Vol. 9, No. 1, 2023 (May) 66-74

The Journal of Knowledge and Innovation

Journal homepage: https://www.nepjol.info/index.php/JKI

Publisher: Research Management Cell , Mahendra Morang A. M. Campus (Tribhuvan University) Biratnagar

Assessment of Thermodynamic and Structural Properties of Al–Er liquid Alloy at Different Temperatures

Shashit Kumar Yadav*

Department of Physics, Mahendra Morang Adarsh Multiple Campus Biratnagar, Nepal.

*Corresponding author. Email: sashit.yadav@mmamc.tu.edu.np

Abstract

Theoretical expressions of quasi–lattice model were used to assess the thermodynamic and structural properties of Al–Er liquid alloy at different temperatures. The model fit parameters were optimised using the available literature data of the thermodynamic properties for the system at 1873 K. The computed values of thermodynamic properties such as excess Gibbs free energy of mixing, enthalpy of mixing, entropy of mixing and activities of Er and Al using the model fit parameters were found to be consistent with the reference data–set. Therefore, the same parameters were used to compute the structural properties such as concentration fluctuation in long wavelength limit, Warren–Cowley short range–order parameter and ratio of mutual to intrinsic diffusion coefficients. Assuming the model fit parameters to be linear temperature–dependent, the above mentioned properties were also assessed in the temperature range 1873–2173 K. The compound forming tendency of the system was found to decrease gradually with increase in temperature.

Keywords

Redlich-Kister polynomial, least square fitting, ordering nature, random mixing.

Article information

Manuscript received: March 10, 2023; Accepted: May 4, 2023

DOI https://doi.org/10.3126/jki.v9i1.54633

1 Introduction

Erbium (Er) falls under the group of rare earth metals or lanthanides with high melting points, high vapor pressure at the melting point and mid-to-low boiling points. It has multi-disciplinary applications, including glass coloring purposes, especially in eyeware and decorative glassware, and as an amplifier in fiber optics for data transfer [1–3]. The mechanical strengths of the rare earth metals varies between aluminum (Al) and titanium (Ti) [4]. Increased mechanical qualities of the materials, such as tensile strength, heat, corrosion and vibration resistances, and extrudability can be achieved by alloying Er with Al [4, 5]. In this regard, the energetic of the Al–Er binary liquid alloys have been studied by several researchers [1, 5–11].

The study of phase diagram showed the existence of Er_2Al, Er_3Al, Er_3Al_2, $ErAl$ and $ErAl_3$ complexes in the system [1, 5, 8]. Literature review shows that only a few works have been carried out to assess the thermodynamic properties of Al–Er binary liquid alloy. The self-consistent parameters for the excess Gibbs free energy of mixing (ΔG_M^{xs}) for the system was optimised by Cacciamani et al. [8] using sub-lattice model. Later, Jin et al. [5] used FactSage computer software coupled with ab-initio data and available experimental data to compute the enthalpy of mixing (ΔH_M) and entropy of mixing (ΔS_M) of the system at 1873 K. Their results greatly deviated with the values computed using the parameters of Ref. [8]. Recently, Xu et al. [11] assessed the phase quilibria and thermodynamics of the system using experimental measurements and CALPHAD software. Thus, it can be concluded that the Al-Er system has drawn the considerable consent of researchers working in this field for decades.

Therefore, an attempt has been made in the present work to assess the thermodynamic and structural properties of the Al–Er system at different temperatures. In thermodynamic properties, excess Gibbs free energy of mixing (ΔG_M^{xs}), enthalpy of mixing (ΔH_M), excess entropy of mixing (ΔS_M^{xs}) and activities of components Al (a_{Al}) and Er (a_{Er}) were computed at 1873 K in the framework of quasi–lattice model [12–14]. Modeling equations of the same model were also used to compute the structural properties such as concentration fluctuation in long wavelength limit ($S_{CC}(0)$), Warren–Cowley short range–order parameter (α_1) and ratio of mutual to intrinsic diffusion coefficients (D_M/D_{id}). The interaction parameters for ΔG_M^{xs} were assumed to be linear temperature–dependent (T–dependent) with the aid of which above mentioned properties were computed in the temperature range 1873–2173 K.

The modeling equations required for the study are presented in the Section 2, results and discussion are presented in the Section 3 and conclusions of the work are highlighted in the Section 4.

2 Formulations

2.1 Quasi–lattice model

Consider one mole of a metallic solution consisting Er (=A) and Al (=B) atoms at constant pressure. Let x_1 (= x_{Er}) and x_2 (= x_{Al}) are the mole fractions of Er and Al respectively in the solution such that $x_1+x_2=1$. The present model is a compound forming in which the expressions for the thermodynamic and structural functions are derived assuming the existence of complex $A_\mu B_\nu$, where μ and ν have small values. Their values are determined from the phase diagram of the system corresponding to the stiochiometric compositions at which stable phases exist. In present case, the complex Er_2Al ($\mu = 2$ and $\nu = 1$) has been assumed to be energetically favoured [1,5,8]. In this regard, the expression for excess Gibbs free energy of mixing ΔG_M^{xs} can be given as [12–14]

$$\Delta G_M^{xs} = N[\Phi\omega + \Phi_{AB}\omega_{AB} + \Phi_{AA}\omega_{AA} + \Phi_{BB}\omega_{BB}] \tag{1}$$

where ω, ω_{AB}, ω_{AA} and ω_{BB} are the interaction energy parameters, also called model parameters. They are assumed to be T–dependent but concentration independent. Φ, Φ_{AB}, Φ_{AA} and Φ_{BB} are the simple polynomials in x_1 and $x_2 = 1 - x_1$, and for the complex of type $A_\mu B_\nu$ having $\nu = 1$, $\Phi_{BB} = 0$. These polynomials for the condition sated above are expressed as

$$\begin{aligned} \Phi &= x_1(1-x_1) \\ \Phi_{AB} &= \frac{x_1}{6} + x_1^2 - \frac{5x_1^3}{3} + \frac{x_1^4}{2} \\ \Phi_{AA} &= -\frac{x_1}{4} + \frac{x_1^2}{2} - \frac{x_1^4}{4} \end{aligned} \tag{2}$$

ΔG_M^{xs} can be expressed in terms of Gibbs free energy of mixing (ΔG_M) as

$$\Delta G_M = \Delta G_M^{xs} + RT[x_1 \ln x_1 + x_2 \ln x_2] \tag{3}$$

where R is the real gas constant and T is the absolute temperature. The excess entropy of mixing (S_M^{xs}) is related to ΔG_M^{xs} as

$$\Delta S_M^{xs} = -\left(\frac{\partial \Delta G_M^{xs}}{\partial T}\right)_P \tag{4}$$

From Equations (1) and (4), one can obtain

$$\Delta S_M^{xs} = -N\left[\frac{\partial \Delta\omega}{\partial T}\Phi + \frac{\partial \Delta\omega_{AB}}{\partial T}\Phi_{AB} + \frac{\partial \Delta\omega_{AA}}{\partial T}\Phi_{AA}\right] \tag{5}$$

Herein, $\frac{\partial \Delta\omega}{\partial T}, \frac{\partial \Delta\omega_{AB}}{\partial T}$ and $\frac{\partial \Delta\omega_{AA}}{\partial T}\Phi_{AA}$ are the temperature derivative terms of interaction energy parameters.

The enthalpy of mixing (ΔH_M) can be related to ΔG_M^{xs} and ΔS_M^{xs} by the well known thermodynamic expression as

$$\Delta H_M = \Delta G_M^{xs} + T\Delta S_M^{xs} \tag{6}$$

Using Equation (4) in Equation (6), yields

$$\Delta H_M = \Delta G_M^{xs} - T\left(\frac{\partial \Delta G_M^{xs}}{\partial T}\right)_P \tag{7}$$

The activity of component i (a_i; $i = Er, Al$) in the binary solution can be expressed in terms of ΔG_M as

$$RT \ln a_i = \Delta G_M + (1 - x_i)\left(\frac{\partial \Delta G_M}{\partial x_i}\right)_{T,P,N} \tag{8}$$

Using Equations (1) and (3) in Equation (8), one can obtain the expression for $\left(\frac{\partial \Delta G_M}{\partial x_i}\right)_{T,P,N}$ as

$$\left(\frac{\partial \Delta G_M}{\partial x_i}\right)_{T,P,N} = \Delta\omega\Phi^{'} + \Delta\omega_{AB}\Phi_{AB}{'} + \Delta\omega_{AA}\Phi^{'}_{AA} + \ln\left(\frac{x_i}{1-x_i}\right) \tag{9}$$

where $\Phi^{'}$ and $\Phi^{'}_{ij}$ are the first order derivatives of respective parameters (in Equation (2)) with respect to concentration of i^{th} element.

To study and understand the arrangement of atoms at atomic level in the initial melt, the structural functions have become an essential tool. Among them, the expression for concentration fluctuation in long wavelength limit ($S_{CC}(0)$) is expressed as [15–18]

$$S_{CC}(0) = RT\left(\frac{\partial^2 G_M}{\partial x_1^2}\right)^{-1}_{T,P,N} = RT\left(\frac{\partial^2 G_M}{\partial x_2^2}\right)^{-1}_{T,P,N} \tag{10}$$

Using Equations (1) and (3) in Equation (10), yields

$$S_{CC}(0) = x_1x_2[1 + x_1x_2RT(\Delta\omega\Phi'' + \Delta\omega_{AB}\Phi^{''}_{AB} + \Delta\omega_{AA}\Phi^{''}_{AA})]^{-1} \tag{11}$$

Herein, Phi'' and Phi_{ij}'' are the second order derivatives of respective parameters with respect to concentration (x_i) and can be obtained from Equation (2). The ideal values of $S_{CC}(0)$ is obtained by the following relation

$$S^{id}_{CC}(0) = x_1x_2 \tag{12}$$

The structural functions, Warren-Cowley short range–order parameter (α_1) and the ratio of mutual to intrinsic diffusion coefficients (D_M/D_{id}) can be expressed in terms of $S_{CC}(0)$ as [13, 16, 19–22]

$$\alpha_1 = \frac{S-1}{[S(Z-1)+1]} \tag{13}$$

with

$$S = \frac{S_{CC}(0)}{S^{id}_{CC}(0)} \tag{14}$$

and

$$\frac{D_M}{D_{id}} = \frac{1}{S} \tag{15}$$

2.2 Redlich-Kister (R-K) polynomial

In this frame, ΔG^{xs}_M is expressed as [5, 23–27]

$$\Delta G^{xs}_M = x_1x_2\sum_{k=0}^{n} L_k(x_1-x_2)^k \tag{16}$$

where L_k are the linear T–dependent coefficients or interaction energy parameters of R-K polynomial. They are expressed in the form $L_k = a_k + b_kT$, where a_k (in J/mol) are ΔH_M contributed terms and b_k (in J/mol-K) are ΔS^{xs}_M contributed terms.

The partial excess Gibbs free energy (ΔG^{xs}_i) of the component i in the binary liquid alloy can be given as [24–26]

$$\Delta G^{xs}_i = \Delta G^{xs}_M + (1-x_i)\left(\frac{\partial \Delta G^{xs}_M}{\partial x_i} - \frac{\partial \Delta G^{xs}_M}{\partial(1-x_i)}\right) \tag{17}$$

The activity coefficient of component i in the binary solution is related to ΔG^{xs}_i as

$$RT\ln\gamma_i = \Delta G^{xs}_i \tag{18}$$

After the computations of γ_i, the activity of component i can be obtained by the relation

$$a_i = x_i\gamma_i \tag{19}$$

The values of S^{xs}_M and H_M can be obtained using Equations (4), (7) and (16). Using Equations (10) and (16), $S_{CC}(0)$ for this system having $k = 0, 1, 2$ can be obtained as [24, 26]

$$S_{CC}(0) = RT[-2L_0 + (-12x_1+6)L_1 + (-48x_1^2+48x_1-10)L_2 + \frac{RT}{x_1(1-x_1)}]^{-1} \tag{20}$$

The values of other structural functions in this frame work can also be obtained using Equations (13-15).

3 Results and Discussion

3.1 Thermodynamic properties

The values of G^{xs}_M for Al–Er liquid alloy at 1873 K were computed in the frame work of R-K polynomial [23] (Equation (16)) using the parameters from ref. [8]. Considering these values as reference data quasi–lattice model was applied to compute the thermodynamic and structural properties of the system. As it is compound formation model, the complex *Er*$_2$*Al* [1, 5, 8] was assumed to be energetically stable in the alloy. T–dependent model parameters for the system at 1873 K were then obtained employing the method of least square fitting with the help of Equations (1) and (2), and determined reference values of G_M^{xs}. The obtained values of model parameters (this work) and the self-consistent values of interaction energy parameters for G_M^{xs} [8] are presented in Table 1.

Table 1: Interaction energy parameters for G_M^{xs} of Al–Er liquid alloy

Parameters [J/mol]	Reference
$L_0 = -176486 + 55.6852 * T$ $L_1 = -3668.5 + 23.4492 * T$ $L_2 = 34349.1 - 8.2352 * T$	[8]
$\Delta\omega = -12185.0 + 70.4 * dT$ $\Delta\omega_{AB} = -8215601 + 1.20 * dT$ $\Delta\omega_{AA} = 138480.9 + 0.0010 * dT$	This work

Among the model parameters, $\Delta\omega$ is called ordering energy parameter. At a given temperature, $\Delta\omega < 0$ indicates ordering or hetero–coordinating tendency and $\Delta\omega > 0$ indicates segregating or homo–coordinating tendency in the alloy. In this work, the computed value of $\Delta\omega < 0$ for Al–Er liquid alloy at 1873 K which supports the assumption of complex formation stated above. The best fit values of $\Delta\omega_{AB} < 0$ indicating the attraction between A (=Er) and B (=Al) atoms in the complex. Additionally, $\Delta\omega_{AA} > 0$ corresponding that the self association among Er atoms is not favoured at this temperature.

The effect of $\Delta\omega$ on G_M^{xs} was observed by arbitrarily varying its values in the range ±4 and keeping $\Delta\omega_{AB}$ and $\Delta\omega_{AA}$ constant. The values of G_M^{xs} were computed in the above mentioned constraints using Equations (1) and (2) and necessary input parameters from Table (1). The values so obtained are plotted as a function of concentration in Figure 1. It can be observed that the deviation between computed and ideal values of G_M^{xs} was found to gradually increase with the increase in negative values of $\Delta\omega$. Moreover, the deviation was found to gradually decrease with increase in the positive values of $\Delta\omega$. These results suggests that the complex forming tendency of the system at 1873 K gradually increases with increase in negative values of $\Delta\omega$ and decreases with increase in positive values of $\Delta\omega$. Therefore, it can be concluded that $\Delta\omega$ have great impact on G_M^{xs} thereby determining the mixing and demixing tendencies of the system.

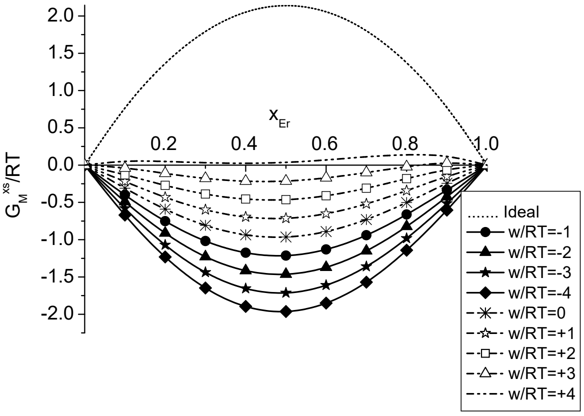

Figure 1: Effect of $\Delta\omega/RT$ on $\Delta G_M^{xs}/RT$ for Al–Er liquid alloy at 1873 K.

The validity of model fit parameters of the work was tested by comparing the computed results of G_M^{xs} with the literature data [8]. The compositional dependence of both of these values are plotted in Figure 2. Both of these values are found to be in excellent agreement, each having optimal value of −18046.90 J/mol at $x_{\mathrm{Er}} = 0.5$. Hence, the system is found to be moderately interacting in nature and symmetric with respect to G_M^{xs}.

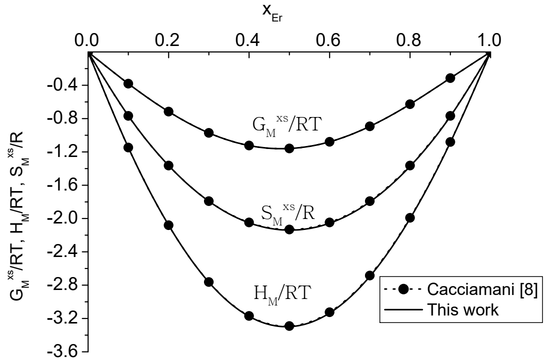

Figure 2: Compositional dependence of $\Delta G_M^{xs}/RT$, $\Delta H_M/RT$ and $\Delta S_M^{xs}/R$ for Al–Er liquid alloy at 1873 K.

As sated earlier, the model parameters in the quasi–lattice model are assumed to be T–dependent. The modeling equation of S_m^{xs} include temperature derivative terms of the interaction energy parameters ($\frac{\partial\Delta\omega}{\partial T}$, $\frac{\partial\Delta\omega_{AB}}{\partial T}$ and $\frac{\partial\Delta\omega_{AA}}{\partial T}$). The literature values of S_m^{xs} for the system at 1873 K were computed using Equations (4), (16) and (17) with the aid of parameters from Table 1. These model parameters were then computed using Equation (5) and the literature data, and are portrayed in Table 1. Likewise, the values of H_M were computed using

Equation (6) and necessary input ingredients from Table 1. The computed and literature values of S_M^{xs} and H_M are plotted as a function of concentration in Figure 2.

The computed and literature values of S_M^{xs} and H_M were found to be consistent with each other at all compositions. Both of them have negative values in the entire concentration range (Figure 2). The minimum values of S_M^{xs} were found to be -17.7873 J/(mol–K) (this work) and -17.7258 J/(mol–K) [8] at $x_{\mathrm{Er}} = 0.5$. Likewise, the minimum values of H_M were found to be -51362.6 J/mol (this work) and -51247.3 J/mol [8] at $x_{\mathrm{Er}} = 0.5$. The accordance between the values of thermodynamic function using model fit parameters of this work and those from ref. [8] validates the present optimisation procedures. Hence, these values were used to compute the other thermodynamic and structural functions of Al–Er liquid alloy at 1873 K.

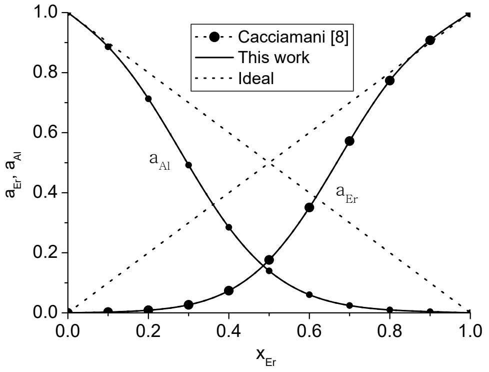

Figure 3: Compositional dependence of a_{Er} and a_{Al} of Al–Er liquid alloy at 1873 K.

The activity is an important thermodynamic function which is directly measured from the experiments in terms of activity coefficient. The activities of monomers Er (a_{Er}) and Al (a_{Al}) of the system were computed using Equations (3), (8) and (9) with help of above determined values of G_M^{xs}. In order to compute a_{Er} and a_{Al} in the frame work of R-K polynomial, the partial excess Gibbs free energies (G_i^{xs}) of the respective components are required. G_{Er}^{xs} and G_{Al}^{xs} were obtained using Equations (16) and (17) with the help of parameters from Table 1 [8]. The literature values of a_{Er} and a_{Al} were then estimated using Equations (18) and (19). The compositional dependence of these values for Al–Er liquid alloy at 1873 K are plotted in Figure 3.

Figure 3 shows that the values of a_{Er} and a_{Al} computed using the model parameters of this work and those of literature [8] were found to be in excellent agreement at all compositions. The activities of both components gradually increased with increase in their respective compositions. They showed high negative deviations from the ideal values at their respective lower concentrations indicating the compound forming tendency in the system at 1873 K. These results are in accordance with those obtained from other thermodynamic functions mentioned above.

The model parameters ($\Delta\omega$, $\Delta\omega_{AB}$ and $\Delta\omega_{AA}$) were assumed to depend linearly on temperature. T-dependence of these parameters in terms of $\partial\Delta\omega/\partial T$, $\partial\Delta\omega_{AB}/\partial T$ and $\partial\Delta\omega_{AA}/\partial T$ can be expressed as [20–22, 28]

$$\Delta\omega(T) = \Delta\omega(T_0) + \frac{\partial\Delta\omega}{\partial T}(T - T_0) \qquad (21)$$

$$\Delta\omega_{ij}(T) = \Delta\omega_{ij}(T_0) + \frac{\partial\Delta\omega_{ij}}{\partial T}(T - T_0) \qquad (22)$$

where T_0 (= 1873 K) is the melting temperature of the system and T is the temperature of interest. T-dependent values of these parameters obtained for this work are presented in Table 1.

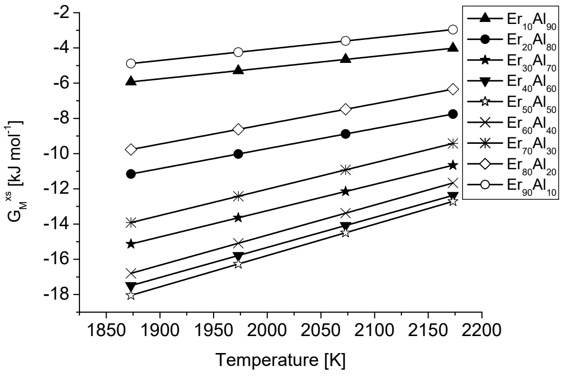

Figure 4: Variation of G_M^{xs} with temperature of Al–Er liquid alloy.

The values of G_M^{xs} were computed in the temperature range $1873 - 2173$ K using Equations (1) and (2) with the help of parameters in Table 1. These values at different composition ratios are portrayed as a function of temperature in Figure 4. It can be observed that the negative values of G_M^{xs} gradually decreases with increase in temperature of the system indicating the decrease in compound forming tendency [22, 28, 29].

The activities of the components of system were also computed at above mentioned temperature range using Equations (1-3), (8) and (9) with the aid of parameters from Table 1. T-dependence of

a_{Er} and a_{Al} at different temperatures and composition ratios are depicted in Figure 5 and Figure 6 respectively. The computed values of a_{Er} and a_{Al} gradually increased with increase in the temperature beyond 1873 K. Thus, theoretical investigations revealed that the compound forming nature of Al–Er liquid alloy gradually decreased at higher temperatures, as mentioned above [22, 28, 29].

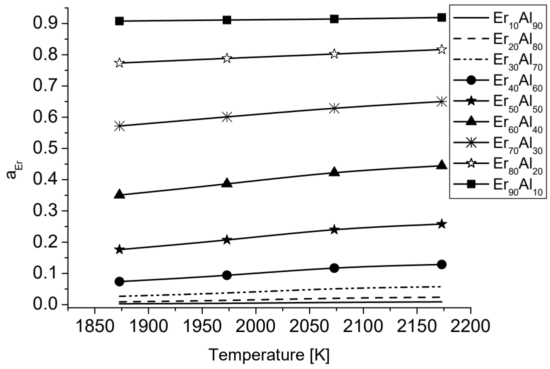

Figure 5: Variation of activity of Er (a_{Er}) with temperature of Al–Er liquid alloy.

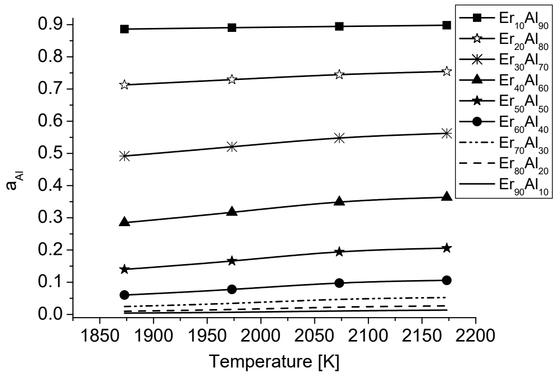

Figure 6: Variations of activity of Al (a_{Al}) with temperature of Al–Er liquid alloy.

3.2 Structural properties

The knowledge of concentration fluctuation in long wavelength limit ($S_{CC}(0)$) gives information regarding the local arrangement or pairing of atoms in the initial melt. At a given temperature and concentration, if $S_{CC}(0) < S_{CC}^{id}(0)$, indicates ordering tendency and if $S_{CC}(0) > S_{CC}^{id}(0)$, reveals segregating tendency. The expressions for structural functions are coupled with the thermodynamic functions, specially G_M^{xs}. Therefore, the model parameters obtained for the investigation of thermodynamic functions were also used for computation of structural properties. Equations (11) and (12) and parameters from Table 1 were used to compute the values of $S_{CC}(0)$ and $S_{CC}^{id}(0)$ for Al–Er liquid alloy at 1873 K. The effect of ordering energy parameter, $\Delta\omega$, on $S_{CC}(0)$ was also studied by varying its values in the range $\Delta\omega = \pm 4$ and keeping the values of $\Delta\omega_{AB}$ and $\Delta\omega_{AA}$ constant.

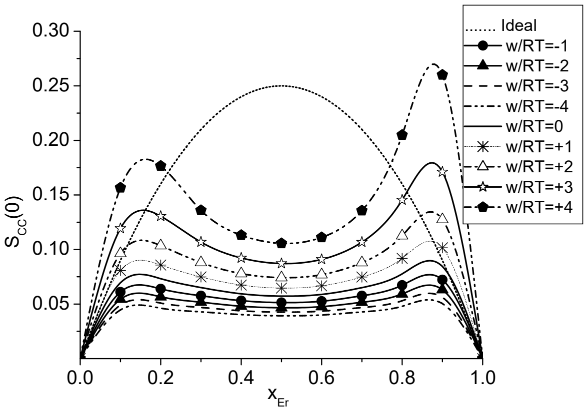

Figure 7: Effect of $\Delta\omega/RT$ on $S_{CC}(0)$ of Al–Er liquid alloy at 1873 K.

From Figure 7, it can be observed that on increasing the negative values of $\Delta\omega$, the negative deviation of $S_{CC}(0)$ from $S_{CC}^{id}(0)$ gradually increases in the entire comcentration range indicating the increase in complex formation capability in the system. But when the positive value of $\Delta\omega$ is gradually increased, the deviation of $S_{CC}(0)$ from $S_{CC}^{id}(0)$ gradually decreases corresponding the decrease in complex formation tendency. For $\Delta\omega = 0$, $S_{CC}(0) > S_{CC}^{id}(0)$ at higher concentration of Er, i.e., $x_{\mathrm{Er}} > 0.9$, predicting the segregating or homoatomic pairing of constituent atoms. For $\Delta\omega = 1$, $S_{CC}(0) > S_{CC}^{id}(0)$ at both lower ($x_{\mathrm{Er}} < 0.1$) and higher ($x_{\mathrm{Er}} > 0.9$) compositions of Er. However, this range gradually increases with increase in positive values of $\Delta\omega$. Similar natures regarding the complex forming tendency of the system were also revealed by the effect of $\Delta\omega$ on G_M^{xs}.

The computed values of $S_{CC}(0)$ as a function of concentration for the system at 1873 K are plotted in Figure 8. The values of $S_{CC}(0)$ computed using the model parameters of this work were found to be less than ideal values throughout the entire concentration indicating the complete ordering nature. But those computed using the parameters of ref. [8] were found to be grater than ideal values in the range $x_{\mathrm{Er}} > 0.9$ indicating the segregating nature in this range and ordering at rest of the concentrations. The values of $S_{CC}(0)$ were also computed at different temperatures using T–dependent model parameters of this work (Table 1) and plotted in

Figure 9. With the increase in temperature, the negative deviation of $S_{CC}(0)$ from $S^{id}_{CC}(0)$ gradually decreases revealing the decrease in tendency towards compound formation.

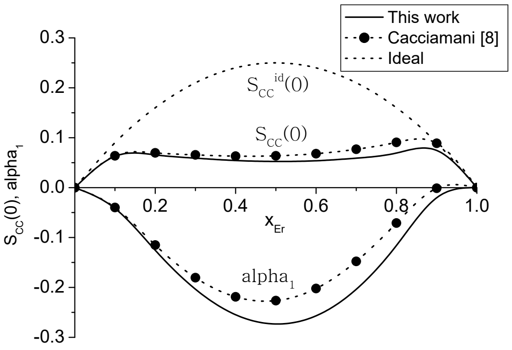

Figure 8: Computed values of $S_{CC}(0)$ and α_1 versus x_{Er} of Al–Er liquid alloy at 1873 K.

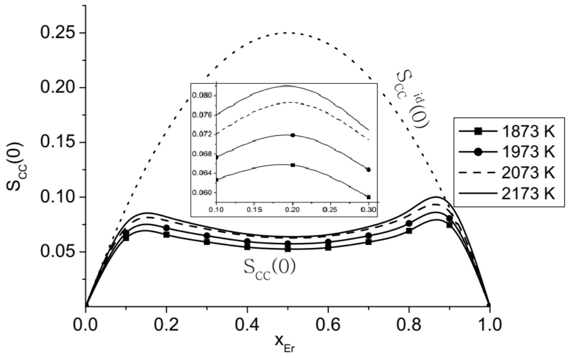

Figure 9: $S_{CC}(0)$ versus x_{Er} of Al–Er liquid alloy at different temperatures.

To further strengthen the mixing and demixing tendency of the system, Warren-Cowley short–range order parameter (α_1) were computed using Equations (13) and (14) with the help of above determined values of $S_{CC}(0)$ and $S^{id}_{CC}(0)$. Both of these values are plotted as a function of concentration in Figure 8.

At a given concentration and temperature, if $\alpha_1 < 0$, then ordering nature is expected and if $\alpha_1 > 0$, then segregating nature is expected. If $\alpha_1 = 0$, then it is assumed that the random mixing takes place in the initial binay melt. It can be observed that the values of α_1 computed using the optimised parameters of this work are less than 0 at all compositions indicating the complete ordering nature of the system at 1873 K. But those computed using the thermodynamic parameters of ref. [8] were found to be greater than 0 in the range $x_{\mathrm{Er}} > 0.9$ revealing the preferential homo-atomic clustering. At rest of the compositions, the nature predicted by both approaches were the same. Employing the same methods, the values of α_1 were computed at different temperatures using T-dependent model parameters of this work and are plotted in Figure 10. The negative values of α_1 gradually decreased with increase in temperature of the system revealing the decrease in mixing behaviour. At T>1873 K, $\alpha_1 > 0$ in the range $x_{\mathrm{Er}} > 0.9$ indicating the segregating tendency.

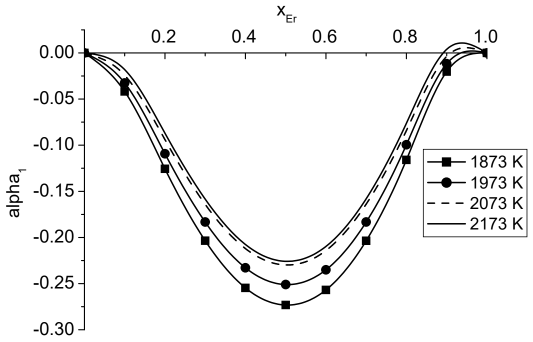

Figure 10: α_1 versus x_{Er} of Al–Er liquid alloy at different temperatures.

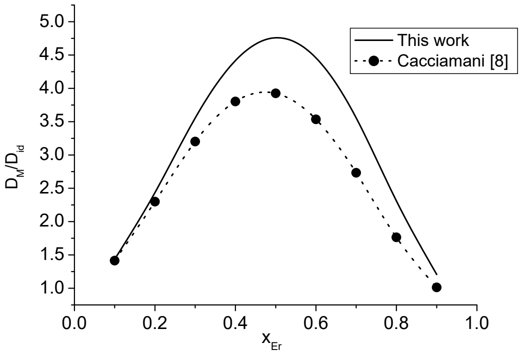

Figure 11: Compositional dependence of D_M/D_{id} of Al–Er liquid alloy at 1873 K.

The structural arrangement of constituent metals at microscopic level can be further analyzed by the studying ratio of mutual to intrinsic diffusion coefficients (D_M/D_{id}). At given concentration and temperature, the values of $D_M/D_{id} > 1$ indicates ordering nature, $D_M/D_{id} < 1$ reveals segregating nature and $D_M/D_{id} = 0$ corresponds to random mixing. The values of D_M/D_{id} for Al–Er liquid alloy at 1873 K and higher temperatures were computed using Equations (14) and (15) with the aid of above determined values of $S_{CC}(0)$ and $S_{CC}^{id}(0)$, plotted in Figures 11 and 12.

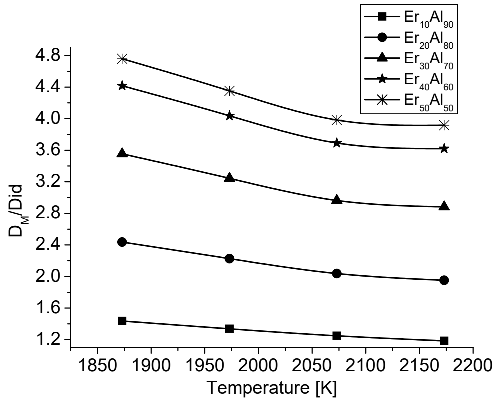

Figure 12: Computed values of D_M/D_{id} of Al–Er liquid alloy at different temperatures.

The perusal of Figure 11 corresponds that the values of D_M/D_{id} computed using the model parameters of this work were found to be greater than 1 at all concentrations indicating the complete ordering nature of the system at 1873 K. But the values computed using the parameters of ref. [8] were found to be less than 1 in the range $x_{\mathrm{Er}} > 0.9$ revealing the segregating nature. Moreover, as the temperature was gradually increased beyond 1873 K, the values of D_M/D_{id} gradually decreased (Figure 12). The nature regarding the mixing behaviour of the Al–Er system predicted by all the thermodynamic and structural functions computed in the work were the same.

4 Conclusions

The computed values of thermodynamic functions using the optimised parameters of this work in the frame work of quasi–latice model were found to be consistent with the literature data thereby providing the validity of respective methodology. The computed values of thermodynamic and structural functions of Al–Er system at 1873 revealed it to be complete ordering in nature. Assuming the model fit parameters to be linear temperature–dependent, the extent of mixing tendency of the system were studied at different temperatures. The present theoretical investigations indicated that the compound forming tendency of the system gradually decreased with increased in temperature.

References

[1] K. A. Gschneidner and F. W. Calderwood. The Al- Er (Aluminum-Erbium) system, 1988.

[2] K. A. Gschneidner Jr. and A. H. Daane. Handbook on the Physics and Chemistry of Rare Earths, vol. KA Gschneidner, Jr. and L. Eyring, 1988.

[3] R. Lundin and J. R. Wilson. Rare earth metals. *Advanced Materials and Processes*, 158(1):52–52, 2000.

[4] K. A. Gschneidner. Physical properties of the rare earth metals. *Bulletin of Alloy Phase Diagrams*, 11(3):216–224, 1990.

[5] L. Jin, Y. B. Kang, P. Chartrand, and C. D Fuerst. Thermodynamic evaluation and optimization of Al–Gd, Al–Tb, Al–Dy, Al–Ho and Al–Er systems using a modified quasichemical model for the liquid. *Calphad*, 34(4):456–466, 2010.

[6] F. Merlo. Heat capacities from 400 to 1200 K of CaAl2, EuAl2, ErAl2 and of the intermediate valence compound YbAl2. *Thermochimica acta*, 64(1-2):115–122, 1983.

[7] H. Okamoto. Al-Er (aluminum-erbium). *Journal of Phase Equilibria and Diffusion*, 32(3):261–262, 2011.

[8] G. Cacciamani, A. Saccone, S. De Negri, and R. Ferro. The Al-Er-Mg ternary system part II: thermodynamic modeling. *Journal of Phase Equilibria*, 23:38–50, 2002.

[9] A. Saccone, G. Cacciamani, S. De Negri, and R. Ferro. The Al-Er-Mg ternary system part I: experimental investigation. *Journal of phase equilibria*, 23(1):29, 2002.

[10] F. Sommer and M. Keita. Determination of the enthalpies of formation of intermetallic compounds of aluminium with cerium, erbium and gadolinium. *Journal of the Less Common Metals*, 136(1):95–99, 1987.

[11] Liping Xu, Xiangbiao Shi, Dechen Xia, Dandan Huang, and Hongqun Tang. Experimental investigation and thermodynamic assessment of the Al–Er system. *Calphad*, 79:102482, 2022.

[12] A. B. Bhatia and R. N. Singh. A quasi–lattice theory for compound forming molten alloys. *Physics and Chemistry of Liquids an International Journal*, 13(3):177–190, 1984.

[13] D. Adhikari, S. K. Yadav, and L. N. Jha. Thermo-physical properties of Mg-Tl melt. *Journal of Basic and Applied Research International*, 9:103–110, 2015.

[14] S. K. Yadav, S. Lamichhane, L. N. Jha, N. P. Adhikari, and D. Adhikari. Mixing behaviour

of Ni–Al melt at 1873 K. *Physics and Chemistry of Liquids*, 54(3):370–383, 2016.

[15] A. B. Bhatia and W. H. Hargrove. Concentration fluctuations and thermodynamic properties of some compound forming binary molten systems. *Physical Review B*, 10(8):3186, 1974.

[16] S. K. Yadav, L. N. Jha, and D. Adhikari. Thermodynamic and structural properties of Bi-based liquid alloys. *Physica B: Condensed Matter*, 475:40–47, 2015.

[17] SK Yadav, LN Jha, and D Adhikari. Segregating to ordering transformation in In–Sn melt. *Physics and Chemistry of Liquids*, 53(4):443–454, 2015.

[18] S. K. Yadav, L. N. Jha, and D. Adhikari. Thermodynamic, structural, transport and surface properties of Pb-Tl liquid alloy. *Bibechana*, 13:100–113, 2016.

[19] D. Adhikari, S. K. Yadav, and L. N. Jha. Thermo-physical properties of Al–Fe melt. *Journal of the Chinese Advanced Materials Society*, 2(3):149–158, 2014.

[20] S. K. Yadav, L. N. Jha, and D Adhikari. Theoretical Modeling to Predict the Thermodynamic, Structural, Surface and Transport Properties of the Liquid Tl–Na Alloys at different Temperatures. *Journal of Nepal Physical Society*, 4(1):101–110, 2017.

[21] S. K. Yadav, M. Gautam, and D. Adhikari. Mixing properties of Cu–Mg liquid alloy. *AIP Advances*, 10(12):125320, 2020.

[22] Shashit Kumar Yadav. *Ordering and Segregation in Liquid Alloys.* PhD thesis, Faculty of Physics, 2018.

[23] O. Redlich and A. T. Kister. Algebraic representation of thermodynamic properties and the classification of solutions. *Industrial & Engineering Chemistry*, 40(2):345–348, 1948.

[24] R. K. Gohivar, S. K. Yadav, R. P. Koirala, and D. Adhikari. Artifacts in Al–Mn liquid alloy. *Physica B: Condensed Matter*, 595:412348, 2020.

[25] R. K. Gohivar, S. K. Yadav, R. P. Koirala, and D. Adhikari. Assessment of thermo-structural properties of Al-Fe and Fe-Si alloys at high temperatures. *Physics and Chemistry of Liquids*, 59(5):679–689, 2021.

[26] R. K. Gohivar, S. K. Yadav, R. P. Koirala, G. K. Shrestha, and D. Adhikari. Temperature dependence of interaction parameters for Al–Li liquid alloy. *Philosophical Magazine*, 101(2):179–192, 2021.

[27] Arjun Dhungana, Shashit Kumar Yadav, and Devendra Adhikari. Thermodynamic and surface properties of Al–Li–Mg liquid alloy. *Physica B: Condensed Matter*, 598:412461, 2020.

[28] Shashit Kumar Yadav, Lok Narayan Jha, Arjun Dhungana, Upendra Mehta, Devendra Adhikari, et al. Thermo-Physical Properties of Al-Mg Alloy in Liquid State at Different Temperatures. *Materials Sciences and Applications*, 9(10):812, 2018.

[29] Shashit Kumar Yadav, Upendra Mehta, Ram Prasad Koirala, and Ramesh Kumar Gohivar. Mixing properties of liquid Al-Au alloys. *Bibechana*, 20(1):86–91, 2023.