

## Temperature dependence of chemical order in liquid Al-Si binary alloys

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### Abstract

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*The concentration-concentration fluctuations in long wavelength limits,  $S_{cc}(0)$  have been computed from experimental data of free energy of mixing ( $G_M/RT$ ) of pure Al and Si components in molten Al-Si alloys at 2000 K, 2400 K and 2473 K, respectively on the basis of a statistical thermodynamic theory within the framework of the quasi-chemical approximation model (QCAM). The  $S_{cc}(0)$  is used to obtain Warren-Cowley short range order parameter ( $\alpha_1$ ) and ratio of mutual and intrinsic diffusion coefficients ( $D_M/D_{id}$ ) for this alloy. Analysis of the result shows that the presence of chemical order leading to complex formation is predominant in liquid Al-Si alloys across the whole concentration range. The atomic interaction between components decreases as temperature increases.*

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**Keywords:** Chemical order, Al-Si, Interchange energy, Chemical complexes

### 1.0 Introduction

The knowledge of thermodynamic properties of liquid alloys is useful in the design and development of reliable materials for high temperature applications. The properties of alloys in the melt often play a prominent role in the understanding of the alloying behaviour in the respective solid states. Thus the determination of thermodynamic functions for alloys in liquid state has been the subjects of active research in recent years. In this regard, a number of compound forming models [1-10] have been proposed to explain the alloying behaviour of molten binary alloys. All the theoretical models led to the fact that interatomic interaction plays a significant role in compound formation. Owing to the presence of strong interatomic interaction, liquid alloys for intermetallic compounds at one or more stoichiometric composition which is often manifested in the phase diagrams [6].

The formation of compound in solid state led many researchers to believe in the existence of chemical complexes, pseudomolecules and privileged group of atoms near the melting temperature in binary liquid alloys. Many theoretical models [4-8] based on the above assumptions have been used to investigate the alloying behaviour of such type of binary liquid alloys. The microscopic properties such as [ $S_{cc}(0)$ ,  $\alpha_1$ ] show maximum deviation from ideal mixture behaviour around compound forming concentration and  $\alpha_1$  has large negative values suggesting chemical order essential for compound formation.

Our interest in Al-Si was aroused by the recently published thermodynamic data for liquid Al-Si alloys obtained using FactSage Thermo-Chemical Software and Databases by Kostov and co-workers [11]. It is therefore quite interesting to investigate the impact of temperature on the intermetallic associates in Al-Si alloys using statistical mechanical model with a view to elucidate the energetic of the alloy formation for the following noteworthy reasons: Firstly, it was observed that thermodynamical study of Al-Si alloys have not been completely reported in literature due to none availability of adequate experimental data. Secondly, the FactSage method [12,13] have been employed by some theoreticians to make thermodynamic predictions of binary liquid alloys such as Ti-Al and Ti-V based alloys and thirdly, we desire to show that useful theoretical thermodynamic information could be deduced from thermodynamic data obtain using FactSage Thermo-Chemical Software and databases for binary liquid alloys as earlier reported in one of the authors earlier work on Si-Ti [14] and therefore, further establishes the suitability of data obtained via FactSage Software for probable comparison with some future critical experimental works.

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In this study, Quasi-Chemical Approximation Model (QCAM) which is an extension of the Bhatia and Hargrove formalism [1] has been chosen to study the temperature dependence of chemical ordering phenomenon and formation of complexes in liquid Al-Si alloys at three different temperatures for which experimental data exist. Aluminum and silicon have various important applications in industries. Aluminum is used for manufacturing overhead cables, roofing sheets, paints and cooking utensils and even in airplanes in which we travel [14,15]. Silicon is used in manufacturing of semiconductor devices and is also used as substrates in thin film technology. As a matter of fact, Al-Si binary alloys have wide applications in diverse fields of science and engineering especially in metallurgy, automotive and aerospace industries [11]. Some other important applications of silicon have been reported in [14].

Theoretical basis of the QCAM is given in section 2, section 3 deals with the numerical results and discussion. Conclusion is provided in section 4.

## 2.0 Theoretical BASIS OF QCAM

The grand partition function  $\Xi$  of a binary molten alloy A-B consisting 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:

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \exp[\mu_A N_A - \mu_B N_B - E] / k_B T \quad (1)$$

where  $q_i^N(T)$  and  $\mu_i$  are atomic partition function and chemical potential of  $i^{th}$  components ( $i = A, B$ ),  $k_B$  is Boltzmann's constant, T is the absolute temperature and E is the configurational energy of the alloy.

After doing some algebra simplification [16], the solution of equation (1) is given as the ratio of the activity coefficient  $\gamma$  ( $\gamma = \gamma_A/\gamma_B$ ) for the compound ( $A_\mu B_\nu$ ) forming alloys as:

$$\ln \gamma = \frac{Z(1-c)}{2c} \cdot \frac{(\beta + 2c - 1)}{(\beta - 2c + 1)} \quad (2)$$

with

$$\beta = \{1 + 4c(1-c)(\eta^2 - 1)\}^{1/2} \quad (3)$$

where

$$\eta^2 = \exp\left(\frac{2\omega}{zk_B T}\right) \exp\left(\frac{2P_{AB}\Delta\epsilon_{AB} - P_{AA}\Delta\epsilon_{AA} - P_{BB}\Delta\epsilon_{BB}}{k_B T}\right) \quad (4)$$

Here Z is the coordination number, R is the universal gas constant and  $\omega$  is the interchange or ordered energy given by

$$\omega = Z[\Delta\epsilon_{AB} - \frac{1}{2}(\Delta\epsilon_{AA} + \Delta\epsilon_{BB})] \quad (5)$$

$\Delta\epsilon_{AB}$ ,  $\Delta\epsilon_{AA}$ ,  $\Delta\epsilon_{BB}$  are the interaction parameters and  $\Delta\epsilon_{ij}$  is the change in the energy of the  $ij$  bond in the complex  $A_\mu B_\nu$ ,  $P_{ij}$  is the probability that  $ij$  bond is a part of the complex.  $P_{ij}$  may be expressed as

$$P_{AB} = c^{\mu-1}(1-c)^{\nu-1}[2 - c^{\mu-1}(1-c)^{\nu-1}] \quad (6)$$

$$P_{AA} = c^{\mu-2}(1-c)^\nu[2 - c^{\mu-2}(1-c)^\nu], \mu \geq 2 \quad (7)$$

$$P_{BB} = c^\mu(1-c)^{\nu-2}[2 - c^\mu(1-c)^{\nu-2}], \nu \geq 2 \quad (8)$$

c is the concentration of atom A.

The excess Gibbs free energy of mixing  $G_M^{XS}$  is obtained from equation (2) using standard thermodynamic relations [17]

as:

$$G_M^{XS} = G_M - RT\{c \ln c + c(1-c) \ln(1-c)\} \quad (9)$$

with  $G_M$  being the free energy of mixing.

$$\frac{G_M^{XS}}{RT} = z \int_0^c [\ln \sigma + (2k_B T)^{-1}(P_{AA}\Delta\epsilon_{AA} - P_{BB}\Delta\epsilon_{BB})] dx + \phi \quad (10)$$

and

$$\ln \sigma = \frac{1}{2} \ln \frac{(1-c)(\beta + 2c - 1)}{c(\beta - 2c + 1)} \quad (11)$$

The constant term  $\phi$  in equation (10) is determined from the requirement that  $G_M^{XS} = 0$  at  $c = 0$  and  $c = 1$ . One observes that for  $\Delta c_{ij} = 0$ , the expression reduces to the regular solution expression [10] and [16].

The concentration-concentration fluctuations in the long-wavelength limit,  $S_{cc}(0)$ , has emerged as one of the most important microscopic functions for understanding the mixing behaviour of liquid alloys in terms of compound formation and phase segregation [17]. The  $S_{cc}(0)$  can be expressed in terms of  $G_M$  as:

$$S_{cc}(0) = RT \left( \frac{\partial^2 G_M}{\partial c_A^2} \right)_{T,P,N}^{-1} \tag{12}$$

For ideal mixing the energy parameters,  $\omega$ , given in equation (5) is equal to zero, and equation (12) becomes:

$$S_{cc}^{id}(0) = c_A c_B \tag{13}$$

Substituting eqn.(9) for  $G_M$  into eqn.(12), we have

$$S_{cc}(0) = \frac{c(1-c)}{1 + \frac{z}{2} \left( \frac{1}{\beta} - 1 \right)} \tag{14}$$

Equation (12) is usually utilized to obtain the experimental values of  $S_{cc}(0)$  from the measured activity or the free energy of mixing data [4,18,19]. The mixing behavior of liquid binary alloys can be inferred from the deviation of  $S_{cc}(0)$  from  $S_{cc}^{id}(0)$ .

The presence of chemical order is indicated by  $S_{cc}(0) < S_{cc}^{id}(0)$ ; on the contrary, if  $S_{cc}(0) > S_{cc}^{id}(0)$ , the segregation and demixing in liquid alloy take place.

The Warren-Cowley short-range order parameter,  $\alpha_1$  [19-21] is computed to quantify the degree of order in the molten alloys. This parameter  $\alpha_1$  is expressed in term of  $\beta$ -function (equation (5)), as

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \tag{15}$$

The mixing behaviour of two molten metals forming alloys at the microscopic scale can further be analyzed in terms of the chemical diffusion. The formalism that relates diffusion and  $S_{cc}(0)$  combines the Darken's thermodynamic equation for diffusion with the basic thermodynamic equations in the form [22]:

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \tag{16}$$

where  $D_M$  is the mutual diffusion coefficient and  $D_{id}$  is the intrinsic diffusion coefficient for an ideal mixture, given as:

$$D_{id} = c_A D_A + c_B D_B \tag{17}$$

with  $D_A$  and  $D_B$  being the self-diffusion coefficient of pure components A and B, respectively. From the above equations it is quite clear that in the case of ideal mixing,  $S_{cc}(0) \rightarrow S_{cc}^{id}(0)$ , i.e.  $D_M D_s^{-1} \rightarrow 1$ . The presence of chemical order is indicated

by  $D_M D_s^{-1} > 1$  as  $S_{cc}(0) < S_{cc}^{id}(0)$ . Likewise,  $D_M D_s^{-1} < 1$  suggests the tendency for self-coordination, leading to phase segregation.

### 3.0 Results and Discussion

Numerical computations of the Gibbs free energy of mixing  $G_M$ , concentration-concentration fluctuations in the long-wavelength limits  $S_{cc}(0)$ , chemical short range order parameter,  $\alpha_1$  and chemical diffusion have been performed based on the theory presented in section 2. Equation (12) was used to obtain experimental  $S_{cc}(0)$  from measured free energy of mixing data which were taken from [11]. The values of the fitted interaction energy parameters  $\omega$  and other quantities required in the model calculations of the various thermodynamic properties are presented in Table 1.

Using equation (9), the interaction energy parameters  $\omega$  which reproduce as closely as possible the experimentally measured concentration dependence Gibbs free energy of mixing for liquid Al-Si alloys at 2000 K, 2400 K and 2473 K, respectively, have been computed based on the available experimental data on the thermodynamic properties as well as the phase diagram information on probable existence of intermetallic compounds in liquid Al-Si alloys. Figure 1 shows the plot of the concentration dependence free energy of mixing for liquid Al-Si alloys at different temperatures. From the figure, it is

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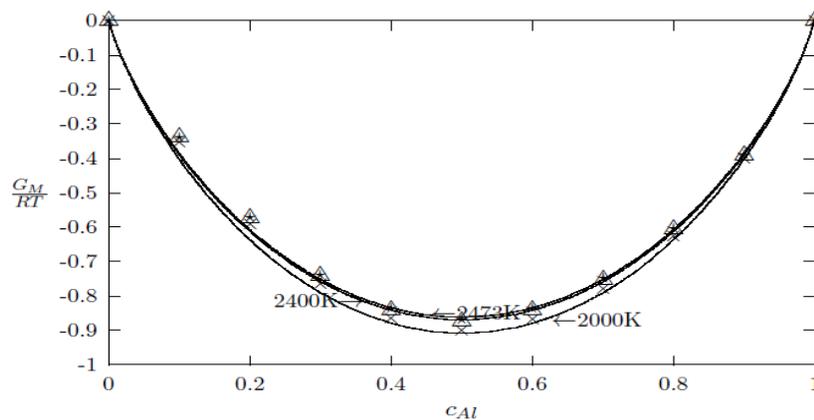
seen that the interaction parameters give a good representation of the experimental free energy of mixing for the alloys at respectively temperatures. A comparison of the curves describing liquid Al-Si alloy reveals that the Gibbs free energy of mixing are negative and almost symmetric around the equiatomic composition  $c_{Al} = 0.5$  (typical of ordered alloy) over the whole concentration range, with Al-Si at 2000 K ( $G_M)_{min} = -0.899RT$  exhibiting the highest tendency for compound formation and is the most interacting at this temperature. Whereas Al-Si at 2400 K, which has  $(G_M)_{min} = -0.871RT$  is more interacting than Al-Si alloy at 2473 K with minimum  $G_M$  value of  $-0.867RT$  at  $c_{Al} = 0.5$ . An indication that the degree of atomic interaction decreases in liquid Al-Si alloys with increasing temperature. From the fitted interaction energy parameters (Table 1), one can see that the interchange energies are all negative which point to the attractive nature of the atomic interaction between corresponding species in the liquid Al-Si alloys [23]. The computed values of activity ratio not given here could not be compared for lack of experimental data on activity at investigated temperatures.

From proper analysis of the nature of ordering in a binary liquid alloys, the first quantity investigated is the concentration-concentration fluctuations in the long-wavelength limit  $S_{cc}(0)$ . The deviation of the  $S_{cc}(0)$  from the ideal  $S_{cc}^{id}(0)$  is an essential parameter in order to visualize the nature of ordering in liquid alloy. Equation (12) can be used directly to obtain  $S_{cc}(0)$  from the experimental free energy of mixing data. Such  $S_{cc}(0)$  are usually termed experimental values in literature [19]. Experimental  $S_{cc}(0)$  used in the present calculations for Al-Si alloys were obtained from equation (12) using the Gibbs free energy of mixing data from [11], while calculated  $S_{cc}(0)$  was obtained from equation (14) and the ideal  $S_{cc}^{id}(0)$  were calculated from equation (13). The computed values of  $S_{cc}(0)$  using Eq. (14) are depicted in Fig. 2 together with experimental and ideal ( $S_{cc}^{id}(0) = c_A c_B$ ) values for liquid Al-Si alloys at respective temperatures. From the figures, it is seen that both the calculated  $S_{cc}(0)$  and experimental values are in reasonable agreement, expect a slight inconsistency between  $0.3 < c_{Al} > 0.6$  with the calculated  $S_{cc}(0)$  less than ideal  $S_{cc}^{id}(0)$  for the alloys across the concentration range indicating the preference for unlike atoms to pair as nearest neighbours (i.e. heterocoordination) in liquid Al-Si alloys.

The computed values of the chemical short range order parameter  $\alpha_1$  through Eq. (15) are shown in Fig. 3. It is to be noted that  $\alpha_1 > 0$  refers to like atoms pairing,  $\alpha_1 = 0$  indicates a random distribution, and  $\alpha_1 < 0$  corresponds to unlike atoms pairing as nearest neighbours. The computed values of this parameter at the different temperatures are shown in Fig. 3. The negative values of  $\alpha_1$  throughout the whole concentration range and temperatures suggest the presence of chemical order. This further indicates that Al-Si binary liquid alloy is an ordered alloy. In addition, the plot of  $\alpha_1$  vs.  $c_{Al}$  becomes shallow with the increase of temperature as can be observed from Fig. 3, indicating a lower degree of association or compound formation with increase in temperature.

**Table 1:** Values of fitted interaction parameters for liquid Al-Si alloys.

Alloys	T(K)	Z	$\omega(eV)$
Al-Si	2000	10	-0.145
Al-Si	2400	10	-0.143
Al-Si	2473	10	-0.141



**Figure 1:** Concentration dependence of free energy of mixing:  $G_M / RT$  for liquid Al-Si alloy at 2000 K, 2400 K and 2473 K, respectively. The solid line denotes theoretical values while the times, triangles and stars denote experimental data for Al-Si at 2000 K, 2400 K and 2473 K, respectively.  $c_{Al}$  is the concentration of Al in the alloy. The experimental data were taken from [11].

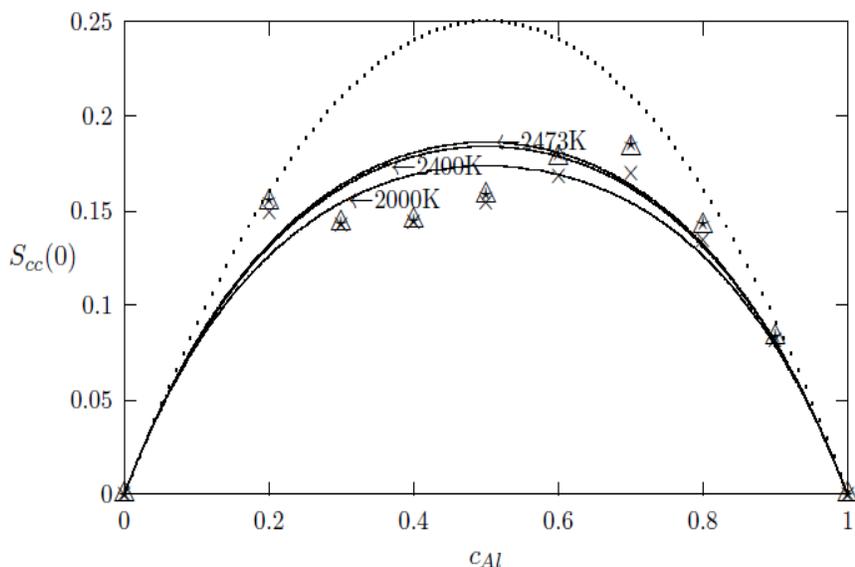


Figure 2: Concentration-concentration fluctuations in the long wavelength limit  $S_{cc}(0)$  and  $S_{cc}^{id}(0)$  versus concentration for liquid Al-Si alloys at 2000 K, 2400 K and 2473 K, respectively. The solid line denotes theoretical values while the times, triangles and stars denote experimental data at 2000 K, 2400 K and 2473 K, respectively. The dot denotes the ideal values  $S_{cc}^{id}(0) \cdot c_{Al}$  is the concentration of Al in the alloys.

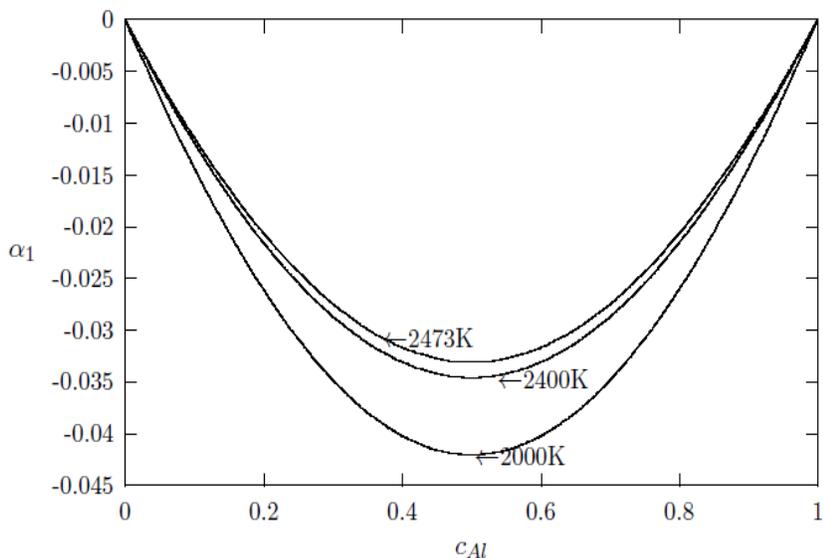


Figure 3: Calculated Warren-Cowley short range order parameter  $\alpha_1$  versus concentration using (15) for liquid Al-Si alloy at 2000 K, 2400 K and 2473 K, respectively.  $c_{Al}$  is the concentration of Al in the alloy.

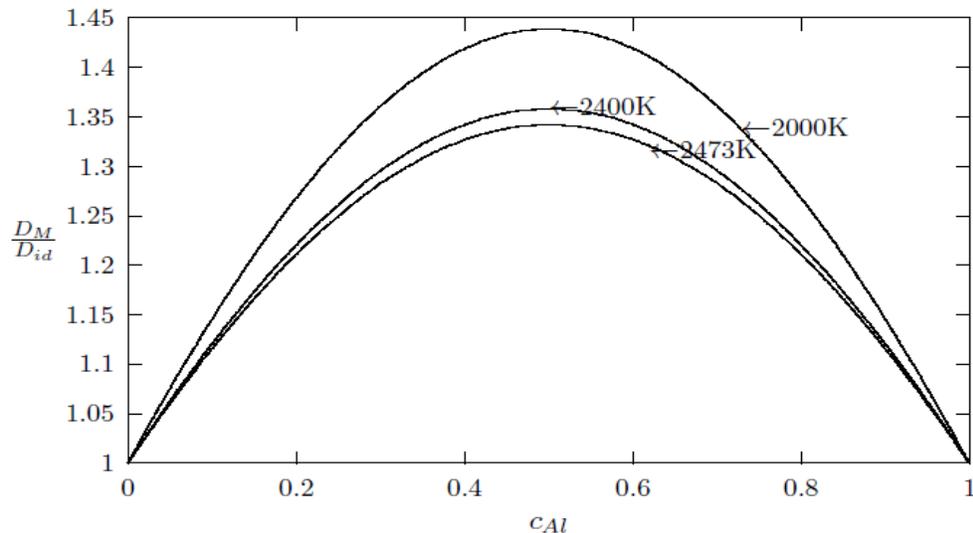


Figure 4: Computed values of the diffusion coefficient using Eq. (16) for liquid Al-Si alloys at 2000 K, 2400 K and 2473 K, respectively.  $c_{Al}$  is the concentration of Al in the alloy.

#### 4.0 Concluding Remarks

The QCAM has been used to investigate the thermodynamic properties of Al-Si binary liquid alloys using the experimental Gibbs free energies of mixing of all phases of the Al-Si alloys at temperatures of 2000 K, 2400 K and 2473K obtained by Kostov and coworkers [11] employing FactSage Thermo-Chemical Software and Databases. From the results presented it is clear that Al-Si alloys exhibit weak negative deviations from the ideal mixture behaviour. The study of  $S_{cc}(0)_{Al}$  and  $D_M/D_{id}$  evidently suggest a conspicuous tendency towards heterocoordination in Al-Si alloys which is not as strong as heterocoordination observed in system such as Si-Ti [14]. One also observed that the tendency for intermetallic associations, which leads to the formation of a chemical compounds, decreases with the increasing temperature. Furthermore, this study has affirmed that experimental data obtained from FactSage Software and Databases could be used to extract useful theoretical thermodynamic information from binary liquid alloys and could as well serve as a basis for comparison with future critical experimental results.

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