THERMODYNAMICS OF PARAEQUILIBRIUM
CARBURIZATION AND NITRIDATION
OF STAINLESS STEELS

by

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for the degree of Master of Science

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11/25/2013

*We also certify that written approval has been obtained for any proprietary material contained therein.
We can all look back on life, however young or old, and say “that was someone who truly made a difference”. Professor Michal was certainly one of those people for me. And I know many others who share the same sentiment. I first met Professor Michal when I arrived at Case Western Reserve in the Fall of 2007, unsure of which field to pursue, but knowing I had a desire to learn why things behave as they do on a most fundamental level. I was on the chemical engineering track and needed an extra elective that first semester, and from a survey of the course catalog, *Materials in Sports* seemed an appropriate choice. As an athlete I was well aware that new, innovative materials were always finding their way into sport. There were only four other students in that class (sadly!)—quite the contrast from the 300+ student lectures that filled the rest of my first semester. To say little about my favorite course of all time, I learned more about what it means to “engineer” from that class than any other in my academic tenure. I don’t remember at what point that autumn it happened, but one day, while walking out of White Building, I had an epiphany. I was made for this: to study materials science and engineering. I went to my then-advisor a few days later, declared my new major, and never looked back.

Those exams on solving the optimal material of choice for a Nike® Air Sole (invented by CIT alum Frank Rudy), or calculating the impulse a running back experiences on being tackled, or the energy transfer of club-to-ball using a metallic glass vs. standard metal golf club head were no trivial task, even as I look at them today! But it taught me a valuable lesson as a young student: what it means to be an engineer, how an engineer looks at the world, and that doing so requires a solid understanding of the basic sciences—‘bread and butter’ as Professor Michal would have put it. The oft abstractions a freshman engineering student is inundated with in his or her introductory coursework do, in fact, matter. The gradual shift in my perception, and awe, of the natural world taking place that first semester as a result of that class probably led me in some capacity to give a more attentive ear in the remainder of my classes.

Professor Michal had the special gift of making the classroom experience fun.
He did not just teach engineering; he inspired learning. He would often find a way to have us go to the front of the class as a team, for example, where one person armed with a racquetball and the others with stopwatches would time the flight of the ball before and after impact, while measuring the time the ball was in actual contact with the wall (a futile task no doubt) to estimate the energy transfer. Other times we would put the hallway to use as our very own bowling lane in the process of learning about the construction and design of the pin and ball. Each and every class there was something for us to examine, and I remember well first holding a block of beryllium (yikes!) in one hand and steel or tungsten in the other. We went over, in minute detail, the array of woods in existence, and how their respectively unique properties adequately suites them in many engineering applications, not the least of which being MLB bats. The five of us looked forward to going to class, to say the least.

Professor Michal was also a Philadelphia lawyer if I ever met one. Nothing could be slipped passed him. His punctilious nature is perhaps best typified from an experience in EMSE 313: Engineering Applications of Materials, while learning the basics of statistical analysis. One of his sources came from a monograph that must have dated back to the 1960s. We were going over one particular example from that book on the linear regression and corresponding confidence intervals through a fit of twenty or so datum. Professor Michal, being the man he was, one day must have painstakingly went through recalculating the fit with pen and paper for his own teaching purposes. Lo and behold, he realized that the lines representing the 95% confidence intervals in the figure were in fact wrong! It turns out, as he demonstrated to us, that one of the datum from the set must have been copied or written incorrectly. Whoever had calculated the regression used one number off by a factor of 10 from that listed in the table. It was simply astounding to think that that person—typist or statistician we may never know—who had misplaced a decimal so many years ago, in a book probably seldom read, and truthfully to no students harm, so many years later had been caught. From that day forward, especially while performing these calculations which you are about to take note of, I made sure every decimal, every digit, was in its correct position before ever walking into his office.

Over the next few years I was fortunate enough to have taken every class
offered by Professor Michal. He will always be remembered for his humorous and creative style in teaching difficult concepts, and for his significant investment in the students. I will for the remainder of my career accredit my foundational knowledge, understanding, and appreciation of materials science, and engineering, to him. He spoke a language that made the most sophisticated of subjects make sense, and would entertain even the most radical of questions. Not only was Professor Michal an extraordinary teacher, but he was also one renowned worldwide in the field of physical metallurgy, as I soon came to learn, for which much could be said here. He epitomized in my mind the very definition of what a professor, researcher, and engineer ought to be, and that trifecta is surely rare to come by.

To him I owe much, and this work, however small, is a start. He helped me discover my own passion for understanding nature, and helped train and refine my thinking process, perhaps the most valuable of all gifts a teacher can bestow, and I cannot say where I would be had I not taken that elective course so many years ago. His legacy will surely continue to reach far beyond the borders of Case Western Reserve University, through his research and mentoring of several generations of engineers. I consider it a great honor to have had the opportunity to learn under, and work beside, such a scholar as him. He is deeply missed by many, but we look forward to running into him again someday.
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# Nomenclature

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<tr>
<td>α</td>
<td>Ferrite</td>
</tr>
<tr>
<td>α′</td>
<td>Martensite (C- or N-containing bct)</td>
</tr>
<tr>
<td>α″</td>
<td>Fe₁₆N₂ (bct)</td>
</tr>
<tr>
<td>β</td>
<td>CALPHAD parameter related to the total magnetic entropy</td>
</tr>
<tr>
<td>χ</td>
<td>Fe₅C₂ (orthorhombic)</td>
</tr>
<tr>
<td>ε</td>
<td>Fe₂₄C (epsilon-phase (orthorhombic))</td>
</tr>
<tr>
<td>ε′</td>
<td>Fe₂C₁₋ₓ (hcp)</td>
</tr>
<tr>
<td>γ</td>
<td>Austenite</td>
</tr>
<tr>
<td>γ′</td>
<td>Fe₄N (cubic)</td>
</tr>
<tr>
<td>γ₃C</td>
<td>Carbon expanded austenite</td>
</tr>
<tr>
<td>γ₅N</td>
<td>Nitrogen expanded austenite</td>
</tr>
<tr>
<td>μᵢφ</td>
<td>Chemical potential of constituent i in the φ state</td>
</tr>
<tr>
<td>τ</td>
<td>Cr₂₃C₆ (fcc)</td>
</tr>
<tr>
<td>τₖC</td>
<td>Critical temperature for magnetic ordering</td>
</tr>
<tr>
<td>θ</td>
<td>Fe₃C (orthorhombic)</td>
</tr>
</tbody>
</table>
NOMENCLATURE

$\varepsilon$ \hspace{1cm} $\text{Fe}_2\text{N}_{1-x}$ (hcp)

$\zeta$ \hspace{1cm} $\text{Fe}_2\text{N}$ (orthorhombic)

$iL_{A:B,C}^\phi$ \hspace{1cm} $i$-th order CALPHAD parameter representing the interaction of constituents A and B with C on the second sublattice

$a, b, c$ \hspace{1cm} Lattice parameters

$a_{\text{N}_2}$ \hspace{1cm} Chemical activity of $\text{N}_2$ gas

$C_i$ \hspace{1cm} Atom fraction of $i$

$D_i^\phi$ \hspace{1cm} Diffusion coefficient of element $i$ in the $\phi$ state

$G'_m$ \hspace{1cm} Total molar Gibbs free energy on atomic basis

$G_{\text{M:N}}^{h\phi}$ \hspace{1cm} Molar Gibbs free energy of a compound in a hypothetical non-magnetic state where all interstitial sites are filled with nitrogen

$G_{\text{M:Va}}^{h\phi}$ \hspace{1cm} Molar Gibbs free energy of an element in a hypothetic non-magnetic state

$G_m^\phi$ \hspace{1cm} Total molar Gibbs free energy of a state $\phi$ on formula unit basis

$H_i^{\text{SER}}$ \hspace{1cm} Enthalpy of the stable state of element $i$ at 298.15 K and 1 atm

$p_i$ \hspace{1cm} Partial pressure of $i$

$R$ \hspace{1cm} Universal gas constant $= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$

$T$ \hspace{1cm} Absolute temperature

$W_i$ \hspace{1cm} Weight fraction of $i$

$X_i$ \hspace{1cm} Mole fraction of $i$

$Y_i$ \hspace{1cm} Site fraction of $i$

$G_m^{\phi}\text{excess}$ \hspace{1cm} Excess energy of mixing contribution to the molar Gibbs free energy
NOMENCLATURE

\( \text{ideal} G_m^\phi \) Ideal entropy of mixing contribution to the molar Gibbs free energy

\( \text{mag} G_m^\phi \) Magnetic contribution to the molar Gibbs free energy of a solution

\( \text{mech} G_m^{h\phi} \) Mechanical mixture of pure components contribution to the molar Gibbs free energy

\( \text{pres} G_m^\phi \) Pressure contribution to the molar Gibbs free energy of a solution

\( bcc \) Body-centered cubic

\( bct \) Body-centered tetragonal

\( fcc \) Face-centered cubic

\( hcp \) Hexagonal close-packed

CALPHAD CALculation of PHAse Diagram

HYSS Hypothetical senary stainless steel used in simulations, composition Fe\(_{60}\)Cr\(_{20}\)Ni\(_{10}\)Mo\(_{5}\)Mn\(_{5}\)

ppm Parts per million

SER Standard element reference at 298.15 K and 1 atm

STP Standard temperature (298.15 K) and pressure (1 atm)

TTT Time-temperature-transformation
Owing to its thermodynamic control and conformal nature, gas-phase nitriding and carburizing of steels has for over a century been a popular method for increasing the hardness, wear-, and fatigue-resistance of ferrous components. Only in recent years (≈ 3 decades) have such processes been successfully applied to stainless steels, under so-called paraequilibrium conditions whereby a truly colossal ($\geq 10^5$ times the equilibrium concentration) supersaturation of interstitials can be achieved, thus imparting extraordinary improvements in the mechanical and electrochemical performance of the alloy. Such novel thermochemical techniques are relatively low-cost, industrially viable, and represent one of few value-added processes of a material that results in all gain and no loss. The thermodynamic origins of this metastable supersaturation, in particular carbon in austenitic 316, have been previously discussed within the context of the CALPHAD-based multi-sublattice model for solid solutions. It is the present effort of this work to review the complete thermodynamic database as applied to stainless steels, and develop a generalized approach for modeling metastable paraequilibria in both $fcc$ austenitic and $bcc$ ferritic (or martensitic) alloys upon low-temperature gas-phase nitriding or carburizing. A flexible and user-friendly program was developed to allow for predictions of the paraequilibrium carbon and nitrogen solubility in model binary to senary systems exposed to some carbon/nitrogen-rich ambient, as well as to model the solubility of carbon or nitrogen when a paraequilibrium, i.e. partitionless, carbide or nitride has
formed. Changes in the paraequilibrium eutectoid temperature as a function of alloy content were also determined to predict the feasibility of an isothermal nitrogen- or carbon-induced ferrite (or martensite) to austenite ($\alpha (\alpha') \rightarrow \gamma$) phase transformation. Such thermodynamic calculations can be used in optimizing interstitial hardening treatments of pre-existing alloys, as well as aid future alloy development. Sound thermodynamic descriptions further provide the basis needed for modeling the kinetics behind paraequilibrium surface treatments, investigations of which are still in their infancy. Lastly, previous sensitivity analyses on published interaction parameters (acquired from high-temperature data) within the chromium-carbon system have led to some parameter revision for better agreement with experiment in the low-temperature regimes of interest. The routine developed and used for the analysis contained herein is readily amenable to parameter optimization and expansion as the thermodynamic database becomes more complete, something which is not presently attainable in commercial thermodynamic platforms such as Thermo-Calc® Software (Stockholm, Sweden).
Chapter 1

Introduction

1.1 Paraequilibrium and the Formation of Expanded Austenite

It is often the case that a material’s in-service performance is regulated by its surface properties and interaction with other media. Stainless steels—ferrous alloys with at least 12 wt. pct. Cr—are a superlative example, most often utilized for the adherent and chemically-inert chromium-rich oxide film present on the surface. It is this passive film that prevents the base metal from corroding, and is self-healing should the steel be scratched. However, stainless steels are not particularly well suited for high-wear and abrasive environments, due in part to their relative softness compared to conventional carbon steels, thus limiting their more widespread use. Thermochemical surface engineering treatments such as carburizing and nitriding are well established industrial processes that have long been used to improve the mechanical and electrochemical performance of many metallic materials, via formation of a carbidic or nitridic surface layer. Certain technical barriers prevailed, however, in applying these treatments to stainless steels, namely the same surface oxide that imparts excellent corrosion resistance also impedes the inward diffusion of carbon or nitrogen needed to create the hardened layer. Furthermore, if the oxide were somehow removed and the stainless steel treated by conventional thermochemical techniques, it would result in a dramatic decrease in corrosion resistance through sensitization of the alloy by precipitation of chromium nitride or carbide phases.\(^1\) This loss of chromium

\(^1\)Precipitates are used as a hardening mechanism in some stainless steels (precipitation-hardened (PH) martensitic and austenitic stainless steels), albeit with non-chromium carbides
from the matrix prevents it from preferentially reacting with oxygen to form the passive layer. It would therefore be futile in the eyes of the engineer to treat such an alloy and lose the primary property that it was likely chosen for in the first place. Yet to do so without compromise of the outstanding intrinsic ductility and corrosion-resistance of stainless steels would be certain to increase their more widespread use in many demanding applications.

Perhaps surprisingly, only in the past 30 years has the potential for a high paraequilibrium solubility of interstitials been realized in austenitic stainless steels for improving their surface hardness, and manifold other properties in the process [1]. The term paraequilibrium is used here to indicate a state of metastability whereby equilibration of only certain chemical species in the system occurs. In the case of nitriding or carburizing at low temperatures, this applies to equilibration of the chemical potentials of carbon or nitrogen in solution with the atmosphere, but not those of metal constituents, which are effectively immobile.

Fig. 1.1 demonstrates the dramatic difference in the diffusion coefficients between interstitial and substitutional species in fcc (face-centered cubic) γ-austenite and bcc (body-centered cubic) α-ferrite matrices. At low temperatures ($\leq 450 ^\circ C$) the diffusional distance of substitutional elements may be no more than a few atomic spacings, while interstitial carbon and nitrogen can diffuse appreciable distances in reasonably short times ($\sim 20$ h). Though not of significance to this work, the lattice expansion associated with the colossal dissolution of carbon and/or nitrogen results in an impressive increase in their respective concentration-dependent diffusion coefficients [3, 4, 5, 6] in fcc stainless steels, though the effect of lattice expansion on substitutional diffusion has yet to be explored. Such paraequilibrium treatments can also be understood with help of the empirical TTT (time-temperature-transformation) diagram, shown in Fig. 1.2 for the precipitation of $M_{23}C_6$ ($M = \text{randomly distributed Fe, Cr, Ni}$) for two 316 stainless steel (Fe-18Cr-12Ni wt. pct.) alloys with concentrations of 0.10 and 0.31 at. pct. carbon. The relatively rapid formation of $M_{23}C_6$ at temperatures above $\approx 700K$ with such low carbon concentrations limits the interstitial hardening effect that could otherwise be achieved in this alloy. It is apparent however that at lower temperatures, appreciable time would be required for nucleation and growth of this or nitrides.
1.1. PARAEQUIL. AND FORMATION OF EXPANDED AUSTENITE

![Arrhenius plot of self- and hetero-diffusion of common stainless steel alloying elements at infinite dilution.][2]

Figure 1.1: Arrhenius plot of self- and hetero-diffusion of common stainless steel alloying elements at infinite dilution. [2]

deleterious secondary phase (primarily dependent upon the diffusivities of substitutional elements) during isothermal annealing, thereby allowing a processing window for carburization (or nitridation) where secondary phases can be kinetically suppressed\(^1\). It is also noted, as will be discussed in detail later, that a prerequisite for dissolution of immense concentrations of interstitial carbon and nitrogen is the presence of carbide and nitride formers (e.g. chromium, molybdenum, vanadium, manganese, etc.) in stainless steels, which have a high affinity for carbon and nitrogen and serve to reduce the activity coefficient \(\gamma_i = a_i/X_i\) of carbon or nitrogen in solution. This allows highly metastable supersaturations to be achieved when secondary phases are kinetically suppressed. Addressing to

\(^1\)It is to be noted here that after sufficiently long treatment times or isothermal holds for temperatures near 400-450 °C, precipitation of secondary phases has been observed in low-temperature carburized or nitrided 316 [1, 8]. Of the more detailed analyses performed, the new phases were found to have formed in a nearly partitionless manner [9].
1.1. PARAEQUIL. AND FORMATION OF EXPANDED AUSTENITE

![TTT Diagram](image)

**Figure 1.2:** Time-temperature-transformation (TTT) diagram for the precipitation of $M_{23}C_6$ in 316 alloys of two carbon contents, 0.10 and 0.31 at. pct., revealing how kinetic suppression of secondary phases is achieved at “low” temperatures. [7]

what extent carbon or nitrogen can be dissolved in solution under the C-curve, and at what interstitial concentrations a driving force for formation of secondary phases exists, in any model stainless steel for which thermodynamic data are available, is the primary objective of this work.

The extreme lattice expansion (up to 3 vol. pct. for carbon [10] and 11 vol. pct. for nitrogen [11]) observed after these treatments in austenitic stainless steels has led this metastable “state” to be referred to as expanded austenite, $\gamma_N$, $\gamma_C$, or sometimes S-phase, to reflect its original moniker as an unidentified phase present in XRD spectra following the first paraequilibrium plasma-nitridation experiments of Zhang and Bell [12] in 1985 and Iichi et al. [13] the following year. Interestingly, near-surface hardness of carburized and nitrided austenitic stainless steels can exceed that of even the hardest carbon or nitrogen martensites [1], which could possibly result from a combination of interstitial-hardening and the
residual biaxial compressive stress. A typical hardness- and carbon-concentration depth-profile through a low-temperature carburized 316L sample can be seen in Fig. 1.3. The residual biaxial compressive stress generated on a monolithic specimen results from the near-surface lattice expansion, whose free expansion is resisted by the core. Such a large residual compressive stress greatly improves the high-cycle fatigue and stress-corrosion cracking performance. The exceptional ductility of austenitic stainless steels is retained after paraequilibrium treatments, and despite the extremely high surface hardness, ductility *within* the carburized or nitrided layer has been evidenced from global and high-resolution techniques [10, [10, [5]...
1.1. PARAEQUIL. AND FORMATION OF EXPANDED AUSTENITE

The electrochemical performance has been found to be unattenuated under most conditions, and with optimal processing can even result in an improvement in corrosion resistances. This improvement of electrochemical performance can be observed in an etched cross-section of carburized 316 sample shown in Fig. 1.4, revealing a featureless layer $\approx 20 \, \mu\text{m}$ thick achieved after 15 h treatment at 430 °C. Lastly, these interstitial hardening paraequilibrium treatments lead to no dimensional changes, they are conformal (as are most gas-phase techniques), and involve essentially the retrofitting of existing operations.

Clearly, the study of this new metastable state is one of both great technological and scientific relevance. It has opened the door for a range of applications not normally considered for stainless steels, and as is true of most engineered materials, allowed metastable states (extremely) far from equilibrium to be explored. The value-added alteration of the material represents one of few that enhances nearly all of desirable properties with zero trade-offs (save the additional processing costs). Several commercial applications of this technology already exist worldwide [16] and the list is growing.

Despite how much is currently known about the nature and properties of expanded austenite, it is still very much an enigma. Most of the conventional

Figure 1.4: Etched cross-section of low-temperature carburized (430 °C for 15 h) AISI 316 revealing a featureless, hardened, and chemically-resistant layer of “expanded austenite”. [15]
1.2. THERMODYNAMIC MODELING AND THE CALPHAD FORMALISM

wisdom stems from treatments of fcc austenitic stainless steels—and of this class, typically AISI 316—which represents only a small fraction of the total stainless steel market. This is in part due to the fact that fcc austenite matrices are able to accommodate much higher levels of carbon and nitrogen, i.e. having a higher equilibrium solubility for these interstitials, than bcc ferrite. The response of low-temperature paraequilibrium treatments applied to stainless steels containing bcc ferrite is largely unknown, as are the thermodynamic simulations involving carbon and nitrogen for many ferritic compositions. Of the limited number of investigations on paraequilibrium treatments of ferritic or duplex stainless steels, several general conclusions can be made: kinetic suppression of secondary phases (carbides and nitrides) in ferrite is nearly always unavoidable [17, 18], case depths have been found to be thicker or thinner than austenitic counterparts exposed to similar treatment, the corrosion performance is highly varied, and several have claimed a ferrite to austenite phase transformation [19, 20, 21, 22, 23, 24, 25], due to the stabilizing nature of carbon and nitrogen for austenite.\(^1\) This has led some to believe that an additional prerequisite for expanded austenite formation is the presence of some volume fraction of austenite in the untreated material. Due to the industrial and economic significance of ferrite-containing stainless steels, it is of great interest to be able to predict the results of a paraequilibrium treatment on ferrite-containing stainless steel, in an effort to help determine processing conditions necessary for ultimately improving their performance. Such thermodynamic calculations will always tell you what can happen, but, perhaps more importantly, they will also tell you what won’t happen.

1.2 Thermodynamic Modeling and the CALPHAD Formalism

Equilibrium phase diagrams, usually in temperature-composition space, are a vital tool to the materials engineer for determining what phases, their composition, and their concentration are present within a system at a particular (equilibrium) state. Most often these are limited to two or sometimes three components.

\(^1\)Nearly all of these studies involved only basic metallographic analyses or bulk characterization techniques such as XRD, and were focused more on the efficacy of the treatment (e.g. hardness, wear, corrosion) than investigation of the formation mechanisms at the atomistic scale.
1.2. THERMODYNAMIC MODELING AND THE CALPHAD FORMALISM

Rarely do useful alloys contain only two or three components. Thus there is a strong need for accurate predictions of thermodynamic behavior in higher-order systems. To circumvent the experimental difficulties in determining equilibrium phase diagrams for multicomponent systems, a computational technique colloquially referred to as the CALPHAD (CALculation of PHase Diagrams) method was developed in the mid-1970s. Built upon the regular solution model, Sundman and Ågren, together in their seminal 1981 paper [26], summarized a general, multi-sublattice, multi-component solid solution thermodynamic model, which laid the foundation for most of the CALPHAD assessments made today, including that behind the well-known Thermo-Calc® Software for which many of the assessments reviewed in this work were originally conducted. The expression “computational thermodynamics” is now used in place of “calculations of phase diagrams” to reflect the fact that a phase diagram is only one piece of information that can be obtained from thermodynamic calculations. The beauty of the CALPHAD method is that it allows for thermodynamic predictions in higher-order systems with data extrapolated from binary or ternary systems, and can describe phases not normally stable within the binary system. It also has the advantage of allowing predictions of metastable phase equilibria and determination of other thermodynamic factors, e.g. chemical potential, activity, heat capacity, etc., not normally present on a phase diagram. Quantifying changes in phase stability with slight modifications in chemistry is relatively straightforward.

To form a thermodynamic database, both phase diagram and thermochemical data are collected, evaluated, and fit in an optimization procedure in accordance with the model parameters. This process is usually referred to in the literature as assessment or optimization of a system. Generally, within the thermodynamic database, all binary and ternary systems are assessed with experimental data. Using these data, reliable extrapolations into higher order systems can be determined with good accuracy. However, it should be remembered that the predictive capacity of the CALPHAD method to interpolate or extrapolate thermodynamic information to compositions and temperatures not easily achieved experimentally ultimately lies in the quality of the parameters used. As such, any predictions need always be taken cum grano salis, especially at lower temperatures ($T \lesssim 800^\circ$C), where kinetic barriers often play a role. The thermodynamic data are of-
ten acquired at high temperatures, and are rarely critically evaluated at lower
temperatures. The paraequilibrium surface treatments described above thus also
provide a unique opportunity for assessing parameters in the current thermo-
dynamic database in a wider temperature and composition range, and may also
permit new parameters to be extracted where low (equilibrium) solubilities would
otherwise be difficult to measure. This is yet another indirect benefit of the pro-
posed paraequilibrium surface hardening technique, in an age where governments
are pushing for more predictive than Edisonian approaches in science and engi-
eering, in particular for creation of new advanced materials, which represents
many of the current bottlenecks in the challenges facing the world today.

As a corollary to what has been discussed above, it is important to note that
some disparity between predictions using parameters in the current CALPHAD
database and experimental data was determined [27]. In the case of carbur-
ization of 316L, the measured paraequilibrium solubility for carbon in the low-
temperature regime was nearly two orders of magnitude too low. This prompted a
reevaluation of the relevant parameters, which were ultimately revised to account
for these low-temperature solubility differences. Of note, the Cr-C interaction
parameters for ferrite and austenite were found to be insufficiently exothermic,
and subtle changes of the parameters led to large changes in predicted paraequi-
librium phase diagrams. The compendium of paraequilibrium solubility data for
low-temperatures gas-phase treatments of stainless steels may not yet be suffi-
ciently complete to perform a rigorous analysis of many of the current parameters,
but it is the goal of this work to provide the future researcher/modeler/engineer
an avenue for doing so.

With regard to the paraequilibrium carburization and nitridation treatments
described above, the CALPHAD formalism allows for a prediction of the follow-
ing:

- the solubility limit of carbon or nitrogen in $\alpha$-ferritic and $\gamma$-austenitic alloys
  in an open system exposed to a carbonaceous or nitrogenous ambient

- the solubility limit of carbon or nitrogen in which a paraequilibrium (adopt-
ing base metal chemistry) carbide ($\tau$-M$_{23}$C$_6$, $\theta$-M$_3$C, $\omega$-M$_7$C$_3$) or nitride
  ($\gamma'$-M$_4$N, $\varepsilon$-M$_2$N$_{1-x}$, MN) has formed
1.2. THERMODYNAMIC MODELING AND THE CALPHAD FORMALISM

- the heterogeneous equilibrium boundaries between ferrite and austenite as a function of alloy and interstitial content
- construction of paraequilibrium phase diagrams, the corresponding eutectoid temperature, and thus the driving force for an isothermal, carbon- or nitrogen-induced $\alpha \rightarrow \gamma$ phase transformation

The maximum metastable, paraequilibrium solubility limit in the first case is determined by equilibration of the chemical potentials of carbon and nitrogen in solution with that defined by the external gas, $\mu_{\text{C,N}}^{\text{bcc, fcc}} = \mu_{\text{C,N}}^{\text{gas}}$. The heterogeneous equilibrium boundaries between two phases, e.g. $\alpha$ and $\gamma$, in a closed system, is determined by the usual convention that the chemical potentials of each constituent, e.g. A and B, must be equal in both phases: $\mu_A^\alpha = \mu_A^\gamma$ and $\mu_B^\alpha = \mu_B^\gamma$. These conditions are most commonly determined using the tangent construction of free energy versus composition curves. The paraequilibrium eutectoid temperature, $T_{\text{paraeq}}$, is then determined by intersection of the maximum solubility limit with heterogeneous equilibrium boundaries. The lowering of the $T_{\text{eut}}$ in stainless steels has already been noted [27] which opens up the prospect for an isothermal $\alpha \rightarrow \gamma$ phase transformation in ferrite-containing stainless steels if the treatment temperature is above $T_{\text{paraeq}}$. The isothermal dissolution of carbon above $T_{\text{eut}}$ in iron has been shown to be an viable means of inducing the $\alpha \rightarrow \gamma$ phase transformation [28], and may well describe the $\alpha \rightarrow \gamma$ transformation apparently observed by several investigators of low-temperature treatments applied to ferrite-containing stainless steels. The derivation and explicit CALPHAD expressions needed to determine the free energy and chemical potential of each constituent, as well as a review of the current database, are presented in the next two chapters.
Chapter 2

Computational Thermodynamics

In this chapter the metastable phases found in the Fe-C and Fe-N (and Cr-C and Cr-N) systems are first presented, as they form the basis for any carburization or nitridation treatment. A brief treatise on the underlying principles behind the CALPHAD formalism is then presented, along with its specific application to modeling paraequilibrium carburization and nitridation. Compared to the more well-established carbon steels, phase diagram information and thermodynamic properties of steels in which nitrogen is a vital alloying element are lesser known from experiment. Fortunately, thermodynamic databases of ferrous alloys—which were the initial driving force for development of the CALPHAD methodology—are also the most complete. A nearly full description of the senary Fe-Cr-Ni-Mo-Mn-(N,C) system (representing the most common stainless steel alloying agents) is therefore available; both the austenitic and ferritic solid solutions, and most relevant carbide and nitride phases can be described for most of these constituents. The data used for all thermodynamic calculations can be found in Appendix A.

2.1 The Fe-C System

Very little needs to be addressed about the Fe-C system as a prelude to describing the CALPHAD method along with the current ferrous database, but it is important to review the equilibrium, as well as metastable phases not shown on the
phase diagram. The well-known metastable\(^1\) Fe-Fe\(_3\)C (cementite) phase diagram determined using Fe-C data from the most current CALPHAD database is shown in Fig. 2.1 for carbon concentrations up to 5 wt. pct. (\(\approx\) 20 at. pct.). The vast majority of steels are hardened through various microstructural combinations of three phases: \textit{bcc} \(\alpha\)-ferrite, \textit{fcc} \(\gamma\)-austenite, orthorhombic Fe\(_3\)C-cementite, and a fourth, if considering \textit{bct} (body-centered tetragonal) \(\alpha'\)-martensite that is formed via a diffusionless transformation upon quenching austenite.

A complete list, including structural information, of all known stable and metastable phases found in the Fe-C and Cr-C binary systems are listed in Table 2.1. Though of modest importance in the hardening of carbon or stainless

\(^1\)It should be remembered that Fe\(_3\)C is not stable with respect to graphite under STP (standard temperature and pressure) conditions. However, the kinetics of the cementite \(\rightarrow\) graphite transformation for all practical purposes are too slow to be of concern in steels, and thus the Fe-Fe\(_3\)C metastable phase diagram is that usually referred to.
2.1. THE FE-C SYSTEM

steels, several paraequilibrium versions of these phases have been identified in 316L subjected to prolonged carburization, namely $M_5C_2$, $M_7C_3$, and $M_{23}C_6$, where M represents randomly distributed constituents on the metal sublattice with near base chemistry. The order of these transformations in paraequilibrium treatments, or conditions favoring the formation of one phase to another, is worthy of further investigation. Note that the $Fe_7C_3$ phase has been described by both trigonal ($hcp$ Bravais lattice) and orthorhombic crystal systems. The important transition points within the Fe-C system are given in Table 2.2.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Alias</th>
<th>Structure</th>
<th>Lattice Parameter</th>
<th>$C_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe</td>
<td>ferrite</td>
<td>bcc (Im$\bar{3}$m)</td>
<td>a [nm]</td>
<td>b [nm]</td>
</tr>
<tr>
<td>γ-Fe(C)</td>
<td>austenite</td>
<td>fcc (Fm$\bar{3}$m)</td>
<td>0.28664</td>
<td>—</td>
</tr>
<tr>
<td>α$'$-Fe(C)</td>
<td>martensite</td>
<td>bct (Im$\bar{3}$m)</td>
<td>0.3572</td>
<td>—</td>
</tr>
<tr>
<td>ε-Fe$<em>2$C$</em>{(1-x)}$</td>
<td>ε-phase</td>
<td>hcp (P6$_3$22)</td>
<td>0.2859</td>
<td>0.2935</td>
</tr>
<tr>
<td>θ-Fe$_3$C</td>
<td>cementite</td>
<td>ortho. (Pnma)</td>
<td>0.2843</td>
<td>0.3070</td>
</tr>
<tr>
<td>χ-Fe$_5$C$_2$</td>
<td>Hägg carbide</td>
<td>mono. $\beta = 97.74^\circ$ (C2/c)</td>
<td>0.4767</td>
<td>0.4354</td>
</tr>
<tr>
<td>ε$'$-Fe$_{2.4}$C</td>
<td>ε$'$-carbide</td>
<td>hcp (P6$_3$/mmc)</td>
<td>1.156</td>
<td>0.4573</td>
</tr>
<tr>
<td>Fe$_7$C$_3$</td>
<td>Eckström-Adcock carbide</td>
<td>hcp (P6$_3$mc)</td>
<td>0.4537</td>
<td>0.6892</td>
</tr>
<tr>
<td>ω-Fe$_7$C$_3$</td>
<td>Fe$_7$C$_3$</td>
<td>ortho. (Pnma)</td>
<td>0.6882</td>
<td>0.4540</td>
</tr>
<tr>
<td>τ-Cr$_{23}$C$_6$</td>
<td>τ</td>
<td>fcc (Fm$\bar{3}$m)</td>
<td>0.4532</td>
<td>0.7015</td>
</tr>
<tr>
<td>Cr$_7$C$_3$</td>
<td>Cr$_7$C$_3$</td>
<td>ortho. (Pnma)</td>
<td>1.0659</td>
<td>20.7</td>
</tr>
<tr>
<td>Cr$_3$C$_2$</td>
<td>Cr$_3$C$_2$</td>
<td>ortho. (Pnma)</td>
<td>0.4540</td>
<td>1.1494</td>
</tr>
</tbody>
</table>

Table 2.1: Structure of known phases present in the Fe-C and Cr-C systems [29, 30, 31, 32, 33]
Table 2.2: Transition points in the stable Fe-C and metastable Fe-Fe$_3$C systems; G = gas and L = liq. [34]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$C_C$ of each phase [at. pct.]</th>
<th>Temperature [$^\circ$C]</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable Fe-C (graphite) system</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G $\leftrightarrow$ L</td>
<td>0</td>
<td>2862</td>
<td>Boiling</td>
</tr>
<tr>
<td>L $\leftrightarrow$ $\delta$-Fe</td>
<td>0</td>
<td>1536</td>
<td>Melting</td>
</tr>
<tr>
<td>$\delta$-Fe $\leftrightarrow$ $\gamma$-Fe</td>
<td>0</td>
<td>1392</td>
<td>Allotropic</td>
</tr>
<tr>
<td>$\gamma$-Fe $\leftrightarrow$ $\alpha$-Fe</td>
<td>0</td>
<td>911</td>
<td>Allotropic</td>
</tr>
<tr>
<td>L + $\delta$-Fe $\leftrightarrow$ $\gamma$-Fe</td>
<td>2.34/0.40/0.74</td>
<td>1493</td>
<td>Peritectic</td>
</tr>
<tr>
<td>$\gamma$-Fe $\leftrightarrow$ $\alpha$-Fe + (C)</td>
<td>2.97/0.096/100</td>
<td>740</td>
<td>Eutectoid</td>
</tr>
<tr>
<td>L $\leftrightarrow$ $\gamma$-Fe + (C)</td>
<td>17.1/9.06/100</td>
<td>1153</td>
<td>Eutectic</td>
</tr>
<tr>
<td>G $\leftrightarrow$ graphite (C)</td>
<td>100</td>
<td>3826</td>
<td>Sublimation</td>
</tr>
<tr>
<td>Metastable Fe-Fe$_3$C (cementite) system</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$-Fe $\leftrightarrow$ $\alpha$-Fe + Fe$_3$C</td>
<td>0.104</td>
<td>727</td>
<td>Eutectoid</td>
</tr>
<tr>
<td>L $\leftrightarrow$ $\gamma$-Fe + Fe$_3$C</td>
<td>9.23</td>
<td>1147</td>
<td>Eutectic</td>
</tr>
<tr>
<td>L $\leftrightarrow$ Fe$_3$C</td>
<td>25</td>
<td>1252</td>
<td>Congruent</td>
</tr>
</tbody>
</table>
The Fe-N system is perhaps the most well-known amongst any pupil of materials science and engineering. Lesser known, but still of great technological significance, is the Fe-N system, which is here reviewed for a proper understanding of any nitriding treatment.

Nitrogen was first noted to be dissolved in iron by Savart in 1828 through the gas flow of ammonia over steel at high temperatures [35]. It was not until later in the first half of the 20th century that a proper structural analysis of the nitride phases formed during these treatments was conducted by Hägg [36], and the thermodynamic description of ammonia nitriding described shortly thereafter by Lehrer [37]. The first full determination of the metastable Fe-N phase diagram was conducted by Jack in the early 1950s [38], which is only marginally different from the currently accepted version by Wriedt et al. [39] shown in Fig. 2.2. In Jack’s analysis he found the interstitial solid solution phases α-ferrite, γ-austenite, and α’-martensite, along with compound phases α''-Fe₁₆N₂, γ′-Fe₄N, ε-Fe₂N₁₋ₓ, and ζ-Fe₂N. The structure, lattice parameter, and composition range of each phase is given in Table 2.3. Note that Fe₄N is treated as a stoichiometric compound, though it does have a narrow stability range as shown on the phase diagram, and is sometimes written more appropriately as Fe₄N₁₋ₓ, where x is the concentration of vacancies on the interstitial sublattice.

Though most of the nitride phases are considered stable at STP, decomposition of α’ and α'' phases into ferrite and Fe₄N given sufficient time and modest

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1 The Fe-N system is gaining increased attention for several reasons. As a relatively “new” alloying element—where scrupulous control of its concentration has been made possible through improved steelmaking—small quantities of nitrogen in nearly all steels greatly improve their performance, including increased strength and corrosion resistance. As a very potent austenite stabilizer, it is also being used more frequently as a substitute for the ever-increasingly expensive nickel. The importance of nitrogen as an alloying element is evidenced by genesis of the International Conference on High Nitrogen Steels in 1989. Additionally, the elusive metastable α''-Fe₁₆N₂ phase, though discovered many years ago, is understandably now a matter of intense research interest, as this phase (so-far produced only in small quantities) has been measured to possess the highest saturation magnetization $M_s$ of any known substance, and is made possible thanks to two highly plentiful elements on earth.

2 Similar to the Fe-Fe₃C system, the phases present in the Fe-N phase diagram are not stable with respect to α-ferrite and N₂ gas at STP, but decomposition kinetics are of impractical significance.
thermal energy has been observed [40]. Concerning the $\varepsilon$-Fe$_2$N$_{1-x}$ phase, there is still ambiguity in the literature regarding under what circumstances there is preferred ordering of nitrogen on the interstitial sites; some have considered $\varepsilon$ to be another interstitial solid solution within the Fe-N system [41]. When the nitrogen content of the $\varepsilon$-Fe$_2$N$_{1-x}$ phase increases from 33.0 at. pct. to 33.2 at. pct. an anisotropic distortion of the hcp lattice occurs, forming the stoichiometric, orthorhombic $\zeta$-Fe$_2$N phase [38, 42]. The FeN phase has not been found during ammonia gas nitriding treatments, but has been successfully produced by several researchers [43, 44] through sputtering techniques. The structure was determined to be either that of ZnS ($\gamma''$) or NaCl ($\gamma'''$). The thermodynamic description for the fcc NaCl-type FeN phase has been assessed based upon the solubilities of nitrogen in austenite as described later.
2.2. THE FE-N SYSTEM

Table 2.3: Structure of known phases present in the Fe-N and Cr-N systems. [39]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Alias</th>
<th>Structure</th>
<th>Lattice Parameter</th>
<th>$C_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Fe</td>
<td>ferrite</td>
<td>bcc (Im$\bar{3}$m)</td>
<td>0.28664</td>
<td>—</td>
</tr>
<tr>
<td>$\gamma$-Fe(N)</td>
<td>austenite</td>
<td>fcc (Fm$\bar{3}$m)</td>
<td>0.3572</td>
<td>—</td>
</tr>
<tr>
<td>$\alpha'$-Fe(N)</td>
<td>martensite</td>
<td>bct (Im$\bar{3}$m)</td>
<td>0.2861 0.2936 2.8</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2848 0.3120 9.5</td>
<td>9.5</td>
</tr>
<tr>
<td>$\alpha''$-Fe$_{16}$N$_2$</td>
<td>$\alpha''$</td>
<td>bct (I4/mmm)</td>
<td>0.572 0.629</td>
<td>11.1</td>
</tr>
<tr>
<td>$\gamma'$-Fe$_4$N</td>
<td>$\gamma'$</td>
<td>fcc (Im$\bar{3}$m)</td>
<td>0.3798</td>
<td>19.3–20.0</td>
</tr>
<tr>
<td>$\varepsilon$-Fe$<em>2$N$</em>{1-x}$</td>
<td>$\varepsilon$</td>
<td>hcp (P$\bar{6}$3/mmc)</td>
<td>0.2705 0.4376</td>
<td>~15–33</td>
</tr>
<tr>
<td>$\zeta$-Fe$_2$N</td>
<td>$\zeta$</td>
<td>bcc (P222)</td>
<td>0.5525 0.4827 0.4422</td>
<td>33.3</td>
</tr>
<tr>
<td>$\gamma''$-FeN</td>
<td>$\gamma''$</td>
<td>fcc (F43m)</td>
<td>0.43</td>
<td>50.0</td>
</tr>
<tr>
<td>$\gamma'''$-FeN</td>
<td>$\gamma'''$</td>
<td>fcc (Fm$\bar{3}$m)</td>
<td>0.45</td>
<td>50.0</td>
</tr>
<tr>
<td>CrN</td>
<td>CrN</td>
<td>fcc (Fm$\bar{3}$m)</td>
<td>0.4148</td>
<td>50.0</td>
</tr>
<tr>
<td>Cr$_2$N</td>
<td>Cr$_2$N</td>
<td>hcp (P31m)</td>
<td>0.4796 0.4470</td>
<td>30–33.3</td>
</tr>
</tbody>
</table>

Several of the important transition points and reaction types within the Fe-N system are listed in Table 2.4
## Table 2.4: Transition points in the Fe-N system [39]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$C_N$ of each phase [at. pct.]</th>
<th>Temperature [$^\circ$C]</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{\text{para.}} \leftrightarrow \alpha_{\text{ferro.}}$</td>
<td>0</td>
<td>770</td>
<td>Curie point</td>
</tr>
<tr>
<td>$\gamma \leftrightarrow \alpha$</td>
<td>0</td>
<td>912</td>
<td>Allotropic</td>
</tr>
<tr>
<td>$\gamma \leftrightarrow \delta$</td>
<td>0</td>
<td>1394</td>
<td>Allotropic</td>
</tr>
<tr>
<td>$L \leftrightarrow \delta$</td>
<td>0</td>
<td>1538</td>
<td>Melting</td>
</tr>
<tr>
<td>$\epsilon \leftrightarrow \gamma'$</td>
<td>19.5</td>
<td>680</td>
<td>Congruent</td>
</tr>
<tr>
<td>$\epsilon \leftrightarrow \zeta$</td>
<td>33.3</td>
<td>$\geq$ 480</td>
<td>Congruent</td>
</tr>
<tr>
<td>$\gamma \leftrightarrow \alpha + \gamma'$</td>
<td>8.8/0.4/19.3</td>
<td>592</td>
<td>Eutectoid</td>
</tr>
<tr>
<td>$\epsilon \leftrightarrow \gamma + \gamma'$</td>
<td>15.9/10.3/19.3</td>
<td>650</td>
<td>Eutectoid</td>
</tr>
<tr>
<td>$\gamma \leftrightarrow \alpha + \alpha''$ †</td>
<td>...</td>
<td>...</td>
<td>Probably eutectoid</td>
</tr>
<tr>
<td>$L + \delta \leftrightarrow \gamma$ †</td>
<td>11/3.5/6</td>
<td>1495</td>
<td>Probably peritectic</td>
</tr>
<tr>
<td>$L + \gamma + \epsilon$ †</td>
<td>...</td>
<td>...</td>
<td>Peritectic or eutectic</td>
</tr>
</tbody>
</table>

† Not observed, though conceptually possible
2.3 The CALPHAD Method

2.3.1 Gibbs Free Energy of Solutions and Compounds Using the Compound Energy Formalism

The CALPHAD method is built on describing the Gibbs free energy, \( G(\equiv H - TS) \), representing the energetic state of a closed system in equilibrium at fixed composition, temperature, and pressure, from which many other important thermodynamic variables can also be derived. The choice of the Gibbs free energy as a minimizing function is due to the fact that the Gibbs energy is a function of temperature and pressure—properties that are conveniently controlled in experiments. The CALPHAD approach begins with the evaluation of thermodynamic descriptions of unary and binary systems. By combining the constitutive binary systems with ternary data, ternary interactions and Gibbs free energy of ternary phases are obtained. The models describing the Gibbs free energy function of a phase are based on its crystal structure. Because of the importance of maintaining a self-consistent description of lower-order systems, the temperature dependence of \( G = f(T) \) relative to the standard state enthalpy for pure elements and compounds is described empirically by Eq. 2.1 using the convention established by the Scientific Group Thermodata Europe (SGTE):

\[
G - H^{\text{SER}} = a + bT + cT \ln(T) + dT^2 + eT^3 + fT^{-1} + ... \tag{2.1}
\]

where \( H^{\text{SER}} \) represents the standard element reference (SER) enthalpy of the stable state as measured at 298.15 K and 1 atm. The coefficients \( a, b, c, d, \text{ etc.} \) represent the model parameters. For simplicity, the pressure dependence and magnetic contribution are handled separately. Normally, the pressure dependence is defined only for the pure elements, and as a consequence, most of the published data are valid only for 1 atm. The SGTE data for the pure elements have been compiled by Dinsdale (Ref. [45]).

In its most generic form, the molar Gibbs free energy of a solid solution, \( G_m \), can be described by Eq. 2.2.

\[
G_m = G^{\text{mech}} + \Delta G^{\text{mix}} \tag{2.2}
\]
2.3. THE CALPHAD METHOD

\[
\Delta G^{\text{mix}} = \Delta H^{\text{mix}} - T \Delta S^{\text{mix}}
\]  \hspace{1cm} (2.3)

\(G^{\text{mech}}\) represents the mechanical mixture of the pure components and \(\Delta G^{\text{mix}}\) represents the additional free energy associated with the interaction between the atoms upon mixing, and can further be reduced to the enthalpic \(\Delta H^{\text{mix}}\) and entropic \(\Delta S^{\text{mix}}\) contributions.

In the CALPHAD-based multiple sublattice description of solid solutions, \(G^{\phi}_m\) represents the free energy of one mole of formula units of phase \(\phi\), and is generically broken down into five independent contributions according to Eq. 2.4.

\[
G^{\phi}_m = \text{mech} G^{h\phi}_m + \text{ideal} G^{\phi}_m + \text{excess} G^{\phi}_m + \text{mag} G^{\phi}_m + \text{pres} G^{\phi}_m
\]  \hspace{1cm} (2.4)

where \(\text{mech} G^{h\phi}_m\) represents the mechanical mixture of end members, \(\text{ideal} G^{\phi}_m\) the ideal (configurational) entropic contribution to the free energy assuming a random mixture, \(\text{excess} G^{\phi}_m\) the additional free energy arising from interactions between atoms on each sublattice, \(\text{mag} G^{\phi}_m\) the magnetic contribution, and \(\text{pres} G^{\phi}_m\) the contribution of a change in pressure to the Gibbs free energy. Each of these contributions is described in more detail in the following sections. The superscript \(h\phi\) represents a hypothetical non-magnetic state of the pure elements and compounds as the magnetic contribution is handled separately.

### 2.3.1.1 Site Fraction

In the CALPHAD modeling of solid solutions, there are often considered two interpenetrating sublattices—one substitutional and one interstitial—whereby the metals atoms, M, reside on the substitutional sublattice and the interstitial species, e.g. C or N, reside on the interstitial sublattice. An important concept within the CALPHAD framework is the so-called site fraction \(Y_i\) of each constituent \(i\), which is analogous to the traditional mole fraction \(X_i\), but for each unique sublattice. The site-fraction concept is used because, while mole fractions are only defined for components, there may be more constituents than components. The site-fraction of constituent \(i\) containing \(n^s_i\) atoms on sublattice \(s\) with
2.3. THE CALPHAD METHOD

\( N^s \) total sites is defined by Eq. 2.5.

\[
Y_i^s = \frac{n_i^s}{N^s}
\] (2.5)

or more explicitly to include the number of vacant sites \( n_{Va} \), which are important in modeling solid solutions by:

\[
Y_i^s = \frac{n_i^s}{n_{Va} + \sum_i n_i^s}
\] (2.6)

where the summation is over all non-vacant sites. The sum of all sites, i.e. \( \sum_i Y_i \), must equal unity on any particular sublattice. In the case of a Fe-Cr-Ni-Mo-Mn alloy containing interstitial nitrogen, the following must hold true (assuming each metal sublattice site is occupied\(^1\)):

\[
Y_{Fe} + Y_{Cr} + Y_{Ni} + Y_{Mo} + Y_{Mn} = 1
\]

\[
Y_{N} + Y_{Va} = 1
\]

Considering a simple, four-constituent, two-sublattice phase \((A,B)_a(C,D)_c\) containing \( a \) number of sites on the first sublattice and \( c \) sites on the second sublattice, the site fractions of \( A \), \( Y_A \), and \( C \), \( Y_C \), on their respective sublattices are given by:

\[
Y_A = \frac{n_A}{n_A + n_B}
\]

\[
Y_C = \frac{n_C}{n_C + n_D}
\] (2.7)

The site fraction of a constituent \( i \) on the substitutional sublattice where the interstitial species is nitrogen can also be related to its mole fraction \( X_i \) through Eq. 2.8.

\[
Y_i = \frac{X_i}{1 - X_N}
\] (2.8)

\(^1\)The number of substitutionally vacant sites from thermal equilibrium is small relative to the total number of sites
2.3. THE CALPHAD METHOD

and for nitrogen on the interstitial sublattice through Eq. 2.9.

\[ Y_N = \frac{a}{c} \left( \frac{X_N}{1 - X_N} \right) \]  

(2.9)

where \( a \) and \( c \) again represent the number of atomic sites on the substitutional and interstitial sublattices respectively.

For the generic case of a multi-sublattice phase containing \( p \) constituents and \( s \) sublattices, the site fractions of all constituents can be represented by an \((s \times p)\) array \( Y \):

\[
Y = \begin{pmatrix}
Y_A^{1} \quad Y_B^{1} \quad \cdots \quad Y_p^{1} \\
Y_A^{2} \quad Y_B^{2} \quad \cdots \quad Y_p^{2} \\
Y_A^{3} \quad Y_B^{3} \quad \cdots \quad Y_p^{3} \\
\vdots \quad \vdots \quad \ddots \quad \vdots \\
Y_A^{s} \quad Y_B^{s} \quad \cdots \quad Y_p^{s}
\end{pmatrix}
\]

where rows represents a common sublattice and columns a constituent dispersed on each sublattice.

### 2.3.1.2 The Mechanical Mixture of End Members

The mechanical mixture contribution to the total Gibbs free energy is defined by its “end members” or compounds whose sublattices are occupied by pure components. For instance, a pure metallic element is described by \( M:Va \) or a pure metal nitride by \( M:N \). Returning again to the simple case of a four-constituent two-sublattice phase represented by \((A,B)\_a(C,D)\_c\) where the number of sites on each sublattice \( a = c = 1 \), the four end members of such a phase would include compounds \( AC \), \( AD \), \( BC \), and \( BD \) whose standard Gibbs free energies are given by \( ^\circ G_{AC} \), \( ^\circ G_{AD} \), \( ^\circ G_{BC} \), and \( ^\circ G_{BD} \) respectively. These four end members, generated when the sublattices are occupied with pure components, e.g. elemental \((M)\_a(Va)\_c\) where the interstitial sublattice is filled with vacancies or compound \((M)\_a(N)\_c\) where the interstitial sublattice is filled with nitrogen, can be plotted on a reference surface for \( a = c = 1 \) as shown in Fig. 2.3. where the non-planar
The surface is given by Eq. 2.10.

$$\text{mech} \, G_m^{\text{ho}} = Y_A Y_C \, ^\circ G_{AC} + Y_A Y_D \, ^\circ G_{AD} + Y_B Y_C \, ^\circ G_{BC} + Y_B Y_D \, ^\circ G_{BD}$$  \hspace{1cm} (2.10)

To generalize the multi-sublattice case, consider a two sublattice phase with $p = 7$ constituents—five on the first sublattice and two on the second sublattice, each containing one site: (A,B,C,D,E)$_1$(F,G)$_1$. The number of possible pure phases is ten, and the standard Gibbs free energy for all phases $^\circ G_I$ can be represented by a $(5 \times 2)$ component array $\mathbf{I}$ where the superscript indicates the first or second sublattice:

$$\mathbf{I} = \begin{pmatrix} ^\circ G_{A1F2} & ^\circ G_{A1G2} \\ ^\circ G_{B1F2} & ^\circ G_{B1G2} \\ ^\circ G_{C1F2} & ^\circ G_{C1G2} \\ ^\circ G_{D1F2} & ^\circ G_{D1G2} \\ ^\circ G_{E1F2} & ^\circ G_{E1G2} \end{pmatrix}$$

The Gibbs free energy of the mechanical mixture can then be represented gener-
ally by Eq. 2.11

\[
\text{mech} G_m^{\phi} = \sum P_I(Y)^{\circ} G_I
\]  

(2.11)

where the \(P_I(Y)\) notation represents the corresponding product of site fraction from the \(Y\) matrix.

### 2.3.1.3 Entropic Contribution

Assuming random mixing of constituents on each sublattice, the ideal entropy contribution to the total Gibbs free energy of a phase is accounted for by the configurational entropy \(S_m^{\text{config}}\), assuming that the volume change on mixing is negligible and therefore the vibrational entropic contribution \(S_m^{\text{vib}}\) can be ignored\(^1\). The configurational entropic contribution to the free energy is given by Eq. 2.12.

\[
\text{ideal} G_m^{\phi} = -T S_m^{\text{mix}} = RT \left( a \sum M Y_M \ln(Y_M) + c \sum I Y_I \ln(Y_I) \right)
\]  

(2.12)

where \(M\) represents all metal atoms on the substitutional sublattice and \(I\) all constituents on the interstitial sublattice. In the simple two-sublattice model \((A,B)_{a}(C,D)_{c}\) introduced above, \(\text{ideal} G_m^{\phi}\) is therefore expressed by Eq. 2.13

\[
\text{ideal} G_m^{\phi} = RT \left[ a \left( Y_A \ln Y_A + Y_B \ln Y_B \right) + c \left( Y_C \ln Y_C + Y_D \ln Y_D \right) \right]
\]  

(2.13)

### 2.3.1.4 Excess Mixing Contribution

The deviation from ideal behavior is included in the excess Gibbs energy contribution arising from interactions between atoms on different sublattices, and is given by the interaction parameters \(i L^\phi \) of \(i\)-th order. To continue with the model two-sublattice phase \((A,B)_{a}(C,D)_{c}\), the excess Gibbs free energy contribution, assuming only zeroth-order interaction parameters, would be expressed

\(^1\)Vibrational entropy can be incorporated into the solution free energy model \([46, 47]\), though the total entropic contribution remains significantly lower in magnitude than the others for the systems in question.
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\[ \text{excess } G_m^\phi = Y_A Y_B Y_C^0 L_{A,B:C} + Y_A Y_B Y_D^0 L_{A,B:D} + Y_A Y_C Y_D^0 L_{A,C,D} + Y_B Y_C Y_D^0 L_{B,C,D} \]  

(2.14)

Following the notation of Sundman and Ågren, the commas separate elements that interact on the same sublattice, while the colons separate elements on different sublattices. For example, \( L_{\text{Fe,Cr:N}}^{\text{fcc}} \) represents the interactions between an \textit{fcc} solution of Fe and Cr on the first sublattice while the second sublattice is completely filled with N, \( L_{\text{Fe,Cr,Va}}^{\text{fcc}} \) the interactions between Fe and Cr with a vacant second sublattice, and \( L_{\text{Fe,Cr:N,Va}}^{\text{fcc}} \) the interactions in a Fe-Cr solution when some N is dissolved on the interstitial sublattice. The interaction parameters are themselves compositionally dependent, and can include higher-order terms according to the phenomenological Redlich-Kister polynomial with Muggiano extrapolation, as shown in Eq. 2.15.

\[ L^\phi = \sum_{i=0}^0 L^\phi (Y_A - Y_B)^i + \sum_{i=0}^1 L^\phi (Y_A - Y_B)^2 + ... \]  

(2.15)

To generalize the excess mixing contribution to include higher-order terms, the four interactions between the four-constituent, two-sublattice phase \((A,B)_a(C,D)_c\) are described by:

\[ L^\phi_{A,B:C} = Y_A Y_B Y_C \sum_{i=0}^m i L^\phi_{A,B:C} (Y_A - Y_B)^i \]

\[ L^\phi_{A,B:D} = Y_A Y_B Y_D \sum_{i=0}^m i L^\phi_{A,B:D} (Y_A - Y_B)^i \]

\[ L^\phi_{A,C,D} = Y_A Y_C Y_D \sum_{i=0}^m i L^\phi_{A,C,D} (Y_C - Y_D)^i \]

\[ L^\phi_{B,C,D} = Y_B Y_C Y_D \sum_{i=0}^m i L^\phi_{B,C,D} (Y_C - Y_D)^i \]  

(2.16)

Here, the order in which the interactions on a similar sublattice are written is crucial for first- and higher-order interaction parameters. The difference term in the Redlich-Kister expansion \textit{must} follow the order of the subscript on the interaction term. For instance, if the first-order term was written as \(^1L_{A,B,C},\)
the difference term must be \((Y_A - Y_B)\) and not \((Y_B - Y_A)\). To again generalize
the excess contribution to any multi-component, multi-sublattice phase using the
constituent array \(I_i\), refer to Eq. 2.17.

\[
\text{excess} G_m^\phi = \sum_{I_1} P_{I_1}(Y)L_{I_1} + \sum_{I_2} P_{I_2}(Y)L_{I_2} + ... \tag{2.17}
\]

where the component array \(I_1\) represents the case where one sublattice contains
two constituents and the other only one, \(I_2\) where each sublattice contains two
constituents, etc..

### 2.3.1.5 Magnetic Contribution

Second-order transitions such as para- to ferromagnetism at the Curie temperature
greatly affect phase stability, as is true in the case of pure iron where the
most stable solid at high temperatures is the non-closest packed \(bcc\) ferrite. The
magnetic contribution \(G_m^{\text{mag}}\) to molar Gibbs free energy is considered separately
within the CALPHAD framework and is given by Eq. 2.18 according to the model
proposed by Hillert and Jarl [48].

\[
G_m^{\text{mag}} = RT \ln(\beta + 1)f(\tau)
\]

\[
\tau = T/T_C \tag{2.18}
\]

where \(\beta\) is the mean magnetic moment or number of unpaired electron spins in
Bohr magnetons \(\mu_B\) and \(T_C\) the critical magnetic ordering temperature, both of
which are compositionally dependent. For ferro- and ferrimagnetic materials, \(T_C\)
represents the Curie temperature and for antiferromagnetic materials the Néel
temperature. The compositional dependence of \(\beta\) and \(\tau\) for the Fe-Cr-Ni-Mo-
Mn system are given in Appendix A. The function \(f(\tau)\) depends on whether the
temperature is above or below \(T_C\) according to Eq. 2.19.

\[
\tau > 1 : f(\tau) = 1 - \frac{1}{A} \left[ \frac{79\tau^{-1}}{140\tau^1} + \frac{474\tau^4}{497} \left( \frac{1}{\tau^6} - 1 \right) \left( \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right]
\]

\[
\tau < 1 : f(\tau) = -\frac{1}{A} \left( \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right) \tag{2.19}
\]
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where

$$A = \left( \frac{518}{1125} \right) + \left( \frac{11692}{15975} \right) \left( \frac{1}{p} - 1 \right)$$  \hspace{1cm} (2.20)

and $p$ is a structurally dependent constant. For bcc phases $p = 0.4$, and for hcp and fcc phase $p = 0.28$.

2.3.1.6 Pressure Effects

The Gibbs free energy is defined only for a fixed temperature and pressure, and therefore varies with a change in pressure. The CALPHAD formalism treats this change in Gibbs free energy with a change in pressure as a separate contribution $\text{pres} G^\phi_m$. Data for $\text{pres} G^\phi_m$ presently exists only for the elements, and consequentially the pressure contribution was not been considered in the thermodynamic analyses considered in this work, as the influence of pressure on the stability of the compound phases is not straightforwardly estimated. It is noted that the low-temperature paraequilibrium carburizing and nitriding of 316L stainless steel has been shown to impart biaxial surface compressive stresses on the order of 3 GPa and 7 GPa respectively [49], which may have an effect on the equilibrium and paraequilibrium stability of various phases. The pressure effect on changing the overall free energy is discussed in more detail in Ch. 5.

2.3.2 The Chemical Potential

The partial molar Gibbs free energy, henceforth referred to as the chemical potential, $\mu_i$, is an important concept in the realm of thermodynamics, and can be thought of as physically representing the change in free energy of a system when changing the composition by one atom or particle. Based on whether the constituent has a high or low chemical potential indicates its willingness to enter, leave, or react within the solution. The chemical potential of a constituent is defined in elementary thermodynamic terms by Eq. 2.21.

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq i}$$ \hspace{1cm} (2.21)
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where \( n \) is the number of moles of constituent \( i \). For systems described by several sublattices, the chemical potential of a zeroth-order component array \( \mu_{I_0}^\phi \) can be defined by Eq. 2.22.

\[
\mu_{I_0}^\phi = \left( \frac{\partial G}{\partial n_{I_0}} \right)_{T,P,n_{I_0}}
\]  

(2.22)

where \( n_{I_0} \) is the number of formula units of \( I_0 \). Eq. 2.22 can further be generalized by Eq. 2.23.

\[
\mu_{I_0}^\phi = G_m^\phi + \sum_s \left( \frac{\partial G_m^\phi}{\partial Y_i^s} - \sum_j Y_j^s \frac{\partial G_m^\phi}{\partial Y_j^s} \right)_{T,P,n_{I_0}}
\]  

(2.23)

where \( i \) is the component on sublattice \( s \) of the component array on sublattice \( s \).

The chemical potential of a metal constituent \( M \) in a fcc solution described by \((Fe, Cr, Ni, Mo, Mn)_{1:(N, Va)}_{1}\) with the addition of nitrogen is given by Eq. 2.24.

\[
\mu_{fcc}^M = G_{fcc}^m + \left( \frac{\partial G_{fcc}^m}{\partial Y_M} \right) + \left( \frac{\partial G_{fcc}^m}{\partial Y_{Va}} \right) - Y_{Fe} \left( \frac{\partial G_{fcc}^m}{\partial Y_{Fe}} \right) - Y_{Cr} \left( \frac{\partial G_{fcc}^m}{\partial Y_{Cr}} \right) - Y_{Ni} \left( \frac{\partial G_{fcc}^m}{\partial Y_{Ni}} \right) - Y_{Mo} \left( \frac{\partial G_{fcc}^m}{\partial Y_{Mo}} \right)
\]  

(2.24)

and similarly for a bcc solution \((Fe, Cr, Ni, Mo, Mn)_{1:(N, Va)}_{3}\) by Eq. 2.25

\[
\mu_{bcc}^M = G_{bcc}^m + \left( \frac{\partial G_{bcc}^m}{\partial Y_M} \right) + \left( \frac{\partial G_{bcc}^m}{\partial Y_{Va}} \right) - Y_{Fe} \left( \frac{\partial G_{bcc}^m}{\partial Y_{Fe}} \right) - Y_{Cr} \left( \frac{\partial G_{bcc}^m}{\partial Y_{Cr}} \right) - Y_{Ni} \left( \frac{\partial G_{bcc}^m}{\partial Y_{Ni}} \right) - Y_{Mo} \left( \frac{\partial G_{bcc}^m}{\partial Y_{Mo}} \right)
\]  

(2.25)

The chemical potential of the interstitial nitrogen in a general two sublattice phase \((M)_{a:(N, Va)}_{c}\) depends upon the site ratios and is given by Eq. 2.26.

\[
\mu_N^\phi = \frac{a}{c} (\mu_{MN}^\phi - \mu_{M:Va}^\phi) = \frac{a}{c} \left( \frac{\partial G_m^\phi}{\partial Y_N} - \frac{\partial G_m^\phi}{\partial Y_{Va}} \right)
\]  

(2.26)
and explicitly for fcc or bcc phases

\[
\mu_{N}^{\text{fcc}} = \left( \frac{\partial G_{m}^{\text{fcc}}}{\partial Y_{N}} \right) - \left( \frac{\partial G_{m}^{\text{fcc}}}{\partial Y_{Va}} \right)
\]

\[
\mu_{N}^{\text{bcc}} = \frac{1}{3} \left[ \left( \frac{\partial G_{m}^{\text{bcc}}}{\partial Y_{N}} \right) - \left( \frac{\partial G_{m}^{\text{bcc}}}{\partial Y_{Va}} \right) \right]
\]

### 2.3.3 Elementary Thermodynamic Model versus Compound Energy Formalism

In elementary thermodynamics, the molar Gibbs free energy curve can be used to establish heterogeneous equilibrium between two or more phases by means of the common tangent construction. Note that in the elementary model the Gibbs free energy of a solution is usually presented in terms of a single sublattice on a mole of atoms basis, henceforth referred to as $G'_{m}$. The relationship between the elementary thermodynamic and multi-sublattice CALPHAD expression for Gibbs free energy of a solution $G_{m}$ described in terms of a mole of formula units basis is given by Eq. 2.27.

\[
G'_{m} = \frac{G_{m} + a c Y_{N}^{2}}{1 + a c Y_{N}}
\]  

(2.27)

where $a$ and $c$ again represent the number of sites on the substitutional and interstitial sublattices respectively. Through Eq. 2.28 the molar free energies of the two conventions can also be related to mole fraction of interstitial species, e.g. nitrogen, through:

\[
G'_{m} = (1 - X_{N})G_{m}
\]  

(2.28)

This conversion is later used for determining the heterogeneous equilibrium boundaries between $\gamma$-austenite and $\alpha$-ferrite in the presence of carbon or nitrogen as described in the next section.

### 2.3.4 Isothermal Phase Transformations

To determine the stability between bcc and fcc phases, it is first necessary to determine the molar Gibbs free energy $G'_{m}$ as a function of interstitial concentration from which the chemical potential of each constituent can be determined.
The conditions satisfying heterogeneous equilibrium in a closed system, i.e., the equilibrium boundaries between \textit{bcc} and \textit{fcc} solid solutions with nitrogen, dictate that the chemical potentials of the metal atoms and nitrogen atoms be equal in both phases as written in Eq. 2.29.

\[
\begin{align*}
\mu_{\text{bcc}}^M &= \mu_{\text{fcc}}^M \\
\mu_{\text{bcc}}^N &= \mu_{\text{fcc}}^N
\end{align*}
\] (2.29)

This equilibrium condition between the two phases is shown schematically in Fig. 2.4 where the equilibrium concentrations of nitrogen \(X_N\) (eq.) in each phase establish the two-phase boundaries of coexisting ferrite and austenite at a par-

\[\text{Figure 2.4: Schematic representation of } G'_m \text{ for } \textit{bcc} \text{ and } \textit{fcc} \text{ solutions as a function of nitrogen concentration } X_N. \text{ The common tangent construction establishes the composition } X_N(\text{eq.}) \text{ and equilibrium phase boundaries between coexisting ferrite and austenite as a function of temperature. Note the maximum } X_N \text{ shown corresponds to 10 at. pct.}\]
2.3. THE CALPHAD METHOD

ticular temperature. Though the free energy curves in this schematic are not extended to higher nitrogen contents, with reference to Eq. 2.5 it can be seen that in fcc solutions with a 1:1 site occupancy between substitutional and interstitial sublattices, when the interstitial sublattice is filled with nitrogen (i.e. $Y_N = 1$), $X_N = 0.5$, and similarly for bcc solutions with a site occupancy of 1:3 the maximum nitrogen concentration occurs at $X_N = 0.75$ (see Fig. 2.5).

![Diagram of Octahedral Interstices Sites in bcc and fcc Lattices](image.png)

**Figure 2.5:** Octahedral interstices sites in bcc and fcc lattices (after [50]).

2.3.5 Solubility Limit Under Paraequilibrium Conditions

Atomic nitrogen diffuses into an activated surface of stainless steel only because it can lower its chemical potential in solution relative to the gas phase. When the chemical potential of nitrogen, for example, in solution is equal to that in the gas phase a balance of chemical forces exists, and hence there is no longer a
driving force for further dissolution. Given sufficient time, the chemical potential of nitrogen at the gas-solid interface should equilibrate, establishing the maximum nitrogen solubility for a particular ambient nitrogen activity. Under the paraequilibrium case where only the interstitial species are equilibrated (due to the limited diffusion of substitutional solutes), the maximum nitrogen solubility $X_N^{\text{max}}$ in both the bcc and fcc phases is established by Eq. 2.30.

$$
\begin{align*}
\mu_{N}^{\text{bcc}} &= \mu_{N}^{\text{gas}} \\
\mu_{N}^{\text{fcc}} &= \mu_{N}^{\text{gas}}
\end{align*}
$$

(2.30)

where the chemical potential of nitrogen $\mu_{N}$ in bcc and fcc solutions is derived from the CALPHAD expressions for $G_{m}^{\text{bcc}}$ and $G_{m}^{\text{fcc}}$, and the chemical potential of nitrogen in the gas is given by Eq. 2.31

$$
\mu_{N}^{\text{gas}} = \frac{1}{2} G_{N_2}^{\text{gas}} + \frac{RT}{2} \ln(a_{N_2})
$$

(2.31)

and is controllable by the NH$_3$ and H$_2$ ratio given by Eq. 2.32

$$
a_{N_2} = \left[ K_{eq} \cdot \frac{p_{NH_3}}{p_{H_2}^{3/2}} \right]^{1/2}
$$

(2.32)

where $K_{eq}$ is the equilibrium constant of the ammonia decomposition reaction and $p_{NH_3}$ and $p_{H_2}^{3/2}$ the partial pressures of ammonia and hydrogen gas respectively.

As described above, the chemical potential of any species is defined by the common tangent to the $G'_{m}$ curve for a given composition at a particular temperature, as shown in Fig. 2.6 for fcc and bcc solutions with nitrogen. From this construct, the chemical potential of nitrogen in bcc or fcc solutions is given where the tangent intersects the ordinate at $X_N = 1$. Following the solubility limit imposed under kinetically-controlled paraequilibrium conditions established by Eq. 2.30, the maximum nitrogen solubility $X_N(\text{max.})$ is determined where the tangent is equal to the chemical potential in the gas phase. As the chemical potential in the gas phase is increased, the tangents intersect the ordinate at higher values, and the maximum solubility in bcc and fcc solutions increase.
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Figure 2.6: Schematic representation establishing the maximum nitrogen solubility $X_N(\text{max.})$ under paraequilibrium conditions in $bcc$ and $fcc$ solid solutions following the elementary thermodynamic model, whereby the chemical potential of nitrogen in solution is equal to the chemical potential of nitrogen in the gas phase.

2.3.6 Solubility Limit by Formation of Paraequilibrium Phases

Continuing with the example of a general metal-nitrogen system, the two scenarios for heterogeneous equilibrium between ferrite and austenite and the solubility of nitrogen ignoring any secondary phase formation have already been discussed. The last topic for consideration is the solubility limit where a paraequilibrium nitride (or carbide) has formed. This situation however does not represent one of true equilibrium because it is assumed that the nitride that has formed does so in a partitionless manner, adopting the base metal chemistry. If the equilibrium nitride were considered to have formed, the metal sublattice composition that yields the lowest free energy as a function of temperature would need to be considered. But, where second phases have been observed in low-temperature
treatments of stainless steels, they were found to be mostly partitionless in nature [9] (see Fig. 1.1). Because the diffusion of interstitial nitrogen is orders of magnitude faster than that of the substitutional solutes at the processing temperatures of interest, any new phase can be considered to have the same composition as the matrix, i.e. the composition is fixed despite the fact that the chemical potential of metal constituents may not be at a global minimum, which is consistent with previous analyses of secondary phases following low temperature carburization and nitridation. Thus in the case of a $M_xN_y$ nitride, $M$ is equivalent to the matrix composition. Therefore, given these constraints, the nitrogen solubility in the ferrite or austenite is established by the free energy of the nitride phase $G_m^{M_xN_y}$ (assuming the pure phase has unit activity) according to Eq. 2.33.

$$G_m^{M_xN_y} = x\mu^\phi_M + y\mu^\phi_N \quad (2.33)$$

Within the M-N stainless steel systems of interest, there are only three equilibrium nitride phases\(^1\) which may form—fcc $MN$, hcp $M_2N_{1-x}$, primitive cubic $M_4N$—or four if separately considering the stoichiometric $M_2N$ (isomorphic with $M_2N_{1-x}$) compound as observed in the Cr-N system. It is possible that a stoichiometric orthorhombic $\zeta$-$Fe_2N$ or the highly metastable $\gamma''$-$Fe_{16}N_2$ (see Table 2.3) could form in a partitionless manner is stainless steels, but thermodynamic descriptions of these compounds are not presently available. The solubility of these nitrides is determined by the nitrogen content that satisfies $\Delta G = 0$ associated with the $\gamma \rightarrow M_xN_y$ or $\alpha \rightarrow M_xN_y$ reaction, i.e. $\Delta G^{\alpha,\gamma \rightarrow M_xN_y} = 0$, as given by Eqs. 2.34–2.37 for the known stable nitrides.

\[
\begin{align*}
\Delta G^{\gamma \rightarrow MN} &= 0 = G_m^{MN} - \mu_M^{fcc} - \mu_N^{fcc} \\
\Delta G^{\alpha \rightarrow MN} &= 0 = G_m^{MN} - \mu_M^{bcc} - \mu_N^{bcc} \\
\Delta G^{\gamma \rightarrow M_2N} &= 0 = G_m^{M_2N} - 2\mu_M^{fcc} - \mu_N^{fcc} \\
\Delta G^{\alpha \rightarrow M_2N} &= 0 = G_m^{M_2N} - 2\mu_M^{bcc} - \mu_N^{bcc} \\
\end{align*}
\]

\(^1\)Though no mention has yet been made on intermetallic formation in stainless steels, they do pose a potential threat to performance when formed during prolonged treatments (many hours) at high temperatures ($\geq 500$), but in the typical processing times and temperatures associated with paraequilibrium carburization and nitridation, their formation is not expected.
2.3. THE CALPHAD METHOD

\[
\Delta G^\gamma \rightarrow M_2N_{1-x} = 0 = G_m^{M_2N_{1-x}} - 2\mu_M^{fcc} - x\mu_N^{fcc}
\]

(2.36)

\[
\Delta G^\alpha \rightarrow M_2N_{1-x} = 0 = G_m^{M_2N_{1-x}} - 2\mu_M^{bcc} - x\mu_N^{bcc}
\]

where again in a hypothetical (Fe,Cr,Ni,Mo,Mn) system \(\mu^\phi_m\) is given by:

\[
\mu^\phi_m = Y_{Fe}\mu_{Fe} + Y_{Cr}\mu_{Cr} + Y_{Ni}\mu_{Ni} + Y_{Mo}\mu_{Mo} + Y_{Mn}\mu_{Mn}
\]

(2.38)

With reference to Table 2.1 there are more carbides phases present within the Fe-C and Cr-C systems than nitrides in the equivalent systems. However, those of concern in stainless steels and for which thermodynamic data are available are orthorhombic \(M_7C_3\), monoclinic \(M_5C_2\), orthorhombic \(M_3C\), and \(fcc\) \(M_{23}C_6\). Of these, only \(M_5C_2\), \(M_7C_3\), and \(M_{23}C_6\) have been observed to form in 316L after prolonged carburization or isothermal annealing [8, 9]. The conditions establishing the solubility limit in the presence of these carbides, \(\Delta G^\alpha,\gamma \rightarrow M_xC_y = 0\), are given in Eqs. 2.39–2.42.

\[
\Delta G^\gamma \rightarrow M_7C_3 = 0 = G_m^{M_7C_3} - 7\mu_M^{fcc} - 3\mu_C^{fcc}
\]

(2.39)

\[
\Delta G^\alpha \rightarrow M_7C_3 = 0 = G_m^{M_7C_3} - 7\mu_M^{bcc} - 3\mu_C^{bcc}
\]

\[
\Delta G^\gamma \rightarrow M_5C_2 = 0 = G_m^{M_5C_2} - 5\mu_M^{fcc} - 2\mu_C^{fcc}
\]

(2.40)

\[
\Delta G^\alpha \rightarrow M_5C_2 = 0 = G_m^{M_5C_2} - 5\mu_M^{bcc} - 2\mu_C^{bcc}
\]

\[
\Delta G^\gamma \rightarrow M_3C = 0 = G_m^{M_3C} - 3\mu_M^{fcc} - \mu_C^{fcc}
\]

(2.41)

\[
\Delta G^\alpha \rightarrow M_3C = 0 = G_m^{M_3C} - 3\mu_M^{bcc} - \mu_C^{bcc}
\]

\[
\Delta G^\gamma \rightarrow M_{23}C_6 = 0 = G_m^{M_{23}C_6} - 23\mu_M^{fcc} - 6\mu_C^{fcc}
\]

(2.42)

\[
\Delta G^\alpha \rightarrow M_{23}C_6 = 0 = G_m^{M_{23}C_6} - 23\mu_M^{bcc} - 6\mu_C^{bcc}
\]

where \(\mu^\phi_m\) has the usual meaning applied to a (Fr,Cr,Ni,Mo,Mn) steel.

In the next chapter, the thermodynamic database and computational methods used in solving the prescribed equations above are discussed. The explicit expressions for the Gibbs free energy of the solution and compound phases using...
the parameters available in the current ferrous database are also presented.
Chapter 3

Computational Methods

The CALPHAD approach to computational thermodynamics, used in this case for predicting phase stability during kinetically-controlled paraequilibrium carburization and nitridation treatments, was introduced in Ch. 2. The specific parameters of this model that have previously been accessed are used to define the Gibbs free energy expression for the specific bcc and fcc Fe-Cr-Ni-Mo-Mn-(C,N) systems. A routine including these most recent thermodynamic assessments with the feasibility of database expansion and parameter revision was written in Wolfram Mathematica® 8.04 and used for all of the following simulations.

3.1 Thermodynamic Database Review

A review of the full Fe-Cr-Ni-Mo-Mn-(C,N) database was first conducted to assess which parameters were available in the descriptions of bcc and fcc solid solutions and the known carbide and nitride phases described in Ch. 2. Within these M-N systems, the complete description for the three primary nitrides $M_2N_{1-x}$ (or $M_2N$), $M_4N$, and $MN$ (described by a fcc solution with full interstitial sublattice) is available, with the exception of $Mo_4N$ for which there is no data. Within the M-C systems, a full description is available for the carbides $\tau$-$M_{23}C_6$, $\theta$-$M_3C$, and $\omega$-$M_7C_3$, while for Hägg carbide $\chi$-$M_5C_2$, only Fe$_5C_2$ and Mn$_5C_2$ have been assessed. This carbide, though rare, is important in the carburization of stainless steels, but was not considered in this analysis due to lack of data. The $\tau$-$M_{23}C_6$ phase is described in the CALPHAD framework as containing three sublattices—two substitutional and one interstitial—i.e. $(M)_{20}(M)_3(C)_6$. A full description
3.2. GIBBS FREE ENERGY EXPRESSIONS FOR SOLUTION AND COMPOUND PHASES

for both metal sublattices is available for Fe, Cr, Ni, and Mn, however Mo has only been assessed for the second metal sublattice. With the assumption that a paraequilibrium carbide will form, where both metal lattices are compositionally invariant, Mo in ferrite and austenite has not been considered in simulating the solubility of carbon upon formation of this phase. It should also be said that some, if not many, parameters within the ferrous database are only available within Thermo-Calc® and are not published values. At present, users do not have access to view these parameters within the Thermo-Calc® database. However, the author of this work did generously receive several of these unpublished parameters from Lee [51] for nitrogen interactions as given in Appendix A. Also, the five revised Cr-C and Cr-Fe-C parameters of Michal et al. [27] were those used in all simulations, as they have been shown to yield better agreement between model and experiment in the low-temperature regimes of interest, while still accurately predicting phase stability at higher temperatures. Use of the previous published interaction parameters of Lee [52] led to calculated solubility limits a factor of 2 too low.

3.2 Gibbs Free Energy Expressions for Solution and Compound Phases

3.2.1 Fe-M-N System

By using Eq. 2.4 in conjunction with the Fe-Cr-Ni-Mo-Mn-N system, the molar Gibbs free energy for fcc austenite and bcc ferrite can be determined. With the compound model, the fcc phase is described by (Fe,Cr,Ni,Mo,Mn)\textsubscript{1}(N,V\textsubscript{a})\textsubscript{1} and bcc by (Fe,Cr,Ni,Mo,Mn)\textsubscript{1}(N,V\textsubscript{a})\textsubscript{3}. It follows that the maximum nitrogen content permissible in the fcc phase is 50 at. pct. when each interstitial site is occupied (a MN nitride), or in bcc solutions, a maximum nitrogen content of 75 at. pct. (a MN\textsubscript{3} nitride). The expression describing the Gibbs free energy of the fcc solution
is given by Eq 3.1 using the available parameters,

\[
G^f_{m} = Y_{Fe}Y_{Va}G^{hfcc}_{Fe;Va} + Y_{Fe}Y_{N}G^{hfcc}_{Fe;N} + Y_{Cr}Y_{Va}G^{hfcc}_{Cr;Va} + Y_{Cr}Y_{N}G^{hfcc}_{Cr;N} \\
+ Y_{Ni}Y_{Va}G^{hfcc}_{Ni;Va} + Y_{Ni}Y_{N}G^{hfcc}_{Ni;N} + Y_{Mo}Y_{Va}G^{hfcc}_{Mo;Va} + Y_{Mo}Y_{N}G^{hfcc}_{Mo;N} \\
+ Y_{Mn}Y_{Va}G^{hfcc}_{Mn;Va} + Y_{Mn}Y_{N}G^{hfcc}_{Mn;N} \\
+ RT\left[ Y_{Fe}ln(Y_{Fe}) + Y_{Cr}ln(Y_{Cr}) + Y_{Ni}ln(Y_{Ni}) + Y_{Mo}ln(Y_{Mo}) \\
+ Y_{Mn}ln(Y_{Mn}) + Y_{N}ln(Y_{N}) + Y_{Va}ln(Y_{Va}) \right] \\
+ Y_{N}Y_{Va}\left[ Y_{Fe}0L^{ffcc}_{Fe;N;Va} + Y_{Cr}0L^{ffcc}_{Cr;N;Va} + Y_{Mo}0L^{ffcc}_{Mo;N;Va} + Y_{Mn}0L^{ffcc}_{Mn;N;Va} \right] \\
+ Y_{Va}\left[ Y_{Cr}Y_{Fe}0L^{ffcc}_{Cr;Fe;Va} + Y_{Cr}Y_{Fe}1L^{ffcc}_{Cr;Fe;Va}(Y_{Cr} - Y_{Fe}) \right] \\
+ Y_{Fe}Y_{Mn}0L^{ffcc}_{Fe;Mn;Va} + Y_{Fe}Y_{Mn}1L^{ffcc}_{Fe;Mn;Va}(Y_{Fe} - Y_{Mn}) \\
+ Y_{Cr}Y_{N}0L^{ffcc}_{Cr;N;Va} + Y_{Cr}Y_{N}1L^{ffcc}_{Cr;N;Va}(Y_{Cr} - Y_{N}) \\
+ Y_{Cr}Y_{Mo}0L^{ffcc}_{Cr;Mo;Va} + Y_{Cr}Y_{Mo}1L^{ffcc}_{Cr;Mo;Va}(Y_{Cr} - Y_{Mo}) \\
+ Y_{Mo}Y_{N}0L^{ffcc}_{Mo;N;Va} + Y_{Mo}Y_{N}1L^{ffcc}_{Mo;N;Va}(Y_{Mo} - Y_{N}) \\
+ Y_{Mn}Y_{N}0L^{ffcc}_{Mn;N;Va} + Y_{Mn}Y_{N}1L^{ffcc}_{Mn;N;Va}(Y_{Mn} - Y_{N}) \\
+ Y_{Mn}Y_{Mo}0L^{ffcc}_{Mn;Mo;Va} + Y_{Mn}Y_{Mo}1L^{ffcc}_{Mn;Mo;Va} \\
+ Y_{Fe}Y_{Ni}Y_{N}Y_{Va}L^{ffcc}_{Fe;Cr;N;Va} + Y_{Cr}Y_{Ni}Y_{N}Y_{Va}L^{ffcc}_{Cr;N;Va} + Y_{Cr}Y_{Ni}Y_{N}Y_{Va}L^{ffcc}_{Cr;N;Va} \\
+ \text{mag}G^{ffcc}_{m} \tag{3.1}
\]
3.2. GIBBS FREE ENERGY FOR SOLUTIONS AND COMPOUNDS

and similarly in Eq. 3.2 for a bec (Fe,Cr,Ni,Mo,Mn,N) solution. It is straightforward to add more interaction terms between the various constituents on each sublattice. As more experimental data are acquired, the system is usually reassessed, and the parameters again optimized. It is hoped that expansion or revision of the database may be achievable using experimental data acquired from low-temperature gas-phase treatments of stainless steels, as has been previously performed in Cr-C system Michal-Gu-Jennings-Kahn-Ernst-Heuer-2009.

\[
G_m = Y_{Fe}Y_{Va}^oG_{Fe,Va} + Y_{Fe}Y_{N}^oG_{Fe,N} + Y_{Cr}Y_{Va}^oG_{Cr,Va} + Y_{Cr}Y_{N}^oG_{Cr,N} + Y_{Ni}Y_{Va}^oG_{Ni,Va} + Y_{Ni}Y_{N}^oG_{Ni,N} + Y_{Mo}Y_{Va}^oG_{Mo,Va} + Y_{Mo}Y_{N}^oG_{Mo,N} \\
+ Y_{Mn}Y_{Va}^oG_{Mn,Va} + Y_{Mn}Y_{N}^oG_{Mn,N} + RT\left[ Y_{Fe}\ln(Y_{Fe}) + Y_{Cr}\ln(Y_{Cr}) + Y_{Ni}\ln(Y_{Ni}) + Y_{Mo}\ln(Y_{Mo}) \right] \\
+ Y_{Mn}\ln(Y_{Mn}) + Y_{N}\ln(Y_{N}) + Y_{Va}\ln(Y_{Va}) \\
+ Y_{Ni}Y_{Fe}^0L_{Fe,Vi,N} + Y_{Cr}Y_{Cr,N}^0L_{Cr,Vi,N} + Y_{Mn}Y_{Mn,N}^0L_{Mn,Vi,N} + Y_{Cr}Y_{Fe}^0L_{Fe,Vi,Mn} + Y_{Ni}Y_{Mn}^0L_{Mn,Vi,Mn} + Y_{Fe}Y_{Ni}^0L_{Fe,Vi,N} + Y_{Fe}Y_{Mn}^0L_{Fe,Vi,Mn} + Y_{Fe}Y_{Mo}^0L_{Fe,Vi,Mo} + Y_{Fe}Y_{Mn}^0L_{Fe,Vi,Mn} + Y_{Fe}Y_{Mo}^0L_{Fe,Vi,Mn} \tag{3.2}
\]

The chemical potential of each constituent in the solution is then determined (within the program) by applying Eqs. 2.24–2.26 to Eqs. 3.1 and 3.2.

The Gibbs free energy of the nitride phases is also described using a two sub-lattice model. The magnetic contribution is not considered for each of the nitrides.
3.2. GIBBS FREE ENERGY FOR SOLUTIONS AND COMPOUNDS

The Gibbs free energy of a stoichiometric MN nitride \((\text{Fe,Cr,Ni,Mo,Mn})_1(\text{N})_1\) is given in Eq. 3.3.

\[
G_{\text{MN}}^{\text{MN}} = Y_{\text{Fe}} Y_{\text{N}}^0 G_{\text{Fe,N}}^{\text{hfc}} + Y_{\text{Cr}} Y_{\text{N}}^0 G_{\text{Cr,N}}^{\text{hfc}} + Y_{\text{Ni}} Y_{\text{N}}^0 G_{\text{Ni,N}}^{\text{hfc}} + Y_{\text{Mo}} Y_{\text{N}}^0 G_{\text{Mo,N}}^{\text{hfc}} + Y_{\text{Mn}} Y_{\text{N}}^0 G_{\text{Mn,N}}^{\text{hfc}}
+ RT \left[ Y_{\text{Fe}} \ln(Y_{\text{Fe}}) + Y_{\text{Cr}} \ln(Y_{\text{Cr}}) + Y_{\text{Ni}} \ln(Y_{\text{Ni}}) + Y_{\text{Mo}} \ln(Y_{\text{Mo}}) + Y_{\text{Mn}} \ln(Y_{\text{Mn}}) \right]
+ Y_{\text{Cr}} Y_{\text{Fe}}^0 L_{\text{Cr,Fe:N}}^{\text{hfc}} + Y_{\text{Cr}} Y_{\text{Fe}}^0 L_{\text{Cr,Fe:N}}^{\text{hfc}}(Y_{\text{Cr}} - Y_{\text{Fe}})
+ Y_{\text{Fe}} Y_{\text{Ni}}^0 L_{\text{Fe,Ni:N}}^{\text{hfc}} + Y_{\text{Fe}} Y_{\text{Ni}}^0 L_{\text{Fe,Ni:N}}^{\text{hfc}}(Y_{\text{Fe}} - Y_{\text{Ni}})
+ Y_{\text{Fe}} Y_{\text{Mo}}^0 L_{\text{Fe,Mn:N}}^{\text{hfc}} + Y_{\text{Fe}} Y_{\text{Mo}}^0 L_{\text{Fe,Mn:N}}^{\text{hfc}}(Y_{\text{Fe}} - Y_{\text{Mo}})
+ Y_{\text{Cr}} Y_{\text{Mo}}^0 L_{\text{Cr,Mn:N}}^{\text{hfc}} + Y_{\text{Cr}} Y_{\text{Mo}}^0 L_{\text{Cr,Mn:N}}^{\text{hfc}}(Y_{\text{Cr}} - Y_{\text{Mo}})
+ Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Mn}}^0 L_{\text{Fe,Cr,Mn:N}}^{\text{hfc}}
\]

(3.3)

The hcp \(\text{M}_2\text{N}_{1-x}\) phase is close-packed thereby yielding one octahedral interstitial site per atom. However, it is assumed that in this nitride phase, two neighboring interstitial sites in the hexagonal \(c\) direction are never simultaneously occupied, and thus the maximum nitrogen content is 33.3 at. pct. The parameters for this phase are actually by a \((\text{Fe,Cr,Ni,Mo,Mn})_1(\text{N, Va})_{0.5}\) nitride for normalized metal constituents, and the free energy then needs only be doubled before use in Eqs. 2.35 and 2.36. If the phase is treated as stoichiometric, i.e. \(Y_{\text{Va}} = 0\), the Gibbs free energy is described by Eq. 3.4

\[
G_{\text{M}_2\text{N}}^{\text{M}_2\text{N}} = 2 \left( Y_{\text{Fe}} Y_{\text{N}}^0 G_{\text{Fe,N}}^{\text{hfc}} + Y_{\text{Cr}} Y_{\text{N}}^0 G_{\text{Cr,N}}^{\text{hfc}} + Y_{\text{Ni}} Y_{\text{N}}^0 G_{\text{Ni,N}}^{\text{hfc}} + Y_{\text{Mo}} Y_{\text{N}}^0 G_{\text{Mo,N}}^{\text{hfc}} + Y_{\text{Mn}} Y_{\text{N}}^0 G_{\text{Mn,N}}^{\text{hfc}}
+ RT \left[ Y_{\text{Fe}} \ln(Y_{\text{Fe}}) + Y_{\text{Cr}} \ln(Y_{\text{Cr}}) + Y_{\text{Ni}} \ln(Y_{\text{Ni}}) + Y_{\text{Mo}} \ln(Y_{\text{Mo}}) + Y_{\text{Mn}} \ln(Y_{\text{Mn}}) \right]
+ Y_{\text{Fe}} Y_{\text{Cr}}^0 L_{\text{Fe,Cr:N}}^{\text{hfc}} + Y_{\text{Cr}} Y_{\text{Ni}}^0 L_{\text{Cr,Ni:N}}^{\text{hfc}} + Y_{\text{Cr}} Y_{\text{Mo}}^0 L_{\text{Cr,Mo:N}}^{\text{hfc}} + Y_{\text{Cr}} Y_{\text{Mn}}^0 L_{\text{Cr,Mn:N}}^{\text{hfc}}
+ Y_{\text{Ni}} Y_{\text{Mo}}^0 L_{\text{Ni,Mo:N}}^{\text{hfc}} + Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Mn}}^0 L_{\text{Fe,Cr,Mn:N}}^{\text{hfc}} \right) \]

(3.4)
3.2. GIBBS FREE ENERGY FOR SOLUTIONS AND COMPOUNDS

or to include vacant interstitial sites by Eq. 3.5

\[
G_{m}^{M_{2}N_{1-x}} = 2\left( Y_{Fe}Y_{Va}G_{Fe:Va}^{hcp} + Y_{Fe}Y_{N}G_{Fe:N}^{hcp} + Y_{Cr}Y_{Va}G_{Cr:Va}^{hcp} + Y_{Cr}Y_{N}G_{Cr:N}^{hcp}
+ Y_{Ni}Y_{Va}G_{Ni:Va}^{hcp} + Y_{Ni}Y_{N}G_{Ni:N}^{hcp} + Y_{Mo}Y_{Va}G_{Mo:Va}^{hcp} + Y_{Mo}Y_{N}G_{Mo:N}^{hcp}
+ Y_{Mn}Y_{Va}G_{Mn:Va}^{hcp} + Y_{Mn}Y_{N}G_{Mn:N}^{hcp}
+ RT\left[ Y_{Fe}ln(Y_{Fe}) + Y_{Cr}ln(Y_{Cr}) + Y_{Ni}ln(Y_{Ni}) + Y_{Mo}ln(Y_{Mo})
+ Y_{Mn}ln(Y_{Mn}) + 0.5Y_{N}ln(Y_{N}) + 0.5Y_{Va}ln(Y_{Va})\right]
+ Y_{Ni}Y_{Va}Y_{Fe}\frac{L_{Fe,Ni:Va}^{hcp}}{L_{Fe,Ni:Va}^{hcp}} + Y_{Fe}Y_{Mo}\frac{L_{Fe,Mo:Va}^{hcp}}{L_{Fe,Mo:Va}^{hcp}} + Y_{Cr}Y_{Mn}\frac{L_{Cr,Mn:Va}^{hcp}}{L_{Cr,Mn:Va}^{hcp}}
+ Y_{Mn}Y_{Mo}\frac{L_{Mn,Mo:Va}^{hcp}}{L_{Mn,Mo:Va}^{hcp}} + Y_{Cr}Y_{Mn}\frac{L_{Cr,Mo:Va}^{hcp}}{L_{Cr,Mo:Va}^{hcp}} (Y_{Cr} - Y_{Mo})
+ Y_{Fe}Y_{Ni}\frac{L_{Fe,Ni:Va}^{hcp}}{L_{Fe,Ni:Va}^{hcp}} + Y_{Fe}Y_{Ni}\frac{L_{Fe,Ni:Va}^{hcp}}{L_{Fe,Ni:Va}^{hcp}} (Y_{Fe} - Y_{Ni}) + Y_{Fe}Y_{Ni}\frac{L_{Fe,Ni:Va}^{hcp}}{L_{Fe,Ni:Va}^{hcp}} (Y_{Fe} - Y_{Ni})^{2}
+ Y_{N}\left[ Y_{Cr}Y_{Fe}\frac{L_{Cr,Fe:Va}^{hcp}}{L_{Cr,Fe:Va}^{hcp}} + Y_{Cr}Y_{Ni}\frac{L_{Cr,Ni:Va}^{hcp}}{L_{Cr,Ni:Va}^{hcp}} + Y_{Cr}Y_{Mo}\frac{L_{Cr,Mo:Va}^{hcp}}{L_{Cr,Mo:Va}^{hcp}} + Y_{Cr}Y_{Mn}\frac{L_{Cr,Mn:Va}^{hcp}}{L_{Cr,Mn:Va}^{hcp}}\right]
+ Y_{Fe}Y_{Cr}Y_{Mn}Y_{Va}\frac{L_{Fe,Y_{Cr,Mn:Va}^{hcp}}}{L_{Fe,Y_{Cr,Mn:Va}^{hcp}}} + Y_{Fe}Y_{Cr}Y_{Mn}Y_{N}\frac{L_{Fe,Y_{Cr,Mn:Va}^{hcp}}}{L_{Fe,Y_{Cr,Mn:Va}^{hcp}}} \right)
\]

(3.5)

The cubic $M_{2}N$ phase, excluding Mo, is treated as a linear compound $(Fe, Cr, Ni, Mn)_{4}N_{1}$, with the Gibbs free energy in Eq. 3.6:

\[
G_{m}^{M_{4}N} = Y_{Fe}G_{Fe:N}^{M_{4}N} + Y_{Cr}G_{Cr:N}^{M_{4}N} + Y_{Ni}G_{Ni:N}^{M_{4}N} + Y_{Mo}G_{Mo:N}^{M_{4}N} + Y_{Mn}G_{Mn:N}^{M_{4}N}
+ 4RT\left[ Y_{Fe}ln(Y_{Fe}) + Y_{Cr}ln(Y_{Cr}) + Y_{Ni}ln(Y_{Ni}) + Y_{Mo}ln(Y_{Mo}) + Y_{Mn}ln(Y_{Mn})\right]
+ Y_{Fe}Y_{Mn}\frac{L_{Fe,Mn:N}^{M_{4}N}}{L_{Fe,Mn:N}^{M_{4}N}} \right)
\]

(3.6)
3.2. GIBBS FREE ENERGY FOR SOLUTIONS AND COMPOUNDS

3.2.2 Fe-M-C

The same descriptions apply to *bcc* and *fcc* solutions containing carbon, and using the available parameters within the Fe-Cr-Ni-Mo-Mn-C system, are presented in Eq. 3.7-3.8 respectively.

\[
G_m^{\text{bcc}} = Y_{\text{Fe}} Y_{\text{Va}} \cdot G_{\text{Fe:Va}}^{\text{bcc}} + Y_{\text{Fe}} Y_{\text{C}} \cdot G_{\text{Fe:C}}^{\text{bcc}} + Y_{\text{Cr}} Y_{\text{Va}} \cdot G_{\text{Cr:Va}}^{\text{bcc}} + Y_{\text{Cr}} Y_{\text{C}} \cdot G_{\text{Cr:C}}^{\text{bcc}} \\
+ Y_{\text{Ni}} Y_{\text{Va}} \cdot G_{\text{Ni:Va}}^{\text{bcc}} + Y_{\text{Ni}} Y_{\text{C}} \cdot G_{\text{Ni:C}}^{\text{bcc}} + Y_{\text{Mo}} Y_{\text{Va}} \cdot G_{\text{Mo:Va}}^{\text{bcc}} + Y_{\text{Mo}} Y_{\text{C}} \cdot G_{\text{Mo:C}}^{\text{bcc}} \\
+ Y_{\text{Mn}} Y_{\text{Va}} \cdot G_{\text{Mn:Va}}^{\text{bcc}} + Y_{\text{Mn}} Y_{\text{C}} \cdot G_{\text{Mn:C}}^{\text{bcc}} \\
+ RT\left[ Y_{\text{Fe}} \ln(Y_{\text{Fe}}) + Y_{\text{Cr}} \ln(Y_{\text{Cr}}) + Y_{\text{Ni}} \ln(Y_{\text{Ni}}) + Y_{\text{Mo}} \ln(Y_{\text{Mo}}) \\
+ Y_{\text{Mn}} \ln(Y_{\text{Mn}}) + Y_{\text{C}} \ln(Y_{\text{C}}) + Y_{\text{Va}} \ln(Y_{\text{Va}}) \right] \\
+ Y_{\text{C}} Y_{\text{Va}} \left[ Y_{\text{Fe}}^0 L_{\text{Fe:Va}}^{\text{bcc}} + Y_{\text{Cr}}^0 L_{\text{Cr:Va}}^{\text{bcc}} \right] \\
+ Y_{\text{Va}} \left[ Y_{\text{Cr}} Y_{\text{Fe}}^0 L_{\text{Cr:Fe:Va}}^{\text{bcc}} + Y_{\text{Fe}} Y_{\text{Mn}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} + Y_{\text{Ni}} Y_{\text{Mo}}^0 L_{\text{Ni:Mo:Va}}^{\text{bcc}} \right] \\
+ Y_{\text{Fe}} Y_{\text{Ni}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} + Y_{\text{Fe}} Y_{\text{Mn}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}}(Y_{\text{Fe}} - Y_{\text{Ni}}) \\
+ Y_{\text{Fe}} Y_{\text{Mo}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} + Y_{\text{Fe}} Y_{\text{Mn}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}}(Y_{\text{Fe}} - Y_{\text{Mo}}) \\
+ Y_{\text{Cr}} Y_{\text{Ni}}^0 L_{\text{Cr:Cr:Va}}^{\text{bcc}} + Y_{\text{Cr}} Y_{\text{Ni}}^0 L_{\text{Cr:Cr:Va}}^{\text{bcc}}(Y_{\text{Fe}} - Y_{\text{Ni}}) \\
+ Y_{\text{Cr}} Y_{\text{Mo}}^0 L_{\text{Cr:Cr:Va}}^{\text{bcc}} + Y_{\text{Cr}} Y_{\text{Mn}}^0 L_{\text{Cr:Cr:Va}}^{\text{bcc}}(Y_{\text{Cr}} - Y_{\text{Mn}}) \\
+ Y_{\text{Mn}} Y_{\text{Ni}}^0 L_{\text{Mn:Cr:Va}}^{\text{bcc}} + Y_{\text{Mn}} Y_{\text{Ni}}^0 L_{\text{Mn:Cr:Va}}^{\text{bcc}}(Y_{\text{Mn}} - Y_{\text{Ni}}) \\
+ Y_{\text{Mn}} Y_{\text{Mn}}^0 L_{\text{Mn:Cr:Va}}^{\text{bcc}} + Y_{\text{Mn}} Y_{\text{Mn}}^0 L_{\text{Mn:Cr:Va}}^{\text{bcc}}(Y_{\text{Mn}} - Y_{\text{Mn}}) \\
+ Y_{\text{C}} \left[ Y_{\text{C}} Y_{\text{Fe}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} + Y_{\text{Fe}} Y_{\text{Mn}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} \right] \\
+ Y_{\text{Fe}} Y_{\text{Ni}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} + Y_{\text{Fe}} Y_{\text{Ni}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} \left( Y_{\text{Fe}} - Y_{\text{Ni}} \right) + Y_{\text{Cr}} Y_{\text{Ni}}^0 L_{\text{Cr:Cr:Va}}^{\text{bcc}} \\
+ Y_{\text{Va}} \left[ Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Ni}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} \right] + Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Mn}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} \\
+ Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Mn}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} \left( Y_{\text{Fe}} - Y_{\text{Mn}} \right) + Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Mn}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} + Y_{\text{Fe}} Y_{\text{Ni}} Y_{\text{Mn}}^0 L_{\text{Fe:Cr:Va}}^{\text{bcc}} \\
+ \text{mag} G_m^{\text{bcc}}
\]

(3.7)
3.2. GIBBS FREE ENERGY FOR SOLUTIONS AND COMPOUNDS

\[
G_{m}^{\text{fcc}} = Y_{\text{Fe}} Y_{\text{Va}} G_{\text{Fe, Va}}^{\text{fcc}} + Y_{\text{Fe}} Y_{\text{C}} G_{\text{Fe, C}}^{\text{fcc}} + Y_{\text{Cr}} Y_{\text{Va}} G_{\text{Cr, Va}}^{\text{fcc}} + Y_{\text{Cr}} Y_{\text{C}} G_{\text{Cr, C}}^{\text{fcc}} + Y_{\text{Ni}} Y_{\text{Va}} G_{\text{Ni, Va}}^{\text{fcc}} + Y_{\text{Ni}} Y_{\text{C}} G_{\text{Ni, C}}^{\text{fcc}} + Y_{\text{Mo}} Y_{\text{Va}} G_{\text{Mo, Va}}^{\text{fcc}} + Y_{\text{Mo}} Y_{\text{C}} G_{\text{Mo, C}}^{\text{fcc}} + Y_{\text{Mn}} Y_{\text{Va}} G_{\text{Mn, Va}}^{\text{fcc}} + Y_{\text{Mn}} Y_{\text{C}} G_{\text{Mn, C}}^{\text{fcc}} + RT \left[ Y_{\text{Fe}} \ln(Y_{\text{Fe}}) + Y_{\text{Cr}} \ln(Y_{\text{Cr}}) + Y_{\text{Ni}} \ln(Y_{\text{Ni}}) + Y_{\text{Mo}} \ln(Y_{\text{Mo}}) + Y_{\text{Mn}} \ln(Y_{\text{Mn}}) + Y_{\text{C}} \ln(Y_{\text{C}}) + Y_{\text{Va}} \ln(Y_{\text{Va}}) \right] + Y_{\text{C}} Y_{\text{Va}} [Y_{\text{Fe}} L_{\text{Fe, C, Va}}^{\text{fcc}} + Y_{\text{Cr}} L_{\text{Cr, C, Va}}^{\text{fcc}} + Y_{\text{Ni}} L_{\text{Ni, C, Va}}^{\text{fcc}} + Y_{\text{Mo}} L_{\text{Mo, C, Va}}^{\text{fcc}} + Y_{\text{Mn}} L_{\text{Mn, C, Va}}^{\text{fcc}}] + Y_{\text{Cr}} Y_{\text{Fe}} [Y_{\text{Cr}} L_{\text{Cr, Fe}}^{\text{fcc}} + Y_{\text{Fe}} L_{\text{Fe, Cr}}^{\text{fcc}} (Y_{\text{Cr}} - Y_{\text{Fe}})] + Y_{\text{Fe}} Y_{\text{Mn}} L_{\text{Fe, Mn}}^{\text{fcc}} (Y_{\text{Fe}} - Y_{\text{Mn}}) + Y_{\text{Cr}} Y_{\text{Ni}} L_{\text{Cr, Ni}}^{\text{fcc}} (Y_{\text{Cr}} - Y_{\text{Ni}}) + Y_{\text{Cr}} Y_{\text{Mn}} Y_{\text{Cr}} L_{\text{Cr, Mn, Va}}^{\text{fcc}} (Y_{\text{Cr}} - Y_{\text{Mn}}) + Y_{\text{Fe}} Y_{\text{Mo}} L_{\text{Fe, Mo}}^{\text{fcc}} (Y_{\text{Fe}} - Y_{\text{Mo}}) + Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Ni}} Y_{\text{Cr}} L_{\text{Cr, Cr, Ni, Va}}^{\text{fcc}} + Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Mo}} Y_{\text{Cr}} L_{\text{Cr, Mo}}^{\text{fcc}} + Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Mn}} L_{\text{Cr, Mn, Va}}^{\text{fcc}} + Y_{\text{Fe}} Y_{\text{Ni}} Y_{\text{Cr}} Y_{\text{Mn}} L_{\text{Cr, Ni, Mn, Va}}^{\text{fcc}} + Y_{\text{Cr}} Y_{\text{Fe}} Y_{\text{Ni}} Y_{\text{Cr}} Y_{\text{C}} L_{\text{Cr, Fe, Ni, C}}^{\text{fcc}} + Y_{\text{Fe}} Y_{\text{Mn}} Y_{\text{Fe}} Y_{\text{Mo}} Y_{\text{Fe}} Y_{\text{Mn}} Y_{\text{Fe}} Y_{\text{Mn}} Y_{\text{Fe}} Y_{\text{Mn}} L_{\text{Fe, Mo, Mn, Va}}^{\text{fcc}} + Y_{\text{Cr}} Y_{\text{Fe}} Y_{\text{Ni}} Y_{\text{Cr}} Y_{\text{C}} (Y_{\text{Fe}} - Y_{\text{Ni}}) + Y_{\text{Cr}} Y_{\text{Fe}} Y_{\text{Mn}} L_{\text{Fe, Mn}}^{\text{fcc}} + Y_{\text{Fe}} Y_{\text{Cr}} Y_{\text{Ni}} Y_{\text{Cr}} Y_{\text{C}} L_{\text{Cr, Cr, Ni, C}}^{\text{fcc}} + Y_{\text{Cr}} Y_{\text{Fe}} Y_{\text{Ni}} Y_{\text{Cr}} Y_{\text{C}} L_{\text{Cr, Fe, Ni, C}}^{\text{fcc}} \tag{3.8} \]
with a two sublattice model \((\text{Fe,Cr,Ni,Mo,Mn})_7(C)_3\) and likewise for \(M_4C\) by \((\text{Fe,Cr,Ni,Mo,Mn})_7(C)_3\). Special mention is made for the \(M_23C_6\) which is described using three sublattices \((\text{Fe,Cr,Ni,Mn})_{20}(\text{Fe,Cr,Ni,Mn})_7(C)_6\) where \(Y_i^1\) represents the site fraction of \(i\) on the first metal sublattice and \(Y_i^2\) the site fraction on the second sublattice. In an equilibrium condition, the metal atoms will partition, in the right proportions, to each sublattice so as to minimize the total energy. However, with limited kinetics for such movement at the processing temperatures of interest, it is assumed here that the carbid is paraequilibrium, i.e. \(Y_i^1 = Y_i^2\).

\[
G_m^{M_23C_6} = Y_{Fe}^{1} \left[ Y_{Fe}^{2} G_{Fe:C}^{M_23C_6} + Y_{Cr}^{2} G_{Cr:C}^{M_23C_6} \right] + Y_{Ni}^{1} \left[ Y_{Fe}^{2} G_{Fe:C}^{M_23C_6} + Y_{Cr}^{2} G_{Cr:C}^{M_23C_6} \right] + Y_{Mn}^{1} \left[ Y_{Fe}^{2} G_{Fe:C}^{M_23C_6} + Y_{Cr}^{2} G_{Cr:C}^{M_23C_6} \right] + 20RT \left[ Y_{Fe}^{1} ln(Y_{Fe}^{1}) + Y_{Cr}^{1} ln(Y_{Cr}^{1}) + Y_{Ni}^{1} ln(Y_{Ni}^{1}) + Y_{Mn}^{1} ln(Y_{Mn}^{1}) \right] + 3RT \left[ Y_{Fe}^{2} ln(Y_{Fe}^{2}) + Y_{Cr}^{2} ln(Y_{Cr}^{2}) + Y_{Ni}^{2} ln(Y_{Ni}^{2}) + Y_{Mn}^{2} ln(Y_{Mn}^{2}) \right]
\]

\[
G_m^{M_4C} = Y_{Fe}^{0} G_{Fe:C}^{M_4C} + Y_{Cr}^{0} G_{Cr:C}^{M_4C} + Y_{Ni}^{0} G_{Ni:C}^{M_4C} + Y_{Mo}^{0} G_{Mo:C}^{M_4C} + Y_{Mn}^{0} G_{Mn:C}^{M_4C} + 3RT \left[ Y_{Fe}^{0} ln(Y_{Fe}^{0}) + Y_{Cr}^{0} ln(Y_{Cr}^{0}) + Y_{Ni}^{0} ln(Y_{Ni}^{0}) + Y_{Mo}^{0} ln(Y_{Mo}^{0}) + Y_{Mn}^{0} ln(Y_{Mn}^{0}) \right] + Y_{Cr}^{0} Y_{Fe}^{0} L_{Cr,Fe:C}^{M_4C} + Y_{Fe}^{0} Y_{Ni}^{0} L_{Fe,Ni:C}^{M_4C} + Y_{Cr}^{0} Y_{Mo}^{0} L_{Cr,Mo:C}^{M_4C}
\]

\[
G_m^{M_4C} = Y_{Fe}^{0} G_{Fe:C}^{M_4C} + Y_{Cr}^{0} G_{Cr:C}^{M_4C} + Y_{Ni}^{0} G_{Ni:C}^{M_4C} + Y_{Mo}^{0} G_{Mo:C}^{M_4C} + Y_{Mn}^{0} G_{Mn:C}^{M_4C} + 7RT \left[ Y_{Fe}^{0} ln(Y_{Fe}^{0}) + Y_{Cr}^{0} ln(Y_{Cr}^{0}) + Y_{Ni}^{0} ln(Y_{Ni}^{0}) + Y_{Mo}^{0} ln(Y_{Mo}^{0}) + Y_{Mn}^{0} ln(Y_{Mn}^{0}) \right] + Y_{Cr}^{0} Y_{Fe}^{0} L_{Cr,Fe:C}^{M_4C} + Y_{Fe}^{0} Y_{Ni}^{0} L_{Fe,Ni:C}^{M_4C} + Y_{Cr}^{0} Y_{Mo}^{0} L_{Cr,Mo:C}^{M_4C}
\]
3.3 Mathematica® Routine

A range of software and programming languages could be used to implement and solve all of the aforementioned equations in determining solubility limits, construction of paraequilibrium phase diagrams, etc., but the symbolic capabilities and user-friendly interface of Mathematica® deemed it appropriate for this work. While the routine (presented in Appendix B) was not optimized for speed, a single simulation took at most several minutes on a standard laptop computer (MS Windows™ 7 Ultimate 64-bit SP1/Intel® Core2™ Duo CPU T400 at 2.00 GHz/4.0 GB RAM). The routine symbolically differentiates the Gibbs free energy expressions to determine the chemical potential of each constituent, applies each to Eqs. 2.34–2.42, and determines the unique root of the nonlinear equations in Eqs. 2.30 & 2.33 using the Newton iterative method. The equilibrium solvus lines between ferrite and austenite as defined by the common tangent construct are determined by first expressing the Gibbs free energy of the bcc and fcc solu-
tions on a per mole basis, \( G_m^{\text{bcc}} \) and \( G_m^{\text{fcc}} \), using Eq. 2.27. Again, Newton’s iterative method is applied to locate the root(s) of a nonlinear equation; the two equilibrium nitrogen (or carbon) concentrations \( X_N^{\text{bcc}} \) (eq.) and \( X_N^{\text{fcc}} \) (eq.) are those two that uniquely satisfy Eq. 3.12.

\[
\frac{G_m^{\text{bcc}} - G_m^{\text{fcc}}}{X_N^{\text{bcc}} \text{(eq.)} - X_N^{\text{fcc}} \text{(eq.)}} = \frac{\partial G_m^{\text{bcc}}}{\partial X_N^{\text{bcc}}} = \frac{\partial G_m^{\text{fcc}}}{\partial X_N^{\text{fcc}}} \quad (3.12)
\]

In its earliest days, Mathematica® was developed for and used primarily by mathematicians, but use of the powerful program is rapidly growing within scientific, engineering, and industrial communities as it has a near endless list of pre-programmed functionality, and fills a unique niche in the realm of computation.
Chapter 4
Simulation Results

The following simulations involve either the pure constituents or hypothetical alloys, but with use of the program similar simulations can be carried out for a commercial alloy containing any combination of (Fe,Cr,Ni,Mo,Mn). For observing the effect of a single constituent on paraequilibrium solubilities of nitrogen or carbon, hypothetical binary (100-x)Fe-xM (at. pct.) alloys were used. To gauge the stability in a high-alloy stainless steel, a hypothetical senary 60Fe-20Cr-10Ni-5Mo-5Mn (at. pct.) alloy was used—henceforth referred to as HYSS. This alloy is to represent typical concentrations of each constituent found across the gamut of stainless steels.

4.1 Chemical Potential of Constituents

It is at first edifying to observe how the chemical potentials of each constituent in ferrite or austenite vary in the presence of carbon or nitrogen. Using the expressions for the chemical potential (relative to the free energy of the respective SER state) of each metal constituent and nitrogen in Eqs. 2.24–2.26, the chemical potentials of pure iron, chromium, nickel, molybdenum, and manganese as a function of nitrogen concentration at 450 °C are shown in Fig. 4.1 for fcc and bcc solutions; again, nitrogen can reach a maximum concentration of 50 at. pct. and 75 at. pct. in fcc and bcc solutions respectively when each interstitial site is occupied. Plotted separately in Fig. 4.2 is the chemical potentials of nitrogen relative to its standard state (N₂ gas) as a function of nitrogen concentration in the elemental and alloy bcc and fcc solutions.
4.1. CHEMICAL POTENTIAL OF CONSTITUENTS

**Figure 4.1:** Chemical potentials of pure Fe, Cr, Ni, Mo, Mn, and each element in HYSS relative to their most stable state at 298.15 K and 1 atm in fcc (solid lines) and bcc (broken lines) as a function of nitrogen concentration at 450 °C.
Interestingly, the chemical potentials of nearly all of the pure metal constituents decrease, i.e. become more stable, with increasing nitrogen content in both fcc and bcc solutions, with the exception of fcc chromium and bcc manganese. The chemical potential of fcc chromium slowly increases and reaches some maximum near 48 at. pct. nitrogen and then slightly decreases, while the chemical potential of bcc manganese reaches it maximum near 60. at. pct. and dramatically drops with increasing nitrogen up to 75 at. pct. Though nearly all of the metal constituents are stabilized in the presence of nitrogen, it is the chemical potential of nitrogen in solution that increases in elemental bcc and fcc states and the HYSS system, which will ultimately determine phase stability. The chemical potential of nitrogen in pure fcc chromium exhibits the same anomalous behavior as the metal, increasing with increasing nitrogen, decreasing, and finally increasing again. In all other M-N systems, the chemical potential of nitrogen increases in bcc and fcc states with increasing nitrogen content. The nearly infinite
chemical potentials of nitrogen approaching zero or maximum concentration can best be understood from entropic considerations: the first nitrogen atom to enter the solution is extremely stable, while filling of the last vacant site represents a highly unstable scenario.

The chemical potentials of each constituent in bcc and fcc HYSS are shown in Fig. 4.1 to be far different from their elemental counterparts, due to the additional metal-metal interactions. Here, the chemical potential of each metal constituent (with the exception of nickel) in the HYSS fcc phase decreases or remains relatively constant until the last few vacant sites are filled, at which point the chemical potential rapidly decreases. The chemical potential of iron is slightly increased until it reaches a maximum near 30 at. pct. nitrogen, at which points it begins to decrease. The chemical potential of chromium in HYSS fcc decreases most rapidly with increasing nitrogen. In the bcc HYSS, chromium is again the most stable element in the presence of nitrogen and continually decreases with increasing nitrogen concentration. The chemical potential of iron remains relatively unchanged until the concentration reaches nearly 60 at. pct., where it decreases rapidly thereafter. The chemical potentials of all other species in the bcc phase increase with increasing nitrogen, until nearly all of the interstitial sites are filled, nickel being the most unstable, followed by molybdenum. The chemical potential of nitrogen in bcc and fcc HYSS is similar to the case of pure bcc and fcc metals, where each nitrogen atom added to the solution is less stable than the previous.

The chemical potentials of pure iron, chromium, nickel, molybdenum, and manganese at 450 °C in the presence of carbon are shown in Fig. 4.3 for fcc and bcc solutions. Likewise the chemical potential of carbon in these solutions in Fig. 4.4.

Like nitrogen, the chemical potentials of the metal constituents all decrease in the solution with the addition of carbon, chromium in the fcc state remaining relatively constant until nearly a full interstitial sublattice, at which point it decreases rapidly. In the hypothetical HYSS alloy, the chemical potentials of nearly all constituents remains unchanged, with the exception of chromium in the bcc and fcc states and molybdenum in the bcc state, all of which continually decrease with increasing carbon concentration. The chemical potential of nickel increases in chemical potential with increasing carbon, as do iron and manganese.
Figure 4.3: Chemical potentials of pure Fe, Cr, Ni, Mo, Mn, and each element in HYSS relative to their most stable state at 298.15 K and 1 atm in fcc (solid lines) and bcc (broken lines) as a function of carbon concentration at 450 °C.
4.1. CHEMICAL POTENTIAL OF CONSTITUENTS

**Figure 4.4:** Chemical potential of C relative to graphite at 298.15 K and 1 atm as a function of carbon concentration in fcc (solid lines) and bcc (broken lines) at 450 °C.

in fcc states. The trend in stability of the interstitial carbon atoms in ferrite and austenite are similar to nitrogen, though to varying magnitudes.

To get a feel for the magnetic contribution added separately to the total Gibbs free energy (and chemical potential), it is plotted as a function of temperature in Fig. 4.5 for the elemental bcc and fcc phases. It is clear that the magnetic contribution in lowering the free energy is most significant only for bcc iron, and this primarily at lower temperatures. The fcc iron, bcc and fcc chromium, and molybdenum have negligible contributions through the range of temperatures from 0 to 1000 °C. There is a marginal lowering of the free energy for both bcc and fcc nickel and manganese at temperatures below ∼300 °C. Although the magnetic contribution is small compared to the total free energy and significant only for the case of bcc iron, its contribution was still considered for both the bcc and fcc solutions in all of the following analyses.
4.2. Paraequilibrium Solubility of Interstitials

4.2.1 Nitrogen

The conditions for the maximum metastable solubility of nitrogen in a \( bcc \) and \( fcc \) matrix as a function of ambient nitrogen activity were given in Eq. 2.30, under the paraequilibrium condition where only the chemical potentials of interstitial nitrogen in the solution and gas phase are equilibrated. The chemical potentials of the metal constituents, which are considered to be effectively immobile at the temperatures of the process, are neglected for the purposes of determining how much nitrogen could be dissolved for a given temperature and nitrogen activity. The solubility of nitrogen, \( \mu_{N}^{\text{gas}} = \frac{1}{2} G_{N_2}^{\text{gas}} \), in binary (100-\( x \))Fe-\( x \)M alloys exposed to an atmosphere of unit activity nitrogen, i.e. that of \( N_2 \) gas, given these conditions and the assumption that no surface oxide is present, can be seen in Fig. 4.6.
4.2. PARAEQUILIBRIUM SOLUBILITY OF INTERSTITIALS

for additions of 5, 10, 15, 20, and 25 at. pct. Cr, Ni, Mo, and Mn to bcc and fcc Fe. It is not suggested that nitrogen gas would ever “precipitate” out of the

solution, but rather these limits represents the maximum surface concentration of nitrogen expected at equilibrium in an atmosphere of nitrogen at unit activity. It is clear that the solubility of nitrogen in pure bcc iron is very low through a range of temperatures. Though not evident in the figure, the solubility for nitrogen in

Figure 4.6: Paraequilibrium solubility limits for bcc (broken lines) and fcc (solid lines) (100-x)Fe-xM alloys in equilibrium with pure N₂ gas (aN₂ = 1). Note change in abscissa for Fe-Ni alloys.
4.2. PARAEQUILIBRIUM SOLUBILITY OF INTERSTITIALS

*bcc* iron is endothermic, increasing with increasing temperature, as is true for all of the Ni, Mo, and Mn *bcc* binaries shown in Fig. 4.6. With the exception of Fe-Cr alloys, the paraequilibrium solubility of nitrogen in *bcc* (Ni,Mo,Mn)-Fe alloys is practically nil at unit activity, though the solubility can be significantly increased by increasing the nitrogen activity. The paraequilibrium solubility of nitrogen in pure *fcc* iron is significantly higher and exothermic. The increasing paraequilibrium solubility of nitrogen with increasing alloy content is most dramatic for chromium. Additions of only 5 at. pct. to *bcc* iron increase the maximum solubility by nearly an order of magnitude. The solubility in *bcc* iron also becomes exothermic near 13–14 at. pct. chromium. The solubility of nitrogen in *fcc* iron is also greatly increased through chromium alloying, but less dramatically when compared to the *bcc* phase. Nickel, having a low affinity for nitrogen, serves to decreases the solubility when added to both *bcc* and *fcc* iron, by roughly an order of magnitude when the alloy content is 25 at. pct. Molybdenum has little effect on the solubility of nitrogen in *bcc* iron, even for a 75Fe-25Mo alloy, but it does serve to increase the solubility in the *fcc* phase. Manganese, also a strong nitride former, increases the maximum solubility of nitrogen in *bcc* and *fcc* iron alloys. The increase in solubility is less in the *bcc* phase than for equivalent Fe-Cr alloys, while the increase in the *fcc* phase is very similar to equal concentration of molybdenum.

Nitriding of ferrous alloys, usually carried out in the ferritic state, works through control of the chemical activity of nitrogen in the gas phase, which can reach very high levels, and serves to increase the paraequilibrium solubility limit, i.e., a shifting of all solubility lines in Fig. 4.6 to the right with increasing nitrogen activity in the gas. Fig. 4.7 shows the paraequilibrium solubility of nitrogen in the ferritic and austenitic phases in the HYSS system for varying nitrogen gas activities. Even at unit activity, the paraequilibrium solubility in *fcc* HYSS is significantly higher compared to the solubility in pure iron. The solubility in the *bcc* is initially very low for low gas activities, but rapidly increases with increasing activity to levels that are comparable with the *fcc* phase. Nitrogen solubility in the *bcc* ferrite exhibits endothermic behavior due to such a high nickel content, while it is exothermic in the *fcc* phase. As with increasing chromium content in Fe-Cr alloys, the solubility limit is increased more dramatically in the *bcc* phase.
4.2. PARAEQUILIBRIUM SOLUBILITY OF INTERSTITIALS

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.7}
\caption{Maximum paraequilibrium nitrogen solubility in HYSS \textit{fcc} (solid lines) austenite and \textit{bcc} (broken lines) ferrite for several ambient nitrogen gas activity.}
\end{figure}

than the \textit{fcc} phase for an increase in nitrogen gas activity. When the activity is greater than $a_{N_2} = 10,000$, the perceivable solubility in \textit{fcc} HYSS is determined to be approaching 50 at. pct., near the theoretical limit.

4.2.2 Carbon

The solubility limit of carbon (graphite) is shown in Fig. 4.8 for the binary alloys and in Fig. 4.9 for HYSS. It is first noted that the solubility for carbon is in all cases lower than nitrogen for the same alloy. The solubility of carbon is also always endothermic, with the exception of high chromium \textit{fcc} and high molybdenum \textit{bcc} alloys which exhibit retrograde solubility. Nickel decreases the solubility of both carbon and nitrogen in \textit{fcc} alloys, most dramatically at temperatures above $\sim$500
4.2. PARAEQUILIBRIUM SOLUBILITY OF INTERSTITIALS

**Figure 4.8:** Paraequilibrium solubility limits for *bcc* (broken lines) and *fcc* (solid lines) (100-*x*)Fe-*x*M alloys in equilibrium with graphite. Note change in abscissa for Fe-Ni alloys.
4.2. PARAEQUILIBRIUM SOLUBILITY OF INTERSTITIALS

![Graph](image)

**Figure 4.9:** Maximum paraequilibrium carbon solubility in HYSS austenite and ferrite.

°C. Ranked in order of increasing the carbon solubility in *fcc* alloys are chromium, molybdenum, and manganese. The strong effect of chromium on increasing the paraequilibrium solubility of nitrogen and carbon in *fcc* iron alloys immediately makes clear why paraequilibrium treatments are so effective. The additions of molybdenum and manganese to the alloy further serves to increase the achievable solubility limit. The *fcc* HYSS alloy has a carbon solubility of almost 17 at. pct. that it nearly independent of temperature. Due to the high nickel content, the carbon solubility in the *bcc* phase is still relatively low, reaching approximately 2 at. pct. at 400 °C. The solubility of carbon in the *bcc* HYSS phase is also greater than nitrogen in the same alloy at unit activity, but is exceeded by nitrogen even at modest nitrogen activities.
4.3 Solubility with Paraequilibrium Secondary Phases

4.3.1 Gibbs Free Energy of Formation: Carbides and Nitrides

It is next important to considering the possibility of secondary phase precipitation within the $bcc$ and $fcc$ solutions, which are expected to have a high driving force for formation. First, the relative stability of each of the four (including a stoichiometric and nitrogen-deficient $M_2N_{1-x}$) nitride phases as a function temperature is considered. The standard Gibbs free energy of formation $\Delta^\circ G$ associated with

$$xM(s) + \frac{y}{2}N_2(g) \rightleftharpoons M_xN_y(s)$$

(4.1)

can be plotted on a so-called Ellingham diagram (minus the reduction potentials usually associated with these diagrams). Using the latest CALPHAD assessments for the $M_4N$, $M_2N_{1-x}$, and MN phases, the Ellingham diagrams for each of the $M_xN_y$ compounds are shown in Fig. 4.10 for $\frac{1}{2}$ mole of $N_2$ gas, excluding Mo$_4$N for which there is currently no data. The $M_2N$ and $M_2N_{1-x}$ compound are included for comparison, where the nitrogen concentration of $M_2N_{1-x}$ represents that which is most stable in the ternary system (described in further detail later). From the Ellingham diagrams it is apparent that in the Fe-N system, all but Fe$_4N$ are unstable with respect to pure $N_2$ gas, and the Fe$_4N$ stable only at lower temperatures. As discussed previously, high nitrogen activities are necessary to realize nearly all nitride phases in iron. The non-stoichiometric Fe$_2N_{0.38}$ (a $hcp$ Fe$_2N$ compound in which only 38% of the available interstices are filled) is much more stable than any of the other phases at temperatures above $\sim$300 °C. This is different for the Cr-N system, in which the stoichiometric Cr$_2N$ phase is most stable, and all of the phases are stable in $N_2$ gas. Nickel is not an avid nitride former, and as expected, each phase cannot be formed without a very large nitriding potential. As in the Fe-N system, a nitrogen-deficient Ni$_2N_{0.24}$ phase is favored over the stoichiometric counterpart, but the lowering in free energy between the stoichiometric and non-stoichiometric phase is even more drastic in the Ni-N system. The NiN compound is highly unstable. Within the Mo-N system it as apparent that Mo has a high affinity for nitrogen, where the Mo$_2N$ and MoN phases can be formed in pure $N_2$ through a wide temperature range.
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

**Figure 4.10:** The standard Gibbs free energy of formation of various $M_xN_y$ compounds for $\frac{1}{2}$ moles $N_2$ gas where $M = Fe$, Cr, Ni, Mo, Mn, and HYSS composition.
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

Like the Cr-N system however, the most stable nitrogen-deficient Mo$_2$N$_{0.33}$ phase is not favored relative to the stoichiometric counterpart. The Mn-N system is similar to the Cr-N system, all of the phases being stable below roughly 500 °C in pure N$_2$, where MnN is the least stable. The lowest energy Mn$_2$N$_{0.22}$ phase is not favored over Mn$_2$N except at temperatures above 850 °C. Assuming a paraequilibrium nitride where the metal composition of the nitride is the same as the matrix in the HYSS system, it appears that all nitride phases are stable in pure N$_2$ at lower temperatures, where Mn$_4$N is the most stable. The Mn$_2$N$_{1-x}$ is highly stabilized by vacant interstitial sites, to the point that entropic contributions to the free energy become significant, and the $\Delta^\circ G$ curves assumes a negative slope (also observed for the Mn$_2$N$_{0.22}$ nitride). The stability of this hcp phase in the HYSS system increases continuously as the nitrogen content decreases, so much so that it might more aptly be viewed as an interstitial solid solution instead of an ordered compound.

Considering the reaction in Eq. 4.1, the equilibrium constant is given by $K_{eq} = a_{N_2}^{-1/2}$ (assuming the pure metal and compound have unit activity), or for one mole of N$_2$, the equilibrium constant is simply $a_{N_2}^{-1}$. Knowing that $K_{eq} = \exp \left( -\frac{\Delta^\circ G}{RT} \right)$, the nitrogen activity in equilibrium with a nitride phase at some temperature can be determined by:

$$\ln(a_{N_2}) = \frac{\Delta^\circ G}{RT}$$

(4.2)

as is shown in Fig. 4.11. As expected from the largely positive $\Delta^\circ G$ for the formation of iron and nickel nitrides, these phases can form only under high nitriding potentials. The FeN phase has not yet been found even with nitriding in pure ammonia, though it has been produced with certain sputtering techniques [43, 44]. Based on the solubility of nitrogen in fcc iron, the CALPHAD method allows for prediction of the stability of a FeN compound.

The Ellingham diagrams for the carbide phases (excluding Mo$_{23}$C$_6$) are shown in Fig. 4.12. In all cases, the elemental and partitionless carbides are stable (negative free energy of formation), and closer in magnitude than the nitrides. The $\tau$-M$_{23}$C$_6$ phase is the most stable for elemental iron, chromium, and manganese, while the $\omega$-M$_7$C$_3$ is least stable for iron, chromium, and nickel. The alloy carbides all have similar stability relative to the differences between each carbide in
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

Figure 4.11: Nitrogen activity required at temperature to maintain equilibrium of $2x\, M_{(s)} + y\, N_{2(g)} \rightleftharpoons 2\, M_x\, N_{y(s)}$. 
Figure 4.12: The standard Gibbs free energy of formation of various $M_xC_y$ compounds for 6 moles of C, where $M =$ Fe, Cr, Ni, Mo, Mn, and HYSS composition.
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

the elemental cases.

4.3.2 Nitrogen

The equilibrium condition $\Delta^\circ G = 0$ for the reaction given in Eq. 4.1 establishes the solubility limit within a $bcc$ and $fcc$ phase (generalized by $\phi$). The $\Delta^\circ G = 0$ criterion is satisfied when:

$$G^M_{mN^y} = x \cdot \mu^\phi_M + y \cdot \mu^\phi_N$$  \hspace{1cm} (4.3)$$

where each expression for the free energy of the nitride and chemical potentials is derived from the appropriate CALPHAD equations.

Simulations were conducted on the solubility limit in the presence of the $M_4N$, $M_2N$, $M_2N_{1-x}$, and $MN$ phases in $bcc$ and $fcc$ iron when alloyed with chromium, nickel, molybdenum and manganese. The solubility limits of the $M_4N$ phase within $fcc$ and $bcc$ Fe-M alloys is shown in Fig. 4.13, up to the maximum 20 at. pct. nitrogen. In the Fe-Mo alloys, the solubility limit assumes formation of a pure $Fe_4N$ compound from a molybdenum containing alloy. It is clear that the addition of chromium increases the solubility limit in the $bcc$ phase and $fcc$ phase, however to a much larger extent within the $fcc$ phase. The near-vertical line at 20 at. pct nitrogen for 5, 10, and 15% additions of chromium to $fcc$ iron indicate that there is no driving force to form the paraequilibrium nitride. Thus a $(Fe,Cr)_4N$ nitride would not be expected to form from an $fcc$ phase when the chromium concentration is greater than 5 at. pct. The addition of nickel to iron serves to increase the stability of the $M_4N$ phase, lowering the solubility limit in both $bcc$ and $fcc$ with increasing nickel. Molybdenum lowers the solubility within the $bcc$ while increasing the solubility in the $fcc$ phase. Manganese, like chromium, increases the solubility limit of the paraequilibrium nitride in both the $bcc$ and $fcc$ phases. A $(Fe,Mn)_4N$ phase could precipitate from a $fcc$ solution before 20 at. pct. nitrogen was reached. In $bcc$ Fe-Mo alloys, the molybdenum stabilizes the $(Fe,Mo)_4N$, while in a $fcc$ phase the solubility increases with increasing molybdenum.

Similar analyses on the formation of a stoichiometric, paraequilibrium $M_2N$ phase in Fe-M alloys was conducted, are shown in Fig. 4.14. The addition of
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

![Graphs showing solubility limits of paraequilibrium $\gamma'$-$M_4N$ in binary fcc (solid lines) and bcc (broken lines) iron alloys as a function of alloy content.](image)

**Figure 4.13:** Solubility limit of paraequilibrium $\gamma'$-$M_4N$ in binary fcc (solid lines) and bcc (broken lines) iron alloys as a function of alloy content.
### 4.3. Solubility with Paraequilibrium Secondary Phases

Solubility limit of $M_2N$ for Fe-$M$ ($M = 0, 5, 10, 15$ at. pct) in $\text{Fe} - 5\%\text{Cr}$, $\text{Fe} - 10\%\text{Cr}$, and $\text{Fe} - 15\%\text{Cr}$.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Nitrogen Concentration (at. pct)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$100%\text{Fe}$</td>
<td></td>
<td>300</td>
</tr>
<tr>
<td>$95%\text{Fe} - 5%\text{Cr}$</td>
<td></td>
<td>400</td>
</tr>
<tr>
<td>$90%\text{Fe} - 10%\text{Cr}$</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>$85%\text{Fe} - 15%\text{Cr}$</td>
<td></td>
<td>600</td>
</tr>
</tbody>
</table>

**Figure 4.14:** Solubility limit of $M_2N$ in $fcc$ (solid lines) and $bcc$ (broken lines) iron alloys as a function of alloy content.

Chromium to iron increases the solubility of $M_2N$ in a $bcc$ phase at low temperatures (less than approximately $650$ °C) with increasing chromium content. The solubility in the $fcc$ phase decreases with increasing chromium concentration, with little changes for chromium concentrations greater than $5$ at. pct. Nickel, molybdenum, and manganese all decrease the solubility of the paraequilibrium $M_2N$ in $bcc$ and $fcc$ iron alloys to roughly the same extent. Like chromium, there is little change in the solubility of $(\text{Fe,Mo})_2N$ for molybdenum concentrations.
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

greater than 5 at. pct.

The solubility limit in the presence of a MN paraequilibrium nitride in Fe-M alloys is shown in Fig. 4.15 for bcc alloys of interest. For chromium, nickel, molybdenum, and manganese additions up to 15 at. pct. in fcc iron, the MN paraequilibrium nitride is destabilized such that no driving force exists for its formation. The solubility limit of MN is still high in the bcc phase for each alloy relative to the other nitrides. Chromium, nickel, and molybdenum serve to de-
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

crease the solubility of paraequilibrium MN in bcc solutions with increasing alloy content, while manganese destabilized the MN phase and increases the nitrogen solubility. As for fcc Fe-M alloys, the precipitation of MN from ferrite is not expected for each of the alloys at higher temperatures.

The possibility of forming a non-stoichiometric, nitrogen-deficient $\varepsilon$-M$_2$N$_{1-x}$ compound is next considered, as it is important in the Fe-N system, and from the Ellingham diagrams in Fig. 4.10, is shown to be very stable for most M-N systems, with the exception of Cr-N where the phase is destabilized by vacancies, i.e. a linear compound is most stable. Fortunately, the CALPHAD data are complete enough to determine the Gibbs free energy for this non-stoichiometric phase with each of the alloy elements in question. Fig. 4.16 shows the solubility limit of the most stable M$_2$N$_{1-x}$ for 1 at. pct. additions of chromium, nickel, molybdenum, and manganese to iron—most stable here meaning that the solubility limit is lowest for the respective concentration of vacancies. The 16 at. pct. nitrogen Fe$_2$N$_{0.38}$ nitride formed from austenite represents that shown on the equilibrium Fe-N diagram in Fig. 2.2. It is seen that by adding even 1 at. pct. nickel, molybdenum, manganese, and (surprisingly) chromium to iron, the $\varepsilon$-Fe$_2$N$_{1-x}$ becomes much more stable with respect to bcc and fcc solid solutions than the pure iron nitride. The most stable paraequilibrium nitrides are also more nitrogen deficient than Fe$_2$N$_{0.38}$. Both manganese and nickel added to iron most highly favor the formation of the hcp phase, decreasing the solubility to very low nitrogen concentrations even in the fcc phase. The formation of the $\varepsilon$-Fe$_2$N$_{1-x}$ phase exhibits endothermic and exothermic behavior in the bcc and fcc solutions respectively. The solubility of the phase for each alloy is again considerably lower in the bcc than fcc phase.

Using the solubility limits of each phase presented above in binary alloys, a pseudo-phase diagram for the HYSS system involving precipitation of M$_4$N$^1$, M$_2$N, M$_2$N$_{1-x}$, and MN from bcc and fcc phases is given in Fig. 4.17. It is first noted that precipitation of a paraequilibrium M$_4$N or MN nitride from the austenitic HYSS is not expected (indicated by the vertical solubility limit at 20 at. pct. and 50 at. pct. nitrogen). There is again a high propensity for secondary phase formation within the bcc phase, that is, there always exists

$^1$(M = 65Fe-20Cr-10Ni-5Mn)
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

Figure 4.16: Solubility limit of the most stable paraequilibrium $\varepsilon$-$M_2N_{1-x}$ phase for \textit{bcc} (broken lines) and \textit{fcc} (solid lines) 99Fe-1M alloys where $M = \text{Cr, Ni, Mo, or Mn}$. 

$\begin{align*}
(99\text{Fe-1Cr})_2N_{0.33} \\
(99\text{Fe-1Ni})_2N_{0.24} \\
(99\text{Fe-1Mo})_2N_{0.37} \\
(99\text{Fe-1Mn})_2N_{0.38}
\end{align*}$
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

![Graph showing solubility limits of various nitrides]

**Figure 4.17**: Solubility limits of $M_4N$, $M_2N$, $M_2N_{1-x}$, and MN nitrides within $fcc$ (solid lines) and $bcc$ (broken lines) HYSS.

...a highest driving force for nitride formation within the ferrite phase of HYSS relative to the austenitic phase. Of the nitrides, $M_4N$ has the highest driving force for formation from a $bcc$ alloy at temperatures below $\sim 400 \, ^\circ C$. However, the $hcp$ phase is extremely stable, the solubility continuously decreasing with decreasing nitrogen in the compound. If the $\varepsilon$ nitride had a nitrogen content of 9.1 at. pct. ($M_2N_{0.20}$) it would be the first expected compound to form from $bcc$ HYSS above $\sim 400 \, ^\circ C$, as well as the first expected to precipitate from $fcc$ HYSS at approximately 1 at. pct. nitrogen at $300 \, ^\circ C$.

### 4.3.3 Carbon

The similar simulations for the solubility limit of carbon in the presence of paraequilibrium $M_{23}C_6$, $M_3C$, and $M_7C_3$ carbides are shown in Figs. 4.18–4.20. For all...
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

![Graphs showing solubility limits of paraequilibrium M₂₃C₆ in binary fcc (solid lines) and bcc (broken lines) iron alloys as a function of alloy content.]

**Figure 4.18:** Solubility limit of paraequilibrium M₂₃C₆ in binary fcc (solid lines) and bcc (broken lines) iron alloys as a function of alloy content.

Binary alloys, the solubility limit increases with increasing chromium, nickel, and manganese additions in M₂₃C₆, to the largest extent for Fe-Mn. Likewise, for all three binary systems, the solubility limit in the bcc phase is extremely low for temperatures below ~400 °C, but increases above this temperature most significantly for Fe-Mn. For high nickel and manganese concentrations, the paraequilibrium M₂₃C₆ is not expected to form from austenite.

Concerning the formation of paraequilibrium cementite the same is true—increasing solubility in fcc with increasing each of the alloy elements. The Fe-Cr
and Fe-Mn systems shows the most pronounced increased in achievable solubility in the fcc state (exhibiting retrograde solubility for 15 at. pct. chromium) while Fe-Mo alloys significantly increase the solubility limit in the bcc. The presence of nickel in the fcc does very little to change the stability of cementite, relative to the other alloying elements.

For $M_7C_3$ carbide, the solubility decreases in fcc with increasing nickel and molybdenum, and the solubility becomes significant in the bcc phase only for...
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

Figure 4.20: Solubility limit of $M_7C_3$ in fcc (solid lines) and bcc (broken lines) iron alloys as a function of alloy content.

Manganese is shown to have very little effect on the stability of a $(Fe,Mn)_7C_3$ carbide, especially at lower temperatures.

The pseudo-phase diagram of HYSS for the solubility of carbon in the presence of these three carbides is shown in Fig. 4.21. The partitionless $M_{23}C_6$ or $M_3C$ (at $T < 500 \, ^\circ C$) would not be expected to form from the austenite, and there is a driving force to form $M_7C_3$ only at carbon concentrations near 15 at. pct., independent of temperature. There is again a high driving force to form the paraequilibrium carbides in ferrite at very low carbon concentrations, though
4.3. SOLUBILITY WITH PARAEQUILIBRIUM SECONDARY PHASES

![Graph showing solubility limits of M\textsubscript{23}C\textsubscript{6}, M\textsubscript{3}C, M\textsubscript{7}C\textsubscript{3} carbides within fcc (solid lines) and bcc (broken lines) HYSS.]

Figure 4.21: Solubility limits of M\textsubscript{23}C\textsubscript{6}, M\textsubscript{3}C, M\textsubscript{7}C\textsubscript{3} carbides within fcc (solid lines) and bcc (broken lines) HYSS.

This limit increases rapidly for M\textsubscript{23}C\textsubscript{6} above \(\sim 300^\circ\text{C}\).
4.4 Heterogeneous Equilibrium and the Eutectoid Reaction

4.4.1 Nitrogen

The conditions for heterogeneous equilibrium between the solid solutions fcc austenite and bcc ferrite in a closed system were given in Eq. 2.29. To determine these equilibrium boundaries as a function of temperature and nitrogen content, the free energy of the solutions given in Eqs. 3.1 and 3.2 are implemented for the common tangent construction. The molar Gibbs free energy of solid solution bcc and fcc phases on a per mole of atom basis, $G'_m$, is shown in Fig. 4.22 for pure iron and the HYSS system as a function of nitrogen content at $T = 450 \, ^\circ\text{C}$. It is clear that for iron, ferrite is more stable at 450 °C at low nitrogen concentration. The molar Gibbs free energy of bcc and fcc HYSS are nearly equal at low nitro-
gen contents, and the free energy of \( fcc \) decreases with increasing nitrogen, until reaching a minimum near 21 at. pct. The molar Gibbs free energy of \( bcc \) and \( fcc \) HYSS at 300 °C is also shown in Fig. 4.23 for low nitrogen concentrations, revealing that HYSS ferrite becomes unstable with respect to austenite at much lower nitrogen concentrations than the Fe-N system.

![Molar Gibbs free energy of bcc (broken lines) and fcc (solid lines) HYSS on per mole of atom basis as a function of nitrogen content at \( T = 300 °C \).](image)

**Figure 4.23**: Molar Gibbs free energy of \( bcc \) (broken lines) and \( fcc \) (solid lines) HYSS on per mole of atom basis as a function of nitrogen content at \( T = 300 °C \).

The equilibrium ferrite-austenite solvus lines were determined for the Fe-N and HYSS system, as shown in Fig. 4.24. The equilibrium ferrite and austenite solvuses in the Fe-N system represent those shown in the currently established phase diagram (see Ref. [39]). The solubility of nitrogen in \( bcc \) iron is quite low, but in comparison to the HYSS system, ferrite is destabilized with respect to austenite at much lower nitrogen contents. Whereas the maximum solubility of nitrogen in \( bcc \) iron is 0.04 at. pct. at 592 °C, the maximum solubility in ferrite in the HYSS system is less than 1 ppm at 380 °C. Above 400 °C, austenite is the
Figure 4.24: Equilibrium boundaries between $\alpha$-ferrite and $\gamma$-austenite in the Fe-N and HYSS-N systems as a function of temperature (note the logarithmic abscissa).
only stable phase in this system. Provided that the nitriding temperature were above the eutectoid temperature, and formation of other nitrides was suppressed, a high driving force for the nitrogen-induced $\alpha \to \gamma$ transformation would exist within the HYSS system with even a small dissolution of nitrogen in the ferrite. Superposition of this figure with the maximum solubility limits of nitrogen at unit activity within the ferritic and austenitic phases of HYSS (see Fig. 4.7) is shown in Fig. 4.25. From this paraequilibrium phase diagram, it is seen that the eutectoid reaction is completely suppressed, that is at all temperatures, the dissolution of nitrogen in ferrite, even at unit activity nitrogen, generates a driving force for austenite formation. The same situation applies to the other M-N systems, even at 1 at. pct. alloying.

**Figure 4.25:** Equilibrium solvus lines between $\alpha$-ferrite and $\gamma$-austenite HYSS-N system and paraequilibrium solubility limit in each phase at unit nitrogen activity.
4.4. HETEROGENEOUS EQUIL. AND THE EUTECTOID REACTION

4.4.2 Carbon

The equilibrium solvuses in the Fe-C system are shown in Fig. 4.26, revealing the eutectoid temperature ($A_1$) of 738 °C and allotropic transformation temperature of 912 °C. Because the eutectoid reaction is not immediately suppressed by alloying with chromium, nickel, molybdenum, or manganese as it is in the M-N systems, it is of interest to determine how the eutectoid temperature changes as a function of alloy concentration. Alloys of iron with 1–3 at. pct. chromium, nickel, molybdenum, and manganese were used to determine the paraequilibrium eutectoid temperature, as shown in Fig. 4.27. Only molybdenum is observed to cause an increase in the paraequilibrium eutectoid temperature. The paraequilibrium eutectoid temperature decreases rapidly at low manganese levels. For all alloy concentrations greater than the maximum shown in the figure for chromium, nickel, and manganese, the eutectoid reaction is completely suppressed, while for molybdenum concentrations greater than 3 at. pct., the maximum carbon con-

![Figure 4.26: Equilibrium boundaries between α-ferrite and γ-austenite in the Fe-C and HYSS-C system as a function of temperature.](image-url)
Figure 4.27: Change in paraequilibrium eutectoid temperature with alloy concentration in the Fe-M-C system. Greater than 2 at. pct. additions of Cr, Ni, Mn in Fe result in complete suppression of the eutectoid reaction.
Chapter 5

Discussion

5.1 Alloying Effect on the Paraequilibrium Solubility of Interstitials

Additions of chromium, molybdenum, and manganese in austenitic stainless steels increases the paraequilibrium solubilities of both carbon and nitrogen. Chromium has the most potent effect, followed by molybdenum and manganese. Nickel in austenitic stainless steel decreases the maximum paraequilibrium solubility of both carbon and nitrogen, but to a lesser extent than chromium increases the solubility. The paraequilibrium solubility for nitrogen is always greater than carbon in austenite at unit activity for a given alloy.

Concerning ferritic or ferrite-containing stainless steels, chromium is the only alloying element that causes a substantial increase in nitrogen solubility in ferrite, and this only at lower temperatures. All ferritic alloys have a very low solubility for nitrogen at unit activity. However, the maximum solubility for nitrogen in ferrite can reach very high levels with even modest nitrogen activities, easily achieved through ammonia gas nitriding. The calculations predict that the solubility limit in a ferritic stainless steel would even exceed that in the austenitic phase when the nitriding potential is high enough. Molybdenum has the most potent effect for increasing the paraequilibrium solubility of carbon in ferritic stainless alloys. The ferritic phase of a high-alloy stainless steel can dissolve significantly more carbon at unit activity than nitrogen, but the nitrogen solubility exceeds carbon as the nitriding potential is increased. The carbon activity in the gas phase can—and often does in industrial paraequilibrium carburization
5.1. ALLOYING EFFECT ON PARAEQUIL. SOLUB. OF INTERSTITIALS

treatments—greatly exceed unity, but the fact that carbon is stable as a solid is why the paraequilibrium solubility has only been considered for equilibrium with graphite, rather than in equilibrium with gaseous carbon at a much higher activity. Were the surface concentration of carbon to exceed the paraequilibrium solvus line, a driving force for formation of graphite at the surface exists, which would impede the further dissolution of carbon. The maximum paraequilibrium solubility for nitrogen in any stainless steel alloy is always increased by increasing the nitriding potential, which is one benefit of this thermochemical treatment over carburization.

Based on the calculated solubility limit for austenite in equilibrium with nitrogen at unit activity, it might be supposed that such a level could be obtained by soaking the surface-activated steel in nitrogen gas at elevated temperatures. However, the kinetics of the nitrogen molecule decomposition–adsorption reaction in nitrogen gas, at the low temperatures required to kinetically suppress nitride formation, are such that very little uptake of nitrogen by the steel would be observed, and hence the reason for ammonia nitriding processes. In recent low-temperature gas-phase nitriding studies of 316, Wu [53] noted a measurable lattice expansion in an ammonia/hydrogen gas atmosphere at unit nitrogen activity. Still, the measured nitrogen content at the surface (∼7.5 at. pct.) after 20 h treatment is far lower than the model prediction of 23 at. pct. Several reasons could account for this difference. First, it is assumed in all simulations that a state of (para)equilibrium exists at the gas-steel interface, and thus nitrogen leaves the solution at the same rate at which it dissolves. In Wu’s investigation of paraequilibrium nitridation treatments of 316, she observed a 25 pct. increase in surface concentration between 20 h and 80 h treatments at constant activity, but the measured surface concentration of 20 at. pct. nitrogen after 80 h is still significantly lower than the predicted value of 35 at. pct. This could either indicate that the gas-metal interface has still not reached equilibrium after 80 h due to a low mass transfer efficiency, or it had reached equilibrium and the predicted values are too high. To determine whether an equilibrium condition is established at the surface, a treatment much longer than 80 h could be conducted and the surface concentration measured to see if it remains constant, or increases and to what extent. Likewise, a series of experiments at lower and higher temperatures
could be conducted, in which the activated surface is isothermally exposed to nitrogen for an extended time, immediately followed by an isothermally treatment at a temperature intermediate of the two. Given sufficient time at this intermediate temperature, the surface concentration of both the previously high- and low-temperature holds will converge to the equilibrium value. As the solubility for nitrogen is exothermic in austenitic stainless steel, the surface concentration of the sample initially treated at a lower temperature will decrease as the nitriding temperature is increased, and vice versa. When considering measured concentration profiles following a paraequilibrium treatment, it is also noteworthy that de-carburization or de-nitridation has not been observed during the prolonged cooling in an inert atmosphere of hydrogen/nitrogen gas. The surface is likely re-passivated as soon as exposed to the lower purity gases in the furnace, and the same surface oxide that prevents the inward diffusion of atomic species also inhibits their outward diffusion.

Another possible cause for the large discrepancy between predicted and previous measurements of nitrogen concentrations in low-temperature nitrided austenitic stainless steel could be that the surface is insufficiently activated and rid of its native oxide by reaction with HCl gas. In other in-situ activation experiments on bulk samples, similar nitrogen concentrations after long treatment times are reported throughout the literature, and to-date such high nitrogen solubilities (greater than 30 at. pct.) in bulk austenitic samples have not been achieved. Recent experiments using the decomposition products of urea in low-temperature nitrocarburizing have demonstrated that comparable surface concentrations and case depths can be achieved in only a fraction of the time of other techniques [53], and hints that there is still much to be learned about the activation process.

Another possibility is that the M-N interaction parameters are too exothermic at the temperatures of interest (the carbon parameters were found to be insufficiently exothermic), predicting a much larger solubility. The revised Cr-C interaction parameters used in these simulations predict solubilities in good agreement with experimental results of paraequilibrium carburized 316 austenitic stainless steel. However, a thorough analysis of these parameters on the carbon solubilities in ferrite has yet to be conducted, mostly due to the lack in experimental data. Recent work by Wang [54] has revealed metastable carbon concentrations in fer-
5.2. ALLOYING EFFECT ON SOLUB. WITH SECONDARY PHASES

rite of almost 10 at. pct., which is again significantly higher than the predicted value of approximately 1–2 pct. Considering these observations—and as more data become available—it would be worthwhile to critically examine the effect of Cr-C in bcc systems, as chromium is observed from the present simulations to have the most significant effect. It is also interesting that the solubility for nitrogen in ferritic and carbon in austenitic stainless steel changes from endothermic to exothermic near 13–14 at. pct. and 20 at. pct. chromium respectively, where at some critical chromium concentration the solubility is predicted to be independent of temperature. The possibility of designing a ferritic or austenitic stainless steel such that the concentration of the hardened case did not change with time could be further explored.

With these discrepancies considered, perhaps the most illuminating result comes from more recent thin-foil nitridation treatments of Christiansen and Somers [11]. Foils of 316 were through-nitrided near 440 °C creating expanded austenite powder lacking any residual compressive stresses. The measured nitrogen concentration in this stress-free expanded austenite following treatment in pure ammonia was approximately 38 at. pct.—much closer to, but still lower than, the predicted value of ~43 at. pct. Wu measured a surface concentration of ~25 at. pct. in 316 following HCl surface activation and nitridation in pure ammonia after 20 h. This effect of stress on the solubility limit is discussed in further detail later, but as Christiansen and Somers also used a proprietary surface activation involving nickel-plating, the effect of surface transparency cannot be ruled out.

5.2 Alloying Effect on the Solubility Limit with Formation of Paraequilibrium Secondary Phases

The solubility limit of nitrogen or carbon in equilibrium with a partitionless second phase is observed to be exceedingly low in all bcc alloys. The solubility limit for a paraequilibrium nitride in bcc is large only for a NaCl-type MN nitride. It is therefore unlikely that this phase would ever form in ferritic stainless steel unless substantial partitioning of the substitutional elements could be achieved. There is never a driving force to form a paraequilibrium MN in any austenitic stainless steel, unless partitioning of chromium, iron, and nickel takes place.
5.2. ALLOYING EFFECT ON SOLUB. WITH SECONDARY PHASES

The nitrogen-deficient $M_2N_{1-x}$ is observed to be the most stable of all the nitrides, having the lowest solubility limit in all ferritic and austenitic stainless steels. Though nickel itself is not a nitride former, it does, in small concentrations increase the stability of this $hcp$ $M_2N_{1-x}$ phase, even more so than nitride-forming chromium or molybdenum. In the high alloy stainless steel there is a driving force to form this phase at very low nitrogen concentrations in the austenite phase (less than 1 at. pct. at 400 °C). This agrees with most precipitates experimentally observed in low-temperature nitrided 316 alloys [53], though it has not been determined if this $hcp$ nitride has the same base metal chemistry, or if the nitrogen concentration is heavily-nitrogen deficient as the simulation suggests, or is nearly stoichiometric as in the Cr-N system.

The solubility for carbon in ferrite is only significantly large relative to formation of a paraequilibrium cementite in high molybdenum alloys, that is, molybdenum is least stable in cementite of the examined alloying elements. A paraequilibrium $M_{23}C_6$ is relatively unstable in austenite at higher alloy contents of chromium, nickel, and molybdenum, and would indicate why this phase has not been observed in carburized stainless steels, although it has the lowest carbon concentration of the carbides. The paraequilibrium $M_7C_3$ is the first expected to form in the case of a high alloy stainless steel, and has been observed to form during prolonged carburization treatments as discussed previously. The Hӓgg carbide has been found to be the most pervasive in low-temperature carburized stainless steels, but its stability relative to the others cannot at present be estimated.

It is rather fortunate that the primary alloying element in stainless steels, chromium, is also the most potent for increasing the paraequilibrium solubility of nitrogen, as well as increasing the solubility with respect to nearly all of the paraequilibrium nitride and carbide phases to comparable levels in austenite. These simulations affirm why there is great success in the paraequilibrium treatment of austenitic stainless steels, which pose very little driving force for any phase transformation. It is a different story for ferritic stainless steels, which favor secondary phase formation at very low interstitial concentrations, as well as having a low paraequilibrium solubility limit for carbon and nitrogen, except at larger nitriding potentials.
5.3 Paraequilibrium Surface Treatments of Ferrite-containing Stainless Steels

The efficacy of paraequilibrium treatments applied to ferrite-containing stainless steels can largely be understood from the thermodynamic predictions: there is very limited tolerance for interstitials in ferrite relative to a carbonaceous/nitrogenous atmosphere or carbide/nitride formation. Furthermore, diffusion of substitutional elements is much faster in ferrite relative to austenite, indicating that ferrite likely has a much lower kinetic barrier to precipitation of secondary phases. With reference to Fig. 1.1 and the relation that the diffusional distance $x$ after time $t$ is proportional to $\sqrt{Dt}$, chromium in ferrite can diffuse approximately 2,700 nm at 400 °C after 20 h, while chromium in austenite may only diffuse 80 nm under similar conditions. The lattice expansion associated with dissolution of interstitial species may further increase the diffusion coefficient of substitutional elements. In situations in which all secondary phases are kinetically suppressed and the nitriding potential is high, a high-nitrogen and deeper case would be expected in a ferritic stainless steel over an austenitic phase of similar composition.

As carbon is an austenite stabilizer, carburization above the eutectoid temperature can result in the isothermal $\alpha \rightarrow \gamma$ phase transformation through dissolution of carbon in ferrite. With use of the CALPHAD model, it is determined that even small quantities, 1–2 at. pct., of chromium, nickel, or manganese in iron significantly lower the paraequilibrium eutectoid temperature. Though chromium is a ferrite stabilizer, its presence in the alloy greatly increases the maximum carbon concentration that can be dissolved under paraequilibrium constraints. Above 3 at. pct., these alloy elements complete suppress the eutectoid reaction, indicating that the $\alpha \rightarrow \gamma$ transformation could occur during carburization of ferritic stainless steels, even at very low interstitial concentrations. Such a transformation would first require that any paraequilibrium carbides, which could form at even lower carbon concentrations, be kinetically suppressed, and second that the $\alpha \rightarrow \gamma$ transformation be kinetically favored at typical treatment temperatures. Convincing experimental evidence on the $\alpha' \rightarrow \gamma$ transformation have been observed (see Ref. [18]) following low-temperature carburization of 17-7 PH
stainless steel, though no such transformation of ferrite in any stainless steel has directly been confirmed.

Nitrogen is a very potent austenite stabilizer. This causes ferrite to have a significantly lower equilibrium solubility for nitrogen than carbon. This fact, combined with the affinity of chromium, molybdenum, and manganese for nitrogen, reveals a suppression of the eutectoid reaction for any concentration of these elements in iron. This includes nickel, whose austenite stabilizing/ferrite destabilizing nature more than make up for a loss in maximum paraequilibrium nitrogen solubility. From Fig. 4.25 it is clear that ferrite in this high alloy stainless steel is unstable with respect to austenite at ppm levels of nitrogen. Therefore, there exists a very high driving force for an isothermal nitrogen-induced $\alpha \rightarrow \gamma$ during any nitriding treatment of a ferrite-containing stainless steel. Even in the absence of nitrogen, there is a driving force for the transformation above $\sim 400 ^\circ C$. The solubility of nitrogen in ferritic stainless steel is lower than any of the paraequilibrium nitrides, and thus it would be the first expected phase to form if permitted by the kinetics of the $\alpha \rightarrow \gamma$ transformation. Isothermal annealing of duplex stainless steels containing large volume fractions of ferrite has been shown to lead to the $\alpha \rightarrow \gamma$ transformation after sufficient time at temperatures above 300 $^\circ C$ [55]. The transformation of the ferrite to austenite between 300–650 $^\circ C$ was likened to a martensitic reaction, in which the austenite formed in the ferritic matrix did so in a partitionless manner.

## 5.4 Residual Stress Effects on Phase Stability

It was discussed previously that low-temperature carburization and nitridation treatments of austenitic stainless steel results in residual compressive stresses on the order of 3 GPa and 7 GPa respectively. The effect of this stress on the Gibbs free energy of the solutions and compound phases, $\text{pres}G^\phi$, should be considered, where such large residual stresses are likely to affect the paraequilibrium solubility in accordance with Le Chatelier’s principle: in response to a biaxial surface stress, the maximum metastable solubility will decrease. The effect of pressure $P$ on the
5.4. RESIDUAL STRESS EFFECTS ON PHASE STABILITY

The free energy of the elements can be determined with use of Eq. 5.1

\[
\text{pres}G^\phi_m = A \exp(a_0T + a_1T^2 + a_2T^3 + a_3T^{-1}) \left( \frac{1}{(K_0 + K_1T + K_2T^2)(n-1)} \right) [\left( 1 + nP(K_0 + K_1T + K_2T^2) \right)^{1-n} - 1]
\]

(5.1)

where \(A, a_i, K_i\), and \(n\) are fitting parameters in accordance with the CALPHAD model. Using the elemental data of Dinsdale [45] the Gibbs free energy of the elements as a function of pressure at 450 °C is shown in Fig. 5.1. It is seen that pressures on the order of several GPa can significantly increase the free energy of the elements. This change in free energy is comparable, if not larger, than the contributions due to the mechanical mixture or non-ideal interactions in stainless steels, and will therefore have a measurable effect on the predicted paraequilibrium solubility limits. The stress-free nitrogen concentration measured by Christiansen and Somers in 316 foils is close to the model predictions, while those of Wu on bulk samples is drastically lower for equal nitriding potential.

**Figure 5.1:** Elemental Gibbs free energy relative to standard state as a function of pressure at 450 °C.
temperature, and time. Though the effect of pressure in changing the stability of compound phases is not presently known, it is of interest to incorporate the stress-effect into the model for more accurate prediction of phase stability. Addition of this pressure contribution to the routine developed in this work would be relatively straightforward once determined how to best estimate the effect for compounds.

5.5 Thermodynamic Modeling with Mathematica®

CALPHAD modeling of phase equilibria in high-order systems has been conducted with great success since its inception, primarily through use of commercial platforms such as Thermo-Calc® Software. There are however several advantages of using the open-source routine presented in this work over commercial software for predicting phase stability in stainless steels under paraequilibrium conditions. At present, there are no means available to the licensed user for viewing the individual thermodynamic parameters within most commercial software packages. As has already been demonstrated by Gu [56], use of the published interaction parameters in the Cr-C system inaccurately predicted solubilities in 316 stainless steel during carburization. Using the experimentally measured values at lower temperatures, he was able to re-fit the available data over a wider temperature range, yielding more accurate predictions at low temperatures, while maintaining consistency with phase stability at higher temperatures. Likewise, by using experimental solubility data for carbon in copper, Lee [57] was able to determine the previously unpublished Cu-C interaction parameters for use in paraequilibrium solubility predictions. As the experimental data on solubilities in both ferritic and austenitic stainless steels continues to increase over a range of temperatures, researchers will now have an efficient means of revising and/or expanding the thermodynamic database. It will also allow future investigations on the effect of residual stress to be directly incorporated into the model. Additionally, with the aid of thermodynamic predictions, time can be spared in applying these treatments for improved performance of other high-alloy systems such as Co-Cr or Ni-based alloys that have important biological applications. As the field of paraequilibrium surface treatments continues to mature, so too will the predic-
5.5. THERMODYNAMIC MODELING WITH MATHEMATICA®

tive capacity on what can happen during such treatments, and how they can be optimized for a given alloy. Having a generalized, open-source platform will also greatly increase the speed at which advances in the field are made.

Wolfram Mathematica® is already available through many research institutions worldwide, and is also affordable for private licensing. Users with little or no background in programming should find the routine relatively straightforward to use and revise as deemed fit.
Chapter 6

Conclusions and Suggestions for Future Work

The application of the CALPHAD formalism to low-temperature gas-phase carburizing and nitriding treatments of stainless steels has been demonstrated in a generalized format. The stability of various phases for which there is thermodynamic data, relative to one other, has been demonstrated in the presence of carbon and nitrogen in ferrite and austenite, using the current parameters within the CALPHAD database. The paraequilibrium solubility limit of carbon and nitrogen is for all phases significantly lower in ferrite than austenite, but can reach large concentrations at high nitriding potentials. Chromium is the preferred alloying element for increasing the paraequilibrium solubility limit of carbon and nitrogen in ferritic and austenitic matrices, as well as increasing the solubility limit if a new paraequilibrium phase were to form. For both carburizing and nitriding of ferrite-containing stainless steels, there exists a large driving force for an isothermal carbon- or nitrogen-induced $\alpha \rightarrow \gamma$ transformation at any temperature. Ignoring kinetic effects, the transformation is most likely to occur upon nitridation of ferrite in stainless steels, which is destabilized relative to austenite at ppm nitrogen concentrations, compared to carburization of ferrite, for which there is a driving force for carbide formation prior to reaching the ferrite/austenite equilibrium solvus.

An open-source routine was developed that allows for thermodynamic database expansion and revision as solubility data over a broader range of temperatures is acquired. It will also permit straightforward inclusion of stress effects on the
6.1 Future Investigations

The next logical step is to determine how well these simulations compare with experiment results, particularly in ferritic stainless steels. As has been discussed, there is some disparity between the predicted solubilities of nitrogen in ferrite and austenite. As was done with Cr-C interaction parameters, it may be of use to perform similar sensitivity analyses on Cr-N interaction parameters, which may be too exothermic. There is a strong need for better understanding of the surface activation effect, and also in determining when a true (para)equilibrium condition has been established at the gas-metal interface. A good thermodynamic model for carburization and nitridation of stainless steels should also consider the effect of pressure on the change in Gibbs free energy of the various phases. A duplex stainless steel would provide a useful avenue for investigation the response of ferrite and austenite subjected to low-temperature interstitial hardening treatments simultaneously. To date, very few studies have been performed to examine at the microstructural level what secondary phases, if any, form in the ferritic phase of stainless steels. As a highly nitrogen-deficient \( \text{M}_2\text{N}_{1-x} \) phase is to be expected to form first in the austenitic phase, it is of interest to better characterize the chemistry and structure of this phase, found previously in low-temperature nitrided 316. Lastly, as kinetic-control of phase transformations forms the basis of any paraequilibrium surface treatment, the question should be answered why the \( \alpha' \to \gamma \) transformation is observed upon low-temperature carburization of a martensitic stainless steel, while the \( \alpha \to \gamma \) transformation is not, even though a very large driving force for such a transformation exists.
Appendix A

Note: All of the following CALPHAD parameters are given in SI units (Joule, mole, Kelvin) with $R = 8.3145 \text{ J mol}^{-1}$ and correspond to one mole of formula units. There is at present no universal criterion for determining the significant digits associated with each CALPHAD parameter, and are thus presented according to each assessment of the calculated phase diagrams. All phases are represented by an excess regular solution model according to a Redlich-Kister polynomial with ternary Muggianu extrapolation. For all reference states, the notation $G_{i}^{\text{SER}}$ is used to denote the Gibbs free energy with respect to the standard element reference enthalpy (at 298.15 K and 1 bar), i.e. the short form of $G_{i}^{\text{SER}} - H_{i}^{\text{SER}}$.

The magnetic contribution $G_{m}^{\phi \text{mag}}$ to the total Gibbs free energy of a solution is given by:

$$G_{m}^{\phi \text{mag}} = RT \ln(\beta + 1) f(\tau)$$

where $\tau = T/T_{C}$.

$$f(\tau) =
\begin{cases}
1 - \frac{1}{A} \left[ \frac{79\tau^{-1}}{140p} + \frac{474}{497} \left( \frac{1}{p} - 1 \right) \left( \frac{\tau^{3}}{6} + \frac{\tau^{9}}{135} + \frac{\tau^{15}}{600} \right) \right] & \tau > 1 \\
-\frac{1}{A} \left( \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right) & \tau < 1
\end{cases}$$

where $A = \left( \frac{518}{1125} \right) + \left( \frac{11692}{15975} \right) \left( \frac{1}{p} - 1 \right)$ and $p$ depends on the structure. For $bcc$ phases, $p = 0.4$ and for $hcp$ and $fcc$ phases, $p = 0.28$. 

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Reference States

\[ G_{\text{Fe}}^{\text{SER}} = +1225.7 + 124.134T - 23.5143T \ln(T) - 0.00439752T^2 \]
\[ (= G_{\text{Fe}}^{\text{bcc}}) - (5.8927 \times 10^{-8})T^3 + 77359T^{-1} \] [45]

\[ G_{\text{Cr}}^{\text{SER}} = -8856.94 + 157.48T - 26.908T \ln(T) - 0.00189435T^2 \]
\[ (= G_{\text{Cr}}^{\text{bcc}}) - (1.47721 \times 10^{-6})T^3 + 139250T^{-1} \] [45]

\[ G_{\text{Ni}}^{\text{SER}} = -5179.159 + 117.854T - 22.096T \ln(T) - 0.0048407T^2 \]
\[ (= G_{\text{Ni}}^{\text{fcc}}) \]

\[ G_{\text{Mo}}^{\text{SER}} = -7746.302 + 131.9197T - 23.56414T \ln(T) - 0.00344396T^2 \]
\[ (= G_{\text{Mo}}^{\text{bcc}}) + (5.66283 \times 10^{-7})T^3 - (1.30927 \times 10^{-10})T^4 + 65812T^{-1} \] [45]

\[ G_{\text{Mn}}^{\text{SER}} = -8115.28 + 130.059T - 23.4582T \ln(T) - 0.00734768T^2 \]
\[ (= G_{\text{Mn}}^{\text{A12}}) + 69827T^{-1} \] [45]

\[ G_{\text{N}_2}^{\text{SER}} = -3750.675 - 9.45425T - 12.7819T \ln(T) - 0.00176686T^2 \]
\[ (= G_{\text{N}_2}^{\text{gas}}) + (2.681 \times 10^{-9})T^3 - 32374T^{-1} \] [45]

\[ G_{\text{C}}^{\text{SER}} = -17369 + 170.73T - 24.3T \ln(T) - (4.723 \times 10^{-4})T^2 \]
\[ (= G_{\text{C}}^{\text{gra}}) + 2562600T^{-1} - (2.643 \times 10^{8})T^{-2} + (1.2 \times 10^{10})T^{-3} \] [45]

\[ \text{bcc (including MN}_3\text{): two sublattice model (Fe,Cr,Ni,Mo,Mn)}_1\text{(N,Va)}_3 \]

\[ \circ G_{\text{Fe, Va}}^{\text{bcc}} = G_{\text{Fe}}^{\text{SER}} \] [45]
\[ \circ G_{\text{Cr, Va}}^{\text{bcc}} = G_{\text{Cr}}^{\text{SER}} \] [45]
\[ \circ G_{\text{Ni, Va}}^{\text{bcc}} = G_{\text{Ni}}^{\text{SER}} + 8715.084 - 3.556T \] [45]
\[ \circ G_{\text{Mn, Va}}^{\text{bcc}} = G_{\text{Mn}}^{\text{SER}} \] [45]
\[ \circ G_{\text{Mo, Va}}^{\text{bcc}} = G_{\text{Mo}}^{\text{SER}} \] [45]
\[ \circ G_{\text{Min, Va}}^{\text{bcc}} = G_{\text{Min}}^{\text{SER}} - 2.209T - 0.2418T \ln(T) - 0.00009503T^2 + 4879.98 \]
\[ - 98277T^{-1} \] [45]
\[ \circ G_{\text{Fe, N}}^{\text{bcc}} = G_{\text{Fe}}^{\text{SER}} + 3G_{\text{N}_2}^{\text{SER}} + 93562 + 165.07T \] [58]
\[ \circ G_{\text{Cr, N}}^{\text{bcc}} = G_{\text{Cr}}^{\text{SER}} + 3G_{\text{N}_2}^{\text{SER}} + 311870 + 29.12T \] [58]
\[ \Delta G^\text{fcc}_{\text{Ni}:\text{N}} = G^\text{H,FER}_{\text{Ni}} + 3G^\text{H,FER}_{N_2} + 20000 + 200T \]  
[59]

\[ \Delta G^\text{fcc}_{\text{Mo}:\text{N}} = G^\text{H,FER}_{\text{Mo}} + 3G^\text{H,FER}_{N_2} + 299700 + 79.73T \]  
[58]

\[ \Delta G^\text{fcc}_{\text{Mn}:\text{N}} = G^\text{H,FER}_{\text{Mn}} + 3G^\text{H,FER}_{N_2} - 36232.7 + 504.952T - 38.6061T \ln(T) 
+ 0.0126483T^2 - (8.043 \times 10^{-9})T^3 + 872192T^{-1} \]  
[60]

\[ L^\text{fcc}_{\text{Fe},\text{N},\text{Va}} = -235433 - 40.5308T \]  
[45]

\[ L^\text{fcc}_{\text{Cr},\text{N},\text{Va}} = -200000 \]  
[58]

\[ L^\text{fcc}_{\text{Mn},\text{N},\text{Va}} = -185000 \]  
[60]

\[ L^\text{fcc}_{\text{Cr},\text{Fe},\text{Va}} = +20500 - 9.68T \]  
[61]

\[ L^\text{fcc}_{\text{Fe},\text{Ni},\text{Va}} = -956.63 - 1.28726T \]  
[59]

\[ L^\text{fcc}_{\text{Fe},\text{Ni},\text{Va}} = +1789.03 - 1.92912T \]  
[59]

\[ L^\text{fcc}_{\text{Fe},\text{Mo},\text{Va}} = +36818 - 9.141T \]  
[62]

\[ L^\text{fcc}_{\text{Fe},\text{Mo},\text{Va}} = -362 - 5.724T \]  
[62]

\[ L^\text{fcc}_{\text{Fe},\text{Mn},\text{Va}} = +2759 + 1.237T \]  
[63]

\[ L^\text{fcc}_{\text{Cr},\text{Ni},\text{Va}} = +17170 - 11.8199T \]  
[64]

\[ L^\text{fcc}_{\text{Cr},\text{Ni},\text{Va}} = +34418 - 11.8577T \]  
[64]

\[ L^\text{fcc}_{\text{Cr},\text{Mo},\text{Va}} = +28890 - 7.962T \]  
[58]

\[ L^\text{fcc}_{\text{Cr},\text{Mo},\text{Va}} = +5974 - 2.428T \]  
[58]

\[ L^\text{fcc}_{\text{Cr},\text{Mn},\text{Va}} = -20328 + 18.7339T \]  
[65]

\[ L^\text{fcc}_{\text{Cr},\text{Mn},\text{Va}} = -9162 + 4.4183T \]  
[65]

\[ L^\text{fcc}_{\text{Mo},\text{Ni},\text{Va}} = +46422 \]  
[66]

\[ L^\text{fcc}_{\text{Mn},\text{Ni},\text{Va}} = -51638.31 + 3.64T \]  
[51]

\[ L^\text{fcc}_{\text{Mn},\text{Ni},\text{Va}} = +6276 \]  
[51]

\[ L^\text{fcc}_{\text{Mn},\text{Mo},\text{Va}} = +49770 - 14.2564T \]  
[51]

\[ L^\text{fcc}_{\text{Mn},\text{Mo},\text{Va}} = -7260 \]  
[51]

\[ L^\text{fcc}_{\text{Cr},\text{Fe},\text{N}} = -799379 + 293T \]  
[61]
\[ \beta_{\text{bcc}} = -0.008Y_{\text{Cr}} + 2.22Y_{\text{Fe}} + 0.85Y_{\text{Ni}} - 0.27Y_{\text{Mn}} - 0.85Y_{\text{Cr}}Y_{\text{Fe}} \\
+ 4Y_{\text{Cr}}Y_{\text{Ni}} + (Y_{\text{Cr}}Y_{\text{Mn}})[0.48643 - 0.72035(Y_{\text{Cr}} - Y_{\text{Mn}})^2 \\
- 1.93265(Y_{\text{Cr}} - Y_{\text{Mn}})^4] \]

\[ \tau_{\text{bcc}} = -311.5Y_{\text{Cr}} + 1043Y_{\text{Fe}} + 575Y_{\text{Ni}} - 580Y_{\text{Mn}} + (Y_{\text{Cr}}Y_{\text{Fe}})[1650 \\
+ 550(Y_{\text{Cr}} - Y_{\text{Fe}})] + (Y_{\text{Cr}}Y_{\text{Ni}})[2373 + 617(Y_{\text{Cr}} - Y_{\text{Ni}})] \\
+ (Y_{\text{Cr}}Y_{\text{Mn}})[-1325 - 1133(Y_{\text{Cr}} - Y_{\text{Mn}})^2 - 10294(Y_{\text{Cr}} - Y_{\text{Mn}})^4 \\
+ 26706(Y_{\text{Cr}} - Y_{\text{Mn}})^6 - 28117(Y_{\text{Cr}} - Y_{\text{Mn}})^8] + 123Y_{\text{Fe}}Y_{\text{Mn}} \\
+ (Y_{\text{Fe}}Y_{\text{Mo}})[335 + 526(Y_{\text{Fe}} - Y_{\text{Mo}})] \]

**fcc (including MN): two sublattice model**

\[ (\text{Fe, Cr, Ni, Mo, Mn})_1(\text{N, Va})_1 \]

\[ ^0G^\text{fcc}_{\text{Fe,Mo,N}} = -151200 \]  
\[ ^0G^\text{fcc}_{\text{Fe,Cr,Ni,Va}} = -2673 + 2.0415T \]  
\[ ^0G^\text{fcc}_{\text{Fe,Cr,Mo,Va}} = +37460 - 20T \]  
\[ ^0G^\text{fcc}_{\text{Fe,Cr,Mn,Va}} = -5996 \]  
\[ ^0G^\text{fcc}_{\text{Fe,Ni,Mo,Va}} = -35743 \]  

\[ ^0G^\text{fcc}_{\text{Fe,Va}} = G^\text{H}_{\text{Fe}}^\text{SER} - 1462.4 + 8.282T - 1.15T \ln(T) + 0.00064T^2 \]  
\[ ^0G^\text{fcc}_{\text{Cr,Va}} = G^\text{H}_{\text{Cr}}^\text{SER} + 7284 + 0.163T \]  
\[ ^0G^\text{fcc}_{\text{Ni,Va}} = G^\text{H}_{\text{Ni}}^\text{SER} \]  
\[ ^0G^\text{fcc}_{\text{Mo,Va}} = G^\text{H}_{\text{Mo}}^\text{SER} + 15200 + 0.63T \]  
\[ ^0G^\text{fcc}_{\text{Mn,Va}} = G^\text{H}_{\text{Mn}}^\text{SER} + 4675.98 + 1.825T - 1.0595T \ln(T) + 0.00134768T^2 \\
- 227T^{-1} \]  
\[ ^0G^\text{fcc}_{\text{Fe,N}} = G^\text{H}_{\text{Fe}}^\text{SER} + G^\text{H}_{\text{N}_2}^\text{SER} - 37460 + 375.42T - 37.6T \ln(T) \]  
\[ ^0G^\text{fcc}_{\text{Cr,N}} = G^\text{H}_{\text{Cr}}^\text{SER} + G^\text{H}_{\text{N}_2}^\text{SER} - 124460 + 142.16T - 8.5T \ln(T) \]  
\[ ^0G^\text{fcc}_{\text{Ni,N}} = G^\text{H}_{\text{Ni}}^\text{SER} + G^\text{H}_{\text{N}_2}^\text{SER} + 38680 + 143.09T - 10.9T \ln(T) + 0.00438T^2 \]  
\[ ^0G^\text{fcc}_{\text{Mo,N}} = G^\text{H}_{\text{Mo}}^\text{SER} + G^\text{H}_{\text{N}_2}^\text{SER} - 65344 + 149.7T - 9.78T \ln(T) \]  
\[ ^0G^\text{fcc}_{\text{Mn,N}} = G^\text{H}_{\text{Mn}}^\text{SER} + G^\text{H}_{\text{N}_2}^\text{SER} - 64074 + 171.621T - 14.0539T \ln(T) \]  

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\[ + 0.00911454T^2 - (2.681 \times 10^{-9})T^3 + 227598T^{-1} \]

\[
0L_{Fe,N, Va}^{fcc} = -26150 \quad [58]
\]
\[
0L_{Cr,N, Va}^{fcc} = +20000 \quad [58]
\]
\[
0L_{Mo,N, Va}^{fcc} = +52565 \quad [58]
\]
\[
0L_{Mn,N, Va}^{fcc} = -69698 + 11.5845T \quad [60]
\]
\[
0L_{Cr,Fe, Va}^{fcc} = +10833 - 7.477T \quad [61]
\]
\[
1L_{Fe,Cr, Va}^{fcc} = +1410 \quad [61]
\]
\[
0L_{Fe, Ni, Va}^{fcc} = -12054.355 + 3.27413T \quad [59]
\]
\[
1L_{Fe, Ni, Va}^{fcc} = +11082.1315 - 4.45077T \quad [59]
\]
\[
2L_{Fe, Ni, Va}^{fcc} = -725.805174 \quad [59]
\]
\[
0L_{Fe, Mo, Va}^{fcc} = +28347 - 17.691T \quad [62]
\]
\[
0L_{Fe, Mn, Va}^{fcc} = -7762 + 3.865T \quad [63]
\]
\[
1L_{Fe, Mn, Va}^{fcc} = -259 \quad [63]
\]
\[
0L_{Cr, Ni, Va}^{fcc} = +8030 - 12.8801T \quad [64]
\]
\[
1L_{Cr, Ni, Va}^{fcc} = +33080 - 16.0362T \quad [64]
\]
\[
0L_{Cr, Mo, Va}^{fcc} = +28890 - 7.962T \quad [71]
\]
\[
1L_{Cr, Mo, Va}^{fcc} = +5974 - 2.428T \quad [71]
\]
\[
0L_{Cr, Mn, Va}^{fcc} = -19088 + 17.5423T \quad [65]
\]
\[
0L_{Mo, Ni, Va}^{fcc} = +4803.7 - 5.96T \quad [66]
\]
\[
1L_{Mo, Ni, Va}^{fcc} = +10880 \quad [66]
\]
\[
0L_{Mn, Ni, Va}^{fcc} = -58158 + 10.878T \quad [51]
\]
\[
1L_{Mn, Ni, Va}^{fcc} = +6276 \quad [51]
\]
\[
0L_{Mo, Mn, Va}^{fcc} = +11174 \quad [51]
\]
\[
0L_{Fe, Cr, N}^{fcc} = -128930 + 86.49T \quad [61]
\]
\[
1L_{Fe, Cr, N}^{fcc} = +24330 \quad [61]
\]
\( 0L_{Fe,Ni,N}^{fcc} = -22710 + 5.19T \) \[59\]

\( 1L_{Fe,Ni,N}^{fcc} = +3334 \) \[59\]

\( 0L_{Fe,Mn,N}^{fcc} = +53968 - 38.102T \) \[60\]

\( 1L_{Fe,Mn,N}^{fcc} = -28787 \) \[60\]

\( 0L_{Cr,Mo,N}^{fcc} = -40000 \) \[58\]

\( 0L_{Cr,Mn,N}^{fcc} = -21237 \) \[72\]

\( 0L_{Fe,Cr,Ni,\text{Va}}^{fcc} = +16580 - 9.783T \) \[51\]

\( 0L_{Fe,Mo,N}^{fcc} = +37460 - 20T \) \[51\]

\( 0L_{Fe,Cr,Mn,\text{Va}}^{fcc} = +6715 - 10.3933T \) \[65\]

\( 0L_{Fe,Ni,Mo,\text{Va}}^{fcc} = -204791 + 163.93T \) \[73\]

\( 1L_{Fe,Ni,Mo,\text{Va}}^{fcc} = +11555 - 55.81T \) \[73\]

\( 2L_{Fe,Ni,Mo,\text{Va}}^{fcc} = +77975 \) \[73\]

\( 0L_{Fe,Ni,Mn,\text{Va}}^{fcc} = -20000 \) \[51\]

\( 0L_{Fe,Mo,Mn,\text{Va}}^{fcc} = +30000 \) \[51\]

\( 0L_{Cr,Ni,Mo,\text{Va}}^{fcc} = -30000 \) \[51\]

\( 0L_{Fe,Cr,Mn,\text{N}}^{fcc} = -118000 \) \[63\]

\( 0L_{Cr,Fe,N,\text{Va}}^{fcc} = -162516 \) \[61\]

\( 0L_{Cr,Ni,N,\text{Va}}^{fcc} = -661270 + 305T \) \[74\]

\( \beta^{fcc} = -2.46Y_{Cr} - 2.1Y_{Fe} - 1.86Y_{Mn} + 0.52Y_{Ni} - 1.91Y_{Cr}Y_{Ni} \)
\[+ (Y_{Fe}Y_{Ni})[9.55 + 7.23(Y_{Fe} - Y_{Ni}) + 5.93(Y_{Fe} - Y_{Ni})^2] \]
\[+ 6.18(Y_{Fe} - Y_{Ni})^3] \) \[69\]

\( \tau^{fcc} = -1109Y_{Cr} - 201Y_{Fe} - 1620Y_{Mn} + 633Y_{Ni} - 3605Y_{Cr}Y_{Ni} \)
\[+ Y_{Fe}Y_{Mn}[-2282 - 2068(Y_{Fe} - Y_{Mn})] + (Y_{Fe}Y_{Ni})[2133 \]
\[ - 682(Y_{Fe} - Y_{Ni})] \) \[69\]
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{\text{hcp Fe:Va}}$</td>
<td>$G_{\text{Fe}}^{\text{SER}} - 3705.78 + 12.591T - 1.15T \ln(T) + 0.00064T^2$</td>
</tr>
<tr>
<td>$G_{\text{hcp Cr:Va}}$</td>
<td>$G_{\text{Cr}}^{\text{SER}} + 4438$</td>
</tr>
<tr>
<td>$G_{\text{hcp Ni:Va}}$</td>
<td>$G_{\text{Ni}}^{\text{SER}} + 1046 + 1.255T$</td>
</tr>
<tr>
<td>$G_{\text{hcp Mo:Va}}$</td>
<td>$G_{\text{Mo}}^{\text{SER}} + 11550$</td>
</tr>
<tr>
<td>$G_{\text{hcp Mn:Va}}$</td>
<td>$G_{\text{Mn}}^{\text{SER}} + 3675.98 + 2.948T - 1.0595T \ln(T) + 0.00134768T^2 - 227T^{-1}$</td>
</tr>
<tr>
<td>$G_{\text{hcp Fe:N}}$</td>
<td>$G_{\text{Fe}}^{\text{SER}} + 0.5G_{\text{N}}^{\text{SER}} - 12015 + 37.98T$</td>
</tr>
<tr>
<td>$G_{\text{hcp Cr:N}}$</td>
<td>$G_{\text{Cr}}^{\text{SER}} + 0.5G_{\text{N}}^{\text{SER}} - 65760 + 64.69T - 3.93T \ln(T)$</td>
</tr>
<tr>
<td>$G_{\text{hcp Ni:N}}$</td>
<td>$G_{\text{Ni}}^{\text{SER}} + 0.5G_{\text{N}}^{\text{SER}} - 4409 + 72.93T - 7.36T \ln(T) + 0.00614T^2$</td>
</tr>
<tr>
<td>$G_{\text{hcp Mo:N}}$</td>
<td>$G_{\text{Mo}}^{\text{SER}} + 0.5G_{\text{N}}^{\text{SER}} - 29450 + 28.7T$</td>
</tr>
<tr>
<td>$G_{\text{hcp Mn:N}}$</td>
<td>$G_{\text{Mn}}^{\text{SER}} + 0.5G_{\text{N}}^{\text{SER}} - 50616.4 + 75802T^{-1} + 85.8485T + 0.00823111T^2 - (1.3405 \times 10^{-9})T^3 - 7.88395T \ln(T)$</td>
</tr>
<tr>
<td>$L_{\text{hcp Fe:N, Va}}$</td>
<td>$+10345 - 19.71T$</td>
</tr>
<tr>
<td>$L_{\text{hcp Fe:N, Va}}$</td>
<td>$-11130 + 11.84T$</td>
</tr>
<tr>
<td>$L_{\text{hcp Cr:N, Va}}$</td>
<td>$+21120 - 10.61T$</td>
</tr>
<tr>
<td>$L_{\text{hcp Cr:N, Va}}$</td>
<td>$-6204$</td>
</tr>
<tr>
<td>$L_{\text{hcp Mn:N, Va}}$</td>
<td>$-7194 - 5.207T$</td>
</tr>
<tr>
<td>$L_{\text{hcp Mn:N, Va}}$</td>
<td>$-11810 + 6.9538T$</td>
</tr>
<tr>
<td>$L_{\text{hcp Fe, Cr:Va}}$</td>
<td>$+10833 - 7.477T$</td>
</tr>
<tr>
<td>$L_{\text{hcp Fe, Ni:Va}}$</td>
<td>$-12054.355 + 3.27413T$</td>
</tr>
<tr>
<td>$L_{\text{hcp Fe, Ni:Va}}$</td>
<td>$+11082 - 4.45077T$</td>
</tr>
<tr>
<td>$L_{\text{hcp Fe, Ni:Va}}$</td>
<td>$-725.8$</td>
</tr>
<tr>
<td>$L_{\text{hcp Fe, Mo:Va}}$</td>
<td>$+28347 - 17.691T$</td>
</tr>
</tbody>
</table>
\[0 L_{\text{Fe,Mn:Va}}^{\text{hcp}} = -5582 + 3.865T \]  
\[1 L_{\text{Fe,Mn:Va}}^{\text{hcp}} = +273 \]  
\[0 L_{\text{Cr,Mo:Va}}^{\text{hcp}} = +28890 - 7.962T \]  
\[1 L_{\text{Cr,Mo:Va}}^{\text{hcp}} = +5974 - 2.428T \]  
\[0 L_{\text{Cr,Mn:Va}}^{\text{hcp}} = -19088 + 17.5423T \]  
\[0 L_{\text{Mo,Mn:Va}}^{\text{hcp}} = +11174 \]  
\[0 L_{\text{Fe,Cr:N}}^{\text{hcp}} = +12826 - 19.48T \]  
\[0 L_{\text{Cr,Ni:N}}^{\text{hcp}} = +1443 \]  
\[0 L_{\text{Cr,Mo:N}}^{\text{hcp}} = -87828 + 71.885T \]  
\[0 L_{\text{Cr,Mn:N}}^{\text{hcp}} = -42187 + 32.48T \]  
\[0 L_{\text{Mo,Ni:N}}^{\text{hcp}} = -80000 \]  
\[0 L_{\text{Fe,Cr,Mn:Va}}^{\text{hcp}} = +34600 \]  
\[0 L_{\text{Fe,Cr,Mn:N}}^{\text{hcp}} = -185400 \]  
\[\beta^{\text{hcp}} = -2.46Y_{\text{Cr}}Y_{\text{Va}} - 1.86Y_{\text{Mn}}Y_{\text{Va}} + 0.52Y_{\text{Ni}}Y_{\text{Va}} \]  
\[\gamma^{\text{hcp}} = -1109Y_{\text{Cr}}Y_{\text{Va}} - 1620Y_{\text{Mn}}Y_{\text{Va}} + 633Y_{\text{Ni}}Y_{\text{Va}} \]

**M₄N: two sublattice model (Fe, Cr, Ni, Mn)₄(N)₁**

\[\circ G_{\text{Fe,N}}^{\text{M₄N}} = 4G_{\text{Fe}}^{\text{HSER}} + G_{\text{N}}^{\text{HSER}} - 38744 + 73.52T \]  
\[\circ G_{\text{Cr,N}}^{\text{M₄N}} = 4G_{\text{Cr}}^{\text{HSER}} + G_{\text{N}}^{\text{HSER}} - 96061.6 + 97.4043T + 0.00644526T^2 \]  
\[\quad - 74395T^{-1} + (4.80936 \times 10^{-6})T^3 - 6.7661T \ln(T) \]  
\[\circ G_{\text{Ni,N}}^{\text{M₄N}} = 4G_{\text{Ni}}^{\text{HSER}} + G_{\text{N}}^{\text{HSER}} - 5393 + 142.97T - 15.65T \ln(T) + 0.0154T^2 \]  
\[\circ G_{\text{Mn,N}}^{\text{M₄N}} = 4G_{\text{Mn}}^{\text{HSER}} + G_{\text{N}}^{\text{HSER}} - 119578 + 180.282T - 20.3181T \ln(T) \]  
\[\quad + 0.0311576T^2 - (2.681 \times 10^{-9})T^3 + 60483.7T^{-1} \]  
\[\circ L_{\text{Fe,Mn:N}}^{\text{M₄N}} = +36297 - 28.8876T \]
bcc (including MC$_3$): two sublattice model (Fe, Cr, Ni, Mo, Mn)$_1$(C, Va)$_3$

\[
\begin{align*}
G_{\text{Fe} \text{Va}}^{\text{bcc}} &= G_{\text{Fe}}^{\text{SER}} \\
G_{\text{Cr} \text{Va}}^{\text{bcc}} &= G_{\text{Cr}}^{\text{SER}} \\
G_{\text{Ni} \text{Va}}^{\text{bcc}} &= G_{\text{Ni}}^{\text{SER}} + 8715.084 - 3.556T \\
G_{\text{Mo} \text{Va}}^{\text{bcc}} &= G_{\text{Mo}}^{\text{SER}} \\
G_{\text{Mn} \text{Va}}^{\text{bcc}} &= G_{\text{Mn}}^{\text{SER}} - 2.209T - 0.2418T \ln(T) - 0.00009503T^2 + 4879.98
\end{align*}
\]

\[
\begin{align*}
G_{\text{Fe} \text{C}}^{\text{bcc}} &= G_{\text{Fe}}^{\text{SER}} + 3G_{\text{C}}^{\text{SER}} + 322050 + 75.667T \\
G_{\text{Cr} \text{C}}^{\text{bcc}} &= G_{\text{Cr}}^{\text{SER}} + 3G_{\text{C}}^{\text{SER}} + 357730 + 13.09T \\
G_{\text{Ni} \text{C}}^{\text{bcc}} &= G_{\text{Ni}}^{\text{SER}} + 3G_{\text{C}}^{\text{SER}} + 366445.084 + 9.534T \\
G_{\text{Mo} \text{C}}^{\text{bcc}} &= G_{\text{Mo}}^{\text{SER}} + 3G_{\text{C}}^{\text{SER}} + 331000 - 75T \\
G_{\text{Mn} \text{C}}^{\text{bcc}} &= G_{\text{Mn}}^{\text{SER}} + 3G_{\text{C}}^{\text{SER}} + 10000 + 30T \\
L_{\text{Fe} \text{C}, \text{Va}}^{\text{bcc}} &= -190T \\
L_{\text{Cr} \text{C}, \text{Va}}^{\text{bcc}} &= -190T \\
L_{\text{Cr}, \text{Fe} \text{Va}}^{\text{bcc}} &= +20500 - 9.68T \\
L_{\text{Fe}, \text{Ni} \text{Va}}^{\text{bcc}} &= -956.63 - 1.28726T \\
L_{\text{Fe}, \text{Ni} \text{Va}}^{\text{bcc}} &= +1789.03 - 1.92912T \\
L_{\text{Fe}, \text{Mo} \text{Va}}^{\text{bcc}} &= +36818 - 9.141T \\
L_{\text{Fe}, \text{Mo} \text{Va}}^{\text{bcc}} &= -362 - 5.724T \\
L_{\text{Fe}, \text{Mn} \text{Va}}^{\text{bcc}} &= -2759 + 1.237T \\
L_{\text{Cr}, \text{Ni} \text{Va}}^{\text{bcc}} &= +17170 - 11.8199T \\
L_{\text{Cr}, \text{Ni} \text{Va}}^{\text{bcc}} &= +34418 - 11.8577T \\
L_{\text{Cr}, \text{Mo} \text{Va}}^{\text{bcc}} &= +28890 - 7.962T \\
L_{\text{Cr}, \text{Mo} \text{Va}}^{\text{bcc}} &= +5974 - 2.428T
\end{align*}
\]
\[0 L_{Cr,Mn:Va}^{bcc} = -20328 + 18.7339T \]  
\[1 L_{Cr,Mn:Va}^{bcc} = -9162 + 4.4183T \]  
\[0 L_{Mo,Ni:Va}^{bcc} = +46422 \]  
\[0 L_{Mn,Ni:Va}^{bcc} = -51538.31 + 3.64T \]  
\[1 L_{Mn,Ni:Va}^{bcc} = +6276 \]  
\[0 L_{Mn,Mo:Va}^{bcc} = +49770 - 14.2564T \]  
\[1 L_{Mn,Mo:Va}^{bcc} = -7260 \]  
\[0 L_{Cr,Fe:C}^{bcc} = -1300000 + 667.7T \]  
\[0 L_{Fe,Ni:C}^{bcc} = -956.63 - 1.28726T \]  
\[1 L_{Fe,Ni:C}^{bcc} = +1789.03 - 1.92912T \]  
\[0 L_{Fe,Mo:C}^{bcc} = -1750000 + 940T \]  
\[0 L_{Cr,Ni:C}^{bcc} = -1226000 + 570T \]  
\[0 L_{Fe,Mn:C}^{bcc} = +34052 - 23.467T \]  
\[0 L_{Fe,Cr,Ni:Va}^{bcc} = -2673 + 2.0415T \]  
\[0 L_{Fe,Cr,Mo:Va}^{bcc} = +37460 - 20T \]  
\[0 L_{Fe,Cr,Mn:Va}^{bcc} = -5996 \]  
\[0 L_{Fe,Ni,Mo:Va}^{bcc} = -35743 \]  
\[\beta^{bcc} = -0.008Y_{Cr} + 2.22Y_{Fe} + 0.85Y_{Ni} - 0.27Y_{Mn} - 0.85Y_{Cr}Y_{Fe} + 4Y_{Cr}Y_{Ni} + (Y_{Cr}Y_{Mn})[0.48643 - 0.72035(Y_{Cr} - Y_{Mn})^2 - 1.93265(Y_{Cr} - Y_{Mn})^4] \]  
\[\tau^{bcc} = -311.5Y_{Cr} + 1043Y_{Fe} + 575Y_{Ni} - 580Y_{Mn} + (Y_{Cr}Y_{Fe})[1650 + 550(Y_{Cr} - Y_{Fe})] + (Y_{Cr}Y_{Ni})[2373 + 617(Y_{Cr} - Y_{Ni})] + (Y_{Cr}Y_{Mn})[-1325 - 1133(Y_{Cr} - Y_{Mn})^2 - 10294(Y_{Cr} - Y_{Mn})^4 + 26706(Y_{Cr} - Y_{Mn})^6 - 28117(Y_{Cr} - Y_{Mn})^8] + 123Y_{Fe}Y_{Mn} + (Y_{Fe}Y_{Mo})[335 + 526(Y_{Fe} - Y_{Mo})] \]
fcc (including MC): two sublattice model \((Fe, Cr, Ni, Mo, Mn)_1(C, Va)_1\)

\[
\begin{align*}
g^{fcc}_{Fe, Va} &= G^{H_{SER}}_{Fe} - 1462.4 + 8.282T - 1.15T \ln(T) + 0.00064T^2 \quad [45] \\
g^{fcc}_{Cr, Va} &= G^{H_{SER}}_{Cr} + 7284 + 0.163T \quad [45] \\
g^{fcc}_{Ni, Va} &= G^{H_{SER}}_{Ni} \quad [45] \\
g^{fcc}_{Mo, Va} &= G^{H_{SER}}_{Mo} + 15200 + 0.63T \quad [45] \\
g^{fcc}_{Mn, Va} &= G^{H_{SER}}_{Mn} + 4675.98 + 1.825T - 1.0595T \ln(T) + 0.00134768T^2 \\
&\quad - 227T^{-1} \quad [45] \\
g^{fcc}_{Fe, C} &= G^{H_{SER}}_{Fe} + G^{H_{SER}}_{C} + 75744.6 - 7.595T - 1.15T \ln(T) + 0.00064T^2 \quad [52] \\
g^{fcc}_{Cr, C} &= G^{H_{SER}}_{Cr} + G^{H_{SER}}_{C} - 21438 - 6.6747T \quad [27] \\
g^{fcc}_{Ni, C} &= G^{H_{SER}}_{Ni} + G^{H_{SER}}_{C} + 62000 - 7.6T \quad [52] \\
g^{fcc}_{Mo, C} &= G^{H_{SER}}_{Mo} + G^{H_{SER}}_{C} - 7500 - 8.3T - 750000T^{-1} \quad [76] \\
g^{fcc}_{Mn, C} &= G^{H_{SER}}_{Mn} + G^{H_{SER}}_{C} + 13.659T \quad [77] \\
\ell^{fcc}_{Fe, C, Va} &= -34671 \quad [52] \\
\ell^{fcc}_{Cr, C, Va} &= +5267.2 - 2.9067T \quad [27] \\
\ell^{fcc}_{Ni, C, Va} &= -14902 + 7.5T \quad [52] \\
\ell^{fcc}_{Mo, C, Va} &= -41300 \quad [76] \\
\ell^{fcc}_{Mn, C, Va} &= -41333 \quad [77] \\
\ell^{fcc}_{Cr, Fe, Va} &= +10833 - 7.477T \quad [61] \\
\ell^{fcc}_{Fe, Cr, Va} &= +1410 \quad [61] \\
\ell^{fcc}_{Fe, Ni, Va} &= -12054.355 + 3.27413T \quad [59] \\
\ell^{fcc}_{Fe, Ni, Va} &= +11082.1315 - 4.45077T \quad [59] \\
\ell^{fcc}_{Fe, Ni, Va} &= -725.805174 \quad [59] \\
\ell^{fcc}_{Fe, Mo, Va} &= +28347 - 17.691T \quad [62] \\
\ell^{fcc}_{Fe, Mn, Va} &= -7762 + 3.865T \quad [63] 
\end{align*}
\]
\begin{align*}
  ^1L_{\text{Fe,Mn:Va}}^{\text{fcc}} &= -259 & [63] \\
  ^0L_{\text{Cr,Ni:Va}}^{\text{fcc}} &= +8030 - 12.8801T & [64] \\
  ^1L_{\text{Cr,Ni:Va}}^{\text{fcc}} &= +33080 - 16.0362T & [64] \\
  ^0L_{\text{Cr,Mo:Va}}^{\text{fcc}} &= +28890 - 7.962T & [71] \\
  ^1L_{\text{Cr,Mo:Va}}^{\text{fcc}} &= +5974 - 2.428T & [71] \\
  ^0L_{\text{Cr,Mn:Va}}^{\text{fcc}} &= -19088 + 17.5423T & [65] \\
  ^0L_{\text{Mo,Ni:Va}}^{\text{fcc}} &= +4803.7 - 5.96T & [66] \\
  ^1L_{\text{Mo,Ni:Va}}^{\text{fcc}} &= +10880 & [66] \\
  ^0L_{\text{Mn,Ni:Va}}^{\text{fcc}} &= -58158 + 10.878T & [51] \\
  ^1L_{\text{Mn,Ni:Va}}^{\text{fcc}} &= +6276 & [51] \\
  ^0L_{\text{Mo,Mn:Va}}^{\text{fcc}} &= +11174 & [51] \\
  ^0L_{\text{Cr,Fe:C}}^{\text{fcc}} &= -246225 + 166.44T & [27] \\
  ^0L_{\text{Fe,Ni:C}}^{\text{fcc}} &= 49074 - 7.32T & [69] \\
  ^1L_{\text{Fe,Ni:C}}^{\text{fcc}} &= -25800 & [69] \\
  ^0L_{\text{Fe,Mo:C}}^{\text{fcc}} &= +6000 & [76] \\
  ^0L_{\text{Fe,Mn:C}}^{\text{fcc}} &= +34052 - 23.467T & [70] \\
  ^0L_{\text{Cr,Ni:C}}^{\text{fcc}} &= -125935 + 95T & [52] \\
  ^0L_{\text{Fe,Cr,Ni:Va}}^{\text{fcc}} &= +16580 - 9.783T & [51] \\
  ^0L_{\text{Fe,Cr,Mo:Va}}^{\text{fcc}} &= +37460 - 20T & [51] \\
  ^0L_{\text{Fe,Cr,Mn:Va}}^{\text{fcc}} &= +6715 - 10.3933T & [65] \\
  ^0L_{\text{Fe,Ni,Mo:Va}}^{\text{fcc}} &= -204791 + 163.93T & [73] \\
  ^1L_{\text{Fe,Ni,Mo:Va}}^{\text{fcc}} &= +11555 - 55.81T & [73] \\
  ^2L_{\text{Fe,Ni,Mo:Va}}^{\text{fcc}} &= +77975 & [73] \\
  ^0L_{\text{Fe,Ni,Mn:Va}}^{\text{fcc}} &= -20000 & [51] \\
  ^0L_{\text{Fe,Mo,Mn:Va}}^{\text{fcc}} &= +30000 & [51]
\end{align*}
\[ 0L_{Cr,Ni,Mo}^{I_{cc}} = -30000 \]  
\[ 0L_{Cr,Fe,Ni,C}^{I_{cc}} = -8215 \]  
\[ \beta^{I_{cc}} = -2.46Y_{Cr} - 2.1Y_{Fe} - 1.86Y_{Mn} + 0.52Y_{Ni} - 1.91Y_{Cr}Y_{Ni} \]  
\[ + (Y_{Fe}Y_{Ni})[9.55 + 7.23(Y_{Fe} - Y_{Ni}) + 5.93(Y_{Fe} - Y_{Ni})^2] \]  
\[ + 6.18(Y_{Fe} - Y_{Ni})^3] \]  
\[ \tau^{I_{cc}} = -1109Y_{Cr} - 201Y_{Fe} - 1620Y_{Mn} + 633Y_{Ni} - 3605Y_{Cr}Y_{Ni} \]  
\[ + Y_{Fe}Y_{Mn}[-2282 - 2068(Y_{Fe} - Y_{Mn})] + (Y_{Fe}Y_{Ni})[2133 \]  
\[ - 682(Y_{Fe} - Y_{Ni})] \]

\[ M_3C: \text{two sublattice model (Fe,Cr,Ni,Mo,Mn)}_3(C) \]

\[ ^{0}G_{Fe-C}^{M_3C} = 3G_{Fe}^{H_{SER}} + G_{C}^{H_{SER}} + 2946.341 + 162.908T - 25.7571T \ln(T) \]  
\[ + 0.01366486T^2 + (1.76781 \times 10^{-7})T^3 - 2794677T^{-1} \]  
\[ + (2.643 \times 10^8)T^{-2} - (1.2 \times 10^{10})T^{-3} \]  
\[ \text{[52]} \]

\[ ^{0}G_{Cr-C}^{M_3C} = 3G_{Cr}^{H_{SER}} + G_{C}^{H_{SER}} - 48000 - 9.2888T \]  
\[ \text{[52]} \]

\[ ^{0}G_{Ni-C}^{M_3C} = 3G_{Ni}^{H_{SER}} + G_{C}^{H_{SER}} + 34700 - 20T \]  
\[ \text{[52]} \]

\[ ^{0}G_{Mo-C}^{M_3C} = 3G_{Mo}^{H_{SER}} + G_{C}^{H_{SER}} + 77000 - 57.4T \]  
\[ \text{[52]} \]

\[ ^{0}G_{Mn-C}^{M_3C} = 3G_{Mn}^{H_{SER}} + G_{C}^{H_{SER}} - 39644 + 3.04T \]  
\[ \text{[52]} \]

\[ 0L_{Cr,Fe,C}^{M_3C} = +25278 - 17.5T \]  
\[ \text{[52]} \]

\[ 0L_{Fe,Ni,C}^{M_3C} = +29400 \]  
\[ \text{[59]} \]

\[ 0L_{Cr,Mo,C}^{M_3C} = +40000 \]  
\[ \text{[52]} \]

\[ M_7C_3: \text{two sublattice model (Fe,Cr,Ni,Mo,Mn)}_7(C)_3 \]

\[ ^{0}G_{Fe-C}^{M_7C_3} = 7G_{Fe}^{H_{SER}} + 3G_{C}^{H_{SER}} + 75000 - 48.2168T \]  
\[ \text{[52]} \]

\[ ^{0}G_{Cr-C}^{M_7C_3} = 7G_{Cr}^{H_{SER}} + 3G_{C}^{H_{SER}} - 87584.4 - 511.422T + 71.079T \ln(T) \]  
\[ - 0.0118435T^2 + 0.0000103405T^3 - 8662550T^{-1} \]  
\[ + (7.929 \times 10^8)T^{-2} - (3.6 \times 10^{10})T^{-3} \]  
\[ \text{[52]} \]
\[ \theta G_{Mn:C}^{M_C} = 7G_{Ni:H}^{HSER} + 3G_{C:H}^{HSER} - 106695 + 9.36T \]

\[ \theta G_{Mo:C}^{M_C} = 7G_{Mo:H}^{HSER} + 3G_{C:H}^{HSER} - 140415 + 24.24T \]

\[ 0L_{Cr,Fe:C}^{M_C} = -4520 - 10T \]

\[ 0L_{Cr,Ni:C}^{M_C} = +100000 \]

\[ 0L_{Cr,Mo:C}^{M_C} = +165280 \]

\[ \pm \theta G_{Fe:Fe:C}^{M_C} = 23G_{Cr:H}^{HSER} + 6G_{C:H}^{HSER} + 89508.61654 + 1208.961512T \]

\[- 197.4711321T \ln(T) + 0.104763926T^2 \]

\[ (3.355321 \times 10^{-6})T^3 - 21425857.85T^{-1} + 2026300887T^{-2} \]

\[- (9.2000004 \times 10^{10})T^{-3} \]

\[ \pm \theta G_{Fe:Cr:C}^{M_C} = 20G_{Fe:H}^{HSER} + 3G_{Cr:H}^{HSER} + 6G_{C:H}^{HSER} + 49912.34411 + 917.6821587T \]

\[- 152.96806687T \ln(T) + 0.06929464T^2 + (5.61017 \times 10^{-6})T^3 \]

\[- 21054443.71T^{-1} + 1968843547T^{-2} \]

\[- (8.939130748 \times 10^{10})T^{-3} \]

\[ \pm \theta G_{Cr:Cr:C}^{M_C} = 23G_{Cr:H}^{HSER} + 6G_{C:H}^{HSER} - 214062.734 - 1024.18T \]

\[ + 143.719T \ln(T) - 0.16716725T^2 + (3.397583 \times 10^{-5})T^3 \]

\[- 18578350T^{-1} + 1585800000T^{-2} - (7.2 \times 10^{10})T^{-3} \]

\[ \pm \theta G_{Cr:Fe:C}^{M_C} = 20G_{Cr:H}^{HSER} + 3G_{Fe:H}^{HSER} + 6G_{C:H}^{HSER} - 174466.46 - 732.9006469T \]

\[ + 99.21593472T \ln(T) - 0.1316979637T^2 \]

\[ + (2.9720981 \times 10^{-5})T^3 - 18949764.14T^{-1} \]

\[ \pm \theta G_{Cr:Ni:C}^{M_C} = 20G_{Cr:H}^{HSER} + 3G_{Ni:H}^{HSER} + 6G_{C:H}^{HSER} - 158750.1946 - 901.6404343T \]

\[ + 124.9730429T \ln(T) - 0.1472991267T^2 + (2.95442 \times 10^{-5})T^3 \]

\[- 16155086.69T^{-1} + 1378956494T^{-2} \]

\[- (6.26086944 \times 10^{10})T^{-3} \]
\[ \Delta G_{\text{NiNi:C}} = 23G_{\text{Ni}}^{\text{SR}} + 6G_{\text{C}}^{\text{SR}} + 210000 - 84.71T \]  \[ \text{[52]} \]

\[ \Delta G_{\text{NiCr:C}} = 20G_{\text{Ni}}^{\text{SR}} + 3G_{\text{Cr}}^{\text{SR}} + 6G_{\text{C}}^{\text{SR}} + 154687.4606 - 207.2495657T \]
\[ + 18.7459571T \ln(T) - 0.019868076T^2 + (4.43163 \times 10^{-6})T^3 \]
\[ - 2423263.311T^{-1} + 206843505.8T^{-2} - 9391305600T^{-3} \]  \[ \text{[52]} \]

\[ \Delta G_{\text{MnMn:C}} = 23G_{\text{Mn}}^{\text{SR}} + 6G_{\text{C}}^{\text{SR}} - 310473 + 53.86T \]  \[ \text{[52]} \]

\[ \Delta L_{\text{Fe, Cr, Fe:C}} = -205342 + 141.6667T \]  \[ \text{[52]} \]

\[ \Delta L_{\text{Fe, Cr, Cr:C}} = -205342 + 141.6667T \]  \[ \text{[52]} \]

\[ \Delta L_{\text{Cr, Ni, Cr:C}} = +100000 \]  \[ \text{[52]} \]

\[ \Delta L_{\text{Cr, Ni, Ni:C}} = +100000 \]  \[ \text{[52]} \]
Appendix B

The routine below, used in simulating solubility limits within the (Fe,Cr,Ni,Mo,Mn)-
carbon system, was written in Wolfram Mathematica® 8.04 and employed the para-
parameters listed in Appendix A. A similar routine was used for the (Fe,Cr,Ni,Mo,Mn)-
nitrogen system using the relevant parameters and nitride phases.

Magnetic Contribution

\[
\begin{align*}
\beta_{\text{bccFeCrNiMoMn}}[y_C, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}] &= -0.008 y_{\text{Cr}} + 2.22 y_{\text{Fe}} + 0.85 y_{\text{Ni}} - 0.27 y_{\text{Mn}} - 0.85 y_{\text{Cr}} y_{\text{Fe}} + 4 y_{\text{Cr}} y_{\text{Ni}} + (y_{\text{Cr}} y_{\text{Mn}})(0.48643 - 0.72035(y_{\text{Cr}} - y_{\text{Mn}})^2 - 1.93265(y_{\text{Cr}} - y_{\text{Mn}})^4) + 0 y_{\text{Mo}} \\
\beta_{\text{bcc}}[y_C, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}] &= \text{If} \left[\# < 0, -\#, \#\right] \& \text{@} \beta_{\text{bccFeCrNiMoMn}}[y_C, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}] \\
T_{\text{cbccFeCrNiMoMn}}[y_N, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}] &= -311.5 y_{\text{Cr}} + 1043 y_{\text{Fe}} + 575 y_{\text{Ni}} - 580 y_{\text{Mn}} + (y_{\text{Cr}} y_{\text{Fe}})(1650 + 550(y_{\text{Cr}} - y_{\text{Fe}})) + (y_{\text{Cr}} y_{\text{Ni}})(2373 + 617(y_{\text{Cr}} - y_{\text{Ni}})) + (y_{\text{Cr}} y_{\text{Mn}})(-1325 - 1133(y_{\text{Cr}} - y_{\text{Mn}})^2 - 10294(y_{\text{Cr}} - y_{\text{Mn}})^4 + 26706(y_{\text{Cr}} - y_{\text{Mn}})^6 - 28117(y_{\text{Cr}} - y_{\text{Mn}})^8) + 123 y_{\text{Fe}} y_{\text{Mn}} + (y_{\text{Fe}} y_{\text{Mo}})(335 + 526(y_{\text{Fe}} - y_{\text{Mo}})) \\
T_{\text{cc}}[y_C, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}] &= \text{If} \left[\# < 0, -\#, \#\right] \& @T_{\text{cbccFeCrNiMoMn}}[y_C, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}] \\
\tau_{\text{bcc}}[y_C, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}] &= T / T_{\text{cbcc}}[y_C, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}] \\
\beta_{\text{bcc}}[y_C, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}] &= \text{If} \left[\# < 1, +1 - 0.905299383\#^{-1} - 0.153008346\#^{-3} - 0.00680037095\#^{-9} - 0.00153008346\#^{-15} - 0.0641731208\#^{-25}\right] \& \text{@} \tau_{\text{bcc}}[y_C, T, y_{\text{Fe}}, y_{\text{Cr}}, y_{\text{Ni}}, y_{\text{Mo}}, y_{\text{Mn}}]
\end{align*}
\]
Gmagbcc \[yC_-, T_-, yFe_-, yCr_-, yNi_-, yMo_-, yMn_-\] := R*T*Log[\[Beta] bcc[yC,T,yFe,yCr,yNi,yMo,yMn]+1]*fbcc[yC,T,yFe,yCr,yNi, yMo,yMn]

\[Beta] fcc[yC_-, T_-, yFe_-, yCr_-, yNi_-, yMo_-, yMn_-] := If [#<0, -#/3, #] & @\[Beta] fccFeCrNiMoMn[yC,T,yFe,yCr,yNi,yMo,yMn]

TcfccFeCrNiMoMn[yC_-, T_-, yFe_-, yCr_-, yNi_-, yMo_-, yMn_-] := -1109yCr -201yFe -1620yMn +6365yNi+yFe*yNi+yMn*(-2282-2068*(yFe-yMn)+(yFe*yNi)(2133-682(yFe-yNi)))

Tcfcc[yC_-, T_-, yFe_-, yCr_-, yNi_-, yMo_-, yMn_-] := T/TcfccFeCrNiMoMn[yC,T,yFe,yCr,yNi,yMo,yMn]

\[Tau] fcc[yC_-, T_-, yFe_-, yCr_-, yNi_-, yMo_-, yMn_-] := If [#<=1, +1 -0.860338755#^~1-0.17449124#^~3-0.00775516624#^~9
-0.001749124#^~15,-0.0426902268#^~5-0.0013552453#^~15
-0.000284601512#^~25] & @\[Tau] fcc[yC,T,yFe,yCr,yNi,yMo,yMn]

Gmagfcc[yC_-, T_-, yFe_-, yCr_-, yNi_-, yMo_-, yMn_-] := R*T*Log[\[Beta] fcc[yC,T,yFe,yCr,yNi,yMo,yMn]+1]*ffcc[yC,T,yFe,yCr,yNi,yMo,yMn]

**Gibbs Free Energy of Solution and Carbide Phases**

fe[yFe_] := yFe*Log[yFe];
fe[0] = 0;

\[yCr_\] := yCr*Log[yCr];

\[yCr_\] := yCr*Log[yCr];

\[yCr_\] := yCr*Log[yCr];

\[yCr_\] := yCr*Log[yCr];

\[yCr_\] := yCr*Log[yCr];

\[yCr_\] := yCr*Log[yCr];
mo[0] = 0;
mn[yMn_] := yMn * Log[yMn]


\[
\begin{align*}
\text{fe} &\{\text{yFe}\} + \text{cr} &\{\text{yCr}\} + \text{ni} &\{\text{yNi}\} + \text{mo} &\{\text{yMo}\} + \text{mn} &\{\text{yMn}\} + 3yC &\text{Log} &\{yC\} + 3yVa &\text{Log} &\{yVa\} + yCyVa &\{(\text{yFeL0bccFeCrVa} &\{T\} + yCrL0bccCrCVa &\{T\}) + \\
yVa &\{(\text{yFeyCrL0bccFeCrVa} &\{T\} + yFeyNiL0bccFeNiVa &\{T\} + \\
yFeyNiL1bccFeNiVa &\{T\}(yFe - yNi) + yFeyMoL0bccFeMoVa &\{T\} + \\
yFeyMoL1bccFeMoVa &\{T\}(yFe - yMo) + yFeyMnL0bccFeMnVa &\{T\} + yCyVa &\{(T\} + yCyVa &\{(T\} + yCyCrL0bccFeCrVa &\{T\} + yFeyNiL0bccFeNiVa &\{T\} + yFeyNiL1bccFeNiVa &\{T\}(yFe - yNi) + yFeyMoL0bccFeMoVa &\{T\} + yFeyMoL1bccFeMoVa &\{T\}(yFe - yMo) + yFeyMnL0bccFeMnVa &\{T\} + \\
yCyCrL0bccCrNiVa &\{T\} + yCyMnL0bccCrMnVa &\{T\}(yCr - yMn) + yCyMnL1bccCrMnVa &\{T\}(yCr - yMn) + yCyMnL0bccCrNiMoVa &\{T\} + yCyMnL1bccCrNiMoVa &\{T\}(yCr - yMn) + yCyMnL0bccCrNiMnVa &\{T\} + yCyMnL1bccCrNiMnVa &\{T\}(yCr - yMn) + yCyMnL0bccCrMnVa &\{T\}(yMn - yMo) + yCyCrL0bccFeCrC &\{T\} + \\
yFeyNiL0bccFeNiC &\{T\} + yFeyNiL1bccFeNiC &\{T\}(yFe - yNi) + yFeyMoL0bccFeMoC &\{T\} + yFeyMnL0bccFeMnC &\{T\} + yCyNiL0bccCrNiC &\{T\} + yVa &\{(T\} + \\
yFeyCryCrL0bccFeCrNiVa &\{T\} + yFeyMnL0bccFeNiMoVa &\{T\} + yFeyMnL1bccFeNiMoVa &\{T\}(yMn - yMo) + yCyCrL0bccFeCrMoVa &\{T\} + yFeyMnL0bccFeCrMoVa &\{T\} + yFeyMnL1bccFeCrMoVa &\{T\}(yMn - yMo) + yCyMnL0bccCrNiMoVa &\{T\} + yFeyMnL0bccCrNiMoVa &\{T\} + yFeyMnL1bccCrNiMoVa &\{T\}(yMn - yMo) + Gmagbcc &\{yC, T, yFe, yCr, yNi, yMo, yMn\} &+ GprimeFCC &\{yC, T, yFe, yCr, yNi, yMo, yMn\} := GmFCC &\{yC, T, yFe, yCr, yNi, yMo, yMn\}(1 + yC)/. yVa -> 1 - yC &+ GprimeBCC &\{yC, T, yFe, yCr, yNi, yMo, yMn\} := GmBCC &\{yC, T, yFe, yCr, yNi, yMo, yMn\}(1 + 3yC)/. yVa -> 1 - yC &+ GpFCC &\{xCf, T, yFe, yCr, yNi, yMo, yMn\} := GprimeFCC &\{yC, T, yFe, yCr, yNi, yMo, yMn\}(1 - xCf) &+ GpBCC &\{xCb, T, yFe, yCr, yNi, yMo, yMn\} := GprimeBCC &\{yC, T, yFe, yCr, yNi, yMo, yMn\}(1 - xCb) &+ eqbound &\{yC, T, yFe, yCr, yNi, yMo, yMn\} := Chop[FindRoot[{(GpFCC &\{xCf, T, yFe, yCr, yNi, yMo, yMn\} - GpBCC &\{xCb, T, yFe, yCr, yNi, yMo, yMn\})(xCf - xCb) == D[GpFCC &\{xCf, T, yFe, yCr, yNi, yMo, yMn\}, xCf] == D[GpBCC &\{xCb, T, yFe, yCr, yNi, yMo, yMn\}, xCb}, {xCf, 0.001}, {xCb, 0.00000001}][[All, 2]]]
\end{align*}
\]
\[ \mu_{\text{Fe FCC}} = \text{Module}\{C, Fe, Cr, Ni, Mo, Mn\}, \text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn] + D[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Fe] + D[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Fe] - yCrD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Cr] - yNiD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Ni] - yMoD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Mo] - yMnD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Mn] - yVaD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], yVal] - yCD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], yVal] \}

\[ \mu_{\text{Cr FCC}} = \text{Module}\{C, Fe, Cr, Ni, Mo, Mn\}, \text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn] + D[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Fe] + D[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Fe] - yCrD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Cr] - yNiD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Ni] - yMoD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Mo] - yMnD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Mn] - yVaD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], yVal] - yCD[\text{Gm FCC}[yC, T, yFe, yCr, yNi, yMo, yMn], yVal] \} \]
\[ \mu_{Febcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] := \text{Module}[\{C, Fe, Cr, Ni, Mo, Mn\}, GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] + D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], y_{Va}] - y_{Fe}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Fe] - y_{Cr}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Cr] - y_{Ni}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Ni] - y_{Mo}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Mo] - y_{Mn}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Mn] - y_{Va}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], y_{Va}] - yCD[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], C]. \] 
\[ \{C->y_C, Fe->y_{Fe}, Cr->y_{Cr}, Ni->y_{Ni}, Mo->y_{Mo}, Mn->y_{Mn}\} \]

\[ \mu_{Crbcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] := \text{Module}[\{C, Fe, Cr, Ni, Mo, Mn\}, GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] + D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Cr] + D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], y_{Va}] - y_{Fe}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Fe] - y_{Cr}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Cr] - y_{Ni}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Ni] - y_{Mo}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Mo] - y_{Mn}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Mn] - y_{Va}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], y_{Va}] - yCD[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], C]. \] 
\[ \{C->y_C, Fe->y_{Fe}, Cr->y_{Cr}, Ni->y_{Ni}, Mo->y_{Mo}, Mn->y_{Mn}\} \]

\[ \mu_{Nibcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] := \text{Module}[\{C, Fe, Cr, Ni, Mo, Mn\}, GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] + D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Cr] + D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], y_{Va}] - y_{Fe}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Fe] - y_{Cr}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Cr] - y_{Ni}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Ni] - y_{Mo}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Mo] - y_{Mn}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Mn] - y_{Va}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], y_{Va}] - yCD[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], C]. \] 
\[ \{C->y_C, Fe->y_{Fe}, Cr->y_{Cr}, Ni->y_{Ni}, Mo->y_{Mo}, Mn->y_{Mn}\} \]

\[ \mu_{Mobcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] := \text{Module}[\{C, Fe, Cr, Ni, Mo, Mn\}, GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] + D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Mo] + D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], y_{Va}] - y_{Fe}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Fe] - y_{Cr}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Cr] - y_{Ni}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Ni] - y_{Mo}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Mo] - y_{Mn}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], Mn] - y_{Va}D[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], y_{Va}] - yCD[GmBCC[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}], C]. \] 
\[ \{C->y_C, Fe->y_{Fe}, Cr->y_{Cr}, Ni->y_{Ni}, Mo->y_{Mo}, Mn->y_{Mn}\} \]
\[ \text{GmBCC}[yC, T, yFe, Cr, yNi, yMo, yMn], Cr] - yNiD[\text{GmBCC}[yC, T, yFe, yCr, yNi, yMo, yMn], Ni] - yMoD[\text{GmBCC}[yC, T, yFe, yCr, yNi, Mo, yMn], Mo] - yMnD[\text{GmBCC}[yC, T, yFe, yCr, yNi, yMo, Mn], Mn] - yVaD[\text{GmBCC}[yC, T, yFe, yCr, yNi, yMo, yMn], yVal] - yCD[\text{GmBCC}[C, T, yFe, yCr, yNi, yMo, yMn], C].\]

\[\{C -> yC, Fe -> yFe, Cr -> yCr, Ni -> yNi, Mo -> yMo, Mn -> yMn\} //. yVa -> 1 - yC\]

\[\text{Cfcc}[yC, T, yFe, yCr, yNi, yMo, yMn] = \text{Module}\{[C, D[\text{GmFCC}[C, T, yFe, yCr, yNi, yMo, yMn], C] - D[\text{GmFCC}[yC, T, yFe, yCr, yNi, yMo, yMn], yVal]/(1/3)\}.\]

\[\text{Cbcc}[yC, T, yFe, yCr, yNi, yMo, yMn] = \text{Module}\{[C, D[\text{GmBCC}[C, T, yFe, yCr, yNi, yMo, yMn], C] - D[\text{GmBCC}[yC, T, yFe, yCr, yNi, yMo, yMn], yVal]]\}.\]

Free Energy Changes

\[\text{\Delta Gfcc}[yC, T, yFe, yCr, yNi, yMo, yMn] = G0C[T] - G0C[T] - \text{Cfcc}[yC, T, yFe, yCr, yNi, yMo, yMn]\]

\[\text{\Delta Gbcc}[yC, T, yFe, yCr, yNi, yMo, yMn] = G0C[T] - G0C[T] - \text{Cbcc}[yC, T, yFe, yCr, yNi, yMo, yMn]\]

\[\text{\Delta GM7C3bcc}[yC, T, yFe, yCr, yNi, yMo, yMn] = \text{Module}\{[a, b, c, d, e, GmM7C3[yC, T, yFe, yCr, yNi, yMo, yMn] - 7(yFe \text{Febcc}[yC, T, yFe, yCr, yNi, yMo, yMn] + yCr \text{Crbcc}[yC, T, yFe, yCr, yNi, yMo, yMn]) + yNi \text{Nibcc}[yC, T, yFe, yCr, yNi, yMo, yMn]]\}.
\[
\text{\textit{\([\text{Delta}]\) GM3CBC}}(y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}) := \\
\text{Module}\{a, b, c, d, e\}, \text{GM3C}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] - 3(y_{Fe} [\text{Mu}]\text{Cbcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}]) + y_{Cr} [\text{Mu}]\text{Crbc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] + y_{Ni} [\text{Mu}]\text{Nibcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] + y_{Mo} [\text{Mu}]\text{Mobcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] - 3y_{Mn} [\text{Mu}]\text{Mnbcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}]) / \{a \rightarrow y_{Fe}, b \rightarrow y_{Cr}, c \rightarrow y_{Ni}, d \rightarrow y_{Mo}, e \rightarrow y_{Mn}\}
\]

\[
\text{\textit{\([\text{Delta}]\) GM23C6CBC}}(y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}) := \\
\text{Module}\{a, b, c, d, e\}, \text{GM23C6}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] - 23(y_{Fe} [\text{Mu}]\text{Fbcc}[y_C, T, a, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}]) + y_{Cr} [\text{Mu}]\text{Crbc}[y_C, T, y_{Fe}, b, y_{Ni}, y_{Mo}, y_{Mn}] + y_{Ni} [\text{Mu}]\text{Nibcc}[y_C, T, y_{Fe}, c, y_{Mo}, y_{Mn}] + y_{Mo} [\text{Mu}]\text{Mobcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, d, y_{Mn}] + y_{Mn} [\text{Mu}]\text{Mnbcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] / \{a \rightarrow y_{Fe}, b \rightarrow y_{Cr}, c \rightarrow y_{Ni}, d \rightarrow y_{Mo}, e \rightarrow y_{Mn}\}
\]

\[
\text{\textit{\([\text{Delta}]\) GM7C3FCC}}(y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}) := \\
\text{Module}\{a, b, c, d, e\}, \text{GM7C3}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] - 7(y_{Fe} [\text{Mu}]\text{Ffcc}[y_C, T, a, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}]) + y_{Cr} [\text{Mu}]\text{Crcc}[y_C, T, y_{Fe}, b, y_{Ni}, y_{Mo}, y_{Mn}] + y_{Ni} [\text{Mu}]\text{Nifcc}[y_C, T, y_{Fe}, y_{Cr}, c, y_{Mo}, y_{Mn}] + y_{Mo} [\text{Mu}]\text{Mofcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, d, y_{Mn}] + y_{Mn} [\text{Mu}]\text{Mncc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] / \{a \rightarrow y_{Fe}, b \rightarrow y_{Cr}, c \rightarrow y_{Ni}, d \rightarrow y_{Mo}, e \rightarrow y_{Mn}\}
\]

\[
\text{\textit{\([\text{Delta}]\) GM3C6FCC}}(y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}) := \\
\text{Module}\{a, b, c, d, e\}, \text{GM3C6}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] - 23(y_{Fe} [\text{Mu}]\text{Ffcc}[y_C, T, a, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}]) + y_{Cr} [\text{Mu}]\text{Crcc}[y_C, T, y_{Fe}, b, y_{Ni}, y_{Mo}, y_{Mn}] + y_{Ni} [\text{Mu}]\text{Nifcc}[y_C, T, y_{Fe}, y_{Cr}, c, y_{Mo}, y_{Mn}] + y_{Mo} [\text{Mu}]\text{Mofcc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, d, y_{Mn}] + y_{Mn} [\text{Mu}]\text{Mncc}[y_C, T, y_{Fe}, y_{Cr}, y_{Ni}, y_{Mo}, y_{Mn}] / \{a \rightarrow y_{Fe}, b \rightarrow y_{Cr}, c \rightarrow y_{Ni}, d \rightarrow y_{Mo}, e \rightarrow y_{Mn}\}
\]
, yFe, yNi, yMo, yMn] + yNi \[\text{Nifcc} \] [yC, T, yFe, yCr, c, yMo, yMn ] + yMo \[\text{Mofcc} \] [yC, T, yFe, yCr, yNi, d, yMo] + yMn \[\text{Mnfcc} \] [yC , T, yFe, yCr, yNi, yMo, e \] - 6 \[\text{Cfcc} \] [yC, T, yFe, yCr, yNi, yMo, yMn ]/. {a->yFe, b->yCr, c->yNi, d->yMo, e->yMn}
References


REFERENCES


