THERMODYNAMIC PROPERTIES OF INTERSTITIAL ELEMENTS IN THE REFRACTORY METALS

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ABSTRACT

The thermodynamic properties of C dissolved in solid Mo, W, Nb, and Ta were estimated from the phase equilibrium diagrams of the respective metal-carbon systems, and knowledge of the free energies of formation of the di-metal carbides in equilibrium with the terminal solid solutions. Values of the partial molar heats and vibrational entropies of carbon in the terminal solid solutions are presented, and the accuracy of the calculations is discussed.
I. INTRODUCTION

The interstitial elements, C, O, N, present in small quantities, exert a potent effect on the mechanical properties of the refractory metals Mo, W, Cb, and Ta. This effect is related to their segregating, compound forming, and precipitating tendencies, and therefore closely connected with their thermochemical properties in solid solution.

The thermodynamic properties of the interstitial elements in the refractory metals have not yet been evaluated. This is an inherently difficult task because of the restricted solubilities and high temperatures involved. Sufficient information about the binary phase equilibria in refractory metal-interstitial element systems has become available however, to suggest that as a first step, an attempt to evaluate the thermodynamic properties from the equilibrium diagrams should be made. Details of such calculations for C in Mo, W, Cb, and Ta are presented in the following.

II. METHOD

The terminal solid solutions of C in the four refractory metals exist in equilibrium with carbides of the formula Me$_2$C. At high temperatures these carbides tolerate an appreciable carbon deficit, and therefore the composition of carbide in equilibrium with the terminal solid solutions is sub-stoichiometric, and variable with temperature. The comprehensive study of phase-equilibria in the refractory carbide systems by Rudy and co-workers$^1$ presents some information about the location of the boundaries of the Me$_2$C phases in the equilibrium diagrams, and this, in conjunction
with a knowledge of the free energies of formation of the carbides, makes it possible to estimate the entropies, enthalpies, and free energies of mixing of carbon in the terminal solutions.

To begin with, it is noted that the thermodynamic properties of C in the terminal solutions can be simply calculated, if the deviation from stoichiometry of the Me$_2$C phase is ignored. The method, which is discussed by Swalin,$^2$ requires a knowledge of the standard free energy of formation of the carbide, $\Delta G_f^0$, and the solubility of carbon in the metal $x^a$, as functions of temperature. As shown by Swalin, for $x^a << 1$

$$\Delta G^a_c = \left( \frac{1-x^a}{b-x^a} \right) \Delta G_f^0$$

(1)

where $b$ = the mol fraction of carbon in the carbide, = 1/3 for Me$_2$C. If now the partial molar enthalpy, $\Delta H^a_c$, and the vibrational entropy, $\Delta S^a_{vc}$, of carbon in the terminal solid solutions are assumed independent of temperature, as well as composition, and furthermore, the distribution of carbon atoms in the terminal solutions assumed to be random the partial molar free energy of carbon may be written

$$\Delta G^a_c = \Delta H^a_c - T(\Delta S^a_{vc} + \Delta S^a_{cc})$$

where $\Delta S^a_{cc}$, the configurational entropy of carbon, may be expressed as

$$\Delta S^a_{cc} = R \ln \left( \frac{3 - 4x^a}{x^a} \right)$$

(2)

Combining the above with equation (1)

$$\Delta H^a_c - T \Delta S^a_{vc} = \left( \frac{1-x^a}{b-x^a} \right) \Delta G_f^0 + RT \ln \left( \frac{3 - 4x^a}{x^a} \right)$$

(3)

A plot of the function on the right of equation (3) vs. $T$ should yield a straight line of slope $-\Delta S^a_{vc}$, and intercept, $\Delta H^a_c$. 
As mentioned, however, in these systems the composition of carbide in equilibrium with the terminal solid solutions is non-stoichiometric, and variable with temperature, i.e., the carbide is stable over a range of compositions. In order to obtain a precise determination of the chemical potential of carbon in the terminal solution from the equilibrium diagram it is therefore necessary to essentially know $\Delta G_f$ as a function of composition, as well as temperature. As might be expected, the variation of the free energy of formation of these refractory carbides with composition has rarely been measured, so that experimentally determined relationships for $\Delta G_f(x)$ do not exist. Wagner has shown, however, that the form of such relationships may be predicted, if simplifying assumptions are made about the nature and distribution of lattice defects in the non-stoichiometric compounds, and it is thus possible to allow for the non-stoichiometry of the carbide in deriving the thermodynamic properties of dissolved carbon from the equilibrium diagram.

The assumptions which must be made about the nature of the lattice defects in the non-stoichiometric $\text{Me}_2\text{C}$ carbides are clearly indicated by the structure of these compounds. The metal atoms form a hexagonal-close-packed structure in these carbides, and the carbon atoms occupy one-half of the octahedral interstitial sites in this structure. In $\text{Mo}_2\text{C}$ it has been shown that the occupancy of the octahedral sites is such that each Mo atom has three equidistant carbon neighbors, and that, considering the structure as a sequence of close-packed planes, carbon atoms in adjacent planes do not lie directly above each other. This differs from the anti-$\text{CdI}_2$ structure proposed for $\text{W}_2\text{C}$, and it has been suggested that the structure
of the dimetal carbides could bear further study. For our purposes, however, it is sufficient to know that the octahedral sites in the hcp metal structure may be divided into two types - those normally occupied by carbon atoms, and those normally empty. We may therefore assume that the principal defects which occur in $\text{Me}_2\text{C}$ are carbon atoms missing from the normally occupied octahedral sites, which may be designated as carbon vacancies, $C_v$, and carbon atoms in the normally empty octahedral sites, designated as carbon interstitials, $C_i$. If $G_{cv}$ and $G_{ci}$ are the molar free energies of formation of carbon vacancies and interstitials, respectively, then, following Wagner, the free energy of formation of the non-stoichiometric carbide, $\Delta G_f^o$, may be written

$$\Delta G_f^o = \frac{N}{N} \Delta G_f^o + \frac{N}{N} G_{cv} + \frac{N}{N} G_{ci} - T S_{cf}$$

(4)

where $\Delta G_f^o$ is the standard free energy of formation of the perfectly ordered alloy at the stoichiometric composition, $S_{cf}$ is the configurational entropy of the defects on their respective sites, $N_s$, $N_{cv}$, $N_{ci}$, and $N$ are the number of normal atom sites, number of carbon vacancies, number of carbon interstitials, and number of atoms in the structure.

If it is now assumed that the distribution of vacancies and interstitials is random, and that the quantities $G_{cv}$ and $G_{ci}$ are independent of composition in the $\text{Me}_2\text{C}$ phase, then the free energy of formation as a function of composition may be written,
\[
\Delta G_f^0 = y \Delta G_f^0 + n_{cv} G_{cv} + n_{ci} G_{ci} - RT \left[ 2x_0 y \ln x_0 y 
- n_{cv} \ln n_{cv} - n_{ci} \ln n_{ci} - (x_0 y - n_{cv}) \ln (x_0 y - n_{cv}) 
- (x_0 y - n_{ci}) \ln (x_0 y - n_{ci}) \right]
\]

and the relative partial molar free energies of metal and carbon in the carbide,

\[
\Delta \tilde{G}_{Me} = \Delta G_f^0 \left[ \left( \frac{1}{1 - x_0} \right) + \left( n_{cv} + \frac{x}{1 - x_0} \right) \ln n_{cv} \ln n_{ci} \right] 
- RT \left[ \frac{2x_0 y}{1 - x_0} \ln x_0 y - \left( n_{cv} + \frac{x}{1 - x_0} \right) \ln n_{cv} \ln n_{ci} \right]
- n_{ci} \ln n_{ci} - \left( \frac{x_0 y}{1 - x_0} - n_{cv} \right) \ln (x_0 y - n_{cv}) 
- \left( \frac{x_0 y}{1 - x_0} - n_{ci} \right) \ln (x_0 y - n_{ci})
\]

\[
\Delta \tilde{G}_c = (n_{cv} - y) \left[ G_{cv} - RT \ln \left( \frac{x_0 y}{n_{cv}} - 1 \right) \right] + n_{ci} \left[ G_{ci} - RT \ln \left( \frac{x_0 y}{n_{ci}} - 1 \right) \right]
\]

where \( x \) = atom fraction of carbon in the carbide, \( x_0 \) = atom fraction in the stoichiometric carbide, \( y = \frac{N_s}{N} \), \( n_{cv} = \frac{N_{cv}}{N} \), etc. Furthermore, since the metal atoms are assumed to be all on normal sites

\[
y = \frac{1 - x}{1 - x_0}
\]

and since at constant \( x \) the number of carbon atoms is constant,
\[ x + n_{cv} - n_{ci} - x_0 y = 0 \] (9)

At equilibrium, the concentration of defects is related to the free energy of formation of defects, therefore,

\[ \frac{n_{cv} n_{ci}}{(x_0 y - n_{cv})(x_0 y - n_{ci})} = \exp \left[ \frac{-(G_{cv} + G_{ci})}{RT} \right] \] (10)

The derivation of these equations is given in Appendix 1.

The key to the use of the equations for our purposes lies in the fact that the relative partial molar free energy of carbon in the carbide, \( \Delta G_c \), as given by equation (7), evaluated at the composition \( x_0 y \), in equilibrium with the terminal solid solution, is equal to the relative partial molar free energy of carbon in the terminal solution, \( \Delta G_c^t \). In order to evaluate \( \Delta G_c^t \), it is necessary to obtain values of the parameters \( G_{cv} \) and \( G_{ci} \) which, with equations (9) and (10), determine the values of \( n_{cv} \) and \( n_{ci} \). This can be done in several ways. The method which we have chosen takes advantage of the fact that the terminal solid solutions are dilute, and hence \( \Delta G_{Me} \) in equation (6) is given by Raoult's law, as

\[ \Delta G_{Me} = \Delta G_{Me}^a = RT \ln (1 - x^a) \] (11)

Since \( x^a \) is generally small, \( \Delta G_{Me} \) is usually close to zero, corresponding to the fact that the carbide is in equilibrium with nearly pure metal.

Advantage is also taken of Rudy and Chang's estimate of the energy difference of a carbon atom in the two types of octahedral sites in the carbide, which yields a value for the quantity \( (G_{cv} + G_{ci}) \) in equation (10). Hence, it is possible to solve equations (6), (9), and (10), to yield values of the parameters \( G_{cv} \) and \( G_{ci} \), and thereby define \( \Delta G_f^c \) and \( \Delta G_c^t \) as functions of...
composition.

III. RESULTS

The experimental data required for application of the methods discussed above are, (1), compositions of the terminal solid solutions, and Me₂C phases in equilibrium, and (2), Free energies of formation of Me₂C in each system. We are able to take advantage of the recent survey of the refractory carbide systems by Rudy and co-workers for much of this information. A summary is given here:

Molybdenum - Carbon:

Compositions of Mo₂C in equilibrium with the terminal solution are, according to Rudy, et.al., as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Atomic % C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2200</td>
<td>26.0</td>
</tr>
<tr>
<td>2000</td>
<td>30.0</td>
</tr>
<tr>
<td>1400</td>
<td>31-32.2</td>
</tr>
</tbody>
</table>

The only recent determination of the solubility of C in Mo has been made by Few and Manning, yielding the following:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Weight % C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1650</td>
<td>0.0075</td>
</tr>
<tr>
<td>1925</td>
<td>0.0125</td>
</tr>
<tr>
<td>2200</td>
<td>0.0200</td>
</tr>
</tbody>
</table>

The most reliable value of the free energy of formation of Mo₂C is, according to the careful survey of Chang, that of Gleiser and Chipman

\[
\text{Mo} + 0.449 \text{C(gr)} \rightarrow \text{MoC}_{0.449}
\]

\[
(\Delta G^0)_{298-1340^\circ K} = -5250 - 0.82T
\]
Rudy and Chang have detected a phase transformation in Mo$_2$C at 1475°C which they interpret as an order-disorder transformation involving the C atoms alone. Their analysis of this transformation indicates that the energy required to transfer a C atom from a normal to an empty octahedral site is about 8500 cal/mol. This process is obviously equivalent to the formation of a pair of defects, and therefore leads to the statement

\[ G_{cv} + G_{ci} = 8500 \text{ cal/mol}, \]  

used in equation (10). Our calculations have shown that the results are relatively insensitive to the precise value assumed for \( G_{cv} + G_{ci} \), because vacancies predominate in the carbon deficient compound.

**Tungsten - Carbon:**

The recent work of Rudy, et.al., yields the following values for the composition of W$_2$C in equilibrium with the terminal solid solution.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Atomic % C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2710</td>
<td>25.6</td>
</tr>
<tr>
<td>2200</td>
<td>29.2</td>
</tr>
<tr>
<td>1250</td>
<td>32.0</td>
</tr>
</tbody>
</table>

According to Chang, the preferred value for the free energy of formation of W$_2$C is

\[ \Delta G_f^0 = (-3,150 \pm 300) - (0.62 \pm 0.5) T \]

This is based upon Mah's determination of the heat of formation of WC$_{1/2}$ as -3150 ± 300 cal/g.atom.W, and an estimate of the entropy of formation at 1523°K as 0.62 ± 0.5 cal./degree, g. atom. W.

The solubility of C in W has been recently redetermined by Goldschmidt
and Brand, with the following results:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Atomic % C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>0.050</td>
</tr>
<tr>
<td>2200</td>
<td>0.120</td>
</tr>
<tr>
<td>2300</td>
<td>0.160</td>
</tr>
<tr>
<td>2425</td>
<td>0.300</td>
</tr>
</tbody>
</table>

Columbium – Carbon:

Data regarding the compositions of Nb₂C in equilibrium with the terminal solid solution have been taken from Storms and Krikorian, Elliot, and Brauer and Lesser, as given below. The preliminary studies of Rudy, et al., suggest that a transformation occurs in Nb₂C at ~2700°K which is not shown by the above authors.

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>Reference (11)</th>
<th>Reference (12)</th>
<th>Reference (13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1870-1975</td>
<td>32.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2223</td>
<td>30.8</td>
<td>26.5</td>
<td></td>
</tr>
<tr>
<td>2497-2503</td>
<td>30.8-32.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2608</td>
<td>28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The solubility of C in Nb from various sources is given as:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Atomic % C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>0.1</td>
</tr>
<tr>
<td>2000</td>
<td>0.258</td>
</tr>
<tr>
<td>2230</td>
<td>0.80</td>
</tr>
<tr>
<td>2335*20</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Based upon the heat of formation of -23,300 cal/g.atom Nb measured by Huber, et al., and the heat content measurements and estimated entropies of Geld and Kusenka, the free energy of formation of Nb₂C is estimated as follows:

\[ \text{Nb} + \frac{1}{2} \text{C(gr)} = \text{NbC}_{1/2} \]
\[ \Delta G^0_f = (-23,300 \pm 1700) - (0.5 \pm 0.5) T \]

The selected entropy value is still uncertain and further study is being given to the question of \( \Delta G^0_f \) for \( \text{Nb}_2\text{C} \).

**Tantalum - Carbon:**

Values of the composition of \( \text{Ta}_2\text{C} \) in equilibrium with the terminal solid solution, taken from the recent work of Rudy, et al., are as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Atomic % C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>~32</td>
</tr>
<tr>
<td>2180</td>
<td>31±1</td>
</tr>
<tr>
<td>28±3</td>
<td>26±0.5</td>
</tr>
</tbody>
</table>

According to these workers \( \text{Ta}_2\text{C} \) changes its form at elevated temperatures, and there is a slight shift in the corresponding phase boundaries. This transformation has not been taken into account in the calculations.

The solubility of C in Ta, according to the recent work of Fromm and Roy, is given as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Atomic % C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>0.6</td>
</tr>
<tr>
<td>2000</td>
<td>2.3</td>
</tr>
<tr>
<td>2400</td>
<td>4.5</td>
</tr>
<tr>
<td>2800</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Finally, the free energy of formation of \( \text{Ta}_2\text{C} \) is given as follows:

\[ \text{Ta} + \frac{1}{2} \text{C} = \text{TaC}_{1/2} \]

\[ \Delta G^0_f = (-22,000 \pm 1700) - (0.56 \pm 0.5) T \]

This is based upon the heats of formation of Mah, Huber, et al., and Krikorian's estimate of the heat capacity and entropy.

The solubility data were interpolated by plotting for the terminal solutions \( \log x^a \) vs. \( \frac{1}{T^0K} \), and for the \( \text{Me}_2\text{C} \) phases \( \log (b - x'^a) \) vs. \( \frac{1}{T^0K} \).
since these yielded roughly straight lines, and from these plots the compositions in equilibrium over a series of temperatures were obtained. These compositions were used in equations (6), (8), (9), and (10) to obtain values of the parameters $G_{cv}$ and $G_{ci}$, under the assumption that $G_{cv} + G_{ci} = 9000$ cal/mol in all of the systems. Then these parameters were used to calculate $\Delta G_c$ at $x_\gamma$ in equation (7), which is equal to $\Delta G_c^a$ in the saturated terminal solid solution. Knowledge of $\Delta G_c^a$ as $f(T)$ in turn permits the calculation of $\Delta H_c^a$ and $\Delta S_c^a$ from the expression, similar to equation (3)

$$\Delta H_c^a - T\Delta S_c^a = \Delta G_c^a(T) + RT \ln \left( \frac{3 - u_{\gamma}}{x_{\gamma}} \right)$$  \hspace{1cm} (12)

under the assumptions that the carbon atoms are distributed randomly, and $\Delta H_c^a$ and $\Delta S_c^a$ are independent of temperature and composition. The solution of these equations was programmed on an IBM 7044/1401 computer and the final results are given below, (method 2) with those obtained from the more approximate method mentioned earlier (method 1).

TABLE I: Thermodynamic Properties of the Terminal Solid Solutions of C in Mo, W, Cb, and Ta

<table>
<thead>
<tr>
<th>System</th>
<th>Method 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_c^a$</td>
</tr>
<tr>
<td></td>
<td>cal/g.atom</td>
</tr>
<tr>
<td>Mo - C</td>
<td>9,300±7,000</td>
</tr>
<tr>
<td>W - C</td>
<td>45,000±7,000</td>
</tr>
<tr>
<td>Nb - C</td>
<td>11,000±5,000</td>
</tr>
<tr>
<td>Ta - C</td>
<td>6,100±5,000</td>
</tr>
</tbody>
</table>
### IV. Discussion

The question which invariably exists with respect to calculations such as the above is how reliable are the results? With so many factors entering into the calculation, the answer is not obvious. If one considers the simpler method, first, however, it appears that the major factors influencing the results are the magnitude of the free energy of formation of the carbide, and the location of the phase boundaries representing the limiting solubilities in the terminal solid solutions. From equation (1) it is apparent, first that the relative error in \( \Delta G^0_c \) will be the same as that in \( \Delta G^0_f \). Allowing for uncertainties in the entropy of formation, the reported uncertainties in \( \Delta G^0_f \) are as follows: Mo\(_2\)C, \( \pm 15\% \); W\(_2\)C, \( \pm 40\% \); Nb\(_2\)C, \( \pm 15\% \); Ta\(_2\)C, \( \pm 15\% \). Separation of \( \Delta G^0_c \) into \( \Delta H^0_c \) and \( \Delta S^0_c \) introduces more serious uncertainties, the latter values depending upon the temperature variation of the solubility limits as well as \( \Delta G^0_f \). From equation (3) it is seen by taking the derivative of both sides with respect to temperature that

\[
\Delta S^0_{vc} = \left( \frac{1 - x^0 \alpha}{1/3 - x^0 \alpha} \right) \Delta S^0_f - \ln \left( \frac{3 - 4x^0 \alpha}{x^0 \alpha} \right) - \frac{3}{T(3 - 4x^0 \alpha)} \frac{d \ln x^0 \alpha}{d(1/T)}
\]
Since \( x^a \ll 1 \), this expression may be written

\[
\Delta S^a_{vc} = 3 \Delta S^o_f + \ln x^a - \frac{1}{T} \frac{d \ln x^a}{d(1/T)}
\]  

(13)

An estimation may be made of the possible error contributed by each of the terms on the right of equation (13). Judging simply from the reported uncertainties, \( \Delta S^o_f \) could vary by about \( \pm 0.5 \) e.u. in all of the systems and the first term therefore contribute a possible error of \( \pm 1.5 \). The possible error contributed by the second term varies from system to system. If we assume that the phase boundaries are correctly located to approximately \( \pm 0.2\% \) \( C \), taking \( x^a \) for the Mo - C and W - C systems to be \( \approx 0.001 \) and for the Nb - C and Ta - C systems \( \approx 0.01 \) the possible error in \( \ln x^a \) is estimated at about \( \pm 1 \) and \( \pm 0.2 \) e.u., respectively. Finally, judging from the scatter of points in the \( \ln x^a \) vs. \( 1/T \) plots shown in Figure 1, the error in the derivative in the third term must be of the order of 20%. Since \( 1/T \frac{d \ln x^a}{d(1/T)} \) is \( \approx 2-5 \), a possible error of \( \approx 1 \) e.u. is again suggested. It appears, therefore, that the error in \( \Delta S^a_{vc} \) could amount to approximately \( \pm 3.5 \) e.u. for Mo - C and W - C, and \( \pm 2.7 \) e.u. for Nb - C and Ta - C. This corresponds to possible errors in \( \Delta H^a_c \) of the order of \( \pm 7,000 \) and \( \pm 5,400 \) cal/mol, respectively. It is evident from Table I that the correction made by allowing for deviation of the \( \text{Me}_2C \) from stoichiometry, while an appreciable one, is not a major correction. (Compare results from method 2 and method 1.) Therefore, it is estimated that the possibilities of further errors due to uncertainty in the \( \text{Me}_2C \) phase boundaries are not large, and an increment of \( \pm 1,000 \) cal/mol in \( \Delta H^a_c \) and \( \pm 0.5 \) e.u./mol in \( \Delta S^a_{vc} \) has been arbitrarily selected.

While the errors in the calculated quantities could evidently be large,
Fig. 1

\[ \log (x^{\alpha_{\text{sat.}}}) \text{ vs. } 1/T \]
it is probable that compensation of error among the various terms leads to a more satisfactory final result. Certain regularities in the data also lend confidence in the calculated values. For example, the values of $\Delta S^a_{vc}$ are of the expected sign and order of magnitude for all except the Mo - C system. However, it will be noted in Figure 1 that the slope of the $\ln x^a$ vs. $1/T$ curve for this system is decidedly out of accord with the others. If the line for C in Mo is drawn parallel to and between those for C in Ta, and C in W, values of $\Delta H^a_c$ and $\Delta S^a_{vc}$ similar to those for the W - C system are obtained, in much better accord with theory. One is led therefore to suspect an error in the presently accepted solubility value for C in Mo. Secondly the corrections introduced by the use of method 2 in values for C in Nb seem excessively large, in comparison with the others. This may be attributed to our acceptance of an excessively large variation of the position of the Nb$_2$C phase boundary with temperature. These factors are being investigated further.

V. FUTURE WORK

Following completion of calculations of the thermodynamic properties of C in the above refractory metal systems, an effort will be made to obtain similar information about O and N in the metals from the respective phase diagrams. An initial search of the literature suggests that it should be possible to obtain results by this approach, since considerable data are available. At the same time attention will be given to the physical theory of such interstitial solutions, in order to rationalize the observed
thermochemical behavior.

During the past year equipment has been procured for the construction of a high temperature electrolytic cell for direct measurement of the thermodynamic properties of the interstitial solutions by the emf method, and attention in the future will be given to the details of cell construction, and assembling of this apparatus. Possible limitations on the use of solid electrolytes for these systems are under study since this factor is important in choice of cell design.
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>Atom fraction of C in Me$_2$C phase.</td>
</tr>
<tr>
<td>$x_0$</td>
<td>Atom fraction of C in Me$_2$C phase at stoichiometry.</td>
</tr>
<tr>
<td>$x_{Ya}$</td>
<td>Atom fraction of C in Me$_2$C phase in equilibrium with terminal solid solution.</td>
</tr>
<tr>
<td>$x^a$</td>
<td>Atom fraction of C in terminal solid solution.</td>
</tr>
<tr>
<td>$\Delta G_f^0$</td>
<td>Standard free energy of formation of Me$_2$C.</td>
</tr>
<tr>
<td>$\Delta S_f^0$</td>
<td>Standard entropy of formation of Me$_2$C.</td>
</tr>
<tr>
<td>$\Delta G_f^a$</td>
<td>Standard free energy of formation of perfectly ordered Me$_2$C at the stoichiometric composition.</td>
</tr>
<tr>
<td>$G_{cv}, G_{ci}$</td>
<td>Molar free energy of formation of carbon vacancies and interstitials, respectively.</td>
</tr>
<tr>
<td>$\Delta G_{Me}^a, \Delta G_{Me}^s$</td>
<td>Partial molar free energy of metal in Me$_2$C and terminal solid solution, respectively.</td>
</tr>
<tr>
<td>$\Delta H_c, \Delta H_c^a$</td>
<td>Partial molar enthalpy of carbon in Me$_2$C and in terminal solid solution, respectively.</td>
</tr>
<tr>
<td>$\Delta S_{vc}^a, \Delta S_{cc}^s$</td>
<td>Partial molar vibrational and configurational entropy of C in terminal solid solution, respectively.</td>
</tr>
<tr>
<td>$S_{cf}$</td>
<td>Configurational entropy of Me$_2$C phase.</td>
</tr>
<tr>
<td>$N, N_s, N_{cv}, N_{ci}$</td>
<td>Number of atoms, normal atom sites, number of carbon vacancies, and number of carbon interstitials in Me$_2$C, respectively.</td>
</tr>
<tr>
<td>$n_{ci} = \frac{N_{ci}}{N}, \ldots$ etc.</td>
<td></td>
</tr>
<tr>
<td>$y = \frac{N_s}{N}$</td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES


5. Ref. (1) Vol. (1)


17. See ref.(6) p. 52


APPENDIX I

DERIVATION OF FREE ENERGY EQUATIONS FOR THE $\text{Me}_2\text{C}$ PHASE

Assuming the defects existing in the carbide are carbon vacancies and interstitials as discussed on p. of the report, the free energy of formation of the compound, as a function of composition, is expressed as

$$\Delta G_f^0 = \frac{N_S}{N} \Delta G_f + \frac{N_{cv}}{N} G_{cv} + \frac{N_{ci}}{N} G_{ci} - T S_{cf}$$

(1)

The symbols are defined in the table of symbols. The configurational entropy, $S_{cf}$, is the configurational entropy of normal carbon sites, plus that of carbon interstitial sites and is derived from the Boltzmann expression assuming random distribution of defects

$$S_{cf} = k \ln W = k \ln \frac{(x_0 N_S)!}{(x_0 N_S - N_{cv})! (N_{cv})!} + k \ln \frac{(x_0 N_S)!}{(x_0 N_S - N_{ci})! (N_{ci})!}$$

or, upon using Stirling’s approximation

$$S_{cf} = R \left[2 x_0 y \ln x_0 y - n_{cv} \ln n_{cv} - n_{ci} \ln n_{ci} - (x_0 y - n_{cv}) \ln (x_0 y - n_{cv}) - (x_0 y - n_{ci}) \ln (x_0 y - n_{ci})\right]$$

(2)

Therefore,

$$\Delta G_f^0 = y \Delta G_f + n_{cv} G_{cv} + n_{ci} G_{ci} - RT \left[2 x_0 y \ln x_0 y \ldots\text{etc.}\right]$$

(3)

In order to find the equilibrium values of $n_{cv}$ and $n_{ci}$, $\Delta G_f^0$ is minimized at constant composition and temperature, under the constraints:

$$x_0 N_S = x N + N_{cv} - N_{ci}$$

(4)

or

$$\phi = x + n_{cv} - n_{ci} - x_0 y = 0$$
and \[(1 - x_o) N_s = (1 - x) N\] (5)

or \[y = \frac{N_s}{N} = \frac{1 - x}{1 - x_o}\]

According to the method of Lagrange,
\[
\frac{\partial \Delta G_f^0}{\partial n_{cv}} + \lambda \frac{\partial \phi}{\partial n_{cv}} = 0
\]
and
\[
\frac{\partial \Delta G_f^0}{\partial n_{ci}} + \lambda \frac{\partial \phi}{\partial n_{ci}} = 0
\]

Since \(\frac{\partial \phi}{\partial n_{cv}} = 1\), and \(\frac{\partial \phi}{\partial n_{ci}} = -1\), the condition is obtained, that
\[
\frac{\partial \Delta G_f^0}{\partial n_{cv}} = -\frac{\partial \Delta G_f^0}{\partial n_{ci}}
\]

Differentiating equation (3), partially, with respect to \(n_{cv}\) and \(n_{ci}\), and substituting in equation (7),
\[
\frac{n_{cv} n_{ci}}{(x_o y - n_{cv}) (x_o y - n_{ci})} = \exp \left( \frac{G_{cv} + G_{ci}}{RT} \right)
\]

Since \(n_{cv} = n_{ci} - x + x_o \frac{(1 - x)}{(1 - x_o)}\) from equation (4) and (5), we may write
\[
n_{ci} = 1/4 \left[ 2x - B (1 - x) + \sqrt{8x^2 - 4x + B^2 (1 - x)^2} \right]
\]

where \(B = \frac{1 + A}{1 - A}, A = \exp \left( \frac{G_{cv} + G_{ci}}{RT} \right)\)

With a knowledge of \(\Delta G_f^0, G_{cv}\), and \(G_{ci}\) equations (8), (9), and (13) define \(\Delta G_f^0\) as a function of composition. By the use of standard formulas, the partial molar free energies can be derived
\[ \Delta \bar{G}_c = \left[ n_{cv} - y \right] \left[ G_{cv} - RT \ln \left( \frac{x_{o}y}{n_{cv}} - 1 \right) \right] \]

\[ - n_{ci} \left[ G_{ci} - RT \ln \left( \frac{x_{o}y}{n_{ci}} - 1 \right) \right] \]

\[ \Delta \bar{G}_{Me} = \frac{x_{o}}{1 - x_{o}} \Delta \bar{G}_{f}^{o} + \left( n_{cv} + \frac{x}{1 - x_{o}} \right) G_{cv} + n_{ci} G_{ci} \]

\[ - RT \left[ \frac{2x_{o} \ln x_{o}y - \left( n_{cv} + \frac{x}{1 - x_{o}} \right) \ln n_{cv} - n_{ci} \ln n_{ci}}{1 - x_{o} - n_{cv}} \right] \ln (x_{o}y - n_{cv}) - \left[ \frac{x_{o}y}{1 - x_{o} - n_{ci}} \ln (x_{o}y - n_{ci}) \right] \]

Equation (11) has been used, with (8) and (9) to evaluate \( G_{cv} \) and \( G_{ci} \) under the assumption that \( G_{cv} \) and \( G_{ci} = 8500 \text{ cal/mol} \), from the estimate of Rudy and Chang for \( \text{Mo}_{2}C \). To a close approximation \( \Delta \bar{G}_{Me} = 0 \) at the composition \( x_{\gamma} \) and \( \Delta \bar{G}_{f}^{o} = \Delta \bar{G}_{f}^{c} \) at the stoichiometric composition as reported in the literature. Knowing \( G_{cv} \) and \( G_{ci} \), equation (10) may then be used to evaluate \( \Delta \bar{G}_c \) at the phase boundary, and thus \( \Delta \bar{G}_c = \Delta \bar{G}_c' \).