Prediction of Multicomponent Equilibrium Diagrams
PREDICTION OF MULTICOMPONENT EQUILIBRIUM DIAGRAMS

by

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A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree
Master of Engineering

McMaster University
April, 1978
TITLE: Prediction of Multicomponent Equilibrium Diagrams

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NUMBER OF PAGES: xi, 163
Abstract

Published standard free energy changes and activity data for iron and its binary and ternary alloys have been used to evaluate the general linear series (Wagner) expansion of the activity coefficient and these were employed in turn for the accurate thermodynamic determinations of the liquidus line and the field in steels with additions of Mn, Si, Ni, Cr, Mo, Cu; W, V, Nb and Co. Computer programs based on several derived analytic formulae were used to predict multicomponent constant composition and isothermal phase diagrams for total alloy additions up to 5 wt%.
Acknowledgements

The author is indebted to his supervisor, Dr. J.S. Kirkaldy, for suggesting the problems treated here and for his continuing guidance. The author also wishes to thank the staff and graduate students of the Department of Metallurgy and Materials Science for their advice and assistance.
TABLE OF CONTENTS

Chapter I

1.1 Review of Empirical Methods 1
1.2 Review of Approximate Thermodynamic Methods 4

Chapter II

Thermodynamic Analysis for Phase Boundaries in the Fe-C-X₁ System 5
II.1 Introduction 5
II.2 The Effect of Alloying Elements on the Phase Boundaries of the Fe-C System 5
II.3 The Effect of Alloying on the Carbide Equilibrium in the Fe-C System 10
II.4 Dependence of T₀ Temperature on Alloying 11

Chapter III

The Thermodynamic Data Set 14
III.1 Introduction 14
III.2 Free Energies: Thermodynamic Analysis 14
III.3 Free Energies: Particular Systems 18
A Fe-C 18
B Fe-Mn 22
C Fe-Si 25
D Fe-Ni 25
E Fe-Cr 25
F Fe-Mo 26
G Fe-Cu 27
H Fe-W 27
I Fe-V 28
J Fe-Nb 29
K Fe-Co 30
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>III.4</td>
<td>Interaction Coefficients</td>
<td>31</td>
</tr>
<tr>
<td>III.5</td>
<td>Partition Coefficients</td>
<td>37</td>
</tr>
<tr>
<td>III.6</td>
<td>Empirical Fe-C Phase Diagram</td>
<td>40</td>
</tr>
<tr>
<td>Chapter IV</td>
<td>Calculations, Discussion and Results</td>
<td>44</td>
</tr>
<tr>
<td>IV.1</td>
<td>Introduction</td>
<td>44</td>
</tr>
<tr>
<td>IV.2</td>
<td>Computer Calculations</td>
<td>44</td>
</tr>
<tr>
<td>IV.2.A</td>
<td>Constant Composition Sections of the Fe-C</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Phase Diagram</td>
<td></td>
</tr>
<tr>
<td>IV.2.B</td>
<td>Isothermal Ternary and Ternary-Constant</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>Composition Sections</td>
<td></td>
</tr>
<tr>
<td>IV.3</td>
<td>Results and Comparison with Experiment</td>
<td>54</td>
</tr>
<tr>
<td>IV.4</td>
<td>Discussion</td>
<td>94</td>
</tr>
<tr>
<td>Chapter V</td>
<td>Conclusions</td>
<td>105</td>
</tr>
<tr>
<td>Appendix I</td>
<td>Derivation of Temperature Deviation Formula</td>
<td>106</td>
</tr>
<tr>
<td>Appendix II</td>
<td>Derivation of Carilige Line Shift</td>
<td>110</td>
</tr>
<tr>
<td>Appendix III</td>
<td>Derivation of Isothermal Conversion Formula</td>
<td>117</td>
</tr>
<tr>
<td>Appendix IV</td>
<td>Program for Calculating Isothermal Phase</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>Diagrams</td>
<td></td>
</tr>
<tr>
<td>Appendix V</td>
<td>Program for Calculating Constant Composition</td>
<td>120</td>
</tr>
<tr>
<td>Sections to Fe-C Phase Diagram</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appendix VI</td>
<td>Program for Calculating Constant Composition</td>
<td>141</td>
</tr>
<tr>
<td>References</td>
<td>158</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Thermodynamic Functions of Iron and Carbon ( \frac{\text{cal}}{\text{mole}} )</td>
<td>21</td>
</tr>
<tr>
<td>II</td>
<td>( \Delta G_i^{\alpha \gamma} ) as Functions of Temperature</td>
<td>32</td>
</tr>
<tr>
<td>III</td>
<td>( \Delta G_i^{\alpha L} ) as Functions of Temperature</td>
<td>33</td>
</tr>
<tr>
<td>IV</td>
<td>( \Delta G_i^{\gamma L} ) as Functions of Temperature</td>
<td>34</td>
</tr>
<tr>
<td>V</td>
<td>( \epsilon_{ci}^L ) as Functions of Temperature</td>
<td>38</td>
</tr>
<tr>
<td>VI</td>
<td>( \epsilon_{ci}^Y ) as Functions of Temperature</td>
<td>39</td>
</tr>
<tr>
<td>VII</td>
<td>Partition Coefficients as Functions of Temperature</td>
<td>41</td>
</tr>
<tr>
<td>VIII</td>
<td>Analytic Formula for Fe-C Phase Diagram</td>
<td>42</td>
</tr>
<tr>
<td>IX</td>
<td>Fe-Ni-C at 973 K in wt.%</td>
<td>56</td>
</tr>
<tr>
<td>X</td>
<td>Fe-Ni-C at 1073 K in wt.%</td>
<td>58</td>
</tr>
<tr>
<td>XI</td>
<td>Fe-Ni-C at 1173 K in wt.%</td>
<td>60</td>
</tr>
<tr>
<td>XII</td>
<td>Fe-Cr-C at 1023 K in wt.%</td>
<td>68</td>
</tr>
<tr>
<td>XIII</td>
<td>Fe-Cr-C at 1073 K in wt.%</td>
<td>69</td>
</tr>
<tr>
<td>XIV</td>
<td>Fe-Cr-C at 1173 K in wt.%</td>
<td>71</td>
</tr>
<tr>
<td>XV</td>
<td>Fe-Cu-C at 1173 K in wt.%</td>
<td>73</td>
</tr>
<tr>
<td>XVI</td>
<td>Fe-Cu-C at 1073 K in wt.%</td>
<td>75</td>
</tr>
<tr>
<td>XVII</td>
<td>Fe-Cu-C at 1023 K in wt.%</td>
<td>77</td>
</tr>
<tr>
<td>XVIII</td>
<td>Fe-Mn-C at 1173 K in wt.%</td>
<td>79</td>
</tr>
<tr>
<td>XIX</td>
<td>Fe-Mn-C at 1073 K in wt.%</td>
<td>81</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Table XX</td>
<td>Fe-Mn-C at 1035 K in wt.%</td>
<td>83</td>
</tr>
<tr>
<td>Table XXI</td>
<td>Fe-Mn-C at 973 K in wt.%</td>
<td>85</td>
</tr>
<tr>
<td>Table XXII</td>
<td>Fe-Si-C at 1073 K in wt.%</td>
<td>87</td>
</tr>
<tr>
<td>Table XXIII</td>
<td>Fe-Si-C at 973 K in wt.%</td>
<td>89</td>
</tr>
<tr>
<td>Table XXIV</td>
<td>Fe-Cr-C at 1043 K in wt.%</td>
<td>91</td>
</tr>
<tr>
<td>Table XXV</td>
<td>Comparison of Partition Coefficients (mole fraction basis) for α/γ in Fe-C-Cr Systems (79)</td>
<td>92</td>
</tr>
<tr>
<td>Table XXVI</td>
<td>α/γ Partition Coefficient, K_{α/γ} = x^γ/x^α</td>
<td>93</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Figure 1</td>
<td>Schematic of $T_0$ temperature</td>
<td>13</td>
</tr>
<tr>
<td>Figure 2</td>
<td>Predicted versus measured $\alpha_3$ temperature for a set of low alloy steels. Steels identified in reference (28)</td>
<td>23</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Predicted versus measured $\alpha_3$ temperature for a set of low alloy steels. Steels identified in reference (28)</td>
<td>24</td>
</tr>
<tr>
<td>Figure 4</td>
<td>The Fe-C phase diagram according to reference (20)</td>
<td>43</td>
</tr>
<tr>
<td>Figure 5</td>
<td>Schematic of an Fe-C-X liquidus and solidus</td>
<td>45</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Set of constant Cr sections through the Fe-C$_2$Cr phase diagram</td>
<td>47</td>
</tr>
<tr>
<td>Figure 7</td>
<td>Set of constant Mo sections through the Fe-C-Mo phase diagram</td>
<td>48</td>
</tr>
<tr>
<td>Figure 8</td>
<td>Set of constant Ni sections through the Fe-C-Ni phase diagram</td>
<td>49</td>
</tr>
<tr>
<td>Figure 9</td>
<td>Set of constant In sections through the Fe-C-In phase diagram</td>
<td>50</td>
</tr>
<tr>
<td>Figure 10</td>
<td>Fe-Cr ternary phase diagram for 1025±5 K</td>
<td>52</td>
</tr>
<tr>
<td>Figure 11</td>
<td>Fe-Ni-C system at 973 K</td>
<td>55</td>
</tr>
<tr>
<td>Figure 12</td>
<td>Fe-Ni-C system at 1073 K</td>
<td>57</td>
</tr>
<tr>
<td>Figure 13</td>
<td>Fe-Ni-C at 1173 K</td>
<td>59</td>
</tr>
<tr>
<td>Figure 14</td>
<td>Predicted $\alpha_3$ versus $\alpha_3$ and $\gamma_3$ temperature for low alloy steels. Steels identified in reference (28).</td>
<td>61a</td>
</tr>
<tr>
<td>Figure 15</td>
<td>Comparison of the Fe-Cu-C system at 1023 K with that of Uhrenius (80)</td>
<td>63</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Figure 16</td>
<td>Fe-Cr-C system at 1028 K with the experimental points of Sharma (79)</td>
<td>65</td>
</tr>
<tr>
<td>Figure 17</td>
<td>Fe-Cr-C system at 1043 K with the experimental points of Sharma (79)</td>
<td>66</td>
</tr>
<tr>
<td>Figure 18</td>
<td>Fe-Cr-C system at 1023 K</td>
<td>67</td>
</tr>
<tr>
<td>Figure 19</td>
<td>Fe-Cr-C system at 1073 K</td>
<td>68a</td>
</tr>
<tr>
<td>Figure 20</td>
<td>Fe-Cr-C system at 1173 K</td>
<td>70</td>
</tr>
<tr>
<td>Figure 21</td>
<td>Fe-Cu-C system at 1173 K</td>
<td>72</td>
</tr>
<tr>
<td>Figure 22</td>
<td>Fe-Cu-C system at 1073 K</td>
<td>74</td>
</tr>
<tr>
<td>Figure 23</td>
<td>Fe-Cu-C system at 1023 K</td>
<td>76</td>
</tr>
<tr>
<td>Figure 24</td>
<td>Fe-Mn-C system at 1173 K</td>
<td>78</td>
</tr>
<tr>
<td>Figure 25</td>
<td>Fe-Mn-C system at 1073 K</td>
<td>80</td>
</tr>
<tr>
<td>Figure 26</td>
<td>Fe-Mn-C system at 1035 K</td>
<td>82</td>
</tr>
<tr>
<td>Figure 27</td>
<td>Fe-Mn-C system at 973 K</td>
<td>84</td>
</tr>
<tr>
<td>Figure 28</td>
<td>Fe-Si-C system at 1073 K</td>
<td>85</td>
</tr>
<tr>
<td>Figure 29</td>
<td>Fe-Si-C system at 973 K</td>
<td>86</td>
</tr>
<tr>
<td>Figure 30</td>
<td>Fe-Cr-C system at 1043 K</td>
<td>90</td>
</tr>
<tr>
<td>Figure 31</td>
<td>Comparison of predicted and observed variations in the eutectoid temperature and composition with additions of Cr. Experimental points after Sharma (79) +, and Ralik et al. (80).</td>
<td>96</td>
</tr>
<tr>
<td>Figure 32</td>
<td>Comparison of predicted and observed variations in the eutectoid temperature and composition with additions of Mn, Si, Ni and Cr. Single points were taken from Bain's experimental curves (91).</td>
<td>96</td>
</tr>
<tr>
<td>Figure 33</td>
<td>Fe-1.0 Mo - 1.0 Cr-C constant composition section</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 34  Fe-Cr-C-1.0 Mo isothermal phase diagram at 1100 K  

Figure 35  Fe-Mo-C-1.0 Cr isothermal phase diagram at 1100 K  

Figure 36  Fe-Cr-C-1.0 Mo isothermal phase diagram at 1000 K  

Figure 37  Fe-Mo-C-1.0 Cr isothermal phase diagram at 1000 K  

Figure 38  Schematic of deviation of $\text{Ae}_3$ and carbide lines with addition of alloying elements  

Figure 39  Schematic of multicomponent eutectoid intersection
CHAPTER I

INTRODUCTION

For more than a century studies have been undertaken to characterize the important transformation parameters for steels. Due to the large number of components that are added to or are naturally found in steel, this is a very complex task.

In this chapter the old empirical methods for determining the transformation temperatures are reviewed. The chapter also contains a brief review of the early approximate thermodynamic formulae.

1.1 Review of Empirical Methods

Since most of the metallurgically important transformations in steel occur at austenitising temperatures and below, the bulk of the work undertaken on the phase diagrams and transformation temperatures in the Fe-C-X and Fe-X systems is found in this range.

The important quantities that one finds discussed in the literature are: the $A_{c3}$ temperature or the temperature under equilibrium conditions at which austenite (f.c.c. iron) begins to decompose to ferrite (b.c.c. iron); the $A_{c1}$ temperature or the temperature at which the apparent transformation occurs on heating; the $A_{r1}$ temperature or the temperature
of the apparent transformation on cooling. The latter two transition
temperatures are normally dilatometrically determined and can vary
widely with heating and cooling rates. The $Ae_3$ temperature is very
difficult to measure accurately because of the slow heating rates and
long times involved to ensure equilibrium.

The majority of efforts at predicting these temperatures have
taken the form of empirical relations derived via regression analysis of
the steel compositions versus the determined temperature. All of these
formulae assume linear terms:

$$Ae_3(Ac_3) = \text{constant} + \sum_{i=1}^{n} a_i w_i$$

with constant coefficients to be sufficient. Baganis (1) has shown by
thermodynamic analysis that this constancy assumption is inadequate in the
ranges over which these relations are employed.

The best known and most widely used empirical formulae are:

(1) Andrews' (2) Formula:

$$Ac_3(\degree C) = 910 - 230\sqrt{C} - 15.2 \text{Ni} + 44.7 \text{Si} + 104 \text{V} + 31.5 \text{Mo} +$$
$$131 \text{W} - 30 \text{Mn} - 11 \text{Cr} - 20 \text{Cu} + 700 \text{P}$$

This was derived from 155 steels over the composition range up
to 0.6% C, 5% Cr, 5% Ni, 5.4% Mo and 4% V.
(2) Kunitake and Ohtani's (3) Formula:

\[ \text{Ac}_3(\text{C}) = 881 - 200 \text{C} + 53.1 \text{Si} - 15 \text{Mn} - 20.1 \text{Ni} - 0.7 \text{Cr} - 26.5 \text{Cu} + 41.1 \text{Mo} \]

This was derived from 85 steels and assumed valid up to 1.70% Cr, 1.05% Mo, 0.98% Cu, 3.09% Ni and in the ranges 0.10 to 0.55% C, 0.30 to 1.67% Mn and 0.13 to 1.68% Si.

(3) Grange's (4) Formula:

\[ \text{Ae}_3(\text{C}) = 854 - 179 \text{C} - 14 \text{Mn} + 22 \text{Si} - 15 \text{Ni} - 23 \text{Cr} \]

derived from careful determinations of 19 steels in the composition range 0.35 to 0.63% C, 0.37 to 1.85% Mn, 0.15 to 0.30% Si, and up to 3.41% Ni, 0.93% Cr and 0.23% Mo.

(4) Andrews' (5) Formula:

\[ \text{Ae}_3(\text{C}) = 913 - \Delta T - 25 \text{Mn} - 11 \text{Cr} - 20 \text{Cu} + 60 \text{Si} + 60 \text{Mo} + 40 \text{W} + 100 \text{V} + 70 \text{P} \]

derived from the results of Grange (4) in conjunction with the binary Fe-X phase diagrams. \( \Delta T \) accounts for the undercooling due to C and Ni where:

\[ \text{C}_{\text{effective}} = C + \frac{\text{Ni}}{10} \]
I.2 Approximate Thermodynamic Formulae

Since the available empirical linear regression formulae give varying results for the same steel composition and have limited ranges of application it was evident that some of the alloy effects could not be treated using a linear formula and that more fundamental thermodynamic data should be used for an adequate quantitative treatment.

The necessary form of the thermodynamic analysis began with Wever (5,6,7) who classified the binary Fe-X phase diagrams by type. This work was built upon by Zener (8) who expressed the thermodynamic quantities (such as free energy) in a form similar to that in use today. Zener's analysis was modified by Andrews (2) to try to predict the effect of alloying elements on the \(\text{A}_\text{g}^3\) temperature.

The lack of good thermodynamic data and the cumbersome calculations involved in these early methods resulted in poor acceptance and inadequate quantitative results.
CHAPTER II
THERMODYNAMIC ANALYSIS FOR PHASE BOUNDARIES IN
THE Fe-C-X₁ SYSTEM

II.1 Introduction

If the thermodynamic data were available, it was thought that
it would be possible to predict the effect of adding alloying elements
to steel by describing their effect on the Fe-C binary phase diagram.
This chapter outlines such an analysis which is applicable to all the
phases which are present in the binary Fe-C system.

II.2 The Effect of Alloying Elements on the Phase Boundaries of
the Fe-C System

In this section is described a rigorous procedure for predicting
dilute two phase regions similar to that of Baganis and Kirkaldy (9) for
the deviation of the Ać₃ temperature of steels from Fe-C binary values.

If any two phases are in equilibrium at any temperature, T,
then the partial molar free energies or chemical potentials of the
alloying elements and the solvent are equal in the two phases. Analytically
we have:
\[ \tilde{G}_i^\gamma = \tilde{G}_i^\alpha \]
\[ \tilde{G}_i^\delta = \tilde{G}_i^\gamma \]
\[ \tilde{G}_i^L = \tilde{G}_i^\delta \]
\[ \tilde{G}_i^L = \tilde{G}_i \]

(II-1)

For the various equilibria in steel where \( \tilde{G}_i^\phi \) is the partial molar free energy of element \( i \) in the phase \( \phi \) and \( \phi \) is delta iron (b.c.c.), gamma iron (f.c.c.), alpha iron (b.c.c.) or the liquid state. This latter quantity can be rewritten:

\[ \tilde{G}_i^\phi = \tilde{G}_i^\phi + RT \ln a_i^\phi \]

(II-2)

where \( \tilde{G}_i^\phi \) is the standard free energy and \( a_i \) is the activity of component \( i \) in phase \( \phi \) or alternatively:

\[ \tilde{G}_i^\phi = \tilde{G}_i^\phi + RT (\ln x_i^\phi + \ln \gamma_i^\phi) \]

(II-3)

where \( x_i^\phi \) is the mole fraction and \( \gamma_i^\phi \) the activity coefficient. This relation can also be expressed in terms of an ideal solution contribution and an excess free energy term to account for the observed departure from ideality:

\[ \tilde{G}_i^\phi = \tilde{G}_i^\phi + RT \ln x_i^\phi + \Delta G_i^\phi \]

(II-4)

Wagner (10) recognized that the excess free energy can be described by a Taylor expansion in the solute concentrations about \( x_o = 1 \) (pure solvent, infinitely dilute solutes), viz.,
\[ \ln \gamma_i = \ln \gamma_i^0 + \left[ x_i \left( \frac{\partial \ln \gamma_i}{\partial x_i} \right) \text{all } x_k = 0 \right] + x_j \left( \frac{\partial \ln \gamma_i}{\partial x_j} \right) \text{all } x_k = 0 + \ldots \]  

(II-5)

It is usual to define the standard states of all solutes at infinite dilution and to introduce the coefficients:

\[ \epsilon_{ii} = \left( \frac{\partial \ln \gamma_i}{\partial x_i} \right) \text{all } x_k = 0 \]  

(II-6)

\[ \epsilon_{ij} = \left( \frac{\partial \ln \gamma_i}{\partial x_j} \right) \text{all } x_k = 0 \]  

(II-7)

evaluated at infinite dilution. These are often called Wagner interaction coefficients. The magnitude and sign of these quantities expresses the attractive or repulsive forces between atoms of element \( i \) or \( j \) in solvent iron. Further simplification is allowed by the symmetry properties of the interaction parameter (10):

\[ \epsilon_{ij} = \epsilon_{ji} \]  

(II-8)

Kirkaldy and Purdy (94) and De Brion (95) have applied the Gibbs-Duhem to this expansion at infinite dilution to obtain the corresponding relation for the solvent:

\[ \ln \gamma_o = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{p} \epsilon_{ij} \phi_i \phi_j \]  

(II-9)
It is now possible to evaluate the equality of chemical potentials (equation (II-1)) to yield the expressions (rigorous up to linear terms in the solute concentrations) for any two phases, 1 and 2:

\[ \frac{o_{G_i}^1 - o_{G_i}^2}{RT} = \ln \frac{x_i}{x_i}, \quad \frac{1}{y_i}, \quad \frac{1}{y_i} \quad (II-10) \]

or:

or finally:

\[ \frac{\Delta o_{G_i}^{2+1}}{RT} = \ln \frac{x_i}{x_i} + \frac{1}{x_i} + \frac{n}{j=1} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{x_i}^{x_i} \frac{x_i}{x_i} x_i x_j i x_j i j i j x_i x_j \quad (II-12) \]

and:

\[ \frac{\Delta o_{G_i}^{2+1}}{RT} = \ln \frac{x_i}{x_i} + \frac{1}{x_i} + \frac{n}{j=1} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{x_i}^{x_i} \frac{x_i}{x_i} x_i x_j i x_j i j x_i x_j \quad (II-13) \]

\( \Delta o_{G_i}^{2+1} \) is the shorthand notation of the standard free energy change for the transformation from phase 1 to phase 2 at equilibrium, viz.,

\[ \Delta o_{G_i}^{2+1} = o_{G_i}^1 - o_{G_i}^2 \quad (II-14) \]

Neglecting the cross interaction terms between alloying elements other than carbon since these ultimately appear in a higher order, one obtains for the transformation from \( \gamma \) to \( L \):
\[ \frac{\Delta^0_{G}^{Y-L}}{RT} = \ln \left[ \frac{1 - x_1^{Y}}{1 - x_1^{L}} \right] - x_1^{Y} \frac{\varepsilon L}{2} x_1^{L} + x_1^{L} \frac{\varepsilon L}{2} x_1^{L} - \varepsilon \frac{(x_1^{Y})^2}{2} \]
\[ + \varepsilon \frac{1}{11} (x_1^{L})^2 \]  
(II-15)

\[ \frac{\Delta^0_{G}^{Y-L}}{RT} = \ln \left[ \frac{x_1^{Y}}{x_1^{L}} \right] + \varepsilon \frac{x_1^{Y}}{11} x_1^{L} - \varepsilon \frac{x_1^{L}}{11} x_1^{L} \quad \text{For carbon (n=1)} \]  
(II-16)

\[ \frac{\Delta^0_{G}^{Y-L}}{RT} = \ln \left[ \frac{x_i^{Y}}{x_i^{L}} \right] + \varepsilon \frac{x_i^{Y}}{11} x_i^{L} - \varepsilon \frac{x_i^{L}}{11} x_i^{L} \quad \text{For component } i, \ i=2,11 \]  
(II-17)

Utilizing, in the linearization of this set of eleven equations, the partition coefficient of component \( i \) in any two phases:

\[ k_i = \frac{x_i^{Y}}{x_i^{L}} = \frac{\frac{\Delta^0_{G}^{Y-L}}{RT} + \varepsilon \frac{x_i^{L}}{11} x_i^{L}}{1 + \varepsilon \frac{x_i^{Y}}{11} x_i^{L} \exp \left[ -\frac{\Delta^0_{G}^{Y-L}}{RT} \right]} \]  
(II-18)

it is possible to arrive at an analytic formula for the temperature change from the binary iron-carbon phase diagram with the addition of alloying elements that is rigorous up to the linear terms in the solute concentrations:

\[ \Delta T = RT \sum_{i=2}^{11} A_i x_i^{L} \]  
(II-19)
where
\[ A_i = \frac{\left[ 1 + x_1^L + (1 - x_1^L)(e^{L_{11}} - e^{L_{11}}) \right] \exp \left( \frac{\Delta^{G_o} (x_1^L)}{RT_o} \right) \left( e^{L_{11}} - e^{L_{11}} \right)}{x_1^{L-o} (1 - x_1^L) \Delta^{H_o} \exp \left( \frac{\Delta^{G_o} (x_1^L)}{RT_o} \right)} \]

The full derivation is given in Appendix (1).

11.3 The Effect of Alloying on the Carbide Equilibrium in the Fe-C System

Although studies of the \( \delta \rightarrow \gamma \), \( \gamma \rightarrow \delta \), and \( \gamma \rightarrow \) transformations in the binary and ternary systems provide sufficient experimental information on the respective free energies to support evaluation in the above manner, the carbide phase equilibria do not. As a consequence, it became necessary to derive another form of the above equation so as to utilize the experimental partition coefficient information available.

Starting with the Gibbs-Duhem equation for any two phases, 1 and 2, at constant temperature and pressure, where phase 1 is the metal and phase 2 the carbide one obtains:

\[ x_1^{L-o} d \mu_o + x_1^{L} d \mu_1 + \frac{n}{2} x_1^{L} d \phi_1 = 0 \]  
\[ (I1-20) \]

\[ x_1^{L-o} d \mu_o + x_1^{L} d \mu_1 + \frac{n}{2} x_1^{L} d \phi_1 = 0 \]  
\[ (I1-21) \]

From these relations one obtains, using the Wagner expansion and expanding about the empirical binary iron-carbon phase diagram, the expression for the change in carbon content of the metal-carbide phase boundary at any temperature, \( T \):
\[ \Delta x_1 = \frac{-x_1^n \sum_{i=2}^n x_i (k_i - 1 + (1+c_{1i})(x_i^c-x_1^c))}{x_1^2 + x_1^c ((x_1^c-x_1^c)(1+c_{1i})-1)} \]  

(II-22)

where the partition coefficient, \( k = \frac{x_1}{x_1^c} \) and \( x_1^c \) is the composition of carbon, in mole fraction of the binary Fe-C metal/carbide phase boundary. The full derivation is given in Appendix (II).

II.4 Dependence of T_0 Temperature on Alloying

The method used to determine the analytic expression for the temperature deviation of the phase boundary can be extended for use in determining the change in the T_0 temperature with alloy additions. This temperature is defined in Figure (1) according to the requirement that the integral free energy curves of the two phases present at equilibrium intersect. This corresponds to the conditions:

\[ G_i^I = G_i^{II} \]  

(II-23)

\[ x_1^I = x_1^{II} \]  

(II-24)

where I and II refer to phases I and phase II respectively. Using this equality of free energies and expanding about the Fe-C binary phase diagram one obtains the following expression for the T_0 temperature of an iron-carbon alloy with dilute additions of other elements:

\[ T_{0,\text{alloy}} = T_{0,\text{Fe-C}} \left( 1 + \frac{1}{R(T_{0,\text{Fe-C}})^2} \right)^n \sum_{\substack{i=1 \text{ to } n \text{ (II-25)}}}^n \left( \frac{x_i^{I_0} - x_i^{II_0}}{x_i^{I_0} - x_i^{II_0}} \right) \left( \frac{x_i^{I_0} - x_i^{II_0}}{x_i^{I_0} - x_i^{II_0}} \right) \]
The full derivation of this formula is to be found in Appendix (III).
Figure 1  Schematic of $T_0$ temperature.
CHAPTER III

THE THERMODYNAMIC DATA SET

III.1 Introduction

Although it is a relatively simple matter to derive thermodynamic equations to describe phase diagrams, it is much more difficult to obtain the thermodynamic quantities necessary to use them.

In this chapter, the free energy and interaction parameter data necessary for the utilization of our formulae are summarized and reviewed. Since it was not always possible to find information in the exact form required, it was sometimes necessary to obtain a method of conversion. The major conversion methods and their thermodynamic background are also included in order to give a comprehensive idea of the problems encountered (and their solutions) when this type of search for data is attempted.

III.2 Free Energies: Thermodynamic Analysis

Since free energy data referred to a standard state at infinite dilution was not available for all of the transformations in all of the binary Fe-X systems encompassed by this study, it was necessary to convert some free energy information in the literature from the pure component
or one weight percent standard states to the infinite dilution or Henrian standard state. In other cases it was necessary to estimate the free energy from the experimental iron binary phase diagrams.

As in Chapter II the Wagner interaction parameter formalism in conjunction with the equality of chemical potentials was used as a basis for the thermodynamic analysis of binary phase diagrams, viz.,

$$\frac{\Delta G_{i}^{1\rightarrow2}}{RT} = \ln \frac{x_i^1}{x_i^2} + \ln \frac{y_i^1}{y_i^2}$$  \hspace{1cm} (III-1)

which by Taylor expansion of \(\ln y_i\) yields:

$$\frac{\Delta G_{i}^{2} - \Delta G_{i}^{1}}{RT} = \ln \frac{x_i^1}{x_i^2} + \epsilon_{ii}^1 x_i^1 - \epsilon_{ii}^2 x_i^2$$ \hspace{1cm} (III-2)

where component \(i\) is the solute and \(\ln y_i^0 \rightarrow 0\) as \(\gamma^0 \rightarrow 1\) in the limit of infinite dilution.

The decision as to whether or not this form or the Henrian approximation to it \(\epsilon_{ii} = 0\) would be used depended upon the reliability of the phase diagram and the size of the interaction parameters in each phase at temperature. This procedure of fitting experimental phase boundary points to the equation and solving for \(\Delta G_{i}^{1\rightarrow2}\) as a function of temperature was employed for the \(\alpha\rightarrow\gamma\) transformation in Fe-Co and the \(\alpha\rightarrowL\) transformations in the Fe-Si, Fe-Nb and Fe-V systems.

Often the free energies available were expressed in terms of a pure component standard state, e.g., all that data compiled for use
with the thermodynamic model developed by Hillert (10) and coworkers. In the Hillert model the molar free energy is expressed in the form:

\[ G_M = \sum_i^n x_i \, \delta G_i + RT \sum_i^n x_i \ln x_i \] + \( E_G \) \hspace{2cm} (III-3)

where \( \delta G_i \) is for the pure component. By applying the equality of chemical potentials and employing the rule (11):

\[ \frac{\Delta G}{\Delta N} = \sum_j x_j \left[ \frac{\partial \Delta G}{\partial x_j} \right]_{x_k} \] + \( \frac{\partial \Delta G}{\partial x_i} \) \hspace{2cm} (III-4)

where \( x_k \) indicates that the ratios between other components are kept constant and \( \Delta G_i \) is the free energy of component \( i \) at infinite dilution, \( \Delta G_M \) being the free energy for the pure component, substitution yields:

\[ \Delta G_{i,j}^{1/2} \text{ (inf. dil.)} = \sum_k \delta G_i \text{ (pure . . . pure)} + \ln \frac{1}{1-x_i} \] \hspace{2cm} (III-5)

The temperature, \( T \), is in degrees Kelvin and the free energies are expressed in cal/mole.

If the excess free energy term in equation (III-5) is expressed as a polynomial of the form (11):

\[ E_G = \frac{1}{2} \sum_{i,j} A_{ij} x_i x_j = \frac{1}{2} \sum_{i,j} A_{ij} x_i (1-x_i) \] \hspace{2cm} (III-6)

for the binary \( i-j \) system in phase 1, this can be transformed, using
equation (III-4) to

\[ E_{G_i}^1 = A_{ij}^1 (1-x_i^1)^2 \]  \hspace{1cm} (III-7)

for solvent i. This excess free energy, referenced to the pure component can now be compared with that for the infinite dilution standard state:

\[ E_{G_i}^1 = RT \ln \gamma_i^1 \]  \hspace{1cm} (III-8)

\[ E_{G_i}^1 = RT \ln \gamma_i^{01} + RT \mathcal{E}_{ij}^1 x_i^1 \]  \hspace{1cm} (III-9)

From the comparison of equations (III-7) and (III-9) as \( x_i \to 0 \) it can be seen that:

\[ \ln \gamma_i^{01} = \frac{A_{ij}}{RT} \]  \hspace{1cm} (III-10)

Substitution back into equation (III-5) gives the transformation necessary to change standard states as a function of the regular solution parameters defined for this model, viz.,

\[ \Delta G_i^{1 \rightarrow 2} \text{ (inf.dil)} = \Delta G_i^{1 \rightarrow 2} \text{ (pure comp.)} - A_{ij}^1 + A_{ij}^2 \]  \hspace{1cm} (III-11)

where \( A_{ij}^1 \) and \( A_{ij}^2 \) are the regular solution parameters in phase 1 and 2 respectively.

This type of analysis was used for the α→L transformations of the Fe-Mo, Fe-Mn and Fe-W as well as the α→γ transformations for the Fe-W, Fe-Mo, Fe-Cr and Fe-Mn systems.
The information from the data set of Elliott et al. (12) which was used for comparison purposes had to be transformed from common logarithms and the one weight percent (1 wt.pct.) standard state. For this purpose, the transformation formula given by Gaskell (13) was used. This is:

\[
\Delta G^\circ_{12} \left( \text{inf.dil.} \rightarrow 1 \text{ wt.pct.} \right) = RT \ln \left( \frac{100 \ \text{wt.pct.}}{1 \text{ wt.pct.}} \right)
\]

(III-12)

where \( j \) is the solvent, \( i \) is the solute and \( MW \) is the molecular weight of component \( i \) or \( j \).

III.3 Free Energies: Particular Systems

III.3.2 Fe-C

The free energy change for the \( \alpha \rightarrow \gamma \) transition in iron carbon was critically analysed by Harvig (14) using the model of Hillert and Staffansson (11) and the free energy difference for \( \alpha \rightarrow Fe \) and \( \gamma \rightarrow Fe \) determined by Orr and Chipman (15) and confirmed by Wada et al. (16). The transformed values of \( \Delta G^\circ_{\alpha \rightarrow \gamma} \) are shown in Table (I), from 900 to 1820 K. The values from 1800 K to 1820 K were determined by interpolation. The free energy for the \( \gamma \rightarrow \delta \) transition was obtained by assuming:

\[
\Delta G^\circ_{\gamma \rightarrow \delta} = - \Delta G^\circ_{\alpha \rightarrow \gamma}
\]

(III-13)

since the \( \alpha \) and \( \delta \) phases both have a body centred cubic structure.

The free energy for the \( \alpha \rightarrow L \) transformation was derived from the tabulated values of \( \Delta G^\circ_{\alpha \rightarrow \gamma} \) and the experimental value for \( \Delta G^\circ_{\gamma \rightarrow L} \) of Orr
and Chipman (15). Both are tabulated from 1600 to 1800 K in Table (1). Utilizing the carbon free energy for α→γ from Harvig (14), referenced to graphite:

\[
\Delta G^\gamma - \Delta G^\alpha = 11030 - 4.594T \text{ cal/mole} \quad (III-14)
\]

\[
\Delta G^\alpha - \Delta G^\gamma = 15670 - 5.692 \text{ cal/mole} \quad (III-15)
\]

the free energy change at infinite dilution due to Sharma and Kirkaldy (17):

\[
\Delta G^\gamma - \Delta G^\alpha = -15323 + 7.686T \text{ cal/mole} \quad (III-16)
\]

and the values for the dissolution of graphite in liquid iron due to Sigworth and Elliott (18) and J. Chipman (19), (C(gr.) + C(inf. dil. in Fe)):

\[
\Delta G_{1}^{\gamma \rightarrow \alpha} = 5400 - 4.0T \text{ cal/mole} \quad (III-17)
\]

one obtains by rearrangement:

\[
\Delta G_{1}^{\alpha \rightarrow L} = -21300 + 6.3T \text{ cal/mole} \quad (III-18)
\]

\[
\Delta G_{1}^{\gamma \rightarrow H} = -5830 + 0.6T \text{ cal/mole} \quad (III-19)
\]

which are consistent with the Fe-C liquidus of Benz and Elliott (20).

The enthalpy values, when unrecorded, were obtained by differentiating the analytic free energy functions:

\[
\Delta H = \Delta G - T\left(\frac{\partial \Delta G}{\partial T}\right) \quad (III-20)
\]
All of the enthalpies concerning carbon were obtained in this fashion. \( \Delta H_0^{\alpha} \gamma \) was fitted in the temperature range 1000 K to 1184 K by Baganis and Kirkaldy (9) and the \( \Delta H_0^{\alpha} \gamma \) determined by this method is:

\[
\Delta H_0^{\alpha} \gamma = \Delta H_0^{\alpha} \gamma + T(0.79 - 0.00461[T-1000])^{0.96} + 0.058 \cos(0.034[T-1000])
\]

(III-21)

Fischer et al. (21) report:

\[
\Delta H_0^{\alpha} \gamma = -0.81T + 1183 \text{ cal/mole}
\]

(III-22)

in the range 1184 K to 1165 K and this agrees favorably with the preceding formula at 1184 K. For temperatures of 900 K to 1000 K, the enthalpy was assumed to be independent of temperature, the value adopted being that at 1000 K from the Baganis and Kirkaldy formula.

The experimental \( \Delta H_0^{\alpha} \gamma \gamma \) shows a wide scatter. Dence and Kubaschewski (22) found 260 cal/mole. Ferrier and Olette (23) reported 263 cal/mole and this was corrected by Orr and Chipman (15) to 192 cal/mole. The value adopted here was 200 cal/mole, independent of temperature.

Values for \( \Delta H_0^{\delta+L} \) have been reported by Ferrier and Olette (23) who found 3292 \( \pm \) 80 cal/mole, Morris et al. (24) who found 5298 \( \pm \) 100 cal/mole and Vollmer et al. (25) who report 3435 \( \pm \) 50 cal/mole, all at 1809 K. The value chosen was 3300 cal/mole, independent of temperature.

The value of \( \Delta H_0^{\gamma+L} \) obtained by subtraction is about 3500 cal/mole at 1809 K. The enthalpy values for iron and carbon are listed in Table (I).
Table I. Thermodynamic Functions of Iron and Carbon (\text{cal/mole})

<table>
<thead>
<tr>
<th>T(K)</th>
<th>(\Delta G^{\alpha\rightarrow\gamma})</th>
<th>T(K)</th>
<th>(\Delta G^{\alpha\rightarrow\gamma})</th>
<th>(\Delta G^{\delta\rightarrow\text{L}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>191.1</td>
<td>1500</td>
<td>-13.95</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>80.80</td>
<td>1600</td>
<td>-7.20</td>
<td>387.8</td>
</tr>
<tr>
<td>1100</td>
<td>22.22</td>
<td>1700</td>
<td>4.08</td>
<td>195.4</td>
</tr>
<tr>
<td>1200</td>
<td>-2.40</td>
<td>1800</td>
<td>19.98</td>
<td>16.00</td>
</tr>
<tr>
<td>1300</td>
<td>-12.87</td>
<td>1820</td>
<td>23.32</td>
<td>-7.34</td>
</tr>
<tr>
<td>1400</td>
<td>-16.10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\Delta^0 G^{\alpha\rightarrow\gamma} & \quad \text{Tabulated} \\
\Delta^0 H^{\alpha\rightarrow\gamma} & = -0.81T + 692 \\
\Delta^0 G^{\delta\rightarrow\gamma} & \quad \text{Tabulated} \\
\Delta^0 H^{Y\rightarrow\gamma} & = 200 \\
\Delta^0 G^{\delta\rightarrow\text{L}} & = -2646 + 39.1693T - 5.277T \ln T + 0.001T^2 \\
\Delta^0 H^{Y\rightarrow\text{L}} & = 3600 \\
\Delta^0 G^{\delta\rightarrow\text{L}} & = \Delta^0 G^{Y\rightarrow\text{L}} - \Delta^0 G^{\alpha\rightarrow\gamma} \\
\Delta^0 H^{\delta\rightarrow\text{L}} & = 3300
\end{align*}
\]

*\(\Delta^0 H_1 = \Delta^0 G_1 - T \frac{\partial \Delta^0 G_1}{\partial T}\)
III.3.B Fe-Mn

Virtually all the work done on the α→γ transformation in this system was based on the binary phase diagram of Troiano and McGuire (26) which contained no experimental points on the phase boundaries or in the two-phase region. The only true-equilibrium point in this system is that of Kirchner et al. (27) on the α/α+γ phase boundary at 0.015 mole fraction manganese and 1075 K. Utilizing this point and the $A^\alpha - A^\gamma$ temperature dependence of Kirchner et al., the free energy of Baganis and Kirkaldy was corrected in an attempt to produce a $\Delta^0G^\alpha_{2γ}$ that would behave correctly out to 2 w/o Mn.

Plots of predicted $A_3$ temperatures versus the experimentally determined values for selected steels (from reference (28)), Figures 2 and 3, show a marked systematic deviation from expected behaviour at lower carbon and higher manganese contents. This was traced back to the uncertainty in the binary phase diagram.

From the experimental phase diagram of Hellawell and Hume-Rothery (29), Kirchner et al. and Hillert and Staffansson (30) demonstrated that it was not possible to extend the $\Delta^0G^\alpha_{2γ}$ obtained for the $A_3$ temperature range up into the $γ→δ$ transformation because of the non-linear nature of the regular solution parameters over this range of temperature. $\Delta^0G^\alpha_{2L}$ and $\Delta^0G^\gamma_δ$ were taken from reference (30) and converted to the infinite dilution standard state using the regular solution parameters suitable to the temperature ranges from references (27) and (30). The values obtained are similar to those reported by Sigworth and
Figure 2. Predicted versus measured $Ae_3$ temperature for a set of low-alloy steels. Steels identified in reference (28).
Figure 3  Predicted versus measured $A_{eq}$ temperature for a set of low alloy steels. Steels identified in reference (28).
Elliott (18). \( \Delta^0 G^\gamma\rightarrow L \) was deduced by subtraction.

III.3.C Fe-Si

The free energy and regular solution parameters determined by Fridberg and Harvig (32) allowed the calculation of a \( \Delta^0 G^\alpha\rightarrow \gamma \) value at infinite dilution which reproduces the gamma loop of the Fe-Si phase diagram of Übelacker (31) up to 1.8 w/o Si.

Since there was insufficient reliable data on \( \Delta^0 G^\gamma\rightarrow L \) at infinite dilution this value was deduced by thermodynamic analysis of the phase diagram of Übelacker in the range 0 to 4 w/o Si. The solidus and liquidus are essentially linear out to this point and assumptions of both ideal solution and regular solution behaviour produced similar results. \( \Delta^0 G^\gamma\rightarrow L \) was obtained by subtraction.

III.3.D Fe-Ni

The \( \alpha \rightarrow \gamma \) transition was studied by Summa and Kinzle (17) whose results were adopted and extended up to 1800 K. For the \( \gamma \rightarrow \delta \) transformation \( \Delta^0 G^\gamma\rightarrow L \) was a combination of Sigworth and Elliott's results and those of Kaufman and Nesor (33). Since Kaufman and Nesor reported a value for the \( L \rightarrow f.c.c. \) transformation in pure nickel it was possible to obtain independent results for the \( \alpha \rightarrow L \) and \( \gamma \rightarrow L \) transitions.

III.3.E Fe-Cr

The free energy for the \( \alpha \rightarrow \gamma \) transformation was first suggested by Kaufman (34) and used by Kirchner et al. (27) who reported the necessary
regular solution parameters for conversion to the infinite dilution standard state. Since the value of the quantity \((A^\gamma - A^\alpha)\) decreased linearly with temperature in the range 1100 K to 1700 K, the \(\Delta^0_{\gamma\alpha}^{\gamma\alpha}\) was extrapolated for use in the \(\gamma\rightarrow\delta\) region (cf. equation (III-4)).

Information on the \(\alpha\rightarrow\gamma\) transformation was obtained from Reese et al. (35) who reported \(\Delta^0_{\gamma\alpha}^{\alpha\rightarrow\gamma}\) as a function of \(x_Fe\) \((x_Fe = 1\) at infinite dilution), Kaufman and Neser (33), Belton and Freuhman (36) and Sigworth and Elliott (18). The adopted value was from Kaufman and Neser and Sigworth and Elliott, assuming an ideal solution in the liquid. \(\Delta^0_{\gamma\alpha}^{\gamma\alpha}\) was obtained from \(\Delta^0_{\gamma\alpha}^{\alpha\rightarrow\gamma}\) and \(\Delta^0_{\gamma\alpha}^{\alpha\rightarrow\gamma}\).

III.3.F Fe-Mo

The \(\alpha\rightarrow\gamma\) free energy was suggested by Kaufman (34) and converted to the infinite dilution standard state using the regular solution parameters of Kirchner et al. (37). Since these parameters were well with respect to temperature, the values obtained were interpolated for use in the \(\gamma\rightarrow\delta\) transformation as well. With this \(\Delta^0_{\gamma\alpha}^{\alpha\rightarrow\gamma}\) it was possible to reproduce the gamma loop of Sinha et al. (38) up to 2 w/o molybdenum.

Little data was available for the free energy of the \(\alpha\rightarrow\gamma\) transformation but the value from Sigworth and Elliott, calculated for an ideal solution produces a good fit between the computed liquid and that reported by Gibson et al. (39). \(\Delta^0_{\gamma\alpha}^{\gamma\rightarrow\delta}\) was obtained from the above results.
III.3.6 Fe-Cu

The value of $\Delta^o G_{\alpha \gamma}^o$ was reported by Baganis and Kirkaldy (9) who fitted the data of Weiss and Tauer (40). By means of a method similar to that used for manganese, Harvig et al. (41), using the phase diagram of Hellywell and Hume-Rothery (29), demonstrated that the temperature dependence of the regular solution parameters were such that $\Delta^o G_{\gamma}^o$ would not be valid if extrapolated out of the range of this transformation. $\Delta^o G_{\gamma}^o$ was determined by using the free energy of the pure component suggested by Kaufman (45) for the $\alpha \rightarrow \gamma$ transition and converting it to the infinite dilution standard state using the regular solution parameters of Harvig et al. evaluated in the region of 1800 K.

Activity measurements through the temperature range of the $\alpha + L$ transformation were performed by Morris and Zellars (43) and Wooley and Elliott (44). The $\Delta^o G_{\gamma}^o$ obtained, when converted to the correct standard state could not reproduce the non-reaction of the phase diagram of Hellywell and Hume-Rothery (29) as well as the value of Kaufman et al. (45). This latter $\Delta^o G_{\gamma}^o$, although independent of temperature was chosen and $\Delta^o G_{\gamma}^o$ was obtained from it and the $\gamma \rightarrow \delta$ values chosen.

III.3.11 Fe-W

When the $\alpha \rightarrow \gamma$ free energy of Kaufman (34) was converted to the infinite dilution standard state by utilizing the regular solution parameters of Kirchner et al. (37) it was found that the resulting expression:

$$\Delta^o G_{\delta}^o = 3710 - 0.3T$$

(III-23).
was a poorer fit to the gamma loop of the Fe-W phase diagram of Sinha and Hume-Rothery (46) than could be obtained by assuming that the self-interaction parameters, $c_{wW}$, are equal in ferrite and austenite. It was assumed, because of insufficient information, that the $\Delta^0 G^\alpha\gamma_8$ derived was also applicable to the $\gamma\rightarrow\delta$ transformation.

The free energy for the $\alpha\rightarrow L$ transformation was reported by Kaufman (57) and Sigworth and Elliott (18). The latter value will reproduce the phase diagram of Sinha and Hume-Rothery to 3 w/o tungsten. $\Delta^0 G^\gamma_8$ was derived with the use of the above values.

III.3.1 Fe-V

$\Delta^0 G^\alpha\gamma_9$ was derived from a thermodynamic analysis of the Fe-V binary phase diagrams of Kirchner and Gemmel (47), Lucas and Fishel (48) and Fischer et al. (21), using the self interaction coefficient, $c_{\gamma\gamma}$, deduced by Wada et al. (49) and assuming the self interaction in ferrite to be negligible. Since no other information was available, the $\alpha\gamma$ free energy was extrapolated for use in describing the $\gamma\rightarrow\delta$ transformation.

The $\alpha\rightarrow L$ transformation was studied by Myles and Aldred (50) over the entire range 0 to 1 mole fraction vanadium and by Fruehan (51) who was able to estimate the activity coefficient of liquid vanadium at infinite dilution. This information was sufficient to attempt a thermodynamic analysis of the liquidus, which yielded $\Delta^0 G^\alpha_9$ up to 2 w/o V. $\Delta^0 G^\gamma_9$ was obtained from the above information.
III.3. J Fe-Nb

The ω→γ transformation in this binary system differs from those already mentioned because of the addition of an intermediate phase field into the gamma loop. In this analysis it was assumed that this extra phase field does not exist and the gamma loop is treated as a normal one. The $\Delta^0_{\omega\rightarrow\gamma}^{10}$ adopted is reported by Rudd et al. (52) and is not to be used over 0.2 w/o Nb. Due to lack of data, this free energy was extrapolated for use in the γ→δ transformation up to 0.2 w/o Nb.

The phase diagram of Ferrier et al. (55) utilized to check the free energy for the α+L transition derived by assuming an ideal solution seemed anomalous because of the narrow width of the solidus-liquidus region. For an ideal solution of an element i in iron it can be shown that:

$$\ln \left( \frac{1-x_i^1}{1-x_i^2} \right) = \frac{\Delta^0 G_{Fe}^{1\rightarrow2}}{RT} \quad (III-21)$$

for the transformation from phase 1 to phase 2. If $x_i^1$ and $x_i^2$ are sufficiently dilute this expression may be approximated (29) by performing a Taylor series expansion on $\ln(1-x_i)$:

$$x_i^2 - x_i^1 = \frac{\Delta^0 G_{Fe}^{1\rightarrow2}}{RT} \quad (III-25)$$

In this case of the α+L transformation, this means that for small additions of alloying element, the width of the α+L phase field is independent of the element added at any given temperature.
Comparison with the phase diagrams of Fe-Mo, Fe-Cr, Fe-Si and Fe-Mn demonstrated that since these phase fields had almost constant widths, the Fe-Nb phase diagram was probably wrong. As a result, the thermodynamic analysis for \( \Delta G_{10}^{\alpha \rightarrow \gamma} \) was carried out on a phase diagram constructed with the width of the solidus-liquidus region of the Fe-Mo system which straddled (i.e. contained) the measured Fe-Nb phase region. The adopted free energy lies between that of an ideal solution and that necessary to reproduce this particular phase diagram using the self interaction parameter of Sigworth and Elliott.

It must be emphasised that this free energy, while similar to that of Sigworth and Elliott is not strictly based on the experimental information.

III.3.K Fe-Co

Analysis by Harvig et al. (41) showed that \( \Delta G_{11}^{\alpha \rightarrow \gamma} \) ranged from -90 cal/mole at 1688 K to 0 cal/mole at 1184 K. The value of the free energy for the \( \alpha \rightarrow \gamma \) transformation was taken to be 0 cal/mole, independent of temperature because it would reproduce the phase diagram of Fischer et al. (21) up to 0.02 atom fraction cobalt. Since -90 cal/mole is of the same order or smaller than the error normally encountered on free energy measurements at higher temperatures, the value of zero was also adopted for the \( \gamma \rightarrow \delta \) transformation.

\( \Delta G_{11}^{\alpha \rightarrow L} \) and \( \Delta G_{11}^{\gamma \rightarrow L} \) were reported by Kaufman and Nesor (33) and adopted assuming an ideal solution behaviour. These free energy values
reproduced the phase diagram of Harris and Hume-Rothery (54) out to .06 atom fraction cobalt.

All of this thermodynamic free energy data is summarized in Tables I to IV.

III.4 Interaction Coefficients

As previously mentioned it has been common practice to express the interaction parameters in terms of common logarithms and the one weight percent standard state or as mole fractions at infinite dilution and natural logarithms:

$$e_{ij} = \left( \frac{\partial \log f_i}{\partial w/o_j} \right)_{w/o_i = w/o_j = 0}$$  \hspace{1cm} (III-26)

$$e_{ij} = \left( \frac{\partial \ln \gamma_i}{\partial x_j} \right)_{x_i = x_j = 0}$$  \hspace{1cm} (III-27)

Since both forms occur in the literature, the conversion from the weight percent form to the mole fraction form required here was accomplished using the method given by Lupis and Elliott (58):

$$e_{ij} = 230 \frac{m_i}{m_o} e_{ij} + \frac{m_o - m_i}{m_o}$$  \hspace{1cm} (III-28)

where \( m \) is the respective molecular weights of the elements of a ternary system with \( x_i > 0 \) and \( x_j > 0 \) in solvent "O" (iron).
Table II. $\Delta G_i^{\alpha+\gamma}$ as Functions of Temperature

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta G_i^{\alpha+\gamma}$ (cal/mole)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$-15323 + 7.686T$</td>
<td>14,17</td>
</tr>
<tr>
<td>Mn**</td>
<td>$-26650 + 42.69T - 0.17T^2$</td>
<td>9,27,29,30,55</td>
</tr>
<tr>
<td>Si</td>
<td>$-5964 + 33.799T - 4.7244TlnT$</td>
<td>32</td>
</tr>
<tr>
<td>Ni</td>
<td>$-4545 + 3.233T$</td>
<td>17</td>
</tr>
<tr>
<td>Cr</td>
<td>$-367 - 4.656T + 0.6568TlnT$</td>
<td>27,34</td>
</tr>
<tr>
<td>Mo</td>
<td>$565 + 0.15T$</td>
<td>34,37</td>
</tr>
<tr>
<td>Cu***</td>
<td>$-25500 + 41.183T - 0.17T^2$</td>
<td>9,41</td>
</tr>
<tr>
<td>W</td>
<td>$2500 + 0.15T$</td>
<td>37</td>
</tr>
<tr>
<td>V</td>
<td>$-8357 + 13.8T - 0.0031T^2$</td>
<td>derived from 47, 50</td>
</tr>
<tr>
<td>Nb</td>
<td>$14.34 - 0.00131T$</td>
<td>52</td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
<td>41</td>
</tr>
</tbody>
</table>

$\Delta G_i^{\gamma+\delta} = -\Delta G_i^{\alpha+\gamma}$

$\Delta G_{\text{Mn}}^{\gamma+\delta} = 650 - 0.305T$

Because of a systematic deviation between observations and predictions, we have taken this as 0.687 times the value given in reference 27.

$\Delta G_{\text{Cu}}^{\gamma+\delta} = 1450 - 0.8T$
Table III. $\Delta G_{i}^{a+L}$ as Functions of Temperature

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta G_{i}^{a+L}$ (cal/mole)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$-21300 + 6.3T$</td>
<td>14, 19, 56</td>
</tr>
<tr>
<td>Mn</td>
<td>$3100 - 2.508T$</td>
<td>30</td>
</tr>
<tr>
<td>Si</td>
<td>$3.97 - 8200$</td>
<td>31, ideal solution</td>
</tr>
<tr>
<td>Ni</td>
<td>$-2120 - 0.38T$</td>
<td>18, 33</td>
</tr>
<tr>
<td>Cr</td>
<td>$2.19T - 4600$</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>$2.29T - 6600$</td>
<td>18, ideal solution</td>
</tr>
<tr>
<td>Cu</td>
<td>$-1200$</td>
<td>45, ideal solution</td>
</tr>
<tr>
<td>W</td>
<td>$3.65T - 7500$</td>
<td>18, 51</td>
</tr>
<tr>
<td>V</td>
<td>$-5100 + 2.5T$</td>
<td>18, 51, ideal solution</td>
</tr>
<tr>
<td>Nb</td>
<td>$2.3 - 5500$</td>
<td>18, ideal solution</td>
</tr>
<tr>
<td>Co</td>
<td>$3550 - 2.19T$</td>
<td>18, 33</td>
</tr>
</tbody>
</table>
Table IV. $\Delta G_{\gamma \rightarrow \delta}^\gamma$ as Functions of Temperature

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta G_{\gamma \rightarrow \delta}^\gamma$ (cal/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>$-5360 \pm 0.6T$</td>
<td>14, 29</td>
</tr>
<tr>
<td>Na</td>
<td>$2860 - 2.05T$</td>
<td>30</td>
</tr>
<tr>
<td>Si</td>
<td>$-2236 - 54.9T + 4.7244T\ln T$</td>
<td>*</td>
</tr>
<tr>
<td>Ni</td>
<td>$-790 - 0.64T$</td>
<td>18, 32</td>
</tr>
<tr>
<td>Cr</td>
<td>$-4233 + 6.89T - 0.6566T\ln T$</td>
<td>*</td>
</tr>
<tr>
<td>Mo</td>
<td>$2.14T - 7165$</td>
<td>*</td>
</tr>
<tr>
<td>Cu</td>
<td>$1.39T - 3150$</td>
<td>*</td>
</tr>
<tr>
<td>W</td>
<td>$3.50T - 10000$</td>
<td>*</td>
</tr>
<tr>
<td>V</td>
<td>$3257 - 11.5T + 0.0051T^2$</td>
<td>*</td>
</tr>
<tr>
<td>Nb</td>
<td>$2.3T - 5500$</td>
<td>*</td>
</tr>
<tr>
<td>Co</td>
<td>$3950 - 2.19T$</td>
<td>18, 19</td>
</tr>
</tbody>
</table>

$\Delta G_{\gamma \rightarrow \delta}^\gamma = \Delta G_{\gamma \rightarrow \delta}^\gamma + \Delta G_{\gamma \rightarrow \delta}^\delta$
Dealy and Pehlke (59) investigated the temperature dependence of the interaction parameter:

\[ \frac{\partial \epsilon_{ij}}{\partial T} = -\frac{1}{RT^2} \left( \frac{\partial^2 H}{\partial x_i \partial x_j} \right) \bigg|_{x_i=x_j=0} \quad (III-29) \]

where the derivative of the molar enthalpy can in principle be deduced from tabulated heat of solution data. Provided that the derivative of the enthalpy as written above for the two solutes at infinite dilution is not a strong function of temperature, it is possible to write equation (III-29) as:

\[ \frac{\partial \epsilon_{ij}}{\partial \left( \frac{1}{T} \right)} = \frac{1}{R} \left( \frac{\partial^2 H}{\partial x_i \partial x_j} \right) \bigg|_{x_k=0} \quad (III-30) \]

which indicates that a relationship of the form:

\[ \epsilon_{ij} = \frac{A}{T} + B \quad (III-31) \]

would be valid for the interaction coefficients. Where data from more than one source or at more than one temperature was used, the values were averaged or a least squares method was used for evaluation, fitting a curve of the above type. Since the greater portion of the data was available at only one temperature, the integration constant was assumed zero and a reciprocal temperature relationship used for determining the value at a different temperature. Where data came from a regular solution model or was used in the form necessary to be used in such a model,
the conversion formula of Nishizawa (60) was utilized:

\[ C^1 = +RT \epsilon_{cj} \]  \hspace{1cm} (III-32)

where \( C^1 \) is the regular solution ternary "correction" for the interaction between carbon and solute \( j \) in solvent iron in phase 1.

The majority of the liquid alloy cross interaction parameters were reported by Sigworth and Elliott (18), with newer or different information being referenced in Table V.

There is much more information available for the cross interaction between carbon and transition metals in austenite than in ferrite or the liquid state. Where more than one reference is listed for \( \epsilon_{11} \) in Table VI, the value adopted was an average over all the reported ones. A case in point is molybdenum, where different researchers (49, 60-66) arrived at similar \( \epsilon_{10} \) values for the temperature range 1000 K to 1273 K but the large variation with temperature outside this range was such that any one determination could not be used for the \( \gamma \)-\( \delta \) transformation.

Little information exists on the cross-interaction parameters for the \( \delta \) and \( \alpha \) phases. The \( \delta \) phase interaction parameter was assumed equal to the austenite interaction parameter extrapolated to the temperature of interest. All high temperature extrapolations were checked for consistency of sign with the liquid interaction values at 1800 K and to ensure that, the adopted values were of the same order of magnitude, e.g.:
\[ \epsilon_{\text{CMO}}^L = -4.2 \text{ at } 1800 \text{ K} \]  
(III-33)

\[ \epsilon_{\text{CMO}}^\gamma = -6.1 \text{ at } 1800 \text{ K} \]  
(III-34)

For ferrite, the mole fraction of carbon, \( x_1 \), is sufficiently small that assuming \( \epsilon_j^\gamma = \epsilon_j^a \) leads to negligible error.

### III.5 Partition Coefficients

Because interaction coefficients and free energies have not been reliably evaluated for the carbide phase, it became necessary to adopt the partition coefficients between austenite and cementite:

\[ k_i = \frac{x_{i}^{\text{cem}}}{x_{i}^{\gamma}} \]  
(III-35)

as the experimental inputs, where \( x_{j}^{\text{cem}} \) is the mole fraction of element \( j \) in the Fe\(_3\)C carbide phase at any temperature.

The only temperature dependent partition coefficients are those of Uhrenius (78). These are expressed in terms of weight percent of solute \( i \), at temperature \( T \), viz:

\[ k_i^{1} = \frac{\text{wt. pct. } i \text{ in cementite}}{\text{wt. pct. } i \text{ in austenite}} \]  
(III-36)

The transformation from \( k^{1} \) to \( k \) is possible knowing \( x_{i}^{\gamma} \) and wt. pct. \( i \) in austenite, if equation (III-36) is expressed as

\[ [\text{wt./o} \_i \text{ in cementite}] = k^{1} [\text{wt./o} \_i \text{ in austenite}] \]  
(III-37)
Table V. $\varepsilon_{ci}^L$ as Functions of Temperature

<table>
<thead>
<tr>
<th>Element</th>
<th>$\varepsilon_{ci}^L$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$0.389 + 7810/T$</td>
<td>12,19,20,65</td>
</tr>
<tr>
<td>Mn*</td>
<td>$-5060/T$</td>
<td>18,30,66</td>
</tr>
<tr>
<td>Si</td>
<td>$-0.428 + 18740/T$</td>
<td>18,65</td>
</tr>
<tr>
<td>Ni*</td>
<td>$5340/T$</td>
<td>18,67</td>
</tr>
<tr>
<td>Cr*</td>
<td>$-9500/T$</td>
<td>18</td>
</tr>
<tr>
<td>Mo*</td>
<td>$-7490/T$</td>
<td>18</td>
</tr>
<tr>
<td>Cu*</td>
<td>$7586/T$</td>
<td>18</td>
</tr>
<tr>
<td>W*</td>
<td>$-12230/T$</td>
<td>18</td>
</tr>
<tr>
<td>V*</td>
<td>$-30100/T$</td>
<td>18</td>
</tr>
<tr>
<td>Nb*</td>
<td>$-46615/T$</td>
<td>18</td>
</tr>
<tr>
<td>Co*</td>
<td>$3550/T$</td>
<td>18,66,67</td>
</tr>
</tbody>
</table>

*Assumed inverse temperature relationship
<table>
<thead>
<tr>
<th>Element</th>
<th>$\gamma_{\text{ci}}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C**</td>
<td>8910/T</td>
<td>68</td>
</tr>
<tr>
<td>Ma**</td>
<td>-5070/T</td>
<td>16,30,61,68</td>
</tr>
<tr>
<td>Si</td>
<td>4.84 - 7370/T</td>
<td>16,68,69</td>
</tr>
<tr>
<td>Ni</td>
<td>-2.2 + 7600/T</td>
<td>70,71,72,73</td>
</tr>
<tr>
<td>Cr</td>
<td>24.4 - 38400/T</td>
<td>49,61,62,71,74</td>
</tr>
<tr>
<td>Mo</td>
<td>3.855 - 17870/T</td>
<td>49,60,61,62,63,64</td>
</tr>
<tr>
<td>Cu**</td>
<td>4200/T</td>
<td>70</td>
</tr>
<tr>
<td>W</td>
<td>23.4 - 36214/T</td>
<td>62</td>
</tr>
<tr>
<td>V**</td>
<td>-24660/T</td>
<td>49,56</td>
</tr>
<tr>
<td>Nb**</td>
<td>-28770/T</td>
<td>62</td>
</tr>
<tr>
<td>Co**</td>
<td>+2800/T</td>
<td>75,76,77</td>
</tr>
</tbody>
</table>

*Assumed $\gamma = \alpha$ and $\gamma = \delta$

**Assumed inverse temperature relationship:
Now, when the weight percent of element i in cementite is converted to mole fraction, it can be put into equation (III-35) which can then be solved for the necessary partition coefficient. The values obtained by this method of analysis for the chromium partition data of Uhrenius were found to be in good agreement with the experimental chromium partition coefficients calculated from the data of Sharma (79). The zero partition coefficient of silicon is reported by Uhrenius (80) and is used here as independent of temperature. This data is listed in Table VII.

III-6 Empirical Fe-C Phase Diagram

The iron-carbon phase diagram in the range 1000 to 1809 K has been reviewed and revised by Benz and Elliott (20) and more recently by Ban-Ya et al. (82). Both papers have extensively searched and commented upon the literature, eventually publishing about 100 phase diagrams. The empirical equations of Table 1A describe the phase diagram of Fig. (4) and are based on the experimental determinations and the corrected experimental values of previous investigators from Benz and Elliott. For temperatures below 1000 K the extrapolation of the Ae₃ line was taken from Kaufman et al. (81) and the carbide phase are simply linearly extended according to the equation in Table (VII).
Table VII. Partition Coefficients as Functions of Temperature

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>( k = -0.0028T + 5.44 )</td>
<td>78</td>
</tr>
<tr>
<td>Ni</td>
<td>( 0.0004T - 0.249 )</td>
<td>78</td>
</tr>
<tr>
<td>Cr</td>
<td>( 163.4 - 22.78\ln T )</td>
<td>78,79</td>
</tr>
<tr>
<td>Mo</td>
<td>( 121 - 16.91\ln T )</td>
<td>78</td>
</tr>
<tr>
<td>Si</td>
<td>( \infty )</td>
<td></td>
</tr>
</tbody>
</table>
Table VIII. Analytic Formula for Fe-C Phase Diagram

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Formula</th>
<th>Temperature</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ→γ+α</td>
<td>$T = 1115 - 150.5 \text{wt%C} + 216[0.765-\text{wt%C}]^{4.26}$</td>
<td>9100°C ≤ $T$ ≤ 1318 K</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>$T = 103 - 108.46 \text{wt%C}$</td>
<td>≤ $T$ ≤ 999 K</td>
<td>81</td>
</tr>
<tr>
<td>L+L+γ</td>
<td>$T = 1804.3 - 61.3 \text{wt%C} - 4.6(\text{wt%C})^2$</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>L+L+δ</td>
<td>$T = 1809 - 29.56 \text{wt%C} - 86(\text{wt%C})^2$</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>γ→γ+δ</td>
<td>$T = 1666 + 981 \text{wt%C} - 1790(\text{wt%C})^2$</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>γ→γ+Fe₃C</td>
<td>$T = 641.3 + 530 \text{wt%C} - 73.4(\text{wt%C})^2$</td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>
Figure 4  The Fe-C Phase Diagram According to Ref. 20.
CHAPTER IV

CALCULATIONS, DISCUSSION AND RESULTS

IV.1 Introduction

In this chapter we review the major sources of verification for our predictive formulae, from the early Ae₃ determinations to latter day experimental equilibria. Although we are forced to centre on the α+γ transformation information to demonstrate the validity of the method, due to lack of reliable experimental and thermodynamic data for the other regions, the formulae are not limited to this range. Also included, is a summary of the computational methods and problems overcome to extend the simple predictive formulae to the prediction of phase diagrams.

IV.2 Computer Calculations

IV.2.A Constant Composition Sections of the Fe-C Phase Diagram

Constant composition sections were calculated and plotted by computer for the temperature range 950 K to 1850 K and the composition range 0 to 2.5 wt.pct. carbon. As shown in Figure (5) for carbon compositions x₁ and x₂, both the stable phase boundaries and metastable extensions had to be calculated indiscriminately. Since both the stable
Figure 5 Schematic of an Fe-C-X Liquidus and Solidus.
phase temperature and the temperature of the metastable phase at any temperature was known, it was possible to determine which phase would be plotted in the following manner.

As shown in Figure (5) for carbon content $x_1$, the $\delta/\delta+L$ line (i.e. $\delta$-liquidus) is the stable phase boundary at a temperature $T_D$. The metastable phase boundary, the $\gamma$-liquidus is denoted by temperature $T_C$. As $x_1$ approaches $x_2$, the two phase boundaries cross over and the stable phase is now the $\gamma$-liquidus at $T_E$ and the metastable phase boundary is the $\delta$-liquidus at temperature $T_G$. Thus the calculation of all phase temperatures results in a form of "memory" of the phase boundary plotted to that point.

This method was used to determine which phase should be plotted for the $\delta+\gamma/\delta+L$ and $\delta+\gamma/\gamma+L$ cross overs as well. Once it was determined which was the stable phase at any temperature, the partition coefficient (cf. equation (II-18)) was used to calculate the carbon composition on the other side of the two phase region. For instance, with reference to Figure (5), when the $\delta+L/\delta$ phase boundary at $x_1$ is stable, the composition of carbon of the $\delta/\delta+L$ phase boundary is given by point $c$, and when the $\gamma/\gamma+L$ phase boundary is stable, at $T_k$, the carbon composition of the $\gamma/\gamma+L$ boundary is given by the carbon content at point $H$. This method was used for determining the carbon composition of one side of a two phase region when that of the other side is known for the $\alpha+\gamma$, $\delta+\gamma$, $\delta+L$ and $\gamma+L$ regions.

The actual plots, as shown in Figures (6 to 9) are contours of
Figure 6  Set of constant Cr sections through the Fe-C-Cr phase diagram.
Figure 7  Set of constant Mo sections through the Fe-C-Mo phase diagram.
Figure 8  Set of constant Si sections through the Fe-C-Si phase diagram.
the Fe-C binary phase diagrams; each contour representing a different amount of the specified alloy. For example, in Figure (6) the contours represent the following constant composition contours:

Fe-C-0 wt.pct. Cr
Fe-C-1.0 wt.pct. Cr
Fe-C-2.5 wt.pct. Cr

IV.2.B Isothermal Ternary and Ternary Constant Composition Sections

There are many isothermal ternary systems documented in the literature, especially for the temperature range 950 to 1350 K where the stable phases are austenite, ferrite and cementite. Since the best thermodynamic data also exists in this temperature regime, this was the one chosen to test the formulae.

Two methods were used for predicting this type of phase diagram. The first consists of setting up a grid of values, say for carbon between 0 and 2 mole percent and alloying element i between 0 and 4 mole percent, holding the composition of the other elements constant. For each point, the temperature at which it exists is calculated and compared with the temperature of interest. This method is expensive in computer time but allows one to gauge the effect of uncertainties in temperature or thermochemical data (see Figure (10)).

The second, and preferable method of prediction was to transform equations (II-19) and (II-22) to a form whereby the deviation in the carbon content rather than the change in temperature from the binary iron
Figure 10: Fe-C-Cr ternary phase diagram for 1025±5 K.
carbon phase diagram is calculated:

$$x^\text{alloy}_1 = x^\text{Fe-C}_1 + \frac{\Delta T}{m_g}$$  \hspace{1cm} (IV-1)

for the $\text{Ae}_3$ temperature, where $m_g$ is the slope of the binary Fe-C $\alpha/\alpha+\gamma$ phase boundary at this temperature, evaluated from the first derivative of its empirical equation. The shift in the carbide line needed no further transformation since it already existed in the required form.

In order to determine if a three phase region existed, it was necessary to evaluate the existence of a ternary eutectic in the plotted equation. An exact equation was derived for this by Kirkaldy et al. (93):

$$T^\text{eutectic}_\text{alloy} = \frac{T_E \left(1 - \frac{m_g}{m_c}\right) + \Delta T + m_g \Delta x_1}{1 - \frac{m_g}{m_c}}$$  \hspace{1cm} (IV-2)

where $m_g$ and $m_c$ are the slopes of the binary $\text{Ae}_3$ and carbide lines and $T_E$ is the binary eutectic temperature.

In the program, the $\alpha+\gamma/\gamma$ and carbide lines were fitted by quadratic equations and these were solved to find the ternary eutectic, rather than introduce this linear expression.

As in the constant composition sections, the $\alpha/\alpha+\gamma$ phase boundary is calculated using the partition coefficient evaluated within the program. In an analogous manner, the corners of the three phase region are determined and lines computed and plotted between them.
Equations IV-1 and IV-2 are derived in Appendix (IV). Examples of this type of plot, are found in Figures (11) to (13) for the system Fe-Ni-C at 973 K, 1073 K and 1173 K. Following each Figure, is a table (Table IX-XI) containing the coordinates of the plotted points in wt. percent.

IV.3 Results and Comparison with Experiment

It was decided the most effective manner for demonstrating the generality of our predictive formulae was to calculate and plot complete constant composition sections of the iron-carbon binary phase diagram as in Figures (6) to (9). These phase diagrams encompass the entire range of temperatures and phases (except higher carbides) of hardenability steels. Although a diagram of this scope may become more than qualitatively useful, at present there are insufficient experimental results available to verify the entire range of this study.

By far the most extensive data set was available for the \( A_{c_3} \) temperature of low alloy steels. Comparison between experimental and predicted \( A_{c_3} \) temperatures provide a check on one carbon value of the corresponding constant composition section in this limited temperature range. The exhaustive work on this single temperature by Bagania and Kirkaldy (9) made the perfect proving ground for the accuracy of the formulae and programming techniques.

Shown in Figure (2) were those steels which were thought to approach closest to equilibrium. For the most part, these were chosen
Figure 11 Fe-Ni-C system at 973 K.
Table IX. Fe-Ni-C at 973 K in wt.%

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>GAMMA</th>
<th>CARBIDE</th>
<th>TEMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>1.00259</td>
<td>0.59659</td>
<td>973.00</td>
</tr>
<tr>
<td>0.2000</td>
<td>0.99899</td>
<td>0.49528</td>
<td>973.00</td>
</tr>
<tr>
<td>0.3000</td>
<td>0.99793</td>
<td>0.49396</td>
<td>973.00</td>
</tr>
<tr>
<td>0.4000</td>
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**Table X.** Fe-Ni-C at 1073 K in wt.%
Figure 13 Fe-Ni-C at 1173 K
Table XI. Fe-Ni-C at 1173 K in wt.%

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from ternary Fe-C-X experiments. The $Ae_3$ temperatures of those steels of Aaronson and Domion (83) and Hall et al. (84) were determined by heating the steels to $1300^\circ$C, quenching to martensite, then reheating and holding at a temperature thought to be near the $Ae_3$. The $Ae_3$ temperature was taken as that intermediate between the highest holding temperature at which ferrite remained in the microstructure and the lowest at which it did not (measured in $5^\circ$C increments). Gilmour (85) and Kirchner and Uhrenius (86) were studying isothermal Fe-C-X sections and subjecting their samples to long periods at carefully controlled temperatures (a method similar to that used by Grange (4)). The results of Swinden and Woodhead (87) were determined dilatometrically with a heating rate of $22^\circ$C/hr. It is interesting to note that the predicted results lie below the experimental results, even for the leaner steels (low carbon, high $Ae_3$ temperature).

Figure (3) showed the results for the steels from the U.S.S. Atlas of Isothermal Transformations (88). It was argued that these are not a true $Ae_3$ temperature (28) since the predictor, while quite good on experimental steels, was predicting consistently low on these commercial steels. Figure (14) shows the $Ac_3$ and $Ar_3$ temperatures for 15 steels from the A.S.M. Data Sheets (89) as compared with the predicted $Ae_3$ temperature. As would be expected, the $Ac_3$ is below and the $Ar_3$ above the predicted value. However, as the carbon content decreases (temperature increases) the $Ar_3$ crosses the predicted value diagonal.

The above irregularities necessitated a further check of the data and closer scrutiny of sources to be made. It was observed that
Figure 14  Predicted Ac₃ versus Ac₅ and Ar₃ temperature for low alloy steels. Steels identified in Reference (28).
manganese was present in most of the steels that deviated strongly at low carbon contents, along with lesser amounts of chromium and nickel. It was also discovered that the $\Delta G_{\alpha-y}^{\text{Mn}}$ being used would not adequately reproduce the Fe-Mn phase diagram; the main reason being the availability of true experimental equilibrium data. $\Delta G_{\alpha-y}^{\text{Mn}}$ was accordingly adjusted to the value in Table II. It is possible that the Cr and Ni equilibrium data are also insufficiently precise.

Although it is possible to verify at least one point on the $\alpha_3$ line for constant composition sections, there exists no similar data set for the $\delta/L$, $\delta/Y$, $\gamma/L$ or carbide transformations. However, it is our view that since the formulae and the program are performing adequately on the $\alpha_3$ portion of the diagram and since the other input data are presumably correct, the other calculated portions should have fair reliability. The only check we have on the validity of the input data is the program's ability to reproduce the respective binary Fe-$\gamma$ phase diagrams. All data tabulated were checked and the program does indeed reproduce all required binary phase diagrams.

Once the binary limits were established, the program and predictive formulae for constant composition isothermal "quasi-ternary" phase diagrams were verified by accurately reproducing, using identical data, the iron-rich portions of the ternary Fe-C-X phase diagrams (where $\chi$ is one of Mn, Si, Ni, Mo, W, V or Cu) published by Uhrenius (80) for temperatures above and below the binary eutectoid. His diagrams are the best self-consistent fit between regular solution theory and the data. The method of comparison used is illustrated in Figure (15). This is an isothermal
Figure 15. Comparison of the Fe-Cu-C system at 1023 K with that of Uhrenius (80)
section of the Fe-Cu-C system at 1023 K plotted by our program with points from Uhrenius' phase diagram superimposed. The equilibrium tie lines (broken) calculated by Uhrenius and those calculated by our program (full lines) are drawn in for comparison purposes. This was the method of comparison used for every phase diagram plotted (Figures (10) to (13) and (15) to (30)) and good agreement was obtained for Cu, Mn, Ni and Si and for the α-γ equilibrium, for all other elements treated by Uhrenius. Some deviation was found for the γ-carbide equilibrium in the Cr and Mo cases, and this is not unexpected because of the extreme sensitivity of the results to the precise values of $k$ and $\epsilon_c$ used in these cases.

The co-ordinates of the plotted points, in wt.pct. for Figures (17) to (29), are in the tables immediately following the respective phase diagrams, i.e.: Tables XII to XXIV.

Figure (16) and (17) contain the comparison between our calculated phase diagrams and the experimental points of Sharma (79) for the Fe-Cu-C system. It was found that there was good agreement at 1023 K and 1043 K, the temperatures at which this work was undertaken. Sharma also reported partition coefficient data for the iron-rich region of this system. Table (XXV) shows the agreement between our calculated $\alpha/\gamma$ partition coefficients and the experimental ones. The $\alpha/\gamma$ partition coefficients for the other elements are tabulated in Table (XXVI).

Since all points of the isothermal phase diagrams were calculated, we automatically obtained the eutectoid temperature and composition and the effects of alloying elements on them. The experimental verification
Figure 16  Fe-Cr-C system at 1028 K with the experimental points of Sharma (79).
Figure 17  Fe-Cr-C system at 1043 K with the experimental points of Sharma (79)
Figure 18  Fe-Cr-C system at 1023 K
Table XII. Fe-Cr-C at 1023 K in wt.%

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Figure 20. Fe-Cr-C system at 1173 K
Figure 21 Fe-Cu-C system at 1173 K
Figure 22  Re-Cu-C system at 1073 K
Figure 23: Fe-Cu-C system at 1023 K
### TABLE XVII

**Fe-Cu-Č at 1023 K in wt.%**

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Figure 24. Fe-Mn-C system at 1173 K.
Figure 25  Fe-Mn-C system at 1073 K
Figure 26  Fe-Mn-C system at 1035 K
### TABLE XX. Fe-Mn-C at 1035 K in wt.%

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Figure 28 Fe-Si-C system at 1073 K
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<th>GAMMA</th>
<th>CARBIDE</th>
<th>TEMP</th>
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Figure 30  Fe-Cr-C system at 1043 K
Table XXV. Comparison of Partition Coefficients (mole fraction basis) for α/γ in Fe-C-Cr Systems (79)

<table>
<thead>
<tr>
<th>T °K</th>
<th>( \frac{x_{Cr}^\gamma}{x_{Cr}^\alpha} ) (expt.)</th>
<th>( \frac{x_{Cr}^\gamma}{x_{Cr}^\alpha} ) (pred.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1043</td>
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<tr>
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<td>1.73</td>
<td>1.74</td>
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<tr>
<td>1023</td>
<td>1.78</td>
<td>1.81</td>
</tr>
</tbody>
</table>
Table XXVI. \( \alpha/\gamma \) Partition Coefficient, \( k^{\alpha/\gamma} = x^\gamma/x^\alpha \)

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>W</th>
<th>V</th>
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<tr>
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<td>0.78</td>
<td>1.49</td>
<td>1.34</td>
<td>0.76</td>
<td>1.35</td>
<td>0.36</td>
<td>0.91</td>
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</table>
of this calculation was initially based on the data of Sharma (79) and of Razik et al. (90) for the Fe-C-Cr system as shown in Figure (31). This information was used initially to check the eutectoid intersections predicted between the $\text{Ae}_3$ and carbide lines for the constant composition sections, then to verify equations (IV-1) and (IV-2) for the eutectoid temperature and carbon composition upon the addition of chromium, with salutory results. After the formula was shown to work adequately for additions of chromium, it was used to predict the eutectoid composition and temperature for Si, Cr, Mn and Ni and compared with the data of Bain and Paxton (91) as shown in Figure (32). It is not known if Bain and Paxton restricted their analysis to only Fe$_3$C-type carbides, so this diagram was limited to 2 wt.pct. alloying element. It is interesting to note that Uhrenius (80) published a similar comparison that showed a deviation comparable to our formulae prediction for Si.

Discussion

As more information on metallic systems becomes available, there is a trend towards developing more complex and comprehensive models (10) in order to explain the findings and to better predict results which are difficult to achieve experimentally. As a result, the calculations can be expensive, demanding long computation times and larger, faster computers.

It was our contention, when embarking on this work, that for most commercially important alloys (i.e.: hardenability steels) it was not necessary and not practical to resort to complex thermodynamic modelling
Figure 31 Comparison of predicted and observed variations in the eutectoid temperature and composition with additions of Cr. Experimental points after Sharma (79) +, O and Razik et al. (90) A.
Figure 32  Comparison of predicted and observed variations in the eutectoid temperature and composition with additions of Mn, Si, Ni and Cr. Single points were taken from Bain's experimental curves (91).
in order to characterize multicomponent dilute alloy phase diagrams. By choosing the Wagner Taylor series expansion as the starting point, we were able to derive equations that are rigorous up to linear terms, that are accurate for small alloy additions and are able to handle efficiently, large numbers of solute additions. Comparison with experimental phase diagrams and phase diagrams computed using more complex models (80) have shown that our formulae give adequate representation of results for quite rich alloys; indeed, to the limits of: 3 wt.pct. Mn, 2.0 wt.pct. Si, 4 wt.pct. Ni, 4 wt.pct. Cr, 1.5 wt.pct. Mo and ≤ 1 wt.pct. W, V, Nb and Co. Since for Nb, V, W, Si and Mo, the binary iron phase diagrams contain gamma loops, we assume that the binary loop extents set some kind of limit on the maximum addition which can be accepted in the binary formula.

The above limits apply only to the α+γ range which is the only region where quantitative verification is possible. The δ/γ, δ/L, γ/L and γ/carbide fields are also assumed to be qualitatively correct to the same alloy limits although there are unknown inaccuracies due to poorly established thermodynamic data, binary iron phase diagrams and lack of experimental multicomponent observations in these regions. Since the reliability of the information in these areas was questionable, no multi-component quasi-ternary phase diagrams were attempted.

Application of the Wagner Formalism for linearization purposes in our formula required that all variables and standard states be defined at infinite dilution. Although the carbon-carbon and carbon cross interactions are rigorously defined for small solute additions, the values
reported in the literature are actually averages over a wide range of carbon compositions, and usually measured as functions of temperature. The free energy data is referenced at the standard state of infinite dilution but is also an average over a range of composition. These averaging processes in obtaining the thermodynamic parameters could facilitate the extension of the formulae to richer alloys.

It was previously mentioned that the predicted values for the \( \text{Ae}_3 \) temperatures tended to fall below these experimental ones. Judging by the agreement of our ternary phase diagrams with those predicted and carefully verified by Uhrenius and the experimental ternary phase diagrams of Gilmour (85) and Sharma (79) it is thought that perhaps the experimental results, particularly U.S. Steel contain a systematic error. The experimental \( \text{Ae}_3 \) temperatures could be affected by segregation, insufficient austenitising temperatures or inadequate holding times. Since the binary and ternary phase diagram determinations were made by holding samples at carefully controlled temperatures for long periods of time, they are probably better than the \( \text{Ae}_3 \) measurements. The latter fault, too short a holding time, would certainly account for the experimental results being consistently higher than predicted. It is nonetheless thought, because of the behaviour of the \( \text{Ae}_3 \) and ternary results at low carbon contents, that our manganese and perhaps nickel and chromium free energy data for this region is in error, or that there exists a higher order cross effect which we are unable to account for in our treatment.
Application to Steels

Baganis and Kirkaldy (9) demonstrated that predictive formulae of this type could be used as a boundary condition for the TTT curve as applied in a hardenability predictor. Although this is an indirect use of this type of work, the potential uses in the future are much greater.

At the moment, it is possible for us to predict the solution temperatures of various Fe₃C-type carbides and their solubility limits at any temperature. Given more partition coefficient data and empirical analogues of the Fe-C carbide line, it would be possible to predict the lowest temperature a steel could be held at for the complete dissolution of carbides.

A much more important and promising use of our constant composition sections of the Fe-C binary lies in its applicability to the development and implementation of steels containing a duplex microstructure (92). These steels are manufactured by austenitising then quenching to martensite, followed by cycles of heating in the α+γ region then quenching to form a structure of ferrite and dislocated martensite. Since the crucial step is the holding step in the two phase region (during which the alloy segregates into ferrite and austenite along the equilibrium tie-line), we hope our formulae will be instrumental in cutting development time and cost by allowing the prediction of a reasonable carbon composition or temperature starting point. Examples of the types of phase diagrams possible are shown in Figures (33) to (37) for a Fe-1.0 wt.pct. Cr-1.0 wt.pct. Mo-C alloy.
Figure 33  Fe-1.0 Mo - 1.0 Cr-C constant composition section
Figure 34  Fe-Cr-C-1.0 Mo isothermal phase diagram at 1100 K
Figure 35  Fe-Mo-C-1.0 Cr isothermal phase diagram at 1100 K
Figure 36  Fe-Cr-C-1.0 Mo isothermal phase diagram at 1000 K
Figure 37  Fe-Mo-C-1.0 Cr isothermal phase diagram at 1000 K
CHAPTER V
CONCLUSION

This thesis describes the derivation of a rigorous formula for the prediction of multicomponent phase diagrams with the following limits: \( \%C < 2 \text{ wt\%}, \%\text{Mn} < 3 \text{ wt\%}, \%\text{Si} < 1 \text{ wt\%}, \%\text{Ni} < 3\%\), \( \%\text{Cr} < 2.5\%\), \( \%\text{Mo} < 2\%\), \( \%\text{Cu} < 3\%\) and \( W, V, \text{Nb} \) and \( \text{Co} < 1 \text{ wt\%}\).

Because the formula is linear in all elements with the exception of carbon, it is capable of describing phase diagrams with any number of components.

The predictive formulae are simple enough to be programmed on a desk calculator.

They can be used to predict constant composition sections of the iron carbon phase diagrams with the composition of the alloying elements held constant and the deviation from the Fe-C binary plotted with respect to different carbon contents. Quasiterminal isotherms of any order can be plotted, with any number of elements at constant composition and carbon and another alloying element changing at constant temperature.

We also offer subsidiary formula for the prediction of the multicomponent eutectoid composition and temperature and for the deviation of the 1\( T_0 \) line with addition of alloy solutes.
APPENDIX 1

To derive the first phase boundary correction formula we start with the expressions for the equality of chemical potentials. For Fe(n=0) we have

\[
\frac{\Delta^{0}_{1}G_{0}^{Y-L}}{RT} = \ln\left[ \frac{1-x_{1}^{L} \frac{\gamma}{2} x_{1}^{L}}{1-x_{1}^{L} \frac{\gamma}{2} x_{1}^{L}} \right] - x_{1}^{L} \frac{\gamma}{2} x_{1}^{L} + x_{1}^{L} \frac{\gamma}{2} x_{1}^{L} - x_{1}^{L} \frac{\gamma}{2} x_{1}^{L} = \frac{\gamma}{2} x_{1}^{L} \frac{\gamma}{2} x_{1}^{L}, \tag{1}
\]

For C(n=1) we have

\[
\frac{\Delta^{0}_{1}G_{1}^{Y-L}}{RT} = \ln\left[ \frac{x_{1}^{Y}}{x_{1}^{L}} \right] + \frac{\gamma}{11} x_{1}^{L} - \frac{\gamma}{11} x_{1}^{L}, \tag{2}
\]

and for component i we have

\[
\frac{\Delta^{0}_{1}G_{i}^{Y-L}}{RT} = \ln\left[ \frac{x_{i}^{Y}}{x_{i}^{L}} \right] + \frac{\gamma}{11} x_{i}^{L} - \frac{\gamma}{11} x_{i}^{L}. \tag{3}
\]

Now rearranging eq. (2)

\[
x_{1}^{Y} \exp(\frac{\gamma}{11} x_{1}^{L}) = x_{1}^{L} \exp(\frac{\Delta^{0}_{1}G_{1}^{Y-L}}{RT} + \frac{\gamma}{11} x_{1}^{L}). \tag{4}
\]

Expanding the exponential and disregarding higher order terms gives

\[
x_{1}^{Y}(1+\frac{\gamma}{11} x_{1}^{L}) = x_{1}^{L} \exp(\frac{\Delta^{0}_{1}G_{1}^{Y-L}}{RT} + \frac{\gamma}{11} x_{1}^{L}). \tag{5}
\]

To a first approximation, for \( x_{1}^{L}, x_{1}^{Y} \) small

\[
x_{1}^{Y} = x_{1}^{L} \exp(\frac{\Delta^{0}_{1}G_{1}^{Y-L}}{RT}). \tag{6}
\]

Substituting for \( x_{1}^{Y} \) in eq. (5) and rearranging we obtain the next higher order approximation

\[
x_{1}^{Y} = \frac{x_{1}^{L} \exp(\frac{\Delta^{0}_{1}G_{1}^{Y-L}}{RT} + \frac{\gamma}{11} x_{1}^{L})}{(1+\frac{\gamma}{11} x_{1}^{L} \exp(\frac{\Delta^{0}_{1}G_{1}^{Y-L}}{RT}))}. \tag{7}
\]
\[ x_i^\gamma (1 + \varepsilon_{11} x_i^\gamma) = x_i^L \exp \left[ \frac{\Delta G_i}{RT} + \varepsilon_{11}^L x_i^L \right] \]  

(8)

Substituting for \( x_i^\gamma \) from (6) and rearranging we obtain

\[ x_i^\gamma = \frac{x_i^L \exp \left[ \frac{\Delta G_i}{RT} + \varepsilon_{11}^L x_i^L \right]}{(1 + \varepsilon_{11} x_i^\gamma \exp \left[ \frac{\Delta G_i}{RT} \right])} \]  

(9)

Now from (1) we write

\[ 1 - x_i^L - \frac{n}{2} x_i^L = (1 - x_i^\gamma - \frac{n}{2} x_i^\gamma) \]

\[ \exp \left[ - \frac{\Delta G_i}{RT} \right] - x_i^\gamma \frac{n}{2} \varepsilon_{11} x_i^\gamma + x_i^L \frac{n}{2} \varepsilon_{11} x_i^L - \varepsilon_{11}^L (x_i^\gamma)^2 + \varepsilon_{11}^L (x_i^L)^2 \]  

(10)

and let

\[ A_i = \frac{\exp \left[ - \frac{\Delta G_i}{RT} - \varepsilon_{11}^L \right]}{1 + \varepsilon_{11} x_i^L \exp \left[ - \frac{\Delta G_i}{RT} \right]} \]  

(11)

So that

\[ x_i^\gamma = x_i^L A_i \]  

(12)

\[ x_i^\gamma = x_i^L A_i \]  

(13)

Next, substituting for \( x_i^\gamma \) and \( x_i^L \) in (10) we obtain

\[ 1 - x_i^L - \frac{n}{2} x_i^L = (1 - x_i^L A_i - \frac{n}{2} x_i^L A_i) \]

\[ \exp \left[ - \frac{\Delta G_i}{RT} - x_i^L A_i \frac{n}{2} \varepsilon_{11} x_i^L A_i + x_i^L \frac{n}{2} \varepsilon_{11} x_i^L - \varepsilon_{11}^L (x_i^L A_i)^2 + \varepsilon_{11}^L (x_i^L)^2 \right] \]  

(14)

Now carrying out a first order expansion about the iron carbon line, \( T = T_0 \), of the quantities \( \exp \left[ - \frac{\Delta G_{0,1}}{RT} \right] \) in the leading term on the right-hand side of (14) (all other temperature-dependent terms appear in higher orders) we obtain
\[
\exp \left[ \frac{\Delta^0 G(T)}{RT} \right] = \exp \left[ -\frac{\Delta^0 S}{R} \right] \exp \left[ -\frac{\Delta^0 H}{RT_0 (1+\frac{\Delta^0 \Delta T}{T_0})} \right] = (1 - \frac{\Delta^0 H \Delta T}{RT_0^2}) \exp \left[ \frac{\Delta^0 G}{RT_0} \right]
\]

(15)

Following these substitutions we can set all the remaining \( A_1 \times^*(T) = A_1, A_i(T_0) = A_1, i \). As a subsidiary relation we can evaluate equation (9) at the limit of the Fe-C phase diagram \((x_1 = 0; T = T_0)\), viz.,

\[
1 - x_1^L = (1 - x_1^L A_1^0) \exp \left[ -\frac{\Delta^0 G}{RT_0} - \frac{\epsilon_1^T}{2} (x_1^L A_1^0)^2 + \frac{\epsilon_1}{2} (x_1^L)^2 \right]
\]

(16)

Next, discarding higher order terms of the type \( x_i \Delta T, x_i x_j \), (14) becomes

\[
1 - x_1^L - \frac{n}{2} x_1 = (1 - (1 - \frac{\Delta^0 H \Delta T}{RT_0^2}) x_1^L A_1^0 - \frac{n}{2} x_1^L A_1^0) (1 + \frac{\Delta^0 H \Delta T}{RT_0^2})
\]

\[
\cdot \exp \left[ -\frac{\Delta^0 G}{RT_0} - x_1^L A_1^0 \frac{n}{2} \epsilon_1 x_1^L A_1^0 + x_1^L \frac{n}{2} \epsilon_1 x_1^L - \epsilon_1 \frac{\epsilon_1}{2} (x_1^L A_1^0)^2 + \epsilon_1 \frac{\epsilon_1}{2} (x_1^L)^2 \right]
\]

(17)

Now since the quantity \( -x_1^L A_1^0 \frac{n}{2} \epsilon_1 x_1^L A_1^0 + x_1^L \frac{n}{2} \epsilon_1 x_1^L \) is \( \ll 1 \) the exponential on the right can be expanded to yield

\[
1 - x_1^L - \frac{n}{2} x_1 = (1 - (1 - \frac{\Delta^0 H \Delta T}{RT_0^2}) x_1^L A_1^0 - \frac{n}{2} x_1^L A_1^0)
\]

\[
\cdot \left[ (1 + \frac{\Delta^0 H \Delta T}{RT_0^2} - x_1^L A_1^0 \frac{n}{2} \epsilon_1 x_1^L A_1^0 + x_1^L \frac{n}{2} \epsilon_1 x_1^L) \right]
\]

\[
\cdot \exp \left[ -\frac{\Delta^0 G}{RT_0} - \epsilon_1 \frac{\epsilon_1}{2} (x_1^L A_1^0)^2 + \epsilon_1 \frac{\epsilon_1}{2} (x_1^L)^2 \right]
\]

(18)

Again since the quantity \( -x_1^L A_1^0 \frac{n}{2} \epsilon_1 x_1^L A_1^0 + x_1^L \frac{n}{2} \epsilon_1 x_1^L \) is \( \ll 1 \), we can rearrange between the left and right hand sides using the binomial theorem to obtain

\[
\ldots
\]
\[
\begin{align*}
\{1 - \frac{\Delta H^o \Delta T}{RT_o^2} \} + x_i A_i^o \sum_{L_i^0} \frac{\Lambda_{i-1}^1}{2} x_i x_{i-1} + x_i L_n \sum_{L_i^1} \frac{\Lambda_{i-1}^1}{2} x_i \Lambda_{i-1}^1 + x_i L \sum_{L_i^1} \frac{\Lambda_{i-1}^1}{2} x_i \Lambda_{i-1}^1 + x_i \frac{\Delta H^o \Delta T}{RT_o^2} - \sum_{i=1}^n \frac{\Lambda_{i-1}^1}{2} x_i + \frac{\Lambda_{i-1}^1}{2} \sum_{i=1}^n \Lambda_{i-1}^1 & \\
= \{1 - x_i A_i^o \sum_{L_i^0} \frac{\Delta H^o \Delta T}{RT_o^2} \} & - \frac{\Lambda_{i-1}^1}{2} x_i + x_i A_i^o \sum_{L_i^0} \frac{\Delta H^o \Delta T}{RT_o^2} & \sum_{i=1}^n \frac{\Delta H^o \Delta T}{RT_o^2} - \frac{\Lambda_{i-1}^1}{2} x_i + x_i A_i^o \sum_{L_i^0} \frac{\Delta H^o \Delta T}{RT_o^2} & (19)
\end{align*}
\]

But from (16)
\[
(1 - x_i A_i^o) = (1 - x_i^L) \exp\left[\frac{\Delta G^o}{RT_o^2} + \frac{\gamma_{i-1}^L}{2} (x_i A_i^o)^2 \right] - \frac{\Lambda_{i-1}^1}{2} x_i + x_i A_i^o \sum_{L_i^0} \frac{\Delta H^o \Delta T}{RT_o^2} & \sum_{i=1}^n \frac{\Delta H^o \Delta T}{RT_o^2} - \frac{\Lambda_{i-1}^1}{2} x_i + x_i A_i^o \sum_{L_i^0} \frac{\Delta H^o \Delta T}{RT_o^2} & (20)
\end{align*}
\]

Substituting in (19) and rearranging gives
\[
\sum_{i=1}^n \frac{\Lambda_{i-1}^1}{2} x_i + x_i A_i^o \sum_{L_i^0} \frac{\Delta H^o \Delta T}{RT_o^2} & \sum_{i=1}^n \frac{\Delta H^o \Delta T}{RT_o^2} - \frac{\Lambda_{i-1}^1}{2} x_i + x_i A_i^o \sum_{L_i^0} \frac{\Delta H^o \Delta T}{RT_o^2} & (21)
\end{align*}
\]

Solving for \( \Delta T \) and rearranging to obtain the \( x_i^L \)'s as common factors yields finally
\[
\Delta T = RT_o^2 \frac{\sum_{i=1}^n A_i x_i^L}{\sum_{i=1}^n A_i x_i^L}
\]

where
\[
A_i = \left[ \frac{\Delta G^o}{RT_o^2} + \frac{\gamma_{i-1}^L}{2} (x_i^L)^2 \right] \exp\left[\frac{\Delta G^o}{RT_o^2} + \frac{\gamma_{i-1}^L}{2} (x_i^L)^2 \right] - \frac{\Lambda_{i-1}^1}{2} x_i + x_i A_i^o \sum_{L_i^0} \frac{\Delta H^o \Delta T}{RT_o^2} & \sum_{i=1}^n \frac{\Delta H^o \Delta T}{RT_o^2} - \frac{\Lambda_{i-1}^1}{2} x_i + x_i A_i^o \sum_{L_i^0} \frac{\Delta H^o \Delta T}{RT_o^2} & (22)
\end{align*}
\]

Other than the Wagner expansions we have made no approximations in the carbon variables, \( x_i^L \). If we assume, as is likely, that the empirical determinations of the linear coefficients in the Wagner expansions are actually averages over linear and quadratic effects then we are justified in retaining the quadratic carbon terms in (22). These are marginally
significant for carbon concentrations above the eutectoid.

APPENDIX 2

To derive the metal(I)-carbide(II) correction formula we proceed from the Gibbs-Duhem equation. At constant \( T \) and \( P \) we have

\[
X_0^I du_0 + X_1^I du_1 + \frac{n}{2} X_1^I du_i = 0
\]  
(1)

and

\[
X_0^{II} du_0 + X_1^{II} du_1 + \frac{n}{2} X_1^{II} du_i = 0
\]  
(2)

Since \( \sum_0^n x_i = 1 \) we can subtract and rearrange to obtain

\[
(X_1^{II} - X_1^I) (du_1 - du_0) + \frac{n}{2} (X_1^{II} - X_1^I) (du_i - du_0) = 0
\]  
(3)

Now using the Wagner expansions with reference states at infinite dilution we have

\[
\frac{du_0}{RT} = - \sum_{i=1} X_i^I - X_i^I
\]  
(4)

\[
\frac{du_1}{RT} = \frac{dx_1}{x_1} + \epsilon_1 11 dx_1 + \frac{n}{2} \sum_{i=2} \epsilon_1 11 dx_i
\]  
(5)

and

\[
\frac{du_i}{RT} = \frac{dx_i}{x_i} + \epsilon_1 11 dx_i + \frac{n}{2} \sum_{k=2} \epsilon_1 11 dx_k
\]  
(6)

Substituting into (3), dropping the superscript I and letting all \( X_i \rightarrow 0 \) yields

\[
\left\{ \frac{x_1^{II}}{x_1^I} - 1 + (x_1^{II} - x_1^I) (1 + \epsilon_1 11) \right\} dx_1 + \frac{n}{2} \sum_{i=2} \left( k_i - 1 + (1 + \epsilon_1 11) (x_1^{II} - x_1^I) \right) dx_i = 0.
\]  
(7)

Noting that we are seeking a limiting solution wherein \( \Delta X_1 \) is linear in the \( X_i \) we can integrate (7) in the limiting approximation that

\[
x_1^{II} - x_1^I = x_1^{II} - x_1^c
\]  
(8)

where \( x_1^c \) is the plain carbon limit of the integral. Thus

\[
x_1^{II} \ln \frac{x_1^I}{x_1^c} + \left( (x_1^{II} - x_1^c) (1 + \epsilon_1 11) - 1 \right) (x_1 - x_1^c) = \sum_{i=2} \frac{k_i - 1 + (1 + \epsilon_1 11) (x_1^{II} - x_1^I)}{2} X_i
\]  
(9)
Letting $X_1 = x_1^c + (x_1^c - x_1^c)$ and expanding the logarithm we obtain

$$\Delta x_1 = x_1 - x_1^c = -\frac{x_1^c \prod_{i=2}^{n} x_i (k_i - 1 + (1 + \epsilon_{11})(x_i^{II} - x_i^c))}{x_1^{II} + x_1^c (x_1^{II} - x_1^c) (1 + \epsilon_{11}) - 1}$$

(10)
APPENDIX III

At the $T_0$ temperature:

\[ G_1^I = G_1^2 \]  \hspace{1cm} (1)

\[ x_1^I = x_1^{II} \]  \hspace{1cm} (2)

which for the binary gives:

\[ x_1^I \nu_1 + x_0^I \nu_2 = x_1^{II} \nu_1^{II} + x_0^{II} \nu_0^{II} \]  \hspace{1cm} (3)

but since $x_1^I = x_1^{II}$:

\[ x_1^I (\nu_1 - \nu_1^{II}) + x_0^I (\nu_0 - \nu_0^{II}) = 0 \]  \hspace{1cm} (4)

Therefore:

\[ x_1^I \left( \frac{\Delta^0 G_1^{I+II}}{RT} \right) + x_0^I \left( \frac{\Delta^0 G_0^{I+II}}{RT} \right) = 0 \]  \hspace{1cm} (5)

Similarly, for a multicomponent system:

\[ x_1^I \left( \frac{\Delta^0 G_1}{RT} \right) + x_0^I \left( \frac{\Delta^0 G_0}{RT} \right) + \frac{n}{2} \left( \frac{\Delta^0 G_1^{III}}{RT} \right) = 0 \]  \hspace{1cm} (6)
At $T = T_o$, for the binary Fe-C system:

$$x^I_1 \frac{\Delta G^0(T_o)}{RT_o} + x^O_0 \frac{\Delta G^0(T_o)}{RT_o} = 0 \quad (7)$$

Expanding $\frac{\Delta G^0_i}{RT}$ about $T = T_o$:

$$\frac{\Delta^0 G(T)}{RT} = \frac{\Delta^0 G(T_o)}{RT_o} - \frac{\Delta^0 H}{RT_o} \Delta T \quad (8)$$

Substituting (8) into (6) and subtracting (7) yields:

$$-x^I_1 \frac{\Delta^0 H_1 \Delta T}{RT^2_o} + x^O_0 \frac{\Delta^0 H_0 \Delta T}{RT^2_o} = \sum \frac{x^I_i \Delta^0 G_i}{RT_o} - \frac{x^I_i \Delta^0 H_1^0}{RT^2_o} \quad (9)$$

Since, in the dilute limit terms of order $x \Delta T$ are negligible:

$$\frac{\Delta T}{RT^2_o} \left( x^I_1 \Delta^0 H_1 + x^O_0 \Delta^0 H_0 \right) = \frac{1}{RT_o} \sum \frac{x^I_i \Delta^0 G_i}{2} \quad (10)$$

Thus, in the binary limit, $\frac{n}{2} x_1 \rightarrow 0$, $x_0 = 1-x_1$ and

$$\Delta T = \frac{1}{RT_o} \sum \frac{x^I_1 \Delta^0 G_1}{x^I_1 \Delta^0 H_1 + (1-x_1) \Delta^0 H_0} \quad (11)$$

where $T_o$ is for the binary Fe-C phase diagram. It can be seen, that upon the addition of alloying elements, for dilute alloys that
\[ T_{o,\text{alloy}} = T_o \left( 1 + \frac{1}{RT_o} \sum_{i}^n \frac{x_i^{I} \Delta H_i^{\text{I}+\text{II}}}{x_i^{I} \Delta H_i^{\text{I}} + (1-x_i^{I}) \Delta H_o^{\text{II}}} \right) \] (12)
APPENDIX IV

If an alloying element $i$, is added to an Fe-C binary alloy, the result is to shift the $\Delta e$ line.

Now at any amount of $i$ added:

$$x^T = x_c + \Delta x_1$$

where $x_c$ is for the Fe-C binary at $T$

$$T^T = T + \Delta T$$

where $T_c$ is for the Fe-C binary at $x_c$

If $m_g$ is the slope of the $\Delta e_3$ ($\alpha + \gamma / \gamma$) line, it is obvious from the diagram (Fig. 1) that

$$x^T = x_c + \frac{\Delta T}{m_g}$$

This means that at any temperature $T$ and amount of alloy addition $i$, that it is possible to calculate the corresponding shift in $x_i$. Thus, the coordinates of the $\alpha + \gamma / \gamma$ phase boundary at temperature $T$ and any amount $x_i$ will be in the form:

$$P = P(x_c + \frac{\Delta T}{m_g}, x_i)$$

where $\Delta T$ is a function $x_i$ of the previously mentioned type:

$$\Delta T = RT^2 \sum_{i=2}^{n} A_i x_i$$
Figure 38 Schematic of deviation of \(Ae_3\) and carbide lines with addition of alloying elements.
Similarly, for the carbide line

\[ x^* = x_c^1 + \Delta x_1 \]

where \( x_c^1 \) is the \( \gamma/\gamma+Fe_3C \) phase limit in the binary Fe-C system. The coordinates of any point on the isothermal diagram (Fig. J) is thus

\[ P = P(x_c^1 + \Delta x_1, x_i) \]

In the same manner it is possible to solve for the intersection of these two points, to calculate the temperature and composition of the eutectic.

Let

- \( \text{GAMMA} = \alpha + \gamma/\gamma \) phase boundary
- \( \text{CARBIDE} = \gamma/\gamma+Fe_3C \) phase boundary

Now, at \( x_i \) = constant, the eutectic point lies on the intersection of the two planes, LM at P.

Now, if \( m_g \) is the slope of the \( Ae_3 \) line (FG) and \( m_c \) is the slope of the carbide line (RS) both at the binary eutectic, the transformation to move L' to P is:

\[ P = L + \Delta T + \Delta X \]

Now, projecting back to the \( T-x_1 \) axis:

\[ x_i^* = x_E + \frac{T^*-T_E}{m_c} + \Delta x_1 \]

and

\[ T^* = T_E + (x_i^*-x_i) \cdot \frac{m_g}{m_c} + \Delta T \]
Figure 39  Schematic of multicomponent eutectoid intersection
Hence, at the eutectic, generalizing over all \( i \):

\[
x_1^* = \frac{m_g}{m_c} \left( 1 - \frac{m_g}{m_c} \right) + \frac{\Delta T}{m_c} + \Delta T x_1
\]

and

\[
T^* = \frac{T_E \left( 1 - \frac{m_g}{m_c} \right) + \Delta T + m_g \Delta x_1}{1 - \frac{m_g}{m_c}}
\]
APPENDIX V

Program for Calculating Isothermal Quasi-ternary Multicomponent phase diagrams

Variable List

Variables

I,K,KL,M,N
CSTORE, DEN, REP1, S,
TEST, V1N, VVK, XD, XP,
YD, YP, ZA, ZB, ZC, SLOPE
ZLS, ZRS

J1, J2, J3, J4, J5,
NOB, IIM, XNUM

A, B, O

CARK

DT

DIC

DTE

DI

GFE

HC

Height

HFE

IER, IERR

NUMPLT

: indices
: dummy variables
: counters
: coefficients of quadratic to be solved
: holds γ/cementite partition coefficients of all elements
: temperature change from Fe-C binary
: carbide line temperature of alloy
: Aez temperature of alloy
: slope of Aez line at temperature
: \( \Delta \sigma G_{O}^{\nu-\gamma} \)
: \( \Delta \sigma H_{I}^{\nu-\gamma} \)
: height of characters to be plotted
: \( \Delta \sigma H_{O}^{\nu-\gamma} \)
: error messages that equal zero if subroutines operate properly
: number of separate phase diagrams to be plotted
Q : number of the ternary alloying element to be plotted
R : gas constant
SA : partition coefficient in calculations
SIGSQ : sum of squares of deviations from fitted quadratic
TDM : temperature of isotherm
THETA : angle of characters to be plotted
TO : temperature from empirical Fe-C phase diagram
XCNLW : composition of carbon of carbide line in alloy in mole fraction
XSOL, XSOIX : carbon composition in mole fraction of α/α+γ boundary
XWCAR : carbon composition of carbide line in wt.pct.
ZLG : complex, larger root of quadratic containing eutectoid carbon composition in mole fraction
ZLC : complex, smaller root of quadratic containing eutectoid carbon composition

Arrays
BX, BZ, C, DXC, WA, WC XWT, Y : dummy or working arrays
D, E, F, P, U : dummy arrays holding calculated points for curve fitting
W1, W2, W3 : dummy arrays holding calculated points in wt.pct.
EA : gamma phase interaction parameters
EB : alpha phase interaction parameters
G : $\Delta^0 G_{i}^{\alpha+\gamma}$ data
POLY : coefficients of quadratic for $\text{Ae}_3$ line
SARRAY : coefficients of quadratic for carbide line
VALP : $\alpha/\gamma$ partition coefficients for all elements
WT : composition of elements in wt.pct.
X : composition of elements in mole fraction
XW : molecular weights of alloying elements
T,V : Tabulated $\Delta G_0^{\alpha-\gamma}$ data; $T(I)$ holds the temperature
and $V(I)$ the $\Delta G_0^{\alpha-\gamma}$ value at that temperature

Results: This program, as written was used to calculate and plot the following isothermal phase diagrams:

Fe-Si-C at 973 and 1073 K
Fe-Mn-C at 973, 1035, 1073 and 1173 K
Fe-Ni-C at 973, 1073 and 1173 K
Fe-Cr-C at 1023, 1045, 1073 and 1173 K
Fe-Cu-C at 1023, 1073 and 1173 K
PROGRAM TST INPUT, OUTPUT, TAPE5=INPUT, TAPE6=OUTPUT

THIS PROGRAM CALCULATES DIRECTLY, ISOTHERMAL PHASE DIAGRAMS OF THE TYPE I Fe-C-X-X-X-X-, WHERE X IS ONE OF Mn, Si, Ni, Cr, Mo, Cu, W, V, A HE Co ; OR ANY COMBINATION OF THESE ELEMENTS. THE PLOT ROUTINES ARE DESIGNED FOR A BENSON-LEHRER PLOTTING DEVICE WITH A CDC-6400 COMPUTER. THE ELEMENT TO BE INCREMENTED ALONG THE ORIGIN IS SPECIFIED BY READING IN THE APPROPRIATE ELEMENT NUMBER (CALLED Q). THE REST OF THE ELEMENTS WHICH ARE HELD CONSTANT IN THE CALCULATIONS ARE READ IN FROM A SINGLE CARD (I, "X") AS IF IT WERE A SINGLE STEEL COMPOSITION BEING ENTERED.

Q = THE NUMBER OF THE ELEMENT TO BE INCREMENTED

TDGH = THE TEMPERATURE OF THE ISOTHERM REQUIRED

WT(I) = THE AMOUNT OF ELEMENT I IN WT

X(I) = THE AMOUNT OF ELEMENT I IN MOLE FRACTION. THIS IS CALCULATED IN THE PROGRAM AND IS CALLED PI(I) FOR THE CARBIDE PHASE.

THE PHASE DIAGRAM IS PLOTTED IN MOLE FRACTION AND THE THREE PHASE REGION IS PLOTTED IF THERE IS A SINGLE THREE PHASE FIELD INTERSECTION IN THE REGION. THIS IS DETERMINED BY FITTING THE GAMA-CARBIDE AND ALPHA-GAMMA PHASE BOUNDARIES WITH QUADRATICS AND FINDING THEIR INTERSECTION. IF NONE EXISTS THEN THE PHASE REGION CONTAINS NO THREE PHASE TRIANGLE.

DIMENSION D(200), E(200), F(200), U(200), Z(200), WA(10), C(12)

DIMENSION X(11), WT(11), XH(11), XHM(11)

DIMENSION T(I), D(I), D(I), BZ(I), B(11), W(I)

DIMENSION X(I), Y(I), Z(I), BZ(I), B(I), W(I), O(I)

DIMENSION POLY(3), X(11), Y(11), Z(11)

DIMENSION J(11), W(I), W(I), W(I), W(I)

COMMON /DELG/ G(I), Z(I), Z(I), G(I)

COMMON /TYP/ TYP

COMMON /SSC/ SSC, T(I), V(I)

COMMON BLOCK SSG, HOLDS HARVIGS DELTA G = O DATA FOR ALPHA GAMA FOR INTERPOLATION USE.

COMMON /AGPAF/ VALP(I)

COMMON /XVAL/ XVAL(I)

COMMON /TEMP/ TEMP

COMMON /ACSXP/ ACSX

COMPLEX ZSM, ZLG

INTEGER Q
REP1=0.01
N=94
NO3=75
E=1.987

XW CONTAINS THE MOLECULAR WEIGHS OF THE ELEMENTS

XH(1)=12.011
XH(2)=16.000
XH(3)=19.015
XH(4)=35.453
XH(5)=51.094
XH(6)=96.54
XH(7)=63.54
XH(8)=153.34
XH(9)=50.942
XH(10)=92.086
XH(11)=98.933

READ IN THE DELTA G DATA, THE ELEMENT AND TEMPERATURE REQUIRED

DO 101 K=1,N
READ (5,115) T(K),V(K)
CONTINUE

READ (5,116) NUMPLT
DO 114 I1M=1,NUMPLT
TSUM=0
J1=J2=J3=0
READ (5,117) Q,TGDH

READ IN THE CONSTANT COMPOSITIONS IN WT. PCT.

READ (5,118) (WT(I),I=1,11)
WRITE (6,119) Q
WRITE (6,120)
DRAW THE GRID OUTLINES

CALL GRID (Q)
WT(Q)=0.0

START TO CALCULATE THE POINTS TO BE PLOTTED

DO 106 KL=1,40
WT(Q)=WT(Q)+0.1
XH(KL)=WT(KL)
XCMH=XCMH+0.3
Q0=Q0
XH(T1)=Q0

CARLIN Calculates THE CARBIDE LINE

CALL CARLIN (XH,P,WT,XHT,XDC,XCMH)
XHCM=XHT(1)
W3(KL)=XHCAR

TAG Calculates THE IRON DATA, NEEDED FOR THE TEMPERATURE CHANGE CALCULATIONS

CALL TAG (XH,WT,X,TO,GFE,HC,HFE)
GAG CALCULATES THE DELTA G AND INTERACTION PARAMETERS NEEDED
CALL GAG (TO)

CALCT DOES THE TEMPERATURE CALCULATIONS
CALL CALCT (TO, X, HC, HFE, DT)
DT2=DT+TO
XSOL=X(1)*SA
J3=J3+1

CALCULATE AND LOCATE THE ALPHA/ALPHA+GAMMA BOUNDARY
N=J3
XSOLX=XSOL
CALL CHANGE (XSOLX, XW, X, XWT)

V'T=VALP(0)
IF (REP1.LT.C.C1) XSOLX=G.G
D(*)=XSOLX
XD=XSOLX
YP=X(0)*VALP(0)
X(0)=YP*100
YO=YP*100
IF (REP1.LT.G.G1) GO TO 102
CALL UNITTO (XD, YD, XP, YC)
CALL GRAW (XP, YP, 0.1J25, 9)
CONTINUE
102

CALCULATE AND PLOT THE AE3 LINE. THE CALCULATIONS MUST BE DONE
IN WT. PCT. THEN CONVERTED TO MOLE FRACTION.

REP1=WT(1)+(TO-DTE)/D1
IF (REP1.LT.G.G1) REP1=J.I
WT(1)=REP1
N2(I)=REP1
A=1.

CONVERT WT. PCT. TO ATOMIC FRACTION
DEH=(4-WT(1)-WT(2)-WT(3)-WT(4)-WT(5)-WT(6)-WT(7)-WT(8)-WT(9)-WT(10))
0.1=WT(11)/55.847*WT(1)/WT(2)+WT(1)/WT(3)+WT(4)/WT(5)+WT(6)/WT(7)+WT(8)/WT(9)+WT(10)/
3*WT(11)/WT(1)/WT(1)
DO 103 I=1,11
X(I)=(WT(I)/XH(I))/DEH
103
CONTINUE
IF (REP1.LT.C.C1) X(1)=G.G
XD=X(1)
YD=X(2)
X(2)=YD*100
YD=YD*100
IF (REP1.LT.G.G1) GO TO 104
CALL UNITTO (XD, YD, XP, YC)
CALL GRAW (XP, YP, 0.1J25, 9)
CONTINUE

PLOT THE CARBIDE POINTS
J1=J1+1
IF (ABS(DTC-TCGHM) .GE. 1.0) GO TO 105
J2=J2+1
M=J2
VVK=CAR(K(Q)
XD=XC+EH
Z(Q)=XCH+EH
YD=P(Q)
U(N)=P(Q)
XD=XD+100
YO=YO+100
CALL UNITTO (XD,YD,XP,YP)
CALL GRAF (XP,YP,0,J25,1)
CONTINUE

105 WRITE THE VALUES PLOTTED IN HEIGHT PCT.
WRITE (6,121) W1(KL),W2(N),W3(KL),TGHM

CALCULATE THE EUTECTOID, IF CHE EXISTS
TSUM=TSUM+W2(N)
CONTINUE
IF (TSUM*EQ*0.0) GO TO 113
IF (TGHM*LE.*10.0) GO TO 110
CONTINUE
VALP(N)=VVT
CAR(H)=VVK
VIN=1/VALP(N)
WRITE (6,122) Q
WRITE (6,123) VALP(N),VIN
WRITE (6,124) CAR(Q)

FIT THE AE3 LINE
W(1)=0.0
CALL CRLSC (F,E,W,H,Z,HK,SIGS0,POLY,IER)
WRITE (6,126) IER
SARRAY(1)=POLY(1)
SARRAY(2)=POLY(2)
SARRAY(3)=POLY(3)

FIT THE CARBIDE LINE
W(1)=0.0
CALL CRLSC (Z,U,W,H,Z,HK,SIGS0,POLY,IER)
WRITE (6,127) POLY(1),POLY(2),POLY(3),SARRAY(1),SARRAY(2),SARRAY(3)
A=POLY(1)-SARRAY(1)
B=(POLY(2)-SARRAY(2))
C=(POLY(3)-SARRAY(3))
WRITE (6,128) A,B,C

SOLVE FOR INTERSECTION
CALL ROOTS(A,B,C,ZLG,ZSM,IER)
WRITE (6,129) IER
ZLG=REAL(ZLG)
ZSM=REAL(ZSM)
WHITE (6,136) ZSM,ZLG
TEST=3**2-A*C
WHITE (6,131) TEST
C(1)=ZRS
C(2)=POLY(3)+POLY(2)+ZRS+POLY(1)*ZRS**2
CSTORE=C(2)
J4=0
IF (C(1),LT,0.0115) GO TO 108
IF (C(2),LE,0.0) GO TO 108
IF (C(2),GE,0.06) GO TO 138
IF (C(1),GE,0.06) GO TO 138
J4=1
CONTINUE
108 CALCULATE AND PLOT THREE PHASE TRIANGLE, IF ONE EXISTS
C(1)=ZLS
C(2)=POLY(3)+POLY(2)+ZLS+POLY(1)*ZLS**2
J5=0
IF (C(1),LT,0.0115) GO TO 109
IF (C(2),LE,0.0) GO TO 109
IF (C(1),GE,0.06) GO TO 109
IF (C(2),GE,0.06) GO TO 109
J5=1
109 IF (J4+J5,EQ,0) GO TO 112
IF (J4+J5,EQ,2) GC TO 111
IF (J4,EQ,1) C(1)=ZRS
IF (J4,EQ,0) C(2)=CSTORE
C(1)=C(1)+100
C(2)=C(2)*10.0
C VALF(I) IS THE INVERSE A/G PART CCCEF FOR ELEMENT I
IF (HGT,EQ,6) M=4-6
D(M)=D(M)+100
ZM=VALP(0)*C(2)
CALL PLT(LN (C(1),ZM,C(1),C(2))
110 CONTINUE
GO TO 113
111 WHITE (5,132)
112 CONTINUE
113 CONTINUE
WHITE NAME AND TEMPERATURE ON PLOT
CALL PLTLET (7,0.325,0.0,3.5,6.2,7/TRED. =)
R=4.85
S=5.2
HEIGHT=0.325
THETA=0.0
ANUM=TOGM
CALL NUMBER (R,S,HEIGHT,ANUM,THETA,6H(5,0))
CALL PLTLET (1,0.325,3.0,5.8,6.2,1/HK)
CALL PLTLET (9,0.75,9.0,-4.0,-2.0,9/HB THOMSON)
CALL PLOT (35,0,0.3,3)
CONTINUE
CALL PLOT (X, Y, 999)
STOP

C
FORMAT (F5.0, F7.3)
FORMAT (I2)
FORMAT (I3, F6.1)
FORMAT (11F5.6)
FORMAT (1H1, /, 36X, 13MELEMENT NO. II)
FORMAT (3H1X, 8H ELEMENT, 20X, 6H GAMMA, 20X, 8H TE
1MP, 1//,
FORMAT (1X, 8.5, 2(20X, F6.5), 20X, F8.2)
FORMAT (1H1, //, //, 25X, #ELEMENT NO. #, II)
FORMAT (10X, #G7A PART COEFF = #, F9.3, 10X, #A/G PART COEFF = #, F9.3, //)
FORMAT (10X, #IER = #, I2)
FORMAT (10X, #IER = #, I2)
FORMAT (10X, 6F6.4)
FORMAT (10X, 6F6.4)
FORMAT (10X, #A = #, F16.5, 15X, #Z = #, F10.5, 15X, #C = #, F10.5)
FORMAT (10X, #IER = #, I2)
FORMAT (10X, 10X, 6F6.4)
FORMAT (10X, #Z = #, F10.5, 15X, #ZLG = #, F10.5, F10.5)
FORMAT (10X, #DISCRIMINANT = #, F10.5)
FORMAT (10X, #INTERSECTIONS IN REGION, POSSIBLE ERROR#)
END

**************************************************************************
SUBROUTINE GRID(Q)
**************************************************************************
DRAWS GRID AND WRITES APPROPRIATE CAPTIONS

DIMENSION WC(7), Z(7), ECD(1)
INTEGER 0
CALL PLOT (X, Y, -2C)
XSCALE=5.0
YSCALE=6.5
CALL PLTN (0.5, 0.5, 5.0, -5.0, -5.0, 11.0, -5.0, 9.0)
CALL PLTN (0.0, 0.0, 7.0, 0.0, 0.0)
CALL PLTN (0.0, 0.0, 7.0, 0.0, 0.0)
CALL PLTN (7.0, 0.0, 7.0, 0.0, 7.0)
A1=1.0
B1=1.0
A2=1.0
B2=1.0
DO 1 I=1, 6
CALL PLTN (A1, B1, A2, B2)
A1=A1+1.0
A2=A2+1.0
CONTINUE
A1=9.0
A2=9.0
B1=1.0
B2=1.0
DO 1 I=1, 6
CALL PLTN (A1, B1, A2, B2)
B1=B1+1.0
B2=B2+1.0
CONTINUE
HC(i)=3.0
Z(i)=0.0
DO 3 I=2,7
HC(I)=HC(I-1)+0.01
Z(i)=HC(I)
3 CONTINUE
S=-8.25
THETA=0.0
HEIGHT=0.25
DO 4 I=1,7
ANUM=HC(I)
4 CALL NUMBER (R,S,HEIGHT,ANUM,THETA,SN(F4.2))
R=R+1.0
CONTINUE
F=-6.0
S=-0.25
THETA=0.0
HEIGHT=0.25
DO 5 I=1,7
ANUM=HC(I)
5 CALL NUMBER (F,S,HEIGHT,ANUM,THETA,SN(F4.2))
S=S+1.0
CONTINUE
IF (Q.GE.2) CALL PLTLET (23.0,325,90.0,-1.0,1.75,23HMOLE FRACTION 1HANAGENES) 1 1SILICON
IF (Q.GE.3) CALL PLTLET (23.0,325,90.0,-1.0,1.76,23HMOLE FRACTION 1NICKEL
IF (Q.GE.4) CALL PLTLET (23.0,325,90.0,-1.0,1.77,23HMOLE FRACTION 1CHROMIUM
IF (Q.GE.5) CALL PLTLET (23.0,325,90.0,-1.0,1.78,23HMOLE FRACTION 1COPPER
IF (Q.GE.6) CALL PLTLET (23.0,325,90.0,-1.0,1.79,23HMOLE FRACTION 1TUNGSTEN
IF (Q.GE.7) CALL PLTLET (23.0,325,90.0,-1.0,1.80,23HMOLE FRACTION 1VANADIUM
IF (Q.GE.8) CALL PLTLET (23.0,325,90.0,-1.0,1.81,23HMOLE FRACTION 1SCENUM
IF (Q.GE.9) CALL PLTLET (23.0,325,90.0,-1.0,1.82,23HMOLE FRACTION 1C02AL
CALL PLTLET (23.0,325,90.0,-1.0,1.83,0.90,23HMOLE FRACTION CARBON)
RETURN
END

SUBROUTINE NUMBER (R,S,HEIGHT,ANUM,THETA,FMT)

ENCODING SUBROUTINE FOR GRID

DIMENSION BCD(I)
ENCODE (10,FMT,BCD) ANUM
CALL PLTLET (10,HEIGHT,THETA,R,S,BCD)
RETURN
SUBROUTINE INTNUM (R,S,HEIGHT,INUM,THETA,FMT)

ENCODING SUBROUTINE FOR GRID

DIMENSION BCD(11)
ENCODC (10,FFT,BCD) INUM
CALL PLTLET (10,0.25,THETA,R,S,BCD)
RETURN
END

SUBROUTINE TAG (XH,A,T,X,T0,GFE,HG,HFE)

CALCULATES THE POINTS FROM THE EMPIRICAL Fe-C PHASE DIAGRAM, THE DELTA G AND DELTA H DATA FOR IRON AND CARBON.

DIMENSION XH(11), WT(11), X(11)
COMMON /SSO/ T(110), V(110)
COMMON /ACSLP/ D1
COMMON /DTEPP/ TDGH
REAL HG, HFE
A=1100.
C
CALCULATES TO
C=3.765
CT= 1.3
IF (TDGH.SLT.1000.) GO TO 2
DO 1 KLK=1,25
DL=-922.3-216.0*(C.765-C)**3.25
BL=1115.4-TDGH-15.5*C+216.0*(0.765-C)**4.26
AI=C-51/D1
CI=A1
IF (ABS(C-CT).LT.0.005) GO TO 4
CT= A1
1 CONTINUE
GO TO 4
2  DO 3 KLK=1,25
DL=-198.46
BL=1653.6-TDGH-108.46*C
AI=C-51/D1
CI=A1
IF (ABS(C-CT).LT.0.005) GO TO 4
3 CONTINUE
GO TO 4
4  DO 5 KLK=1,25
DL=530.0-156.78*C
WT(1)=C
IF (C.GT.3.765) C=3.765
TO=1115.4-15.5*C+216.0*(0.765-C)**4.26
IF (C.GT.3.765) TO=1115.4-15.5*C+216.0*(0.765-C)**4.26
C CONVERT WT, PCT, TO ATOM FRACTION
DE=(A-WT(1)-WT(2)-4T(3)-WT(4)-WT(5)-WT(6)-WT(7)-WT(8)-WT(9)-WT(10)-WT(11))/55.847+WT(1)/XH(1)+WT(2)/XH(2)+WT(3)/XH(3)+WT(4)/XH(4)+WT(5)/XH(5)+WT(6)/XH(6)+WT(7)/XH(7)+WT(8)/XH(8)+WT(9)/XH(9)+WT(10)/XH(10)+WT(11)/XH(11)
DO 5 I=1,11
X(I)=(AT(I)/XW(T))/DEN
CONTINUE
C
CALCULATES DELTA G FOR FE
K=INT((TO-8.5)/1Q+1)
GFE=SQR(K)+(SQR(K+1)-SQR(K))*((K+1)-TO)/10
HCE=-1.5323
TSAVE=TO
IF (TO*5.5*1.036+1.0)=1.020
IF (TO*5.5*7.6)*1.036
HFE=GFE+TO*(0.069*TO-1.526*TO-1.526)**0.96
HFE=GFE+0.56*COS(0.034*(TO-1.0)*0.96)*TO
TO=TSAVE
RETURN
END

C*****************************************************************************

C
SUBROUTINE GAG (TO)

C
CALCULATES THE DELTA G AND INTERACTION PARAMETER DATA AT A GIVEN
TEMPERATURE FOR ELEMENTS 1 TO 11 .

C
COMMON /DELG/ G(11),EA(11),EB(11),GFE
T=TO
G(1)=-1.5323+7.686*T
G(2)=-2.6658+2.69*T-0.017*T**2
G(3)=3.2563+3.675*T
G(4)=4.5493+3.233*T
G(5)=3.67-4.656*T+3.6568*T*ALOG(T)
G(6)=5.5+1.15*T
G(7)=2.5064+1.183*T-0.17*T**2
G(8)=2.5064+3.15*T
G(9)=3.97-1.3*T-0.651*T**2
G(10)=4.34+0.013*(T-273)
G(11)=0
SA=1100/T
EA(1)=8.4*SA
EA(2)=5670/T
EA(3)=4.84+7.370/T
EA(4)=4.65/T+4.557
EA(5)=24.4-34.5/T
EA(6)=3.45-17.37/T
EA(7)=3.8-12.37/T
EA(8)=4.1323/T
EA(9)=19.4-12.37/T
EA(10)=4.1273/T
EA(11)=2.3-12.37/T
DO 1 I=1,11
EB(I)=0
1 CONTINUE
RETURN
END

C*****************************************************************************

C
SUBROUTINE CARLIN (XH,X,W,T,XWT,XNT,CTC,XCW,EW)
CALCULATES THE CARBON SHIFT FROM THE Fe-C BINARY AT A GIVEN TEMPERATURE USING PARTITIONING DATA

DIMENSION WK(11), DXC(11), XH(11), WT(11), X(11), XHT(11)
DIMENSION Y(11), SX(11), 3Z(11)
COMMON /XKAL/ CAFK(11)
COMMON /DEGM/ G(11), EA(11), EE(11), GFE
COMMON /DTEF/ TUDG
CT=0.75
C=1.765
DO 1 I=1,25
BI=641.3-TDGM*53G*C-78.39*C**2
DI=53G*C-156.78*C
AI=C-0.01/D1
C=AI
IF (ABS(C-CT).LT.0.0005) GO TO 2
CT=AI
CONTINUE
1 CONTINUE
TO=641.3+536*WT(1)-78.39*(WT(1)**2)
IF (TO.LE.274.0) RETURN
TT=TO-274.0
CALL GAC (TO)
A=100
C CONVERT WT.PCT. TO ATCM FRACTION
DEN=(A-WT(1)-WT(2)-WT(3)-WT(4)-WT(5)-WT(6)-WT(7)-WT(8)-WT(9)-WT(10)
1-WT(11))/55.647/WT(1)/XH(1)+WT(2)/XH(2)+WT(3)/XH(3)+WT(4)/XH(4)+
2*WT(5)/XH(5)+WT(6)/XH(6)+WT(7)/XH(7)+WT(8)/XH(8)+WT(9)/XH(9)+WT(10)/
3*XH(10))/XH(11)
DO 3 I=1,11
X(I)=(WT(I)/XH(I))/DEN
CONTINUE
3 CONTINUE
DO 4 I=1,11
BZ(I)=WT(I)
BX(I)=X(I)
WK(I)=0.0
CONTINUE
4 CONTINUE
DXSMH=0.0
DXC(1)=0.0
A=100.0
C PARTITION COEFFICIENTS AS FUNCTIONS OF TEMPERATURE,
IN DEGREES CELSIUS

WK(2)=-0.05289*TO+5.44
WK(3)=1e-3
WK(4)=5.0-7.0*TO+3.249
WK(5)=22.78+ALOG(1+1)*163.444
WK(5)=WK(5)**2.0
WK(6)=-18.9+ALOG(1+1)*121.
10 5 I=1,11
WT(I)=WK(I)*WT(I)
DEN=(A-WT(1)-WT(2)-WT(3)-WT(4)-WT(5)-WT(6)-WT(7)-WT(8)-WT(9)-WT(10)
1-WT(11))/55.647/WT(1)/XH(1)+WT(2)/XH(2)+WT(3)/XH(3)+WT(4)/XH(4)+
2*WT(5)/XH(5)+WT(6)/XH(6)+WT(7)/XH(7)+WT(8)/XH(8)+WT(9)/XH(9)+WT(10)/
3*XH(10))/XH(11)
Y(I) = (WT(I) / XW(I) / DEN)
IF (X(I) > 0.0, C) X(I) = 1.0E-14
XK = Y(I) / X(I)
CARK(I) = XK
DA = XK * (1 + EA(I)) * (1 - 0.25 - X(1))
DB = X(I) * ((1 + EL(1)) * (1 - 0.25 - X(1)) - 1.0)
DXC(I) = -X(1) * X(I) * DA / (0.25 + DB)
DXSUM = DXSUM + DXC(I)
CONTINUE
X(1) = 3 * X(1)
XNEW = X(1) + DXSUM
CALL CHANGE (XCI EW, XW, X, XHT)

XHT(1) IS THE ACTUAL CARBON CONTENT IN HT. PCT.
XNEW IS THE ACTUAL CARBON CONTENT IN AT. PCT.

DO 6 I = 1, J1
WT(I) = X(I)
X(I) = DX(I)
CONTINUE
RETURN
END

**SUBROUTINE CHANGE (XSCLX,XW,X,XHT)**

CHANGES ALL VALUES FROM POLE FRACTION TO WT. PCT.

DIMENSION XW(11) X(I) XHT(11)
DEN = (1 - XSCLX * X(2) - X(3) - X(4) - X(5) - X(6) - X(7) - X(8) - X(9) - X(I) - X(I) - X(11)) * 155.64 + XSCLX * XW(1) * X(2) * XW(2) * X(3) * XW(3) * X(4) * XW(4) + X(5) * XW(5) * X(6) * XW(6) + X(7) * XW(7) + X(8) * XW(8) + X(9) * XW(9) + X(I) * XW(11) + X(I) * X(I) + X(11) * X(11)
XPH = 150 * XSCLX * XW(1) / DEN
XHT(I) = XPH
DO 1 I = 2, J1
XHT(I) = XHT(I) * XW(I) / DEN
CONTINUE
RETURN
END

**SUBROUTINE CALCT (TO,X,H,F,HFE,FH)**

CALCULATES TEMPERATURE DEVIATION FROM FE-C PHASE DIAGRAM.

COMMON /TTY / SA
COMMON /DELG/ G(I), EA(I), EB(I), GFE
COMMON /APAR/ VALP(I)
REAL HC, HFE

CALCULATE NUMERATOR
R = 1.957
RT = 1.987 * TO
FC=G(I)
XC=X(I)
EC=EA(I)
XNUM(I)=0.0
SUMNUM=0.0
SA=(EXP(-FC/FRT)*EC*XC)/(1+EXP(-EC*FC/FRT))
PHIC=EXP(GFE/S**T-(XC**2)/2*(EC-EB(I)*SA**2))
GG=FC/FRT
DO 1 I=2,11
F=G(I)
E=EA(I)
PA=EXP(-F/FRT)*E*XC/(1+EXP(-F)*XC*EXP(GG))
VALF(I)=PA
C CALCULATE I-TH TERM
XNUM(I)=X(I)*(PA-(1+XC*(1-XC)*(E-EB(I)*SA*PA))*PHIC)
C DOES SUMMATION OF NUMERATOR
SUMNUM=SUMNUM+XNUM(I)
CONTINUE
C CALCULATE DENOMINATOR
DEN=((XC*HC*SA)+(1-XC)*HFE*PHIC)
C CALCULATE TEMPERATURE DIFFERENCE
DT=((TO**2)**SUMNUM/DE
C END
C

-----------------------------
SUBROUTINE QPLSO (X,Y,H,N,M,WK,SIGS,POLY/IERP)
DIMENSION X(1), Y(1), H(1), POLY(1), WK(1)

X IS THE ARRAY OF ABSICISSAE AND Y THE ARRAY OF COXAS.
W(1),EQ.C, IMPLIES UNIT WEIGHTS ARE TO BE USED.
C An ARRAY OF WEIGHTS OF SIZE M
H Is A WORK SPACE OF SIZE 3N+SIGS SIGNALS ARE RETURNED IN WK(1...)
M IS THE DEGREE OF POLYNOMIAL TO BE FITTED.
P OLY IS AN ARRAY OF SIZE (M+1) AND RETURNS THE COEFFICIENTS OF X
ORDERED FROM HIGHEST POWER TO LOWEST.
P OL(Y(M+1) IS CONSTANT TERM
SIGS RETURN THE SUM OF SQUARED DEVIATIONS.
IERP IS INITIALLY SET TO 0 IF THERE IS AN ILEGAL VALUE OF M
IERP IS SET TO 1 ALSO WE RETURN TO THE CALLING PROGRAM.
M MUST BE >.1 AND .LT.(N-1) AND LE.15
DIMENSION A(15), U(15), V(15)

LOGICAL WP

WE USE WP TO SIGNAL WHICH SECTION 12-AD. OR 3-RD. BLOCK OF M+SIGS
OF WK WHICH CURRENTLY CONTAINS P//M/(X(I)) AND WHICH P//T-1/(X(I
IERP=0
IF ((M.GT.1).AND.(H.LT.(N-1))ACD.(H.LT.1.5)) GO TO 1
IERP=1
RETURN
1 IF (W(1).EQ.0) GO TO 3
S=0.
WE DENOTE THE WEIGHTS IN WHAT FOLLOWS BY $w(i) + 2$ EVEN THOUGH THEY CAME FROM THE ARRAY $w(i)$.

DO 2 I=1,N
WK(I)=C(I)
S=S+WK(I)
CONTINUE
GO TO 5
3 DO 4 I=1,N
WK(I)=1.
4 CONTINUE
S=S
5 DO =
DO 6 I=1,N
S=S*WK(I)
6 CONTINUE
T=S/D0
U(1)=T
WP=.FALSE.


K=N+N
DO 7 T=1,N
KI=K+1
MI=M+1
WK(I)=X(I)-T
WK(H)=1.
7 CONTINUE

WE EVALUATE $V(1), C1, A(1), A(2)$

S=0.
D1=0.
T=0.
TT=0.
DO 8 T=1,N
KI=K+1
T1=X(K-1)
T2=X(K)
T3=Y(K)*T2
S=S+X(K)*T1*T2
D1=D1+T1*T1*T2
T=T*T3
TT=TT*T3*T1
8 CONTINUE
V(1)=S/D0
A(1)=T/D0
A(2)=TT/D1

WE NOW HAVE...
$U_1 = (\sigma^2 - x_i^2) / \sigma$

$DU = \sigma^2 \cdot 2 \cdot x_i / \sigma$

$P_1 = 1 / \sigma \cdot (x_i - \bar{y}) / \sigma$

$V_1 = (\sigma^2 - x_i^2) \cdot 2 \cdot \bar{y} / \sigma$

$A_0 = \sigma^2 - x_i^2 / \sigma$

$A_1 = (\sigma^2 - x_i^2) / \sigma$

WE GO ON NOW TO THE GENERAL CASE

DO 14 I = 2, N
  IF (IP) GO TO 9
  IP = N + 1
  IP = N + 1
  GO TO 10

9 IF IS THE INCREMENT TO BE ADDED TO J TO GET $P / / N - 1 / (X(J))$
  WHILE (IP = J) YIELDS $P / / N - 2 / (X(J))$
  WE SHALL CALCULATE $P / / N$ AND OVERWRITE IT ON $P / / N - 2$, REVERSING W

10 WP = NOT. WP

$U / / I = (\sigma^2 - x_i \cdot \sigma / / I - 1 / (X(J)) \cdot \bar{y} / / I - 1 / \sigma)$

S = J.

DO 11 J = 1, N
  K = IP + J
  S = S * XJ * WK(K) * WK(K) * WK(J)
  CONTINUE
  T = S / D1
  UI = T
  S = V(I-1)

P / / I = (X(J) - \sigma / / U / / I) * P / / I - 1 / (X(J)) - \sigma / / U / / I - 1 / P / / I - 1 / (X(J)) - \sigma / / U / / I - 1

OVERWRITE P / / I - 2 / (X(J)) WITH T

11 DO 12 J = 1, N
  K = IP + J
  WK(K) = WK(K) * (X(J) - T) - WK(K) * S
  CONTINUE

WE CALCULATE $O / / I = \sigma^2 - x_i^2 / \sigma$, SHOWING $O / / I = \sigma$ TO SHORTEN THE PLACES.

$V / / I = (\sigma^2 - x_i^2 / \sigma / / I / (X(J)) \cdot \bar{y} / / I / (X(J)) \cdot \sigma / / I / \sigma)$

A / / I = $\sigma^2 - x_i^2 / \sigma / / I / (X(J)) \cdot \bar{y} / / I / \sigma$

D0 = 01
D1 = J
S = J.
T = J.

DO 13 J = 1, N
  K = IP + J
  T1 = WK(K)
  T2 = WK(J) * T1
  D1 = D1 + T1 * T2
  S = S * X(J) * WK(K) * T2
T=T+Y(J)*T2
CONTINUE
V(I)=S/D0
A(I+1)=T/D1
CONTINUE

WE HAVE NOW CALCULATED THE ARRAYS U, V, FROM 1 TO M AND
A FROM 0 TO M INDEXED 1 TO M+1
WE GO ON TO CALCULATE THE COEFFICIENTS OF THE POWERS OF X.

H1=M+1
WH(1)=1.
WH(2)=U(1)
DO 15 I=2,M
I1=I-1
WH(I1)=U(I)*WH(I)-V(I1)*WH(I1)
15 CONTINUE
S=A(I)
DO 16 I=2,M
S=S+A(I)*WH(I)
16 CONTINUE
POLY(M1)=S
DO 20 I=2,M
I1=I-1
DO 17 K=1,M
L=M1-K
WH(L+1)=WH(L)
17 CONTINUE
WH(I1)=0.
WH(I)=1.
DO 18 J=I,M
K=J-1
L=K+2
WH(L)=WH(L)-U(J)*WH(J)-V(K)*WH(K)
18 CONTINUE
S=9.
HM1=M1-I1
DO 19 J=I,M1
S=S+A(J)*WH(J)
19 CONTINUE
POLY(M1+M1)=S
CONTINUE
POLY(1)=A(M1)

WE CALCULATE THE RESIDUALS AND SIGSQ

WP=TRUE.
IF (WH(1).EQ.0.) WP=.FALSE.
SIGSQ=0.
DO 23 I=1,N
S=9.
DO 21 J=1,M
K=M1-J
S=S+POLY(J)*X(I)**K
21 CONTINUE
T=S+POLY(M1)-Y(I)
WH(I)=T
IF (WP) GO TO 22
SIGSQ=SIGSQ+T**2
22 GO TO 23
SUBROUTINE FCOTS(A, B, C, ZS, ZLG, IER)

SUBROUTINE FROOTS(A, B, C, ZS, ZLG, IER)

FIND ROOTS OF THE QUADRATIC EQUATION

A*X**2 + B*X + C = 0

COMPLEX ZL, ZS, ZSM, ZLG
DOUBLE PRECISION CIS, CISA
BS=8
IPS=(LLOG(ABS(A)) + LLOG(ABS(C)) + LLOG(Z.0)) / (2*LLOG(Z.0))
SCALE=2.0**IPS
DISA=ABLE(ABS(B))
DIS=DISA+SCALE
DIS=DIS+DISA
IF(SNLG(DIS).EQ.0.0) GO TO 200
B=8.0
DIS=DISA+SCALE
IF(SNLG(DIS).NE.0.0) E=(BS/SCALE)*2.0
A=A/SCALE
C=C/SCALE
DIS=DISA+SCALE
DISC=ABLE(B)**2-ABLE(A)*ABLE(C)
SQDIS=SQRT(ABS(DISC))
IF(DISC.GT.0.0) GO TO 100
ZL=COMPLY(B/A, 0.0)
ZS=CONJ(ZL)
IER=1
GO TO 700
100 B=SIG4(SQDIS, B)+8
200 ZS=COMPLY(C/B, C)
ZL=COMPLY(B/A, C)
IF(ABS(REAL(ZL)).LT.0.0) ZS=-ZL
IER=9
300 ZSH=ZS
ZLG=ZL
RETURN
END
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<tr>
<td>1920</td>
<td>1073</td>
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</tr>
<tr>
<td>1940</td>
<td>1173</td>
</tr>
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</table>
APPENDIX VI

Program for Calculating Constant Composition
Sections to the Fe-C Binary Phase Diagram

Variable List

Variables

I, JJ, K, KL, M, NOB : indices and counters
A, DEN, DTS, DTT, THELP, XD, XP, YD, YP : dummy variables
DT : dummy variable returned from CALCT containing the temperature difference
DTA : Predicted delta/liquid temperature
DTC : Predicted carbide temperature
DTE : Predicted Ae₃ temperature
DTG : Predicted gamma/liquid temperature
GFE : Dummy variable containing $\Delta^O G_o$
HC : Dummy variable containing $\Delta^O H_1$
HFE : Dummy variable containing $\Delta^O H_o$
NCOUNT : Number of constant composition sections to be plotted
R : gas constant
SA : Dummy variable containing the partition coefficient
TO : Dummy variable containing empirical temperature value from the binary Fe-C phase diagram
XCNEW : Carbide line carbon content in mole fraction
XSOL : dummy variable containing carbon compositions
XSOLA : Delta solidus carbon composition
XSOLD : Delta/delta + gamma carbon composition
XSOLG : Gamma solidus carbon composition
XSOLX : Alpha/alpha + gamma carbon composition
XWCAR : Carbide line carbon composition in wt.pct.

Arrays
BX, BZ, DMC, WC, WK, XNUM, XWT, Y, Z : Dummy arrays
EA : Dummy array holding interaction parameters: $\epsilon_{1i}^1$
EB : Dummy array holding interaction parameters: $\epsilon_{1i}^2$
G : Dummy array containing $\Delta^O G_{i}^{2+1}$
T, V : Tabulated $\Delta^O G_{0}^{\alpha+\gamma}$ values; T(I) holds the temperature and V(I) the $\Delta^O G_{0}^{\alpha+\gamma}$ value at that temperature
WT : Composition of element i in alloy in wt.pct.
X : Composition of element i in alloy in mole fraction
XW : Molecular weights of the alloying elements

Results: This is a copy of the program utilized to calculate the silicon sections shown in Fig:(8).
PROGRAM TST(INPUT, OUTPUT, TAPE5=INPUT, TAPE6=OUTPUT)

THIS PROGRAM CALCULATES THE EFFECT OF ADDING ALLOYING ELEMENTS TO THE FEO-BINARY AND FLEO-TRINARY COMPOSITION CONTOURS OF THE FEO PHASE DIAGRAM. THIS PROGRAM IS VALID FOR THE TEMPERATURE RANGE 1350 TO 1820 K AND FOR THE ELEMENTS K, CO, O, W, V, B AND Cu (ELEMENTS 1 THROUGH 11) AND THEIR RESPECTIVE CONCENTRATIONS IN WT. PCT. MUST BE READ IN.

WT(I) = WT. PCT. OF ELEMENT I , 1 < I < 11

W(I) = MOLE FRACTION OF ELEMENT I, CALCULATED IN THE PROGRAM

XW(I) = MOLECULAR WEIGHTS OF THE ELEMENTS

DIMENSION X(11), WT(11), XW(11), XWJH(11)
DIMENSION Y(11), WY(11), YXG(11), YX(11), BX(11)
DIMENSION XWT(11), YWT(11), Z(12), B(12)
COMMON /CELG/G(11), EA(11), EB(11), GFE
COMMON /TIV/X1
COMMON /SSD/T(10), V(10)
COMMON BLOCK SSD HOLDING ALL THE VALUES OF G0 FOR ALPHA.
COMMON FOR INTERPOLATION USE.

A=1.0
M=94
N03=75
THELP=1800
R=1.07

SET THE VALUES OF THE MOLECULAR WEIGHTS

XW(1)= 12.411
XW(2)= 54.438
XW(3)= 22.986
XW(4)= 93.71
XW(5)= 91.996
XW(6)= 195.94
XW(7)= 83.91
XW(8)= 143.45
XW(9)= 53.942
XW(10)= 92.926
XW(11)= 66.933
DO 11, K=1,M

READ IN THE IRON DELTA G VALUES, NUMBER OF CONTOURS

READ (5, 119) T(K), V(K)
101 CONTINUE
READ (5, 121) ACCOUNT
DO 11 J=1, ACCOUNT
C READ IN VALUES IN WT. PCT.
READ (5,121) (WT(I),I=1,11)

DRAW THE GRID OUTLINE

CALL JRAWH

IF (WT(1).GE.0.50) NOE=1
IF (WT(1).LE.0.49) WT(1)=-3.329999
DTC=1.0
CALL JNEWPen (1)

INCREMENT THE CARBON COMPOSITION

DO 117 KL=1,NOE
IF (WT(1).LE.1.1) WT(1)=WT(1)+0.03
IF (WT(1).GT.1.1) WT(1)=WT(1)+0.1

CONVERT WT. PCT. TO ATCH FRACTION

GE=1-(WT(1)-WT(2)-WT(3)-WT(4)-WT(5)-WT(6)-WT(7)-WT(8)-WT(9)-WT(10)-WT(11))/5.72
HGT=WT(1)/XW(1)+WT(2)/XW(2)+WT(3)/XW(3)+WT(4)/XW(4)+WT(5)/XW(5)+WT(6)/XW(6)+WT(7)/XW(7)+WT(8)/XW(8)+WT(9)/XW(9)+WT(1)
XW(11)+WT(11))/XW(11)
DO 112 I=1,11
X(I)=(WT(I)/XW(I))/GEN
CONTINUE.

CALCULATE THE CARBIDE LINE: SHIFT

XGEN=6.0
IF (WT(1).LE.6.0).OR. WT(1).GT.2.3) GO TO 103
CALL CARLIN (XW,X,WT,XWT,DTC,XC;Xew)
XWCA=XWT(1)
CONTINUE.

CALCULATE THE EMPIRICAL FE-C TEMPERATURE, IRCH AND CARBON ALPHA-GAMMA

IF (WT(1).GE.2.3) GO TO 114
CALL TAG (WT,X,TO,SGF,HC,HFE).

CALCULATE DELTA G AND INTERACTION PARAMETER DATA FOR ALPHA-GAMMA

CALL GAG (TO)

CALCULATE TEMPERATURE SHIFT

CALL CALCT (TO,X,HC,HFE,DT)
DT=70+DT

CALCULATE ALPHA/ALPHA+GAMMA LINE:

XSOX=X(1)*SA
DTE=DT

PLOT THE CALCULATED VALUES

IF (DTE.GE.1350) GO TO 107
XSOX=XSOX
CALL CHANGE (XSOX,XW,X,XWT)
CALL UNIT20 (X0, Y0, Xp, Yp)
CALL GAF (X0, Y0, 1.125, 0)
IF (XT, GE, CTY) SC TO 165
X0 = XT (1)
Y0 = 0
CALL UNIT20 (X0, Y0, Xp, Yp)
CALL GAF (X0, Y0, 1.125, 5)
GO TO 166
CONTINUE
IF (XMAF, GT, 2.5) G0 TO 166
IF (XC, GE, CTQ) SC TO 166
Y = XTC
X = XC
CALL UNIT20 (X0, Y0, Xp, Yp)
CALL GAF (X0, Y0, 1.125, 0)
CONTINUE
CALCULATE THE EPRIICAL FE-C TEMPERATURE , IRON AND CARBOII DATA
FOR ALPHA-LIQUID
IF (WT (1), GE, 2.5) GO TO 138
CALL TAL (WT, X, TO, GFE, HC, HFE)
CALCULATE DELTA G AND INTERACTION PARAMETER DATA FOR
FOR ALPHA-LIQUID
CALL GAL (TO)
CALCULATE TEMPERATURE SHIFT
CALL CALCT (TO, X, HC, HFE, CT)
DT = TO + DT
CONTINUE
CALCULATE THE SOLIDUS
XSO = X (1) * 5A
DTA = DT
XSOA = XSO
CONTINUE
CALCULATE THE EPRIICAL FE-C TEMPERATURE , IRON AND CARBOII DATA
GAMMA-LIQUID
CALL TGL (WT, X, TO, GFE, HC, HFE)
CALCULATE DELTA G AND INTERACTION PARAMETER DATA FOR
GAMMA-LIQUID
CALL GGL (TO)
CALCULATE TEMPERATURE SHIFT
CALL CALCT (TO, X, HC, HFE, BT)
DT = TO + DT
CALCULATE THE SOLIDUS

XSGL=X(1)*SA
DTG=DT
XSGL=XSGL

Determine and Plot the Correct Liquidus

DT=DTA
OTS=DTG
IF (DTA, GE, CTG) DTG=DTA
IF (MT(1), GT, 2.5) GO TO 129
XP=MT(1)
YD=DTG
CALL UNITTO (XD, YC, XP, YF)
CALL GRIP (XP, YF, J25, 9)
CONTINUE

CALCULATE THE EXPERIMENTAL Fe-C TEMPERATURE, IRON AND CARBON DATA DELTA-GAMMA

IF (MT(1), GT, 2.5) GO TO 115
IF (MTLPG, GT, 150, 125) GO TOL155
CALL TCG (MT, X, TO, GFE, HC, HFE)

CALCULATE DELTA G AND INTERACTION PARAMETER DATA FOR DELTA-GAMMA

CALL DAEV (TO)

CALCULATE TEMPERATURE SHIFT

CALL CALCT (TO, X, HC, HFE, DT)
DT=TO+DT
THELP=DT
CALL PLOTPT (CT, X(1), 4)

CALCULATE THE DELTA/GAMMA+DELTA PHASE BOUNDARY

XSGL=X(1)*SA
DTG=DT
XSGL=XSGL
CONTINUE

PLOT THE CORRECT SOLIDUS OR DELTA PHASE EXTENT

IF (XCHN, GE, XSGL, ANC, CTG, GT, DTG) GO TO 111
CALL TMA, GE (XSGL, XH, XH, XH)
IF (XCH(1), GE, 2.5) GO TO 122
XP=MT(1)
YD=DTG
CALL UNITTO (XD, YC, XP, YF)
CALL GRIP (XP, YF, J25, 9)
CONTINUE

IF (DTG, LT, 150) GO TO 113
IF (MT(1), GT, 2.5) GO TO 112
IF (MT(1), GT, 2.3) GO TO 112
XP=MT(1)
YD=DTG
CALL UNITTO (XD, YD, XP, YP)
CALL GZF (XP, YF, J25, 9)
112 CONTINUE
113 CONTINUE
IF (XL.LT.65555) GC TO 114
114 CONTINUE
IF (OTE.NE.0) GC TO 116
CALL CHANGE (XSCLA, XW, X, XWT)
115 CONTINUE
YD=DATA
CALL UNITTO (XD, YG, XP, YF)
CALL GZF (XP, YF, J25, 9)
116 CONTINUE
117 CONTINUE
118 CONTINUE
END THE PLOT
CALL NEWPEN (2)
CALL PLTL4 (4.0, 850.0, J, 4.0, 189.0, C)
CALL PLOT (X, Y, 999)
STOP
C
FORMAT (F5.3, F7.3)
C
119 FORMAT (I, F5.3)
120 FORMAT (I, F5.3)
121 FORMAT (I, F5.3)
END

SUBROUTINE DRAW

CALLS AND LABELS THE GRID

DIMENSION WC(6), Z(3), BCD(1)
XSCALE=0.2
YSCALE=45.
CALL PLOT (X, Y, -2C)
CALL PLTN (1.2, 40. ) , -1.2, 940.0, -1.2, 5.0, 840.0, 1900.0)
CALL NEWPEN (5)
CALL PLTN (2.5, 165.0, J, 2.5, 95.0, C)
CALL PLTN (1.0, 165.0, J, 1.0, 95.0, C)
CALL NEWPEN (2)
A1=5
B1=65.0
A2=1.0
B2=95.0, 1.0, 0.2, YSCALE
DO 10 I=1, 5
CALL PLTN (A1, O1, A2, B2)
A1=A1+5.5
A2 = A2 + 3.5
CONTINUE
A1 = 3.0
B1 = 1.5, 0.6
A2 = i, 0.5 * XSCALE
B2 = i, 0.5 * XSCALE
DO 2 I = 1, 9
CALL PLTLET (A1, E1, A2, B2)
D1 = 31.1 + 10.0
D2 = 32.1 + 10.0
CONTINUE
HC(1) = 0.0
DO 3 I = 2, 6
HC(I) = HC(I - 1) + 0.5
CONTINUE
F(1) = 0.06
S = 3, 4, 5
THETA = 0.0
HEIGHT = 1.25
DO 4 I = 1, 6
HC(I) = HC(I)
ANUM = HC(I)
CALL HUMEP (S, THETA, HEIGHT, ANUM, THETA, B(N))
P = 4 + 5
G = 3
CONTINUE
7(1) = 4.0, 4.5
DO 6 I = 2, 9
7(1) = 7(1 - 1) + 100.0
CONTINUE
R = 4, 24
S = 100.0, 0
DO 6 I = 1, 9
INUM = INUM + 1
CALL INTNUM (S, THETA, INUM, THETA, B(N))
CONTINUE
END

SUBROUTINE NUMBER (R, S, HEIGHT, ANUM, THETA, FMT)

ENCODE ROUTINE FOR REAL NUMBERS

DIMENSION BCC(1)
END OF (IN1, FM1, BCC) ANUM
CALL PLTLET (10.0, 25, THETA, R, S, BCC)
RETURN

SUBROUTINE INTNUM (R, S, HEIGHT, INUM, THETA, FMT)

ENCODE ROUTINE FOR INTEGERS

DIMENSION BCC(1)
SUBROUTINE CHANGE (XSLX, XH, X, XHT)

CHANGES ALL VALUES FROM CLE FRACTION TO WT, PCT.

DIMENSION XW(11), X(11), XHT(11)
C = (1-XSLX-X(2)-X(3)-X(4)-X(5)-X(7)-X(8)-X(9)-X(10)-X(11))
155.347*XSLX*XH(1)+X(2)*XH(2)+X(3)+X(5)+X(7)+X(8)+X(9)+X(10)+X(11)
XPT = 113.4*XSLX*XH(1)/T
XHT(I) = XP
DO 1 I = 2, 11
XHT(I) = 100.*X(I)*XW(I)/CEN
CONTINUE
RETURN
END

SUBROUTINE TAG (WT, X, TC, GFE, HC, HFE)

CALCULATES THE DELTA G FOR IRON, THE DELTA H FOR IRON AND CARBON AND THE EMPIRICAL TEMPERATURE FROM THE Fe-C PHASE DIAGRAM FOR ALPHA/GAMMA

DIMENSION WT(11), X(11)
COMON /SS0/ T(100), V(100)
REAL HC, HFE
C = WT(I)

TO = 1150
C = 153.36 + 216.5*(T - 765) + 4.25
T = INT((TO - 950) / 10 + 1)
GFE = V(K) + (V(K+1) - V(K))*(T(K+1) - TO) / 10
HC = 15323
HFE = GFE + TO*(0.85 - 0.046*(TO - 1050.))**0.96
RETURN
END

SUBROUTINE GAG (TC)

CALCULATES THE DELTA G AND INTERACTION PARAMETERS DATA FOR ALPHA/GAMMA

COMMON /DELG/ G(11), EA(11), EB(11), GFE
T = TO
SUBROUTINE TDG (WT;X;TC;GFE;HC,HFE)

CALCULATES THE DELTA G FOR IRON I, THE DELTA H FOR IRON I AND CARBON I AND THE EMPIRICAL TEMPERATURE FROM THE Fe-C PHASE DIAGRAM FOR DELTA/GAMMA

DIMENSION WT(11), X(11)
GO TO 100
SSD = T(100), V(100).
REAL 4C,HFE
XC=WT(1)
C CALCULATES TO
TO=1532*3+6.6*7
C CALCULATES DELTA G = FFE
K=INT(TO-9.6)/10+1
GFE=V(K)*(V(K+1)-V(K))^(T(K+1)-TO)/10
GFE=-GFE
HC=19323
HFE=2.3
RETURN
END

SUBROUTINE DAD (TO)
CALCULATES THE DELTA G AND INTERACTION PARAMETER DATA FOR DELTA/GAMMA

COMMON /DELG/ G(11), EA(11), EB(11), GFE
T=TO
G(1)=5.3*T+7.4*G
G(2)=653-T+3.5*T
G(3)=5364-36.7*T+4.7244*T-ALOG(T)
G(4)=4545+3.233*G
G(5)=367+4.556*T+0.5568*T-ALOG(T)
G(6)=565+0.15*T
G(7)=2557+41.183*T+2.17*T**2
G(8)=-2500+4.15*T
G(9)=6357+1383*T+0.151*T**2
G(11)=14.346+0.6613*(T-273)
G(11)=3*G
SA=11.10/T
EA(1)=5.1*SA
EA(2)=6.76/T
EA(3)=4+7370/T
EA(4)=835/T+0.557
EA(5)=24+36.46/T
EA(6)=7.71-1553/T
EA(7)=3/6+1273/T
EA(8)=4,1+1323/T
EA(9)=19,4+1273/T
EA(11)=4+1273/T
EA(11)=2.5+1273/T
DG 1 I=1,11
EB(I)=EA(I)
CONTINUE
RETURN
END

SUBROUTINE TGL (WT,X,T0,GFE,HG,HFE)

CALCULATES THE DELTA G FOR IRON I, THE DELTA H FOR IRON AND CARBON AND THE EMPERICAL TEMPERATURE FROM THE Fe-C PHASE DIAGRAM FOR GAMMA/LIQUID

DIMENSION WT(11), X(11)
REAL HG,HFE
CALCULATE TO
C=WT(I)
TO=12.4,5-51.3*C-4.6+C**2
C=WT(I)
C=2546+35.1653*T0-5.27*T0+ALLOG(T0)+3.3*1*T0**2
HG=54.6
HFE=3524
RETURN
END

SUBROUTINE GGL (TC)
CALCULATES THE DELTA G AND INTERACTION PARAMETER DATA FOR GAMA/ LIQUID

COMMON /DELG/ G(11), ZA(11), EB(11), GFE
T=0
XX=183.3/T
G(1)= -56.33 + 6.6*T
G(2)= 256.0 - 2.03*T
G(3)= -6236 - 34.5*T + 4.7244*T - ALOG(T)
G(4)= 3.8*T - 2.060
G(5)= 790 - 5.64*T
G(6)= 460 + 2.15*T
G(7)= 390 - 2.31*T
G(8)= 619 - 2.67*T
G(9)= -245 - 1.27*T
G(10)= 909 - 2.3*T
G(11)= 411 - 2.19*T
A(1)= 7513 / T + 390
A(2)= -2.7 + XX
A(3)= 18476 / T - 0.429
A(4)= 2.5*XX
A(5)= 5.7*XX
A(6)= 4*XX
A(7)= 4.5*XX
A(8)= 5.53*XX
A(9)= -16.07*XX
A(10)= -23.52*XX
A(11)= 1.79 - XX
B(1)= 81.11 - XX
B(2)= 50.77 / T
B(3)= 4.64 + 7370 / T
B(4)= 4839 / T + 6.957
B(5)= -24.4 - 38.4*/ T
B(6)= 7.53 - 1503 / T
B(7)= 3.1 - 1237 / T
B(8)= 4.51 + 1323 / T
B(9)= -19.41 + 1273 / T
B(10)= -4.5 - 1273 / T
B(11)= 2 - 1273 / T
RETURN
END

SUBROUTINE TAL (WT, X, IO, GFE, HC, HFE)


COMMON /SSO/ T(100), V(110)
DIMENSION WT(11), X(11)
REAL HC, HFE
G CALCULATE TO
C = W(1)
TC = 13(9-29,56*C-96.6*C**2
CALCULATE GFE
K = INT(TTO-960)/10+1
GAA = V(K)+(V(K+1)-V(K))*((T(K+1)-T)/10
GFE = 2.56+39.1653*T-5.27*T**ALOG(TO)+0.651*T**2
GFE = GAA+GGB
HGE = 540.
HFE = 3524.
RETURN.
END

SUBROUTINE GAL (TTO)

CALCULATES THE DELTA G AND INTERACTION PARAMETER DATA FOR
DELTA/ LIQUID

COMMON / DELG/ G(11), EA(11), EB(11), GFE
T = TTO
XX = 13 0/T
G(1) = 213.39+6.8*T
G(2) = 3.160-2.326*T
G(3) = 6.9*T+2.8260
G(4) = 2.127*T+0.5365
G(5) = 2.29+1.35800
G(6) = 2.207+2.377T
G(7) = 1.160+2.45*T
G(8) = 4.95+1.823*T
G(9) = 7.61+1.39+T
G(10) = 5.60+2.373+T
G(11) = 3.05+1.19*T
EA(1) = 16.75/T-T+0.399
EA(2) = 2.79+XX
EA(3) = 1.475/T-T+0.423
EA(4) = 2.55+XX
EA(5) = 5.17+XX
EA(6) = 4+XX
EA(7) = 5.37+XX
EA(8) = 4+XX
EA(9) = 4.55+XX
EA(10) = 6.53+XX
EA(11) = 15.37+XX
EA(12) = 1.73+XX
EB(1) = 4.1+1.15+XX
EB(2) = 5+77/T
EB(3) = 4.64+7.375/T
EB(4) = 4.635/T+0.557
EB(5) = 24.4-354.33/T
EB(6) = 7.83+1593.3/T
EB(7) = 3.6*1273/T
EB(8) = 4.3*1273/T
EB(9) = 19.4*1273/T
EB(10) = 4*1273/T
EB(11) = 2.3*1273/T
RETURN.
SUBROUTINE CARLIN (XH, X, WT, XH1, DT3, XCNW)

CARLIN CALCULATES THE SHIFT IN THE CARBON CONTENT OF THE CARBIDE LINE, AT ANY GIVEN TEMPERATURE, WITH THE ADDITION OF ALLOYING ELEMENTS.

DIMENSION WK(11), DXC(11), XW(11), HT(11), X(11), XWT(11)
DOUBLE PRECISION Y(11), HT(11), BZ(11)
COMMON /ELG/ G(11), EA(11), EE(11), GEE
TO=1375*0.673+0.485*WT(1)+0.052*WT(1)**2
CALL GAG (TO)
Y=TO
EA(1)=4.54+7336/T
TT=TO-273.15
CALL GAG (TO)
DO 1 I=1, 11
20 BX(I)=WT(I)
BX(I)=X(I)
WK(I)=G(I,C)
CONTINUE
DXSU=C*0
DXSU=C*0
A=1.0*0

PARTITION COEFFICIENTS, CALCULATED AT TEMPERATURE

WK(2)=0.60284*TO+5.44
WK(3)=1.2-J4
WK(4)=0.636*TO-0.249
WK(5)=22.782*ALOG(TT)+163.464
WK(6)=WK(9)-2.06
WK(6)=16.95*ALOG(TT)+11
DO 2 I=2, 11
WT(I)=WK(I)*HT(I)
DEN=(A-WT(1)-WT(2)-WT(3)-WT(4)-WT(5)-WT(6)-WT(7)-WT(8)-WT(9)-WT(11))/XH(I)
1:Y(I)=WT(I)/XH(I)/DEN
IF (X(I).GE.0.01) X(I)=1.0*E-16
XK=Y(I)/X(I)
DXK=XK=1.0*(1+EA(I))+(1.25-X(I))
DXK=XK=X(I)**(1.0+EA(I))-((1.25-X(I))-1.0))
DXC(I)=X(I)**X(I)-X(I)**25/25+30
DXSU=DXSU+GXC(I)
CONTINUE
X(I)=3*X(I)
XCNEW=X(I)+DXSU
CALL CHANGE (XCNW, XH, X, XHT)

XHT(1) IS THE ACTUAL CARBON CONTENT IN WT. PCT.
XCNW IS THE ACTUAL CARBON CONTENT IN AT. PCT.

DTG=TO
DO 3 I=1,11
    WT(I)=BZ(I)
    X(I)=3*X(I)
    CONTINUE
    RETURN
END

SUBROUTINE CALCT (T0, X, Hc, HFE, DT)

CALCT Determines the shift in temperature caused by the addition of alloying elements.

COMMON /TTY/ SA
DIMENSION X(11), XNUM(11)
COMMON /DEG/ G(11), E(A(11), E(B(11), GFE
REAL Hc, HFE

CALCULATE NUMERATOR

P=1.387
RT=1.987*RT
FC=G(I)
XC=X(I)
EC=E(A(1)
XNUM(I)=0.6
SUMNUM=G
SA=(\e^{FC/RT+EC*XC} / (1+EC(1)*XC*\e^{FC/RT}))
PHIC=E^{GFE/(\e^{GFE/RT}-(1+EC)*2) / (EC-E(B(I)*SA**2))}
G=G/RT
DO 1 I=2,11
F=G(I)
E=E(A(I)

PA=\e^{FC/RT+EC*XC} / (1+EC(I)*XC*\e^{GFE(G)})
CALCULATE I-TH EFF.
XNUM(I)=X(I)*\e^{GFE(PA/(1+EC*(1-XC)*\e^{(E-E(B(I)*SA*PA))/PHIC))}

DOES SUMMATION OF NUMERATOR:

SUMNUM=SUMNUM+XNUM(I)
CONTINUE

CALCULATE DENOMINATOR

DEN=(XC*Hc*SA)+(1-XC)*HFE*PHIC

CALCULATE TEMPERATURE DIFFERENCE

DT=(T0**2)*SUMNUM/DEN
RETURN
END

SUBROUTINE NEWPEN (U)

DUMMY ROUTINE NECESSARY IN ORDER TO ACCOMMODATE DIFFERENT PLOTTER...
References

1. E. A. Baganis, Private Communication.


4. R. A. Grange, Met. Progress, 79 (1961), No. 4, p. 73.


89. A.S.M. Metal Progress Data Sheets, Metal Progress Reprint Service, American Society for Metals, Metals Park, Ohio, U.S.A.


