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Thermodynamic assessment of the K–Na and Cr–V system

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Abstract

The assessment of the thermodynamic properties of K–Na and Cr–V molten alloys has been theoretically examined using a simple statistical mechanical model based on pairwise interaction to obtain higher-order conditional probabilities that describe the occupation of the neighbouring atoms in molten binary alloys. The optimised values of order energy ω obtained are used to describe a number of thermodynamic quantities computed for different concentrations in the alloys at 384 and 1550 K, respectively. The study shows that there is a tendency for homocoordination (like atoms pairing as nearest neighbour) in K–Na and the existence of heterocoordination in Cr–V at all concentrations. Thus, the consistency between calculated and reported experimental thermodynamic values enforces the legitimacy of the findings.

Keywords: Order energy; Homocoordination; Conditional probabilities; Alkali metal

1. Introduction

There has been significant increase in experimentalists and theoreticians interest in understanding the thermodynamic properties of liquid alkali metal alloys due to their use as coolants in nuclear reactors. Some efforts to create the coolants with controlled properties has led to increase in attention to multicomponent liquid alkali metal alloys. A number of theoretical studies have been performed on various properties of metals in the liquid state [1–10] which has greatly improved the understanding of the thermodynamics of molten alloys containing strongly interacting metals. Advances in these studies has been made possible due to the combination of the following theoretical approaches such as electron theory [11], pseudopotential formalism [12] with thermodynamic perturbation theories.

In the present study, the assessment of the thermodynamic properties of K–Na an alkali metal alloy and Cr–V a transition molten alloy has been performed using a four atom cluster model (FACM) proposed by Singh [13] which is a simple statistical mechanical model based on pairwise interaction to obtain higher-order conditional probabilities that describe the occupation of the neighbouring atoms in molten binary alloys. The optimised values of order energy ω obtained are used to calculate a number of thermodynamic quantities for different concentrations of the alloys at different temperatures.

Apart from a high-academic interest, liquid K–Na and Cr–V alloys have been chosen for investigation because of their great commercial significance and the wide diversity of their physical and chemical properties. Besides, K and Na are alkali metals found in group 1A of the periodic table. Alloys of this group exhibit very fascinating properties in the liquid state. This group of metals are used primarily as a reducing agent in pharmaceutical, perfumery and general chemical industries. Due to excellent physical properties of alkali metals, mainly high-thermal conductivity coupled with low viscosity and low density, K–Na alloys are used in the heat-transfer systems as coolant in the valves of internal combustion engines and in nuclear reactors [14].

Chromium is alloyed (that is, mixed) with steel to make it corrosion resistant or harder. An example is its use in the production of stainless steel, a bright, shiny steel that is strong and resistant to oxidation (rust). It is also widely used in electroplating for appearance and wear in textile industries, in powder metallurgy, and to make X-ray

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targets and mirrors [15]. In addition, its component vanadium also has various industrial applications. It is used as an alloying element in different types of steel, where it increases strength and fatigue resistance. Aluminium is also alloyed with vanadium to produce master alloys, which are then added to titanium alloys used in jet engines, automotive industries and high-speed airframes [16,17]. Furthermore, vanadium is also used in speciality stainless steel for surgical instruments and high-speed tool steels. Vanadium foil is used as a bonding agent in binding titanium to steel and, because of its low fission neutron cross-section, vanadium also has nuclear applications. Vanadium pentoxide is used as a catalyst for the production of sulphuric acid by the contact process and for the production of maleic anhydride.

All mentioned above confirm that for a proper understanding of the thermodynamic properties of these alloys reliable and comprehensive information regarding the energetics of mixing in binary alloys through the study of microscopic functions such as concentration–concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$ and Warren–Cowley chemical short-range order parameter, (CSRO), α_1, [2,4,7,18] are essential.

In this study, a FACM based on pairwise interaction has been successfully used to compute the conditional probabilities enumerating the occupation of neighbouring sites by the atoms of the constituent elements in the liquid alloys. These are then utilised to compute the CSRO parameter, α_1 as a function of concentration. It has been shown that conditional probabilities is closely related to the activity through the order energy, ω. Thus, other thermodynamic quantities such $S_{cc}(0)$, free energy of mixing, chemical diffusion, heat of mixing and entropy of mixing are computed. The theoretical formalism of the FACM are discussed in Section 2, after which the results obtained are given in Section 3. In the final section, some concluding remarks are given.

2. Theoretical formalism

The grand partition function Ξ of a binary molten alloy AB, which consists of $N_A = Nc$ and $N_B = N(1-c)$ atoms of elements A and B, respectively, where the total number of atoms, N, is equal to $N_A + N_B$, can be expressed as

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T)\, e^{\beta(\mu_A N_A + \mu_B N_B - E)}, \quad \beta = \frac{1}{k_B T}, \tag{1}$$

where $q_i(T)$ are the particle functions of atoms i (A or B) associated with inner and vibrational degrees of freedom, μ_A and μ_B are the chemical potentials and E is the configurational energy. Solving Eq. (1), requires two simplifying assumptions [13], the first assumption requires that the interactions between atoms should be of short-range and effective only between nearest neighbours. The second assumption is that the atoms are located on lattice sites such that each site has Z-nearest neighbours. The lattice sites are further subdivided into smaller cluster of just a few lattice sites in domain 1 and the remainder in domain 2.

Arising from the above assumptions, one can define parameters P_{ij} and the ε_{ij}'s as the bond energies for ij nearest neighbour bond such that

$$P_{ij} = e^{-\beta\varepsilon_{ij}}, \quad (i,j = A,B). \tag{2}$$

The complete discussion of FACM are given in Ref. [13]. After doing some algebra [13], one obtains an expression of the form

$$\sigma^{12} - B_1\sigma^9 - B_2\sigma^6 - B_3\sigma^3 - B_4 = 0, \tag{3}$$

where

$$\sigma = \frac{\phi_B}{\phi_A}\left(\frac{P_{AA}}{P_{BB}}\right), \tag{4}$$

$$wB_1 = \frac{1-3x}{\eta^3}, \tag{5}$$

$$B_2 = 3x\frac{(1-x)}{\eta^4}, \tag{6}$$

$$B_3 = 3x^2\frac{(1-x/3)}{\eta^3}, \tag{7}$$

$$B_4 = x^3, \tag{8}$$

$$x = \frac{1-c}{c} \quad \text{and} \quad \eta = \exp\left(\frac{\beta\omega}{Z}\right), \tag{9}$$

$w = Z(\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2)$ is the interatomic interaction energy, usually termed the order energy in regular solution theory and the parameter ϕ in Eq. (4) is a constant which has to be eliminated in the final result.

The activity ratio a defined as ($a = a_B/a_A$) is related to σ by the expression given as

$$cf_1(a,\sigma) = (1-c)f_2(a,\sigma), \tag{10}$$

where $f_1(a,\sigma)$ and $f_2(a,\sigma)$ are defined as

$$f_1(a,\sigma) = a^4\sigma^{4ZL} + \frac{3a^3\sigma^{3ZL}}{\eta^3} + \frac{3a^2\sigma^{2ZL}}{\eta^4} + \frac{a\sigma^{ZL}}{\eta^3} \tag{11}$$

and

$$f_2(a,\sigma) = \frac{a^3\sigma^{3ZL}}{\eta^3} + \frac{3a^2\sigma^{2ZL}}{\eta^4} + \frac{3a\sigma^{ZL}}{\eta^3} + 1 \tag{12}$$

here $ZL = Z - 3$ in Eqs. (11) and (12), Eq. (12) is solved numerically to determine the activity ratio for a given binary alloy from the knowledge of σ obtained from the numerical solution of Eq. (3). The value of σ required in the calculations is optimised in such a way that it gives a good overall representation of activity at all concentrations [19].

The main objective of the FACM is to express the degree of CSRO in terms of probabilities. To achieve this, one observes that in the framework of the model, the probability of finding an A atom or B atom on any lattice site depends on the nature of atoms already existing in the