A Statistical Model for Ternary Solid Solutions Containing both Substitutional and Interstitial Solute Atoms

By Donald H. Coplin*, John E. McGinness* and Rex B. McLellan*

A statistical model of ternary solid solutions involving both substitutional and interstitial solutes has been devised. In this model the substitutional solute atoms are distributed randomly in the lattice and the interstitial solute atoms are regarded as being apportioned into two sub-assemblies. In one sub-assembly the interstitial atoms have nearest neighbors which are all solvent atoms and in the other sub-assembly interstitial atoms can have one or more substitutional solute nearest neighbors. It is shown that, within certain limits, the fraction of interstitial atoms in each sub-assembly remains constant when the atom fraction of interstitial atoms in the ternary solution is varied but the atom fraction of substitutional atoms is held fixed.

The available data for the activity of carbon in Fe–u–C ternary solid solutions have been shown to be in excellent agreement with the theoretical activity equation for the interstitial solute deduced from the model.

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I. Introduction

This work represents an attempt to understand the thermodynamic behavior of dilute ternary solid solutions containing both substitutional and interstitial solute atoms in terms of composition-independent interaction energies and the statistical degeneracy of the solid solution crystal. Excess thermodynamic quantities are also considered but these arise from non-configurational terms in the entropy and are not dependent on composition. The solutions involved in this treatment have compositions in the range of less than about 10 at% substitutional solute and less than about 2% interstitial solute.

At this time much data is available on the thermodynamic behavior of this type of solution where the interstitial component is carbon. Several recent investigations have provided data for the variation of the carbon activity with both the interstitial and substitutional solute content. Some attempts have been made to explain the available activity data and a brief discussion of these previous models will be given before the present model is described in detail.

Iwase and Kachi(1) calculated the partition function of the ternary solution by assuming that the C-atoms were distributed in a non-random manner determined by the number of C-C nearest neighbors and the number of substitutional solute atoms. However, their treatment did not contain any contribution to the free energy arising from non-configurational terms and their expression for the concentration dependence of the C-activity is not consistent with the experimental data.

An atomistic model was also developed by Kirkaldy and Purdy(2) who described the energetics of the solution by pairwise interaction energies. However, C-atoms were assumed to be distributed in a regular manner despite the presence of the substitutional solutes which can interact strongly with the C-atoms. Furthermore this model contained no excess terms due to non-configurational effects.

Aaronson, Domian, and Pound(3) have discussed binary Fe–C alloys in terms of the Lacher, Fowler and Guggenheim(4) model for interstitial solutions. The most important parameter in this model is \( \omega_p \), the pairwise interaction energy between adjacent C-atoms in austenite. Aaronson, Domian and Pound(5) extended this treatment to ternary Fe–u–C alloys (u is any substitutional element) by assuming that non-localized interactions were involved so that they could apply the theoretical expression for the activity of C in a binary Fe–C solution without modification to the ternary case. The substitutional solute had the effect of changing the value of \( \omega_p \) from the binary Fe–C case. They found that the C-activity data could be represented quite well by this means but that both chromium and silicon additions decrease \( \omega_p \) even though chromium and silicon have the opposite effect on the C-activity \( a_C \); chromium decreases \( a_C \) very strongly whereas additions of silicon increase \( a_C \) for a given C-content.

Zupp and Stevenson(6) have given semi-empirical equations for the C-activity in ternary Fe–u–C systems by combining an empirical relation for \( a_C \) for binary

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Fe-C alloys and Fe-\textit{u}-C alloys and the well-known expression for the activity of C in the binary system deduced from the geometrical blocking model. This model in which the C-atoms are all located at sites of the same energy and all the excess configurational free energy arises from the non-random entropy has been discussed by many authors \cite{7,8}.

Wada and Saito \cite{9} have considered an atomistic model for ternary solid solutions in which each binary system was regular. They showed that the Wagner interaction parameters for interstitial solutes are independent of interactions between the other two components.

In the next section a model for dilute ternary Fe-\textit{u}-C alloys will be presented which is based on a more direct atomistic approach. The activity data for many ternary solutions have been analyzed using the equations for \( \alpha_C \) developed in this treatment. The results show that the thermodynamic behavior of many ternary systems can be described by this model.

II. The Model for the Solid Solution

The postulates underlying the model are as follows:

(a) The binary solvent (\( v \))-substitutional solute (\( u \)) system is quasi-regular. The \( u \)-atoms are distributed randomly in the \( v \)-matrix and the partial energy of solution is not dependent on concentration. There is an excess partial entropy of solution which can arise from a number of causes such as the perturbation in the phonon spectrum of the pure solvent when the \( u \)-atoms are introduced or electron spin uncoupling but this is not dependent on composition.*

(b) The interstitial atoms (\( i \)) are partitioned into two groups. In one group, the \( v \)-\( i \) sub-assembly, all the nearest neighbors of an \( i \)-atom are \( v \)-atoms. In the other group, the \( u \)-\( i \) sub-assembly, the \( i \)-atoms have at least one \( u \)-type nearest neighbor.

(c) The \( v \)-\( i \) sub-assembly can be regarded as a pseudo-binary interstitial solid solution in which the \( i \)-atoms have a constant partial energy but the configurational entropy is not random due to the fact that a given \( i \)-atom excludes an integral number of nearest neighbor sites from occupation by other \( i \)-atoms.

(d) The \( u \)-\( i \) sub-assembly consists of \( i \)-atoms contained in the available nearest neighbor sites to the

\* The term quasi-regular solution has been used by Lupis and Elliod \cite{10} to describe a solution where the partial excess entropy does vary with composition but the term had been used previously with the meaning in the text of this paper \cite{11,13}.


substitutional solute (\( u \)) atoms. It is assumed that the energy and non-configurational entropy involved in placing an \( i \)-atom in a site which is nearest neighbor to a \( u \)-atom is independent of how many other \( i \)-atoms are also nearest neighbors of the given \( u \)-atom.

(e) Cognizance is taken of the fact that the presence of \( u-u \) pairs will decrease the number of interstitial sites in the \( u \)-\( i \) sub-assembly and concomitantly will increase the number of interstitial sites in the \( v \)-\( i \) sub-assembly.

Within the framework of these postulates the solution crystal has just one energy level and if its degeneracy is known we can write the canonical state sum at a given temperature, pressure, and composition and thus deduce all the thermodynamic properties.

Consider a crystal with \( N \) lattice sites. It contains \( N_v \) solvent atoms, \( N_i \) interstitial atoms and \( N_u \) substitutional solute atoms. The total number of interstitial sites of a given kind is \( \beta N \) (we will consider the octahedral sites in the fcc lattice in which \( \beta = 1 \)). The concentrations of \( i \)-atoms and \( u \)-atoms will be expressed by the atom ratios

\[
\theta_i = \frac{N_i}{N_u + N_v}; \ \theta_u = \frac{N_u}{N_u + N_v}; \ \theta_v = \frac{N_v}{N_u + N_v}.
\]

Let \( xN_i \) \( i \)-atoms be associated with the \( u \)-\( i \) sub-assembly and \( (1-x)N_i \) \( i \)-atoms be associated with the \( v \)-\( i \) sub-assembly. The parameter \( x \) can be regarded as a partitioning parameter which indicates to what extent the interstitial atoms crowd around the substitutional solutes (or are repelled away from them). The numerical value of \( x \) will vary between 0 and 1 and will depend on the \( u \)-content of the solution, increasing as \( u \)-increases. We will regard \( x \) as being constant in a solution of fixed \( u \)-content and justify this assumption later in this section.

We have to find the number of sites of equal energy in the \( u \)-\( i \) sub-assembly amongst which the \( xN_i \) \( i \)-atoms are to be distributed and the number of energetically equivalent sites in the \( v \)-\( i \) sub-assembly amongst which the \( (1-x)N_i \) \( i \)-atoms are to be distributed.

Consider a given \( u \)-atom. It has \( C_N \) nearest neighbor lattice atoms \((C_N=12 \text{ for fcc lattices})\). For a random distribution of \( u \)-atoms the probability that one of the \( C_N \) is a \( u \)-atom is

\[
p = \frac{N_u - 1}{N - 1} \approx \theta_u.
\]

Thus the number of \( u-u \) pairs involving the given \( u \)-atom is \( C_N \theta_u \). Summing over all \( u \)-atoms in a random solution gives a total of \( 1/2N_uC_N \theta_u \) \( u-u \) pairs. Since each pair reduces the number of interstitial sites which are nearest neighbor to a \( u \)-atom by 2 for the fcc lattice, pair formation decreases the number of interstitial sites in the \( u \)-\( i \) sub-assembly by \( N_uC_N \theta_u \) sites. Second nearest neighbors in the fcc lattice share only one octahedral interstitial site so we will ignore the effect of second nearest neighbor \( u-u \) pairs in counting the complexities. Now each lattice
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The model has been developed for ternary solutions containing both substitutional and interstitial solute atoms. The total number of interstitial sites in the u-i sub-assembly is

\[ N_u g_0 - N_u C_N \theta_u = N_u (g_0 - C_N \theta_u). \]

The degeneracy in the u-i sub-assembly is thus,

\[ g_u = \frac{[N_u (g_0 - C_N \theta_u)]!}{[N_u (g_0 - C_N \theta_u) - x N_i]! (x N_i)!}. \quad (1) \]

The total number of interstitial sites in the v-i sub-assembly is,

\[ \beta (N_r + N_u) - N_r (g_0 - C_N \theta_u) = \beta N_r - N_u (g_0 - \beta) + N_u C_N \theta_u = \beta N_r - N_u (\gamma - C_N \theta_u) \]

where \( \gamma = g_0 - \beta \) (=5 for the fcc lattice).

It has been shown that the simple geometrical blocking model of an interstitial solution gives a very accurate description of the thermodynamic properties of C in austenite(6)(7). In this model the interstitial atoms prohibit an integral number (\( z-1 \)), of nearest neighbor interstitial sites from being occupied by other interstitial solute atoms. Further support for the validity of this model for carbon austenite stems from the fact that it has been shown that the small effect on the thermodynamic functions of C in \( \gamma \)-Fe at high concentrations arising from the overlap of prohibited sites is consistent with the experimental thermodynamic data(11). For this model the degeneracy of the binary solution of \( N_v \) lattice atoms and \( N_i \) interstitial atoms is(12)

\[ g = \frac{[N_v \beta']! z^{N_v} \beta}{[N_v \beta - N_v]! N_v}. \quad (2) \]

Now in the ternary solution in the v-i sub-assembly we have \( \beta N_r - N_u (\gamma - C_N \theta_u) \) interstitial sites and \( (1-z) N_i \) interstitial solute atoms so we can write the degeneracy as

\[ g_v = \frac{[N_v \beta - N_v (\gamma - C_N \theta_u)]! z^{(1-z) N_i}}{[N_v \beta - N_v (\gamma - C_N \theta_u)]! z^{(1-z) N_i}! \{(1-z) N_i\}!}. \quad (3) \]

This assumes that the value of \( z \) is not affected by the presence of the u-atoms. In this work we will take \( z=5 \), the value found most appropriate for Fe-C solutions(13). The canonical state sum for the whole crystal is thus,

\[ Q(V, T) = \frac{(N_r + N_u)!}{N_u! N_u} \times \frac{[N_u (g_0 - C_N \theta_u)]!}{[N_u (g_0 - C_N \theta_u) - x N_i]! (x N_i)!} \times \frac{[N_v \beta - N_v (\gamma - C_N \theta_u)]! z^{(1-z) N_i}}{[N_v \beta - N_v (\gamma - C_N \theta_u)]! z^{(1-z) N_i}! \{(1-z) N_i\}!} \times \Omega_0 \exp \left( \frac{-E}{kT} \right). \quad (3) \]

where \( \Omega_0 \) is the part of the state sum which accounts for the internal degrees of freedom of the crystal, \( E \) is the total energy, and the initial factor counts the number of ways of arranging the u-atoms on the lattice sites. Now if \( E_u \) is the energy per atom of pure solvent, \( E_u \) is the energy needed to put a u-atom into the v-u binary solution, \( E_{ui} \) is the energy required to insert an i-atom into an interstitial site in the u-i sub-assembly and \( E_{vi} \) is the energy required to insert an i-atom into an interstitial site in the v-i sub-assembly, then

\[ E = N_u E_u^o + N_u E_u + z N_i E_{ui} + (1-z) N_i E_{vi}. \quad (4) \]

The energy zero will be regarded as the energy of an atom at rest in a vacuum.

Similarly the total non-configurational entropy of the crystal is,

\[ S = k \ln \Omega_0 = N_u S_u^o + N_u S_u + z N_i S_{ui} + (1-z) N_i S_{vi}. \quad (5) \]

This equation can now be differentiated to give the chemical potential of an interstitial atom in solution, \( \mu_i \)

\[ \mu_i = \langle \partial F / \partial N_i \rangle_{N_u, N_v} = E_i - T S_i + k T \ln \left[ \frac{z \theta_i}{\theta_u (g_0 - C_N \theta_u)} \right]^{x} \times \left\{ \beta \theta_i - \theta_u (\gamma - C_N \theta_u) - z (1-z) \theta_i \right\}^{(1-z)}. \quad (6) \]

In this equation \( E_i = \langle \partial E / \partial N_i \rangle_{N_u, N_v} \) is the partial energy of an i-atom in solution and \( S_i = \langle \partial S / \partial N_i \rangle_{N_u, N_v} \) is the partial non-configurational entropy of an i-atom in solution. If we put \( z=0, \theta_u=0, \theta_i=1 \) in this formula it reduces to,
\[ \mu_i = \frac{E_i^c - TS_i^c + kT \ln \left( \frac{\theta_i}{\beta} \right)}{1 - x \theta_i / \beta}, \] (9)

the chemical potential of an interstitial atom in the geometrical blocking model for a binary interstitial solid solution(13).

The two logarithmic factors in brackets in eq. (8) are just the partial configurational entropies of an i-atom in the u-i and v-i sub-assemblies,

\[ S_{vi} = \left( \frac{\partial \ln g_v}{\partial N_i} \right)_{N_u,N_v} = -N_x \ln \left( g_0 - C_i \theta_u \right) - x \theta_i, \] (9)

\[ S_{ui} = \left( \frac{\partial \ln g_u}{\partial N_i} \right)_{N_w,N_v} = -\left( 1 - x \right) \beta \theta_u - \theta_i \right) \theta_i. \] (10)

At this stage we will justify the assumption that the parameter \( \chi \) can be regarded as a constant for a given value of \( \theta_u \). Assume we have a ternary solution with a fixed content of substitutional solute atoms. The solution also contains some interstitial atoms appportioned between the v-i and u-i sub-assemblies in the manner already discussed. Further additions of interstitial solute will be appportioned between the two sub-assemblies according to the partial free energy of an i-atom in the two sub-assemblies regarded as pseudo-binary systems. In this model the partial energy and non-configurational entropy of the i-atoms are not functions of composition so that the partitioning of further additions of interstitial solute, and thus \( \chi \), will depend on how the partial configurational entropy of the i-atoms in each sub-assembly changes with composition. If the ratio of these two partial entropies is constant in the range of compositions involved, then we can assume that \( \chi \) will not depend on \( \theta_u \). The relevant partial entropies can be obtained from eqs. (9) and (10) if we write \( \chi = 1 \) in (9) and write \( \theta_u = \theta_u' \) and put \( \chi = 0 \) in (10) and again write \( \theta_u = \theta_u' \). A plot of the partial configurational entropies \( S_{ui}' \) and \( S_{vi}' \) for the pseudo-binary systems vs \( \theta_u \) is given in Fig. 1. It is seen that the two plots are reasonably parallel over the range of interstitial solute contents encountered in most solutions for which experimental data is available. In fact from \( \theta_u' = 0.001 \) to \( \theta_u' = 0.05 \), the ratio \( S_{ui}' / S_{vi}' \) varies from 1.183 to 1.56. The entropy plots were made for \( \theta_u = 0.05 \).

Finally we calculate the activity \( a_i \) of the interstitial solute in solution. This may be defined through the equation,

\[ \mu_i = E_i - TS_i + kT \ln a_i \] (11)

although there is some doubt about the appropriateness of this way of defining activities for interstitial solutes(13). In this equation \( E_i \) and \( S_i \) are the energy and entropy of pure i in its standard state at the same temperature and pressure as the solution. Combining eqs. (8) and (11) we get for the activity of i with respect to pure i,

\[ \alpha_i = \left[ \frac{\chi \theta_i}{\theta_u \left( g_0 - C_i \theta_u \right) - x \theta_i} \right] \left[ \frac{1 - x \theta_i}{\beta \theta_u - \theta_i} \right] \left[ \frac{1 - x \theta_i}{\beta \theta_u - \theta_i} \right], \] (12)

This equation will be used to analyze the available activity data of this type of ternary system in order to show to what extent the model is compatible with the experimental activity data.

III. Analysis of the Experimental Data

The expression for the activity of the interstitial solute developed in the preceding section has been compared with the carbon activity data available for single-phase austenitic solid solutions within the composition limits delineated. The data of Smith were used for the Fe-Si-C and Fe-Mn-C systems(14), that of Schenck and Kaiser(15) for the Fe-Cr-C and Fe-Al-C systems, and further data for the Fe-Cr-C system were obtained from the work of Flender and Wever(16). The activity data is illustrated in Fig. 2. Only data for the highest and lowest u-content used in the computer analyses is shown and the arrows indicate whether or not increasing the u-content at a constant i-content increases or decreases the carbon activity.

Extensive determinations of \( a_C \) have been made by Zupp and Stevenson(6) for Fe-V-C alloys but these measurements are not appropriate for the present analysis since most of their data refers to either two-phase alloys or to a single-phase alloy containing a very small u-content in comparison with the i-content.

Many activity data are also available for the Fe-Ni-C system. Measurements at 1000°C within the

(14) R. P. Smith : Trans. AIME, 70 (1948), 2724.
The experimental activity data discussed above was used to estimate the unknown constants \( x \) and \( \varphi \), the exponential factor in the theoretical activity eq. (12). The values of \( x \) and \( \varphi \) and their behavior with composition will be used in a later section to assess the plausibility of the model.

The parameters \( x \) and \( \varphi \) were estimated by making a least squares fit of the activity data to eq. (12). In the program the values of \( x \) were restricted to range from \( 1.0 \times 10^{-5} \) to 0.999 but no restriction was placed on \( \varphi \). The calculated activities for an assumed value of \( x \) were determined by minimizing the square of the difference between the measured and calculated activity. Once the calculated activity for a given \( x \) was found the error sum of squares was obtained. The best value of \( x \) was selected by performing this process for a range of \( x \)-values and choosing that \( x \) which gave the minimum error sum of squares. The concomitant value of \( \varphi \) was taken as the best value for this parameter. The analysis was performed on an IBM 7040 digital computer. The values of \( x \) and \( \varphi \) for a given \( \theta_u \) are shown in Table 1.

### Table 1

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<th>( \theta_u )</th>
<th>( \theta_v )</th>
<th>( \theta_w )</th>
<th>( x )</th>
<th>( \varphi )</th>
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### IV. Discussion of Results

The values obtained for the partitioning parameter \( z \) and the exponential term in the activity \( \varphi \) agree well with the thermo-chemical behavior of the solutions investigated.

Fig. 2 shows that Al, Mn, and Cr are increasingly more effective in reducing the carbon activity in the ternary solution. This may be seen in Fig. 4 which shows \( a_i \) as a function of \( \theta_i \) at a constant carbon content of \( \theta_i=0.03 \). These plots also show that Si behaves in the opposite sense and, for a given C-content, increasing \( \theta_u \) increases \( a_i \). Now if \( a_i \) were only determined by the concentration of C in the \( i \)-subassembly then the \( z \)-values should decrease in the order Cr->Mn->Al->Si at a given \( \theta_u \)-content. The \( z \)-values are plotted against \( \theta_u \) in Fig. 5. Values of \( z \) taken from this plot for \( \theta_u=0.05 \) are given in Table 2. Chromium has the highest value of \( z \) indicating strong bonding between the C and Cr atom resulting...
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Fig. 4 The variation of carbon activity with substitutional solute concentration at a fixed carbon concentration

Fig. 5 The variation of $\chi$ with substitutional solute concentration

Table 2

<p>| | |</p>
<table>
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<td>Cr</td>
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<tr>
<td>Si</td>
<td>0.09</td>
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in a crowding of C-atoms around the Cr-atoms and a large decrease of the C-activity in solution. Silicon has the lowest $\chi$-value commensurate with its behavior in increasing the C-activity in solution; the C-atoms tend to avoid the Si-atoms.

Al and Mn lower the C-activity at a fixed $\theta_i$ but not as effectively as Cr. The $\chi$-values in Table 2 indicate that despite the lower C-activity in the Fe–Mn–C solution for a given $\theta_u$ compared to $\theta_u$ in the Fe–Al–C system, the C-atoms cluster round the Al-atoms to a greater extent than they do around the Mn-atoms. This could be explained if the C-atoms were more loosely bound to the Fe-atoms in the v-i sub-assembly for the Fe–Al–C system than the Fe–Mn–C system. This could be a result of long-range forces acting in the v-i sub-assembly due to the presence of the u-atoms.

Table 1 shows that the $\chi$-values decrease smoothly with $\theta_u$ as they should and Fig. 5 shows that in all cases the value of $\chi$ extrapolates unambiguously to zero when $\theta_u=0$ as consistency requires.

The numerical values of $\chi$ show that even when the substitutional solute is present in small concentrations with respect to Fe, the C-atoms tend to cluster round the u-atoms. In the case of Cr, Al, and Mn this is certainly due to the fact that the u-C bonds have a higher binding energy than the v-C bonds. However, an entropy factor also tends to cluster the C-atoms around the u-atoms. The interstitial sites surrounding the Fe-atoms in the v-i sub-assembly are not unique and are shared by nearest neighbor Fe-atoms. There is only one site per Fe-atom. In the u-i sub-assembly however, neglecting the formation of u-u pairs, each of the $g_0$ nearest neighbor interstitial sites is unique; the u-i pair forms an orientable dipole with a $g_0$-fold degeneracy. Thus the configurational entropy per u-atom in the u-i sub-assembly is greater than the entropy per v-atom in the v-i sub-assembly.

Let us now consider the values of $\varphi$, the exponential function in the equation for $a_i$. From eqs. (4) and (5) we see that

$$E_i = x E_{vi} + (1 - x) E_{ui}$$

and

$$S_i = x S_{ui} + (1 - x) S_{vi}.$$  \hspace{1cm} (13)

Thus

$$\varphi = \exp \left\{ \frac{E_i - E_{vi}}{kT} \right\} \exp \left\{ \frac{S_i - S_{vi}}{k} \right\}$$

$$= \exp \left\{ \frac{E_i - [x S_{vi} + (1 - x) E_{vi}]}{kT} \right\}$$

$$\times \exp \left\{ \frac{S_i - [x S_{vi} + (1 - x) S_{vi}]}{k} \right\}. \hspace{1cm} (14)$$

Fig. 6 shows plots of $\varphi$ vs. $\theta_u$. The positive slope of the plot for the Fe–Si–C system is consistent with the Si-C binding energy being less than the Fe-C binding energy. The negative slopes of the other three plots indicate that C-atoms are more strongly bound to the u-atoms than to the Fe-atoms.

Now in the limit when $\theta_u$ is zero and $x=0$ the value of $\varphi$ becomes,

$$\varphi_0 = \exp \left\{ - \frac{E_i - E_{vi}}{kT} \right\} \exp \left\{ \frac{S_i - S_{vi}}{k} \right\} \hspace{1cm} (15)$$

where $E_{vi}$ is the partial energy of a C-atom in the pure Fe-C binary and $S_{vi}$ is the partial non-configurational entropy of a C-atom in the pure Fe-C binary. The values of $(E_i - E_{vi})$ and $(S_i - S_{vi})$ have been determined by McLellan(16) from the measurements of Smith(19). Using these values we get $\varphi_0 = 8.1$. Fig. 6 shows that the values of $\varphi$ extrapolate linearly to values very close to 8.1 in the case of Si, Mn, and Cr and to a somewhat higher value in the case of Al. This is consistent with the idea that the C-atoms are more loosely bound in the v-i sub-assembly in the Fe–Al–C ternary than in the pure Fe-C binary so that the activity of carbon in the Fe–Al–C system is higher than the $\chi$-values would indicate. For the Al-case $E_{vi}$ is less negative than $E_{vi}$ and thus the $\varphi$-

values and hence the activity of carbon is increased compared to the systems for which $E_{vi} = E_{vi}^{b}$.

We can estimate the $u$-$i$ binding energy from the slopes of plots of $\ln \varphi$ vs $\chi$, which, from (15) are given by

$$\frac{d \ln \varphi}{d \chi} = \frac{(E_{ui} - E_{vi})}{kT} - \frac{(S_{ui} - S_{vi})}{k}.$$  

Now for the systems containing Cr, Mn, and Al the C-atoms are bound more tightly to the $u$-atoms than to the Fe-atoms. Thus they will vibrate in a stiffer average force field and hence their vibrational frequency will be less than that of a C completely surrounded by Fe-atoms. This implies that $S_{ui} > S_{vi}$. For the ternary system containing Si where the C-atoms are more loosely bound to the Si-atoms than to the Fe-atoms, the converse applies and $S_{ui} < S_{vi}$. The values calculated for $(E_{ui} - E_{vi})$ from the slopes of plots of $\ln \varphi$ vs $\chi$ and assuming that $(S_{ui} - S_{vi})/k = -1$ for the systems containing Cr, Mn, and Al, and $(S_{ui} - S_{vi})/k = +1$ for the solution containing Si are given in Table 3.

Now Fig. 6 shows that at least for the systems containing Cr, Si and Mn the partial energy in the $v$-$i$ sub-assembly $E_{vi}$ can be closely approximated by its value in pure Fe-C binary system ($-155.2$ kcal/mole). Using this value for $E_{vi}$ the corresponding values of $E_{vi}$ have been calculated and are given in Table 3. The energies given in Table 3 are at best only tentative due to the assumption involving the entropies and the small number of data points in the $\ln \varphi$ vs $\chi$ plots. However, they do bear the relationship to $E_{vi}^{b}$ that would be expected from the activity data.

The fact that an equation involving two parameters, $\chi$ and $\varphi$, can be fitted to the experimental activity data is in itself not significant. However, it is significant that the numbers $\chi$ and $\varphi$ generated by the computer fitting agree so well with the thermodynamic behavior of the solutions and the physical limitations on $\chi$ and $\varphi$. The only restriction placed on the parameters in the numerical analysis was that $0 \leq \chi \leq 1$. There was no restriction placed on the values of $\varphi$. The fact that the values of $\chi$ and $\varphi$ for the different systems investigated are in the order that would be expected from the activity data and that they vary in the expected way with $u$-content is hard to explain unless the model is valid and the parameters $\chi$ and $\varphi$ have the physical significance ascribed to them. The fact that the values of $\chi$ and $\varphi$ for the different systems investigated are in the order that would be expected from the activity data and that they vary in the expected way with $u$-content is hard to explain unless the model is valid and the parameters $\chi$ and $\varphi$ have the physical significance ascribed to them. The fact that the values of $\chi$ and $\varphi$ give the known values for these constants for binary solutions in the limit when $\theta_{u} \rightarrow 0$ adds further credence to the validity of the model since again this agreement is in no way "built into" or guaranteed by the numerical analysis.

**Acknowledgment**

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<table>
<thead>
<tr>
<th>$u$</th>
<th>$(E_{ui} - E_{vi})$ kcal/mole</th>
<th>$E_{vi}$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>$-9.32$</td>
<td>$-164.5$</td>
</tr>
<tr>
<td>Al</td>
<td>$-0.17$</td>
<td>$-$</td>
</tr>
<tr>
<td>Mn</td>
<td>$-7.74$</td>
<td>$-162.9$</td>
</tr>
<tr>
<td>Si</td>
<td>$+40.00$</td>
<td>$-115.2$</td>
</tr>
</tbody>
</table>