Study of energy of formation for Fe$_x$Ni$_{1-x}$ liquid binary alloys

M. S. S. Chowdhury[*1]**, Mohammad A. Rashid**[2]**, M. A. Rahman**[3]
and A. Z. Ziauddin Ahmed[4]

[1]*Plasma Physics Division, Atomic Energy Centre, Dhaka-1000, Bangladesh*
[2]*Department of Physics, Jashore University of Science and Technology, Jashore-7408, Bangladesh*
[3]*Electronics Division, Atomic Energy Centre, Dhaka-1000, Bangladesh*
[4]*BSB Cambrian Education Group, Dhaka, Bangladesh*

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Abstract

In this present study we have systematically calculated the free energy of formation for Fe$_x$Ni$_{1-x}$ binary alloys at a thermodynamic state $T = 1920$ K. A microscopic theory bases on first order perturbation theory along with a reference hard sphere liquid has been applied. The interionic interaction is described by Bretonnet-Silbert local pseudopotential that capable of takes into account the s-d hybridization in electro-ion interaction in transition metals. The effective hard sphere diameters have been determined using linearized Weeks-Chandler-Andersen (LWCA) perturbation theory and the partial structure calculated in line with Ashcroft and Langreths original work. The calculated theoretical value and available experimental data for free energy of formation are in agreement quite satisfactorily.

Keywords: Free energy, Energy of formation, Liquid binary alloys, Pseudopotential

1 Introduction

The measurement of thermodynamic properties of the liquid binary alloys have great importance in industrial metallurgy. Often it is very difficult and expensive to measure them experimentally, due to extreme conditions, like high temperature, high pressure, high reactivity, etc [1]. Hence, theoretical or computational studies are popular. In this paper we have presented a systematic theoretical investigation on free energy of formation of Fe$_x$Ni$_{1-x}$ liquid binary alloys at 1920 K.

For years, understanding the mixing behavior of alloys is of great interest to both scientist and industrialist due to the fact that often interionic properties, and consequently physical properties of alloys sometimes largely differ from their constituent elements. Studying the energy of formation of binary alloy is very important to understand their characteristic properties; for example, compound formation, segregation or phase separation, etc.

Fi-Ni alloys are of great interest because of a broad range of magnetic properties. This alloys are among the most important soft magnetic alloys [2]. Permalloy, 20% Fe and 80% Ni, is an

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*Corresponding author: E-mail:salekin@baec.gov.bd

interesting candidate for magnetic core and magnetic shielding applications for exceptionally high magnetic permeability. Permalloy also has prospect a wide range of application in nanotechnologies considering (/due to) low coercivity, negligible magnetic restriction, large anisotropic magnetoresistance and possibility of reducing its size at nanoscale [3]. Superalloys, a Ni-Fe or Ni-Fe and Co alloys, used in jet engines for exceptional heat resistance capacity [4].

Till date, there are several established theories to study energy of formation for liquid binary alloys. For example, the empirical linear free energy theory [5], quasi lattice theory [6], computer simulations [7], the general microscopic theory (GMT) [8], etc. The empirical linear free energy theory has a limitation that it can be applicable only when solute concentration is very low [9]. In quasi lattice theory, the activity expressed in terms of the formation of mixing and the average interionic interaction energy through Gibbs free energy and then energy of formation is extracted by fitting with experimental data [10]. DFT and similar computer simulations are computationally much expensive. The general microscopic theory (GMT) is built on electronic theory of metals, the static structure factor and first order perturbation theory. The static structure factor can be obtained from interionic pair interaction with the help of statistical mechanics and perturbation theory [8]. All the components in GMT are easily understandable from physical point of view, simple for calculation and proved successful for liquid binary alloys [11].

In our current system, Fe_xNi_{1-x}, both elements, Fe and Ni, are transition metals and both have completely filled $4s$ band and partially filled $3d$ band. Physical properties of transition metals are greatly influenced by d band electrons through $s-d$ hybridization [12, 13]. The effect of $s-d$ hybridization is very important in alloys and sometimes it changes with the proportion of the constituent elements [14]. Therefore a model is required which can properly take into account the d band effect in the interionic interactions.

In 1992, Bretonnet and Silbert (BS) proposed a model [15] to describe interionic interactions for liquid transition metals. Bretonnet and Silbert model considers $s-p$ and d bands separately within conventional/traditional pseudopotential formalism where $s-p$ band described through the empty core model and d band is derived from the d band scattering phase-shift via inverse scattering approach. The BS pseudopotential has a very simple from and easy to handle numerically. This is why in our current study BS pseudopotential is used.

Another essential component of the first principle perturbation theory is a reference liquid of hard spheres (HS) of two effective hard sphere diameters that resembles the real system of our interest [16, 17]. We have employed HS liquid within Percus-Yevick approximation (HSPY) [18] as reference system here and determined the effective hard sphere diameters using Linearized Week-Chandler- Andersen (LWCA) theory [19].

2 Theories

The applied theories to calculate the free energy of formation are briefly presented below:

2.1 The effective pair potentials

We have used BS potential in our current research. The BS potential single component metallic system [15]

$$
W_{\text{BS}}(r) \;=\; \begin{cases} \displaystyle\sum_{m=1}^{2} B_m \exp\left(\dfrac{-r}{ma}\right) & \text{for } r < R_c \\[2em] \dfrac{-Z}{r} & \text{for } r > R_c, \end{cases}
\tag{2.1}
$$

where a, R_c and Z are softness parameter, core radius and the effective s-electron occupancy number. The coefficients in the core are

$$B_1 \quad = \quad \frac{Z_s e^2}{R_c}\left(1 - \frac{2a}{R_c}\right)\exp\left(\frac{R_c}{a}\right) \tag{2.2}$$

$$B_2 \quad = \quad \frac{2Z_s e^2}{R_c}\left(\frac{a}{R_c} - 1\right)\exp\left(\frac{R_c}{2a}\right) \tag{2.3}$$

The mapping of the equation (2.1) onto a binary system is straight forward [20] and can be represented as $(i = 1, 2)$,

$$W_{i\text{BS}}(r) \quad = \quad \begin{cases} \sum\limits_{m=1}^{2} B_{mi}\exp\left(\frac{-r}{ma}\right) & \text{for } r < R_c \\ -Z_i/r & \text{for } r > R_c \end{cases} \tag{2.4}$$

and,

$$B_{1i} \quad = \quad \frac{Z_i e^2}{R_{ci}}\left(1 - \frac{2a_i}{R_c}\right)\exp\left(\frac{R_{ci}}{a_i}\right) \tag{2.5}$$

$$B_{2i} \quad = \quad \frac{2Z_i}{R_{ci}}\left(\frac{a_i}{R_{ci}} - 1\right)\exp\left(\frac{R_{ci}}{2a_i}\right) \tag{2.6}$$

The effective interionic interaction can be represented as follows

$$\phi_{ij}(r) \quad = \quad \frac{Z_i Z_j}{r}\left[1 - \frac{2}{\pi}\int F_{ij}{}^N(q)\frac{\sin(qr)}{q}\,\mathrm{d}q\right] \tag{2.7}$$

where i and j refer the ionic species in the liquid binary alloys and $F_{ij}{}^N(q)$ is the normalized energy wavenumber characteristic

$$F_{ij}{}^N(q) \quad = \quad \left[\frac{q^2}{\pi a \rho \sqrt{Z_i Z_j}}\right]^2 W_i(q)\,W_j(q)\left[1 - \frac{1}{\varepsilon(q)}\right]\left[\frac{1}{1 - G(q)}\right] \tag{2.8}$$

where $W(q)$, $\varepsilon(q)$ and $G(q)$ are unscreened form factor, dielectric function and local form factor respectively [21].

The ionic number density is defined as

$$\rho \quad = \quad \frac{\rho\rho'}{C_1\rho_2 + C_2\rho_1}, \tag{2.9}$$

where $C_1 = x$ and $C_2 = 1 - x$.

2.2 Partial pair correlation function for HS binary liquids

Partial structure factor $S_{ij}(q)$ has been calculated according to Ashcroft and Langreth (AL) original work [22]. The essential components of $S_{ij}(q)$ are concentrations of two HS in mixtures and the effective hard sphere diameters. The values of HSD are calculated using LWCA perturbation theory [19]. The pair correlation function can be obtained by the Fourier transform of corresponding partial structure factor as follows

$$g_{ij}(r) \quad = \quad 1 + \frac{1}{(2\pi)^3\rho\sqrt{C_i C_j}}\int_0^\infty (S_{ij} - \delta_{ij})\exp(i\bar{q}.\bar{r})\mathrm{d}^3 r \tag{2.10}$$

2.3 Energy of formation for liquid binary alloys

The Helmholtz free energy per ion for an alloy within first perturbation theory can be written as:

$$F = F_{vol} + F_{eg} + F_{HS} + F_{Tail}, \tag{2.11}$$

where F_{eg}, F_{HS}, F_{Vol} and F_{Tail} denote the electron gas, hard sphere, volume dependent and tail dependent contribution in free energy.

The electron gas contribution, in Rydberg units, [23] to the free energy per electron can be written as,

$$F_{eg} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.031 \ln r_s - 0.115 \tag{2.12}$$

where r_s is the dimensionless parameter defined as,

$$r_s = \frac{1}{a_0}\left(\frac{3}{4\pi\rho Z}\right)^{\frac{1}{3}} \tag{2.13}$$

with a_0 being the first Bohr radius.

Free energy per atom of the reference HS liquid is [16]

$$
\begin{aligned}
\frac{F_{HS}}{Nk_BT} &= \sum_i C_i\left[-\ln(\Lambda_i^3 v) + \ln C_i\right] - \frac{3}{2}\left(\frac{5}{3} - y_1 + y_2 + y_3\right) \\
&\quad + \frac{(3y_2 + 2y_3)}{(1-\xi)} + \frac{3}{2}\left(1 - y_1 - y_2 - \frac{1}{3}y_3\right)\frac{1}{(1-\xi)^2} \\
&\quad + (y_3 - 1)\ln(1-\xi)
\end{aligned} \tag{2.14}
$$

where

$$
\begin{aligned}
\Lambda &= \left[\frac{2\pi\hbar^2}{m_i^{C_i} m_j^{C_j} k_B T}\right]^{\frac{1}{2}} \\
\xi &= \sum_i \frac{C_i \pi \rho_i \sigma_{ii}^3}{6} \\
y_1 &= \sum_{j>i} \Delta_{ij}\left[\frac{\sigma_{ii} + \sigma_{jj}}{(\sigma_{ii}\sigma_{jj})^{\frac{1}{2}}}\right] \\
y_2 &= \sum_{j>i} \Delta_{ij}\sum_\gamma \left[\frac{\xi_\gamma}{\xi}\right]\left[\frac{(\sigma_{ii}\sigma_{jj})^{\frac{1}{2}}}{\sigma_{\gamma\gamma}}\right] \\
y_3 &= \left[\sum_i \left(\frac{\xi_i}{\xi}\right)^{\frac{2}{3}} C_i\right]^3 \\
\Delta_{ij} &= \left[\frac{(\xi_i\xi_j)^{\frac{1}{2}}}{\xi}\right]\left[\frac{(\sigma_{ii} - \sigma_{jj})^2}{\sigma_{ii}\sigma_{jj}}\right](C_iC_j)^{\frac{1}{2}}
\end{aligned}
$$

In these equations C_i, ρ_i, ξ_i, and σ_{ii} denote the atomic concentration, ionic number density, ionic mass and the effective hard sphere diameter of the ith component respectively.

The volume contribution to the free energy is [24],

$$F_{vol} = \frac{1}{32\pi^3}\int_{q=0}^{\infty} q^4\left\{\frac{1}{\varepsilon(q)} - 1\right\}|v_i(q)|^2 \mathrm{d}q - \frac{ZE_F}{3P} \tag{2.15}$$

where Z is the effective valency of the concerned alloy, defined as $Z = xZ_1 + (1-x)Z_2$, and $v(q)$ is the average form factor of the of the electron-ion interaction for the alloy, $\epsilon(q)$ is the dielectric function, E_F Fermi energy for electrons. Here,

$$P \quad = \quad \frac{\chi_{el}}{\chi_F}$$

where χ_{el} and χ_F are the isothermal compressibility of the interacting and non-interacting electrons respectively. Lastly, the potential tail contribution to the free energy is,

$$F_{Tail} \quad = \quad D\sum_{ij} C_i C_j M_{ij} \tag{2.16}$$

where

$$
\begin{aligned}
D &= 2\pi\rho \\
M_{ij} &= \int_\sigma^\infty v_{ij}(r) g_{ij}^{\mathsf{HS}}(r, \sigma_{ij}, \rho) r^2 \mathrm{d}r
\end{aligned}
$$

In above equation $v_{ij}(r)$ and $g_{ij}^{\mathsf{HS}}(r)$ are partial pair potential and the correlation functions respectively.

Now, the energy of formation reads,

$$
\begin{aligned}
\Delta F &= F - \sum_i C_i F^{(i)} \\
&= \Delta F_{vol} + \Delta F_{HS} + \Delta F_{eg} + \Delta F_{Tail} \tag{2.17}
\end{aligned}
$$

where $F^{(i)}$ represents the free energy of the constituent elements of the liquid binary alloys.

3   Results and Discussion

We have calculated free energy of formation using the first order perturbation theory and the general microscopic theory (GMT) of metals. The knowledge of the effective pair potentials and the pair distribution functions have been required in this formalism. The partial interionic interactions (effective partial pair potentials) were calculated from the Bretonnet-Silbert (BS) model [15]. The reason behind using BS-model was that it can take into account the necessary d-band effects which is crucially important for study of transition metal alloys of our concern. There are three essential parameters: the empty-core radius R_c, the effective s-electron occupancy number Z, and the softness parameter a, to be adjusted in the BS-model for an effective calculation.

Generally, the empty-core radii, R_c values, are determined by fitting the physical properties of the system of interest, such as bulk modulus, electrical resistivity or structural data [25]. Since the energy of formation is a very small quantity, it considerably changes with values of R_c. So, the most reliable values for R_c [26] are taken . During choosing Z we have followed the concept that the effect of hybridization between $s-p$ and d electrons can be approximately accounted for by changing the relative occupancy of $s-p$ band for elemental systems [27, 28]. The value of $Z = 1.4$ and 1.5 for Fe and Ni are chosen, respectively. These values are in agreement with the self-consistent study of Moriarty [29]. It is shown that the values of Z lie in the range from 1.1 to 1.8 for $3d$ transition metals [29]. Though, in principle, there is no such restriction to use different but suitable values of Z for different systems as long as the self-consistent calculations of charge transfer support these values. For example, Bhuiyan et al. used $Z = 1.4$ for $3d$ metals [27, 30] and $Z = 1.3 - 1.7$ for less simple metals [11] and and Wills and Harrison used $Z = 1.5$ for all metals of $3d$, $4d$ and $5d$ series [26]. Finally, the values of softness parameter have been determined by fitting to the experimental data for static structure factors at low q values [31]. The values of core radius R_c, softness parameter a, number density ρ, and effective valency Z which are used in the calculation are listed in Table 1.

Table 1: Values of different parameters for Fe and Ni that are used in the present study.

Element	R_c (a.u.)	a (a.u.)	ρ (Å^{-3})	Z
Fe	1.42	0.3	0.07504	1.4
Ni	1.06	0.22	0.07862	1.5

Figure 1 shows the effective partial pair potentials for three different alloys of Fe$_x$Ni$_{1-x}$ for $x = 0.1$, 0.5 and 0.9, respectively. The position of the principal minima and the depth of the potential are the result of the balance between the repulsive and attractive interactions in metals. In the pseudopotential formalism this is demonstrated by the direct interaction between different ion cores and the indirect interaction via the conduction electrons. From figures it is seen that the depth of the well of the potential is largest for $v_{22}(r)$ and the smallest for $v_{11}(r)$ for all concentrations. The well for $v_{12}(r)$ lies in between. These results show that the binding energy of Fe is larger than Ni, which is supported by experiments.
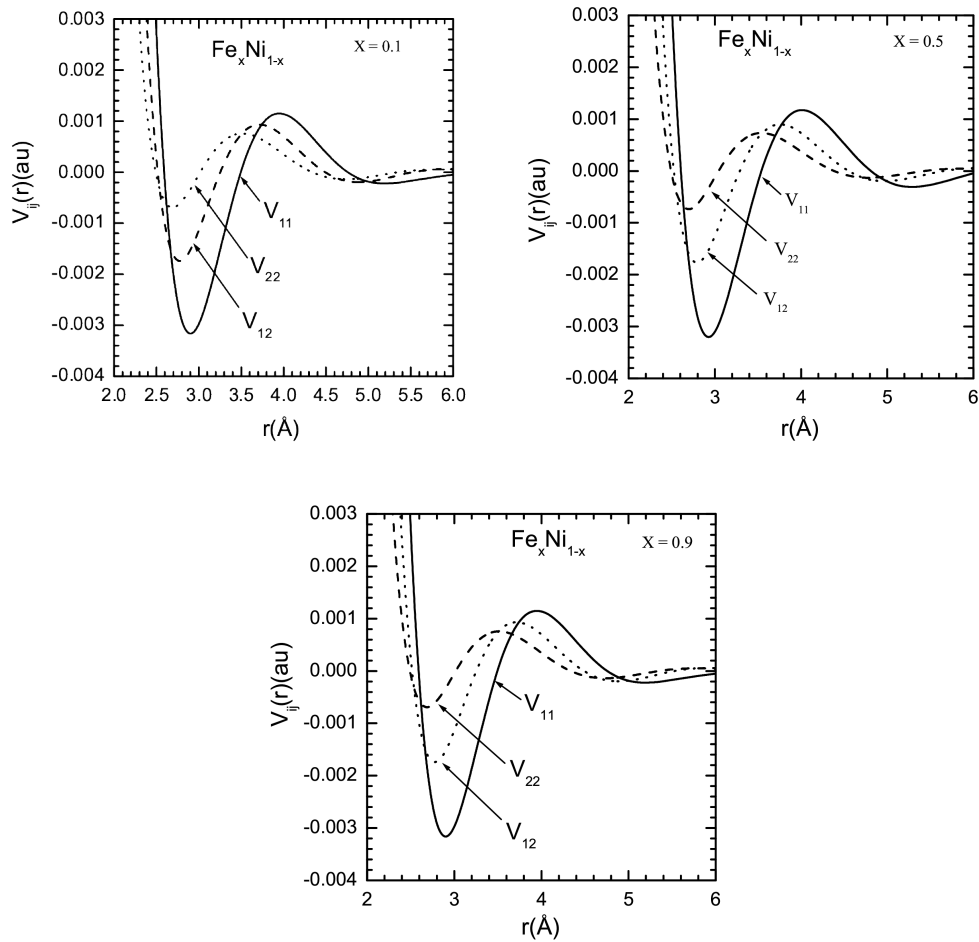
Figure 1: Partial pair potentials for Fe$_x$Ni$_{1-x}$ binary alloy at $x = 0.1$, 0.5 and 0.9.

To calculating the partial pair correlation functions, the essential ingredients are the effective hard sphere diameters (HSDs) of the elements of the alloy. The effective HSDs are determined by using the LWCA perturbation theory [19]. In our calculation the hard sphere diameters for Fe and Ni are found to be $\sigma_1 = 2.5351$ Å and $\sigma_2 = 2.2931$ Å, respectively. In Table 2, the effective hard sphere diameters of elements for $Fe_x Ni_{1-x}$ liquid binary alloy at different concentration are presented.

Table 2: Effective HSDs for Fe and Ni at different concentration in $Fe_x Ni_{1-x}$ binary alloys.

$C_1 (= x)$	σ_{11} (Å)	σ_{22} (Å)
0.1	2.4987	2.2952
0.2	2.5034	2.2963
0.3	2.5073	2.2982
0.4	2.5120	2.3001
0.5	2.5154	2.3004
0.6	2.5193	2.3030
0.7	2.5234	2.3048
0.8	2.5270	2.3060
0.9	2.5300	2.3080

Figure 2 displays the partial pair correlation functions $g_{ij}(r)$, for the effective reference hard sphere liquids. The figures show a comparative feature of Fe and Ni for the effective pair correlation functions. For $x = 0.1$, the principal peak for $g_{22}(r)$ is much larger than that of $g_{11}(r)$. But the situation gradually changes as the concentration x increases and for $x = 0.9$, $g_{11}(r)$ becomes greater. Because for $x = 0.1$ the probability of finding Fe is lesser than that of Ni and it increases with the increase in concentration and so the $g_{11}(r)$.
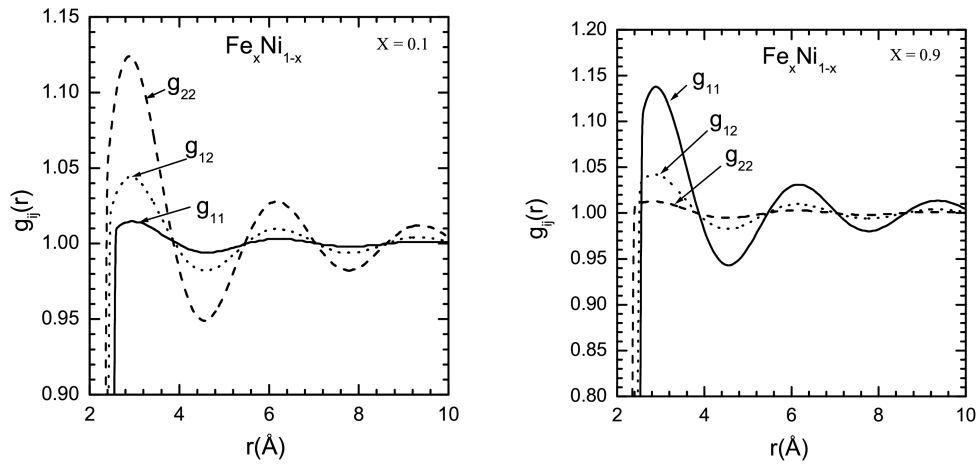

Figure 2: Partial pair correlation functions for $Fe_x Ni_{1-x}$ liquid binary alloy at $x = 0.1$, and 0.9.

The contributions of different parts to the free energy and the total free energy of the liquid binary alloys $Fe_x Ni_{1-x}$ at 1920 K temperature is presented in Figure 3. It was found that the largest contributions arises from electron gas part, F_{eg} while the least is from tail part, F_{Tail}. It can also be

noted from the plots that the variation in the total free energy with the variation of concentration x is mostly from the hard sphere part, F_{HS}. As the concentration x increases F_{HS} increases almost exponentially. It can also be noted from the plots that with the increase of concentration of Fe in the liquid binary alloy $Fe_x Ni_{1-x}$, the tail part F_{Tail} decreases while the values of all the other components of the total free energy increase resulting an increase in the total free energy of the alloy. For the $Fe_x Ni_{1-x}$ alloys the total free energy is minimum at $x = 0.1$ and continue to increase with the increase of x without decreasing and reaches its maximum value at $x = 0.9$ as shown in the figure.
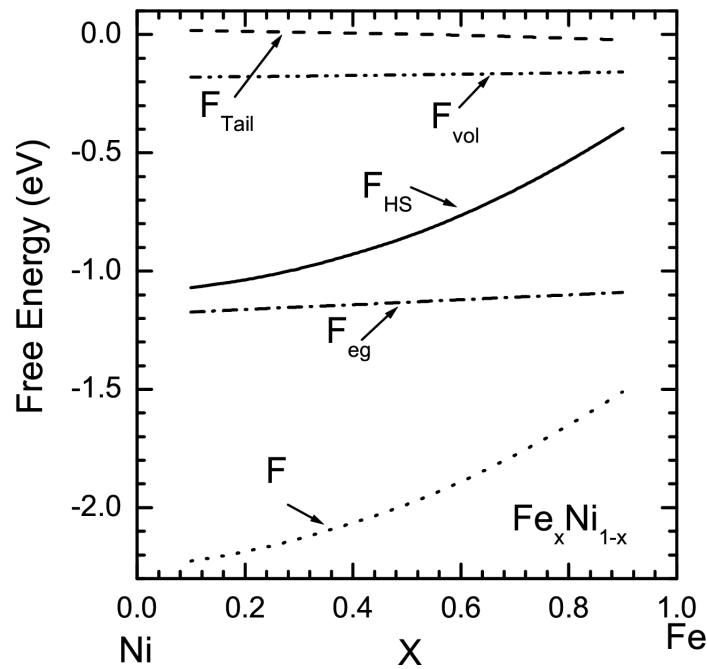

Figure 3: Free energy for $Fe_x Ni_{1-x}$ liquid binary alloys at the temperature 1920 K at different concentration x. Total free energy F, the sum of all the contributing parts, is presented by the doted line. All the symbols are defined in the text.

In Figure 4, we present the calculated energy of formation for $Fe_x Ni_{1-x}$ liquid binary alloys at 1920 K temperature. Total excess free energy, ΔF, is marked by solid line. The free energy of formation due to tail part of potential, electron gas, the reference HS liquid, and the volume term are labeled by ΔF_{Tail}, ΔF_{eg}, ΔF_{HS}, and ΔF_{Vol}, respectively. It can be noted from the plot that most of the contribution to the ΔF are comes from the hard sphere part. The value of ΔF for the binary alloy $Fe_x Ni_{1-x}$ decreases with the increase of concentration of Fe in the alloy. Around the equiatomic composition the value of ΔF reaches its minimum and then increases again with the increase of x in the $Fe_x Ni_{1-x}$ liquid alloy. From Figure 4 it can be noticed that, (i) the value of ΔF_{eg} remain almost constant for all concentrations of Fe, (ii) the value of ΔF_{Tail} first increases and then decreases with increasing concentrations of Fe, and (ii) the value of ΔF_{HS} have minimal value around the equiatomic composition and gradually increase on both sides.

We compare our theoretical result of energy of formation of the $Fe_x Ni_{1-x}$ liquid binary alloys with the available experimental data taken from Ref. [17]. The data that are found in literature for the alloy
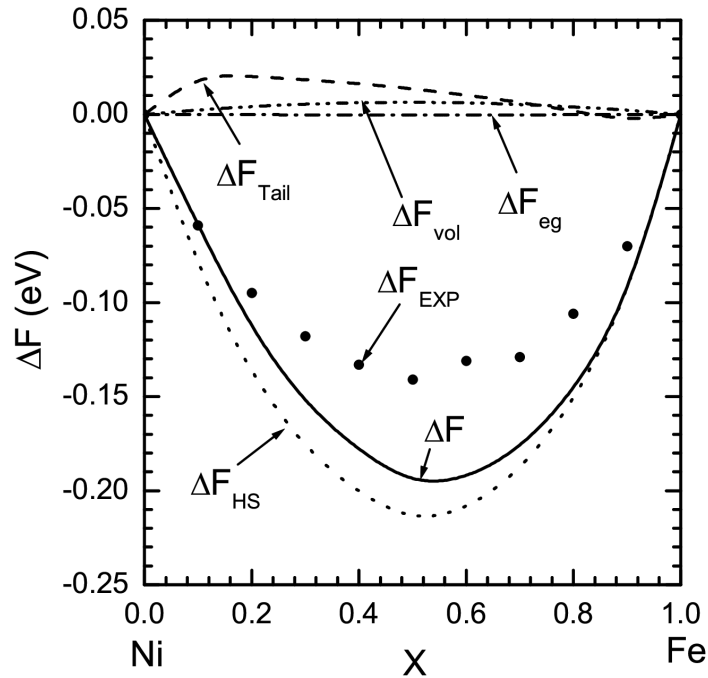
Figure 4: Energy of formation (and contributions of different parts to it) for Fe_xNi_{1-x} liquid binary alloy as a function of concentration x. Theoretical results, ΔF ($T = 1920$ K), are presented by solid line while the experimental data, ΔF_{EXP} ($T = 1873$ K), are marked by small filled black circles. All the symbols are defined in the text.

is at 1873 K while our calculations are performed at 1920 K. This is because during the calculation at 1873 K we found that for some concentration of Fe the alloy is in amorphous state rather than the liquid state. Despite the variation in temperature, we found an exact match with the experiment at $x = 0.1$ and the maximum deviation was found at $x = 0.5$ for the Fe_xNi_{1-x} liquid binary alloy. For other concentrations of Fe in Fe_xNi_{1-x} least deviations of the calculated values from the experiment are found at $x = 0.2$ and at $x = 0.8$. Overall, the theoretical values are close to the experimental results.

4 Conclusion

In this paper, we have presented a detailed systematic study of the energy of formation for Fe_xNi_{1-x} liquid binary alloys. The investigation was performed at an elevated temperature $T = 1920$ K. The results for energy of formation for liquid transition metals are found to be quite satisfactory, as far as agreement with experimental data is concerned. Bretonnet-Silbert model is used to describe the effective interionic interaction. We have used noninteger numbers for Z to account for the effect of $s - d$ hybridization in the potential. The LWCA theory was employed to determine the effective hard sphere diameter. Theoretical results also predict that a mixture of any proportion of liquid Fe and Ni forms an alloy which is in agreement with the experimental data.

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