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Equation of state and artificial neural network to predict the thermodynamic properties of pure and mixture of liquid alkali metals

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ABSTRACT

A statistical mechanical equation of state is developed to predict the volumetric properties of pure and mixture liquid alkali metals at different temperatures, pressures and compositions. The temperature dependent parameters of the equation of state have been calculated using corresponding states correlation based on the normal boiling point parameters as scaling constants. It is shown that the knowledge of just normal boiling point and its liquid density are sufficient to estimate the thermodynamic properties of pure and mixture liquid alkali metals in different conditions. Besides, the performance of artificial neural network (ANN) based on back propagation training with 10 neurons in hidden layer for prediction of behavior of presented systems was investigated. A collection of 512 data points for above systems in different temperatures and pressures was used. The Tao–Mason equation of state (TM EOS) and ANN model results have good agreement with the experimental data with absolute average deviations of 0.74% and 0.299%, respectively.

1. Introduction

Metals, both in liquid and vapor states, have complex structures. They widely used in modern science and technology, including in nuclear energetic, emission electronics, new power-intensive chemical current sources, medicine and act as coolant in nuclear power plants [1,2]. They could be also more effectively used in extraction metallurgy, especially in that some precious metals from their ores and wastes [2]. These applications need the knowledge of high temperature properties of alkali metals because these metals are heated to high-temperatures in these applications [3]. The achievement of high temperature in real case is a difficult protocol and studying the theoretical treatment of metals is good choice to predict and correlate the high-temperature properties of liquid alkali metals. In these circumstances the development and application of novel modeling such as equation of state and artificial neural network to predict the thermodynamic properties of liquid alkali metals is great interest.

Liquid alkali metal and their alloys have been studied widely during the last decades by several researchers [4–11]. For example Eslami [7,8] applied the Ihm–Song–Mason (ISM) equation of state for pure alkali metals and their alloys using the corresponding states correlation based on heat of vaporization and the freezing point density. A perturbed hard sphere EOS has been developed for pure alkali metals by Maftoon-Azad et al. [9]. Six hundred and ninety four data points at different pressures and temperatures are examined and the average absolute deviation of predicted liquid density data compared to experiments is 1.41%. Besides, Mozaffari et al. [11] extended this equation of state to calculate the liquid density of alkali metal alloys over a wide range of temperature. Mousazadeh et al. [12] focused on application of perturbed-chain statistical associating fluid theory (PC-SAFT) for prediction of pure and mixtures alkali metal properties. It was found that the method efficiently is able to predict the density of binary and ternary alkali metal alloys of Cs–K, Na–K, Na–K–Cs, at various temperatures in the range of freezing point up to several hundred degrees above the boiling point. Besides, Moosavi and Sabzevari [13] extended a new equation of state (EOS) which reported for pure liquid alkali metals [14] to predict the density and other thermodynamic properties of binary molten alloys of Na–K and Cs–K in range of freezing point up to several hundred degrees above the boiling point using quadratic mixing rules along with the mean geometry approximation (MGA).

However different authors used different equations of state (EOS) and auxiliary methods to predict and reproduce the thermodynamic properties of these systems. Some of these attempts are restricted to the limited ranges of temperature and pressure

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and their results to predict the thermodynamic properties of these systems show different degrees of accuracy.

However, in spite of their applicability there are some limitations with these models due to using of many adjustable parameters or mixing rules that they sometimes need a sufficient amount of data for calibration and validation purposes that makes them computationally inefficient. In such cases, an artificial neural network (ANN) can be a suitable alternative to model the different thermodynamic properties. The relationship between the physical and thermodynamic properties is highly nonlinear, and an artificial neural network (ANN) is an especially efficient algorithm to approximate a certain function (such as density) by learning the relationships between the input and output vectors [15].

Accordingly, ANN method can be an alternative tool to model the different thermodynamic properties [16,17]. In the past decades, ANNs have been intensively used in various fields. The major reason for this rapid growth and diverse applications of neural networks is their ability to virtually approximate any function in a stable and efficient way.

In the previous studies, Tao–Mason equation of state TM EOS [18] has been successfully extended to fluid and fluid mixtures [19–22]. Besides, the applications of equation of state and artificial neural networks approaches [15,23] were studied to estimate the properties of pure polymers. Generally, ANN is powerful and successful method for complex non-linear systems due to unique advantages such as high speed, simplicity and large capacity which reduce engineering attempt. In recent years, ANN modeling has been successfully used for prediction of thermophysical properties of pure and mixture fluids [24–27].

This research focus on the capability of both TM EOS and ANN to estimate of thermodynamic properties of liquid alkali metals and their alloys in different temperatures, pressures and mole fractions. Finally, the efficiency of these approaches is compared with experimental data and other equations of state.

2. Theory

2.1. Tao–Mason equation of state

In most cases, the common equations of state are based on the van der Waals family of cubic equations, the extended family of virial equations, or equations based more closely on the results from statistical mechanics and computer simulations [28–30]. The TM EOS falls in the latter category. In 1994, Tao and Mason described a perturbation correction term which affect on the attractive forces and combined it with the ISM equation of state [31] to present an improved equation of state (TM EOS) [18]. The TM EOS for pure substances is as follow:

$$\frac{P}{\rho KT} = 1 + (B_2 - \alpha)\rho + \frac{\alpha\rho}{1-\lambda b\rho} + A_1(\alpha - B)b\rho^2\frac{(e^{\kappa T_C/T} - A_2)}{1 + 1.8(b\rho)^4} \quad (1)$$

where

$$A_1 = 0.143$$

$$A_2 = 1.64 + 2.65[e^{(\kappa - 1.093)} - 1]) \quad (2)$$

$$\kappa = 1.093 + 0.26[(\omega + 0.002)^{1/2} + 4.50(\omega + 0.002)] \quad (3)$$

where, ω is the Pitzer acentric factor, λ is an adjustable parameter, ρ is the number density, T_c is the critical temperature, kT has usual meaning, B_2 is the second virial coefficient, α is the scaling parameter, and b is the effective van der Waals co-volume.

The TM EOS requires the usage of the second virial coefficient, B_2, along with the parameters α, and b. It should be mentioned that if the intermolecular potential is not available, the knowledge of experimental second virial coefficient data is sufficient to calculate values of the other two temperature-dependent parameters [18]. In this case, there are several correlation scheme, usually based on the corresponding state principal that lead to the calculation of the second virial coefficient.

Tao and Mason formulated α, and b in terms of the Boyle temperature (T_B) and the Boyle volume (υ_B).

$$\frac{\alpha}{V_B} = a_1 e^{-c_1\left(\frac{T}{T_B}\right)} + a_2\left[1 - e^{-c_2/\left(\frac{T}{T_B}\right)^{1/4}}\right] \quad (4)$$

$$\frac{b}{V_B} = a_1\left[1 - c_1\left(\frac{T}{T_B}\right)\right]e^{-c_1\left(\frac{T}{T_B}\right)} + a_2\left\{1 - \left[1 + \frac{c_2}{4\left(\frac{T}{T_B}\right)^{1/4}}\right]e^{\frac{-c_2}{\left(\frac{T}{T_B}\right)^{1/4}}}\right\} \quad (5)$$

where the constant a_1, a_2, c_1, c_2 are −0.0648, 1.8067, 2.6038, 0.9726, respectively.

In the absence of sufficient experimental data, the B_2 values can be calculated from the Tsonopolous correlation [32].

$$B_2\left(\frac{P_C}{RT_C}\right) = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \quad (6)$$

$$f^{(0)}(T_r) = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} \quad (7)$$

$$f^{(1)}(T_r) = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8} \quad (8)$$

To achieve the higher accuracy, a corresponding state correlation was investigated in order to TM EOS could be applied to alkali metals and their alloys. In this respect, the following correlation equation for B_2 using new scaling parameters (such as temperature and molar density at the boiling point) has been developed. The resulting correlation for second virial coefficient is presented as follow:

$$B_2\rho_{bp} = 1.033 - 3.0069\left(\frac{T_{bp}}{T}\right) - 10.588\left(\frac{T_{bp}}{T}\right)^2 + 13.096\left(\frac{T_{bp}}{T}\right)^3 - 9.8968\left(\frac{T_{bp}}{T}\right)^4 \quad (9)$$

where ρ_{bp} and T_{bp} are density and temperature at boiling point.

Tao and Mason observation show that the dimensionless quantities α/υ_B and b/υ_B as almost universal functions of the reduced temperature (T/T_B) can be calculated from the exponential formulas based on a LJ(12-6) model potential [18]. At this point the scale factors (T_B and υ_B) are the Boyle temperature and Boyle volume, which can be expressed in terms of the boiling point parameters. The empirical equations given in Ref. [18] for α/υ_B and b/υ_B as a function of T/T_B can be rescaled by T_{bp} and ρ_{bp}, temperature and density in boiling point, instead of T_B and υ_B as Eslami [33].

$$\alpha\rho_{bp} = a_1 e^{-c_1\left(\frac{T}{T_{bp}}\right)} + a_2\left[1 - e^{-c_2/\left(\frac{T}{T_{bp}}\right)^{1/4}}\right] \quad (10)$$

$$b\rho_{bp} = a_1\left[1 - c_1\left(\frac{T}{T_{bp}}\right)\right]e^{-c_1\left(\frac{T}{T_{bp}}\right)} + a_2\left\{1 - \left[1 + \frac{c_2}{4\left(\frac{T}{T_{bp}}\right)^{1/4}}\right]e^{\frac{-c_2}{\left(\frac{T}{T_{bp}}\right)^{1/4}}}\right\} \quad (11)$$

where the constants a_1, a_2, c_1, c_2 are −0.0860, 2.3988, 0.5624, 1.4267, respectively. Therefore, known value of the boiling point