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ON THE KINETICS AND THERMODYNAMICS OF METALLIC SOLID SOLUTIONS

by

Daniel C. Parris

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

Thesis Director's Signature:

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Houston, Texas

April, 1976
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PART I

Diffusion of Carbon in Austenite
Introduction

The mobility of interstitial solute atoms in high temperature metallic solid solutions is ordinarily expressed in terms of the diffusivity, $D$, which is defined with reference to the macroscopic flux, $J$, of that specie and its concentration gradient, $\partial C/\partial x$, where $C$ is expressed in terms of moles per unit volume. Fick's first law states this relation as,

$$ J = -D \nabla C $$  \hspace{1cm} (I-1)

In practice, however, the actual flux is not generally measured. Rather the divergence of the flux

$$ \nabla \cdot J $$ \hspace{1cm} (I-2)

is determined from the concentration profile which obtains after a given time at the elevated temperature in a system in which the initial boundary conditions as well as the final boundary conditions are known. This information is related to the diffusivity by Fick's second relation

$$ \partial C/\partial t = \nabla \cdot (D \nabla C) $$ \hspace{1cm} (I-3)
For the case where $D$ is a constant, independent of position, equation I-3 becomes

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad (I-4)$$

an equation which has been solved for various boundary conditions (e.g., by Crank$^2$).

In a real metallic system, $D$ is seldom strictly constant in that it is dependent on solute concentration. For composition dependent $D$, equation I-3 can be solved in a given system by graphical integration, the Boltzmann-Matano method$^1$. Wells, Batz, and Mehl$^3$ applied this method to the diffusion of carbon in austenite with good results. Nonetheless, the approach is greatly limited in its precision due to the uncertainties inherent in the integration method.

The steady state method, as employed by Smith$^4$, is better suited to precise determination of the diffusivities. This approach requires knowledge only of the concentration profile, $\frac{\partial C}{\partial x}$, at a given plane and of the flux of diffusant through that plane at steady state, in this case measured directly.

Recognizing that by definition

$$\hat{\nabla} \cdot \hat{J} = -\frac{\partial C}{\partial t} \quad (I-5)$$

one sees that at steady state
\[ \nabla \cdot \mathbf{j} = 0 \] (I-6)

since the term steady state implies no variance of macroscopic solution variables with time. In particular, \( \partial C/\partial t = 0 \). In a flat plate with flux normal to the surface this implies that the flux is equal through all planes parallel to the surface. Applied to radial cylindrical flux, it means that the flux through any internal cylindrical surface normal to the radius is proportional to \( r^{-1} \). This relation follows from the fact that the flux can be expressed as

\[ J = \rho/2\pi lr = \rho/A \] (I-7)

where \( A \) is the area of a given closed surface at radius \( r \), where \( l \) is the effective length of the cylinder, and where \( \rho \) is the rate of diffusant transfer through the external surface. From equation I-1, expressed in cylindrical coordinates,

\[ D = -\rho/2\pi lr (\partial C/\partial r) \] (I-8)

or

\[ D = -\rho/2\pi l (\partial C/\partial ln r) = K(\partial C/\partial ln r) \] (I-9)

where \( K \) is a constant for a given sample. Thus by measuring \( K \) at
the elevated temperature and by determining the concentration profile quenched into the sample one can solve I-9 for the diffusivity at any concentration extant in the sample. Smith's measurements using this technique have produced reliable data.

In both steady state and Boltzmann-Matano analyses the measurement of $D$ relies on the presence of a concentration gradient. Though indeed it is of interest to evaluate the diffusivity in this case, it can be shown that the presence of the gradient itself affects the diffusivity in a complex manner and creates substantial problems in relating thus measured diffusivities to mobilities in systems having a uniform concentration of the mobile species.

The compositional gradient affects the observed mass transport in several ways. First, there is the variance of the atomic mobility itself. This is induced in part by a change in specific volume, or lattice parameter, with solute concentration and in part by the change in the total of solute-solute interactions experienced by the solute atom at a given site. This is accompanied by an interaction gradient. That is to say that the solute atoms experience more interactions in jumping up the gradient than in jumping down the gradient. Further, the relative availability of sites for diffusive motion of a given migrating atom is a function of direction in a gradient. This is due to prior occupancy of some potential jump sites by other solute atoms. It is apparent that the last two effects mentioned are differential effects in a gradient.

These differential effects are relatively unimportant when the
concentration of solute atoms is very small. Such is the case for the flow of carbon through BCC iron where the diffusivity can be considered constant over the entire range of solubility. In FCC iron however, the carbon solubility is much higher and $D$ increases rapidly with carbon concentration.

This increase of diffusivity with $e$, the atom ratio of carbon to iron, has been previously discussed by Siller and McLellan$^{5,6}$. Their work consisted of analysis of the diffusivities measured by Smith$^4$ with respect to a simple blocking model after Speiser and Spretnak$^7$ and to first order mixing statistics$^{8,9}$. This analysis met with some success.

It is of interest to apply this same analysis to data collected in an experiment which obviates differential effects leaving only the direct compositional effects. In this way one can more precisely relate the measured system to the thermodynamic model and hopefully extract better defined information on the general relation of diffusion kinetics to equilibrium thermodynamics in interstitial metallic solid solutions.

It is the object of the present investigation to extract and analyze just such information. In the experiment described hereafter the diffusivities of carbon in $\gamma$-iron have been measured in a zero-gradient system.

In such a system the gradient effects are largely eliminated and the mobility is governed primarily by the thermodynamics of the solution. The experiment consisted of measurement of the diffusion of radioactive tracer atoms in an otherwise homogeneous solution. The
method is closely analogous to the tracer diffusion measurements carried out for pure metals.

Here the diffusion of radioactive C$^{14}$ in a diffusion couple containing a uniform overall carbon concentration was measured. Except for the effect of isotopic mass, which can be readily estimated, the mobilities of the two species should be identical. Though the two isotopes differ thus physically they can be considered chemically identical. In a manner of speaking, the atoms of opposite types look identical to each other yet can be distinguished by an outside observer. So for a system with a constant overall carbon to iron atom ratio there is no specific volume gradient and no "interaction gradient" to bias atomic jumps in a given direction.

By choosing a set of standard boundary conditions in designing the couple, such that the solution to equation I-4 is known, it was possible to determine the diffusivity as a function of $\theta$ directly from knowledge of $\theta^*(x,t)$, the tracer concentration profile as a function of distance from the interface and the time at the diffusing temperature and from $\theta$ the overall carbon atom ratio. Since, as will be shown, this measurement differs qualitatively from that of Wells, Batz, and Mehl$^3$ and of Smith$^4$ it is necessary to distinguish between $D$ as measured previously in those works and $\bar{D}$ as measured in this work.
Theory

Theoretical attempts to correlate the equilibrium thermodynamics of an interstitial solid solution with the diffusion kinetics of that solution can be classified as either phenomenological or mechanistic. The former appeal to defined constants of proportionality to link the two types of measurement. A good example is Fick's law which relates a measured flow to a gradient of a thermodynamic variable, the concentration. The mechanistic theories look to a specific solution model defining, more or less precisely, certain unmeasurable thermodynamic quantities, such as the chemical potential of an activated complex, to use as parameters for linking the measured quantities.

Another good example of the phenomenological approach is that of Darken. Assuming the driving force on a solute atom in a solid solution to be the gradient of the partial molar Gibb's free energy, or chemical potential, one can formally equate the mean solute atom diffusion velocity, \( v_i \), to the product of this force and the velocity per unit force, or mobility, \( B_i \). That is

\[
   v_i = -B_i \frac{\partial \mu_i}{\partial x}
\]  

(I-10)

where \( x \) is measured in the direction of the gradient and where a one dimensional gradient has been assumed. Thus the molar flux, \( J_i \), of solute across a given plane normal to the diffusion direction, which is just the velocity, \( v_i \), multiplied by the concentration expressed in moles per unit volume, \( C_i \), is written
\[ J_i = -B_iC_i \frac{\partial\mu_i}{\partial x} \]  \hspace{1cm} \text{(I-11)}

From Fick's first law, equation I-1,

\[ J_i = -D \frac{\partial C_i}{\partial x} \]  \hspace{1cm} \text{(I-12)}

Equating the fluxes in equations I-11 and I-12

\[ D \frac{\partial C_i}{\partial x} = B_iC_i \frac{\partial\mu_i}{\partial x} \]  \hspace{1cm} \text{(I-13)}

or

\[ D = B_iC_i \frac{\partial\mu_i}{\partial x} \]  \hspace{1cm} \text{(I-14)}

Now, defining the activity, \( \alpha_i \), as

\[ d(\ln \alpha_i) = \frac{1}{kT} d\mu_i \]  \hspace{1cm} \text{(I-15)}

one finds,

\[ D = kTB_i \frac{\partial\ln \alpha_i}{\partial \ln c_i} \]  \hspace{1cm} \text{(I-16)}

where \( c_i \) is the atom fraction of \( i \) and where the partial molar volume is assumed constant. Further, defining the activity coefficient
\[ \gamma_i = \alpha_i / c_i \]  
(I-17)

one can express equation I-16 as

\[ D = kT \beta_i (1 + c_i \ln \gamma_i / \partial c_i) \]  
(I-18)

The mechanistic approach of Fisher, Holloman and Turnbull\textsuperscript{11} is based on the so-called absolute rate theory which assumes the existence of a definable quasi-stable activated state at the apex of the potential profile between two stable interstitial sites. Consider a diffusing atom making a jump between two equilibrium sites. For a jump made reversibly, the rest of the lattice adjusts its configuration so as to remain in equilibrium. The energy of the system as a function of position of the diffusing atom can be illustrated schematically by Figure I. At the position of maximum energy (*) the diffusing atom with the locally perturbed lattice can be said to constitute an activated complex. The jump frequency from A to A' can be expressed in terms of the mean forward velocity of the activated complex.

Glasstone et al.\textsuperscript{12} have shown that the lattice configuration corresponding to the activated state has all of the properties of an equilibrium configuration except that the vibration frequency of the migrating atom in the decomposition coordinate, i.e., parallel to the jump direction, has an imaginary value. So, if we assume these activated complexes to be in equilibrium with the rest of the crystal, we
FIGURE 1. Lattice potential energy as a function of solute displacement along a jump path.
can express the transition rate of activated complexes as

\[ v_i = \frac{kT}{m} \frac{c_i^*}{c_i} \]  \hspace{1cm} (I-19)

where \( l/m \) is the transmission coefficient, allowing for the possibility that not every activated complex will lead to a diffusive jump, and where \( c_i \) and \( c_i^* \) are the concentrations of the normal and activated complex configurations respectively in moles per unit volume.

From the assumption that the activated complexes are in equilibrium with the atoms in the normal state we know, from the Maxwell-Boltzmann distribution, that

\[ \frac{\alpha_i^*}{\alpha_i} = \exp \left( \frac{-\Delta G^*}{kT} \right) \]  \hspace{1cm} (I-20)

where again the starred quantities refer to the activated state and where \( \Delta G^* \) is the difference in free energy between the standard state and the activated complex. Thus from I-17 and I-20 we find

\[ v_i = \frac{kT}{m} \frac{z_i}{\gamma_i^*} \exp \left( \frac{-\Delta G^*}{kT} \right) c_i \]  \hspace{1cm} (I-21)

Assuming \( \gamma^* \) constant and defining \( c_i v_i \) as the number of atoms making a transition per unit volume per unit time, \( \Gamma_i \), we see
\[ \Gamma_i = C_i \frac{kT}{m} \frac{\gamma_i}{\gamma_i^*} \exp(-\Delta G/kT) \]
\[ = C_i \frac{\mathcal{K}_O(T)}{m} \gamma_i \]

The net flux through a given plane can be expressed as the difference between the rate of transitions in the forward direction and that in the reverse direction per unit area. If \( m \) is independent of jump direction the forward flux through a plane normal to the diffusion direction midway between interstitial sites can be written

\[ j^+ = \frac{\mathcal{K}_O}{m} C_i \gamma_i \bar{d} \]

(I-23)

where \( \bar{d} \) is the distance between adjacent interstitial sites. Likewise the reverse flux can be written

\[ j^- = \frac{\mathcal{K}_O}{m} (C_i + \delta \partial C_i / \partial x) (\gamma_i + \delta \partial \gamma_i / \partial x) \]

(I-24)

Therefore the net flux through the plane is

\[ J = j^+ - j^- = -\delta^2 \frac{\mathcal{K}_O}{m} (\gamma_i \partial C_i / \partial x + C_i \partial \gamma_i / \partial x) \]
\[ = -\delta^2 \frac{\mathcal{K}_O}{m} (\gamma_i + C_i \partial \gamma_i / \partial C_i) \partial C_i / \partial x \]

(I-25)

Thus from equation I-12
\[ D = \delta^2 k_0 / m \left( \delta_i + c_i \frac{\partial \delta_i}{\partial c_i} \right) \]  \hspace{1cm} (I-26)

or

\[ D = D_0 / m \left( \delta_i + c_i \frac{\partial \delta_i}{\partial c_i} \right) \]  \hspace{1cm} (I-27)

where

\[ D_0 = \delta^2 k_0 = \delta^2 kT / h \delta_i^* \exp(\Delta G^*/kT) \]  \hspace{1cm} (I-28)

and where the partial molar volume of the solute has been assumed constant. The case where \( m \) is dependent upon jump direction has been treated previously\(^5\)\(^6\). In the zero-gradient case \( m \) is properly treated in the above derivation. This point is clarified by recognition of the transmission coefficient as the probability of an activated complex completing a successful diffusive jump, a process which has no directional bias in the absence of a potential gradient.

Therefore, from the definition of \( D \), the tracer diffusivity, in Chapter 1 one sees from equation I-27 that

\[ D = D_0 / m \left( \delta_i + c_i \frac{\partial \delta_i}{\partial c_i} \right) \]

\[ = D_0 / m \left( \alpha_i + (1 + \varepsilon) \frac{\partial \alpha_i}{\partial \theta} \right) \]  \hspace{1cm} (I-29)
Defining

\[ \omega(\theta) = \alpha_1 + (1+\theta) \frac{\partial \alpha_1}{\partial \theta} \]  \hspace{1cm} (I-30)

and

\[ \ell(\theta) = \frac{1}{m(\theta)} \]  \hspace{1cm} (I-31)

one finds that

\[ \mathcal{D}(\theta) = \mathcal{D}_0 \omega(\theta) \ell(\theta) \]  \hspace{1cm} (I-32)

where practically all of the compositional dependence has been separated into the terms explicitly functional in \( \theta \). \( \mathcal{D}_0 \) is strictly a constant except for the dependence of \( \delta \) on \( \theta \), a small effect which can be assumed negligible. Since \( \omega(\theta) \) is comprised of well known thermodynamic quantities, the problem becomes merely that of evaluating \( \ell(\theta) \) explicitly.

Referring again to the definition of the transmission coefficient as the ensemble average probability that a given nearest-neighbor site will be involved in the next jump of a particular solute, one can see that,

\[ \ell(\theta) = \frac{1}{N_v} \left( N_v - N_{\text{f}} - B(\theta) \right) \]  \hspace{1cm} (I-33)
The term $N_i/N_v$ accounts for the direct reduction in $f$ due to the occupation of potential sites by other solutes. $N_i$ is the number of solute atoms per unit volume and $N_v$ the number of solvent atoms per unit volume. The term $B(\theta)/N_v$ accounts for the reduction in probability due to repulsive interactions between $i$ atoms which would be experienced by a solute were it to jump into the given nearest-neighbor site. It is clear that when $\theta \to 0$, $1/m \to 1$ and there are no such restrictions on the mobility. In any case, $B(\theta)$ can be written

$$B(\theta) = N_e N_i^2 p'$$  \hspace{1cm} (I-34)$$

where $N_e$ is the number of occupied-empty site pairs on the given plane and its two adjacent planes normal to the diffusion direction, and $p'$ is the probability that an interstitial atom will not jump into a site adjacent to another such atom. The probability $p'$ can be easily calculated from the simple first order theory for interstitial solutions. It is given by

$$p' = 1 - N_i/N_{ii}$$  \hspace{1cm} (I-35)$$

where $N_{ii}$ is the equilibrium number of $i$-$i$ pairs (occupied-occupied pairs) and $N_{ii}$ is the corresponding number for a completely random solution. The assumption has been made here that the equilibrium number of pairs of any kind exist in an elemental volume surrounding the atom plane under consideration. For the case of carbon in austenite the
i-i interaction is repulsive so \( N_{i i} / \langle N_{i i} \rangle \) is less than one.

In the first order treatment of C-austenite

\[
N_{ei} = \frac{z \bar{\lambda}}{2} \quad (I-36)
\]

where \( z = 12 \) is the coordination number for octahedral interstitial sites, those occupied primarily by the carbon atoms, and where

\[
\bar{\lambda} = \frac{N_v}{2 \sigma} \left( 1 - (1 - 4 \sigma \theta (1 - \theta)^{1/2}) \right) = \frac{N_v \chi}{2} \quad (I-37)
\]

with

\[
\sigma = 1 - \exp(\Delta \varepsilon / kT) \quad (I-38)
\]

In equation I-38 \( \Delta \varepsilon \) is the i-i pairwise interaction energy. Now, since

\[
N_{i i} = \frac{z (N_u - \bar{\lambda})}{2} \quad (I-39)
\]

and

\[
\langle N_{i i} \rangle = \frac{z N_u^2}{2N_v} \quad (I-40)
\]

combination of equations I-35, I-39, and I-40 is possible yielding
\[ p^* = 1 - (N_u - \bar{\lambda}) \frac{N_v}{N_u^2} \]  

and from equation I-37

\[ B(\theta) = \frac{z}{2} N_v \frac{\chi}{2\sigma} \left(1 - (N_u - \bar{\lambda}) N_v / 2\sigma N_u^2\right) \]

\[ = \frac{zN_v \chi}{4\sigma} \left(1 - 1/\theta \left(1 - \frac{\chi}{2\sigma\theta}\right)\right) \]  

Finally combination of I-33 and I-42 yields

\[ \left\{ \begin{array}{c}
\frac{1}{\theta} = m^{-1} = 1 - \theta - (1 - \theta(1 - \frac{\chi}{2\sigma\theta})/\chi)^2 \sigma^{-1} \\
\end{array} \right. \]  

By inserting proper values of the thermodynamic functions in I-30 and I-43 and calculating \( \rho/\omega(\theta) \) \( \left\{ \theta \right\} \) from measured values of \( \rho \) one should be able to demonstrate the constancy of \( \rho_0 \). It should be noted here, due to the timely caution of Wagner that the proper thermodynamic functions are those taken in constant pressure experiments in that the diffusivities are measured under isobaric laboratory conditions.
EXPERIMENTAL PROCEDURE

Experimental Design

The experiment consisted of five steps of sample preparation and analysis:

1. Solution annealing
2. Welding
3. Diffusion annealing
4. Sectioning and counting
5. Chemical analysis

In this chapter the overall experimental design is discussed and the equipment and procedures for each of the above steps are presented.

The basic premise of the experimental design lay in the assumption of the chemical identity of the radioactive isotope $\text{C}^{14}$ with $\text{C}^{12}$. Given this identity one can say that even if the observer can discern a compositional profile due to isotopic concentration gradients it is possible to have a configuration in which neither the solvent lattice nor the various solute atoms is "aware" of these gradients. This assumption is the same as is employed in using tracer diffusion methods to determine self-diffusivities in pure metals.

For a dilute interstitial solution, though, the tracer experiment is somewhat different from the substitutional case of self-diffusion. First, it is noted that the latter case is characterized as a quasi-binary solution of tracers and normal atoms whereas the former is similarly quasi-ternary. This difference is of little moment since in the
interstitial solution the solvent lattice can be considered effectively static and inert. It is static since the interstitial diffusivities are much higher at all temperatures than the substitutional diffusivities. For example, the diffusivity of carbon in nickel at 1000°C is approximately $2.5 \times 10^{-7}$ cm$^2$/second. Self-diffusion in nickel at the same temperature is on the order of $4 \times 10^{-12}$ cm$^2$/second, a factor of $10^5$ slower. The effective inertness of the solvent is due to the symmetry of the lattice, that is, since every solute experiences a like interaction to every other solute, the solute-solvent interactions can be smoothed over the entire solution and can be considered a parameter of the solution independent of detailed configuration. Thus the tracer doped interstitial solution can be viewed as a quasi-binary tracer-normal solute solution residing on a geometric lattice defined by the solvent atoms.

In addition to this distinction between the substitutional quasi-binary and interstitial quasi-ternary systems it is of note that a vacancy mechanism is responsible for diffusive motion of the solute in either case. In the substitutional solution the equilibrium concentration of vacancies is extremely low even at high temperatures. This paucity of freely mobile species, vacancies, leads to correlation effects, geometrical factors which are due to the possibility of multiple interchanges between a given vacancy and a given tracer and which are required to relate measured tracer diffusivities to the mobilities of the normal atom in a homogeneous solution. The interstitial atom experiences no such geometrically imposed correlation, that is the correlation factor
is unity. This is due to the fact that vacant interstices are plentiful even in relatively concentrated solutions. In this case it is meaningless to discuss the identity of one of these vacant sites much less to calculate the effect of multiple interchanges of a given vacancy with a given solute. The subject of correlation effects in solid solutions has been carefully presented by Bardeen and Herring.\textsuperscript{14}

Having characterized the solution it was necessary to define initial and boundary conditions which fit the constraints of the experiment and which would yield data amenable to analysis by equation I-4. The doubly infinite sample geometry was chosen with an initial radioactive profile describing a step function. This arrangement had the advantage of bilateral symmetry and of a well known solution to I-4 for $\theta^*$, the tracer to solvent atom ratio, as a function of distance from the interface $x$ and diffusion time $t$, to wit

$$\theta^*(x,t) = \theta_0^*(1 - \text{erf}(x/2\sqrt{Dt}))$$  \hspace{1cm} (I-44)

where $x$ is measured positive in the direction of decreasing tracer concentration and $\theta_0^*$ is the tracer concentration at the interface. This function is shown in Figure II. It must be remembered that the overall atom ratio was held constant throughout the couple at all times and that the $\theta^*$ in equation I-44 refers only to the heavy isotope.

The diffusion couples were formed by butt welding two sample halves containing like quantities of carbon by a resistive technique similar to that employed by Wells and Mehl\textsuperscript{15} and by Wells, Batz and Mehl\textsuperscript{3}. Using
FIGURE 2. \((1 - \text{erf}(kx))\) vs. \(x\)
$\frac{\theta}{\theta_{1/2}}$ vs $x$ for different times $t_1$ and $t_2$. The graph shows two curves $F(x,t_1)$ and $F(x,t_2)$ with $0 < t_1 < t_2$.
this technique it was possible to dissolve radioactive and non-radioactive carbon into the halves independently prior to welding and to hold interdiffusion across the interface due to welding at a minimum.

The welded couples were annealed at a calibrated temperature in a vacuum for a set period of time and air quenched. Then they were sectioned by grinding as described further in this chapter. Due to the extremely short range of the low energy β emissions (E_{max} = .154 mev) from the Cl⁴ it was possible to obtain an activity profile by counting emissions from successively exposed surfaces of the couple with an end window Geiger-Müller tube and to relate this profile directly to that of ⁴θ. Finally \( \theta = (\theta' + \theta^*) \) where \( \theta' \) is the atom ratio of Cl¹² and \( \theta \) is thus the overall atom ratio of carbon was determined by a combustion technique.

From \( \theta_{EXP}(x,t) \) the measured profile of Cl⁴, and equation I-44 one can determine \( \bar{D}^* \), the diffusivity of Cl⁴, by a numerical fitting technique. \( \bar{D}^* \) differs from \( \bar{D} \), the diffusivity of Cl¹², by a factor related to isotopic mass. Vineyard¹⁶ has shown this factor to be \( \sqrt{m^*/m'} \) in the classical case. Thus the equation

\[
\bar{D} = (m^*/m')^{1/2} \bar{D}^*
\]  
(I-45)

could be used to relate tracer diffusivities to normal diffusivities thereby completing the analysis.
Materials

The metals used in the experiment were MARZ grade zone-refined nickel and iron in the form of polycrystalline rods obtained from Materials Research Corporation, Orangeburg, New York. Batch analyses of each are exhibited in Tables I and II. The normal carbon was obtained from reactor grade graphite and the radioactive carbon from finely powdered graphite supplied by International Chemical and Nuclear Corporation, Irvine, California.
TABLE I

Analysis of Nickel

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</tr>
<tr>
<td>Bal.</td>
<td>&lt;60.0</td>
</tr>
</tbody>
</table>
TABLE II

Analysis of Iron

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Content (wt. ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>90.0</td>
</tr>
<tr>
<td>C</td>
<td>35.0</td>
</tr>
<tr>
<td>N</td>
<td>120.0</td>
</tr>
<tr>
<td>B</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>0.3</td>
</tr>
<tr>
<td>S</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Na</td>
<td>0.5</td>
</tr>
<tr>
<td>Mn</td>
<td>3.0</td>
</tr>
<tr>
<td>Bal.</td>
<td>&lt;20.0</td>
</tr>
</tbody>
</table>
Solution Annealing

Solution annealing was carried out by sealing sample halves in evacuated quartz glass ampoules with measured amounts of graphite. The iron sample halves, \( \frac{1}{4} \)" diameter rods \( \frac{1}{2} \)" in length, were cleaned and weighed to .001 gram on a Mettler single pan balance. The amount of carbon required to raise the concentration of a given sample to the desired level was calculated and weighed out to like accuracy. Nickel samples of like dimension were sealed with excess carbon and heated to controlled temperatures. This process allowed control of concentration by use of the slope of solubility with temperature.

Both sample and graphite then were placed in a quartz tube which had previously been sealed at one end. The tube was necked almost to closure at the open end and was connected to the vacuum apparatus illustrated in Figure III. Under the low vacuum of the mechanical pump (approximately 100 torr) the ampoule was torched with an oxy-hydrogen flame to remove any absorbed water vapor. Then the neck was drawn closed with the same flame. An oxy-hydrogen flame was chosen for its broad feathered almost colorless flame which gave more even heating and allowed close observational control over the glass blowing operation.

A Tesla coil was used to determine the success or failure of the sealing operation. The high tension discharge was directed at the ampoule ionizing the contained gases. Any porosity in the seals was observed as a preferred ionization path. Further, in cases of insufficient vacuum, the gas would fail to ionize generally. Each capsule failing either to ionize generally or to indicate a complete lack of
FIGURE 3. Apparatus for sealing samples in quartz glass ampoules under vacuum.
To Vacuum Pump
Liquid Nitrogen
Vapor Trap

Bleed Valve

Rotary Quick Connect

Location of Seal

Sample

Graphite
porosity was opened, the sample washed and the carbon discarded.

The well sealed ampoules were paired by carbon content, tied together with nichrome wire and placed in a high temperature tube furnace at a temperature in excess of 1000°C. They were left in the furnace for from $5 \times 10^2$ hours to $10^3$ hours, the shorter times for low concentration samples. Upon removal they were air quenched, examined for residual graphite and opened. The resulting sample halves were smooth, almost satin in finish.

Several pilot samples were run, of both nickel and iron, to determine the radial homogeneity of solutions. Microhardness profiles were taken across the diameter of an internal surface. The times required to produce a uniform hardness profile was taken as the time required for solution annealing.
Welding

The prepared sample halves were then readied for welding. It is necessary for the faces to be welded together to be polished to a moderately fine finish to assure complete binding with minimal porosity. The faces must be closely perpendicular to the axis of the cylinder yet some slight doming was found to yield more consistent welds, presumably due to the sweeping action of the liquid interface as it passed radially outward. The sample holding device designed to allow this facial configuration is illustrated in Figure IV. The upper piston is a solid block with a ground surface facing the sample end and is closely fit to the cylinder in which it slides. The exterior diameter of the lower piston is likewise machined to a close sliding fit. The diameter of the interior hole in the lower piston is slightly oversized to allow some wobble while retaining perpendicularity of the grinder itself. The body of the grinder is of a hard low alloy steel and was graciously furnished by A. Oates of the University of Newcastle, New South Wales, Australia. The surface of the grinder, being of such greater area than the sample, was but little affected by the grinding though it was dressed periodically to assure its continued flatness and perpendicularity to the grinder axis. Using this holder the sample faces were ground to a 600 grit metallographic finish on grinding papers. Thus prepared they were mounted in the welding jig illustrated in Figure V. The basic frame was designed to have minimal stress compliance so the pressure applied by the positioning screws could be relieved with minimal flaring distortion at the weld. The insulation of the current carrying members
Grinding jig for preparation of sample halves for welding.

FIGURE 4.
from one another was accomplished using glass microscope slides on the sides and bottom of the holder channel. The positioning screws pressed against pads of high temperature low vapor pressure epoxy. The rear faces of the copper sample mounting block and the contact surfaces of the brass terminal strips were kept highly polished to assure high conductivity at this junction. With the samples mounted the holder was placed in a vacuum chamber which was pumped to a hard vacuum of better than $10^{-5}$ torr.

Current for welding was supplied by a Variac controlled 7kva transformer. It was conducted into the chamber through high current feedthroughs manufactured by Consolidated Vacuum Corporation. Welding currents required were on the order of 200 amperes.

Operator control of the welding operation was facilitated by observation of the heated couple through the vacuum bell jar. Prior to fusion the interface could be distinguished as a bright orange circumferential line which effectively vanished at the time of interfacial welding.

Total times at elevated temperature for the welding operation ranged from 30 seconds to one minute, a sufficiently short time to disallow measurable solid state transfer. Mixing at the interface in the liquid phase was also negligible as is demonstrated by the autoradiogram in Figure VI. The dotted lines delineate the edges of the specimen.

Pilot samples were run and sectioned lengthwise to determine weld quality visually. On actual experimental runs, however, it was not possible to exercise any prior screening. Rather, it was necessary to
FIGURE 6. Autoradiogram of longitudinally sectioned diffusion couple after welding. (actual size).
proceed with the sectioning and counting through the sample until the exposed face reached the weld interface. At such time visual inspection was possible both with respect to weld quality and to inclination of the counting axis with respect to the sample axis. Samples having porosity in the central counting region or exhibiting overall porosity spanning an area in excess of one percent of the interface were discarded.
Diffusion Annealing

The diffusion annealing, holding the sample for a given time at an elevated temperature, in this case 10000°C, to allow diffusive motion of the solute, was carried out in an evacuated furnace tube in a three zone Lindberg tube furnace. The annealing system is illustrated in Figure VII. The couple was placed in an alumina boat connected by a stiff molybdenum rod to an iron slug. Translation of the sample into and out from the hot zone of the furnace was accomplished by manipulating the iron slug, and thus the entire holder assembly, with a permanent magnet moved along the outside of the quartz furnace tube.

The hot zone of the furnace consisted of approximately three inches which was within two degrees Celsius of the nominal 10000°C. Calibration of the furnace was carried out before each diffusion run. A chromel-alumel thermocouple connected to a Leeds and Northrup potentiometer and referenced to ice water served as the calibration standard. It was required to stabilize the system for some 24 hours when starting from room temperature. With such stabilization the controller managed to maintain a temperature within 5°C of the nominal value as monitored for periods of 24 hours at various times over the term of the experiment by a continuous chart recording using a platinum/platinum-10% rhodium, type R, thermocouple.

As the couples were removed from the furnace the tube was flooded with argon to quench the sample. With such a quench the cooling time was held extremely low, less than one minute. Rise time, as determined from a slug of comparable mass to that of a couple connected to a
FIGURE 7. Apparatus for annealing diffusion couples under vacuum.
chromel alumel thermocouple being inserted into the furnace, was on the order of one minute with furnace stabilization being achieved within about five minutes. Since this time is negligible with respect to the 48 hours over which diffusion was allowed, no correction was made for the effect of heating time and cooling time on the effective diffusion time.
Serial Sectioning and Counting

The low energy of the $\beta$ particles emitted by C$^{14}$ ($E_{\text{max}} = .154$ mev) allowed counting to be carried out from one exposed end of the specimen. That is, due to the strong $\beta$ absorption by the metals only those particles emitted extremely close to the surface could escape the body of the metal to be counted. Thus the effective counting depth is extremely small (20$\mu$m) and the distribution of solute over this depth can safely be approximated as constant. Though, in interaction with heavy atoms, the $\beta$ particles generate far reaching $\gamma$ emissions, bremsstrahlung radiation$^{17}$, this amounts to an extremely low intensity compared with the direct $\beta$ emissions and did not measurably effect the shape of the concentration profile whether these data were collected up or down the gradient. Therefore it was possible to relate directly the measured activities less background to the C$^{14}$ concentration at the exposed surface.

The apparatus used for sectioning and counting is illustrated in Figures VIII and IX. The counting tube is a gas flow end window Geiger-Muller tube from Baird Atomic Incorporated, Bedford, Massachusetts. The counting gas employed was 1% isobutane in helium and window density was .09 mg/cm$^2$. Scaling was done with a Tracerlab Model scaler-counter.

The sample grinding jig was the same as shown in Figure IV in the section on welding except that the loose mount sample holding piston was replaced by one designed to hold the sample firmly parallel to the axis of the grinder. The couple, once mounted in the holding piston, was held firm with a low melting sealing wax and was not removed until the
entire counting procedure was completed. By using the same mount for both grinding and counting, consistent geometries were assured among successive measurements. The sample faces were ground on successively finer grades of metallographic papers and were then polished on a rotary lapping wheel with 5µ diamond paste prior to each measurement. Using this technique it was possible to remove as little as .01 cm in a given section.

The thickness of the removed layers was measured with micrometer calipers from the face of the sample to the back face of the mounting piston. Since the piston remained isolated from the grinding operation and since the sample mounting was not changed from count to count the butt of the mounting piston served as a reliable point of reference for these length measurements.

After each grinding the sample and the holding jig were carefully washed and dried and were mounted, inverted, into the counting jig of Figure IX. The masks in Figure X were designed to eliminate surface decarburization effects on the counting. They also provided assurance of a constant counting area and a linear counting axis in the sample. Two sizes of aperture were employed to check the radial depth of possible decarburization zones. In every case reported, count rates determined from a given surface with the different masks were in the ratio of the exposed areas thus indicating homogeneous solutions.

Standardization of the counting system was by means of a standard C¹⁴ source of 0.2 µCi from New England Nuclear, Boston, Massachusetts. The gas flow tube exhibited remarkable stability over the term of the
Mask A  \[ a = \frac{1}{8}'' \quad b = \frac{1}{4}'' \]

Mask B  \[ a = \frac{3}{16}'' \quad b = \frac{5}{16}'' \]
experiment. Since count rates were less than $10^3$ cps, correction of observed rates for counter dead time was not required. Such correction would have been on the order of $0.1^0$ at the highest rates due to the extremely short dead time of the counting tube ($\sim10^{-4}$ sec). Background levels measured between every two counting runs or every hour during a series of counts were found by inserting a piston from the same bar stock as the sample mounting piston with a blank section of the pure iron mounted. The counting rates measured varied from 15 to 30 cps with short term variation in a seemingly random manner over the experimental term.

The sectioning scheme is illustrated in Figure XI. In order to solve equation I-44 for D it is necessary to determine the relative intensity profile $\theta^*(x,t)$ normalized to $\theta^*(\infty, t) = 1$. This equation implies further that the atom ratio at the interface should remain at one half the high end value for all times, $\theta^*(0,t) = \frac{1}{2}\theta^*(\infty, t)$. Thus normalization counts were carried out far from the interface at each end yet sufficiently distant from the sample ends to obviate surface effects. The high activities were averaged with the low and the result averaged with the interpolated counting rate at the interface to find a consistently determined value for $\frac{1}{2}\theta^*(\infty, t)$.

The profile of interest was that ranging a few millimeters on either side of the interface. This was measured at exposed faces separated by about .05 cm. As this exposed surface progressed across the weld interface, it was possible to determine visually the inclination of the weld to the grinding axis. The angle was less than
FIGURE 11. Scheme for sectioning and count normalization.
20 in all cases reported.

Counting was carried to $2.0 \times 10^5$ counts or 200 minutes whichever was less. This allowed counting error due to randomness of nuclear disintegrations, calculated as $1/\sqrt{N}$, where $N$ is the number of counts, to be held to about 1% for count levels substantially in excess of background.

High concentration end activities ranged as high as $10^3$ counts/second and as low as 400 cps. Count rates did not necessarily decrease linearly with solute concentration since different levels of C14 were used for samples of varying concentration. This variance was intended to keep the count level approximately constant over the various samples. Low end activities remained close to background levels.
Chemical Analysis

Analysis of the sample segments to determine overall carbon concentration was carried out using a Leco low-carbon analyzer. This apparatus uses a combustion method to extract the carbon as \( \text{CO}_2 \) and an absorption scheme for measurement. As the apparatus is subject to drift, standardization was required between each sample analysis run. Standards were supplied by Leco Corporation and by the National Bureau of Standards. The former are traceable to the National Bureau of Standards. At least four standards were analyzed before each sample run, two high carbon and two low. Several analysis runs were carried out in sequence to provide for standard conditions of measurement.

Sections to be analyzed were taken far from the sample ends and ground several millimeters on each diameter to eliminate surface effects. At least two, and ordinarily four, sections were analyzed for each couple. High to low variance was no greater than \( \Delta \theta = .008 \) in any sample reported.
Results

The diffusivities $D$ were measured at 1000°C for concentrations spanning the $\gamma$ phase field of the Fe-C system. A typical radioactivity profile is shown in Figure XII. A more illuminating method of displaying the data is by plotting, with reference to equation I-44, $\text{erf}^{-1}(1-2\frac{\delta^*/\delta_0}{\delta_0})$ versus $x$. This plot should yield a straight line of slope $(4\bar{D}t)^{-\frac{1}{2}}$. The results for each sample are given in Appendix A.

The best value of $\bar{D}$ for each sample was determined by a least squares fitting routine performed on a digital computer. The two highest concentration samples of iron were counted in opposite directions to evaluate the effect of activities far from the surface on measured concentration profiles and the effect is seen to be negligible. Isotope effects were assumed classical, effecting only the vibrational frequencies of the solutes. Therefore correction of the measured $\bar{D}^*$ to the values appropriate to C$^{12}$, $\bar{D}$, was made by multiplying $\bar{D}^*$ by the factor

$$\left(\frac{m_{\bar{D}^*}}{m_{\bar{D}}^{12}}\right)^{\frac{1}{2}} = 1.08$$  \hspace{1cm} (I-46)

as derived by Vineyard. $\bar{D}$ values along with overall $\theta$ values are exhibited in Tables III and IV for Ni and Fe respectively.

The nickel data spanned a very short composition range due to the limited solubility of carbon. It is notable, however, that $\bar{D}$ measured close to $\theta = 0$ is very close to that given by Kovenski$^{18}$.

The $D$ values in iron were found, by a least squares fitting routine,
FIGURE 12. Typical activity profile.
to be described by

$$\bar{D}(\theta) = (2.47 + 1.36\theta + 319\theta^2) \times 10^{-7} \text{cm}^2/\text{sec}$$  \hspace{1cm} (I-47)

Figure XIII shows $\bar{D}$, calculated by equation I-47, versus $\theta$ along with a curve matched to the $D$ values of Smith$^4$. It is notable that $\bar{D} \to D$ as $\theta \to 0$ as would be expected.
FIGURE 13. Measured finite-gradient and zero-gradient diffusivities vs. atom ratio, $\theta$. 
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>( \theta )</th>
<th>( \mathcal{D}^* \times 10^{-7} \text{ cm}^2/\text{sec} )</th>
<th>( \mathcal{D} \times 10^{-7} \text{ cm}^2/\text{sec} )</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>.008</td>
<td>2.31</td>
<td>2.50</td>
<td>Ni</td>
</tr>
<tr>
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<td>.010</td>
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<td>2.53</td>
<td>&quot;</td>
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<td>201</td>
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<td>.047</td>
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<td>&quot;</td>
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<td>206</td>
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<td>&quot;</td>
</tr>
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<td>207</td>
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<td>3.18</td>
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<tr>
<td>212</td>
<td>.072</td>
<td>3.84</td>
<td>4.15</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Discussion

As seen from Figure XIII the \( D \) values measured here are consistently lower than the \( D \) values of Smith. It is of interest to compare the data with the predictions of equation I-44.

Ban-ya, Elliott, and Chipman have performed very careful and thorough measurements of the thermodynamic activity, \( \alpha_c \), of carbon in austenite as a function of both temperature and atom ratio, \( \theta \). They obtained an analytic expression for \( \alpha_c \) with respect to graphite, which is

\[
\ln \alpha_c = 8681/T - 6.261n\cdot T - 24.24 + 8888\theta/T
\]  

(I-48)

McLellan and Dunn have shown the value \( \Delta_c = -1.95 \) kcal/mole to allow good agreement between these observations and first order statistics.

Using the above expressions for \( \alpha_c \) and \( \Delta_c \), \( D_0 \) was calculated using equation I-32. If the model holds \( D_0 \) is expected to be essentially constant. Figure XIV displays the calculated values of \( D_0 \) over the range of \( \theta \) investigated. The invariance of the calculated \( D_0 \) is evident from the figure.

The constancy in \( D(\theta)/\xi(\theta)\omega(\theta) \) with respect to carbon concentration is somewhat surprising in view of the assumptions made in the calculation. Although the measurement of the "tracer" diffusion coefficient does not involve a gradient of specific volume which could differentially influence the flow rates of diffusing atoms in the
forward and reverse direction, the mean iron-carbon interatomic distances are different at each composition due to the expansion of the lattice caused by the dissolved C atoms. This effect has been neglected in using the first order model with a constant carbon-carbon interaction energy to calculate \( f(\theta) \). It has been pointed out that the lattice expansion would lead to a decrease in the activation energy for diffusion and concomitantly an increase in \( C \) with concentration\(^{21} \). It is at this point difficult to estimate the magnitude of this effect. The difference in energy at infinite dilution between insertion of a C atom into the austenite lattice at constant volume, \( E_i \), and at constant pressure, \( \Pi_i \), (allowing lattice relaxation) can be estimated from recent measurements of the elastic properties of austenite at high temperatures\(^{22} \). The quantity \( H_i - E_i \) at the infinite dilution is 3.7 kcal/mole. It is difficult to estimate the corresponding change in activation energy for diffusion.

In the case of "tracer" diffusion of the kind measured in the present experiments, the mobility factor, \( f(\theta) \), does not affect the fluxes of the diffusing species in a differential manner and always decreases \( D \). The effect however is relatively small. In the limit \( \theta \to 0 \), \( f(\theta) \to 0 \) and at \( \theta = 0.072 \), the highest carbon concentration investigated in the current experiments, \( f(\theta) = 0.72 \). The increase in \( D \) with carbon concentration is due to the increase in chemical driving force. The function \( \omega(\theta) \) increases from 9.8 at \( \theta = 0 \) to a value of 23.9 at \( \theta = 0.072 \) (the activity is measured with respect to graphite).
FIGURE 14. $P_0$ vs. atom ratio, $g$. 
\[ \Delta \varepsilon = -1.95 \text{ kcal/mole} \]
REFERENCES


10. L. S. Darken: Trans. AIME, 175, 184 (1948).


APPENDIX A

The graphs in this appendix detail the measurements carried out on each of the samples referred to in the text. The sample numbers correspond to those given in Table I. Note that 100 series samples are those with nickel as the solvent and 200 series are those in which the solvent is iron. The graphs herein are plotted in units of millimeters on the abscissa and in the unitless quantity erf^{-1} (1-2θ/θ_o) on the ordinate. These units have been omitted in the individual graphs for clarity. Each graph indicates by means of an arrow the direction in which the concentration profile was measured.
PART II
Thermodynamics of Substitutional Solid Solutions
Introduction

A certain degree of positional information always is necessary as a basic starting point in setting up any statistical-mechanical model for solid solutions. The most fundamental information concerns the basic structure of the solution, i.e., whether it is of the substitutional or interstitial type.

Even this most basic information is not always well established. A classic example is the Fe-B system. The substitutional solubility of boron in BCC iron is supported by lattice parameter measurements and the value of the migration energy (62 kcals/mole). However, internal friction work by Thomas and Leak and by Tavadze, Bairamashvili, Metreveli and Tzagareishvili, in which a Snoek peak has been found, supports the interstitial sites for boron in α-iron. On the other hand, other workers have failed to detect a boron peak. The recent careful internal friction study of Hayasaki and Sugeno showed an internal friction peak at 500°C (due to carbon) and a weaker peak at -13°C which appeared only when the sample contained boron. They concluded from the height of the peak at -13°C that most of the boron dissolves substitutionally but about a fifth of it is present in interstitial sites. In FCC iron there is little doubt that the boron is interstitially dissolved since the migration energy is only 21 kcals/mole.

Fortunately, in most cases, this kind of uncertainty is not present and the choice between interstitial and substitutional structure is clear. For such well determined solutions a geometric
approach such as the so-called Kirkwood expansion technique can be applied to model the solution thermodynamics provided that the ratio of the solute interaction energy to kT is sufficiently small, i.e.,

$$|\alpha| \leq 1 \quad (\text{II-1})$$

for

$$\alpha = -\omega / kT \quad (\text{II-2})$$

where

a) $$\omega = \varepsilon_{ii}$$

b) $$\omega = 2\varepsilon_{uv} - \varepsilon_{uu} - \varepsilon_{vv} \quad (\text{II-3})$$

and where $$\varepsilon_{ij}$$ is the interaction energy of an i-j pair.

The Kirkwood expansion by which one expands the free energy of the solution in terms of $$\alpha$$ was first proposed by Kirkwood. It was later expanded upon by Bethe and Kirkwood and by Chang. Recent work has been done in applying this method to interstitial solid solutions and extending it to include second, third, and more distant neighbor interactions. This work by Alex and McLellon has proved successful in treating high temperature solutions where the solute interaction energy is small, e.g., carbon austenite, in spite of the implicit assumption of central force interactions. In the
present work an attempt has been made to apply the expansion method to metallic substitutional solid solutions which exhibit complete solid solubility.
Theory

Krivoglaz and Smirnov\textsuperscript{16} have given a thorough treatment of the Kirkwood expansion method for substitutional solutions. It is upon this work that the following derivation is based.

The configurational partition function for an A-B substitutional solid solution is written

\[ Z_C = \exp\left(-\frac{E_i^C}{kT}\right) \]  \hspace{1cm} (II-4)

where \( E_i^C \) is the configurational energy of the solution, that is the sum of all atomic interaction energies for the solution in a given configuration, \( i \), and where the sum is carried over all accessible configurations. If one considers only pairwise nearest neighbor interactions, the configurational energy can be written

\[ E_i^C = N_{AA}^i \epsilon_{AA} + N_{AB}^i \epsilon_{AB} + N_{BB}^i \epsilon_{BB} \]  \hspace{1cm} (II-5)

where \( N_{jk}^i \) is the number of \( jk \) pairs in configuration \( i \).

It is clear that the number of A-A pairs can be calculated by subtracting the number of A-B pairs from the total number of pairs formed by A atoms, \( zN_A \), where \( z \) is the lattice coordination number, and then dividing by two as each A-A pair is counted twice. That is to say,
\[ N_{AA} = \frac{1}{2}(zN_A - N_{AB}) \]  
(II-6)

Likewise,

\[ N_{BB} = \frac{1}{2}(zN_B - N_{AB}) \]  
(II-7)

Making use of equations II-3b, II-5, II-6 and II-7 one can write

\[ E_i = \frac{z}{2}(N_A(2\epsilon_{AB} - \epsilon_{BB}) + N_B \epsilon_{BB}) - N_{AA} \omega \]  
(II-8)

So combining equations II-4 and II-8 leads to

\[ Z_C = \exp(-z/2kT \cdot (N_A(2\epsilon_{AB} - \epsilon_{BB}) + N_B \epsilon_{BB})) \cdot \exp(-N_{AA}^{(i)} \omega/\kappa T) \]  
(II-9)

If we expand the summand in terms of \( \alpha \) from equation II-1 and replace the summation over configurations by terms involving the mean values of the expansion terms we can write

\[ \exp(N_{AA}^{(i)} \alpha) = W(1+\alpha N_{AA} + \alpha^2/2! \overline{N_{AA}^2} + \cdots) \]  
(II-10)
where

$$W = \frac{(N_A + N_B)!}{N_A! N_B!} \quad (II-11)$$

is the total number of configurations and where the bar denotes an average over all configurations.

This partition function is related to the configurational free energy by

$$F^C = -kT \ln Z_C \quad (II-12)$$

Expanding equation II-10 in a power series in $\alpha$ one arrives at the expression

$$F^C = \frac{1}{2} z (N_A (2\varepsilon_{AB} - \varepsilon_{BB}) + N_B \varepsilon_{BB}) - kT \ln W - kT f(c_A, \alpha) \quad (II-13)$$

where

$$f(c_A, \alpha) = \sum_k \lambda_k \alpha^k / k! \quad (II-14)$$

The $\lambda_k$ in equation II-12 are combinations of the a priori averages of the $k$ powers of $N_A$, the so-called moments of $N_A$. 

$$M_k = \frac{N_k}{N_{AA}}$$  (II-15)

The first few of these terms are

a) \( \lambda_0 = 0 \)

b) \( \lambda_1 = M_1 \)

c) \( \lambda_2 = M_2 - M_1^2 \)  (II-16)

d) \( \lambda_3 = M_3 - 3M_2M_1 + 2M_1^3 \)

e) \( \lambda_4 = M_4 - 4M_3M_1 - 3M_2^2 + 12M_2M_1^2 - 6M_1^4 \)

Krivoglaz and Smirnov\textsuperscript{16} have given a clear account of the calculation of the individual moments for any given lattice, a calculation too involved to reproduce here. Suffice it to say that the calculation depends upon the possibility of decomposing the lattice into independent sub-lattices such that any given site has only nearest neighbor sites on sub-lattices other than that on which it is located. This requirement is satisfied for FCC and BCC lattices which can be decomposed into four and two interpenetrating simple cubic sub-lattices, respectively. It should be noted again that the expansion coefficients are not statistical-mechanical averages dependent upon the specific energetics of the solution but are composed of a priori pair averages and depend only upon the concentration of the solution.
and the lattice geometry.

So long as the summation in equation II-14 converges (and within the approximation of using only pairwise nearest-neighbor interactions) that equation is an exact representation of the configurational free energy. However, the \( \lambda_k \) become increasingly difficult to evaluate with increasing \( k \) for a given lattice, so one is limited in practice to consideration of those solid solutions for which the summation converges rapidly in the first few terms.

In the BCC lattice the first six coefficients have been evaluated and in the FCC lattice the first four are known. Expressions for these quantities are given in reference 16.

One relates \( F^C \) to measured thermodynamic data in the following way. The configurational chemical potential is

\[
\mu_A^C = \frac{1}{2}z(2\epsilon_{AB} - \epsilon_{BB}) + kT(\ln c_A + g(c_A, \infty)) \quad \text{(II-17)}
\]

where

\[
g(c_A, \infty) = \sum_k \left( \frac{\lambda_k}{\sigma_{NA}^{k}} \right)_{T,V,N_B} \ll \frac{k}{k!} = \sum_k \lambda_k \frac{k}{k!} \quad \text{(II-18)}
\]

The expressions for the first few \( \lambda_k \) are given in Table I and they are plotted in Figures I and II. The first term in equation II-15 is identical to \( \tilde{E}_A^\infty \), the partial free energy of A in the infinitely dilute A-B solution. The second term is merely \( -(\tilde{T}_A^{id}) \), minus the
TABLE I

B.C.C. and Simple Cubic

\[ \lambda_1 = \frac{1}{2}ZC^2 + ZC(1-C) \]
\[ \lambda_2 = \frac{1}{2}ZC^2(1-C)^2 + ZC(1-C)^2(1-2C) \]
\[ \lambda_3 = \frac{1}{2}ZC^2(1-C)^2(1-2C)^2 + ZC(1-C)^2(1-2C)(1-6C+6C^2) \]
\[ \lambda_4 = \frac{1}{2}ZC^2(1-C)^2(1-6C+6C^2)^2 + 3(Y-Z)C^4(1-C)^4 + 8C \]
\[ (1-C)^2(1-2C)(1-6C+6C^2)((1-6C+6C^2)-6) + 12(Y-Z)C^3(1-C)^4(1-2C) \]
\[ \lambda_5 = \frac{1}{2}ZC^2(1-C)^2(1-2C)^2(1-12C+12C^2)^2 + 30(Y-Z)C^4 \]
\[ (1-C)^4(1-2C)^2 + ZC(1-C)^2(1-2C)(1-12C+12C^2) \]
\[ ((1-6C+6C^2)(1-12C+12C^2) - 12C(1-C)(1-2C)^2) + 120(Y-Z)C^3(1-C)^4(1-2C)^3(1-6C+6C^2) \]
\[ \lambda_6 = \frac{1}{2}ZC^2(1-C)^2(1-60C(1-C)(1-2C)^2) + 15(13Y+17Z)C^4 \]
\[ (1-C)^4 + 60(J_1-30Y-28Z)C^5(1-C)^5 + 60(J_2-4J_1+66Y+42Z)C^6(1-C)^6 + ZC(1-C)^2(1-2C)((1-60C(1-C)(1-2C)^2) - 30C(1-C)(1-6C+6C^2)) + 60(13Y+17Z)C^3(1-C)^3(1-2C) + 300(J_1-30Y+28Z)C^4(1-C)^4(1-2C) + 360(J_2-4J_1+66Y+42Z)C^5(1-C)^5(1-2C) \]

B.C.C.: Z=8; Y=96; J_1=144; J_2=1776
Simple Cubic: Z=6; Y=24; J_1=0; J_2=264
TABLE I  (Cont'd)

F.C.C.

\[ \lambda_1 = 6c^2 + 12c(1-c) \]
\[ \lambda_2 = 6c^2(1-c)^2 + 12c(1-c)^2(1-2c) \]
\[ \lambda_3 = 6c^2(1-c)^2(1-2c)^2 + 8c(1-c) \]
\[ \lambda_4 = 6c^2(1-c)^2(1-6c+6c^2)^2 + 24c(1-c)(1-2c)^2 + 22c \]
\[ \lambda_4 = 6c^2(1-c)^2(1-6c+6c^2)^2 + 24c(1-c)(1-2c)^2 + 126c \]
\[ \lambda_4 = 6c^2(1-c)^2(1-6c+6c^2)^2 + 24c(1-c)(1-2c)^2 + 126c \]
\[ \lambda_4 = 6c^2(1-c)^2(1-6c+6c^2)^2 + 24c(1-c)(1-2c)^2 + 126c \]
\[ \lambda_4 = 6c^2(1-c)^2(1-6c+6c^2)^2 + 24c(1-c)(1-2c)^2 + 126c \]
FIGURE 1. The expansion coefficients $\lambda'_{k}$ for F.C.C. solutions. The numbers on the curves indicate the order of the coefficients.
FIGURE 2. The expansion coefficients \( \lambda_k \) for B.C.C. solutions. The numbers on the curves indicate the order of the coefficients.
temperature times the ideal partial molar entropy. Thus equation II-17 becomes

$$\mu_A^{\text{c}} = \frac{E_A}{T} - TS_A + kTg(c_A, \infty)$$  \hspace{1cm} (II-19)

Since,

$$\mu_A^{\text{id}} = \frac{E_A}{T} - TS_A + \mu_A^{\text{o}}$$  \hspace{1cm} (II-20)

then

$$\mu_A^{\text{c}} = \mu_A^{\text{id}} - \mu_A^{\text{o}} + kTg(c_A, \infty)$$  \hspace{1cm} (II-21)

where $\mu_A^{\text{o}} = \frac{E_A}{A} - TS_A^o$ is the free energy per mole of pure A.

Now we note that the $\lambda^i_k$ vanish at infinite dilution and thus $g(c_A, a)$ vanishes there as well. Further, the activity coefficient, neglecting non-configurational terms in $\mu_A^{\text{c}}$ can be expressed as

$$\mu_A^{\text{c}} - \mu_A^{\text{id}} = kT \ln \gamma_A$$  \hspace{1cm} (II-22)

Therefore, combining II-21 and II-22, we can say finally that

$$\ln (\gamma_A(c_A)/\gamma_A(0)) = g(c_A, \infty)$$  \hspace{1cm} (II-23)
Results

The functions $g(c_A, \alpha)$ are plotted in Figures III and IV for FCC and BCC solutions. In each case the order of the expansion is noted on the figure. The dashed lines correspond to taking one less term in the expansion. This has been illustrated only for the largest values of $\alpha$ (i.e., $\alpha = 1$) and it can be seen that the final term does not make a large contribution to the sum. The contribution of the last term for $\alpha < 1$ is much smaller.

From the tabulated thermodynamic data collected and evaluated by Hultgren, Orr, Anderson and Kelley\textsuperscript{17}, experimental values of $\ln(\gamma_A(c_A)/\gamma_A(0))$ versus $c_A$ have been calculated and are plotted in Figures V and VI. These particular binary systems were chosen since they each exhibit complete solid solubility and are closely related in the periodic table. The values for $\alpha$ obtained by fitting the experimental data to equation II-21 by a least-squares fitting routine are given in Table II. The specie considered the solute is listed first in the solution nomenclature.

According to the model, both components should behave identically with respect to $\ln(\gamma_A(c_A)/\gamma_A(0))$. That they do not is shown clearly from Table II, and from Figures V and VI.
<table>
<thead>
<tr>
<th>Solute-Solvent</th>
<th>Structure</th>
<th>$\alpha$</th>
<th>$T^{\circ\text{K}}$</th>
<th>$\omega$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au–Ag</td>
<td>FCC</td>
<td>-0.50</td>
<td>800</td>
<td>0.795</td>
</tr>
<tr>
<td>Ag–Au</td>
<td>FCC</td>
<td>-0.25</td>
<td>800</td>
<td>0.397</td>
</tr>
<tr>
<td>Ni–Cu</td>
<td>FCC</td>
<td>0.15</td>
<td>973</td>
<td>-0.290</td>
</tr>
<tr>
<td>Ni–Au</td>
<td>FCC</td>
<td>0.20</td>
<td>1150</td>
<td>-0.457</td>
</tr>
<tr>
<td>Cu–Ni</td>
<td>FCC</td>
<td>0.35</td>
<td>973</td>
<td>-0.677</td>
</tr>
<tr>
<td>Au–Ni</td>
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<td>0.45</td>
<td>1150</td>
<td>-1.03</td>
</tr>
<tr>
<td>V–Cr</td>
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<td>1550</td>
<td>1.85</td>
</tr>
<tr>
<td>Cr–V</td>
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<tr>
<td>Cr–Mo</td>
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<td>1471</td>
<td>-0.877</td>
</tr>
<tr>
<td>Mo–Cr</td>
<td>BCC</td>
<td>0.60</td>
<td>1471</td>
<td>-1.75</td>
</tr>
</tbody>
</table>
FIGURE 3. The functions $g(C_i, \alpha)$ plotted against $C_i$ for F.C.C. solutions.

Different values of $\alpha$ are shown.
FIGURE 4. The functions $g(C_i, \alpha)$ plotted against $C_i$ for B.C.C. solutions. Different values of $\alpha$ are shown.
FIGURE 5. Experimental variation of $\ln \gamma_i(C_i)/\gamma_i(0)$ with $C_i$ for selected F.C.C. solid solutions.
FIGURE 6. Experimental variation of $\ln \frac{\gamma_i(C)}{\gamma_i(0)}$ with $C_i$ for selected B.C.C. solid solutions.
Conclusions

Indeed, the assumptions that $\alpha$ and the partial excess entropies are independent of composition cannot be generally valid. The view could be taken that the thermodynamics of the system could be described by composition-independent $\alpha$'s specific to each species and valid for a certain composition range only. However, the utility of such an approach is doubtful given the much simpler approaches available, such as the parabolic representation of Darken\textsuperscript{18}. It must, however, be emphasized that such representations are merely ways of presenting data in a concise form and have little theoretical significance.

Although the expansion of the free energy in terms of cumulants has proved to be of great value in treating interstitial solutions, the same cannot be said with regard to substitutional solutions. There is a real need to build up a larger body of positional information in substitutional solutions particularly concerning cluster formation and partial ordering.
REFERENCES


