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Optimization of Thermodynamic Properties of Liquid Au-Ni Alloys

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ABSTRACT

The best fitted values of the size ratio $(\Omega)$and the order energy parameter (W) have been used to calculate the thermodynamic properties of liquid Au-Ni alloys at temperature of 1150 K, using the Quasi-Lattice Theory. The temperature dependent values of order energy parameter $(\frac{\partial W}{\partial T})$ were then used to optimize various thermodynamic properties such as the excess free energy of mixing, activity and activities coefficients of the components, partial excess free energy of mixing, the concentration-concentration fluctuations in long-wavelength limits, the heat of mixing, the entropy of mixing as well as the chemical diffusion at different temperatures. The positive deviations observed in various calculated thermodynamic properties and the microscopic functions, (Scc(0) and α_1) show that liquid Au-Ni alloy is a segregating system. The degree of segregation in the alloy is weak though. The values of W are positive and decrease as the temperature increases. These values of W and $\frac{\partial W}{\partial T}$ were utilized in predicting the various thermodynamic properties of the liquid Au-Ni alloys at different temperatures.

1. Introduction

The Au-based alloy system is an important subsystem for designing materials used in many technological applications. Gold-Nickel alloys have long been utilized in electronic devices as contact materials, switching components, and substrate protection [1]. Gold has a significant place in our culture and society today due to its relevance in both fundamental and applied research. For instance, gold is used in making most valuable objects as wedding ring, jewellery, money, Olympic medals and so on. It is the most inert and softest metal with respect to the unique cohesive energy it offers [2]. Apart from commercial value of gold, the unique chemical and physical properties offered by gold have attracted attention of researchers across fields in a growing number of applications. Thus, gold is use within the fields of nanotechnology and medicine for products such as smart cards, automotive electronics, sensors, medical implants and drug delivery systems [1-4]. On the other hand, nickel plays a key role in the automobile industries for it uses in transportation, fabricated metal products, electrical equipment, petroleum and chemical industries household appliances and industries machinery [5]. In order to meet the desire needs for new products in the field of material science, it is cumbersome to develop new technology, optimize simulation and control system by experiments. As a result, with rapid development in science and technology, finding a method that can use small amount of the experimental data to obtain a large amount of information rather than by direct experimentation has become a necessity. In other words, required data can be predicted theoretically using only limited available experimental data. Over the years, a great deal of efforts have been made by metal physicists, metallurgists and chemists through proposition of several models to study the thermodynamic and transport properties of alloys in liquid state which are important prerequisites in proper understanding of the energetics of mixing behaviour in the liquid alloys. Some of the models in use include the Self-Association model [6-8], four-atom-cluster-model [8], complex formation model [9], Quasi-chemical approximation model [10], molecular interaction volume model [11-12], Quasi Lattice theory [13] and others [14]. In the present work, the Quasi Lattice Theory of liquid mixture which account for the effect of size ratio, entropic and enthalpic effects have been used to explain the various thermodynamic and transport properties of liquid Au-Ni alloys at a specified temperature T =1150 K. The purpose of this study is to provide a simplified method to verify the capability for using relevant expressions derived within the frame of the Quasi Lattice Theory of liquid mixture in conjunction with the Redlich-Kister polynomial equation [15] to predict the various thermodynamic properties for liquid Au-Ni alloy systems at different working temperatures via optimization. Thus, the results of various properties for the liquid Au-Ni alloys at the temperature T = 1150 K have been calculated and compared with their corresponding experimental values. Likewise, the optimization procedure has been employed to compute the excess free energy of mixing at different temperatures and hence the optimized coefficients for liquid Au-Ni alloys were then used to determine the partial excess free energy of mixing as well as activity of both the components as well as concentration fluctuations in long wave-length limit ($S_{cc}(0)$) at different temperatures in the entire range of concentration. In the next section the theoretical formulation is presented, follow by the results and discussion with conclusion in the last section.

2. Theoretical formulation

2.1 Thermodynamic properties and activities

Let us assume that one mole of a binary liquid mixture of constituents $c_A = c$ of constituent atom A (= Au) and $c_B = (1\text{-}c)$ of constituent atom B (= Ni) such that $c_N = N_A$ (No. of constituent atom A) and (1-c) N = N_B (No. of constituent atom B) in the alloy. Suppose also that the constituent atoms A and B of the binary mixtures are of different sizes and shapes, so the entropic and enthalpic effects of the binary mixture require that $H_M \neq 0$ within the framework of the Quasi-Lattice Theory (QLT) of liquid mixture as proposed by Guggenheim [13] in the limit of Z → infinity at a Temperature T. Based on the QLT, an expression for the free energy of mixing, G_M is given by:

$$G_M = RT[(1-c)\ln\psi + c\ln(1-\psi) + c\psi W] \tag{1}$$

where R is the universal gas constant , $\psi = \dfrac{\Omega(1-c)}{c+\Omega(1-c)}$ with $\Omega\left(=\dfrac{\Omega_B}{\Omega_A}\right)$; $\Omega_A > \Omega_B$ is the atomic size ratio of the alloy and the ordering energy parameter, W, is defined as:

$$W = \gamma_A\left(\frac{w}{k_B T}\right) \tag{2}$$

With
$$w = Z\left[\varepsilon_{AB} - \left(\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right)\right] \tag{3}$$

Here, *w* is the interchange energy, Z is the coordination number of atoms, k_B is the Boltmann's constant and ε_{ij} (i, j = Au, Ni) are bonding energies of i-j bond in the complex. γ_A is the activity coefficient of atom A (i.e. Au). With the help of Eq. (1), the component activity a_i can be obtained using:

$$RT \ln a_i = \left(\frac{\partial G_M}{\partial N_i}\right)_{T,P,N} \tag{4}$$

Recalling that N = N_A +N_B with $C_A = N_A/N$ and putting Eq. (1) in Eq.(4), the activities of component A and B are expressed as:

$$\ln a_A = \ln(1-\psi) + \psi\left\{\frac{\Omega - 1}{\Omega}\right\} + \psi^2 \frac{W}{RT} \tag{5}$$

$$\ln a_B = \ln \psi - (1-\psi)(\Omega - 1) + \Omega(1-\psi)^2 \frac{W}{RT} \tag{6}$$

Once the expressions for G_M and a_i are known, other thermodynamic functions can readily be obtained using standard thermodynamic relations. Thus, the entropy of mixing is expressed as:

$$S_M = -\left(\frac{\partial G_M}{\partial T}\right)_P \tag{7}$$

so putting Eq.(1) in Eq. (7), we obtain

$$S_M = -R\left[(1-c)\ln \psi + c\ln(1-\psi) + c\psi\left(W + T\frac{\partial W}{\partial T}\right)\right] \tag{8}$$

and

$$\frac{H_M}{RT} == \frac{G_M}{RT} + \frac{S_M}{R} = -\psi c T \frac{\partial W}{\partial T} \tag{9}$$

The ordered energy, W, is temperature dependent and its temperature dependence has been well reported by [6]. The long-wavelength limit q → 0 of the structure factor $S_{cc}(q)$ which is known as the concentration-concentration fluctuations, $S_{cc}(0)$, have been widely used to study the stability of the binary liquid mixtures and in gauging the nature of interactions in liquid alloys [6]. The calculated $S_{cc}(0)$ is therefore expressed as:

$$S_{cc}(0) = \frac{c(1-c)}{1 - c(1-c) f(\Omega, W)} \tag{10}$$

where

$$f(\Omega, W) = \frac{2\Omega^2\left(\frac{W}{RT}\right) - (\Omega - 1)^2\left[(c + \Omega(1-c)\right]}{\left[(c + \Omega(1-c)\right]^3} \tag{11}$$

for ideal mixing the energy parameter, *w*, defined by Eq. (3) is equal to zero, and Eq. (11) reduces to

$$S_{cc}^{id}(0) = c(1-c) \tag{12}$$

Once $S_{cc}(0)$ is determined from Eq. (11), the chemical short-range order parameter, α_1, can be computed as a measure of the tendency for compound formation or segregation of atoms in liquid binary alloys [8, 14, 16, 17]. In terms of unlike constituent atoms α_1 can be defined as:

$$\alpha_1 = \frac{P-1}{P(Z-1)+1}, \qquad P = \frac{S_{cc}(0)}{S_{cc}^{id}(0)} \tag{13}$$

The coordination number is taken as 10 [18-21].

The relationship between $S_{cc}(0)$ and chemical diffusion, (D_M), can as well be used at the microscopic level to examine the alloying behaviour of two atomic species forming a binary liquid alloy due to its importance in industrial and corrosion phenomena. The relation between $S_{cc}(0)$ *and* D_M is given as [6, 9, 14, 18]

$$\frac{D_M}{D_{id}} = \frac{S_{cc}(0)}{S_{cc}^{id}(0)} \tag{14}$$

where D_M is the mutual diffusion coefficient and D_{id} is the intrinsic diffusion coefficient for an ideal mixture. It is instructive from Eq. (14), that for ideal mixing $S_{cc}(0) \rightarrow S_{cc}^{id}(0)$, i.e. $D_M D_{id}^{-1} \rightarrow 1$. The presence of chemical order is indicated by $D_M D_{id}^{-1} > 1$ as calculated $S_{cc}(0)$ is less than ideal $S_{cc}^{id}(0)$. Likewise, $D_M D_{id}^{-1} < 1$ suggests the tendency for homo-coordination of atoms leading to phase separation in the liquid alloys.

2.2 The Optimization Method

The optimization approach is a procedure employs for the description of thermodynamic properties within the frame of statistical thermodynamics and polynomial expressions [6, 22]. One major feature of the approach is its high potential in obtaining a consistent set of model parameters analytically which allows for projection into temperature and concentration regions where direct experimental measurements are infeasible. The adjustable coefficients are estimated by the least-square method. The various thermodynamic properties which are expressed by a power-series law with coefficients A, B, C, D, E, etc, determined using the least-square method. The heat capacity at a temperature T is given by:

$$C_p = -C - 2DT - 2ET^{-2} \tag{15}$$

Using standard thermodynamic relations, the enthalpy is given by [6]

$$\begin{aligned} H &= H(T_0) + \int_0^T C_p dT \\ &= A - CT - DT^2 + 2ET^{-1} - ..... \end{aligned} \tag{16}$$

and the entropy is expressed as [6]:

$$S = S(T_0) + \int_0^T \frac{C_p}{T} dT \qquad (17)$$
$$= B - C(1 - \ln T) - 2DT + ET^{-2} - .....$$

Hence, using Eq. (16) and (17), the thermodynamic relation G = H - TS gives the temperature dependence free energy of mixing as:

$$G = A + BT + CT \ln T + DT^2 + ET^{-1} + ... \qquad (18)$$

With the aid of the Redlich-Kister polynomial equation, the concentration dependent excess free energy of mixing is obtained as [6, 22]:

$$G_M^{XS}(c,T) = c(1-c)\sum_{l=0}^{m} K_l(T)[c-(1-c)]^l \qquad (19)$$

where $$K_l(T) = A_l + B_l T + C_l \ln T + D_l T^2 \qquad (20)$$

Similar to G in Eq. (18), the coefficients $K_l(T)$ are temperature dependent. The least-square method was used to determine the unknown parameters in Eq. (19) through Eq. (20). In this method, the excess free energy of mixing, G_M^{xs}, of the binary liquid alloys at different temperatures can be computed using the equation:

$$G_M^{XS} = G_M - G_M^{id}$$
$$= G_M - RT[c \ln c + (1-c)\ln(1-c)] \qquad (21)$$

The values of free energy of mixing, (G_M) for the binary liquid alloys at different temperatures can be computed using Eq.(1) once the values of order energy parameter (W) at different temperatures are determined from:

$$W(T_K) = W(T) + \frac{\partial W}{\partial T}(T_K - T) \qquad (22)$$

$W(T)$ is the order energy parameter at the given temperature T, while $W(T_K)$ is the order energy parameter at the required temperature T_K. The temperature dependence of the order energy parameter for the specified liquid alloy is denoted by $\frac{\partial W}{\partial T}$.

3. Results and Discussion

The free energy of mixing (G_M) and activity (a_i) of the constituents in binary liquid Au-Ni alloys were computed at T = 1150 K using the physical properties of the pure component metals such as the atomic volume and melting temperature (T_m) in the formalism described in the preceding section. The size ratio (Ω) of the binary liquid Au-Ni alloys was determined using the atomic volume of the constituent metals at the specified temperature, T, via the relation:

$$\Omega_i(T) = \Omega_i(T_m)[1 + \alpha_{pi}(T - T_m)] \qquad (23)$$

where $\Omega_i(T_m)$ is the atomic volume of the constituent i at the melting temperature T_m and α_{pi} is the coefficient of thermal expansion of the constituent *i*. The value of the size ratio (Ω) for the binary liquid Au-Ni alloy at 1150 K used in the model calculation is 1.61 while the values of α_{pi} and $\Omega_i\,(T_m)$ were taken from [23-24]. The order energy parameter (W) for binary liquid Au-Ni alloys was treated as a free parameter which was adjusted until there is a reasonable agreement between the theoretical and experimental values for both the free energy of mixing (Eq. (1)) and activity (Eq. (5 & 6)) using the data taken from [25]. The best fitted values for Ω and W for binary liquid Au-Ni alloys at 1150 K are 1.1125 and 1.6898, respectively. The plot of the G_M/RT versus concentration of Au for Au-Ni alloys in the entire concentration range from 0 to1 is shown in Fig.1. A look at the figure shows that there is a good agreement between the calculated and experimental values especially at the lower Au concentration region with some inconsistencies in the concentration range around $0.5 < c_{Au} < 0.8$. The theoretical values of G_M/RT has a minimum of -0.25965 at the concentration of Au, $c_{Au} = 0.4$ while the experimental value has a minimum of -0.25345 when $c_{Au} = 0.4$. This indicates that while Au-Ni alloys at 1150 K is a compounding forming the degree of interactions between Au-atoms and Ni-atoms are not very strong compared to Bi-Mg with minimum $G_M/RT = -3.38RT$ and liquid Hg-K with minimum $G_M/RT = -3.35RT$ [14, 19] around the equiatomic composition. The results of both the calculated and experimental activity values are presented in Fig. 2 with the experimental data shown as symbols. It is clearly seen that there is a reasonably agreement between the two results. Activity is one of the fortunate thermodynamic properties that can be obtained experimentally.

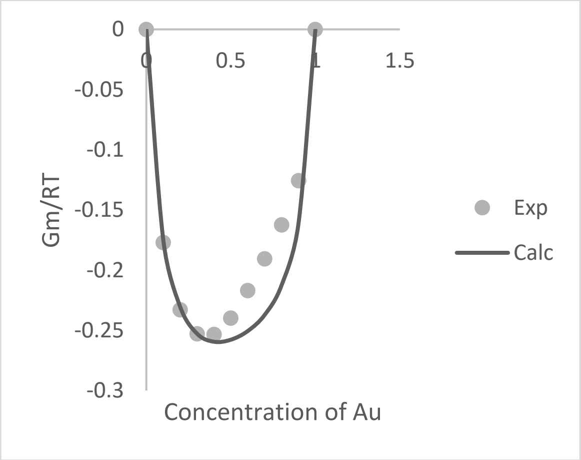


Fig. 1: Free energy of mixing versus concentration of Au in Liquid Au-Ni alloys at 1150 K

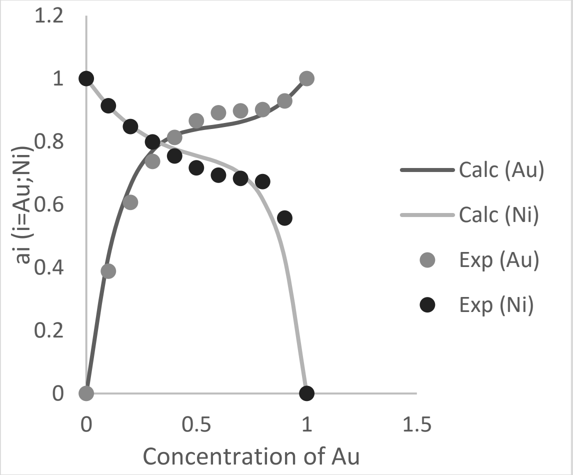
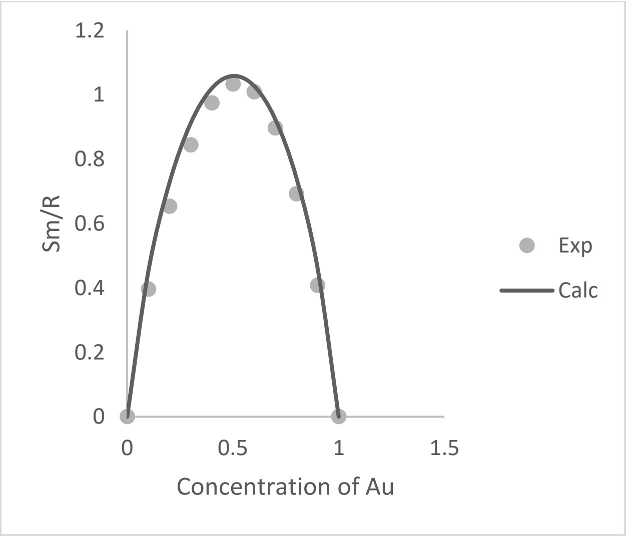


Fig. 2: Computed value of activity coefficients of ($_{Au}$ and a_{Ni}) in liquid Au-Ni alloy at 1150 K

The temperature derivative of the order energy parameter, $\left(\frac{\partial W}{\partial T}\right)$, for Au-Ni binary liquid alloy has been calculated using equations (8) or (9) to reproduce simultaneously an overall fit for experimental values of entropy of mixing (S_M) or heat of mixing (H_M) of Au-Ni liquid alloy at 1150 K in the concentration range of 0.1 to 0.9. The best fit value of $\left(\frac{\partial W}{\partial T}\right)$ for Au-Ni liquid alloy is found to be – 0.002645 K-1. The theoretical values of S_M/R as computed by using equation (8) and the corresponding experimental values of Au-Ni liquid alloys at 1150 K in the entire concentration range are shown in Fig.3, which are in excellent agreement. The theoretical value of S_M/R at 1150 K is maximum at the concentration, c = 0.5 which is found to be 1.05869 while the experimental value of S_M/R at 1150 K is maximum at the same concentration, c = 0.5, which is found to be 1.033026. Also Fig. 4, the theoretical values of H_M/RT (on taking $\left(\frac{\partial W}{\partial T}\right)$ = - 0.002645 K-1) and experimental values of H_M/RT of Au-Ni liquid alloys at 1150 K in the entire concentration range are presented, which are in good agreement. The maximum theoretical value of H_M/RT at 1150 K is 0.800934 at the concentration, C = 0.5, but the maximum experimental value of H_M/RT at 1873 K is 0.79374 at the concentration, C= 0.5.



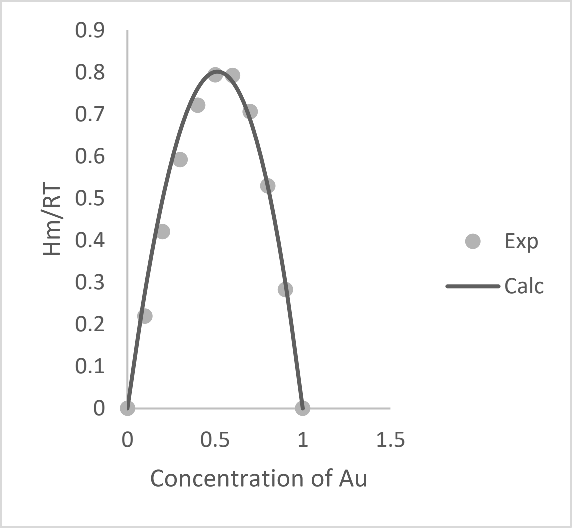


Fig. 3: Entropy of mixing versus concentration for liquid Au-Ni alloys at 1150 K

Fig. 4: Heat of mixing versus concentration for liquid Au-Ni alloys at 1150 K

The theoretical values of $S_{cc}(0)$ for binary liquid Au-Ni alloys at 1150 K in the entire concentration range were calculated using equation (10) (on taking $\Omega = 1.1125$ and W = 1.6898). The experimental values of concentration fluctuations in the long wave-length limit ($S_{cc}(0)$) for Au-Ni alloys at 1150 K is not available. Figure 5, shows the theoretical of Scc (0) for Au-Ni liquid alloys over the entire concentration range.

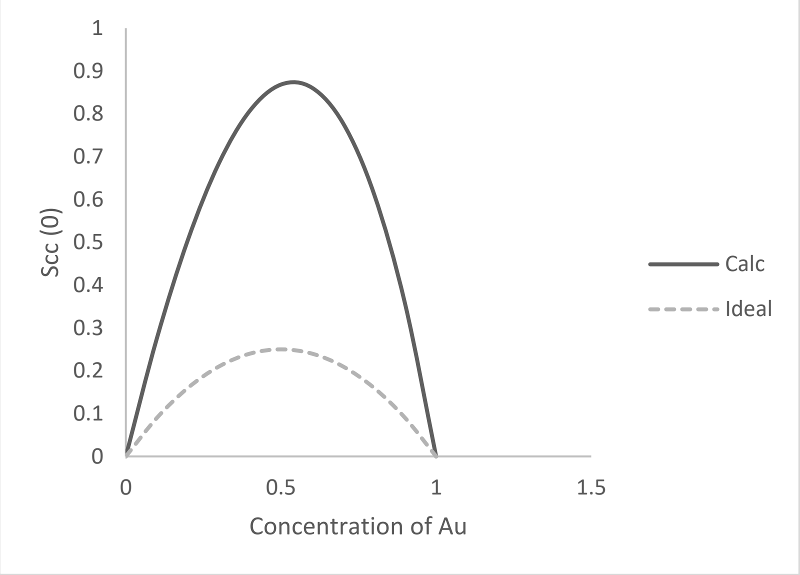


Fig. 5: Concentration-concentration fluctuations in the long wavelength limit, $S_{cc}(0)$ versus concentration of Au in liquid Au-Ni alloys at 1150 K

The theoretical maximum value of ($S_{cc}(0)$) is found to be 0.868308 at the concentration c = 0.5. The concentration-concentration fluctuations in the long wave-length limit ($S_{cc}(0)$ of liquid Au-Ni alloys at 1150 K is clearly greater than the ideal value of $S_{cc}^{id}(0)$ at all concentration, indicating that liquid Au-Ni alloy has a segregating nature. The calculated values of the fitted parameters for liquid Au-Ni alloy at 1150 K are $\Omega = 1.1125$, W=1.6589, and $\left(\frac{\partial W}{\partial T}\right) = -0.002645\ K^{-1}$. These values were used in an optimization technique to predict the thermodynamic and transport properties of liquid Au-Ni alloys at different temperatures. The values of $W(T_k)$ for temperatures T_k = 1173 K, 1273 K, 1373 K, 1473 K and 1573 K were calculated and the results are listed in Table 1 using the values of fitted parameters for liquid Au-Ni alloys in equation (22).

Table 1: Calculated values of order energy parameter (W) at different temperature for liquid Au-Ni alloys

Temperature (T_k) in K	Order Energy parameter, $W(T_k)$
1150	1.658900
1173	1.598065
1273	1.333565
1373	1.069065
1473	0.804565
1573	0.540065

The values of free energy of mixing (G_M) for the liquid Au-Ni alloys at various temperatures were determined using the corresponding values of W in Eqn.(1) over the entire concentration range. The results are shown in Fig. 6 and the corresponding excess free energy of mixing (G_M^{XS}) for the liquid Au-Ni alloys were calculated using Eqn.(21) at investigated temperatures. The parameters in Eqn.(19) were calculated using the least-square method, and then the optimized coefficients for liquid Au-Ni alloys were computed, which are listed in Table 2.

Table-2: Calculated values of optimized coefficients $A_l,\ B_l,\ C_l,\ D_l\ (l = 0\ to\ 2)$ for Au-Ni liquid alloy.

Value of *l*	$A_l(Jmol^{-1})$	$B_l(Jmol^{-1}K^{-1})$	$C_l(Jmol^{-1}K^{-1})$	$D_l(Jmol^{-1}K^{-2})$
0	-0.000000021	0.0000000435	0.00000003172	0.0000002165
1	0.000000000	0.0000000000	0.00000000000	0.0000000000
2	0.000001100	0.0000021000	0.00000010000	0.0000001100

In addition, the optimized partial excess free energy of mixing of the constituents A (≡Au) and B (≡Ni) in the liquid Au-Ni alloys are given by:

$$\overline{G}_{MA}^{XS}(c,T) = (1-c)^2 \sum_{l=0}^{m} K_l(T)[2c(l+1)-1](2c-1)^{l-1} \qquad (24)$$

and

$$\overline{G}_{MB}^{XS}(c,T) = c^2 \sum_{l=0}^{m} K_l(T)[2c(l+1)-2l-1](2c-1)^{l-1} \qquad (25)$$

Eqns.(24) and (25) were used in computing the partial excess free energy of mixing of both components Au and Ni in liquid Au-Ni alloys at different temperatures over the entire concentration range using optimized coefficients listed in Table 2. Figure 7 shows the optimized values of excess free energy of mixing for the liquid Au-Ni alloys at investigated temperatures over that concentration range.

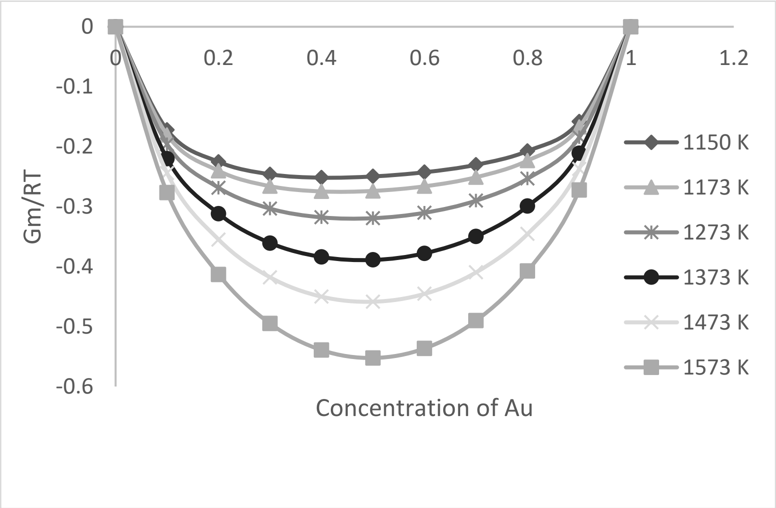


Fig. 6: Optimized G_M/RT versus concentration for liquid Au-Ni alloys at different temperatures

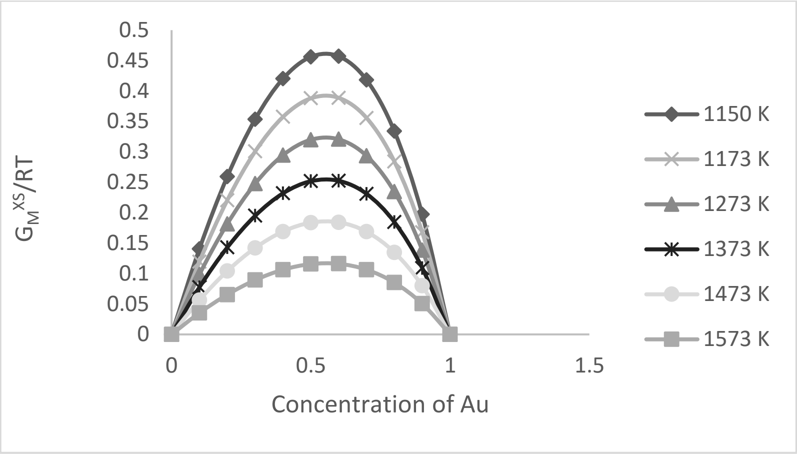


Fig. 7: Optimized excess free energy of mixing versus concentration for liquid Au-Ni alloys at different temperatures

The optimized values of activity coefficients γ_i in the entire concentration range of the component i (γ_i) (i≡Au; Ni) at the corresponding temperature were determined from the relation:

$$\bar{G}_{M,i}^{XS} = RT \ln \gamma_i \tag{26}$$

with

$$\gamma_i = \frac{a_i}{c_i} \tag{27}$$

where a_i and c_i are the activity and concentration of the component i in the liquid alloys at corresponding temperature. Table 3 – Table 8 show the optimized values of partial excess free energy of mixing, the corresponding activity coefficients, and activity of both components involved in liquid Au-Ni alloys in the entire concentration range at temperatures T = 1150 K - 1573 K, respectively.

Table 3: **Optimized value of partial excess free energy of mixing, activity coefficient and activity of both the components in liquid Au-Ni alloys at 1150 K**

Au-Component						Ni-Component				
c$_{Ni}$	$\bar{G}_{M,}^{XS}$ Au	Inɣ$_{Au}$	ɣ$_{Au}$	a$_{Au}$	Ina$_{Au}$	$\bar{G}_{M,}^{XS}$ Ni	Inɣ$_{Ni}$	ɣ$_{Ni}$	a$_{Ni}$	Ina$_{Ni}$
0.1	14290.266	1.495	4.458	0.446	-0.808	21155.596	2.213	9.140	0.914	-0.090
0.2	11615.108	1.215	3.370	0.674	-0.395	13857.622	1.449	4.260	0.852	-0.160
0.3	9169.424	0.959	2.609	0.783	-0.245	9486.610	0.992	2.697	0.809	-0.212
0.4	6969.605	0.729	2.073	0.829	-0.187	6392.069	0.669	1.951	0.781	-0.248
0.5	5033.133	0.526	1.693	0.846	-0.167	4014.538	0.420	1.522	0.761	-0.273
0.6	3378.664	0.353	1.424	0.854	-0.157	2029.520	0.212	1.236	0.742	-0.299
0.7	2026.108	0.212	1.236	0.865	-0.145	114.027	0.012	1.012	0.708	-0.345

0.8	996.737	0.104	1.110	0.888	-0.119	-2286.867	-0.239	0.787	0.630	-0.462
0.9	313.272	0.033	1.033	0.930	-0.073	-6816.074	-0.713	0.490	0.441	-0.818

Table 4: Optimized value of partial excess free energy of mixing, activity coefficient and activity of both the components in liquid Au-Ni alloys at 1173 K

Au-Component						Ni-Component				
c_{Ni}	$\bar{G}^{XS}_{M,\ Au}$	In$Ɣ_{Au}$	$Ɣ_{Au}$	a_{Au}	Ina$_{Au}$	$\bar{G}^{XS}_{M,\ Ni}$	In$Ɣ_{Ni}$	$Ɣ_{Ni}$	a_{Ni}	Ina$_{Ni}$
0.1	13836.540	1.419	4.132	0.413	-0.884	21570.501	2.212	9.132	0.913	-0.091
0.2	11989.519	1.154	3.170	0.634	-0.456	14101.266	1.446	4.246	0.849	-0.163
0.3	9469.934	0.911	2.487	0.746	-0.293	9599.367	0.984	2.676	0.803	-0.220
0.4	720s2.905	0.693	2.000	0.800	-0.223	6380.168	0.654	1.924	0.769	-0.262
0.5	5206.397	0.501	1.650	0.825	-0.192	3871.805	0.397	1.487	0.744	-0.296
0.6	3499.582	0.337	1.400	0.840	-0.174	1742.005	0.179	1.196	0.717	-0.332
0.7	2102.920	0.202	1.224	0.857	-0.154	-340.051	-0.035	0.966	0.676	-0.392
0.8	1038.267	0.100	1.105	0.884	-0.123	-2941.856	-0.302	0.740	0.592	-0.525
0.9	328.974	0.032	1.032	0.929	-0.074	-7740.730	-0.794	0.452	0.407	-0.899

Table 5: Optimized value of partial excess free energy of mixing, activity coefficient and activity of both the components in liquid Au-Ni alloys at 1273 K

Au-Component						Ni-Component				
c_{Ni}	$\bar{G}^{XS}_{M,\ Au}$	In$Ɣ_{Au}$	$Ɣ_{Au}$	a_{Au}	Ina$_{Au}$	$\bar{G}^{XS}_{M,\ Ni}$	In$Ɣ_{Ni}$	$Ɣ_{Ni}$	a_{Ni}	Ina$_{Ni}$
0.1	12702.051	1.200	3.321	0.332	-1.102	23383.739	2.209	9.110	0.911	-0.093
0.2	10969.452	0.977	2.657	0.531	-0.632	16117.885	1.436	4.204	0.841	-0.173
0.3	8680.407	0.773	2.167	0.650	-0.431	10792.437	0.962	2.616	0.785	-0.242
0.4	6618.393	0.590	1.803	0.721	-0.327	6879.187	0.613	1.846	0.738	-0.303
0.5	4799.574	0.428	1.534	0.767	-0.266	3715.965	0.331	1.392	0.696	-0.362
0.6	3241.208	0.289	1.335	0.801	-0.222	916.085	0.082	1.085	0.651	-0.429
0.7	1961.709	0.175	1.191	0.834	-0.182	-1905.744	-0.170	0.844	0.591	-0.526

0.8	980.755	0.087	1.091	0.873	-0.136	-5407.495	-0.482	0.618	0.494	-0.705
0.9	319.363	0.028	1.029	0.926	-0.077	-11524.766	-1.027	0.358	0.322	-1.132

Table 6: **Optimized value of partial excess free energy of mixing, activity coefficient and activity of both the components in liquid Au-Ni alloys at 1373 K**

Au-Component						Ni-Component				
c_{Ni}	$\bar{G}^{XS}_{M,}$ Au	$\mathrm{In}\gamma_{Au}$	γ_{Au}	a_{Au}	Ina_{Au}	$\bar{G}^{XS}_{M,}$ Ni	$\mathrm{In}\gamma_{Ni}$	γ_{Ni}	a_{Ni}	Ina_{Ni}
0.1	11204.002	0.982	2.668	0.267	-1.321	25192.942	2.207	9.088	0.909	-0.096
0.2	9656.162	0.801	2.228	0.446	-0.808	17192.373	1.426	4.163	0.833	-0.183
0.3	7661.680	0.636	1.888	0.566	-0.568	11317.525	0.939	2.557	0.767	-0.265
0.4	5861.921	0.486	1.626	0.650	-0.430	6890.690	0.572	1.771	0.708	-0.345
0.5	4270.778	0.354	1.425	0.713	-0.339	3196.327	0.265	1.304	0.652	-0.428
0.6	2903.080	0.241	1.272	0.763	-0.270	-185.484	-0.015	0.985	0.591	-0.526
0.7	1774.657	0.147	1.159	0.811	-0.209	-3673.467	-0.305	0.737	0.516	-0.661
0.8	902.418	0.075	1.078	0.862	-0.148	-7979.537	-0.662	0.516	0.413	-0.885
0.9	304.429	0.025	1.026	0.923	-0.080	-15188.229	-1.260	0.284	0.255	-1.365

Table 7: **Optimized value of partial excess free energy of mixing, activity coefficient and activity of both the components in liquid Au-Ni alloys at 1473 K**

Au-Component						Ni-Component				
c_{Ni}	$\bar{G}^{XS}_{M,}$ Au	$\mathrm{In}\gamma_{Au}$	γ_{Au}	a_{Au}	Ina_{Au}	$\bar{G}^{XS}_{M,}$ Ni	$\mathrm{In}\gamma_{Ni}$	γ_{Ni}	a_{Ni}	Ina_{Ni}
0.1	9342.391	0.763	2.144	0.214	-1.540	26998.109	2.205	9.066	0.907	-0.098
0.2	8049.655	0.625	1.868	0.374	-0.985	18250.389	1.416	4.122	0.824	-0.193
0.3	6413.748	0.498	1.645	0.493	-0.706	11804.776	0.916	2.499	0.750	-0.288
0.4	4933.484	0.383	1.466	0.587	-0.533	6833.492	0.530	1.699	0.680	-0.386
0.5	3620.005	0.281	1.324	0.662	-0.412	2567.045	0.199	1.220	0.610	-0.494
0.6	2485.198	0.193	1.213	0.728	-0.318	-1448.353	-0.112	0.894	0.536	-0.623
0.7	1541.760	0.120	1.127	0.789	-0.237	-5665.538	-0.440	0.644	0.451	-0.796
0.8	803.254	0.062	1.064	0.851	-0.161	-10851.094	-0.842	0.431	0.345	-1.065
0.9	284.171	0.022	1.022	0.920	-0.083	-19239.250	-1.493	0.225	0.202	-1.598

Table 8: **Optimized value of partial excess free energy of mixing, activity coefficient and activity of both the components in liquid Au-Ni alloys at 1573 K**

Au-Component	Ni-Component

c_{Ni}	$\bar{G}^{XS}_{M,}$ Au	Inγ_{Au}	γ_{Au}	a_{Au}	Ina$_{Au}$	$\bar{G}^{XS}_{M,}$ Ni	Inγ_{Ni}	γ_{Ni}	a_{Ni}	Ina$_{Ni}$
0.1	7117.216	0.544	1.723	0.172	-1.758	28799.244	2.202	9.044	0.904	-0.100
0.2	6149.927	0.448	1.566	0.313	-1.161	19291.931	1.406	4.081	0.816	-0.203
0.3	4936.617	0.360	1.433	0.430	-0.844	12254.181	0.893	2.443	0.733	-0.311
0.4	3833.087	0.279	1.322	0.529	-0.637	6707.596	0.489	1.631	0.652	-0.427
0.5	2847.256	0.208	1.231	0.615	-0.486	1828.127	0.133	1.143	0.571	-0.560
0.6	1987.561	0.145	1.156	0.694	-0.366	-2872.526	-0.209	0.811	0.487	-0.720
0.7	1263.018	0.092	1.096	0.768	-0.265	-7881.964	-0.575	0.563	0.394	-0.931
0.8	683.266	0.050	1.051	0.841	-0.173	-14022.165	-1.022	0.360	0.288	-1.245
0.9	258.591	0.019	1.019	0.917	-0.087	-23677.823	-1.726	0.178	0.160	-1.831

Figure 8 presents the optimized values of activities of both components of liquid Au-Ni alloys at various temperatures T= 1150 K, 1173 K, 1273 K, 1373 K, 1473 K, and 1573 K, over the entire concentration range. Using Equation (10) the optimized values of the concentration-concentration fluctuations in the long wavelength limit $S_{cc}(0)$ of liquid Au-Ni alloys at different temperatures over the entire concentration range have been computed and presented in Fig. 9. The concentration fluctuations in the long wavelength limit decrease as the temperature increases, shifting towards the ideal value of concentration fluctuations $S_{cc}^{id}(0)$ as the temperature increases, but remaining greater than the ideal value of concentration fluctuations $S_{cc}^{id}(0)$ at each concentration, this suggests that the liquid Au-Ni alloy exhibits segregating characteristics throughout the concentration range, but that the segregation characteristics diminish as the temperature increases.

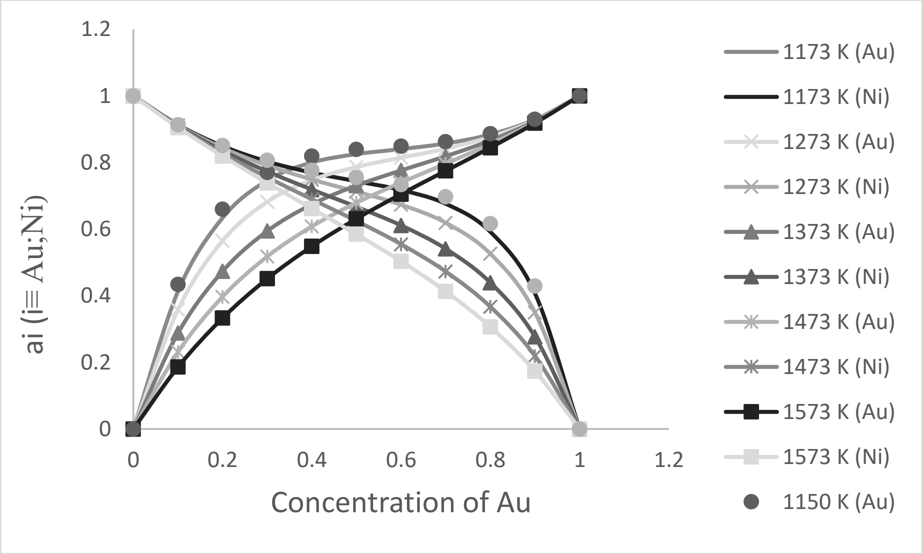


Fig. 8: Optimized activity coefficients (a_i) (I ≡Au ; Ni) versus concentration of liquid Au-Ni alloys at different temperatures

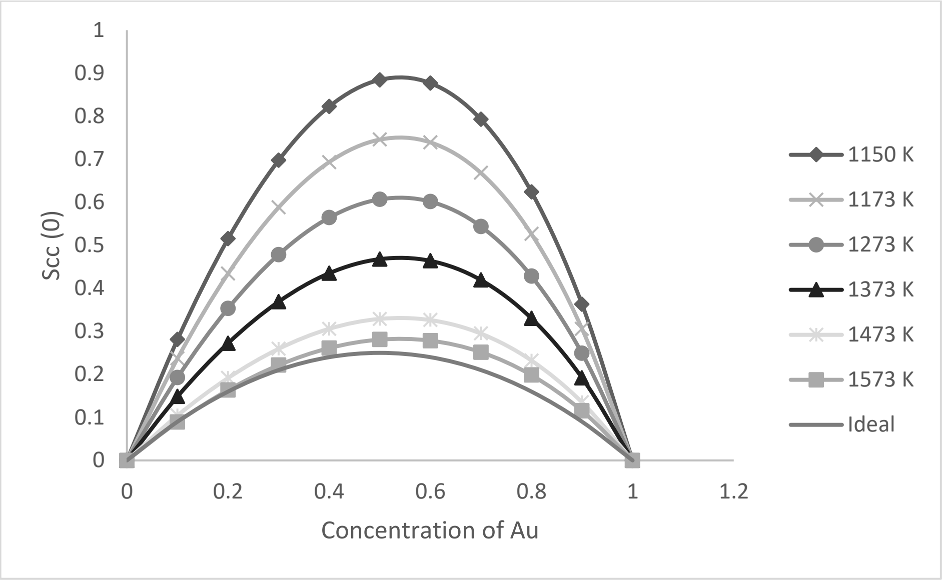


Fig. 9: Optimized Scc(0) versus concentration of liquid Au-Ni alloys at different temperatures

Figure 10 and 11 shows the optimized values of heat of mixing and entropy of mixing for liquid Au-Ni alloys at different temperatures, T= 1150 K, 1173 K, 1273 K, 1373 K, 1473 K and 1573 K over that concentration range, respectively.

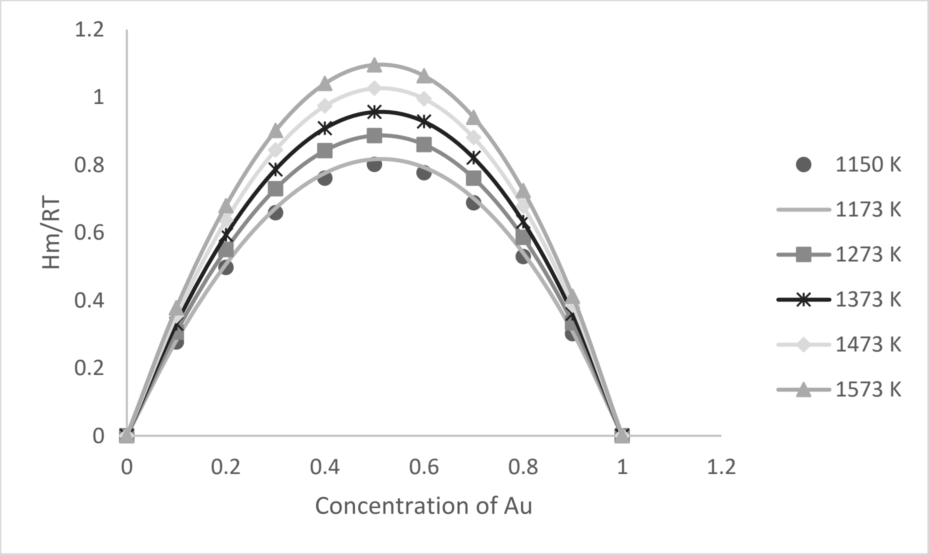


Fig. 10: Optimized values heat of mixing versus concentration for liquid Au-Ni alloys at different temperatures

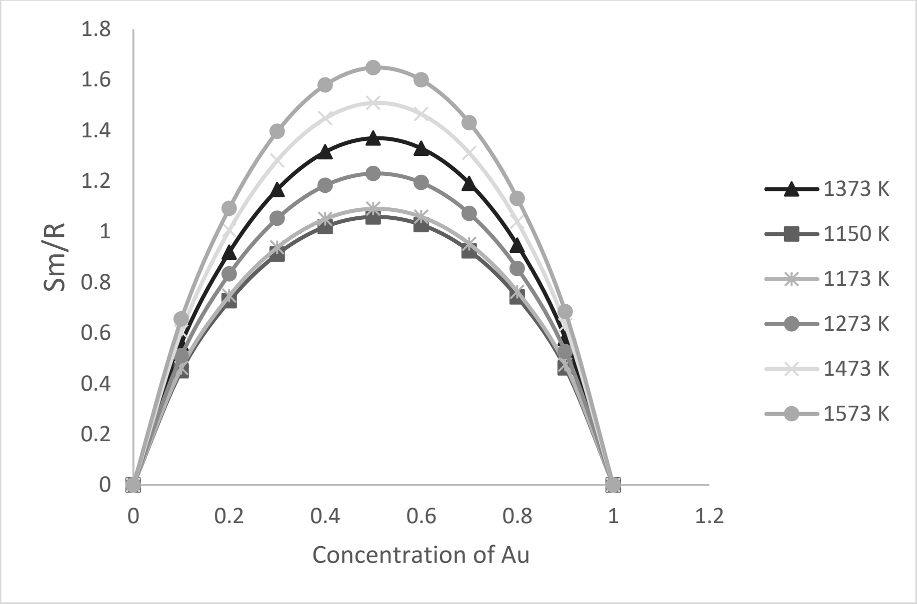


Fig. 11: Optimized values entropy of mixing versus concentration for liquid Au-Ni alloys at different temperatures

The temperature dependence of Warren-Cowley chemical short order parameter **(α_1)** in the entire concentration range is shown in Fig. 12, which shows the optimized values of Warren-Cowley chemical short order parameter **(α_1)** obtained from relation (13) on taking Z = 10 for liquid Au-Ni alloys at different temperatures. Using the optimized parameters, the diffusion coefficients of liquid Au-Ni alloys at different temperatures in the entire concentration range were computed, as shown in Fig.13. The diffusion coefficient for liquid Au-Ni alloys increases as the temperature increases across the entire concentration range.

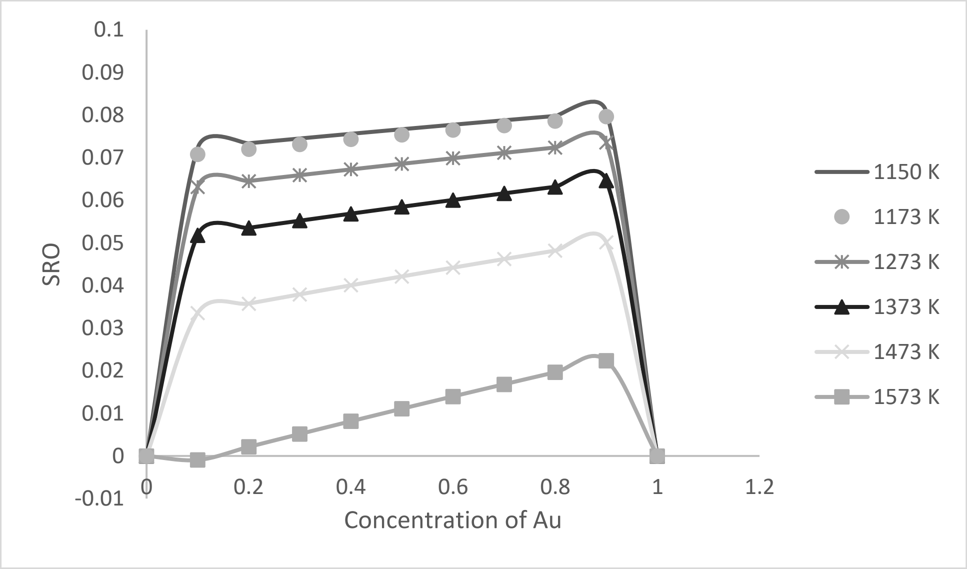


Fig. 12: Optimized SRO versus concentration for liquid Au-Ni alloys at different temperatures

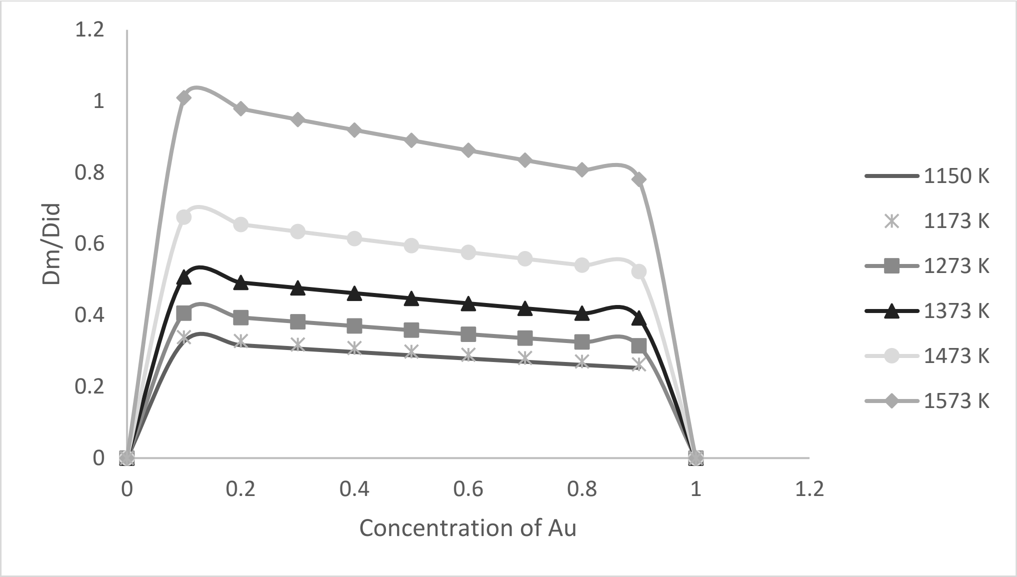


Fig. 13: Optimized D_M/D_{id} versus concentration for liquid Au-Ni alloys at different temperatures

4. Conclusion

The energetics of mixing in binary liquid Au-Ni alloys has been investigated with particular attention on the mixing and transport properties within the frame of Quasi Lattice Theory through optimization method. The model as used has successfully predicted the various thermodynamic properties investigated and the transport properties with a view to correlating the thermodynamics and transport properties for a better understanding of the energetics of mixing behaviour in the liquid Au-Ni alloy melts. The study shows that liquid Au-Ni alloy is a segregated system. The order energy parameter (W) which plays a significant role in determining the mixing properties of the liquid Au-Ni alloys with their values fixed at each temperature (Table 1) in liquid Au-Ni alloys are positive. These values decrease with increasing temperature thus indicating that the degree of segregation in the liquid Au-Ni alloys decreases as the temperature increases. The study shows that the optimization approach is useful to obtaining consistent set of thermodynamic model parameters theoretically which helps in extrapolating into the temperature and concentration regions in which the direct experiment is not feasible.

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