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Quasichemical Model for Interstitial Solutions

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ABSTRACT

An ideal solution is one in which the enthalpy of mixing is zero so that the only contribution to the free energy of mixing comes from the change in configurational entropy when atoms mix at random. Regular solutions have a finite enthalpy of mixing but nevertheless assume random mixing. Quasichemical models avoid this approximation of random mixing. This work deals with an amendment to some of the equations in the quasichemical theory for Fe–C solutions, making the equations, for example, more reliable at large C–C repulsions.

INTRODUCTION

The regular solution model assumes a random distribution of atoms even though the enthalpy of mixing is not zero. In reality, a random solution is only expected at very high temperatures when the entropy term overwhelms any tendency for ordering or clustering of atoms. It follows that the configurational entropy of mixing should therefore vary with the temperature. The *quasi–chemical* solution model has a better treatment of configurational entropy which accounts for a non–random distribution of atoms. The model is so–called because it has a mass–action equation which is typical in chemical reaction theory [1,2].

There is a particularly useful application of the quasi–chemical model to the solution of carbon in austenite [3]. The theory is founded on the fact that there is a repulsion between the carbon atoms which has the effect of reducing the probability by which a neighbouring interstitial site is occupied. The history of such "site exclusion models" has been reviewed by McLellan and Dunn [3,4], but we shall focus on their model which removes many of the difficulties of earlier treatments. Furthermore, the model appears to have considerable physical significance, both in explaining fine detail in thermodynamic data and in the prediction of diffusion phenomena.

The purpose of the present work is to correct a subtle difficulty with the McLellan and Dunn model, which does not seem to cope well with the limit of infinite repulsion, and is not consistently developed in its zeroth and first order approximations†. The theory is generally applicable but will be discussed in the context of Fe–C solutions. Almost half of the paper is devoted to a repitition of published work in order to introduce a subject which is not commonly known in metallurgy.

THE THEORY

Partition Function

The general methodology in summarised in Fig. 1. The essential problem in the construction of a quasi–chemical model is the partition function. Although the function is standard theory, its meaning is introduced below for the sake of readability.

† The zeroth approximation of quasichemical theory is identical to a regular solution model.

Consider a total number N of atoms in a system where there are just two energy levels. At any finite temperature a number N_0 of the atoms are in the ground state, whereas a number N_1 ($= N - N_0$) belong to the higher level with an energy E_1 relative to the ground state. The fraction of atoms in the two states at a temperature T and at zero pressure is given by:

$$\frac{N_o}{N} = \frac{g_0}{g_0 + g_1 \exp\{\frac{-E_1}{kT}\}} \tag{1}$$

$$\frac{N_1}{N} = \frac{g_1 \exp\{\frac{-E_1}{kT}\}}{g_0 + g_1 \exp\{\frac{-E_1}{kT}\}}$$

where g_i represents the degeneracy of the ith energy level. The degeneracy gives the number of states with the same energy. In each of these equations, the term in the denominator, is called the partition function Ω; in general, for a multi–level system,

$$\Omega = \sum_i g_i \exp\left\{\frac{-E_i}{kT}\right\}$$

where E_i is the energy relative to the ground state.

Carbon in Austenite

The treatment that follows is due to McLellan and Dunn [3,4]. Carbon dissolves interstitially in the octahedral holes in the crystal structure of the austenite. The number of Fe–Fe pairs and the number of Fe–C pairs does not change for a given composition for all configurations. The partition function can therefore be described solely in terms of the carbon atoms u in the octahedral sites (u_o).

Consider a system with N_u carbon atoms, N_{Fe} iron atoms and therefore, $\beta_i N_{Fe}$ octahedral sites where β_i is the number of octahedral interstices per iron atom ($\beta_i = 1$ for octahedral holes in austenite and $\beta_i = 3$ for octahedral interstices in ferrite). The variety of pairs of species is listed in Table 1, where the number of u–u_o and u_o–u pairs is written $W\lambda$, where $W = 12$ (for austenite) is the number of octahedral sites around a single such interstice. Naturally, W is the same for the carbon atoms.

Kind of pair	No. of such pairs	Energy per pair	Total energy
u_o–u_o	$\frac{1}{2}W(N_{Fe}\beta_i - N_u - \lambda)$	0	0
u_o–u and u–u_o	$W\lambda$	ϵ_u	$W\lambda\epsilon_u$
u–u	$\frac{1}{2}W(N_u - \lambda)$	ϵ_{uu}	$\frac{1}{2}W(N_u - \lambda)\epsilon_{uu}$
Total	$\frac{1}{2}WN_{Fe}\beta_i$		$W\left[\lambda\epsilon_u + \frac{N_u-\lambda}{2}\epsilon_{uu}\right]$

Table 1: Pair interactions in Fe(γ)–C quasi–chemical model (after McLellan and Dunn [3]). The energy zero is for an atom at rest in a vacuum so that the energies listed are numerically negative.

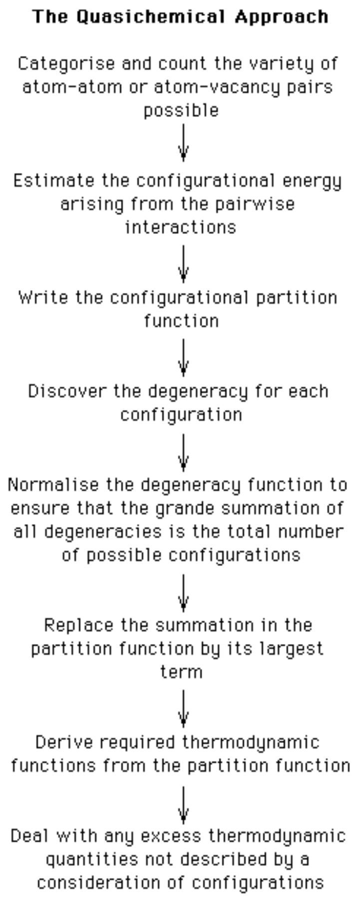

Fig. 1: The steps involved in the construction of a quasichemical solution model.

The configurational partition function using the data listed in Table 1 is, therefore,

$$\Omega = \sum_\lambda g_\lambda \exp\left\{ -W\left[\lambda \epsilon_u + \frac{N_u - \lambda}{2}\epsilon_{uu}\right]/kT \right\} \tag{2}$$

For a given value of λ, the different non–interacting pairs of atoms can be arranged in the following number of ways:

$$g_\lambda \propto \frac{[\frac{1}{2}WN_{Fe}\beta_i]!}{\underbrace{[\frac{1}{2}W(N_{Fe}\beta_i - N_u - \lambda)]!}_{u_o - u_o}\;\underbrace{[\frac{1}{2}W(N_u - \lambda)]!}_{u-u}\;\underbrace{[\frac{1}{2}W\lambda]!\;[\frac{1}{2}W\lambda]!}_{u-u_o \text{ and } u_o-u}} \tag{3}$$

It is usual to convert this proportionality into an equality by using a normalisation procedure which considers the degeneracy of a completely random solution, for which λ has the value λ^* given by the product of the number of solute atoms (N_u) and the chance of finding an unoccupied octahedral site:

$$\lambda^* = N_u\left(1 - \frac{N_u}{N_{Fe}\beta_i}\right) \tag{4}$$

Therefore,

$$\begin{aligned} g_\lambda = & \frac{[N_{Fe}\beta_i]!}{[N_{Fe}\beta_i - N_u]!\ N_u!} \\ & \times \frac{[\frac{1}{2}W(N_{Fe}\beta_i - N_u - \lambda^*)]!\ [\frac{1}{2}W(N_u - \lambda^*)]!\ [\frac{1}{2}W\lambda^*]!\ [\frac{1}{2}W\lambda^*]!}{[\frac{1}{2}W(N_{Fe}\beta_i - N_u - \lambda)]!\ [\frac{1}{2}W(N_u - \lambda)]!\ [\frac{1}{2}W\lambda]!\ [\frac{1}{2}W\lambda]!} \end{aligned} \tag{5}$$

The partition function Ω is now solved, but to proceed and obtain some useful thermodynamic quantities, we follow the normal approximation which is to replace the summation in equation 2 by the largest term corresponding to $\lambda = \overline{\lambda}$, which can be obtained by differentiation with respect to λ:

$$\overline{\lambda} = \frac{N_{Fe}\beta_i}{2\phi}\left\{1 - \left[1 - 4\phi\frac{\theta}{\beta_i}\left(1 - \frac{\theta}{\beta_i}\right)\right]^{\frac{1}{2}}\right\} \tag{6}$$

where $\theta = N_u/N_{Fe}$,

$$\phi = 1 - \exp\left\{\frac{-\omega_\gamma}{kT}\right\} \tag{7}$$

and $\omega_\gamma = \epsilon_{uu} - 2\epsilon_u$ is the carbon–carbon (repulsive) interaction energy.
The partition function now becomes

$$\begin{aligned} \Omega = & \frac{[N_{Fe}\beta_i]!}{[N_{Fe}\beta_i - N_u]!\ N_u!} \\ & \times \frac{[\frac{1}{2}W(N_{Fe}\beta_i - N_u - \lambda^*)]!\ [\frac{1}{2}W(N_u - \lambda^*)]!\ [\frac{1}{2}W\lambda^*]!\ [\frac{1}{2}W\lambda^*]!}{[\frac{1}{2}W(N_{Fe}\beta_i - N_u - \overline{\lambda})]!\ [\frac{1}{2}W(N_u - \overline{\lambda})]!\ [\frac{1}{2}W\overline{\lambda}]!\ [\frac{1}{2}W\overline{\lambda}]!} \\ & \times \exp\left\{-W\left[\overline{\lambda}\epsilon_u + \frac{N_u - \overline{\lambda}}{2}\epsilon_{uu}\right]/kT\right\} \end{aligned} \tag{8}$$

which clearly reduces to a partition function for a random solution when $\overline{\lambda} = \lambda^*$. This can happen when the temperature is very high so that thermal agitation mixes up the atoms irrespective of their binding tendencies. The configurational free energy F and chemical potential (μ) follow:

$$F = -kT\ln\{\Omega\} \tag{9}$$

$$\mu = -kT\ln\left\{\frac{\partial \ln\{\Omega\}}{\partial N_u}\right\}_{N_{Fe},T} \tag{10}$$

To obtain the configurational part of the chemical potential, McLellan and Dunn took (using Stirling's approximation):

$$\begin{aligned} \frac{\partial}{\partial N_u}\ln\left\{\frac{[N_{Fe}\beta_i]!}{[N_{Fe}\beta_i - N_u]!\ N_u!}\right\} &= -\ln\left\{\frac{\theta/\beta_i}{1 - \theta/\beta_i}\right\} \\ \frac{\partial}{\partial N_u}\ln\left\{[\frac{1}{2}W(N_{Fe}\beta_i - N_u - \lambda)]!\right\} &= \frac{-W}{2}\ln\left\{\frac{W}{2}[N_{Fe}\beta_i - N_u - \lambda]\right\} \\ \frac{\partial}{\partial N_u}\ln\left\{[\frac{1}{2}W(N_u - \lambda)]!\right\} &= \frac{W}{2}\ln\left\{\frac{W}{2}(N_u - \lambda)\right\} \\ \frac{\partial}{\partial N_u}\ln\left\{[\frac{1}{2}W\lambda]!\right\} &= 0 \\ \frac{\partial}{\partial N_u}\left\{-W\left(\overline{\lambda}\epsilon_u + \frac{N_u - \overline{\lambda}}{2}\epsilon_{uu}\right)\right\} &= \frac{-W\epsilon_{uu}}{2} \end{aligned} \tag{11}$$

Noting that $W\epsilon_{uu}/2 = W\epsilon_u + W\omega_\gamma/2$, the chemical potential per atom is given by

$$\begin{aligned}\mu =&kT\ln\left\{\frac{\theta/\beta_i}{1-(\theta/\beta_i)}\right\}\\ &-kT\ln\left\{\left(\frac{\theta/\beta_i}{1-(\theta/\beta_i)}\right)^W\left(\frac{1-(\theta/\beta_i)-(\overline{\lambda}/N_{Fe}\beta_i)}{(\theta/\beta_i)-(\overline{\lambda}/N_{Fe}\beta_i)}\right)^{\frac{W}{2}}\right\}+W\epsilon_u+W\frac{\omega_\gamma}{2}\end{aligned} \tag{12}$$

The term $W\epsilon_u$ is interpreted as the partial energy of solution of carbon in austenite at infinite dilution, a component of μ_o in $\mu = \mu_o + RT\ln\{a\}$ where a is the activity. The activity of carbon is in this derivation, with respect to pure carbon with the crystal structure of austenite. It is more convenient to define the activity of carbon relative to pure graphite as the standard state. This is easily done, since

$$\begin{aligned}\frac{a_C\{\text{graphite}\}}{a_C\{\text{austenite}\}} &= \exp\left\{\frac{\mu_C^{o,\text{austenite}}-\mu_C^{o,\text{graphite}}}{kT}\right\}\\ &= \exp\left\{\frac{\Delta\mu_C^o}{kT}\right\}\end{aligned} \tag{13}$$

where $\Delta\mu_C^o$ is the change in free energy accompanying the transfer of carbon from its standard state of graphite to a standard state based on an infinitely dilute solution as the references state (it is also called the *relative* partial free energy of a solute atom in solution with respect to the pure solute at infinite dilution). The value of $\Delta\mu^o$ is determined experimentally from thermodynamic data measured at sufficiently low concentrations (Fig. 2).

It follows that the activity of carbon with respect to graphite is, according to McLellan and Dunn,

$$\begin{aligned}a_u =&\frac{\theta/\beta_i}{1-(\theta/\beta_i)}\exp\left\{\frac{\Delta\mu^o}{kT}\right\}\\ &\times\left(\frac{\theta/\beta_i}{1-(\theta/\beta_i)}\right)^{-W}\left(\frac{1-(\theta/\beta_i)-(\overline{\lambda}/N_{Fe}\beta_i)}{(\theta/\beta_i)-(\overline{\lambda}/N_{Fe}\beta_i)}\right)^{\frac{-W}{2}}\exp\left\{\frac{W\omega_\gamma}{2kT}\right\}\end{aligned} \tag{14}$$

Note that the term containing ϵ_u is absorbed in $\Delta\mu^o$.

All the work described above is already available in the published literature [3,4].

Difficulty

There is a difficulty in the particular derivation of the chemical potential presented above because λ^* and $\overline{\lambda}$ are assumed, in the process of differentiation (equation 11), not to be functions of N_u, which they clearly are. This is also inconsistent with other work on a zeroth order quasi–chemical model [7]. We therefore develop here a version which allows for the dependence of λ on N_u (*cf.* equation 11):

$$\begin{aligned}\frac{\partial}{\partial N_u}\ln\left\{[\tfrac{1}{2}W(N_{Fe}\beta_i-N_u-\lambda)]!\right\} &= -\frac{W}{2}\left(1+\frac{\partial\lambda}{\partial N_u}\right)\ln\left\{\frac{W}{2}[N_{Fe}\beta_i-N_u-\lambda]\right\}\\ \frac{\partial}{\partial N_u}\ln\left\{[\tfrac{1}{2}W(N_u-\lambda)]!\right\} &= \frac{W}{2}\left(1-\frac{\partial\lambda}{\partial N_u}\right)\ln\left\{\frac{W}{2}(N_u-\lambda)\right\}\\ \frac{\partial}{\partial N_u}\ln\left\{[\tfrac{1}{2}W\lambda]!\right\} &= W\left(\frac{\partial\lambda}{\partial N_u}\right)\ln\left\{\frac{W}{2}\lambda\right\}\\ \frac{\partial}{\partial N_u}\left\{-W\left(\overline{\lambda}\epsilon_u+\frac{N_u-\overline{\lambda}}{2}\epsilon_{uu}\right)\right\} &= -\left(\frac{\partial\lambda}{\partial N_u}\right)W\epsilon_u-\frac{W\epsilon_{uu}}{2}+\left(\frac{\partial\lambda}{\partial N_u}\right)\frac{W\epsilon_{uu}}{2}\end{aligned} \tag{15}$$

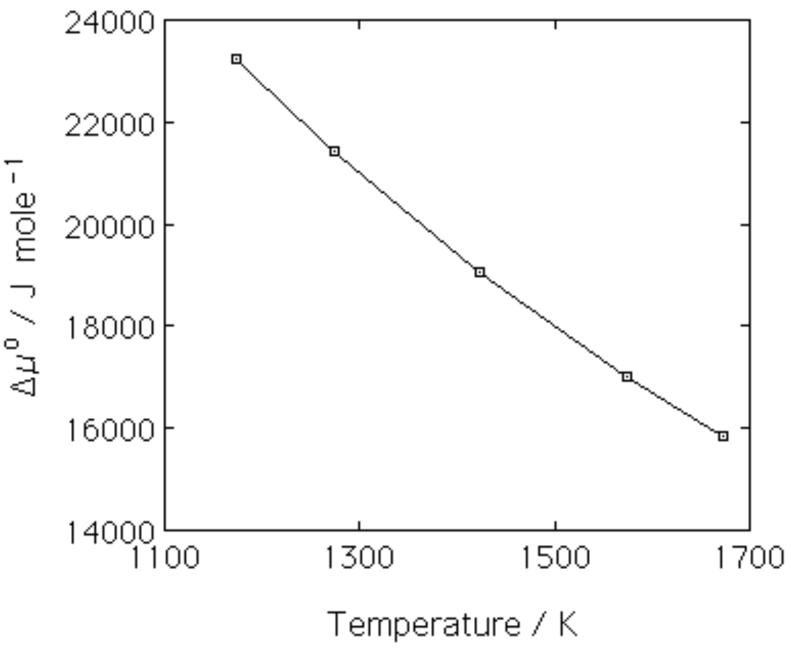

Fig. 2: Variation of the experimentally determined relative partial free energy of carbon in solution in austenite, with respect to pure graphite at infinite dilution (after Ban–ya, Elliott and Chipman, [5,6]).

Writing

$$\begin{aligned}\dot{\lambda}^* &= \frac{\partial \lambda^*}{\partial N_u} = 1 - 2(\theta/\beta_i) \\ \dot{\overline{\lambda}} &= \frac{\partial \overline{\lambda}}{\partial N_u} = \frac{1 - 2(\theta/\beta_i)}{[1 - 4\phi(\theta/\beta_i) + 4\phi(\theta/\beta_i)^2]^{\frac{1}{2}}}\end{aligned} \tag{16}$$

The configurational chemical potential thus becomes

$$\begin{aligned}\mu =& kT \ln\left\{\frac{\theta/\beta_i}{1-(\theta/\beta_i)}\right\} \\ &- kTW \ln\left\{\theta^{\frac{2\theta}{\beta_i}}\left[\frac{\theta}{\beta_i} - \left(\frac{\theta}{\beta_i}\right)^2\right]^{1-\frac{2\theta}{\beta_i}}\left[1 - \frac{\theta}{\beta_i} - \left(\frac{\overline{\lambda}}{N_{Fe}\beta_i}\right)\right]^{\frac{1}{2}(1+\dot{\overline{\lambda}})}\right\} \\ &+ kTW \ln\left\{\left(\frac{\overline{\lambda}}{N_{Fe}\beta_i}\right)^{\dot{\overline{\lambda}}}\left[\frac{\theta}{\beta_i} - \frac{\overline{\lambda}}{N_{Fe}\beta_i}\right]^{\frac{1}{2}(1-\dot{\overline{\lambda}})}\left[1 - 2\frac{\theta}{\beta_i} + \left(\frac{\theta}{\beta_i}\right)^2\right]^{1-\frac{\theta}{\beta_i}}\right\} \\ &+ W\dot{\overline{\lambda}}\epsilon_u + \frac{1}{2}W(1-\dot{\overline{\lambda}})\epsilon_{uu}\end{aligned} \tag{17}$$

and the activity of carbon in austenite with respect to graphite is

$$
\begin{aligned}
a_u = & \frac{\theta/\beta_i}{1-(\theta/\beta_i)} \exp\left\{\frac{\Delta\mu^o}{kT}\right\} \\
& \times \left\{ \frac{\theta}{\beta_i}^{\frac{2\theta}{\beta_i}} \left[\frac{\theta}{\beta_i} - \left(\frac{\theta}{\beta_i}\right)^2\right]^{1-\frac{2\theta}{\beta_i}} \left[1 - \frac{\theta}{\beta_i} - \left(\frac{\overline{\lambda}}{N_{Fe}\beta_i}\right)\right]^{\frac{1}{2}(1+\dot{\overline{\lambda}})} \right\}^{-W} \\
& \times \left\{ \left[\frac{\overline{\lambda}}{N_{Fe}\beta_i}\right]^{\dot{\overline{\lambda}}} \left[\frac{\theta}{\beta_i} - \frac{\overline{\lambda}}{N_{Fe}\beta_i}\right]^{\frac{1}{2}(1-\dot{\overline{\lambda}})} \left[1 - 2\frac{\theta}{\beta_i} + \left(\frac{\theta}{\beta_i}\right)^2\right]^{1-\frac{\theta}{\beta_i}} \right\}^{W} \\
& \times \exp\left\{\frac{(1-\dot{\overline{\lambda}})W\omega_\gamma}{2kT}\right\}
\end{aligned}
$$

Note that the term with $W\epsilon_u$ is again absorbed into $\Delta\mu^o$.

We have verified that the new equations are numerically virtually identical when compared against those derived by McLellan and Dunn for realistic values of the thermodynamic parameters and concentrations. Large differences occur when the interaction energies become strongly repulsive, as might be expected since the McLellan and Dunn equation 11 has a term $(\theta/\beta_i) - (\overline{\lambda}/N_{Fe}\beta_i)$ in the denominator, which tends to zero as the solution becomes random. Large repulsive energies are believed to occur for carbon in ferrite. We shall now proceed to show that the new equation does not suffer from this difficulty for limiting cases.

Dilute solution, $\omega_\gamma \rightarrow 0$ limit

In the limit that ω_γ tends to zero, $\overline{\lambda} \rightarrow \lambda^*$ and $\dot{\overline{\lambda}} \rightarrow 1 - 2(\theta/\beta_i)$. Noting that $\omega_\gamma = \epsilon_{uu} - 2\epsilon_u$, we see that in this limit equation 17 becomes

$$
\mu\{\omega_\gamma \rightarrow 0\} = kT \ln\left\{\frac{\theta/\beta_i}{1-(\theta/\beta_i)}\right\} + W\epsilon_u + W(\theta/\beta_i)\omega_\gamma. \tag{18}
$$

Naturally, $\overline{\lambda}$ must also tend to λ^* at high temperatures so that the high temperature limit of this first–order quasi–chemical theory will then become equivalent to the zeroth–order mixing treatment where the solute atoms are distributed at random [7].

The infinite repulsion limit

In this case, as $\omega_\gamma \rightarrow \infty$, $\overline{\lambda} \rightarrow N_u$ and $\dot{\overline{\lambda}} \rightarrow 1$. Therefore,

$$
\begin{aligned}
\mu\{\omega_\gamma \rightarrow \infty\} = & kT \ln\left\{\frac{\theta/\beta_i}{1-(\theta/\beta_i)}\right\} \\
& - kT \ln\left\{\left(1 - 2\frac{\theta}{\beta_i}\right)\left(1 - \frac{\theta}{\beta_i}\right)^{1-2\frac{\theta}{\beta_i}}\right\} \\
& + kT \ln\left\{\left(1 - \frac{\theta}{\beta_i}\right)^{2-2\frac{\theta}{\beta_i}}\right\} \\
& + W\epsilon_u
\end{aligned} \tag{19}
$$

which, at values of θ *sufficiently small* to allow the expansion $\ln\{1-\theta\} \simeq -\theta$, can be rewritten as

$$
\mu\{\omega_\gamma \rightarrow \infty\} = kT \ln\left\{\frac{\theta/\beta_i}{1-(W+1)(\theta/\beta_i)}\right\} + W\epsilon_u. \tag{20}
$$

This is consistent with all the interstitial sites adjacent to a carbon atom being blocked from occupation. Notice that the term $-W(\theta/\beta_i)\omega_\gamma$ is absent from all these complete–blocking equations since there are no carbon–carbon near neighbour pairs in that scenario.

Zeroth–Order Quasi–Chemical Model

The zeroth approximation of quasi–chemical theory has the solute atoms distributed at random. The partition function and all associated functions for the zeroth–order treatment can be deduced from the corresponding equations for the first–order treatment simply by setting $\overline{\lambda} = \lambda^*$. It is nevertheless interesting to compare the first and zeroth approximations as was first reported by Alex and McLellan [7].

From equation 2, the partition function is obtained as

$$\Omega = \frac{[N_{Fe}\beta_i]!}{[N_{Fe}\beta_i - N_u]!\ N_u!} \times \exp\left\{-W\left[\lambda^*\epsilon_u + \frac{N_u - \lambda^*}{2}\epsilon_{uu}\right]/kT\right\} \tag{21}$$

On substituting for λ^* (equation 4) and ϵ_{uu} this becomes: †

$$\Omega = \frac{[N_{Fe}\beta_i]!}{[N_{Fe}\beta_i - N_u]!\ N_u!} \times \exp\left\{-W\left[(N_u\epsilon_u - \frac{N_u^2}{N_{Fe}\beta_i}\epsilon_u + \frac{N_u^2}{N_{Fe}\beta_i}\omega_\gamma\right]/2kT\right\} \tag{22}$$

The configurational chemical potential therefore becomes:

$$\mu = kT\ln\left\{\frac{\theta/\beta_i}{1-(\theta/\beta_i)}\right\} + W\epsilon_u + W\omega_\gamma\frac{\theta}{\beta_i} \tag{23}$$

which is consistent with a regular solution model (*i.e.* the zeroth approximation).

CONCLUSIONS

A better behaved set of equations has been derived for the quasichemical representation of iron–carbon solutions. Although this makes negligible numerical difference to the chemical potential of carbon in austenite over the typical range of interest, the equations give the correct limit when the carbon–carbon interaction energy becomes very large. Unlike the earlier model, the new equations are also consistent with the details in the formulation of the zeroth approximation of the quasichemical model.

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† It is worth emphasizing again that this substitution for λ^* recognizes implicitly that λ^* is a function of N_u. This is in contrast to the first order quasi–chemical theory by Dunn and McLellan, where during the differentiation of the partition function with respect to N_u, λ was treated as a constant. The comparison reported by Alex and McLellan is therefore between models based on different assumptions. Our comparison is, on the other hand, with the corrected first–order quasi–chemical theory.