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2 THERMODYNAMIC PROPERTIES OF INTERSTITIAL ELEMENTS IN THE REFRACTORY METALS 4

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First semi-annual report, June 1, 1966 - December 1, 1966. /

NASA Research Grant NGR-33-015-035 2/

TABLE OF CONTENTS

Abstract	i
I. Introduction	1.
II. Method	1.
III. Results	7.
IV. Discussion	12.
V. Future Work	14.
List of Symbols	16.
References	17.
Appendix I	18.

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_2C . 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-workers¹ presents some information about the location of the boundaries of the Me_2C 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_2C phase is ignored. The method, which is discussed by Swalin,² requires a knowledge of the standard free energy of formation of the carbide, ΔG_f° , and the solubility of carbon in the metal x^α , as functions of temperature. As shown by Swalin, for $x^\alpha \ll 1$

$$\Delta \bar{G}_c^\alpha \approx \left(\frac{1 - x^\alpha}{b - x^\alpha} \right) \Delta G_f^\circ \quad (1)$$

where b = the mol fraction of carbon in the carbide, = 1/3 for Me_2C . If now the partial molar enthalpy, $\Delta \bar{H}_c^\alpha$, and the vibrational entropy, $\Delta \bar{S}_{vc}^\alpha$, 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 $\Delta \bar{G}_c^\alpha = \Delta \bar{H}_c^\alpha - T(\Delta \bar{S}_{vc}^\alpha + \Delta \bar{S}_{cc}^\alpha)$ where $\Delta \bar{S}_{cc}^\alpha$, the configurational entropy of carbon, may be expressed as

$$\Delta \bar{S}_{cc}^\alpha = R \ln \left(\frac{3 - 4x^\alpha}{x^\alpha} \right) \quad (2)$$

Combining the above with equation (1)

$$\Delta \bar{H}_c^\alpha - T \Delta \bar{S}_{vc}^\alpha = \left(\frac{1 - x^\alpha}{b - x^\alpha} \right) \Delta G_f^\circ + RT \ln \left(\frac{3 - 4x^\alpha}{x^\alpha} \right) \quad (3)$$

A plot of the function on the right of equation (3) vs. T should yield a straight line of slope $-\Delta \bar{S}_{vc}^\alpha$, and intercept, $\Delta \bar{H}_c^\alpha$.

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 ΔG_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 $\Delta G_f^\circ(x)$ do not exist. Wagner has shown,³ 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 Me_2C 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 Mo_2C it has been shown⁴ 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- CdI_2 structure proposed for W_2C , 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 Me_2C 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, ΔG_f^0 , may be written

$$\Delta G_f^0 = \frac{N_s}{N} \Delta G_f^* + \frac{N_{cv}}{N} G_{cv} + \frac{N_{ci}}{N} G_{ci} - TS_{cf} \quad (4)$$

where ΔG_f^* 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 Me_2C phase, then the free energy of formation as a function of composition may be written,

$$\begin{aligned} \Delta G_f^0 = & y \Delta G_f^* + n_{cv} G_{cv} + n_{ci} G_{ci} - RT \left[2x_0 y \ln x_0 y \right. \\ & - n_{cv} \ln n_{cv} - n_{ci} \ln n_{ci} - (x_0 y - n_{cv}) \ln (x_0 y - n_{cv}) \\ & \left. - (x_0 y - n_{ci}) \ln (x_0 y - n_{ci}) \right] \end{aligned} \quad (5)$$

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

$$\begin{aligned} \Delta \bar{G}_{Me} = & \Delta G_f^* \left[\frac{1}{1-x_0} \right] + \left[n_{cv} + \frac{x}{1-x_0} \right] G_{cv} + n_{ci} G_{ci} \\ & - RT \left[\left[\frac{2x_0}{1-x_0} \right] \ln x_0 y - \left[n_{cv} + \frac{x}{1-x_0} \right] \ln n_{cv} \right. \\ & - n_{ci} \ln n_{ci} - \left[\frac{x_0 - x}{1-x_0} - n_{cv} \right] \ln (x_0 y - n_{cv}) \\ & \left. - \left[\frac{x_0 y}{1-x_0} - n_{ci} \right] \ln (x_0 y - n_{ci}) \right] \end{aligned} \quad (6)$$

$$\Delta \bar{G}_c = (n_{cv} - y) \left[G_{cv} - RT \ln \left[\frac{x_0 y}{n_{cv}} - 1 \right] \right] + n_{ci} \left[G_{ci} - RT \ln \left[\frac{x_0 y}{n_{ci}} - 1 \right] \right] \quad (7)$$

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

$$y = \frac{1-x}{1-x_0} \quad (8)$$

and since at constant x the number of carbon atoms is constant,

$$x + n_{cv} - n_{ci} - x_0y = 0 \quad (9)$$

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

$$\frac{n_{cv} n_{ci}}{(x_0y - n_{cv})(x_0y - n_{ci})} = \exp\left[\frac{-(G_{cv} + G_{ci})}{RT}\right] \quad (10)$$

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, $\Delta\bar{G}_c$, as given by equation (7), evaluated at the composition $x_{\gamma\alpha}$, in equilibrium with the terminal solid solution, is equal to the relative partial molar free energy of carbon in the terminal solution, $\Delta\bar{G}_c^\alpha$. In order to evaluate $\Delta\bar{G}_c$, 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 $\Delta\bar{G}_{Me}$ in equation (6) is given by Raoult's law, as

$$\Delta\bar{G}_{Me} = \Delta\bar{G}_{Me}^\alpha = RT \ln(1 - x^\alpha) \quad (11)$$

Since x^α is generally small, $\Delta\bar{G}_{Me}^\alpha$ 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's⁵ 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 $\Delta\bar{G}_f^\circ$ and $\Delta\bar{G}_c$ 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 Me_2C phases in equilibrium, and (2), Free energies of formation of Me_2C in each system. We are able to take advantage of the recent survey of the refractory carbide systems by Rudy and co-workers⁶ for much of this information. A summary is given here:

Molybdenum - Carbon:

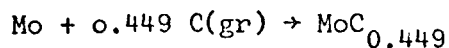
Compositions of Mo_2C in equilibrium with the terminal solution are, according to Rudy, et.al., as follows:

<u>Temperature °C</u>	<u>Atomic % C</u>
2200	26.0
2000	30.0
1400	31-32.2

The only recent determination of the solubility of C in Mo has been made by Few and Manning,⁷ yielding the following:

<u>Temperature °C</u>	<u>Weight % C</u>
1650	0.0075
1925	0.0125
2200	0.0200

The most reliable value of the free energy of formation of Mo_2C is, according to the careful survey of Chang,⁶ that of Gleiser and Chipman⁸



$$(\Delta G_f^\circ)_{298-1340^\circ\text{K}} = -5250 - 0.82T (\pm 700)$$

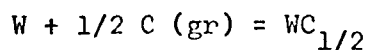
Rudy and Chang have detected a phase transformation in Mo_2C at 1475°C which they interpret as an order-disorder transformation involving the C atoms alone. Their analysis of this transformation indicates that the energy required to transfer a C atom from a normal to an empty octahedral site is about 8500 cal/mol. This process is obviously equivalent to the formation of a pair of defects, and therefore leads to the statement $G_{cv} + G_{ci} = 8500$ 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_2C in equilibrium with the terminal solid solution.

<u>Temperature °C</u>	<u>Atomic % C</u>
2710	25.6
2200	29.2
1250	~32.0

According to Chang,⁶ the preferred value for the free energy of formation of W_2C is



$$\Delta G_f^\circ = (-3,150 \pm 300) - (0.62 \pm 0.5) T$$

This is based upon Mah's⁹ determination of the heat of formation of $\text{WC}_{1/2}$ 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,¹⁰ with the following results:

<u>Temperature °C</u>	<u>Atomic % C</u>
2000	0.050
2200	0.120
2300	0.160
2425	0.300

Columbium - Carbon:

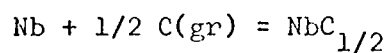
Data regarding the compositions of Nb₂C in equilibrium with the terminal solid solution have been taken from Storms and Krikorian,¹¹ Elliot,¹² and Brauer and Lesser,¹³ as given below. The preliminary studies of Rudy, et.al., suggest that a transformation occurs in Nb₂C at ~2700°K which is not shown by the above authors.

<u>Temperature °K</u>	<u>Atomic % C</u>		
	<u>Reference (1)</u>	<u>Reference (2)</u>	<u>Reference (3)</u>
1870-1975			32.9
2223		30.8	26.5
2497-2503	30.8-32.0		
2608	28		

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

<u>Temperature °C</u>	<u>Atomic % C.</u>
1800	0.1
2000	0.258
2230	0.80
2335±20	1.02

Based upon the heat of formation of -23,300 cal/g.atom Nb measured by Huber, et.al.,¹⁴ and the heat content measurements and estimated entropies of Geld and Kusenka,¹⁵ the free energy of formation of Nb₂C is estimated as follows:



$$\Delta G_f^\circ = (-23,300 \pm 1700) - (0.5 \pm 0.5) T$$

The selected entropy value is still uncertain and further study is being given to the question of ΔG_f° for Nb_2C .

Tantalum - Carbon:

Values of the composition of Ta_2C in equilibrium with the terminal solid solution, taken from the recent work of Rudy, et.al., are as follows:

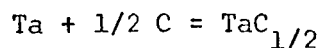
<u>Temperature °C</u>	<u>Atomic % C</u>
1600	~32
2180	31±1
2843	26±0.5

According to these workers Ta_2C 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,¹⁶ is given as follows:

<u>Temperature °C</u>	<u>Atomic % C</u>
1600	0.6
2000	2.3
2400	4.5
2800	7.5

Finally, the free energy of formation of Ta_2C is given as follows:



$$\Delta G_f^\circ = (-22,000 \pm 1700) - (0.56 \pm 0.5) T$$

This is based upon the heats of formation of Mah,¹⁷ Huber, et.al.,¹⁸ and Krikorian's¹⁹ estimate of the heat capacity and entropy.

The solubility data were interpolated by plotting for the terminal solutions $\log x^\alpha$ vs. $\frac{1}{T^\circ K}$, and for the Me_2C phases $\log (b - x_{\gamma\alpha})$ vs. $\frac{1}{T^\circ K}$

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 $G_{cv} + G_{ci} \approx 9000$ cal/mol in all of the systems. Then these parameters were used to calculate $\Delta\bar{G}_c^\alpha$ at $x_{\gamma\alpha}$ in equation (7), which is equal to $\Delta\bar{G}_c^\alpha$ in the saturated terminal solid solution. Knowledge of $\Delta\bar{G}_c^\alpha$ as $f(T)$ in turn permits the calculation of $\Delta\bar{H}_c^\alpha$ and $\Delta\bar{S}_{vc}^\alpha$ from the expression, similar to equation (3)

$$\Delta\bar{H}_c^\alpha - T\Delta\bar{S}_{vc}^\alpha = \Delta\bar{G}_c^\alpha(T) + RT \ln \left[\frac{3 - 4x^\alpha}{x^\alpha} \right] \quad (12)$$

under the assumptions that the carbon atoms are distributed randomly, and $\Delta\bar{H}_c^\alpha$ and $\Delta\bar{S}_{vc}^\alpha$ 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

System	Method 1	
	$\Delta\bar{H}_c^\alpha$	$\Delta\bar{S}_{vc}^\alpha$
	cal/g.atom	cal/degree g.atom
Mo - C	9,300±7,000	-4.5±3.5
W - C	45,000±7,000	7.5±3.5
Nb - C	11,000±5,000	6.5±2.7
Ta - C	6,100±5,000	11.2±2.7

System	Method 2	
	$\Delta\bar{H}_c^\alpha$ cal/g.atom	$\Delta\bar{S}_{vc}^\alpha$ cal/degree g.atom
Mo - C	7,200±8,000	-6.7±4.0
W - C	40,300±8,000	4.2±4.0
Nb - C	-350±6,000	10.9±3.2
Ta - C	4,200±6,000	9.2±3.2

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 $\Delta\bar{G}_c^\alpha$ will be the same as that in ΔG_f° . Allowing for uncertainties in the entropy of formation, the reported uncertainties in ΔG_f° are as follows: Mo_2C , ±15%; W_2C , ± 40%; Nb_2C , ± 15%; Ta_2C , ± 15%.

Separation of $\Delta\bar{G}_c^\alpha$ into $\Delta\bar{H}_c^\alpha$ and $\Delta\bar{S}_{vc}^\alpha$ introduces more serious uncertainties, the latter values depending upon the temperature variation of the solubility limits as well as ΔG_f° . From equation (3) it is seen by taking the derivative of both sides with respect to temperature that

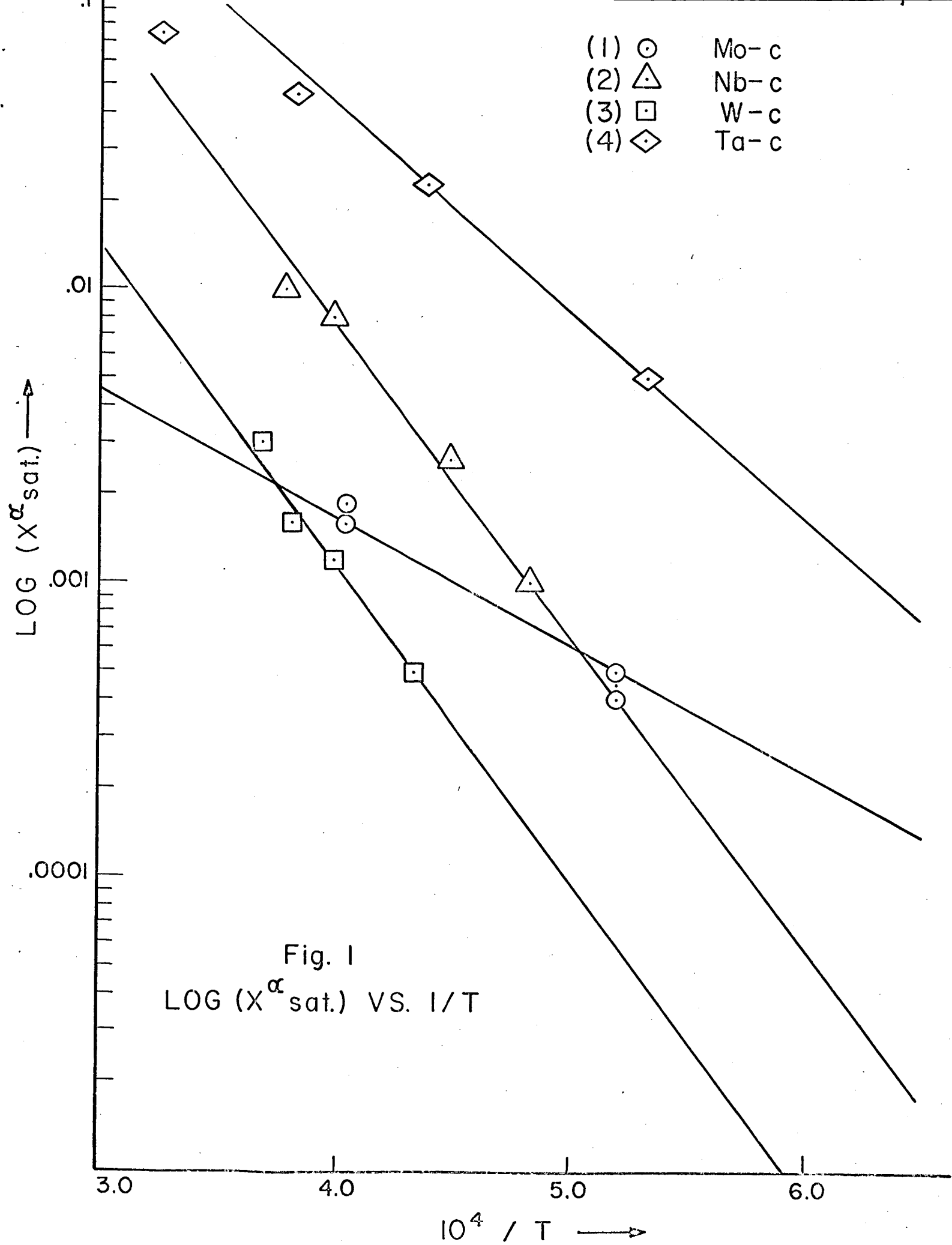
$$\Delta\bar{S}_{vc}^\alpha = \left(\frac{1 - x^\alpha}{1/3 - x^\alpha} \right) \Delta S_f^\circ - \ln \left(\frac{3 - 4x^\alpha}{x^\alpha} \right) - \frac{3}{T(3 - 4x^\alpha)} \frac{d \ln x^\alpha}{d(1/T)}$$

Since $x^\alpha \ll 1$, this expression may be written

$$\Delta \bar{S}_{vc}^\alpha = 3\Delta S_f^\circ + \ln x^\alpha - \frac{1}{T} \frac{d \ln x^\alpha}{d(1/T)} \quad (13)$$

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, ΔS_f° could vary by about ± 0.5 e.u. in all of the systems and the first term therefore contribute a possible error of ± 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^α for the Mo - C and W - C systems to be ~ 0.001 and for the Nb - C and Ta - C systems ~ 0.01 the possible error in $\ln x^\alpha$ is estimated at about ± 1 and ± 0.2 e.u., respectively. Finally, judging from the scatter of points in the $\ln x^\alpha$ 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 $1/T \frac{d \ln x^\alpha}{d(1/T)}$ is $\sim -2-5$, a possible error of $\sim \pm 1$ e.u. is again suggested. It appears, therefore, that the error in $\Delta \bar{S}_{vc}^\alpha$ could amount to approximately ± 3.5 e.u. for Mo - C and W - C, and ± 2.7 e.u. for Nb - C and Ta - C. This corresponds to possible errors in $\Delta \bar{H}_c^\alpha$ 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 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 Me_2C phase boundaries are not large, and an increment of $\pm 1,000$ cal/mol in $\Delta \bar{H}_c^\alpha$ and ± 0.5 e.u./mol in $\Delta \bar{S}_{vc}^\alpha$ has been arbitrarily selected.

While the errors in the calculated quantities could evidently be large,



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 $\Delta\bar{S}_{vc}^{\alpha}$ 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 $\ln x^{\alpha}$ 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 $\Delta\bar{H}_C^{\alpha}$ and $\Delta\bar{S}_{vc}^{\alpha}$ 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_2C 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

x	Atom fraction of C in Me_2C phase.
x_0	Atom fraction of C in Me_2C phase at stoichiometry.
$x_{\gamma\alpha}$	Atom fraction of C in Me_2C phase in equilibrium with terminal solid solution.
x^α	Atom fraction of C in terminal solid solution.
ΔG_F°	Standard free energy of formation of Me_2C .
ΔS_F°	Standard entropy of formation of Me_2C .
ΔG_F^\ddagger	Standard free energy of formation of perfectly ordered Me_2C at the stoichiometric composition.
G_{cv}, G_{ci}	Molar free energy of formation of carbon vacancies and interstitials, respectively.
$\bar{\Delta G}_{\text{Me}}, \bar{\Delta G}_{\text{Me}}^\alpha$	Partial molar free energy of metal in Me_2C and terminal solid solution, respectively.
$\bar{\Delta H}_c, \bar{\Delta H}_c^\alpha$	Partial molar enthalpy of carbon in Me_2C and in terminal solid solution, respectively.
$\bar{\Delta S}_{vc}^\alpha, \bar{\Delta S}_{cc}^\alpha$	Partial molar vibrational and configurational entropy of C in terminal solid solution, respectively.
S_{cf}	Configurational entropy of Me_2C phase
N, N_s, N_{cv}, N_{ci}	Number of atoms, normal atom sites, number of carbon vacancies, and number of carbon interstitials in Me_2C , respectively.
$n_{ci} = \frac{N_{ci}}{N}, \dots \text{etc.}$	
$y = \frac{N_s}{N}$	

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APPENDIX I

DERIVATION OF FREE ENERGY EQUATIONS FOR THE Me₂C PHASE

Assuming the defects existing in the carbide are carbon vacancies and interstitials as discussed on p⁴. of the report, the free energy of formation of the compound, as a function of composition, is expressed as

$$\Delta G_f^0 = \frac{N_s}{N} \Delta G_f^* + \frac{N_{cv}}{N} G_{cv} + \frac{N_{ci}}{N} G_{ci} - TS_{cf} \quad (1)$$

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

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

or, upon using Stirling's approximation

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

Therefore,

$$\Delta G_f^0 = y \Delta G_f^* + n_{cv} G_{cv} + n_{ci} G_{ci} - RT \left[2x_o y \ln x_o y \dots \text{etc.} \right] \quad (3)$$

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

$$x_o N_s = xN + N_{cv} - N_{ci} \quad (4)$$

or

$$\phi = x + n_{cv} - n_{ci} - x_o y = 0$$

and
$$(1 - x_0) N_s = (1 - x) N \quad (5)$$

or
$$y = \frac{N_s}{N} = \frac{1 - x}{1 - x_0}$$

According to the method of Lagrange,

$$\frac{\partial \Delta G_f^0}{\partial n_{cv}} + \lambda \frac{\partial \phi}{\partial n_{cv}} = 0 \quad (6)$$

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

$$\frac{\partial \Delta G_f^0}{\partial n_{cv}} = - \frac{\partial \Delta G_f^0}{\partial n_{ci}} \quad (7)$$

Differentiating equation (3), partially, with respect to n_{cv} and n_{ci} , and substituting in equation (7),

$$\frac{n_{cv} n_{ci}}{(x_0 y - n_{cv})(x_0 y - n_{ci})} = \exp - \left[\frac{G_{cv} + G_{ci}}{RT} \right] \quad (8)$$

Since $n_{cv} = n_{ci} - x + \frac{x_0(1-x)}{(1-x_0)}$ from equation (4) and (5), we may write

$$n_{ci} = 1/4 \left[2x - B(1-x) + \sqrt{8x^2 - 4x + B^2(1-x)^2} \right] \quad (9)$$

where $B = \frac{1+A}{1-A}$, $A = \exp - \left[\frac{G_{cv} + G_{ci}}{RT} \right]$

With a knowledge of ΔG_f^0 , G_{cv} , and G_{ci} equations (8), (9), and (13) define ΔG_f^0 as a function of composition. By the use of standard formulas, the partial molar free energies can be derived

$$\Delta \bar{G}_c = \left[n_{cv} - y \right] \left[G_{cv} - RT \ln \left(\frac{x_o y}{n_{cv}} - 1 \right) \right] - n_{ci} \left[G_{ci} - RT \ln \left(\frac{x_o y}{n_{ci}} - 1 \right) \right] \quad (10)$$

$$\Delta \bar{G}_{Me} = \frac{x_o}{1 - x_o} \Delta G_f^{\ddagger} + \left[n_{cv} + \frac{x}{1 - x_o} \right] G_{cv} + n_{ci} G_{ci} - RT \left[\frac{2x_o}{1 - x_o} \ln x_o y - \left[n_{cv} + \frac{x}{1 - x_o} \right] \ln n_{cv} - n_{ci} \ln n_{ci} - \left[\frac{x_o - x}{1 - x_o} - n_{cv} \right] \ln (x_o y - n_{cv}) - \left[\frac{x_o y}{1 - x_o} - n_{ci} \right] \ln (x_o y - n_{ci}) \right] \quad (11)$$

Equation (11) has been used, with (8) and (9) to evaluate G_{cv} and G_{ci} under the assumption that G_{cv} and $G_{ci} = 8500$ cal/mol, from the estimate of Rudy and Chang for Mo_2C . To a close approximation $\Delta \bar{G}_{Me} = 0$ at the composition $x_{\gamma\alpha}$ and $\Delta G_f^{\ddagger} \approx \Delta G_f^{\circ}$ 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 $\Delta \bar{G}_c^{\alpha} = \Delta \bar{G}_c$.