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STATE UNIVERSITY OF NEW YORK AT STONY BROOK

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THERMODYNAMIC PROPERTIES OF INTERSTITIAL
ELEMENTS IN THE REFRACTORY METALS

by

P. P. Bansal, N. C. Birla

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Fourth semiannual report, December 1, 1967 - May 31, 1968

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TABLE OF CONTENTS

Abstract	i.
I. Introduction	i.
II. Derivation of the Thermodynamic Properties from Phase Equilibrium Diagrams	i.
III. Theory of Interstitial Solutions	4.
IV. Experimental Studies	7.
V. Future Work	8.
Figure 1	10.
Figure 2	11.
Figure 3	12.
References	13.

ABSTRACT

Calculations of the thermodynamic properties of C in Mo, W, Cb, and Ta have been completed, allowing for the deviations from stoichiometry of the carbide phases in equilibrium with the terminal solid solutions. This allowance produces a minor correction in the previously determined values. Work is under way to extend the method to the oxygen and nitrogen containing systems. Values of the thermodynamic properties have also been calculated using elasticity theory to predict the "misfit" energy of the interstitial atoms in solution. For the carbon metal systems these are in reasonable agreement with the results of the phase diagram calculations.

The solid electrolyte galvanic cell was used successfully to determine the free energy of formation of MoO_2 up to about 1100°C .

I. INTRODUCTION

It is well known that the properties of the refractory metals Mo, W, Cb, and Ta are strongly affected by small quantities of C, O, and N dissolved interstitially, and control of interstitials is a major consideration in the processing of refractory alloys. The effect of interstitials is closely related to their thermodynamic properties in solid solution, and a study of these properties, therefore, is of practical as well as theoretical interest. It is the aim of this project to clarify the thermodynamic behavior of the interstitial elements in the refractory metals, and relate this to the practical utilization of these metals on the one hand, and the theory of interstitial solutions on the other.

II. DERIVATION OF THE THERMODYNAMIC PROPERTIES FROM PHASE EQUILIBRIUM DIAGRAMS

Since very high temperature studies are inherently difficult, it is important in this project to make the best use of all available experimental data, and for this reason considerable attention has been devoted to the problem of deriving thermodynamic properties from phase equilibrium diagrams. Attention has been initially concentrated on the metal-carbon systems, and the available data and methods of calculation have been discussed in previous reports.¹ These calculations have been completed in the present report period, and the results and conclusions may be summarized as follows.

A. Metal-carbon systems: The most precise method of calculation takes account of the fact that the terminal solid solutions of carbon in the refractory metals are in equilibrium with carbide phases of variable composition. Knowing the positions of the carbide as well as the terminal solution phase boundaries, it is possible, with the aid of Wagner's theory of defect compounds², to allow for the non-stoichiometry of the carbide phases. A difficulty which arises with the method is lack of knowledge of certain parameters for the carbide phases, and it was necessary to determine how much uncertainty this introduced into the final results.

The applicable equations are given in Appendix I of the First Semi-annual Report¹. In essence, the free energy of formation of the defect carbide is given as a function of composition by means of a series of equations containing the parameters G_{cv} and G_{ci} , the molar free energies of formation of carbon vacancies and carbon interstitials, respectively, as well as the standard free energy of formation of the stoichiometric compound, ΔG_f^0 , which is presumed known. Two relationships are required to determine G_{cv} and G_{ci} at given temperature but only one is available--the fact that at the composition in equilibrium with the terminal solid solution, the chemical potential of metal in the carbide is very close to zero. In order to solve for the chemical potential of carbon, therefore, it is necessary to assume a value for G_{cv} or G_{ci} , or equivalently, $\Delta G = G_{cv} + G_{ci}$.

In the previous calculations a value of $\Delta G = 8500$ cal/mol was used, suggested by Rudy, et. al.³, for Mo_2C . However the basis for selection of this value was not too sound, and in later work the effect of varying

ΔG was investigated. Values of the partial molar enthalpies, entropies, and free energies of C, $\Delta\bar{H}_C^\alpha$, $\Delta\bar{S}_C^\alpha$, and $\Delta\bar{G}_C^\alpha$ were calculated for ΔG assumed from 500 - 50,000 cal/mol. As exemplified by the data for the Mo - C solutions, shown in Fig. 1, it appeared that the calculated thermodynamic properties were not seriously dependent on the magnitude of ΔG . The values of the thermodynamic properties of C in the four refractory metals thus derived from the phase equilibrium diagrams are given in Table I.

Table I - Thermodynamic Properties of C in Mo, W, Cb, and Ta

System	Method 2		Method 1	
	$\Delta\bar{H}_C^\alpha$ (Kcal/mol)	$\Delta\bar{S}_{VC}^\alpha$ (cal mol ⁻¹ dgr ⁻¹)	$\Delta\bar{H}_C^\alpha$ (Kcal/mol)	$\Delta\bar{S}_{CV}^\alpha$ (cal mol)
Mo-C	29.6 - 31.9	8.5 - 10.4	30.4	7.2
W-C	21.6 - 24.5	-0.3 - 1.5	21.1	-1.8
Cb-C	-7.3 - -9.3	7.8 - 10.1	-9.6	7.3
Ta-C < 2000°K	-2.2 - -4.5	10.5 - 12.8	-4.5	9.8
Ta-C > 2000°K	-17.5 - -20.3	2.9 - 4.8	-18.5	2.6

Method 2 is the method just discussed, which takes into account the deviation from stoichiometry of the subcarbides. The range of values presented corresponds to varying ΔG from 500 - 50,000 cal/mol. Method 1 is a slightly modified version of the simple method suggested by Swalin⁴, which neglects variations in the composition of the subcarbides. It is obvious that allowing for non-stoichiometry of the subcarbides produces a minor correction in the calculated results, leading to slightly increased values of both the heat of solution, $\Delta\bar{H}_C^\alpha$, and the vibrational entropy, $\Delta\bar{S}_{VC}^\alpha$.

The values in Table I may be considered the final values of the thermodynamic properties of C in the refractory metals, as calculated from the phase diagrams.

B. Metal-oxygen and metal-nitrogen systems: In order to apply the above methods of calculation to the oxygen and nitrogen containing interstitial solutions, data have been assembled concerning phase diagrams of the gas-metal systems, and free energies of formation of the suboxides and subnitrides. In addition, considerable information is available about the equilibrium of solid phases in these systems with gaseous O_2 and N_2 , so it is clear that a meaningful analysis of the thermodynamic properties of most of the terminal solid solutions can be carried out. This analysis is now in progress, and the results will be reported at a later date.

III. THEORY OF INTERSTITIAL SOLUTIONS

Interpretation of thermodynamic properties is considerably aided by an understanding of the atomic interactions which underlie the thermochemical behavior of substances. For this reason a phase of the project is devoted to an attempt to analyze the thermodynamic properties of interstitial solutions in atomistic terms. Some of the factors which come into question are the size, location, and distribution of the interstitial atoms in solution, the distortion of the host lattice by the interstitials, and the nature of bonding between the interstitial and metal atoms.

As previously mentioned, these problems can be approached by considering the interaction between the interstitial atom and metal lattice to consist of separate "chemical" and "elastic distortion" factors, and to treat the "distortion" or "misfit" factor by continuum elasticity theory. This approach

has been pursued at length for all systems of concern, and the results for the carbon-metal systems will be presented at this time.

It may be mentioned that elasticity theory has been applied in the past to calculation of the size and distortional energy of atoms in substitutional solid solution⁵, but the equations derived for this case require modification before they can be applied to interstitial solutions, due to the often more drastic misfit between interstitial atom and interstitial site. When the higher degree of misfit has been taken into account, the misfit free energy, ΔG_s , and the misfit entropy, ΔS_s , become

$$\Delta G_s = 2\pi N_0 \left\{ 4\mu_m (\gamma_f - \gamma_c)^2 (2/3\gamma_f + 1/3\gamma_c) + 3K_i (\gamma_f - \gamma_i)^2 (2/3\gamma_f + 1/3\gamma_i) \right\}$$

$$\Delta S_s = 2\pi N_0 \left\{ 4(2/3\gamma_f + 1/3\gamma_c) (\gamma_f - \gamma_c)^2 \frac{d\mu_m}{dT} + 3(2/3\gamma_f + 1/3\gamma_i) (\gamma_f - \gamma_i)^2 \frac{dK_i}{dT} \right\}$$

and the radius of the compressed interstitial atom, γ_f , is given by

$$\frac{\gamma_i - \gamma_f}{\gamma_f - \gamma_c} = \frac{4\mu_m}{3K_i}$$

In these equations γ_i and K_i are the initial radius and effective bulk modulus of the interstitial atom, γ_c and μ_m the initial radius of the interstitial site in the metal, and the shear modulus of the metal, and γ_f the final radius of the compressed interstitial atom as well as the expanded interstitial site. These equations lead to values of misfit enthalpies, entropies, free energies and final radii for C in the octahedral interstitial sites, as given below.

Table 2 - Theoretical Misfit Energies, Entropies,
and Sizes of C in Solution at 2000°C

System	$\Delta\bar{G}_C^\alpha$ (cal/mol)	$\Delta\bar{S}_C^\alpha$ (cal mol ⁻¹ dgr ⁻¹)	$\Delta\bar{H}_C^\alpha$ (cal/mol)	γ_f (A°)
Mo - C	40,700	8.02	58,900	.670
W - C	48,300	7.15	64,600	.651
Cb - C	11,800	5.16	23,500	.742
Ta - C	27,600	4.64	38,100	.710

As expected, fairly large positive values are obtained. Before comparing these to the values determined from the phase diagram, allowance must be made for the chemical interaction between the carbon and metal atoms, which adds a negative term to the total enthalpy. The magnitude of this negative term is indicated by the standard heat of formation of the carbides in these systems, and if, as an approximation, the standard heats and entropies of formation of the carbides are added to the misfit terms in Table 2, the following results are obtained for the predicted thermodynamic properties:

Table 3 - Predicted Enthalpies and Entropies
of C in Solution at 2000°C

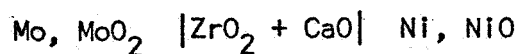
System	$\Delta\bar{H}_C^\alpha$ (cal/mol)	$\Delta\bar{S}_C^\alpha$ (cal mol ⁻¹ degree ⁻¹)
Mo - C	29,000	9.8
W - C	42,000	8.4
Cb - C	-34,800	6.2
Ta - C	-17,400	5.7

There is a striking agreement for the Mo - C and Ta - C systems between the predicted properties in Table 3 and those calculated from the phase diagrams in Table 1, but the values for the Cb - C and W - C systems appear somewhat out of line. Possible errors in the elevated temperature elastic constants, or in the location of the solvus lines are the most likely causes for these discrepancies.

Similar calculations have been completed for the oxygen-metal and nitrogen-metal systems, which will be discussed at a later date, when analysis of these systems has been completed.

IV. EXPERIMENTAL STUDIES

It would be highly desirable to supplement calculation of the thermodynamic properties from the phase equilibrium diagrams by direct measurement, where possible, and therefore attention is being given to experimental techniques for the determination of thermodynamic properties in these systems at high temperatures. Since the emf method has been successfully used in the past for such purposes, an electrolytic cell using CaO doped ZrO_2 as an electrolyte was constructed. Details of the apparatus and experimental technique have been given in a previous report⁶. In the present report period this apparatus was used to re-determine the free energy of formation of MoO_2 , using the cell



The cell operated satisfactorily at temperatures up to about 1100°C, and reproducible values of emf vs. temperature could be obtained, as shown in Fig. 2. At higher temperatures the cell potential decreased steadily.

with time, and it was evident that side reactions were interfering with the operation of the cell. Even below 1100°C it was found necessary to isolate the electrodes from each other, in order to prevent the transport of material from one side of the cell to the other through the vapor phase, but once this was done the cell voltages were stable for extended periods of time, e.g. one hour at 1035°C , and eight hours at 900°C .

Values of the standard free energy of formation of MoO_2 from the present study are compared with those of other workers in Fig. 3, and it may be seen that the agreement of our data with that of Gokcen, and Gleiser and Chipman, is good, and actually better than that of Barbi⁸, who used a similar technique. There is no doubt that the electrolytic cell is a useful instrument for the determination of thermodynamic properties. However it appears that extension of its range of usefulness to very high temperatures for these systems might entail serious difficulties, due to the volatility and reactivity of the compounds involved. For this reason attention is being given to the use of gas equilibration methods, and a sensitive thermogravimetric unit has been ordered for exploration of such methods.

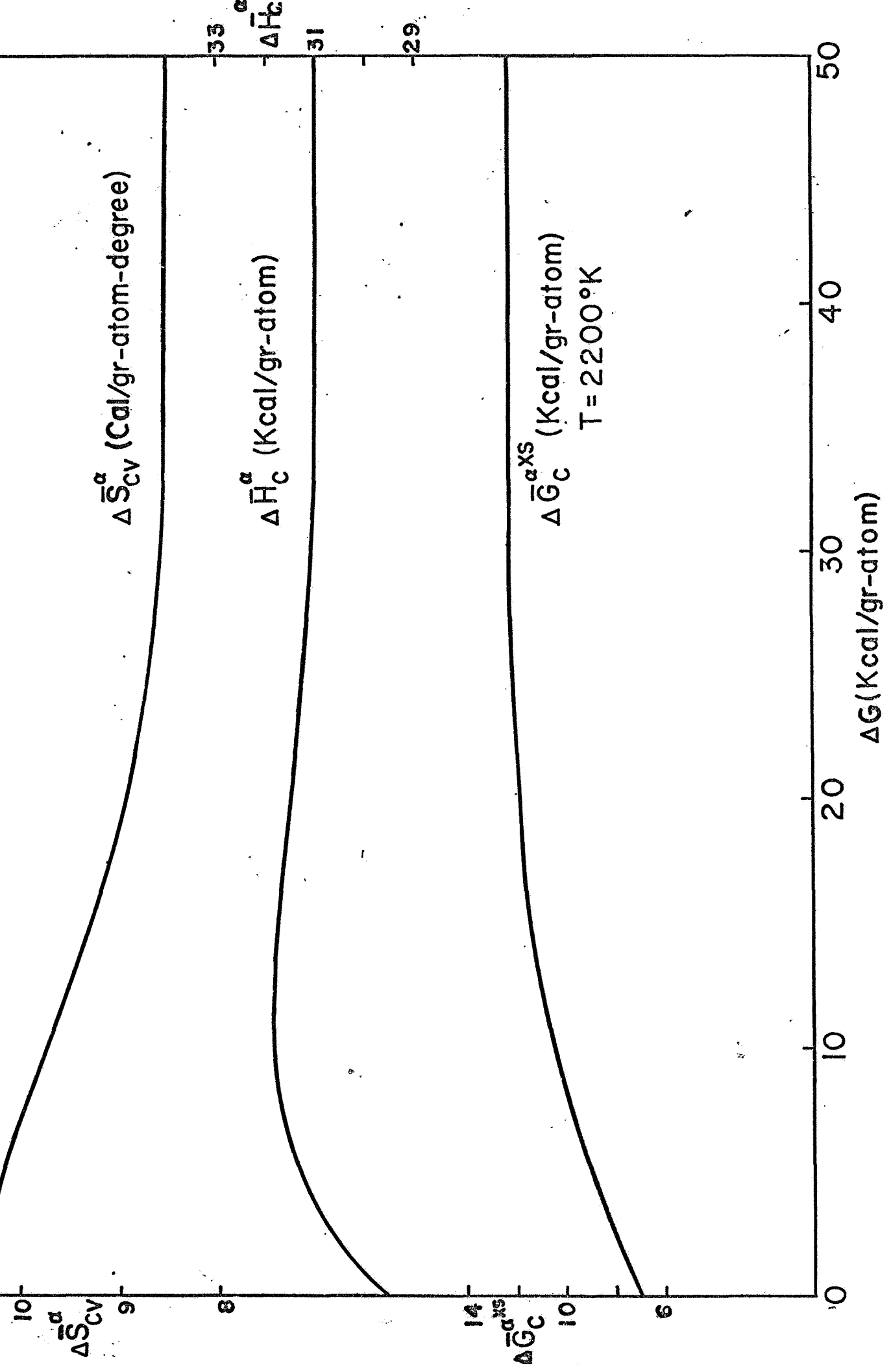
V. FUTURE WORK

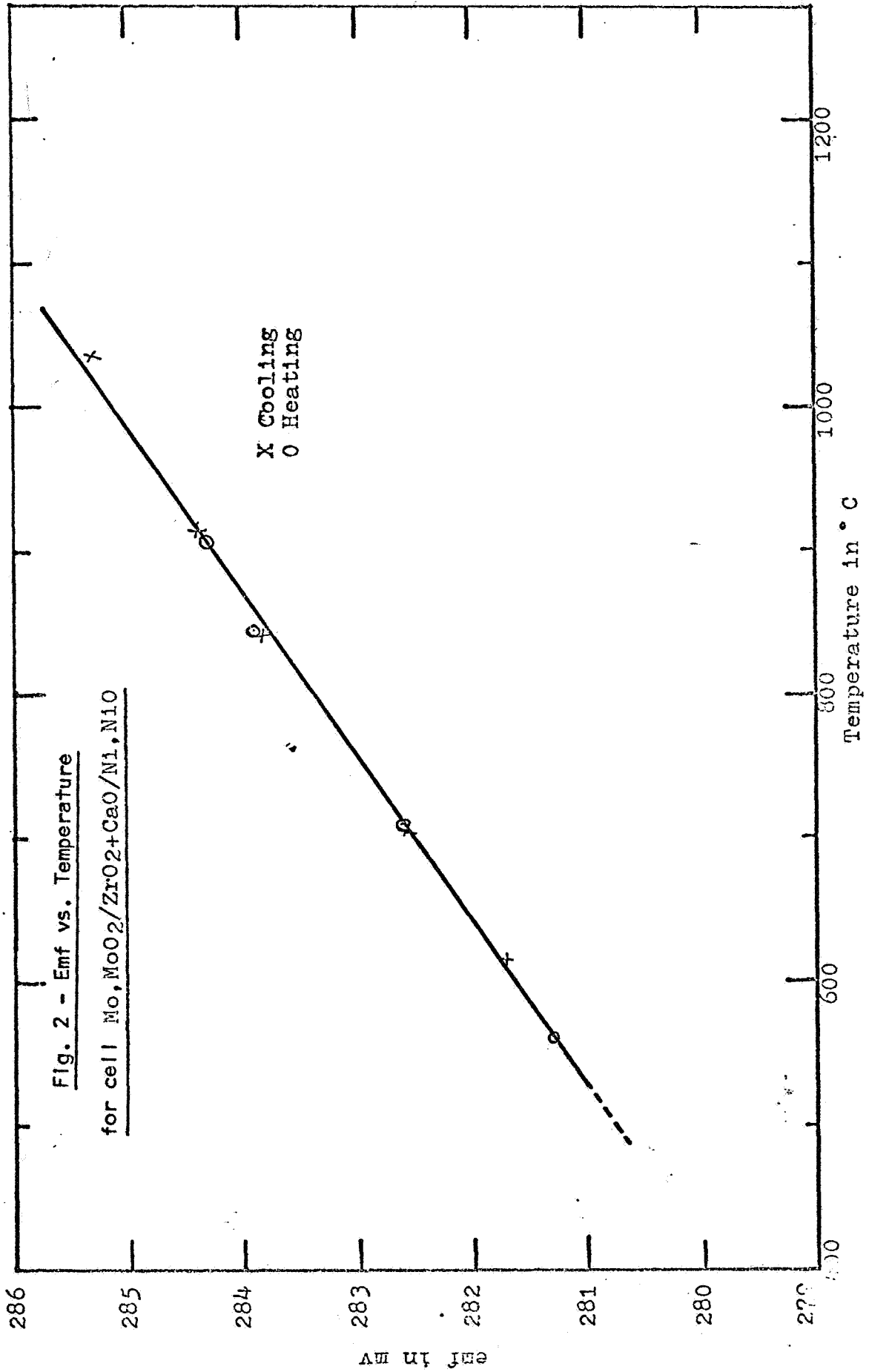
Major effort will be devoted in the immediate future to completing the analysis of the thermodynamic properties of oxygen and nitrogen in the four refractory metals based upon available gas equilibrium as well as phase diagram data. Methods for treating the theory of interstitial solutions will also be extended to these binary systems.

The feasibility of using the galvanic cell method for determination of the thermodynamic properties of oxygen in Cb, Ta, and W will be explored. In addition it is proposed to set up apparatus for the study of gas-solid equilibria. Particularly, the use of a thermogravimetric technique is being considered for this purpose, and equipment has recently been ordered.

Efforts will also continue to improve the theory of interstitial solutions. A more detailed analysis of the atom displacements in the immediate vicinity of the interstitial atom would help, it is felt, in distinguishing between occupancy of the octahedral vs. the tetrahedral site in the bcc structures. Such treatments have been developed, for example, by Johnson¹². Better methods of dealing with the "chemical" factor in the interaction energy are also needed.

FIG. 1 $\Delta \bar{H}_C^\alpha$, $\Delta \bar{S}_{CV}^\alpha$ & $\Delta \bar{G}_C^{\alpha XS}$ vs. ΔG FOR Mo-C SYSTEM.





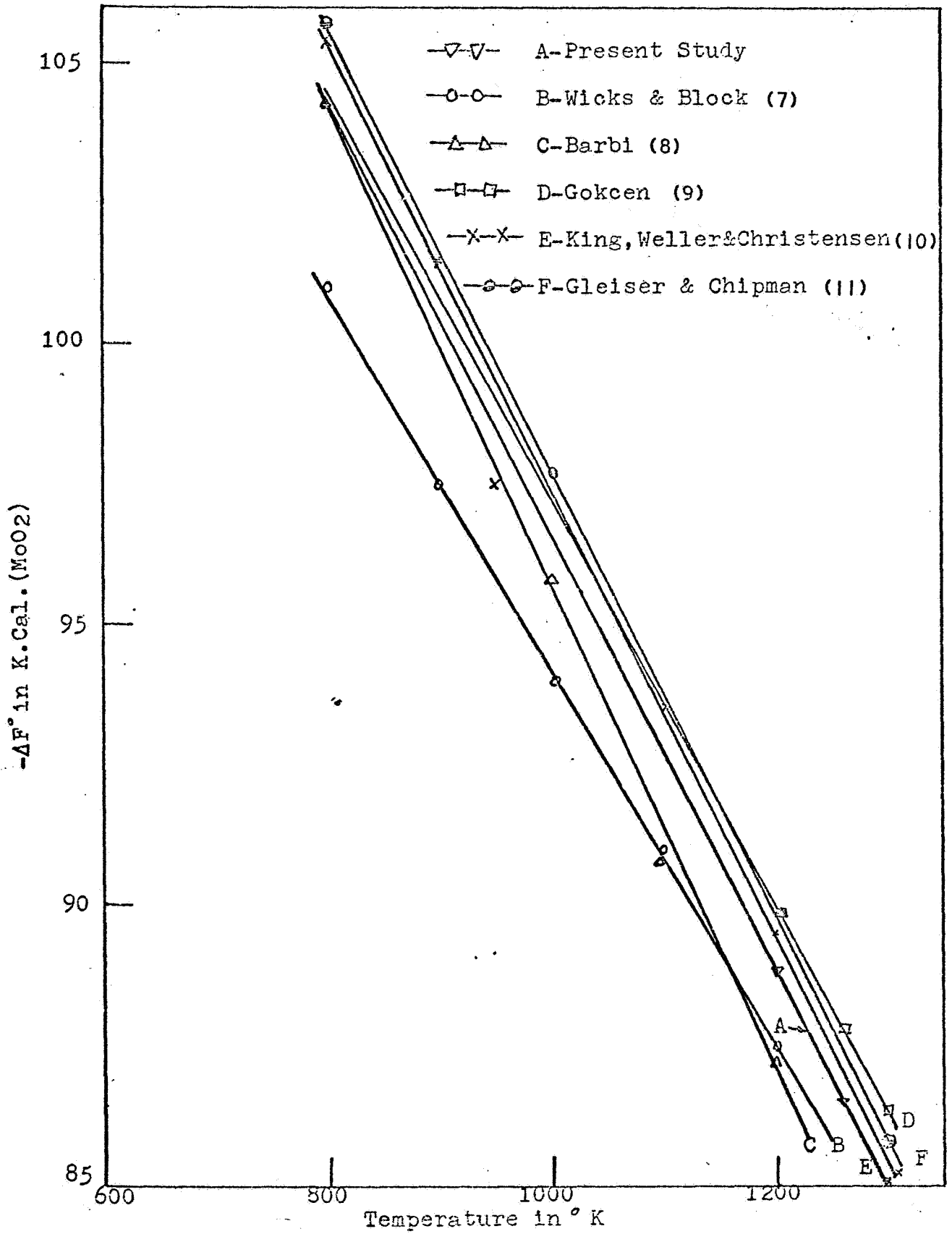


Fig. 3

ΔG° for MoO_2

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