B_2T \ln T)}, \tag{6}$$

$$p_i = (B_1 + B_2T)\rho_m^5 + (A_1 + A_2T)\rho_m^4. \tag{7}$$

average deviation (AAD), the average percentual deviation (bias), and the root mean-square deviation (RMSD).

2. Theoretical basis

A general equation of state for liquids has been recently derived by Goharshadi et al. [6] which has been found to be valid for polar, nonpolar, and hydrogen-bonded fluids. The equation of state is based on the average potential energy and that is

$$(2Z - 1)V_m^3 = A(T) + B(T)\rho_m, \tag{1}$$

where Z, V_m, and ρ_m are the compressibility factor, molar volume, and molar density, respectively. The intercept and the slope of this equation both depend on temperature via the equations

$$A(T) = A_0 - \frac{2A_1}{RT} + \frac{2A_2 \ln T}{R}, \tag{2}$$

$$B(T) = B_0 - \frac{2B_1}{RT} + \frac{2B_2 \ln T}{R}, \tag{3}$$

3. Results and discussion

We have used the experimental PVT data of liquid alkali metals [7] at various temperatures and pressures to examine the linearity of (2Z-1) V_m^3 versus ρ (Eq. (1)). Fig. 1 presents the isotherms of (2Z-1)
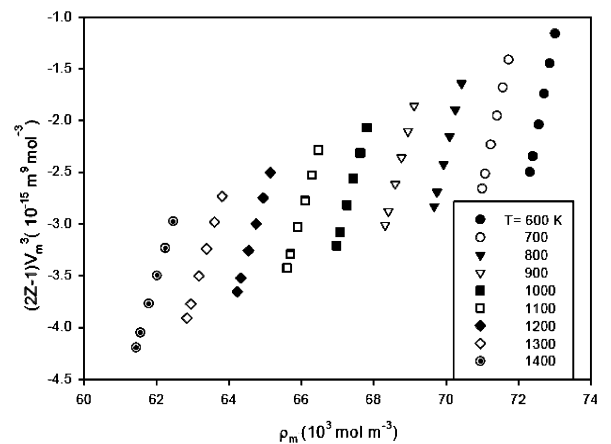

Fig. 1. The isotherms of (2Z-1) V_m^3 versus ρ_m for lithium [8].

V_m^3 versus density for lithium. As the figure shows the linearity holds very well and the slope and the intercept both depend on temperature. The results are summarized in Table 1, including the intercept and slope of the fitted straight line (Eq. (1)) at each temperature, the square of the correlation coefficient (R^2), and the pressure range of the experimental data of liquid alkali metals. Considering the values of R^2

of the different liquid alkali metals, it seems that this linearity is a universal feature for these liquids. Table 2 shows the values of the constants and the square of the correlation coefficients of Eqs. (2) and (3). The ranges of pressure and temperature of this table are the same as Table 1.

A more sensible test for the equation of state is to calculate density at different temperatures and pres-

Table 1
The intercept (A), slope (B), square of correlation coefficient (R^2) of Eq. (1), and pressure range of the data for liquid alkali metals

Substance	T (K)	B (10^{-12} m^{12} mol^{-4})	A (10^{-9} m^9 mol^{-3})	R^2	ΔP (MPa)
Li	600	1.89E−06	−1.39E−04	0.99998	10–100
	700	1.69E−06	−1.23E−04	0.99998	
	800	1.54E−06	−1.10E−04	0.99997	
	900	1.43E−06	−1.01E−04	0.99996	
	1000	1.35E−06	−9.36E−05	0.99996	
	1100	1.29E−06	−8.78E−05	0.99996	
	1200	1.24E−06	−8.31E−05	0.99994	
	1300	1.20E−06	−7.94E−05	0.99994	
	1400	1.18E−06	−7.65E−05	0.99993	
Na	500	2.56E−05	−1.01E−03	0.99992	10–100
	600	2.21E−05	−8.58E−04	0.99994	
	700	1.98E−05	−7.51E−04	0.99994	
	800	1.81E−05	−6.71E−04	0.99991	
	900	1.68E−05	−6.11E−04	0.99989	
	1000	1.59E−05	−5.65E−04	0.99985	
	1100	1.53E−05	−5.30E−04	0.99981	
	1200	1.48E−05	−5.03E−04	0.99973	
	1300	1.46E−05	−4.84E−04	0.99962	
K	500	3.22E−04	−6.62E−03	0.99995	20–100
	600	2.72E−04	−5.47E−03	0.99964	
	700	2.42E−04	−4.75E−03	0.99977	
	800	2.14E−04	−4.10E−03	0.99957	
	900	1.99E−04	−3.73E−03	0.99977	
	1000	1.87E−04	−3.41E−03	0.99904	
	1100	1.77E−04	−3.16E−03	0.99934	
	1200	1.70E−04	−2.95E−03	0.99864	
	1300	1.64E−04	−2.77E−03	0.99865	
Rb	500	6.79E−04	−1.14E−02	0.99981	20–100
	600	5.76E−04	−9.41E−03	0.99975	
	700	5.11E−04	−8.15E−03	0.99977	
	800	4.63E−04	−7.20E−03	0.99963	
	1000	3.97E−04	−5.85E−03	0.99891	
	1100	3.75E−04	−5.38E−03	0.99882	
	1200	3.61E−04	−5.02E−03	0.99868	
	1300	3.51E−04	−4.75E−03	0.99814	
Cs	600	1.30E−03	−1.68E−02	0.99985	40–100
	700	1.14E−03	−1.44E−02	0.99986	
	800	1.04E−03	−1.27E−02	0.99994	
	900	9.74E−04	−1.16E−02	0.99908	
	1000	9.01E−04	−1.04E−02	0.9995	
	1100	8.62E−04	−9.70E−03	0.99829	
	1200	8.18E−04	−8.93E−03	0.99747	
	1300	7.81E−04	−8.26E−03	0.9978	
	1400	7.54E−04	−7.72E−03	0.9959	

Table 2
The values of constants and the square of the correlation coefficients of Eqs. (2) and (3)

Substance	A_0 (L^3 mol^{-3})	A_1 (L^4 atm. mol^{-4})	A_2 (L^4 atm. mol^{-4} K^{-1})	R^2	B_0 (L^4 mol^{-4})	B_1 (L^5 atm. mol^{-5})	B_2 (L^5 atm. mol^{-5} K^{-1})	R^2
Li	0.00012631	0.00343973	−8.08E−07	0.999979	−3.06E−06	−4.82E−05	1.92E−08	0.999902
Na	0.0012153	0.0234072	−7.20E−06	0.999923	−5.12E−05	−6.14E−04	3.10E−07	0.999642
K	0.00843063	0.163989	−4.65E−05	0.999669	−5.95E−04	−7.95E−03	3.49E−06	0.999492
Rb	0.00926367	0.260934	−5.21E−05	0.999865	−9.57E−04	−1.55E−02	5.81E−06	0.999719
Cs	−0.0016183	0.383773	2.99E−06	0.999264	−1.02E−03	−2.96E−02	7.12E−06	0.998895

Table 3
The calculated thermodynamic properties and their percent deviations (dev%)[a] with corresponding experimental data for liquid lithium at various temperatures and pressures based on GMA EoS

T (K)	P (MPa)	$\rho_{m,calc}$ (10^3 mol m^{-3})	dev%	$\alpha_{P,calc} \times 10^4$ (K^{-1})	dev%	$\beta_{T,calc} \times 10^5$ (bar^{-1})	dev%	$p_{i,calc}$ (bar)	dev%
800	10	70.22	−0.79	1.903	0.83	1.253	−0.19	12004.967	1.37
	20	70.31	−0.80	1.895	0.84	1.244	−0.12	11993.445	0.96
	40	70.48	−0.79	1.880	0.79	1.214	0.99	11970.277	−0.04
	60	70.65	−0.78	1.864	0.85	1.184	2.12	11945.252	−0.98
	80	70.82	−0.80	1.849	0.86	1.165	2.46	11918.344	−1.90
	100	70.98	−0.78	1.836	0.76	1.135	3.74	11891.276	−2.93
1000	10	67.47	−0.75	2.065	−1.72	1.451	−1.38	14175.147	−0.63
	20	67.57	−0.76	2.054	−1.68	1.431	−0.78	14198.118	−1.23
	40	67.76	−0.74	2.035	−1.70	1.392	0.53	14240.792	−2.43
	60	67.95	−0.76	2.015	−1.66	1.352	1.88	14282.169	−3.62
	80	68.13	−0.74	1.997	−1.68	1.322	2.62	14320.149	−4.81
	100	68.31	−0.74	1.980	−1.75	1.293	3.37	14356.920	−6.00
1200	10	64.70	−0.73	2.109	2.18	1.678	−1.44	14955.096	3.78
	20	64.81	−0.75	2.096	2.19	1.658	−1.16	15007.584	3.11
	40	65.02	−0.74	2.072	2.22	1.599	0.69	15107.361	1.86
	60	65.23	−0.74	2.048	2.29	1.559	1.43	15206.557	0.60
	80	65.43	−0.74	2.027	2.27	1.510	2.96	15300.467	−0.70
	100	65.63	−0.74	2.006	2.29	1.471	3.89	15393.808	−1.93

[a] dev% $= \left(\frac{x_{exp}-x_{calc}}{x_{exp}}\right) \times 100$ (x is a thermodynamic property).

sures and compare with the corresponding experimental data. The density of liquid alkali metals in the wide ranges of temperature and pressure has been calculated using GMA EoS and the results for lithium are shown in Table 3.

The thermodynamic properties of liquid alkali metals such as isobaric expansion coefficient, isothermal compressibility, and internal pressure as a function of temperature and pressure have been calculated. Table 3 represents the results of these calculations for lithium. Fig. 2 presents the isotherms of the inverse of isobaric expansion coefficient versus pressure for rubidium.

The ability of this EoS in the prediction of density and thermodynamic properties at different temperatures and pressures for all liquid alkali metals may be evaluated by statistical parameters, namely
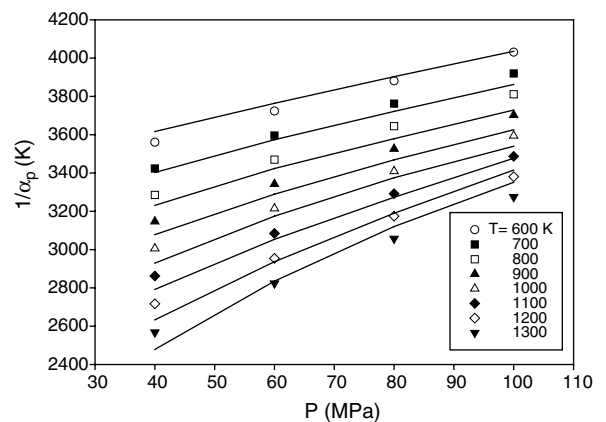

Fig. 2. The isotherms of the inverse of isobaric expansion coefficient versus pressure for rubidium. The solid lines show our calculated values and the symbols stand for experimental data [8].

Table 4
The statistical parameters of different calculated thermodynamic properties of liquid alkali metals

Substance	AAD[a]	bias[b]	RMSD[c]
Density			
Li	0.76	−0.76	0.77
Na	0.21	−0.20	0.27
K	0.15	0.02	0.19
Rb	0.49	−0.49	0.52
Cs	0.35	−0.35	0.37
Isobaric expansion coefficient			
Li	2.04	0.84	2.65
Na	2.47	−1.25	2.79
K	3.21	−1.12	3.44
Rb	2.71	0.78	3.26
Cs	1.99	0.61	2.45
Isothermal compressibility			
Li	1.82	1.20	2.19
Na	2.49	−1.00	2.99
K	2.85	−1.26	3.62
Rb	3.34	0.30	4.10
Cs	3.84	1.88	4.64
Internal pressure			
Li	2.67	−0.47	3.26
Na	2.90	−0.41	3.57
K	2.76	0.03	3.29
Rb	3.45	0.33	4.07
Cs	4.64	−1.82	5.99

[a] Absolute average deviation.
[b] Average percentual deviation.
[c] Root mean-square deviation.

the absolute average deviation (AAD), the average percentual deviation (bias), and the root mean-square deviation (RMSD) (Table 4). These parameters are defined as

$$AAD = \frac{1}{N} \sum_{i=1}^{N} 100 \left| \frac{\rho_{exp} - \rho_{cacl}}{\rho_{exp}} \right|, \tag{8}$$

$$bias = \frac{1}{N} \sum_{i=1}^{N} 100 \left(\frac{\rho_{exp} - \rho_{calc}}{\rho_{exp}} \right), \tag{9}$$

$$RMSD = \left\{ \frac{1}{N} \sum_{i=1}^{N} \left[100 \left(\frac{\rho_{exp} - \rho_{calc}}{\rho_{exp}} \right) \right]^2 \right\}^{0.5}. \tag{10}$$

The AAD characterizes that the experimental points are more or less close to calculated values. The bias characterizes the quality of the distribution of the experimental points on either side of the calculated data. The values of statistical parameters in Table 4 confirm the reliability of GMA EoS in predicting and reproducing the thermodynamic properties of liquid alkali metals. The ranges of temperature and pressure of this table are the same as Table 1.

To assess and compare the performance of GMA EoS with another EoS in prediction of density of

Table 5
The AAD values between experimental density data and those predicted using our work and another EoS

Substance	This work	Iglesias-Silva and Hall's work [9]
Li	0.76	0.77
Na	0.21	0.44
K	0.15	0.38
Rb	0.49	0.50
Cs	0.35	0.12

liquid alkali metals, the AAD values have been used (Table 5). Again, the lower AADs (except cesium) are obtained by GMA EoS supports the ability of this EoS in predicting the density of liquid alkali metals.

4. Conclusion

In the present paper, GMA EoS has been used to predict the different thermodynamic properties of liquid alkali metals. The generally excellent agreement with corresponding experimental data indicates that GMA EoS can be used to calculate the thermodynamic properties of liquid alkali metals with a high degree of certainty.

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