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THERMODYNAMIC PROPERTIES OF TERNARY SOLID  
SOLUTIONS WITH INTERSTITIALLY DISSOLVED CARBON

by

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## PROLOGUE

Parts of this thesis have been or will be published  
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1. R. B. McLellan and P. Chráska, "Thermodynamics of Iron-Carbon Solid Solutions," to appear in Mater. Sci. Eng., 1971.
2. P. Chráska and R. B. McLellan, "Thermodynamic Properties of Carbon in BCC and FCC Iron-Silicon-Carbon Solid Solutions," submitted to Acta Met., 1971.
3. R. B. McLellan and P. Chráska, "A Vapor Transport Study of Nickel-Copper-Carbon Solid Solutions," Mater. Sci. Eng. 6 (1970) 176.
4. P. Chráska and R. B. McLellan, "Residual Carbon in Hydrogen-Annealed Iron," submitted to Met. Trans., 1971.

## INTRODUCTION

The iron-carbon binary system and iron-carbon-metal systems have been of prime importance in technology for a very long time. However, only several past decades have seen a serious effort to study in detail the equilibrium and kinetic properties of these systems, knowledge of which is so important in today's engineering for developing new materials with better mechanical properties, better corrosion resistivity and so on. Many of the recent findings have shaken some of the "old" concepts, but many more data are needed before these systems can be understood completely. The main difficulty stems from the fact that carbon in all of these systems is in the form of interstitial solute. Despite the fast progress of the development of the theory of interstitial solutions in the last few years, the behavior of carbon atoms in iron-based systems has not been fully clarified. In many instances it is much easier to understand the carbon behavior in non-ferrous metals and therefore, new models are often tested on such materials.

The purpose of this thesis is to review the present state of research, to add more experimental data on carbon behavior in iron-based alloys ( Fe-Si ) and to

develop a theoretical model which can be used to explain experimentally measured thermodynamic properties of the Ni-Cu-C system. Finally, in Appendix I a small contribution to the problem of the residual carbon in pure iron has been made.

## I. THERMODYNAMICS OF IRON-CARBON SOLID SOLUTIONS

### 1. Body-Centered Cubic Solutions

#### 1.1 Thermodynamics of Binary Systems

The thermodynamic properties of binary B.C.C. iron-carbon solid solutions, and to a lesser extent those of ternary ferrites, have been the object of numerous experimental investigations.

The basic method of studying the thermodynamic parameters of a phase is to measure its equilibrium with another phase of known free energy. Early major investigations of the thermodynamic properties of ferrite utilized the gas-solid equilibrium involving a gaseous phase of known free energy. Among these early measurements were those of Smith<sup>1</sup> and Dünwald and Wagner<sup>2</sup>. Smith<sup>1</sup> investigated the equilibrium between CH<sub>4</sub>-H<sub>2</sub> mixtures and ferrite at 750°C and determined the carbon content of the equilibrated solid solution as a function of the gas composition, expressed by the pressure ratio,

$$r_1 = \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2} .$$

In these experiments the total gas pressure was maintained at one atmosphere.

Dünwald and Wagner<sup>2</sup> measured the equilibrium between CO-CO<sub>2</sub> mixtures and Fe-C solid solutions. Only one temperature (800°C) was used in the B.C.C.-range and



the variation of C-content in the equilibrated solid was measured as a function of total pressure at a fixed value of the ratio

$$r_2 = \frac{P_{CO}^2}{P_{CO_2}}$$

Both Smith<sup>1</sup> and Dünwald and Wagner<sup>2</sup> used combustion analysis to measure the C-content of the ferrite.

In order to determine both the partial enthalpy  $\bar{H}_i^\alpha$  and the entropy  $\bar{S}_i^{C\alpha}$  of solution, it is necessary to measure the equilibrium at a minimum of two different temperatures. Thus, it is not possible to determine  $\bar{H}_i^\alpha$  and  $\bar{S}_i^{C\alpha}$  from the results of Dünwald and Wagner<sup>2</sup> alone. However, it has been shown<sup>3</sup> that their data are compatible with those of Smith<sup>1</sup> and that, assuming a random solute atom distribution in these dilute solutions, the values of  $\bar{H}_i^\alpha$  and  $\bar{S}_i^{\alpha\alpha}$  (the partial excess entropy) concomitant with these experimental data are -147.2 k.cals/mole and 5.2k. The energy value is given with respect to an atom at rest in a vacuum. Using tabulated data for pure graphite, the relative partial enthalpy  $\Delta\bar{H}_i^\alpha$  at 1000°K is 20.2 k.cals/mole.

Smith<sup>1</sup> recalculated his estimate of  $\Delta\bar{H}_i^\alpha$  using a value for the carbon activity  $\alpha_C$  at 1490°C calculated from the measurements of Adcock<sup>4</sup> on the equilibrium between the  $\delta$  and  $\gamma$  solutions and the liquid phase, and the measurements of Marshall and Chipman<sup>5</sup> of  $r_1$  for

the equilibrium with liquid iron-carbon solutions.

Smith's<sup>1</sup> revised value of  $\Delta\bar{H}_i^\infty$  is 26.0 k.cals/mole.

Other early investigations of the thermodynamic properties of ferrite show a sharp disparity with these gas-solid equilibration data. The temperature dependence of the solid-solid metastable equilibrium between ferrite and cementite has been studied by Dijkstra<sup>6</sup> and by Wert.<sup>7</sup> The precipitation of the carbide was followed by anelastic damping techniques. A determination of the carbon solubility in ferrite in equilibrium with cementite was also made by Stanley<sup>8</sup>. His method involved a study of the diffusion of carbon from pearlite. The solubilities determined in these solid-solid equilibrium studies have been shown<sup>7</sup> to be in good mutual agreement. However, the heat of solution of cementite in ferrite deduced from these data is 9.7 k.cals/mole in comparison with the value 15.1 k.cals/mole calculated from the gas-solid equilibrium data (using  $\Delta\bar{H}_i^\infty = 20.2$  k.cals/mole). Later work by Lindstrand<sup>9</sup>, again using the anelastic damping technique to study the cementite precipitation confirmed the earlier solid-solid equilibrium studies.

The discrepancy described above between the results of the gas-solid and solid-solid equilibrations

was largely resolved by Swartz<sup>10</sup>, who ascribed the difference in the observed heats of solution to the effects of pre-precipitation stresses in the ferrite matrix on the solubility of cementite.

A number of other investigations have also been made which do not show consistency with either of the two groups of experiments described above. They will be mentioned briefly. Borelius<sup>11</sup>, and Borelius and Berglund<sup>12</sup> have reported calorimetry studies of the precipitation of cementite that indicate a ferrite-cementite phase boundary about 50% lower than the internal friction measurements<sup>6, 7, 9</sup>. Petrova, Lapshina, and Shvartsman<sup>13</sup> used a gas-solid equilibrium technique to determine the saturation solubility between 400°C and 723°C while Bruk<sup>14</sup> used a C<sup>14</sup>-tracer method between 620°C and 700°C. Both these determinations showed a higher saturation solubility at higher temperatures than had previously been reported. Singer and Anolick<sup>15</sup> have also studied the saturation solubility of carbon in ferrite in equilibrium with cementite. They used a magnetic aftereffect and found solubilities even lower than those indicated by the calorimetric studies of Borelius and Berglund<sup>11, 12</sup>.

The general situation with regard to the earlier investigations is illustrated schematically in Fig. 1. Not all of the results are shown in order to

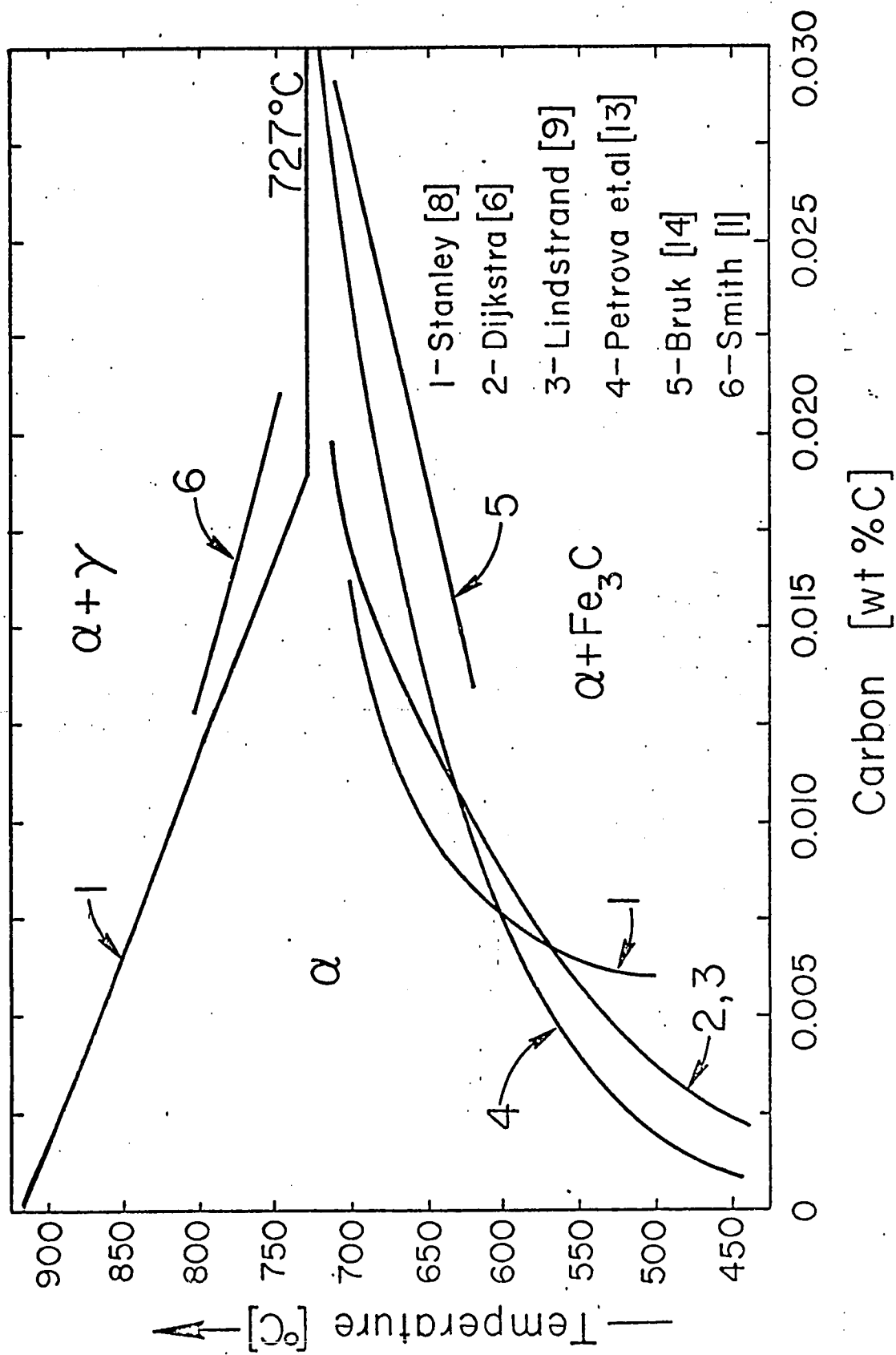


Figure 1

avoid cluttering the diagram.

It is clear from the work of Swartz<sup>10</sup> that the best method of determining the thermodynamic properties of ferrite is to study the gas-solid equilibrium and thus to avoid any stress effects accompanying the precipitation of a second phase in the ferrite. Recent gas-solid equilibration studies have been made by Swartz<sup>16</sup>, Schürmann, Schmidt, and Tillmann<sup>17</sup> (S.S.T.), and Dunn and McLellan<sup>18</sup>.

S.S.T. measured the temperature dependence of the  $\text{CH}_4\text{-H}_2$  equilibrium with ferrite between 600°C and 800°C for eight different fixed gas compositions varying from  $r_1 = 0.0102$  to  $r_1 = 0.0945$ . A careful analysis of the S.S.T. data using a closed solubility equation has revealed<sup>19</sup> that the data taken at each  $r_1$ -value are mutually inconsistent. In fact, the  $\Delta\bar{H}_1^\alpha$  corresponding to the different  $r_1$ -values varies between 14.5 k.cals/mole and 22.5 k.cals/mole.

Swartz<sup>16</sup> used primarily  $\text{CO-CO}_2$  gas mixtures for carburization and measured the carbon content of the solid solution by internal friction methods. Since Swartz carburized some samples at high temperatures in the  $\delta$ -region, his data encompass a large temperature range enabling accurate estimates of  $\Delta\bar{H}_1^\alpha$  and  $\bar{S}_1^{\nu\alpha}$  to be made.

Dunn and McLellan<sup>18</sup> employed the  $\text{CH}_4\text{-H}_2$  equilibration technique in the temperature range from

575°C to 825°C. The carbon content of the equilibrated samples was measured by combustion analysis. The equilibrium measurements at each temperature were analyzed by a closed solubility equation using a temperature-independent standard state so that  $\bar{H}_i^\alpha$  could be obtained directly. The measured value of  $\bar{H}_i^\alpha$  is -144.06 k.cals/mole and it is independent of temperature. The calculated value of  $\Delta\bar{H}_i^\alpha$ , using standard tables<sup>20</sup>, is 23.34 k.cals/mole at 1000°K. The thermodynamic parameters of ferrite found by Swartz<sup>16</sup> and Dunn and McLellan<sup>18</sup> are compared in Table I.

TABLE I

Authors	$\Delta\bar{H}_i^\alpha$ k.cal/mole	$\bar{S}_{i/k}^{\nu\alpha}$
Swartz <sup>16</sup>	24.0	6.89
Dunn & McLellan <sup>18</sup>	23.3	6.56
Smith <sup>1</sup>	20.2	5.2

It can be seen from Table I that the results of Swartz<sup>16</sup> and Dunn and McLellan<sup>18</sup> are in reasonably good accord. However, it cannot be said that the thermodynamics of ferrite are completely understood until the so-called "intercept effect" has been cleared up. This effect was

found by Smith<sup>1</sup> who discovered that his plots of  $r_1$  vs C% did not pass through the origin. A small residual carbon content ( 0.004 - 0.0008 wt. %) was found. The same phenomenon was also found by Dunn and McLellan<sup>18</sup>. It is believed that the "intercept" effect is also seen in the work of Swartz<sup>16</sup> and reflected in the fact that  $k$ , the Snoek peak proportionality constant relating the C-content to the height of the Snoek peak, differs from specimen to specimen and is apparently dependent on the equilibration temperature and polycrystalline structure of the ferrite.

## 1.2 Thermodynamics of Ternary Systems

Compared with ternary austenites, the thermodynamic data available for ternary ferrites are scant.

Leak and Leak<sup>21</sup> determined the solubility of carbon in B.C.C. iron containing 3% Si. The method used was to measure the amount of carbon dissolved in equilibrium with a precipitated carbide. The results showed that the carbon solubility is much lower than that for the binary ferrite in equilibrium with cementite, but the heat of solution of  $\text{Fe}_3\text{C}$  in the ternary ferrite is identical with that in the binary case, i.e., 9.7 k.cal/mole. However, these measurements are open to the same criticism discussed previously for the equilibrium between

binary ferrites and a carbide.

The equilibrium between  $\text{CH}_4\text{-H}_2$  mixtures and Fe-Si solutions of several different Si-contents has been studied by Schürmann, Schmidt and Tillmann<sup>22</sup>. The analysis of the data indicated that the relative partial enthalpy of carbon in solutions containing from 3.55 to 9.6 wt. % Si is independent of both temperature and composition, and, furthermore,  $\Delta\bar{H}_1^\alpha$  is identical to the value found previously by these authors for the binary Fe-C system<sup>17</sup> (20 k.cal/mole). However, this conclusion may not be justified in view of the inconsistencies found<sup>19</sup> in the S.S.T. investigation of binary ferrites<sup>17</sup>.

Smith<sup>23</sup> has studied the  $\text{CH}_4\text{-H}_2$  equilibrium with ferritic solid solutions containing silicon at one temperature only (1000°C). Unfortunately, the number of data points is small so that an accurate estimate of the thermodynamic parameters of the Fe-Si-C solution is not possible.

Petrova, Lapshina, and Shvartsman<sup>24</sup> have investigated the  $\text{CO-CO}_2$  equilibrium with ternary ferrites containing Co, Si, Mn and Cr. Their findings are of a qualitative nature due to the limited number of data points. They show that Si and Co strongly increase the activity of carbon in solution, whereas, Mn and Cr have the opposite effect. It will be shown in a later section



that this behavior is also reflected in the ternary austenitic solutions.

### 1.3 Theoretical Models

Because of the very limited solubility of carbon in binary ferrites, solute atom mutual interactions do not manifest themselves in the equilibrium thermodynamic properties of these solutions. Accordingly, the partial Gibbs free energy  $\mu_i$  is found<sup>3, 18</sup> to be given adequately by the expression

$$\mu_i = \bar{H}_i^\alpha - T \bar{S}_i^{\alpha\alpha} + kT \ln \frac{\theta_i/\beta}{1 - \theta_i/\beta} \quad (1.1)$$

corresponding to the simple quasi-regular approximation<sup>25</sup>. The last term in Eq. (1) involving  $\theta_i$ , the atom ratio of solute atoms, arises from the configurational entropy of the completely random solution. The quantity  $\beta$  is the number of interstitial sites per solvent atom. There is ample evidence that carbon predominantly occupies the octahedral sites in the B.C.C. iron lattice<sup>26, 27</sup> so that  $\beta = 3$ . The partial enthalpy  $\bar{H}_i$  and partial excess entropy  $\bar{S}_i^{\alpha\alpha}$  are independent of both composition and temperature.

Much work has, however, been done on the calculation of simulated carbon atoms (or C-atom clusters)

in B.C.C.-iron. Johnson, Dienes, and Damask<sup>28</sup> calculated by a computer-simulation process, the energy of solution of a C-atom in ferrite relative to  $\text{Fe}_3\text{C}$ . Their results were in reasonable accord with experimental data. In this calculation the Fe-Fe interaction was derived from a two-body central force model. The form of the interaction is derivable from the elastic properties of the B.C.C. iron crystal. The iron-carbon potential was represented by a cubic equation. These potentials were also used to calculate the binding energy of a C-C nearest-neighbor pair. The result (3.1 k.cal/mole) is close to the value (2.0 k.cal/mole) deduced by Keefer and Wert from their low-temperature anelastic damping studies<sup>29</sup>.

Larger clusters of carbon atoms containing four (and more) C-atoms have also been treated by Johnson<sup>30</sup> using the same force model. In this study the binding energies of clusters in several different configurations were calculated.

#### 1.4 Diffusion in Ferrite

The diffusivity of carbon in ferrite has been studied extensively both by anelastic damping techniques and by mass flow methods. Due to the small solubility of carbon in B.C.C.-iron, the variation of the diffusivity  $D$  with temperature has been the object of most of the

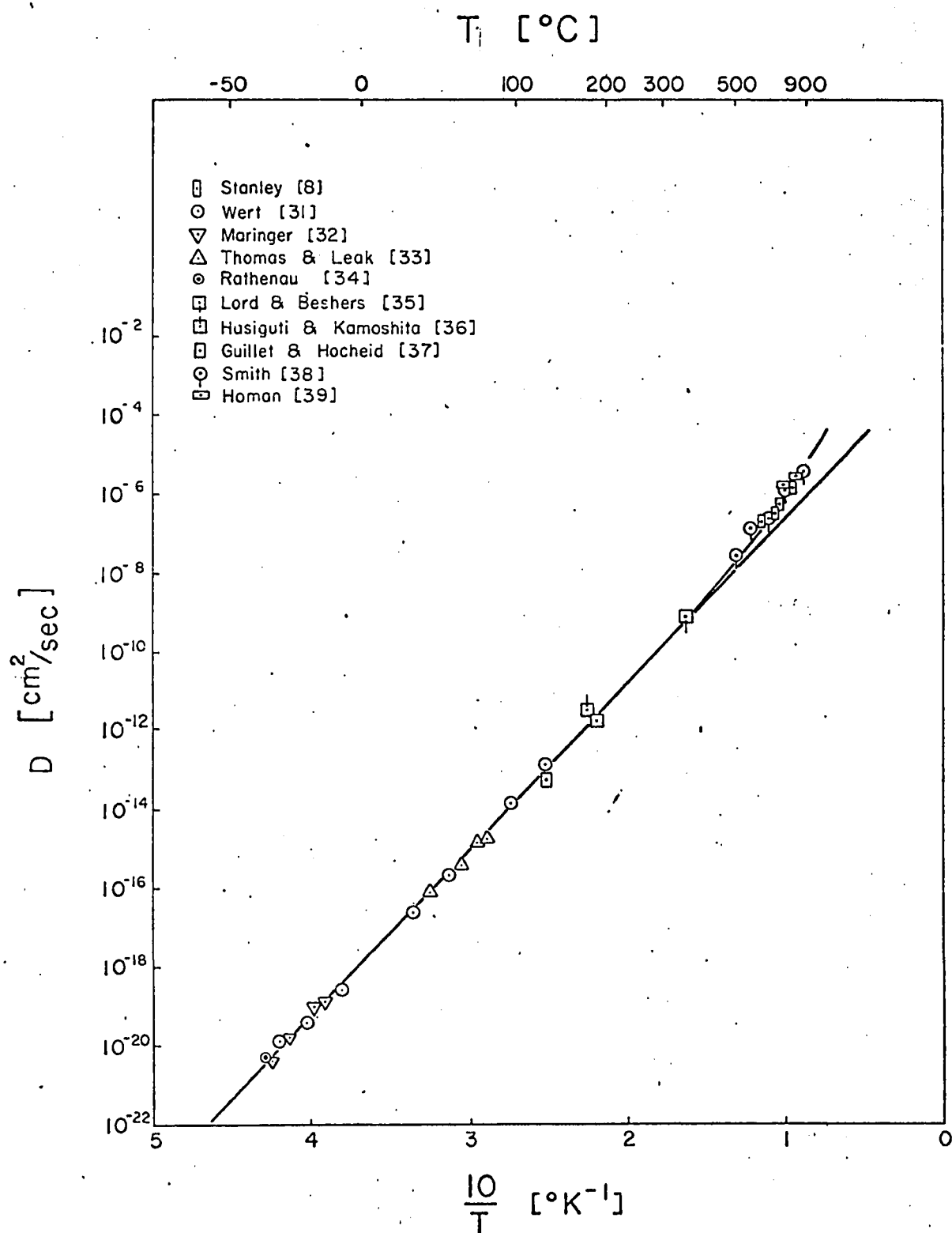


Figure 2

investigations: variations in  $D$  with composition have not been found.

The bulk of the anelastic damping data covers the temperature range from  $-50^{\circ}\text{C}$  to  $450^{\circ}\text{C}$ . In this temperature range the diffusivity varies by a factor of  $10^{11}$  and the Arrhenius plot appears to be linear. The data are illustrated in Fig. 2. The data for the linear Arrhenius region are taken from the investigations of Wert<sup>31</sup>, Maringer<sup>32</sup>, Thomas and Leak<sup>33</sup>, Rathenau<sup>34</sup>, Lord and Beshers<sup>35</sup>, Hasiguti and Kamoshita<sup>36</sup>, and Guillet and Hocheid<sup>37</sup>. The mass flow measurements, usually involving  $\text{C}^{14}$ , cover the remaining temperature range up to the transition temperature. The measurements of Stanley<sup>8</sup>, Smith<sup>38</sup>, and Homan<sup>39</sup> are in good mutual agreement and show that  $D$  increases with temperature much more quickly than the Arrhenius behavior at lower temperatures would predict.

It has been shown by a least squares regression<sup>40</sup> that the best fit to the lower temperature data using the Arrhenius equation

$$D = D_0 e^{-Q/kT}$$

is found when  $D_0 = 0.0033 \text{ cm}^2/\text{sec}$  and  $Q = 19.3 \text{ k.cals/mole}$ . These values should be regarded as giving the best representation of the carbon diffusivity in ferrite in the linear region.

The departure from Arrhenius behavior at higher temperatures has been the object of numerous suggestions. Homan<sup>39</sup> proposed that the accelerated diffusivity could be explained by a proportion of the diffusing C-atoms being associated with lattice vacancies. However, Damask and his co-workers<sup>41, 42, 43, 44</sup> have indicated that the C-atom-vacancy complex in  $\alpha$ -iron dissociates above 250°C.

McLellan, Rudee and Ishibachi<sup>40</sup> proposed an alternative mechanism to explain the enhanced diffusivity. In their model, a small fraction of the C-atoms is located on tetrahedral (T) sites in the B.C.C. lattice. This small fraction increases with temperature and at high temperatures T-T diffusions jumps enhance the observed diffusivity even though the number of atoms at T-sites is too small to have an observable effect on the equilibrium thermodynamic behavior of the system. In an elastic calculation Beshers<sup>45</sup> has indicated that for a C-atom in  $\alpha$ -iron the octahedral site is energetically only slightly more favorable than the tetrahedral site. Condit and Beshers<sup>46</sup> have also discussed a model in which the enhanced diffusivity is ascribed to tetrahedral occupancy.

More recently, Wuttig<sup>47</sup> has considered the contribution of the magnetic exchange energy to the free

energy of activation for diffusion. Since the free energy depends on the saturation magnetization, a function of temperature, the entropy of activation for diffusion is temperature dependent, leading to a departure from Arrhenius behavior.

## 2. Face-Centered Cubic Solutions

### 2.1 Thermodynamics of Binary Systems

The solution of F.C.C.-iron containing carbon has been studied from a thermodynamic point of view, even more extensively than B.C.C.-iron-carbon solutions. As in the case of ferrite, much of the work on austenite involves the equilibrium between a carburizing gas of known properties and the austenitic solution.

The early major investigations were those of Smith<sup>1</sup> and Dünwald and Wagner<sup>2</sup>. Smith<sup>1</sup> measured the equilibrium between austenite and both CO-CO<sub>2</sub> and CH<sub>4</sub>-H<sub>2</sub> gas mixtures. Dünwald and Wagner<sup>2</sup> studied only the equilibrium with CO-CO<sub>2</sub> mixtures. The bulk of Dünwald and Wagner's measurements and many of those of Smith were made in the range of composition where austenite is a henrian solution. In such an interstitial solution, the activity is not strictly a linear function of composition<sup>25</sup>, but its departure from linearity at low solute compositions

( $\theta_i < 0.02$ ) is very small. In this range, the results of both Smith<sup>11</sup> and Dünwald and Wagner<sup>2</sup> are completely compatible with each other and the analysis of McLellan<sup>3</sup> showed that  $\bar{H}_i^{\gamma\infty}$  is -155.2 k.cals/mole and  $\bar{S}_i^{\gamma\infty} = 5.75$  k. This partial enthalpy at infinite dilution gives, using standard tables<sup>20</sup>, a partial relative enthalpy with respect to graphite at 1250°K of  $\Delta\bar{H}_i^{\gamma\infty} = 10.86$  k.cals/mole. The heat of solution of cementite in austenite concomitant with this value of  $\Delta\bar{H}_i^{\gamma\infty}$  is 8.3 k.cals/mole<sup>3</sup>.

Now at concentrations greater than  $\theta_i = 0.03$ , Smith's activity measurements showed that  $\alpha_i$  increased with composition much more strongly than henrian behavior would dictate. This large thermodynamic effect is a manifestation of solute atom mutual interactions. It has been the motivation for many studies and has provided unique opportunity to test theoretical models for interstitial solid solutions, since, with the exception of hydrogen, interstitial atoms have such a low solubility in metals that interactions between solute atoms are rarely reflected in thermodynamic measurements.

Following the early work of Smith<sup>1</sup> and Dünwald and Wagner<sup>2</sup>, several investigators employed the gas-solid equilibration technique to study the thermodynamic properties of austenite. A large proportion of these measurements were made at 1000°C. The gas-solid equilibration method

was employed by Schenck and Kaiser<sup>48</sup>, Schenck, Froberg, and Jaspert<sup>49</sup>, Bungardt, Preisendanz and Lehnert<sup>50</sup>, Scheil, Schmidt and Wünnig<sup>51</sup>, Schürman, Schmidt, and Wagner<sup>52</sup>, and Ellis, Davidson, and Bodsworth<sup>53</sup>.

Activity measurements taken from the above authors, and Smith<sup>1</sup>, are compared in Fig. 3. Two different series of  $\alpha_1$ -measurements due to Schenck and Kaiser<sup>48</sup> are included. A galvanic cell using a fused salt electrolyte and electrodes of carbon and Fe-C solid solution was used by Hawkes and Morris<sup>54</sup> in the temperature zone 800 - 1000°C to study the thermodynamics of austenite. Their results at 1000°C are in substantial accord with the gas-solid data.

However, the best thermodynamic data on austenite are those resulting from the extensive measurements of Ban-ya, Elliott, and Chipman<sup>55, 56</sup>, who employed the CO-CO<sub>2</sub>-austenite equilibrium technique to measure the C-activity in austenite at 900°C, 1000°C, 1150°C, 1300°C and 1400°C over wide compositions ranges. These data are in good accord with the previous data, but they cover a much wider range of temperatures and compositions. Ban-ya, Elliott, and Chipman<sup>56</sup> used numerical fitting techniques and reported their findings in the form of empirical equations for the thermodynamic quantities. The activity with respect to graphite is given by

$$\log_{10} \alpha_i = \frac{3770}{T} + 2.72 \log_{10} T - 10.525 + \frac{3860}{T} \theta_i + \log_{10} \frac{\theta_i}{1 - \theta_i} \quad (1.2)$$



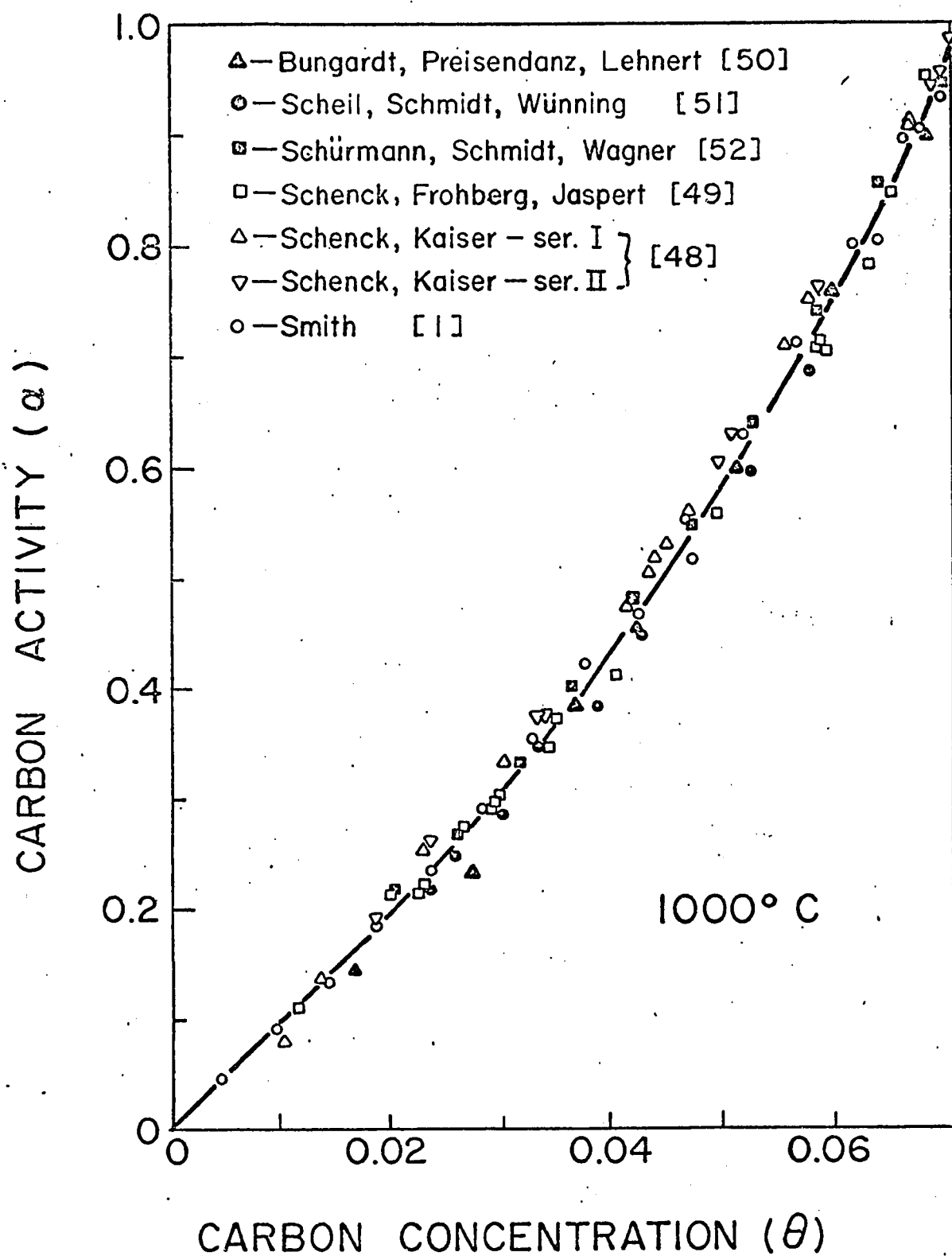


Figure 3

and the partial enthalpy  $\bar{H}_1^\gamma$  relative to that at infinite dilution,  $\bar{H}_1^{\gamma^\infty}$ , is given by

$$\bar{H}_1^\gamma - \bar{H}_1^{\gamma^\infty} = 17760 \theta_1 \text{ cal} \quad (1.3)$$

This linear variation of  $\bar{H}_1^\gamma$  with  $\theta_1$  is of great theoretical interest.

The present review does not seek to emphasize the geometry of the Fe-C phase diagram. This is a large topic and we will content ourselves by referring to the review of Benz and Elliott<sup>57</sup>. Ban-ya, Elliott, and Chipman<sup>56</sup> also give useful data on the geometry of the phase boundaries delineating the  $\gamma$ -field.

## 2.2 Theoretical Models (Binary $\gamma$ -Solutions)

The large deviation from henrian behavior exhibited by austenite has given rise to many theoretical models. These models can be classified into two groups: geometrical exclusion models and atomic interaction models.

The simplest form of the geometrical exclusion model was given by Speiser and Spretnak<sup>58</sup>. The solute atom effectively excludes from occupancy by other solute atoms an integral number  $Z'$  of nearest-neighbor interstitial sites. This concept is not realistic since it implies that a C-atom nearest neighbor pair can have a zero or

infinite potential energy depending upon its orientation. The simple blocking model is athermal in nature: all the deviation from regular behavior is due to the non-ideal configurational entropy and the partial enthalpy is independent of composition. Despite its simplicity, this model is compatible with the experimental C-activities in austenite. It has been used by Kaufman, Radcliffe and Cohen<sup>59</sup> in their discussion of the bainite reaction ( $Z' = 5$ ). Scheil<sup>60</sup> fitted Smith's<sup>1</sup> data to the activity equation of the simple blocking model ( $Z' = 5$ ). However, Temkin and Schwarzmann<sup>61</sup> again analyzed Smith's<sup>1</sup> data and concluded that  $Z' = 4$ .

The simple blocking model has been modified from time to time. The overlapping of sites excluded by different solute atoms has been considered by McLellan, Garrard, Horowitz and Sprague<sup>62</sup>. This leads to an extra quadratic term in the entropy. Equations 4, 5, and 6 compare the partial configurational entropy for the ideal interstitial solution, the simple blocking model and the complex blocking model

$$\frac{\bar{S}_i^c}{k} = -\ell_n \frac{\theta_i}{1 - \theta_i} \quad (1.4)$$

$$\frac{\bar{S}_i^c}{k} = -\ell_n \frac{\theta_i}{1 - \theta_i Z'} \quad (1.5)$$

$$\frac{\bar{S}_i^c}{k} = -\ell n \frac{\theta_i}{1 - \theta_i Z' + \theta_i^2 \chi} \quad (1.6)$$

The constant  $\chi$  was calculated<sup>62</sup> to be 8.67 for F.C.C. lattices. A further modification to the simple blocking model has been made by Gallagher, Lambert, and Oates<sup>63</sup> who introduced a composition dependent  $Z'$ .

The atomic interaction models for austenite are attempts to deduce the thermodynamic properties of the solution by considering specific forms for a non-infinite solute atom mutual interaction.

The simplest form of statistical interaction model for interstitial solid solutions is the zeroth order approximation in which the configurational entropy is that of a random solution and the internal energy is written as a summation over pairwise first nearest neighbor interaction energies. This simple model has been discussed by McLellan and Chráska<sup>64</sup> and by Alex and McLellan<sup>65</sup> and has been applied to the thermodynamics of austenite by Poirer<sup>66</sup>. In this simple model, the configurational entropy is that of a random solution but the energy of solution is dependent on composition due to the composition-dependence of the numbers of pairs of C-atoms located on nearest neighbor interstitial sites. This treatment

resulted in an equation for the C-activity in austenite in good accord with the experimental data.

Darken<sup>67</sup> presented a treatment based on a consideration of the partition functions of configurations involving C-C nearest-neighbor pairs where, again, the solute-solute interaction does not extend beyond first nearest neighbors. Darken's equation for the activity yielded good agreement with experiment. His equation can be written in the form,

$$\ell_n \frac{\alpha_i}{\theta_i} = \theta_i \left[ (Z+1) - Z e^{\Delta \epsilon / kT} \right] + \frac{\Delta \bar{G}_i^\infty}{kT} \quad (1.7)$$

where  $Z = 12$ ,  $\Delta \bar{G}_i^\infty$  is the quantity,

$$\Delta \bar{G}_i^\infty = \Delta \bar{H}_i^\infty - T \Delta \bar{S}_i^\infty$$

and  $\Delta \epsilon$  is the C-C pairwise interaction energy. Darken deduced that a reasonable value for  $\Delta \epsilon$  would be -1.5 k.cals/mole. The equation deduced by Poirer<sup>66</sup> can also be put into the form given by (1.7).

The quasi-chemical approach developed by Guggenheim<sup>68</sup> has been used a number of times in the development of statistical mechanical models for austenite.

Aaronson, Domian, and Pound<sup>69</sup> have discussed an equation derived by Fowler and Guggenheim<sup>70</sup> and by Lacher<sup>71</sup> which is based on a quasi-chemical treatment of surface adsorption. Aaronson, Domian and Pound point out that this approach does not give the correct expression for  $\alpha_i$  when  $\Delta\epsilon$  becomes infinite and further that the model is consistent with the experimental data only if  $\Delta\epsilon$  is strongly dependent on temperature.

Moon<sup>72</sup> has given a statistical treatment of a one-dimensional Ising model for interstitial solutions. As is well known<sup>73</sup>, the one-dimensional Ising model can be solved exactly. Moon has made inferences concerning three-dimensional solutions from his results and applied them to hydrogen-metal systems.

McLellan and Dunn<sup>74</sup> have given a quasi-chemical (or first-order) treatment of interstitial solid solutions. The expression for the activity of the solute atoms in this model is,

$$\alpha_i = \frac{\theta_i/\beta}{1 - \theta_i/\beta} e^{\Delta G_i^\circ / kT} \left\{ \left( \frac{\theta_i/\beta}{1 - \theta_i/\beta} \right)^2 \left( \frac{1 - \theta_i/\beta - \phi_i}{\theta_i/\beta - \phi_i} \right) \right\}^{-\frac{Z}{2}} e^{-Z\Delta\epsilon/2kT} \quad (1.8)$$

where  $Z$  is the coordination number for interstitial sites and the function  $\phi$ , is given by

$$\phi_1 = \frac{1 - \{1 - 4(1 - e^{\Delta\epsilon/kT}) \theta_i/\beta (1 - \theta_i/\beta)\}^{1/2}}{2(1 - e^{\Delta\epsilon/kT})} \quad (1.9)$$

This expression for  $\alpha_i$  was fitted to the available data for austenite at 1000°C using a Cramer's Rule technique. The best value for  $\Delta\epsilon$  was found to be -1.05 k.cals/mole. However, the later data of Ban-ya, Chipman and Elliott<sup>55,56</sup> was fitted to equation 8 for all the temperatures at which  $\alpha_i$  was measured<sup>75</sup>. The best values of  $\Delta\epsilon$  found were not strongly dependent on temperature: they are given in Table II, together with the values of  $\Delta\bar{G}_i^{\uparrow\infty}$  appropriate to each temperature.

TABLE II

T °C	$\Delta\bar{G}_i^{\uparrow\infty}$ k.cals/mole	$-\Delta\epsilon$ k.cals/mole
900	5.558	2.15
1000	5.123	2.02
1150	4.551	1.89
1300	4.064	1.89
1400	3.783	<u>1.92</u>
		< 1.97 >

The difference between the latest evaluation of  $\Delta\epsilon$ , -1.97 k.cals/mole, and the previous value, -1.05 k.cals/mole, is due to the data of Schenck and Kaiser<sup>48</sup> showing higher  $\alpha_i$ -values for a given composition than the other sets of data (see Fig. 3).

Now Ban-ya, Elliott and Chipman<sup>55, 56</sup> drew two conclusions from their data which are relevant to the comparison of the various theoretical models for austenite. These conclusions were:

- (a) The configurational entropy of the solution is approximately that of an ideal interstitial solution.
- (b) The partial energy of a solute atom does not vary with temperature, but it does vary strongly with composition and is directly proportional to  $\theta_i$ .

These conclusions represent a radical departure from the geometrical blocking models, which are athermal in nature since the partial energy is constant and all of the departure from regular mixing behavior is explained by the non-ideal configurational entropy. Now the configurational chemical potential in the first-order<sup>74</sup> treatment is

$$\mu_i^c = -kT \ln \left\{ \left( \frac{\theta_i}{1-\theta_i} \right)^{(Z-1)} \left( \frac{1-\theta_i-\phi_i}{\theta_i-\phi_i} \right)^{Z/2} \right\} + \bar{H}_i^{\infty} - \frac{Z\Delta\epsilon}{2} \quad (1.10)$$



where we have put  $\beta=1$ . The concomitant partial configurational entropy and enthalpy are given by,

$$\begin{aligned} \frac{\bar{S}_i^c}{k} = \ln \left\{ \left( \frac{\theta_i}{1-\theta_i} \right)^{(Z-1)} \left( \frac{1-\theta_i-\phi_1}{\theta_i-\phi_1} \right)^{Z/2} \right\} \\ - \frac{Z\Delta\epsilon}{2kT} \left\{ \frac{e^{\Delta\epsilon/kT} [\theta_i(1-\theta_i)]^2}{[2\phi_1(1-e^{\Delta\epsilon/kT})]-1} \right\} \left\{ \frac{(1-2\theta_i)}{\theta_i(1-\theta_i)-\phi_1(1-\phi_1)} \right\} \end{aligned} \quad (1.11)$$

and

$$\begin{aligned} \bar{H}_i^c - \bar{H}_i^{\infty} = -\frac{Z\Delta\epsilon}{2} \left\{ 1 + \left[ \frac{e^{\Delta\epsilon/kT} [\theta_i(1-\theta_i)]^2}{[2\phi_1(1-e^{\Delta\epsilon/kT})]-1} \right] \right. \\ \left. \left[ \frac{(1-2\theta_i)}{\theta_i(1-\theta_i)-\phi_1(1-\phi_1)} \right] \right\} \end{aligned} \quad (1.12)$$

These functions have been shown<sup>76</sup> to be consistent with the conclusions of Ban-ya, Elliott and Chipman. Plots of  $\bar{S}_i^c$  from equation 11 using  $\Delta\epsilon = -1.97$  k.cals/mole are close to the ideal value from 900 to 1400°C and  $\bar{H}_i^c - \bar{H}_i^{\infty}$  from equation 12 is virtually independent of temperature in the range 900 - 1400°C and directly proportional to  $\theta_i$ . It is also interesting to note that in the limit when  $\theta_i$  is small, equation 8 for  $\alpha_i$  yields equation 7 due to Darken<sup>67</sup>. Furthermore, recent measurements of the thermodynamic properties of nitrogen in austenite<sup>77</sup> have also been analyzed in terms of the first-order model<sup>78</sup> and

shown to be consistent with this formulation.

The quasi-chemical formulation contains two basic assumptions. One is that only first-nearest neighbor pairwise interactions need be considered and the other is that the degeneracy,  $g_c$ , of the solution can be adequately counted by utilizing the fact that the summation of  $g_c$  over all possible complexions must equal the known total number of possible configurations of the atoms in the crystal. However, it is possible, provided  $\Delta\epsilon < kT$  (high temperatures) and the concentration is not too high, to calculate the degeneracy, and thus the entropy, exactly by the method of Kirkwood expansions<sup>79</sup>. This calculation has been performed<sup>80</sup> and it has been shown that the error introduced into the entropy by the use of the first-order counting scheme is small.

Computer simulation calculations of carbon in austenite have not been performed due to the unavailability of a suitable force model for F.C.C. iron. However, Machlin<sup>81</sup> has considered the Friedel oscillations of the electrostatic contribution to  $\Delta\epsilon$ . He shows that if this interaction energy, which covers more than first-nearest neighbors, is introduced into a form of Darken's<sup>67</sup> model generalized so as to include further than nearest-neighbor pairs, an equation for  $\alpha_i$  can be deduced which

is compatible with the observed variation of  $\alpha_i$  with composition.

### 2.3 Diffusion of Carbon in Austenite

There have been several determinations of the diffusivity  $D$  of carbon in austenite covering wide ranges of temperature and composition. Wells and Mehl<sup>82</sup>, Wells, Batz and Mehl<sup>83</sup> and Smith<sup>84</sup> have all shown that  $D$ , at a given temperature, increases strongly with an increase of carbon concentration. Smith<sup>84</sup> used a steady state method, whereas Wells, Batz and Mehl<sup>83</sup> used a non-steady state technique. However, their results for the variation of  $D$  with composition show very good agreement. The most extensive data are at 1000°C and at this temperature  $D$  increases by almost a factor of 5 from  $\theta_i = 0.01$  to  $\theta_i = 0.07$ . A summary of the data is given in Fig. 4.

The variation of  $D$  with composition has been the object of much discussion. Darken<sup>85</sup> showed that the diffusivity  $D$  of an interstitial solute depends on its activity coefficient  $\gamma_i$  and concentration  $C_i$  (number per unit volume) in the form,

$$D = B kT \left( 1 + C_i \frac{d \ln \gamma_i}{d C_i} \right) \quad (1.13)$$

where  $B$  is the mobility of the solute atom. Smith's<sup>84</sup>

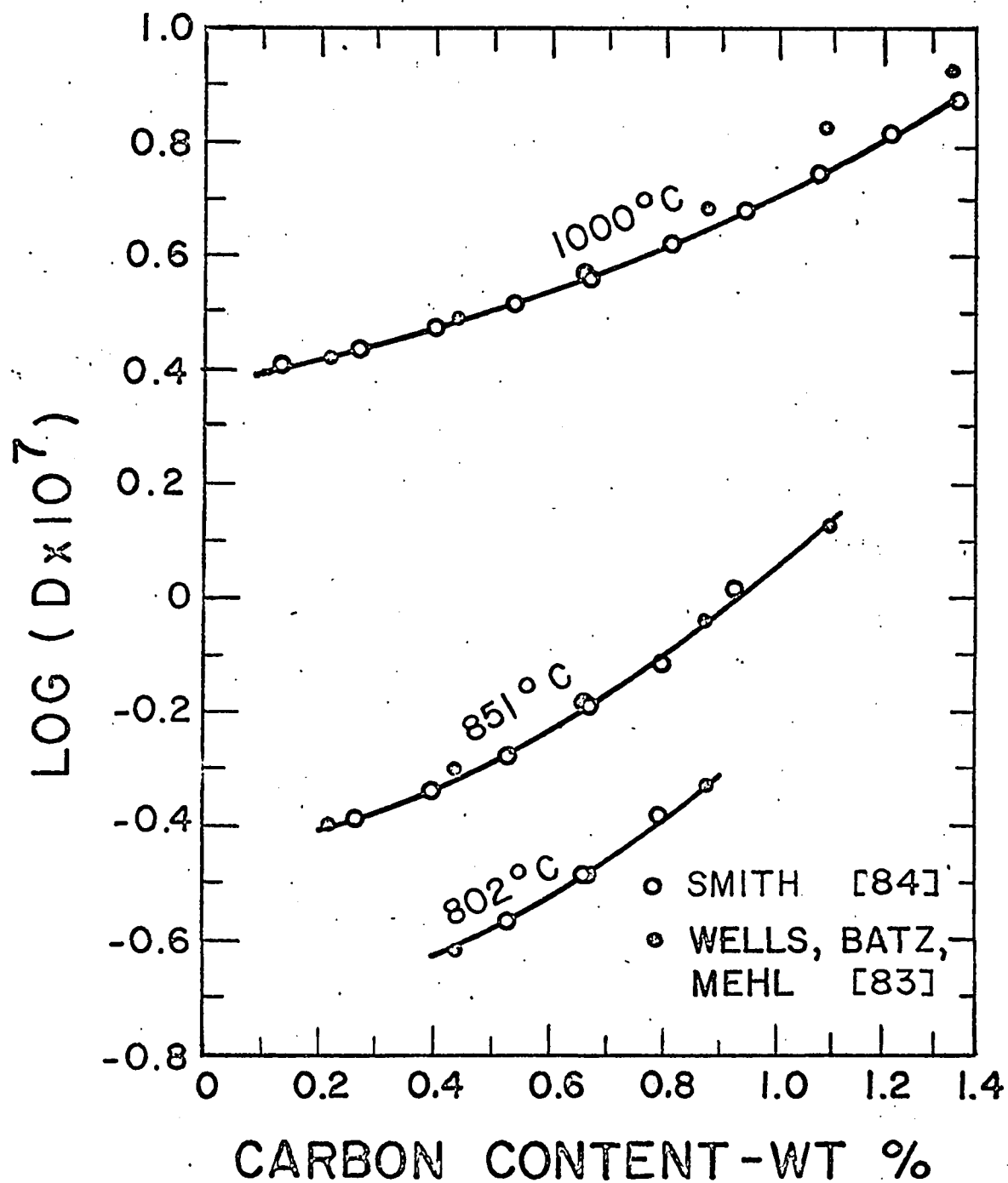


Figure 4

attempt to reconcile the observed variation of  $D$  with an equation derived by Fisher, Hollomon and Turnbull<sup>85</sup> and with equation 13 using a composition independent  $B$ , was not successful. This, however, is not surprising since, as Darken<sup>85</sup> pointed out, there is no reason to assume that  $B$  is constant. An explanation of the effect has been proposed by Siller and McLellan<sup>87, 88</sup>. The greater proportion of the increase in  $D$  with composition arises from the variation in  $\gamma_i$  with  $\theta_i$ . However, in calculating the composition dependence of  $D$ , it must be recognized that the number of available sites for jumps, forward or backward, along the concentration gradient is a function of composition because of the repulsive nature of the solute mutual interactions and the fact that some sites are already occupied by solute atoms. This effect gives rise to a composition dependent mobility. The restriction of available jump sites was calculated using the first-order model for austenite<sup>74</sup> and the measured variation in  $D$  was found to be compatible with the equilibrium thermodynamic properties (the activity data) using the same value of the pairwise interaction energy  $\Delta\epsilon$  that was found to be appropriate for the thermodynamic data.

Computer simulations of the migration of carbon in austenite have not been performed due to the lack

of appropriate force models. Simulation techniques have been used to study both the thermodynamic and kinetic properties of carbon dissolved in nickel<sup>89, 90</sup> and the results provide an interesting comparison with carbon in iron at low concentrations.

## 2.4 Thermodynamics of Ternary Systems

There are many data available for the thermodynamic behavior of the interstitial component of ternary solid solutions in which the solvent (v) contains both substitutional (u) and interstitial (i) solute atoms. In this review, we consider the cases where v is iron and i is carbon. The principal method of investigating the properties of these solutions has been the gas-solid equilibration technique.

Smith<sup>91</sup> used the CO-CO<sub>2</sub> technique at 1000°C to measure the activity of carbon in Fe-Ni-C solutions. Heckler and Winchell<sup>92</sup> measured the activity of carbon in Fe-Ni-C austenites by equilibrating the ternary solution in a sealed capsule with a binary Fe-C austenite of known C-activity.

The Fe-Si-C system has been investigated by Schürmann, Schmidt, and Tillmann<sup>22</sup> (CH<sub>4</sub> - H<sub>2</sub>) and by Smith<sup>23</sup> (CH<sub>4</sub> - H<sub>2</sub>).

The Fe-Mn-C system was studied by Smith<sup>23</sup> ( $\text{CH}_4 - \text{H}_2$ ) and by Schürmann and Schröder<sup>93</sup> ( $\text{CH}_4 - \text{H}_2$ ).

Carbon activity data for the Fe-Cr-C system and the Fe-Al-C system were obtained by Schenck and Kaiser<sup>48</sup> ( $\text{CH}_4 - \text{H}_2$ ) and further data on the Fe-Cr-C system were obtained by Flender and Wever<sup>94</sup> ( $\text{CH}_4 - \text{H}_2$ ) and by Bungardt, Preisendanz and Lehnert<sup>50</sup> ( $\text{CH}_4 - \text{H}_2$ ).

Carbon activities were measured in Fe-Co-C solutions by Smith<sup>95</sup> ( $\text{CO}-\text{CO}_2$ ).

There have been two investigations of the Fe-V-C system<sup>96, 97</sup>, but in both cases the solid contained two phases (solution + vanadium carbide) in the composition range investigated.

Representative experimental data are illustrated in Fig. 5 which shows plots of  $\alpha_i$  with respect to graphite vs  $\theta_i$ . The experimental data for Ni have been omitted due to the inconsistencies in the sets of data. This point has been discussed previously<sup>98</sup>. In each case the  $\alpha_i$ -data corresponding to the largest value of u-atom concentration is plotted. Data for the Fe-C binary system are also included for comparison. Fig. 6 shows the variation of  $\alpha_i$  at a fixed C-concentration ( $\theta_i = 0.03$ ) with  $\theta_u$ , the atom ratio of substitutional solute. It can

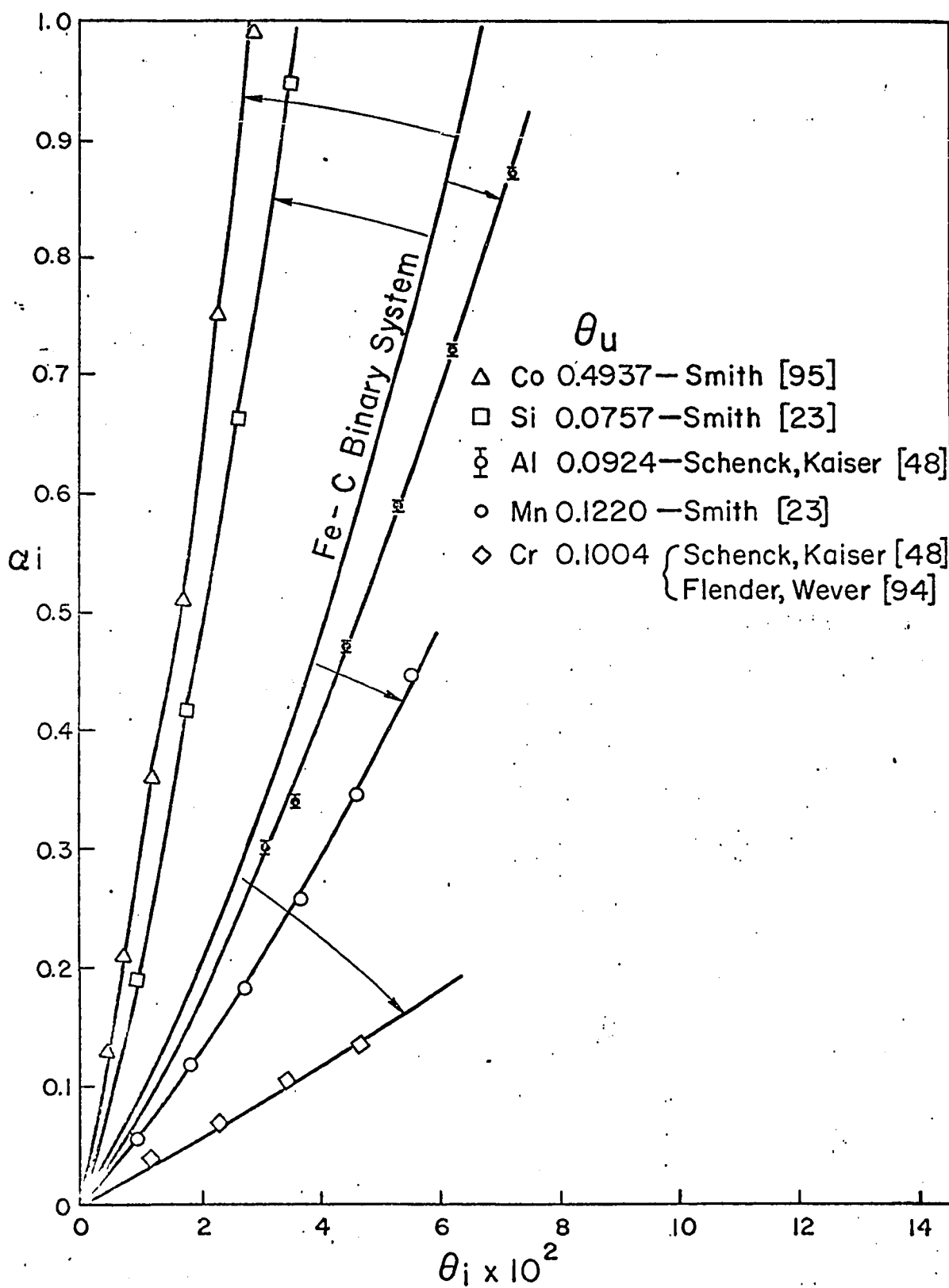


Figure 5



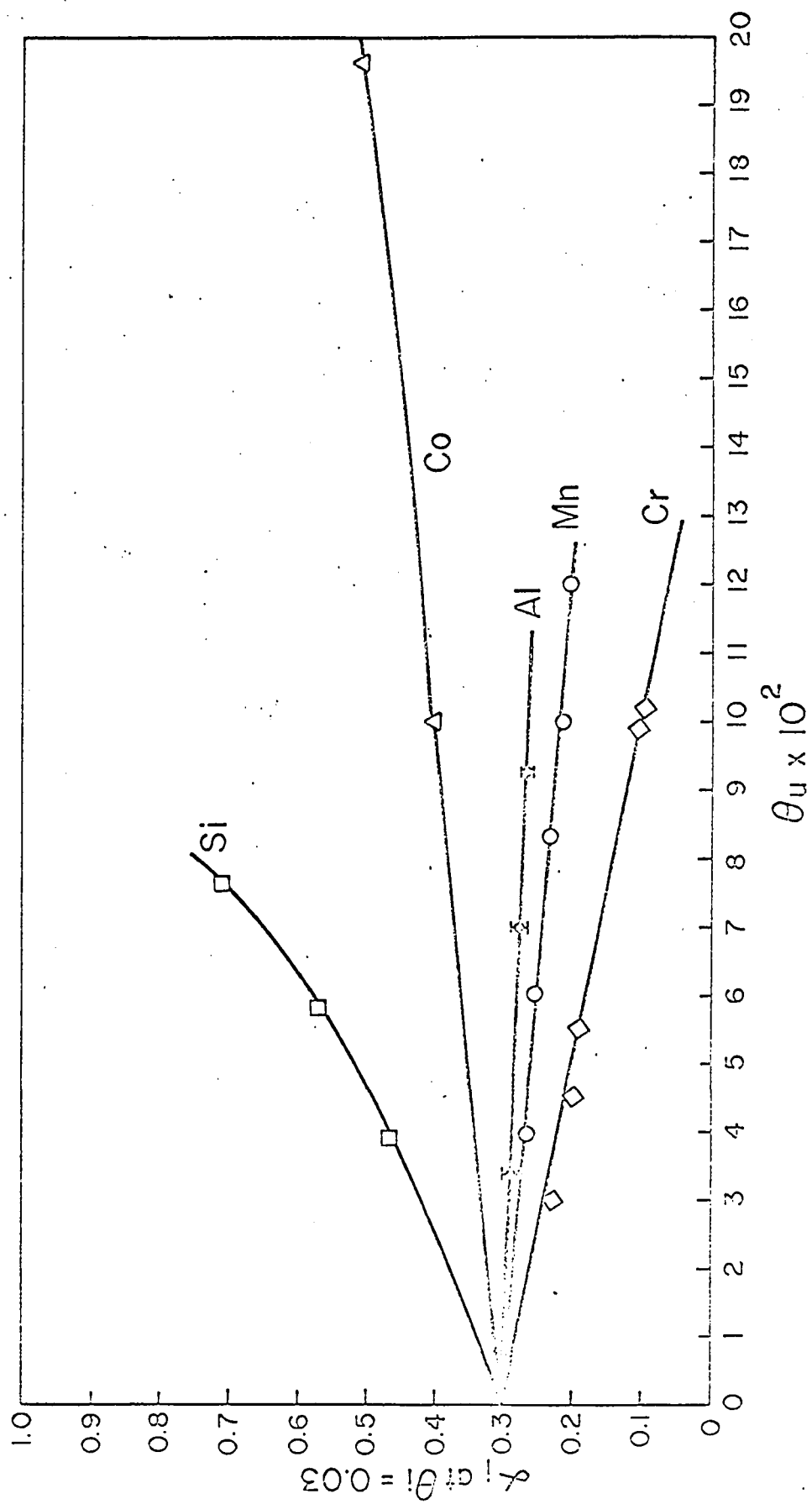


Figure 6

be seen that Si has a pronounced effect in increasing the activity of carbon in solution. The same is true of Co, but not to the same degree. Aluminum slightly depresses the carbon activity in solution. Mn and Cr have the same effect and that of Cr is most pronounced.

It is interesting to note that, for the substitutional solute elements which occupy, along with Fe, the First Transition Series of the Periodic Table, those which lie to the right of Fe, enhance the carbon activity (Co, Ni) and those which lie to the left decrease the carbon activity (Mn, Cr).

## 2.5 Theoretical Models for Ternary Systems

A simple statistical model for the ternary austenites was proposed by Kirkaldy and Purdy<sup>99</sup> in which the entropy was that of a completely random solution and no excess entropy contributions were considered. The energy of the solid solution was written as the sum of nearest-neighbor pairwise bonding energies.

Several models have been proposed which relate to the simple geometrical blocking concept discussed in the case of binary austenite. Zupp and Stevenson<sup>100</sup> considered a model in which each carbon atom excluded a number of interstitial sites from occupancy by other carbon atoms

and the exclusion number is influenced by the substitutional solute. A similar model has been discussed by Bodsworth, Davidson, and Atkinson<sup>101</sup>. The solvent and substitutional solute atoms are randomly distributed in the metal atom sublattice and the carbon atoms are distributed on the lattice gas of interstitial sites according to the simple blocking scheme. This model leads to a semi-empirical relation for the carbon activity in the ternary solution in which the effect of the substitutional solute is accounted for by the addition of linear coefficients.

Wada and Saito<sup>102</sup> have considered a simple model in which the configurational entropy was that of a random ternary system. They showed that the Wagner interaction parameters for the interstitial solute are independent of the interactions between the other two components. This is a well-known result that has been discussed more recently for general ternary systems involving interstitial components in binary metal solvents<sup>103</sup>. Experimental values of the Wagner interaction parameters for the Fe-Co-C system have been discussed by Brown and Kirkaldy<sup>104</sup> and for the Fe-Cr-C system by Brigham and Kirkaldy<sup>105</sup>.

A simple statistical model was considered by Coplin, McGinness and McLellan<sup>98</sup>, in which the substitutional

solute atoms are distributed randomly in the lattice and the interstitial atoms are apportioned into two sub-assemblies. In one sub-assembly the interstitial atoms have nearest-neighbors which are all solvent atoms and in the other sub-assembly interstitial atoms can have one or more substitutional solute nearest neighbors. The expression for the activity of i-atoms deduced from this model is compatible with the experimental data.

The first order formulation can be applied to ternary solid solutions. Stringfellow and Greene<sup>106</sup> have shown that closed solutions of the quasi-chemical equations cannot be obtained when all three components occupy the same lattice. However, closed solutions are obtainable when one of the components occupies a different sub-lattice as is the case for an interstitial solute. Iwase and Kachi<sup>107</sup> have given a first-order treatment. This was, however, an approximate treatment since the substitutional solute concentration was restricted to low levels and no contribution to the free energy arising from non-configurational terms was considered.

A formal first-order treatment has recently been given by Alex and McLellan<sup>108</sup>. The expression derived for the chemical potential of interstitial solute atoms is,

$$\mu_i = \bar{H}_i^{\infty} - T \bar{S}_i^{\infty} + kT \ln \frac{\theta_i}{1 - \theta_i} - \frac{Z_1 kT}{2} \ln \left[ \left( \frac{\theta_i}{1 - \theta_i} \right)^2 e^{\Delta \epsilon / kT} \left( \frac{1 - \theta_i - \phi_1}{\theta_i - \phi_1} \right) \right] - Z_2 kT \ln \left\{ \frac{\theta_i}{1 - \theta_i} \left[ \frac{1 - \theta_u - \theta_i + \phi_2}{\theta_i - \phi_2} \right] \right\} \quad (1.14)$$

In this equation  $\bar{H}_i^{\infty}$  and  $\bar{S}_i^{\infty}$  are the partial enthalpy and excess entropy of interstitial solute in the infinitely dilute v - i binary system. These quantities are thus experimentally known.  $Z_1$  is the number of interstitial sites which are nearest neighbor to a given interstitial site and  $Z_2$  is the number of sites on the v - u lattice which are nearest neighbors to an interstitial site. The i - i pairwise binding energy is  $\Delta \epsilon$  and  $\phi_1$  is defined by equation 9. The function  $\phi_2$  is written in terms of the u-concentration ( $\theta_u = N_u / (N_u - N_v)$ ) and the interaction energy  $\Delta \epsilon'$  which is the difference between the i - u and i - v pairwise interaction energies.

$$\phi_2 = \frac{[\{1 - (\theta_i + \theta_u)(1 - \delta)\}^2 + 4 \theta_u \theta_i \delta (1 - \delta)]^{1/2} - [1 - (\theta_i + \theta_u)(1 - \delta)]}{2 (1 - \delta)} \quad (1.15)$$

where

$$\delta = e^{-\Delta \epsilon' / kT}$$

It has been shown<sup>108</sup> that, assuming  $\Delta\epsilon$  has the same value as it has in the Fe-C binary system, that with the exception of the Fe-Si-C system, equation 14 is in excellent agreement with the thermodynamic properties of ternary Fe-U-C systems. The values of  $\Delta\epsilon'$  obtained by comparing the activities derived from equation 14 with experimental data are given in Table IV.

TABLE IV

Substitutional Solute (u)	$\Delta\epsilon'$ k.cals/mole
Co	+ 1.52
Al	- 0.18
Mn	- 0.93
Cr	- 2.99

It can be seen from Fig. 6 that the numerical values of  $\Delta\epsilon'$  reflect the thermochemical behavior of the ternary systems; the values of  $\Delta\epsilon'$  ranging from large and positive for Co to large and negative for Cr.

The partial enthalpy and configurational entropy of the interstitial species have been calculated<sup>109</sup> from equation 14 using  $\Delta\epsilon = -1.97$  k.cals/mole and a range of  $\Delta\epsilon'$  values covering those given in Table IV. The partial

thermodynamic functions in the ternary system are similar to those in binary austenite<sup>76</sup>. The partial configurational entropy is close to ideal and the partial enthalpy is strongly composition dependent. It does depend on temperature, but not strongly.

In addition to the atomistic models for ternary solid solutions, it should be pointed out that Chipman and Brush<sup>110</sup> and Chipman<sup>111</sup> have given useful empirical equations for the thermodynamic activity of carbon.

This review will not attempt to consider diffusion in Fe-based ternary systems. This is a large topic which has recently been reviewed in detail<sup>112</sup>.

## CONCLUSION

This work is an attempt to review some of the interesting thermodynamic features associated with the iron-carbon system. It does not purport to be complete: for reasons of brevity, many interesting topics have been omitted and we have restricted ourselves to solid solutions. These solutions exhibit interesting departures from the relatively simple behavior often exhibited by dilute solutions. These deviations have been discussed in terms of the many models which have been proposed for their explanation. A collection of some of the

thermodynamic functions of the binary Fe-C solutions at infinite dilution is given in Table V. The energies in this table are in units of k.cals/mole. The reference state for  $\bar{H}_i^\infty$  is an atom at rest in a vacuum and that for the relative partial quantities is pure graphite at 1000°K in the case of B.C.C. solutions and 1250°K for the F.C.C. systems. The B.C.C. diffusivity data refers to the low temperature region in which the Arrhenius plot is linear.



TABLE V

Quantity	B.C.C.	Reference	F.C.C.	Reference
$\bar{H}_i$	- 147.2 - 148.0 - 144.1 - 146.4	(1) analysis (3) (16) (18) average	- 155.2 - 155.3 - 155.25	(1) analysis (3) (55) (56) average
$\Delta \bar{H}_i^{\infty}$	20.2 24.0 23.3 22.5	(1) analysis of (3) (16) (18) average	10.86 10.77 10.81	(1) analysis (3) (55) (56) average
$\bar{S}_{i/k}^{\infty}$	5.20 6.89 6.56 6.22	(1) analysis (3) (16) (18) average	5.75 5.78 5.77	(1) analysis (3) (55)(56) see also (75) average
$\Delta \bar{S}_{i/k}^{\infty}$	2.28 3.97 3.64 3.30	(1) analysis (3) (16) (18) average	2.10 2.13 2.12	(1) analysis (3) (55)(56) see also (75) average
$\Delta \bar{G}_i^{\infty}$	15.67 16.12 16.07 15.95	(1) analysis (3) (16) (18) average	5.65 5.22 5.43	(1) analysis (3) (55) (56) average
$Q$ (diffusion)	19.3	(31) (32) (33) (34)(35)(36)(37) Analysis (40)		
$D$ cm <sup>2</sup> /sec	$3.3 \times 10^{-3}$	(31)(32)(33) (34)(35)(36)(37) Analysis (40)		

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## II. THERMODYNAMIC PROPERTIES OF CARBON IN B.C.C. AND F.C.C. IRON-SILICON SOLID SOLUTIONS

### INTRODUCTION

This paper is the report of an extensive thermodynamic investigation of both body-centered cubic and face-centered cubic solid solutions of iron containing silicon and carbon. The thermodynamic properties of the carbon in solid solution have been deduced from measurements of the equilibrium between the solid, containing a fixed Si-concentration, and a series of  $\text{CH}_4$ - $\text{H}_2$  carburizing gas mixtures of varying composition. The equilibrium was studied at several different temperatures in both the B.C.C. and F.C.C. phase fields.

There are many reasons why Fe-Si-C solid solutions are worthy of study. The data previously available for this system are limited, but they do show clearly that the effect of Si on the thermodynamic parameters of carbon dissolved in austenite is much greater than the effect of other substitutional solute elements dissolved in ternary austenites. Recent statistical mechanical models<sup>1, 2</sup>, which have been found to be consistent with the experimental data for austenites containing Mn, Cr, Al, and Co were found to be inconsistent with the Fe-Si-C data. A

further reason for this investigation is that it provides an opportunity to compare the behavior of the interstitial solute atom simultaneously in both B.C.C. and F.C.C. solutions in similar composition ranges.

In this investigation the thermodynamic activity of carbon in B.C.C. and F.C.C. solid solutions, up to the saturation limit, has been found. The solutions investigated had a fixed Si-content of 3.38 weight percent. The measurements were made at several temperatures ranging from 835 to 1050°C.

### 1. Previous Investigations

Before discussing the previous experimental work on Fe-Si-C solid solutions, a quick perusal of the thermodynamic properties of the Fe-Si binary system will be given. The alloy used in this investigation contained 3.38 weight percent Si.

In Fe-Si alloys with higher Si-contents there is no doubt that ordering and antiphase domains can be produced by a suitable heat treatment. Both B2 and DO<sub>3</sub> type superlattices are found in the Fe-Si alloys. The occurrence and morphology of the antiphase domains have been observed and described by many authors.<sup>3, 4, 5, 6</sup> For solutions containing less than about 4.5 weight percent

Si, there is some doubt about the extent to which ordering occurs. Stearns<sup>7</sup>, using Mössbauer spectroscopy, measured the internal magnetic fields and Isomer shifts in a series of Fe-Si solutions containing from 0-27 weight percent Si. The results were interpreted as indicating that below 5 weight percent Si the solution, at room temperature, was substantially disordered. However, more recent Mössbauer spectra measurements by Gustin and Gielen<sup>8</sup> on an Fe-Si alloy containing 3.3 weight percent Si indicate that material quenched from 1200°C and then annealed for 3 hours at 570°C does not have a random atomic configuration. A slight difference in the secondary peaks in the quenched and annealed material is consistent with some degree of short range order in the annealed alloy.

A recent thermodynamic study of the Fe-Si system has been made by Elliott.<sup>9</sup> His thermodynamic data, obtained from e.m.f. measurements, indicate that the B.C.C. phase, even at low Si-concentrations, exhibits short range order.

The data available for the thermodynamic properties of the ternary Fe-Si-C system are scant and not definitive. Leak and Leak<sup>10</sup> measured the solubility of carbon in B.C.C. iron containing 3 weight percent Si. The method used was

to measure the amount of carbon dissolved in equilibrium with a precipitated carbide. The results showed that the C-solubility is much lower than for the binary ferrite in equilibrium with cementite, but the heat of solution of  $\text{Fe}_3\text{C}$  in the ternary ferrite is identical with that in the binary case, i.e. 9.7 k.cal/mole. However, Swartz<sup>11</sup> has shown that stress effects accompany the precipitation of a second phase in ferrite and this can give rise to ambiguities in the interpretation of experiments involving a precipitate.

The equilibrium between  $\text{CH}_4\text{-H}_2$  gas mixtures and Fe-Si solutions containing several different Si-concentrations has been studied by Schürmann, Schmidt, and Tillmann.<sup>12</sup> Their analysis of the data indicated that the relative partial enthalpy of carbon in solutions containing from 3.55 to 9.6 weight percent Si is independent of both temperature and composition, and, furthermore it is identical to the value found previously by these authors for the Fe-C binary system<sup>13</sup> (20 k.cal/mole). However it should be pointed out that the data found by Schürmann, Schmidt, and Tillmann<sup>12</sup> (S.S.T.) for the ternary system may be subject to the same inconsistencies found in their Fe-C binary data.<sup>14</sup>

Smith<sup>15</sup> has studied the  $\text{CH}_4\text{-H}_2$  equilibrium with Fe-Si-C

solid solutions. Unfortunately the number of data points obtained was small and it is not possible to make an accurate estimate of the thermodynamic parameters of the solution. Petrova, Lapshina, and Shvartsman<sup>16</sup> have presented the results of a study of the CO<sub>2</sub>-CO equilibrium with Fe-Si-C solid solutions, but again the findings are of a qualitative nature due to the small number of data points given.

## 2. Experimental Procedure

This investigation was based on a study of the equilibrium between the solid solution and a carburizing gas. The metal samples in the form of carefully polished, thin foils about 0.04" thick, of Fe-3.38 weight percent Si alloy were suspended inside a ceramic cage in the center of the hot zone of a horizontal tube furnace. The chemical composition of the starting material is given in Table I.

TABLE I

Analysis of Fe-Si Alloy (Figures are wt. %)	
Cr 0.004	Mo 0.009
Cu 0.003	Ni 0.004
Mn 0.010	Ti 0.003
	C 0.002

The carburizing gas, methane hydrogen mixtures, was made to flow through the tube. The details of the apparatus and the means used to ensure that the gases were mixed in a accurately predetermined volume ration have been given previously.<sup>17</sup> The methane used was Matheson's Ultra High Purity containing 40 ppm CO<sub>2</sub>, 5.2 ppm O<sub>2</sub>, 36.6 ppm N<sub>2</sub>, 13.7 ppm C<sub>2</sub>H<sub>6</sub> and less than 5 ppm C<sub>3</sub>H<sub>8</sub>. The hydrogen had a nominal purity of 99.9995% by volume. The gases were flowed through a cleaning train.<sup>17</sup>

The equilibrations were performed at several fixed temperatures for a series of varying gas compositions. In some of the experiments the total flow rate recommended by Darken and Gurry<sup>18</sup> was used (0.9 cm/sec). However, in most of the measurements the total flow velocity was 0.5 cm/sec. No inconsistency in the results was found to ensue from the use of the lower flow velocity.

After equilibration the metal sample was quickly withdrawn from the hot zone and quenched on a copper block at the cold end of the furnace. The initial cooling rate was about 150°C per minute. The minimum equilibration time was 15 hours, but some samples were equilibrated for as long as 30 hours. The long times were used periodically to check whether or not equilibrium had been achieved.



Finally the equilibrated, quenched foils were cleaned, and weighed and their carbon contents determined by combustion analysis using a Leco system with an estimated accuracy of  $\pm 3$  ppm carbon.

### 3. Results

The experimental data are given in Table II (p. 62) (B.C.C. solutions) and Table III (F.C.C. solutions). In these tables  $r$  is the gas ratio,  $r = P_{\text{CH}_4}/P_{\text{H}_2}^2$ , and  $\theta_i$  is the atom ratio of carbon in solution. The atom ratio,  $\theta_i$ , is defined in terms of the numbers of moles  $n$  of the constituents of the solution in the form  $\theta_i = n_c/(n_{\text{Fe}} + n_{\text{Si}})$ .

The data for the F.C.C. solution taken at  $835^\circ\text{C}$  are purposely given at the end of Table III since the limited number and relatively scattered nature of the data points taken at this temperature precludes their use in calculating the activity of the interstitial solute.

All of the measured data are depicted in Fig. 1 in the form of plots of  $\log r$  versus  $\log$  weight percent C. The logarithmic scale is used for convenience. The numbers 1 through 11 in Fig. 1 (and in the later Figs. 2 and 3) refer to phase boundaries of the 3.38 weight percent Si section of the Fe-Si-C phase diagram. Figures 2 and 3

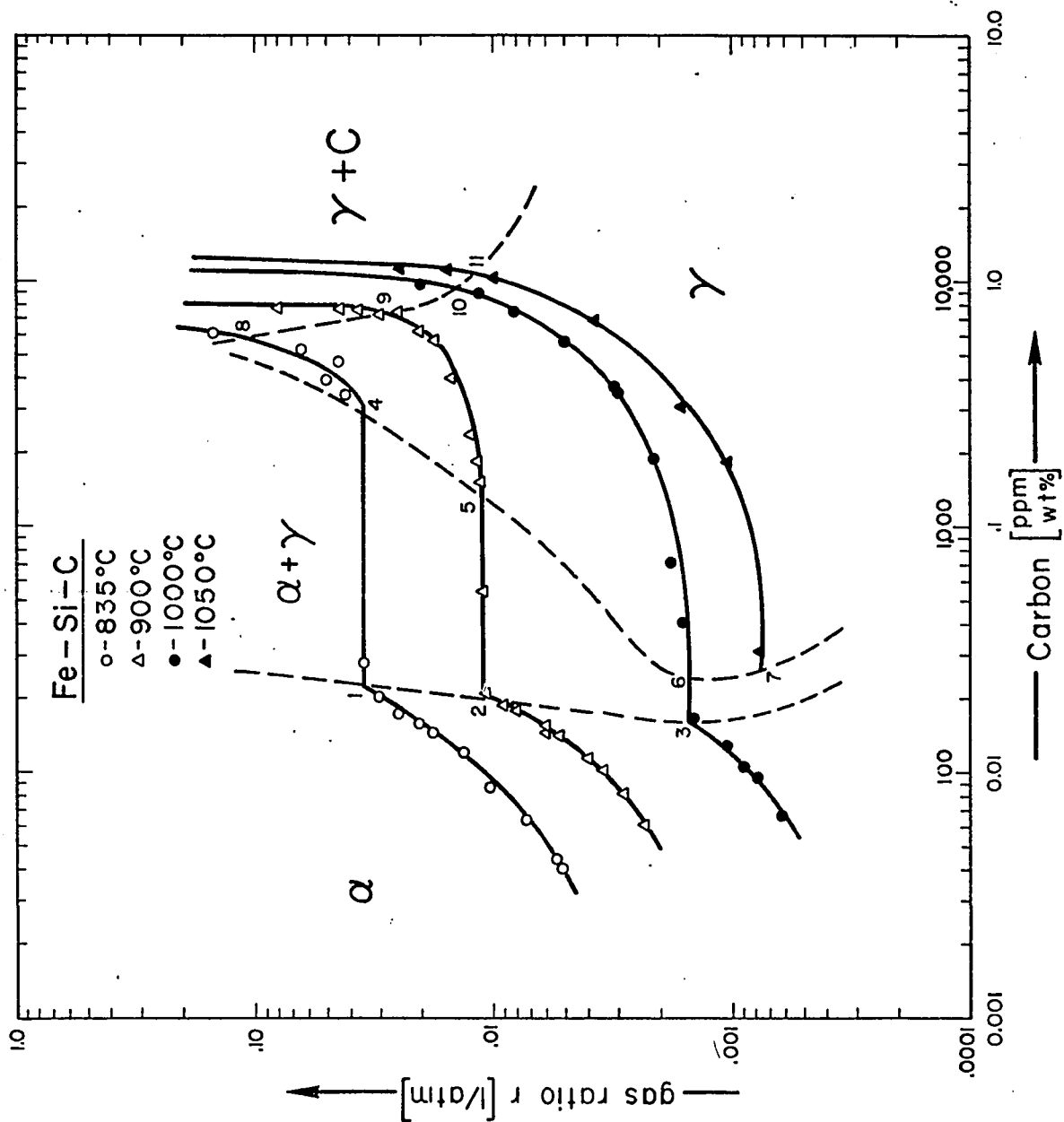


Fig. 1

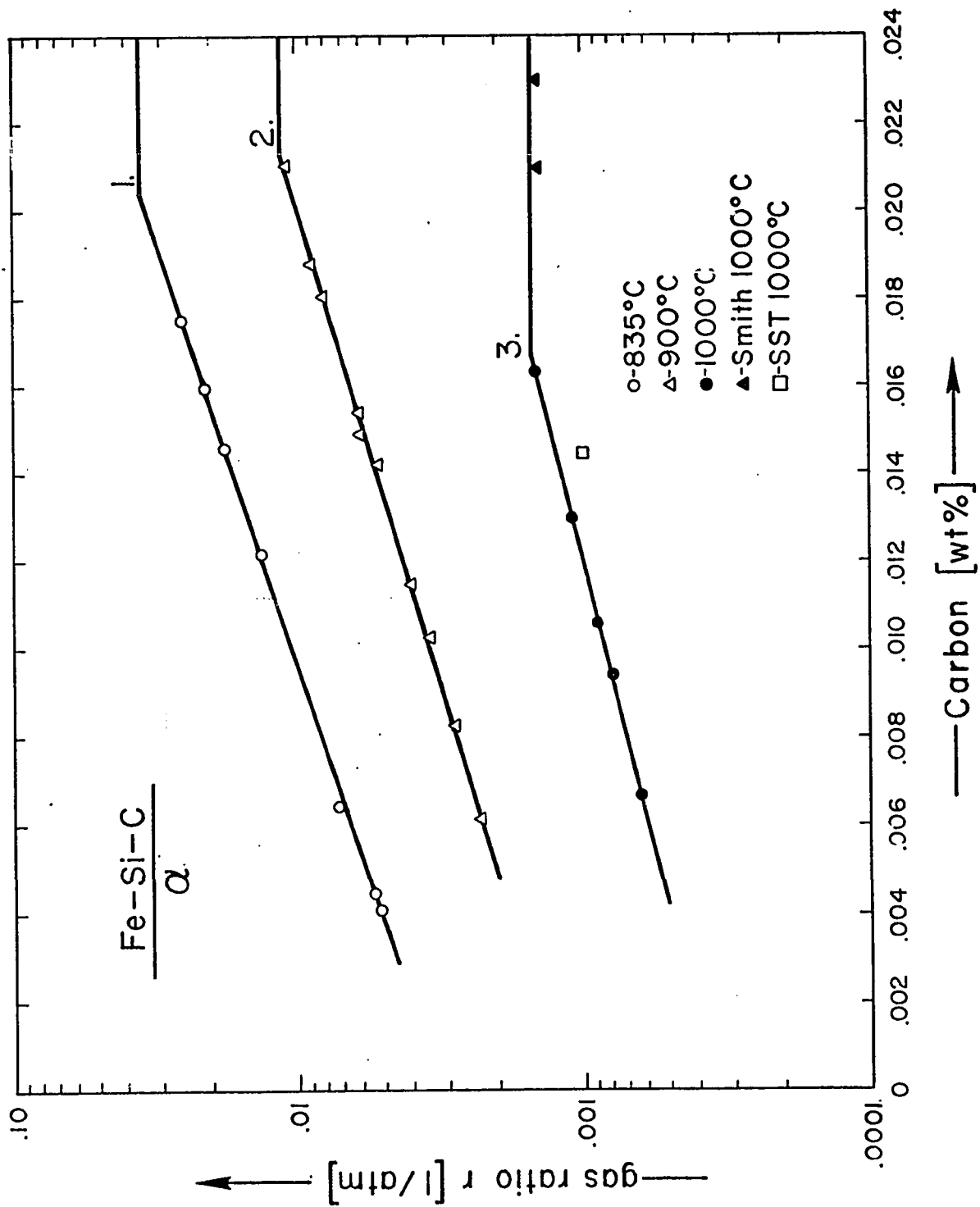


Fig. 2

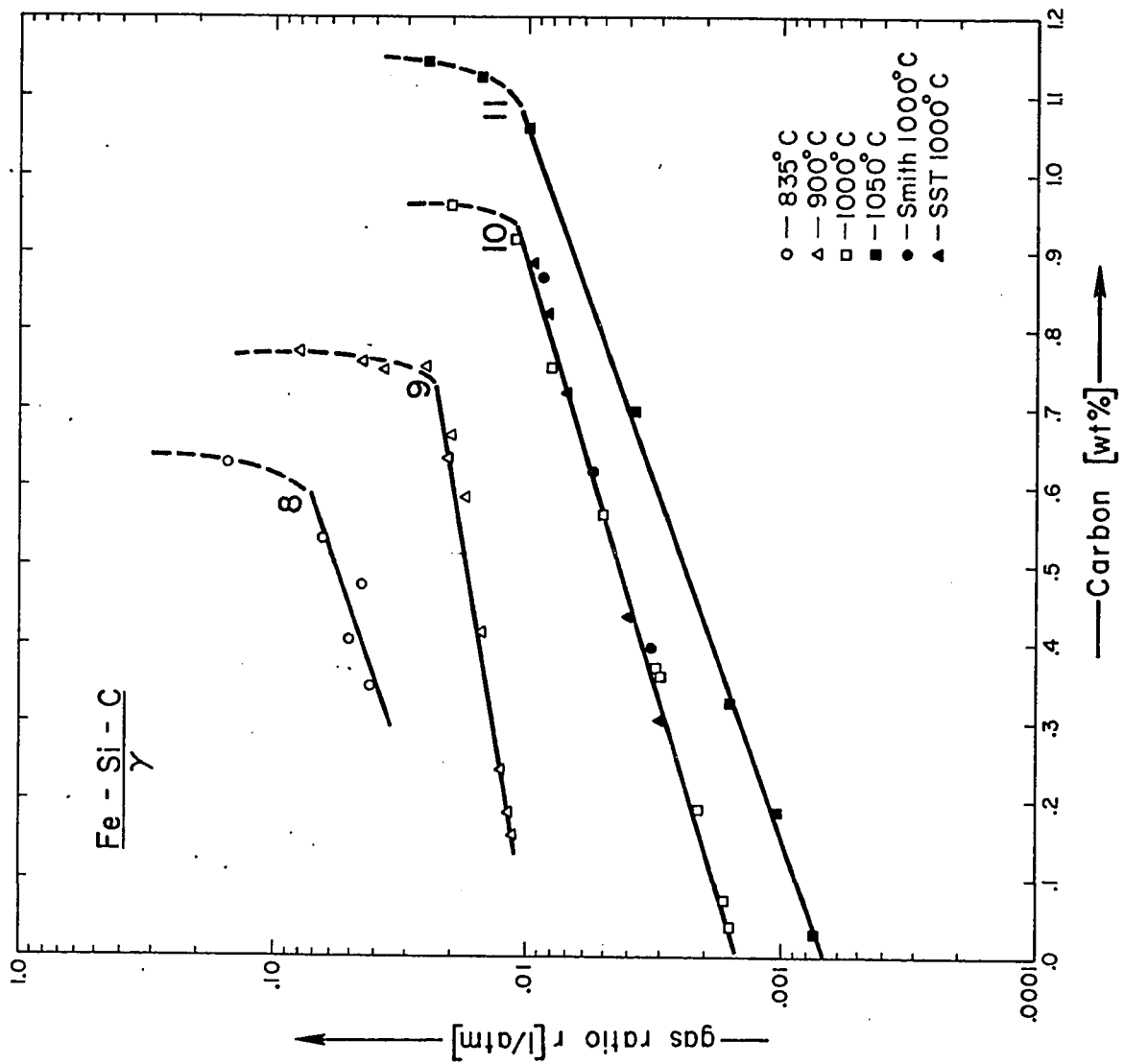
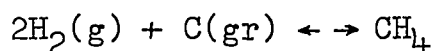


Fig. 3

show plots of  $\ln r$  versus weight percent C. Since the chemical potential of the interstitial component  $\mu_1$  is directly proportional to  $\ln r$ <sup>19</sup>, these plots show that, in the composition and temperature range covered by the data, the chemical potential is proportional to the C-content. Figure 3 was used to determine the phase boundary between the  $\gamma$  and ( $\gamma + C$ ) fields. The ends of the linear regions of the  $\ln r$  versus weight percent C plots were taken as the saturation solubility of C in the ternary austenite.

Figures 5 and 6 depict plots of the activity of carbon in solution relative to graphite, as functions of the C-content. It is well known that the C-activity,  $\alpha_1$ , is given by  $\frac{kr}{p}$  where  $k$  is the equilibrium constant for the reaction,



In the plots of figs. 5 and 6 the activities were deduced from the measured  $r$ -values and values of  $k$  calculated from the properties of the molecular species in the gas<sup>19</sup>, rather than the experimentally determined  $k$ -data given by Smith<sup>20</sup> or S.S.T.<sup>13</sup>. The quantities needed to calculate  $k$  are all accurately known.<sup>17</sup>

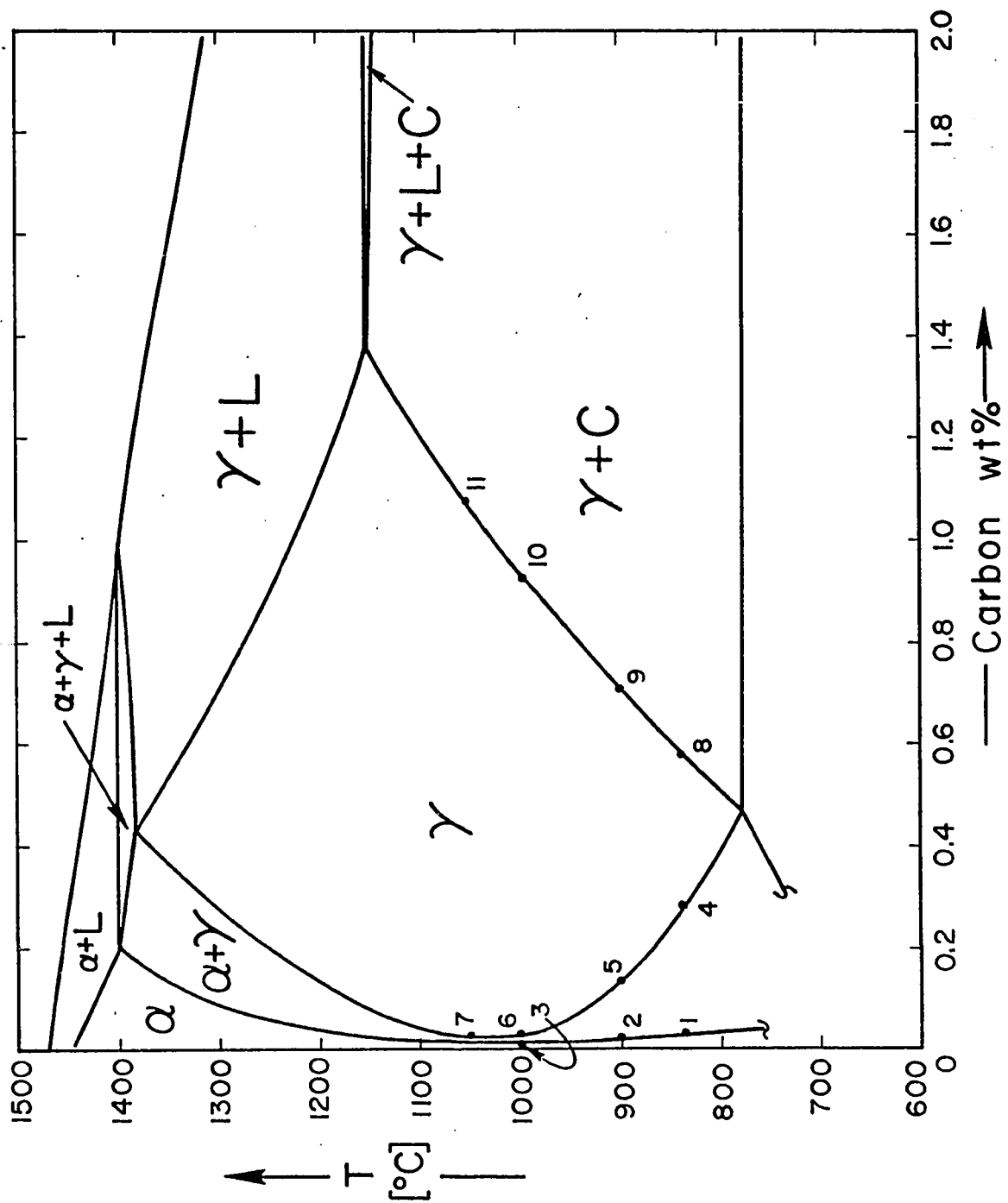


Fig. 4

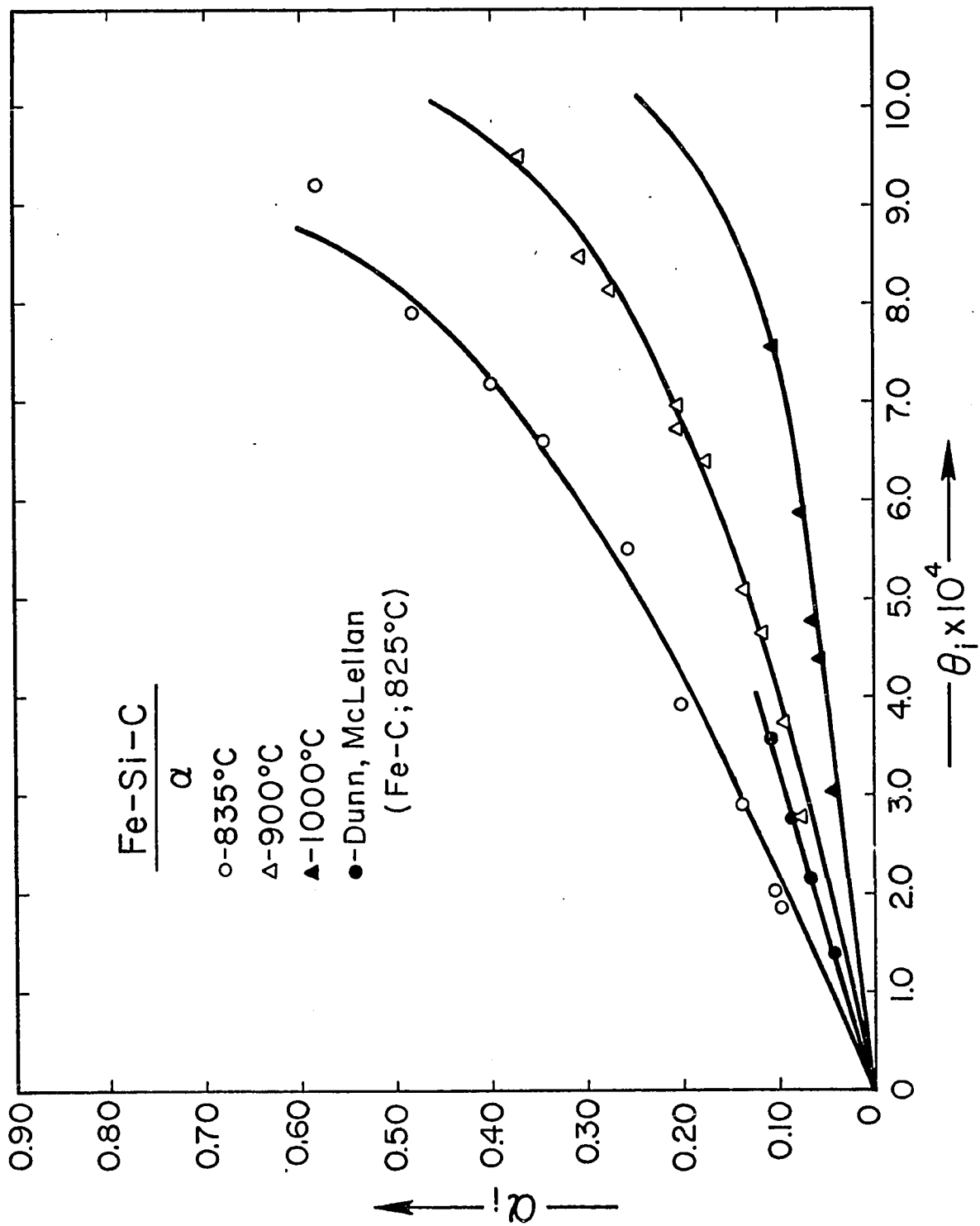


Fig. 5

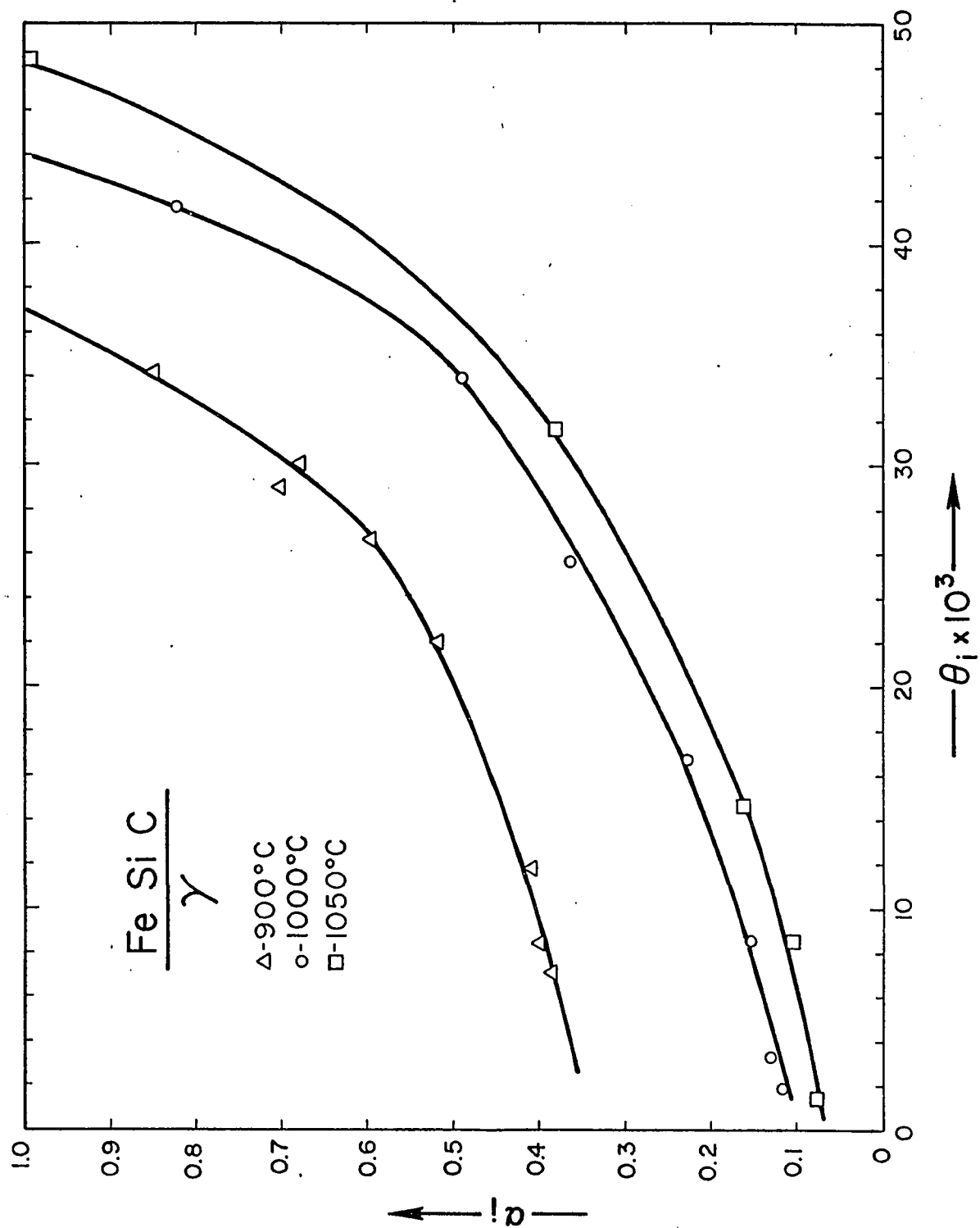


Fig. 6



Finally, figs. 7 and 8 show the variation of the partial entropy  $\bar{S}_i$  of the carbon in solution as a function of concentration. The values of  $S_i$  were calculated from the relation

$$\bar{S}_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{V,n}$$

Values of the chemical potential  $\mu_i$  were calculated<sup>19</sup> from the r-values for a given temperature and composition. The  $\mu_i$  was then expressed as a function of  $\theta_i$  for a constant T by a polynomial fitting technique. This function was transformed so as to express  $\mu_i$  as a function of T for a fixed  $\theta_i$ . The temperature derivative of this latter function given  $S_i$  directly in terms of  $\theta_i$ .

In this investigation 55 separate equilibrations were made. A preliminary statistical study showed that to obtain the variation of  $\bar{S}_i$  and  $\bar{H}_i$  with temperature and composition unequivocally would demand the measurement of at least 15 equilibrations at at least 6 different temperatures in each phase field. Part of the difficulty discussed in the conclusion in evaluating the  $\bar{S}_i$ -data in terms of physical models, may be due to the limitations in the extent of the data.

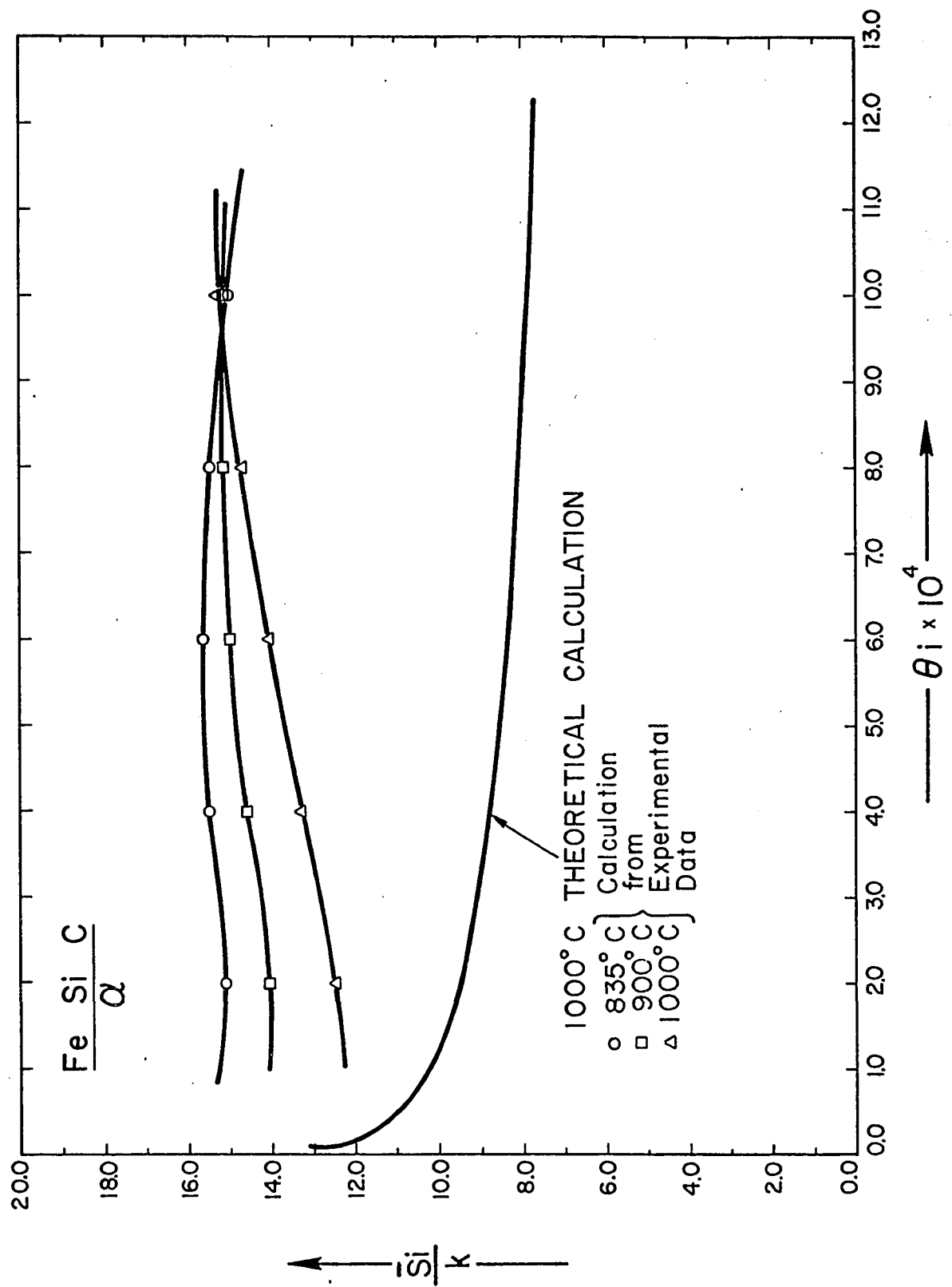


Fig. 7

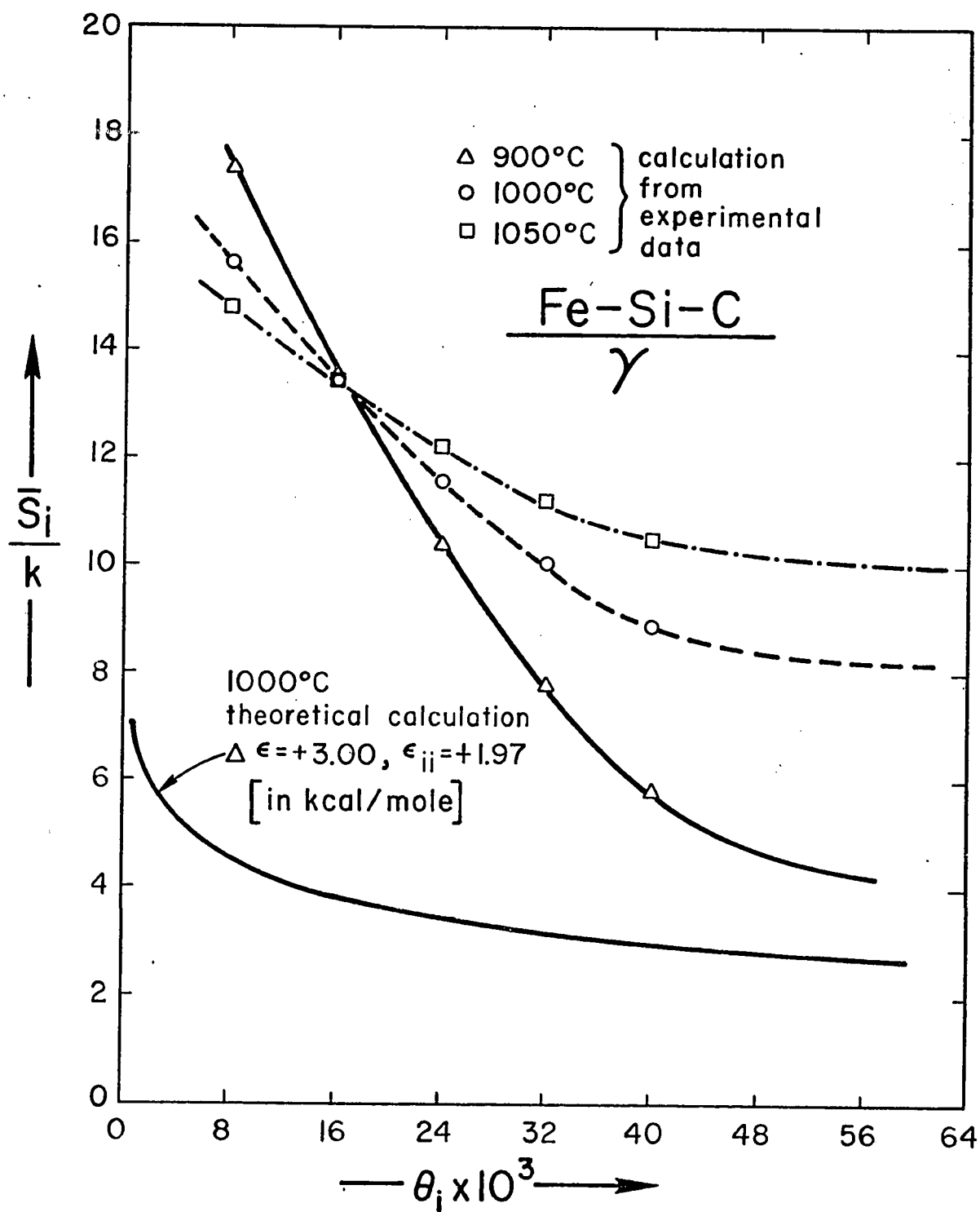


Fig. 8

#### 4. Discussion of Results

##### 4.1 Phase Equilibrium Diagram

The iron-rich portion of the Fe-Si-C ternary system has been studied by many investigators. The most extensive and widely used report is that of Hilliard and Owen.<sup>21</sup> Their results and diagrams have been reviewed and re-evaluated by Phelps in his recent survey of the Fe-Si-C system.<sup>22</sup> The 3.38 weight percent Si section of the phase diagram deduced from our results and the peritectic and eutectic data of Hilliard and Owen is given in Fig. 4. It differs in two respects from the 3.5 weight percent Si section given by Hilliard and Owen. Firstly the minimum in the C-solubility in the B.C.C. phase between the peritectic and eutectoid lines was found to lie at  $\sim 1000^{\circ}\text{C}$  in this work whereas Hilliard and Owen found a minimum at a higher temperature ( $1270^{\circ}\text{C}$ ) and a much higher C-concentration. Secondly Hilliard and Owen indicated that the  $(\alpha + \gamma)$  field was of a rather constant width over a wide temperature range whereas the present results show that the  $(\alpha + \gamma)$  field narrows markedly at a temperature of  $\sim 1050^{\circ}\text{C}$ . The present findings agree with the conclusions of Piwowarsky in his review of the Fe-Si-C system.<sup>23</sup> However, there is general agreement that the eutectoid temperature is close to the value

obtained by extrapolating the present  $(\alpha + \gamma)/\gamma$  and  $(C + \gamma)/\gamma$  boundaries (780°C).

#### 4.2 Comparison with Previous Results and Models

Both Smith<sup>15</sup> and S.S.T.<sup>12</sup> used similar methods to study the solubility of C in Fe-Si alloys. In both cases measurements were made on solutions of several Si-contents and in the case of S.S.T. at several temperatures. Unfortunately there are practically no data for the  $\alpha$ -region which could be compared with the present data since the bulk of the earlier measurements were made on solutions with a considerably higher Si-content. Nevertheless, two data points of Smith at 3.41 weight percent Si and one of S.S.T. at 3.55 weight percent Si are included in Fig. 2. They both show a slightly higher C-solubility than the present results. However, Smith's data points are apparently already in the two phase region which may explain the higher C-content.

It is readily apparent from Fig. 5 that the presence of Si in the B.C.C. solid solution enhances the C-activity above the value found in the Fe-C binary solution of the same C-content. The most recent data<sup>17</sup> for the binary system is included in Fig. 5 for

comparison. The  $\alpha_i$ -values lie about 50% higher in the ternary solution for a given  $\theta_i$ .

S.S.T. derived the partial excess entropy  $\Delta \bar{S}_i^V$  of the C-atoms from their activity data. They indicate that, for a given Si-content,  $\Delta \bar{S}_i^V$  is largely independent of C-content. However, this conclusion cannot be construed to mean that the partial non-configurational entropy is independent of the C-concentration since the C-atom distribution in the ternary solid solution probably deviates strongly from random behavior. Moreover, it should be noted that, for the interstitial component in such a ternary solution, the ideal partial configurational entropy  $\bar{S}_i^{cid}$  is not simply given by  $-k \ln C_i$  ( $C_i$  is the mole fraction) and secondly that  $\bar{S}_i^{cid}$  also contains a factor relating the number of interstitial sites to the total number of solvent and substitutional solute atoms.<sup>24</sup>

In the case of the F.C.C. solutions Fig. 3 shows that the present data are in relatively good accord with those of Smith and S.S.T. Again the large increase in C-activity of the austenite containing Si over the binary austenite is apparent. S.S.T. treated their data for the  $\gamma$ -region in a similar manner to their measurements on the B.C.C. phase, and concluded that the excess partial

entropy of the C-atoms decreased linearly with the mole fraction of carbon in solution.

As mentioned in the introduction, the application of the first order theory of ternary solid solutions<sup>1</sup> did not appropriately describe the previously available thermodynamic data for the  $\gamma$ -Fe-Si-C solution. In this model<sup>1</sup> the activity of the interstitial solute species can be written in terms of the known partial free energy of the carbon atoms in the Fe-C binary system at infinite solute dilution  $\bar{G}_i^\infty$  and two inter action energies  $\epsilon_{ii}$  and  $\Delta\epsilon = \epsilon_{iu} - \epsilon_{iv}$ . An interstitial atom has interactions  $\epsilon_{iv}$  with nearest neighbor solvent (v) atoms and  $\epsilon_{iu}$  with nearest neighbor substitutional solute (u) atoms. If two interstitial (i) atoms occupy adjacent sites on the lattice gas of interstitial sites, there is an additional pairwise interaction  $\epsilon_{ii}$ . Second nearest neighbor interactions on a given sublattice are neglected.

Now  $\bar{G}_i^\infty$  is known accurately from a large body of experimental data both for B.C.C.<sup>17, 25</sup> and F.C.C.<sup>26,27</sup> binary Fe-C solid solutions. In the case of B.C.C. Fe-Si-C solutions there is, however, no obvious way of estimating  $\epsilon_{ii}$  or even of deciding whether or not the C-C mutual interaction is attractive or repulsive. Thus a

direct comparison of the present data for the B.C.C. phase and statistical mechanical models is not possible.

In the case of the  $\gamma$ -Fe-Si-C system a direct comparison of the measured C-activity and that calculated from the first order approximation using the value of  $\epsilon_{ii}$  deduced<sup>28</sup> from experimental data<sup>26, 27</sup> ( $\epsilon_{ii} = 1.97$  k.cals/mole), did not indicate that a fit could be found for any realistic value of  $\Delta\epsilon$ . The computer fitting technique has been discussed previously.<sup>1</sup>

The variation of the partial entropy of the C-atoms with composition in the B.C.C. solution is given in Fig. 7. Quite surprisingly there is little evidence of the increase in  $\bar{S}_i$  which must occur in the limit as  $\theta_i \rightarrow 0$ . This may mean that the Si-C repulsive interaction is so strong that the subgroup of interstitial sites energetically available to the C-atoms is severely restricted. If, moreover, the C-atoms themselves had either a strong repulsive or attractive interaction, the partial entropy for a given concentration would be even smaller and would be expected to show only a small dependence on composition, even at small solute compositions. Figure 7 contains the theoretical partial configurational entropy  $S_i^C$  calculated<sup>1</sup> at 1000°C for  $\Delta\epsilon = 4$  k.cal/mole



and  $\epsilon_{ii} = -3$  k.cal/mole (attractive). It can be seen that, even at small C-concentrations,  $\bar{S}_i^C$  hardly changes with composition. However, it must be emphasized that a direct comparison of  $\bar{S}_i$  and  $\bar{S}_i^C$  is not possible since  $\bar{S}_i$  contains the non-configurational contributions to the entropy and these may vary strongly with composition. Indeed if the Si-C potential is strongly repulsive, the number of C-C nearest neighbors would be expected to vary sharply with C-content at low concentrations.

Figure 8 shows the variation of  $\bar{S}_i$  with  $\theta_i$  for the  $\gamma$ -solutions. In this case  $\bar{S}_i$  approaches the low-concentration limit at higher C-concentration than was found for the B.C.C. case. The theoretical first order mixing curve<sup>1</sup> for  $\Delta\epsilon = 3.0$  k.cals/mole and  $\epsilon_{ii} = 1.97$  k.cals/mole is included for comparison. The theoretical curve is relatively insensitive to temperature<sup>2</sup> and the temperature dependence of  $\bar{S}_i$  should be noted.

The difficulty encountered in analyzing the measured activity data in the light of statistical models is predictable. It is felt that this difficulty is largely due to the strong interaction potentials which undoubtedly characterize this system. It has been shown recently<sup>29</sup> that when the characteristic pairwise inter-

action energies are less than  $kT$  the counting errors inherent in the first-order counting scheme are small, and furthermore, that even quite strong second nearest neighbor interactions play only a minor role in determining the thermodynamic properties of the system.<sup>30</sup> However, when strong interactions are involved, large deviations from the simple statistics occur and furthermore the variation of the excess thermodynamic partial functions with composition may be large.

The results of Elliott<sup>9</sup> indicate that the atomic distribution in the binary Fe-Si solid solutions is far from random. It is easy to show that, in the first order treatment of ternary systems of the type v-u-i, small departures from random mixing of the atoms on the v-u sublattice have little effect on  $\mu_i$ . However, it is well known<sup>31</sup> that the quasi-chemical technique is not successful for many binary substitutional systems and it may be that large departures from random mixing in the v-u sublattice have considerable effect on  $\mu_i$  in the ternary v-u-i system.

TABLE II  
Compilation of Data for B.C.C.

Temperature [°C]	r[l/atm]	wt. % C	$i \times 10^4$
835	0.005207	0.004140	1.8630
	.005473	.004507	2.0282
	.007260	.006446	2.9009
	.013450	.012220	5.4997
	.018041	.014630	6.5845
	.020969	.015965	7.1854
	.025259	.017550	7.8989
900	0.002314	0.006180	2.7812
	.002848	.008304	3.7371
	.003473	.010330	4.6490
	.004032	.011520	5.1846
	.005235	.014230	6.4044
	.006036	.014920	6.7150
	.006036	.015454	6.9554
	.008064	.018050	8.1240
	.008990	.018824	8.4724
	.010865	.021090	9.4925
1000	0.000623	0.006714	3.0215
	.000784	.009429	4.2434
	.000890	.010596	4.7687
	.001069	.013043	5.8701
	.001459	.016300	7.3362

TABLE III

Compilation of Data for F.C.C.

Temperature [ $^{\circ}\text{C}$ ]	$r$ [1/atm]	wt. % C	$i \times 10^2$
900	0.011388	0.157290	0.708920
	.011788	.185593	0.836721
	.012602	.241293	1.096381
	.015147	.414491	1.884050
	.017460	.588918	2.665831
	.020000	.665800	3.016182
	.020560	.638450	2.891486
	.025020	.756370	3.429605
	.030113	.740780	3.318473
	.036819	.751460	3.407174
	.045518	.762626	3.458190
	.080180	.773730	3.508935
1000	0.001604	0.041440	0.186557
	.001796	.072070	0.324549
	.002125	.189630	0.854956
	.003009	.359420	1.623224
	.003134	.370450	1.673223
	.005025	.544720	2.573878
	.008129	.750695	3.403731
	.011335	.917770	4.068220
	.020280	.967002	4.393990

Table III (Con'd.)

Temperature [ $^{\circ}\text{C}$ ]	$r[\text{l/atm}]$	wt. % C	$i \times 10^2$
1050	0.000749	0.031342	0.141083
	.001033	.187703	0.846252
	.001604	.324647	1.465670
	.003767	.698652	3.166054
	.009881	1.059559	4.819076
	.015225	1.124167	5.116267
	.024898	1.142320	5.199838
835	0.042029	0.351470	1.590217
	.045580	.473622	2.130174
	.050874	.404390	1.827144
	.063186	.529198	2.394060
	.152998	.629740	2.851789

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III.           A ZEROth ORDER TREATMENT OF TERNARY  
              INTERSTITIAL SOLID SOLUTIONS

INTRODUCTION

In recent years many new experimental measurements of the thermodynamic behavior of the interstitial component in ternary solid solutions, where the third component is a substitutional solute, have extended the now perhaps classical measurements made for example by Smith<sup>1, 2</sup> and others. At the same time much effort has gone into developing a suitable theoretical model which could explain, as well as predict, the behavior of that interstitial solute. Two different approaches have been employed for that purpose: the classical thermodynamic treatment and statistical interactions models. To the former group belong Darken's<sup>3</sup> application of the Gibbs-Duhem equation to multicomponent systems and subsequent modification by Alcock and Richardson<sup>4</sup>, Belton and Tankins<sup>5</sup> and others. Most of the interactions models are based on the concept of geometrical blocking and have been recently reviewed by Coplin, McGinness and McLellan<sup>6</sup>.

In this chapter, the zeroth-order mixing treatment is developed. The first-order treatment has been simultaneously worked out by Alex and McLellan<sup>7, 8</sup>.

### The solution model

The calculation is based on the zeroth order formalism given by Guggenheim<sup>9</sup> in which the total energy of the solution is assumed to be a function of pairwise interaction energies between nearest neighbors atoms only. Furthermore, assuming the configurational entropy to be random, then, as it has been pointed out by Oates and McLellan<sup>10</sup>, the thermodynamic properties of the interstitial atoms in a ternary solid solution containing both interstitial (i) and substitutional (u) solute atoms are independent of the thermodynamic properties of the binary solvent lattice.

The solid solution is represented in Fig. 1 with open

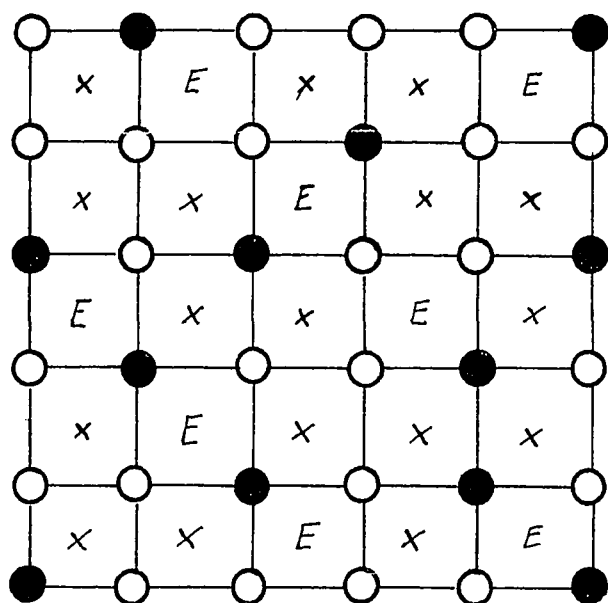


Fig. 1

circles representing the solvent atoms; full circles, the substitutional solute atoms; and crosses and E's being interstitial atoms and empty sites, respectively.

Using notation from Table I, we can

TABLE I

Symbol	Definition
$N$	no. of lattice sites
$N_v$	no. of solvent atoms
$N_u$	no. of solute atoms
$N_i$	no. of interstitial sites
$\beta$	no. of interstitial sites per lattice site
$Z_1$	coord. no. for interstitial sites
$Z_2$	no. of nearest neighbor lattice sites to an interstitial site
$\lambda$	distribution factor
$\theta_i$	$= \frac{N_i}{N_u + N_v} = \frac{N_i}{N}$
$\theta_u$	$= \frac{N_u}{N_u + N_v} = \frac{N_u}{N}$
$\theta_v$	$= \frac{N_v}{N_u + N_v} = \frac{N_v}{N}$

determine the number of nearest neighbor pairs involving interstitial atoms with substitutional solute and solvent atoms. These numbers are calculated by assuming random mixing and are given in Table II, together with assigned energy per pair and total energy per given kind of pairs.

Table II does not include interactions involving only  $\underline{u}$  and  $\underline{v}$  atoms as this is superfluous in specifying the chemical potential of the  $i$ -atoms<sup>11</sup>.  $\epsilon_{ii}$  represents an interaction when two interstitial atoms occupy adjacent sites on the thought lattice of interstitial sites and is independent of the nearest neighboring  $\underline{v}$  and  $\underline{u}$  atoms of the interstitial pair.

Now, we can write the configurational energy  $E_c$  arising from the pairwise interactions as a sum of total energies for the given kind of paris from Table II:

$$E_c = \epsilon_{ie} Z_1 \lambda + \frac{1}{2} \epsilon_{ii} Z_1 (N_i - \lambda) + \epsilon_{iv} Z_2 \frac{N_i N_v}{N} + \epsilon_{iu} Z_2 \frac{N_i N_u}{N} \quad (3.1)$$

The configurational partition function for the interstitial lattice gas sub-assembly is then:

$$\Omega_i^c = \sum_{\lambda} g(N_v N_u N_i \lambda) \exp \left[ -E_c / kT \right] \quad (3.2)$$

where  $g(N_v N_u N_i \lambda)$  is the number of distinguishable

TABLE II

Kind of pair	No. of such pairs	Energy per pair	Total Energy
$i-e$ $e-i$	$Z_1 \lambda$	$\epsilon_{ie}$	$\epsilon_{ie} Z_1 \lambda$
$i-i$	$\frac{1}{2} Z_1 \lambda (N_i - \lambda)$	$\epsilon_{ii}$	$\epsilon_{ii} \frac{1}{2} Z_1 \lambda (N_i - \lambda)$
$e-e$	$\frac{1}{2} Z_1 (N\beta - N_i - \lambda)$	0	0
$i-v$	$Z_2 \frac{N_i N_v}{N}$	$\epsilon_{iv}$	$\epsilon_{iv} Z_2 \frac{N_i N_v}{N}$
$i-u$	$Z_2 \frac{N_i N_u}{N}$	$\epsilon_{iu}$	$\epsilon_{iu} Z_2 \frac{N_i N_u}{N}$

configuration belonging to the energy level  $E_c$ .

The essence of the zeroth order treatment is to consider that the solute atoms are randomly distributed on their interstitial sites with the value of the distribution factor<sup>9</sup>

$$\lambda = \frac{N_i (N\beta - N_i)}{N\beta} \quad (3.3)$$

so that the sum over all the states can be replaced by a single degenerate state of energy  $E_c$ . Thus

$$\Omega_i^e = g(N_v N_u N_i \lambda) \exp[-E_c/kT] \quad (3.4)$$

and the configurational free energy is

$$F_c = -kT \ln \Omega_i^e \quad (3.5)$$

Since  $g(N_v N_u N_i \lambda) = \frac{(N\beta)!}{(N\beta - N_i)! (N_i)!}$  and using  $\Delta \varepsilon_i = 2\varepsilon_{ie} - \varepsilon_{ii}$  we obtain

$$F_c = -kT \ln \frac{(N\beta)!}{(N\beta - N_i)! (N_i)!} + N_i \left[ \frac{Z_1}{2} (2\varepsilon_{ie} - \frac{\theta}{\beta} \Delta \varepsilon_i) + Z_2 (\theta_v \varepsilon_{iv} + \theta_u \varepsilon_{iu}) \right] \quad (3.6)$$

The configurational chemical potential is then

$$\mu_i^c = \left( \frac{\partial F_c}{\partial N_i} \right)_T \quad (3.7)$$

Using Stirling's theorem, we obtain

$$\begin{aligned} \mu_i^c = kT \ln \frac{\theta_i/\beta}{1 - \theta_i/\beta} + Z_1 \epsilon_{ie} - Z_1 \frac{\theta_i}{\beta} \Delta \epsilon_i + \\ + \theta_v Z_2 \epsilon_{iv} + \theta_u Z_2 \epsilon_{iu} \end{aligned} \quad (3.8)$$

Now, let us consider the limiting case when  $N_u \rightarrow 0$ . Then we have for the v-i binary system

$$\mu_i^{cb} = kT \ln \frac{\theta_i/\beta}{1 - \theta_i/\beta} + Z_1 \epsilon_{ie} - Z_1 \frac{\theta_i}{\beta} \Delta \epsilon + \theta_v Z_2 \epsilon_{iv} \quad (3.9)$$

and considering the infinitely dilute solution when  $\theta_i \rightarrow 0$  and  $\theta_v \rightarrow 1$  we get

$$\mu_i^{cb\infty} = kT \ln \frac{\theta_i/\beta}{1 - \theta_i/\beta} + Z_1 \epsilon_{ie} + Z_2 \epsilon_{iv} \quad (3.10)$$

and we can write the partial enthalpy of  $\underline{i}$  in the infinitely dilute limit of the v-i binary solution in the form

$$\bar{H}_i^{v-i} = Z_1 \epsilon_{ic} + Z_2 \epsilon_{iv} \quad (3.11)$$

and similarly we can get

$$\bar{H}_i^{u-i} = Z_1 \epsilon_{ic} + Z_2 \epsilon_{iu} \quad (3.12)$$

Multiplying (3.11) by  $\theta_v$  and (3.12) by  $\theta_u$  and plugging into eqn. (3.8) for  $\theta_v Z_2 \epsilon_{iv}$  and  $\theta_u Z_2 \epsilon_{iu}$ , respectively and assuming that the partial non-configurational entropy of the i-atoms is a constant  $\bar{S}_i$ , we get for the chemical potential of the interstitial atoms the final equation in the following form:

$$\mu_i = kT \ln \frac{\theta_i/\beta}{1-\theta_i/\beta} - Z_1 \theta_i \Delta \epsilon + \bar{H}_i^{v-i} \theta_v + \bar{H}_i^{u-i} \theta_u - T \bar{S}_i \quad (3.13)$$



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#### IV. THERMODYNAMICS OF Ni-Cu-C SYSTEM: AN APPLICATION OF THE ZERO-ORDER FORMALISM

##### INTRODUCTION

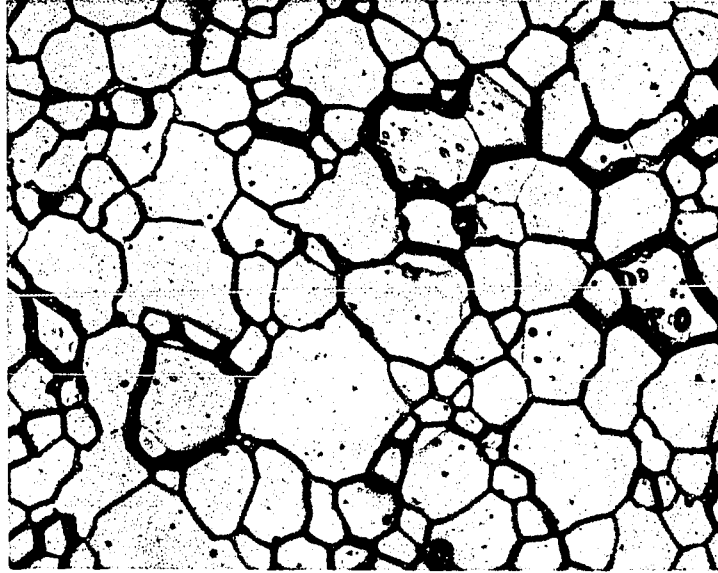
Comprehensive data on the solubility of interstitially dissolved carbon in either pure Ni or Cu are available now from studies by McLellan<sup>1</sup>, Dunn, McLellan and Oates<sup>2</sup>, Schenk and coworkers<sup>3</sup>, Smith<sup>4</sup>, Rao and Nicholson<sup>5</sup>, Alcock and Stavropoulos<sup>6</sup>, etc. However, very few data are known about carbon dissolved in a binary Ni-Cu system, the only reliable work being that of Nicholson<sup>7</sup> on the solubility of C at 1000°C.

The measurements on the binary Ni-C and Cu-C systems clearly show that both systems are Henrian interstitial solid solutions.<sup>8</sup> Furthermore, the partial molar enthalpy of a solute atom in the two solid solutions are very close; that for Ni-C is -160.5 k.cal/mole and that for Cu-C is -159.3 k.cal/mole. These values indicate that the solvent-solute interactions in both systems are very similar and, therefore, we may expect that the thermodynamic properties of the Ni-Cu-C ternary system might be explainable in terms of relatively simple statistical interaction model.

This work has been undertaken, then, for two simple reasons: first, to add more data on the Ni-Cu-C system, and second, to verify our assumption of a simple statistical thermodynamic model.

### 1. Experimental procedure

In our experiments the saturation solubility of pure graphite as a function of temperature in a series of Ni-Cu alloys containing 5, 10, 20, 30, and 40 At. % Cu, respectively, was measured using the vapor transport technique<sup>1, 2, 9</sup>. Small samples of the Ni-Cu alloys (about 0.5 g) in the form of thin foils about 0.025'' (0.6mm) thick were sealed in silica ampoules together with an excess of graphite powder (Grade #38, Fisher Sci. Co.) and a trace of air ( $\sim 50\mu$  of Hg) and annealed. During the annealing equilibrium is established between the two solid phases and a transport gas formed from the residual air. Thus carbon dissolves in the metal until the saturation limit with respect to pure graphite is reached. Equilibrium was obtained by both, carburization and decarburization and equilibrations for different times at the same temperature were made to ensure that the equilibrium had been achieved. The average annealing time was from 50 to 70 hours.



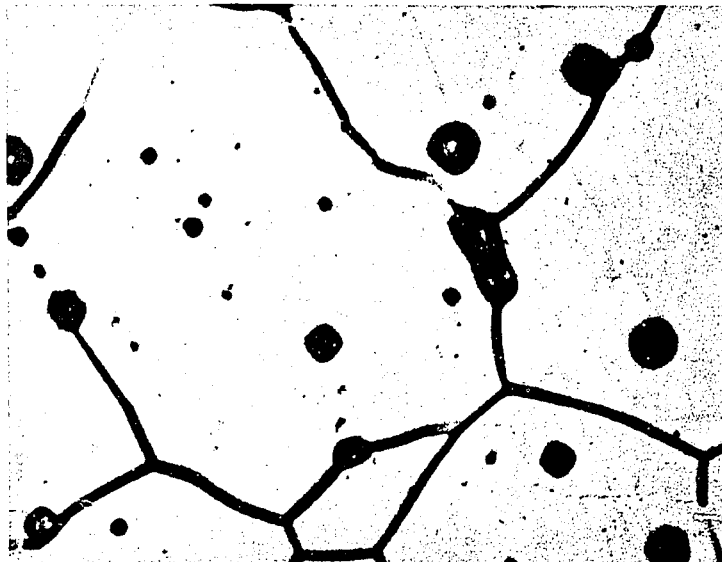
Ni - 10 at% Cu

860° C

200 x

slow cooling

Fig. 1.



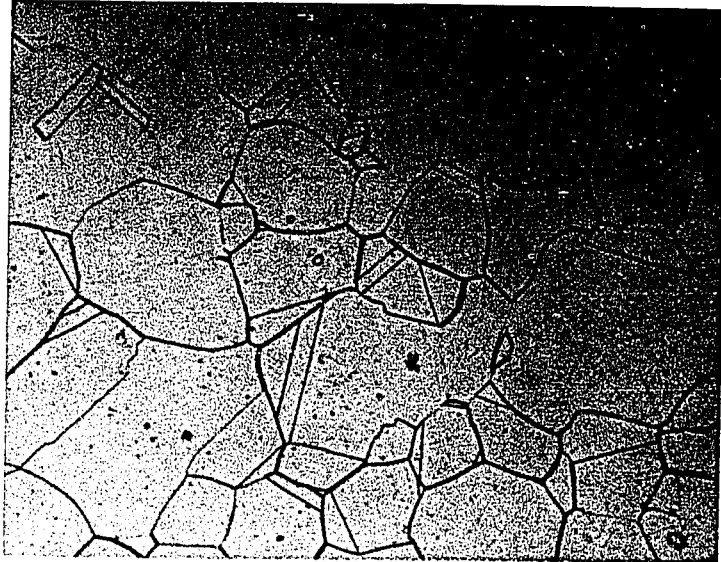
Ni - 30 at% Cu

990° C

500 x

slow cooling

Fig. 2.



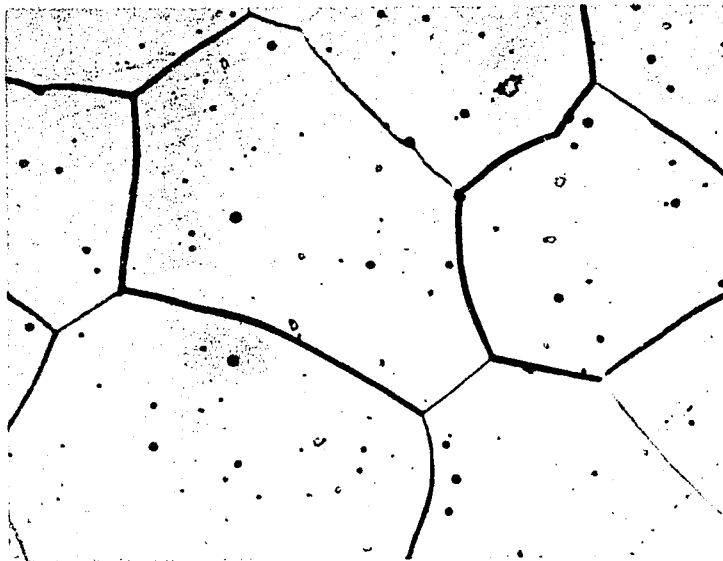
Ni - 10 at% Cu

860° C

200 x

quenched

Fig. 3.



Ni - 30 at% Cu

990° C

500 x

quenched

Fig. 4.

The equilibrated samples were then cleaned and some of them subjected to a metallographic examination. After weighing the samples on a Metler microbalance, the carbon content was determined by a Leco low-carbon combustion analyser.

The metallographic examination of the Ni-Cu-C samples revealed the presence of a precipitate mostly at the grain boundaries but in some instances also inside the grains: Figs. 1 and 2. Microhardness measurements showed the precipitate two to four times softer than the Ni-Cu matrix. For example, in a sample of the composition of Ni-30 At.%Cu after 50 hours annealing at 990°C (Fig. 2), the black spots showed an average hardness in Knoop units equal to 24 while that of the matrix equal to 94. So it was concluded that during cooling carbon from the solid solution precipitated in the form of graphite. This graphite precipitate (or segregation) has been previously reported by Nicholson<sup>7</sup> and Thompson<sup>10</sup>.

In the present experiments most of the equilibrated foils were cooled from the furnace temperature simply by slowly inserting the silica capsule in RT water. This slow cooling resulted in the above-mentioned graphite precipitation. However, some samples were quenched by

breaking the ampoule in agitated water. This fast quenching suppressed the graphite precipitation as shown on Figs. 3 and 4, which show the microstructures of alloys of the same compositions as those in Figs 1 and 2, equilibrated for the same time at the same temperature. The small spots in the grains which look like inclusions are mostly due to atmospheric corrosion after etching by a solution of nitric and acetic acid in water; they were seen to form during the course of the metallographic examination.

## 2. Results and discussion

The measured solubilities are given in Table I,(p.83) and are shown in Fig. 5, in the form of plots of  $\ln \frac{\theta_i}{1-\theta_i}$  vs  $1/T$ , where  $\theta_i$  is the atom ratio of carbon. For comparison, the data of Dunn, McLellan and Oates<sup>2</sup> for the Ni-C binary system are also included. A constant  $A_i$  has been added to the values of  $\ln \frac{\theta_i}{1-\theta_i}$  in Fig. 5 so as to displace the lines relative to each other.

Fig. 6 gives the carbon solubility as a function of copper content for three selected temperatures. The results of Nicholson<sup>7</sup> who carburized Ni-Cu foils at 1000°C only in crucibles containing powdered graphite in the

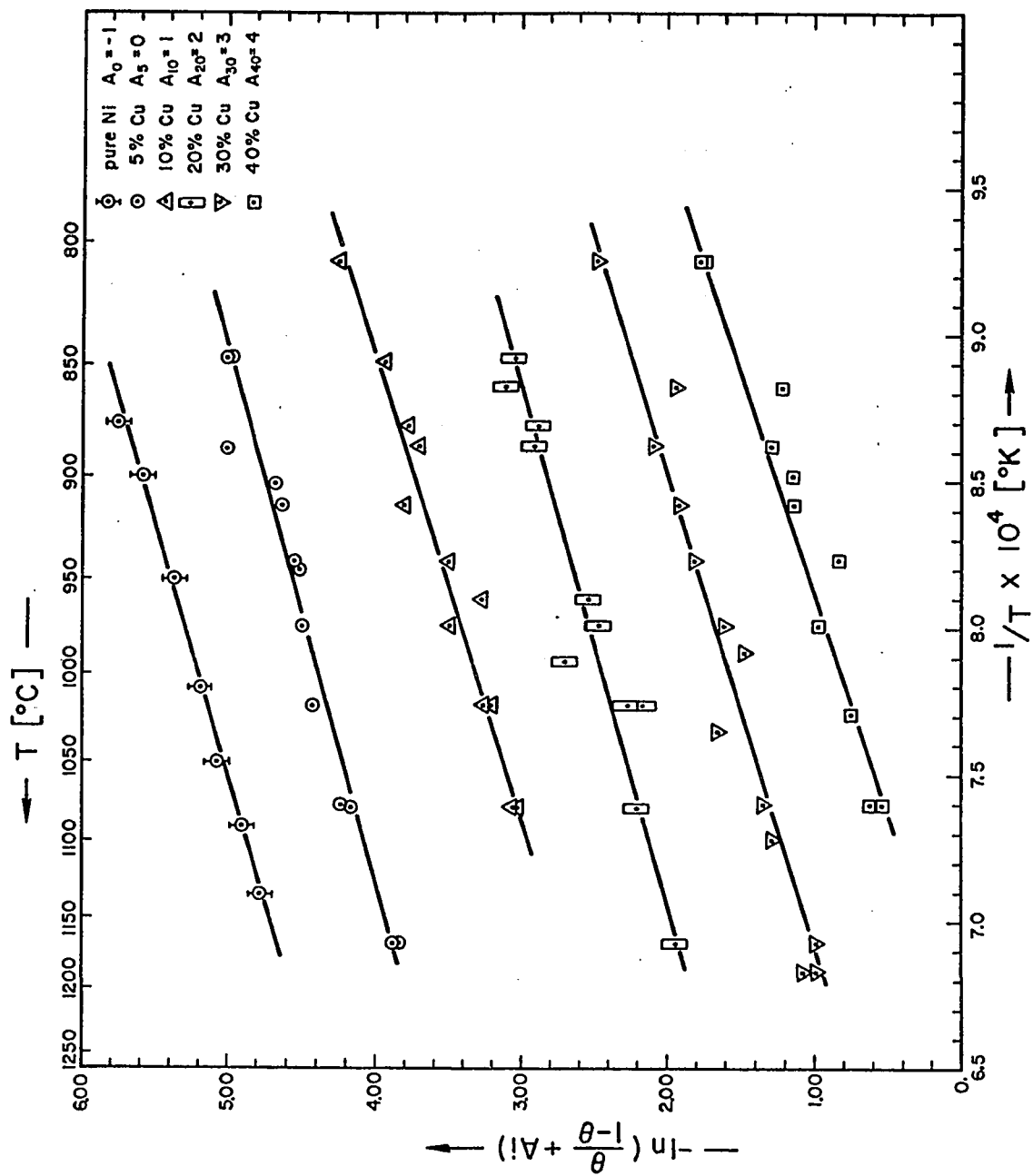


Fig. 5



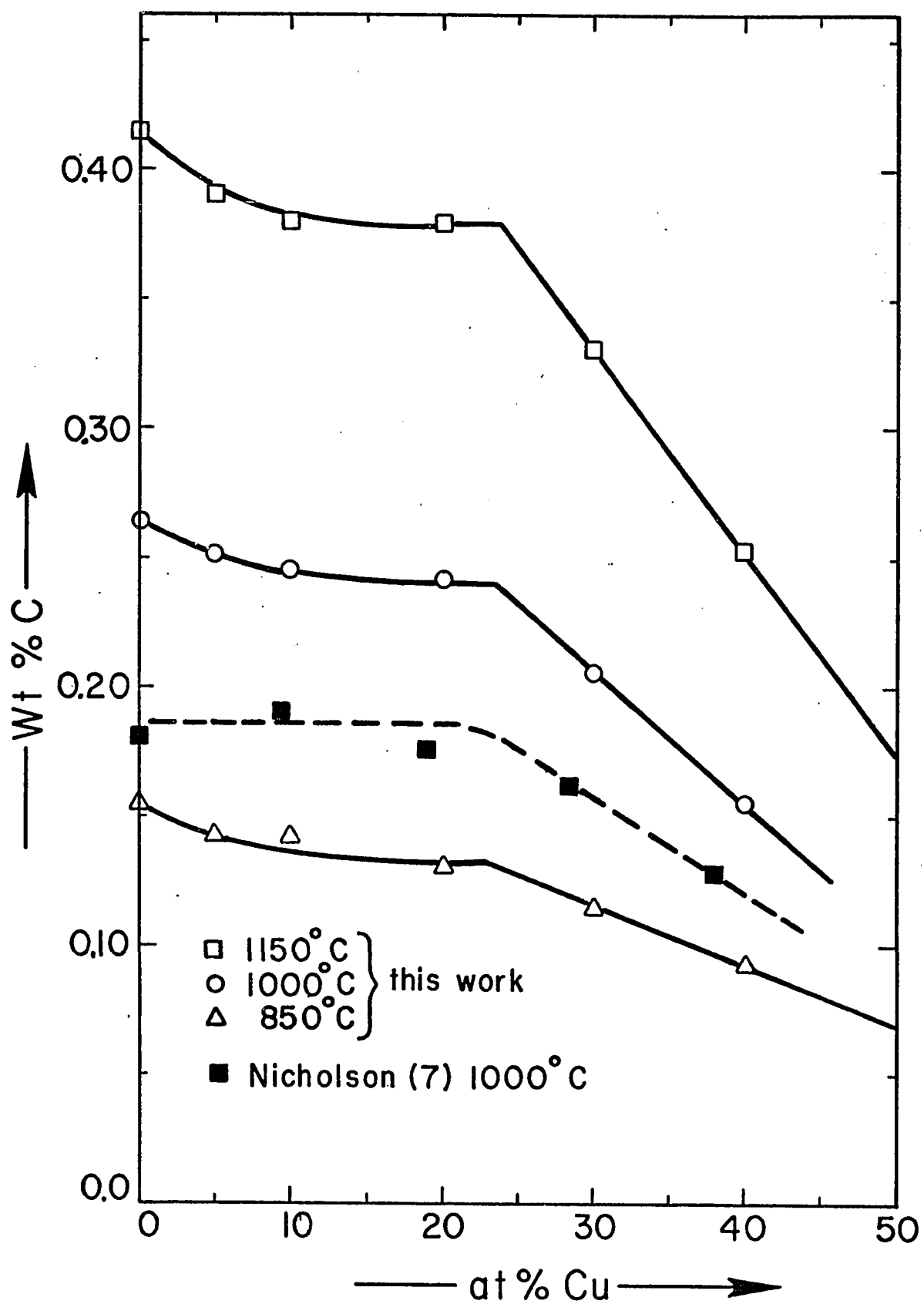


Fig. 6

carbon monoxide atmosphere are also included for comparison. As shown in the diagram, although Nicholson's data are somewhat lower, reflecting his relatively short equilibration times (in most experiments, only 18 hours, as compared to the minimum 50 hours in the present study), the carbon solubility is not a strong function of Cu content (in Nicholson's data, there is no dependency at all) over a wide range of Cu concentrations up to about 25 At.% of Cu and then is a decrease in carbon content.

Before proceeding in the discussion one very important aspect remains to be mentioned, that is the ordering. As is very well known, ordering is common in both Cu-based alloys (CuZn, CuAu, CuPd, Cu<sub>3</sub>Al, . . .) and Ni-based alloys (NiPt, Ni<sub>3</sub>Fe, CoNi, . . .). However, in general, the critical temperature  $T_c$  (i.e., the temperature below which ordering takes a place) of all these alloys very seldom exceeds 600°C with an exception of few alloys, where in the range of another 100°C can exist some kind of the short range order. In spite of these facts, no evidence of ordering in the Ni-Cu system has been found yet, although subjected to many investigations. Some investigators, including Dey<sup>11, 12</sup>, Köster and Schüle<sup>13</sup>, Mozer, Keating and Moss<sup>14</sup>, have detected

clustering in this system with  $T_c$  between 500 - 650°C, but not at higher temperatures. In the present work where the lowest equilibrium temperature was 807°C, we will assume that the substitutional Ni-Cu solvent lattice is random even when carbon atoms are dissolved in it.

The chemical potential  $\mu_i$  of the interstitial atoms in the simple zeroth-order mixing statistic is given by equation (3.13). Now, in the equilibrium with graphite:  $\mu_i = \mu_c^{graph}$ , where  $\mu_c^{graph}$  is equal to the free energy of a carbon atom in pure solid graphite

$$\mu_c^{graph} = H_c^\circ - TS_c^\circ \quad (4.1)$$

Equating equations (3.13) and (4.1) gives

$$\ln \frac{\theta_i/\beta}{1 - \theta_i/\beta} = - \frac{(\Delta \bar{H}_i^{v-i} \theta_v + \Delta \bar{H}_i^{u-i} \theta_u)}{kT} + \frac{Z_i \Delta \bar{E}_i}{kT\beta} \theta_i - \frac{\Delta \bar{S}_i}{k} \quad (4.2)$$

In this equation  $\Delta \bar{H}_i^{v-i}$  and  $\Delta \bar{H}_i^{u-i}$  are the relative partial molar enthalpies of  $i$  in the v-i (Ni-C) and u-i (Cu-C) binaries in the infinitely dilute solution limit and

$$\Delta \bar{S}_i = S_{graph}^\circ - \bar{S}_i .$$

TABLE I

At. % Cu	T°C	Wt. % C	$\theta_i$
5	848	0.1345	0.006653
	848	0.1384	0.006847
	887	0.1320	0.006528
	905	0.1849	0.009173
	914	0.1970	0.009781
	914	0.1987	0.009866
	942	0.2110	0.010484
	946	0.2173	0.010801
	975	0.2230	0.011089
	1018	0.2370	0.011795
	1078	0.2860	0.014275
	1079	0.3020	0.015088
	1169	0.4150	0.020876
	1169	0.4020	0.020206
10	807	0.1050	0.005206
	848	0.1420	0.007056
	878	0.1660	0.008260
	887	0.1800	0.003965
	914	0.1610	0.008009

TABLE I (Con'd.)

At. % Cu	T°C	Wt. % C	$\theta_i$
10	942	0.2200	0.010983
	961	0.2770	0.013876
	975	0.2210	0.011034
	1018	0.2790	0.013978
	1018	0.2910	0.014590
	1079	0.3380	0.016994
	1079	0.3430	0.017251
20	848	0.1260	0.006307
	860	0.2100	0.006307
	878	0.1490	0.007462
	887	0.1450	0.007266
	961	0.2090	0.010513
	975	0.2240	0.011278
	993	0.1790	0.008988
	1018	0.2720	0.013735
	1018	0.3020	0.015277
	1079	0.2910	0.014711
	1169	0.3740	0.019003

TABLE I (Con'd.)

At. % Cu	T°C	Wt. % C	$\theta_i$
30	807	0.0815	0.004102
	860	0.1410	0.007121
	887	0.1210	0.006104
	914	0.1430	0.007223
	942	0.1600	0.008090
	975	0.1940	0.009830
	990	0.2230	0.011319
	1035	0.1860	0.009420
	1078	0.1540	0.012917
	1100	0.2680	0.013641
	1169	0.3590	0.018375
	1190	0.3550	0.018166
	1190	0.3270	0.016704
40	807	0.0612	0.003101
	807	0.0615	0.003116
	860	0.1060	0.005386
	887	0.0987	0.005013
	900	0.1140	0.005195
	914	0.1150	0.005846
	942	0.1550	0.007899

TABLE I (Con'd.)

At. % Cu	T°C	Wt. % C	$\theta_i$
40	975	0.1350	0.006871
	1023	0.1670	0.008517
	1078	0.1900	0.009703
	1078	0.2050	0.010479
	1169	0.1780	0.009084
	1190	0.2160	0.011049

Assuming that  $\Delta \epsilon_i$ , the binding energy of an i-i pair is a relatively small means that the second term in equation (4.2) can be neglected since  $\theta_i$  is small (of the order of  $10^{-2}$ ) and T is of the order of  $10^3$ . Thus, with these approximations the slope of a plot of  $\ln \frac{\theta_i/\beta}{1 - \theta_i/\beta}$  vs.  $1/T$  is given by

$$\phi = - \frac{\Delta \bar{H}_i^{v-i} \theta_v + \Delta \bar{H}_i^{u-i} \theta_u}{k} \quad (4.3)$$

The experimental data were subjected to a least squares regression, and the best values of  $\phi$  and  $\Delta \bar{S}_i/k$

(the intercept of the plots) are given in Table II:

At%Cu	$-\phi \times 10^3(\text{exp})$	$-\phi \times 10^3(\text{calc})$	$\frac{\Delta \bar{S}_i}{k}$	$\frac{\bar{S}_i}{k}$
5	5.437-0.25	5.65	-0.128-0.20	3.54
10	6.232-0.33	5.68	-0.589-0.27	2.82
20	6.000-0.41	5.73	-0.277-0.33	3.13
30	5.650-0.27	5.79	-0.146-0.21	3.56
40	6.034-0.37	5.85	-0.069-0.31	3.48

This table also includes the values of  $\phi$  calculated from equation (4.3) using the values of  $\Delta \bar{H}_i^{v-i} = 11.24 \text{ kcal/mole}$  and  $\Delta \bar{H}_i^{u-i} = 12.40 \text{ kcal/mole}$  found for the v-i and u-i binary systems<sup>1, 2</sup>. The values of  $\bar{S}_i/k$ , also given, were calculated from the  $\Delta \bar{S}_i/k$  values and the standard entropy of graphite.<sup>15</sup>

It can be seen from Table II that the  $\phi$ -values taken from the slopes of the plots are essentially the same as those calculated from the simple model. Furthermore, the partial excess entropies are close to the value for a C-atom in pure Ni ( $\bar{S}_i/k = 3.95$ ). This fact is probably due to the similarity of the binding forces in the



two Ni-C and Cu-C binary solutions.

### 3. Conclusions

1. The solubility of carbon in a series of Ni-Cu-C solid solutions is not a strong function of increasing Cu content up to about 25 At% of Cu. Then the carbon solubility rapidly decreases.

2. The thermodynamic properties of carbon in Ni-Cu solid solutions are also relatively unaffected by the presence of Cu over a wide range of compositions and can be described by a simple zeroth-order solution model. This might be explained by the similarity of the binding forces in the two Ni-C and Cu-C solid solutions.

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## APPENDIX I

### The "intercept" effect

#### Introduction

In an early work on the solubility of C in Fe, Smith<sup>1</sup> came across an interesting discrepancy. For his solubility measurements, Smith carburized pure iron foils using a mixture of H<sub>2</sub> and CH<sub>4</sub> gases of a known composition expressed by the gas ratio  $r = \frac{P_{CH_4}}{P_{H_2}}$ . CH<sub>4</sub> in this mixture represents the carburizing element, H<sub>2</sub> on the other hand as is very well known, is a strongly decarburizing gas. Thus it would be only natural to assume, that after carburizing a sample at some higher r and subsequently annealing in an atmosphere with r = 0, e.g. in pure hydrogen, there would not be any carbon remaining in the iron foil after a certain time. However, the result did not show this--for all his three equilibrium temperatures Smith found a small residual amount of carbon ranging from 0.0008 to 0.0040 wt% of C. Almost 25 years later before starting a similar set of measurements an assumption has been made by Dunn<sup>2</sup> that the discrepancy (or so-called "intercept effect") of Smith's data was due to the relatively low purity of the material (99.836 and 99.957 wt% Fe)

and poor experimental procedure. Dunn, using a high purity Marz Grade I Iron with the total impurity content less than 40 ppm (e.g. 99.996 wt% Fe), the gases of the highest purity available and a low carbon analyser Leco capable of analyzing with ppm accuracy, hoped to avoid the intercept effect. However, after extrapolation of his experimental data to  $r = 0$ , the intercept effect values of 0.0004 to 0.0022 wt% C were found.

The purpose of this work is to relate the intercept effect to the structure of the material as it was felt, that this is the only possible source of it. The work was started originally as a side-project, but during its course a necessity for additional measurements appeared, the work became very time-consuming and was eventually aborted. In this Appendix, a short outline of experiments performed is given together with their results and proposals for further study are made.

### Experimental Results

Note: The material used in this study was the same as Dunn used in his work, that is, the Marz Grade I Iron from the Materials Research Corp. in the form of a thin foil 0.001" thick and 1" wide.

The first set of measurements was aimed at determining the role of the grain size on the amount of the residual

carbon. The assumption was: the smaller grains, the larger grain boundary area and the more carbon can be retained in it. Samples of iron foil about 6" long were annealed for 10 hours in vacuum ( $\sim 10^{-6}$  mm Hg) at various temperatures and afterwards the average grain size<sup>3</sup> of each one was determined - Fig. 1. Then each sample was carburized by mixture of  $\text{CH}_4\text{-H}_2$  at the temperature of the previous vacuum annealing. The composition of the carburizing gas mixture was selected so that the resulting carbon content would be about 50-80 ppm. After maintaining the equilibrium for 16 hours methane as a carburizing element was cut off and the sample was decarburized in the flow of pure hydrogen. Decarburization lasted 24 hours which should be a sufficient time for removal of practically all carbon from such a thin foil<sup>4</sup>. After the average grain size was again measured, the carbon content of each sample was determined using the low carbon analyser Leco. Results of both those measurements are also given in Fig. 1. As is clearly seen, there has been a finite carbon content almost constant over the temperature range with the mean value equal to 28.1 ppm, which is about 3.5 times higher than the nominal amount of carbon in the Marz Grade I Iron (8 ppm),

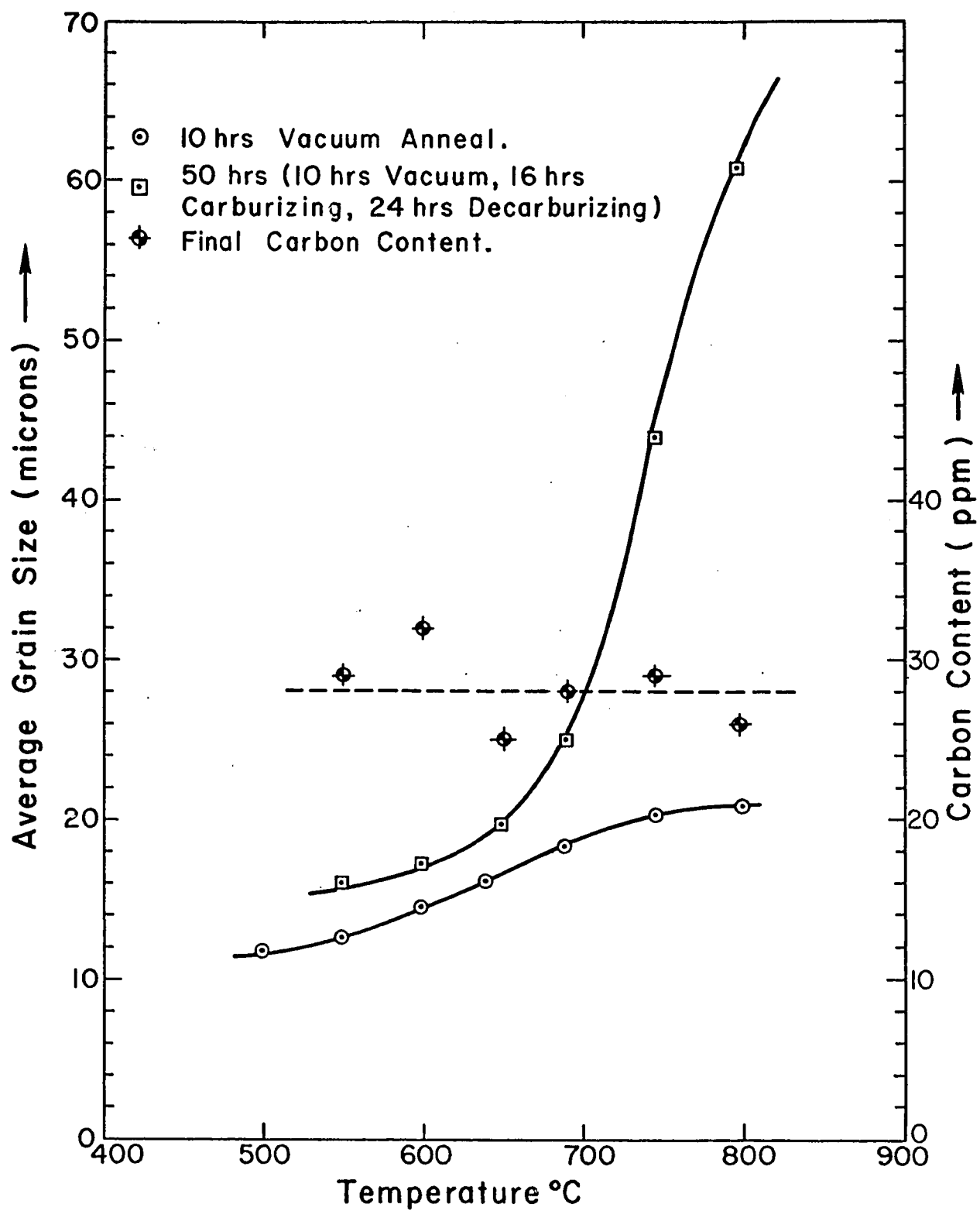


Fig. 1

while there has been a large difference in the average grain size of individual samples. This seems to indicate that there is no relation between the grain size and the amount of the residual carbon.

The only other low energy sites which could play the role of carbon traps, then, are the subgrain boundaries. The subgrain structure is considered to be fairly independent of the annealing temperatures and depends only on the material composition and on previous treatments<sup>5</sup>--that is mainly on the amount of the cold work. Now, let us consider the results of Smith<sup>1</sup>, Dunn<sup>2</sup> and this work in the light of the last statement. Smith made his measurements at two different temperatures--at 750°C he used electrolytic iron of a lower purity while at 800°C he used carbonyl iron of a higher purity as well as the same electrolytic iron used for 750°C. Looking at his intercept effect values, we see that in spite of a difference in temperatures, the results for the electrolytic iron are the same: 40 ppm, while that for the carbonyl iron is only 8 ppm. On the other hand, Dunn was using only one material for all his measurements. However, we can divide his results into two groups of 3 values each according to



the thickness of foils used, and then we will see that in both groups two out of three values are very close to each other. Thus, we could say that the difference in Smith's values of the intercept effect was due to different compositions and hence, to a different substructure and in Dunn's measurements, to different amounts of the cold work and hence, to a different substructure, and accordingly, in our measurements using the same material in the same form, we have gotten a constant value of the intercept effect in agreement with the assumption of the same substructure. Therefore, the possibility of the substructure as a decisive factor determining the amount of the residual carbon appears, but for further clarification another set of experiments needs to be made in which thorough electron microscopy measurements of the substructure would be performed.

Since the total annealing time in our first set of experiments was 50 hours (10 hours vacuum, 16 hours carburization, 24 hours decarburization) a similar set of annealings for 50 hours now in vacuum only was performed and the average grain size measured in order to determine the effect of the annealing atmosphere. The comparison of these two sets is given in Fig. 2, and we can see

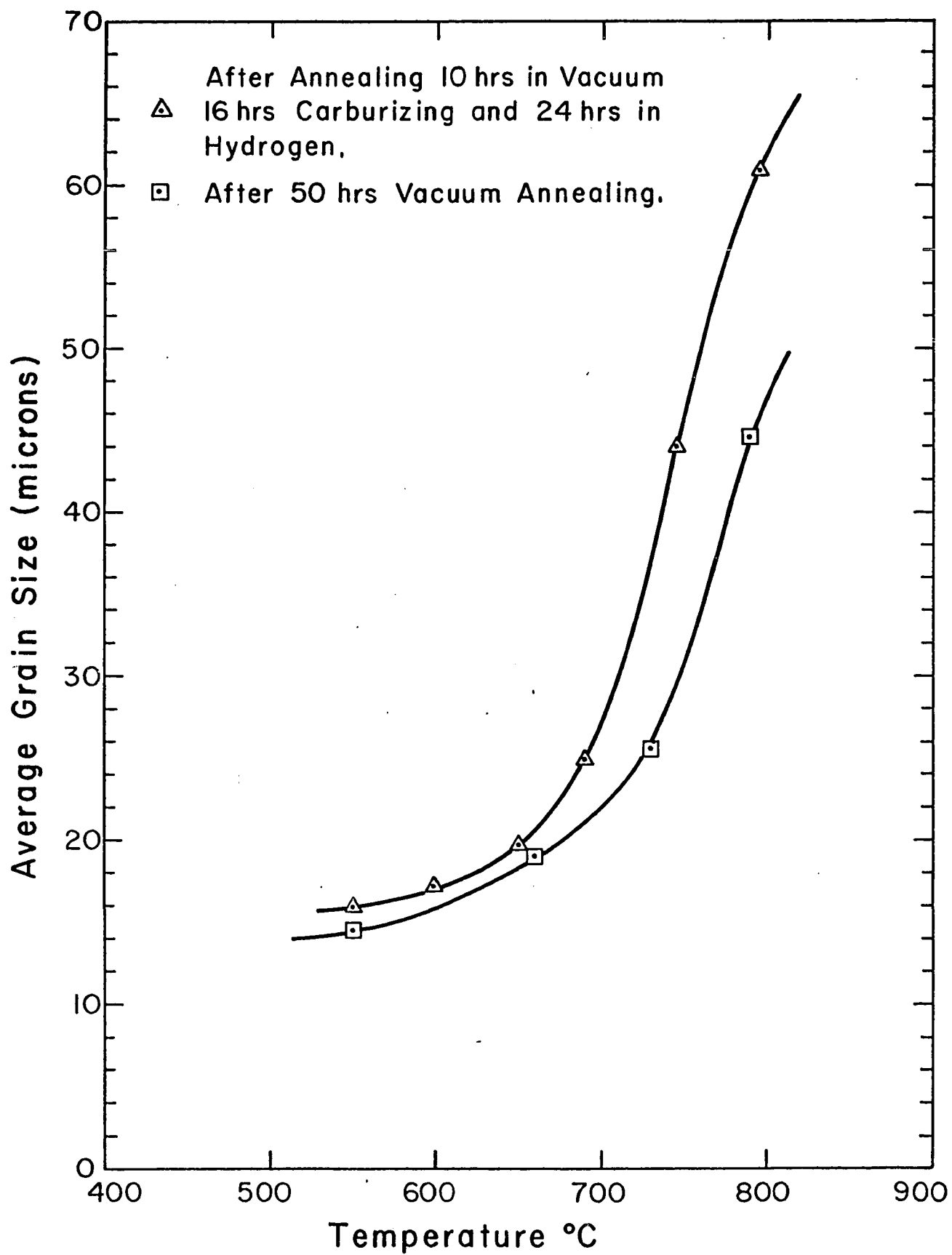


Fig. 2

that either carburizing or decarburizing enhances the grain growth. To clarify this further, three sets of annealing experiments have been made. First, ten hours annealing in vacuum of about  $10^{-6}$  mm Hg (circles in Fig. 3); second, ten hours annealing in pure hydrogen atmosphere (triangles in Fig. 3); and finally, ten hours annealing in carburizing atmosphere of  $\text{CH}_4\text{-H}_2$ --the gas ratio at each temperature corresponding to a resulting composition of 50 ppm of C (squares in Fig. 3). From these results we can tentatively conclude that the enhanced grain growth is due rather to the presence of hydrogen than carbon.

At this point the work has been aborted.

#### Conclusions and suggestions for further study

Conclusion 1: There seems to be no relation between the amount of the residual carbon and the average grain size. The intercept effect rather might be related to the subgrain structure of the material.

Suggestion 1: To make several sets of annealing and carburizing experiments and using the transmission electron microscopy to find relations between the average subgrain size and the amount of carbon dissolved in it, and to look for any precipitation in the solution, as well.

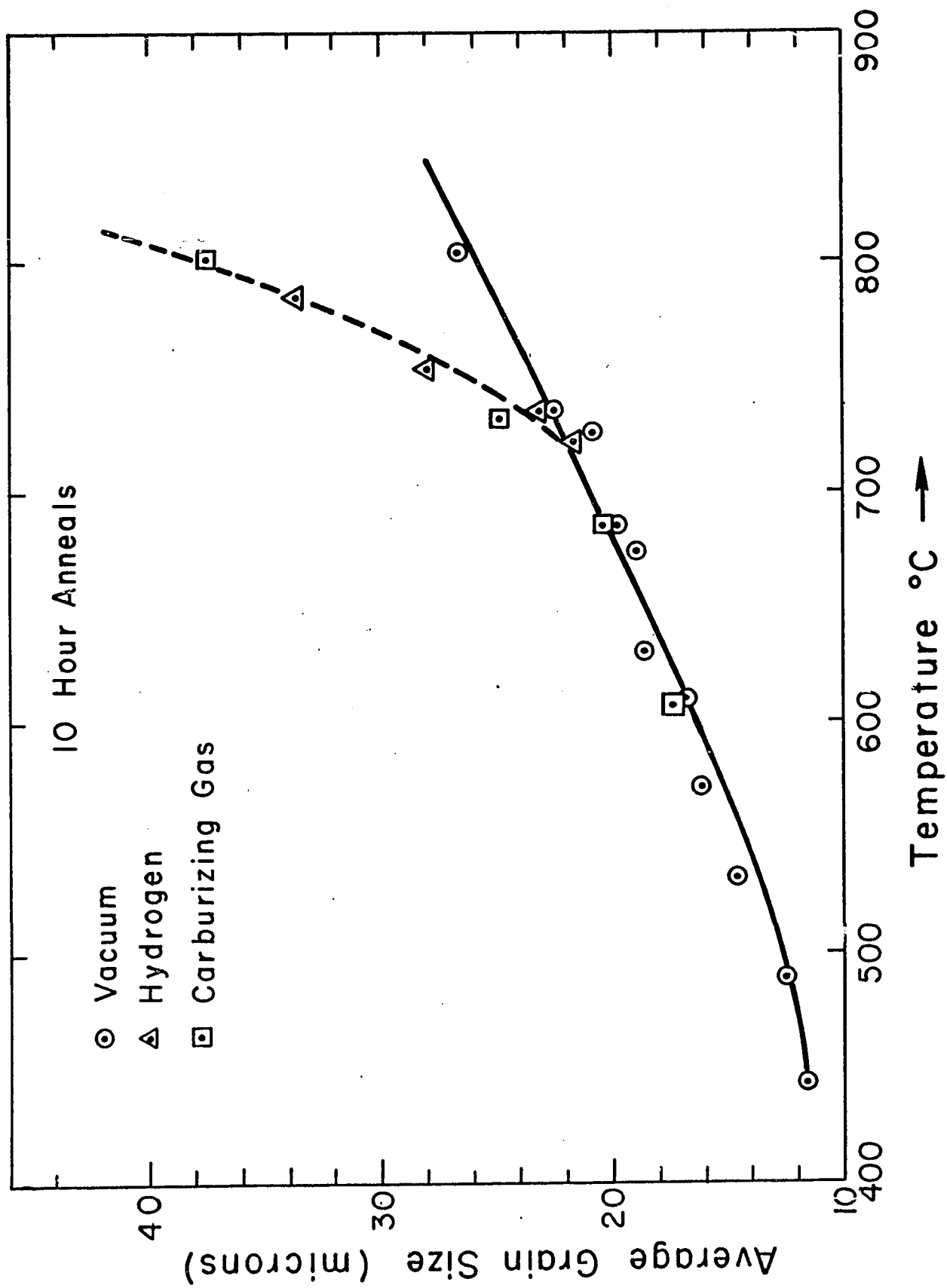


Fig. 3

Conclusion 2: Hydrogen from the carburizing mixture  $\text{CH}_4\text{-H}_2$  seems to enhance the grain growth in iron.

Suggestion 2: To perform additional measurements over a wider range of temperatures and for varying time periods of annealings. To look on the effect of carburizing by a mixture of  $\text{CO-CO}_2$  instead of  $\text{CH}_4\text{-H}_2$ .

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APPENDIX IICalculation of  $\theta_i$  for ternary systems.

The atom ratio  $\theta_i$  is defined as

$$\theta_i = \frac{N_i}{N_v + N_u} \quad (\text{A.1})$$

where N's are numbers of interstitial (i), solvent (v) and substitutional solute (u) atoms respectively.

Now, let us rewrite eqn. (A.1) as:

$$\theta_i = \frac{\frac{N_i}{N_v + N_u + N_i}}{\frac{N_v + N_u}{N_v + N_u + N_i}} = \frac{\alpha_i^T}{1 - \alpha_i^T} \quad (\text{A.2})$$

since the atom fraction of interstitial atoms in ternary systems is given by definition as

$$\alpha_i^T = \frac{N_i}{N_v + N_u + N_i} \quad (\text{A.3})$$

Also from the definition the weight fraction of i-atoms

$$W_i^T = \frac{N_i M_i}{N_v M_v + N_u M_u + N_i M_i} \quad (\text{A.4})$$

where M's are the atomic weights.

From equation (A.4)

$$N_i = \frac{w_i^T}{M_i} (N_v M_v + N_u M_u + N_i M_i) \quad (\text{A.5})$$

Substituting (A.5) into equation (A.3) we get:

$$a_i^T = \frac{w_i^T}{M_i} \frac{N_v M_v + N_u M_u + N_i M_i}{N_v + N_u + N_i} \quad (\text{A.6})$$

and thus

$$\begin{aligned} \frac{1}{a_i^T} &= \frac{M_i}{w_i^T} \frac{N_v + N_u + N_i}{N_v M_v + N_u M_u + N_i M_i} = \frac{M_i}{w_i^T} \left[ \frac{M_v}{M_v} \frac{N_v}{N_v M_v + N_u M_u + N_i M_i} + \right. \\ &\quad \left. + \frac{M_u}{M_u} \frac{N_u}{N_v M_v + N_u M_u + N_i M_i} \right] + \frac{M_i}{w_i^T} \frac{N_i}{N_v M_v + N_u M_u + N_i M_i} = \frac{M_i}{w_i^T} \left[ \frac{w_v^T}{M_v} + \frac{w_u^T}{M_u} \right] + 1 \end{aligned} \quad (\text{A.7})$$

since from definitions

$$w_v^T = \frac{M_v N_v}{N_v M_v + N_u M_u + N_i M_i} \quad ; \quad w_u^T = \frac{M_u N_u}{N_v M_v + N_u M_u + N_i M_i}$$

Rewriting equation (A.7) using a common denominator and then making a reciprocal value



$$a_i^T = \frac{w_i^T M_v M_u}{M_i [M_u w_v^T + M_v w_u^T] + w_i^T M_v M_u} \quad (\text{A.8})$$

Now, plugging equation (A.8) in (A.2):

$$\theta_i = \frac{w_i^T M_v M_u}{M_i [M_u w_v^T + M_v w_u^T]} \quad (\text{A.9})$$

This equation gives  $\theta_i$  in terms of the weight fractions in a ternary system. However, usually we know the composition of an original binary substitutional solution -  $w_v^B$  and  $w_u^B$  so it would be preferable to have  $\theta_i$  as a function of these weight fractions. It is very easy to show that in general

$$w^T = w^B (1 - w_i^T)$$

and thus we can write the final equation for  $\theta_i$  in terms of the original binary composition as

$$\theta_i = \frac{w_i^T M_v M_u}{M_i (1 - w_i^T) [M_u w_v^B + M_v w_u^B]} \quad (\text{A.10})$$

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Psalms 63:7.