

N 69 34914
NASA CR 104092

STATE UNIVERSITY OF NEW YORK AT STONY BROOK

COLLEGE OF
ENGINEERING

CASE FILE
COPY

THERMODYNAMIC PROPERTIES OF INTERSTITIAL
ELEMENTS IN THE REFRACTORY METALS

by

D. K. Gupta, S. C. Srivastava, and L. Seigle

Sixth semiannual report

December 1, 1968 - May 31, 1969

NASA Research Grant NGR-33-015-035

STATE UNIVERSITY OF NEW YORK AT STONY BROOK

THERMODYNAMIC PROPERTIES OF INTERSTITIAL ELEMENTS
IN THE REFRACTORY METALS

D. K. Gupta, S. C. Srivastava, and L. Seigle

Sixth semiannual report, December 1, 1968 - May 31, 1969

NASA Research Grant NGR-33-015-035

TABLE OF CONTENTS

Abstract	
I. Introduction	1
II. Experimental Measurement of the Activity of Carbon in the Refractory Metals	1
III. Conclusions	11
References	14

ABSTRACT

Experimental methods for determination of the activity of carbon in the refractory metals are reviewed and analyzed. The activity of C in Mo and W may be determined by several techniques, among which determination of the calcium vapor pressure over mixtures of Me, Me₂ C, and Ca C₂ appears most promising. Measurement of the CO pressure over mixtures of Me + C, and Me O offers a possibility for determining the activity of C in Nb and Ta at high temperatures.

I. INTRODUCTION

In the initial phases of this project, effort has been concentrated on deriving a set of thermodynamic properties for C, O, and N dissolved interstitially in Mo, W, Nb, and Ta by analysis of existing phase equilibrium diagrams and other data. Although a few details of these calculations remain to be finished, it is clear that additional experimental data are required in order to obtain a complete and accurate picture of the thermodynamic behavior of the interstitial elements in the refractory metals. The shortcomings and gaps in existing information were discussed in the last progress report⁽¹⁾ and suggestions for the direction of further experimental work offered. In the latest report period, the feasibility of certain experimental approaches has been studied more closely, and the results of this study are given in the following.

II. EXPERIMENTAL MEASUREMENT OF THE ACTIVITY OF CARBON IN THE REFRACTORY METALS

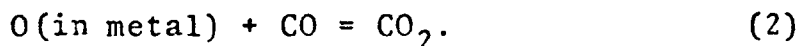
As mentioned in the last progress report⁽¹⁾, there are gaps in the available data for almost all of the carbon-metal systems which make these logical candidates for experimental investigation. Particularly, the free energies of formation of the lower carbides of W, Nb, and Ta have not been accurately

measured, which introduces an uncertainty in the values of thermodynamic properties of C in the terminal solid solutions as calculated from the phase diagrams. Attention has initially been given, therefore, to experimental methods for C in the refractory metals.

A. Gas Equilibration Methods: The free energy of formation of Mo_2C has been determined by Gleiser and Chipman⁽²⁾ by the equilibration of a mixture of Mo, Mo_2C , and MoO_2 with an atmosphere of CO and CO_2 . The same method can be applied in principle to the determination of the activity of C in solution in the metal according to the reaction



The oxygen equilibrium must be simultaneously satisfied,



It is evident that the maximum values which the activities of C and O can assume are those above which the lower carbide or oxide will form. The gas pressures and compositions in equilibrium with the carbide and oxide simultaneously, therefore, represent limiting pressures and compositions whose values may be used to judge the feasibility of using CO - CO_2 mixtures to determine the activities of C in solution. Since the terminal solubilities are quite low, these values may be calculated from known or estimated free energies of formation of the respective carbides and oxides, and free energies of

TABLE 1: LIMITING VALUES OF CO-CO₂ PRESSURES AND RATIOS
OVER METAL-CARBON SYSTEMS

Temp. °K	Molybdenum		Tungsten		Columbium		Tantalum	
	P _{co} (atm)	P _{co2} /P _{co}	P _{co}	P _{co2} /P _{co}	P _{co}	P _{co2} /P _{co}	P _{co}	P _{co2} /P _{co}
1000	1.2 x 10 ⁻³	0.35	1.3 x 10 ⁻²	0.39	1.1x10 ⁻¹⁷	1.3 x 10 ⁻⁷	5.1 x 10 ⁻¹⁷	3.2 x 10 ⁻⁷
1100	1.4 x 10 ⁻²	0.38	9.3 x 10 ⁻²	0.41	1.6x10 ⁻¹⁵	5.3 x 10 ⁻⁷	1.2 x 10 ⁻¹⁴	1.2 x 10 ⁻⁶
1200	9.8 x 10 ⁻²	0.39	0.80	0.43	1.4x10 ⁻¹³	1.7 x 10 ⁻⁶	1.1 x 10 ⁻¹²	4.4 x 10 ⁻⁶
1300	5.5 x 10 ⁻¹	0.41	3.8	0.45	6.5x10 ⁻¹²	4.4 x 10 ⁻⁶	3.5 x 10 ⁻¹¹	8.7 x 10 ⁻⁶
1400	2.0	0.43	14.4	0.47	1.7x10 ⁻¹⁰	1.0 x 10 ⁻⁵	8.1 x 10 ⁻¹⁰	1.9 x 10 ⁻⁵
1500	6.9	0.45	45.7	0.48	3.6x10 ⁻⁹	2.6 x 10 ⁻⁵	1.2 x 10 ⁻⁸	3.8 x 10 ⁻⁵
1600	20	0.46	126	0.49	3.8x10 ⁻⁸	4.4 x 10 ⁻⁵	1.3 x 10 ⁻⁷	6.9 x 10 ⁻⁵
1700	52	0.47	306	0.50	3.9x10 ⁻⁷	8.9 x 10 ⁻⁵	1.1 x 10 ⁻⁶	1.2 x 10 ⁻⁴
1800	123	0.48	623	0.51	2.8x10 ⁻⁶	1.5 x 10 ⁻⁴	7.0 x 10 ⁻⁶	1.9 x 10 ⁻⁴
1900	265	0.49	1465	0.52	1.6x10 ⁻⁵	2.4 x 10 ⁻⁴	3.9 x 10 ⁻⁵	3.0 x 10 ⁻⁴
2000	526	0.50	3262	0.53	7.7x10 ⁻⁵	3.7 x 10 ⁻⁴	1.7 x 10 ⁻⁴	4.2 x 10 ⁻⁴
2100	958	0.53			3.9x10 ⁻⁴	4.0 x 10 ⁻⁴	6.4 x 10 ⁻⁴	5.8 x 10 ⁻⁴
2200	1680	0.54			8.9x10 ⁻⁴	5.6 x 10 ⁻⁴	2.2 x 10 ⁻³	7.9 x 10 ⁻⁴
2300	2820	0.54			2.6x10 ⁻³	7.5 x 10 ⁻⁴	6.7 x 10 ⁻³	1.0 x 10 ⁻³

formation of CO and CO₂.

$$\text{Me}_2\text{C} + \text{CO}_2 = 2\text{Me} + 2\text{CO}$$

$$K_3 = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \exp\left(-\frac{\Delta G_3^\circ}{RT}\right) \quad (3)$$

$$\text{MeO}_n + n\text{CO} = \text{Me} + n\text{CO}_2$$

$$K_4 = \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}}\right)^n = \exp\left(-\frac{\Delta G_4^\circ}{RT}\right)$$

$$\text{or } \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \exp\left(-\frac{\Delta G_4^\circ}{nRT}\right) \quad (4)$$

The simultaneous solution of equations (3) and (4) give the required limiting pressures and compositions, and these are tabulated for the various systems in Table 1, as calculated using values of the free energies of formation of the lower carbides and oxides given in previous progress reports⁽³⁾ in order to obtain ΔG_3° and ΔG_4° .

It is evident that equilibration with CO + CO₂ might be feasible for the Mo-C and W-C systems over the range of temperatures, approximately 1200-1600°K. For the Nb-C and Ta-C systems, the critical CO₂/CO ratios as well as the CO pressures are low over most of the temperature range. The gas in equilibrium with a mixture of Nb + C in solution, and NbO would be almost pure CO. A determination of the total pressure over such a mixture should therefore suffice, knowing the free energy of formation of NbO, to ascertain the C activity. The CO pressures above 1700°K are in a

range where they might be determined using an effusion method.

A problem with the use of CO-CO₂ mixtures is the tendency of the refractory metals to form oxy-carbides of variable composition. This introduces a degree of error whose estimation is difficult because of the lack of detailed information about the mutual solubility of the oxides and carbides.

A second gas equilibration method which it is obvious to consider is equilibration with H₂-CH₄ mixtures. Since hydrides do not form at hydrogen pressures below one atm. in the systems of concern, the critical CH₄/H₂ ratio may be calculated from the following equation, assuming that the total pressure is one atmosphere.

$$\text{Me}_2\text{C} + 2\text{H}_2 = \text{Me} + \text{CH}_4$$

$$K_5 = \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2} = \exp \left(-\frac{\Delta G_5^{\circ}}{RT} \right)$$

Using a value of ΔG_5° obtained from the free energy of formation of methane, and previously given values of the free energy of formation of the lower carbides⁽³⁾, the following values of the critical $P_{\text{CH}_4}/P_{\text{H}_2}^2$ ratios are obtained.

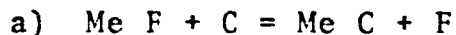
TABLE 2: LIMITING VALUES OF CH₄-H₂ RATIOS OVER
METAL-CARBON SYSTEMS

Temp. °K	$P_{\text{CH}_4}/P_{\text{H}_2}^2$ (Total Pressure = 1 atm.)			
	Mo	W	Cb	Ta
1000	2.2×10^{-4}	2.2×10^{-3}	5.4×10^{-12}	9.9×10^{-12}
1100	1.3×10^{-4}	1.1×10^{-3}	1.1×10^{-11}	3.6×10^{-11}
1200	8.4×10^{-5}	5.8×10^{-4}	2.7×10^{-11}	8.2×10^{-11}
1300	5.4×10^{-5}	3.3×10^{-4}	5.9×10^{-11}	1.6×10^{-10}
1400	3.2×10^{-5}	2.1×10^{-4}	1.1×10^{-10}	2.8×10^{-10}
1500	2.2×10^{-5}	1.3×10^{-4}	1.9×10^{-10}	4.6×10^{-10}
1600	1.6×10^{-5}	9.1×10^{-5}	3.1×10^{-10}	6.8×10^{-10}
1700	1.2×10^{-5}	6.4×10^{-5}	4.5×10^{-10}	9.7×10^{-10}
1800	9.0×10^{-6}	4.7×10^{-5}	6.4×10^{-10}	1.3×10^{-9}
1900	9.5×10^{-6}	4.7×10^{-5}	1.2×10^{-9}	2.3×10^{-9}
2000	5.6×10^{-6}	2.6×10^{-5}	1.1×10^{-9}	2.1×10^{-9}
2100	4.5×10^{-6}	2.1×10^{-5}	1.5×10^{-9}	2.6×10^{-9}
2200	3.7×10^{-6}	1.6×10^{-5}	1.8×10^{-9}	3.1×10^{-9}
2300	3.1×10^{-6}	1.3×10^{-5}	2.2×10^{-9}	3.6×10^{-9}

For the C-Mo, and C-W systems these values while low are still measurable, while the ratios are too low to make this method feasible for the C-Nb and C-Ta systems. Ellis, et. al.⁽⁴⁾, have pointed out the danger of experimental error arising from the use of CH₄-H₂ mixtures at low ratios of P_{CH₄} : P_{H₂}, due to traces of moisture in the atmosphere. Possible solution of hydrogen in Mo₂C and W₂C might also be a cause of error.

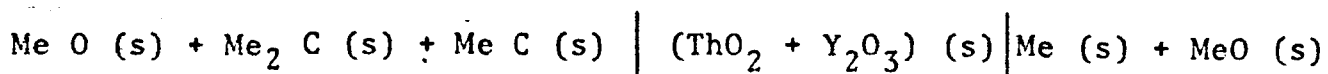
(5)

B. Galvanic Cell Method: Egan and Aronson have used cells of the type C (s) + Me C (s) + Me F (s) | Ca F₂ (s) | Me (s) + Me F (s) to determine the free energies of formation of thorium carbides. The transfer of fluorine is equivalent to the reactions:



A limitation to the use of this type of cell is imposed by the melting points of the halides, about 1050°C in the case of Th F₄. The melting points of the refractory metal halides appear to be much lower than 1050°C, however. For example, NbF₅ melts at 78°C, MoF₅ at 67°C, W F₄ at 281°C, and TaF₅ at 220°C.

An analogous cell which overcomes this objection and might be considered is:



The overall cell reaction produced by the transfer of oxygen is:



Hence the free energy of formation of $\text{Me}_2 \text{ C}$ could be obtained from the emf of a cell of this type, if the free energy of formation of MeC were known. Such a cell is feasible only if the $\text{CO} + \text{CO}_2$ pressure over the left electrode is low enough to be easily contained, and values of such pressures for the various systems are as follows:

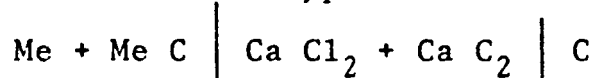
TABLE 4: CO PRESSURES OVER MIXTURES OF
Me O, Me₂ C, and Me C

Temp. °U	CO Pressure (atm)		
	W	Nb	Ta
1000	8.1×10^6	5.5×10^{-8}	1.2×10^{-8}
1200	---	3.3×10^{-5}	6.6×10^{-6}
1400	---	3.1×10^{-3}	1.6×10^{-3}
1600	---	0.96	6.5×10^{-2}
1800	---	38.0	5.1×10^{-1}
2000	---	---	1.6
2200	1.1×10^9	---	74.0

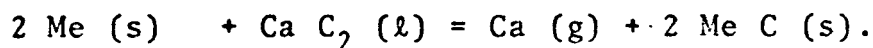
It is clear that the method is not feasible for the W and undoubtedly also the Mo-C systems but might be practical for the Nb and Ta-C systems up to about 1600-1800°K.

Another possible emf method, suggested by the recent work of Hawkes and Morris ⁽⁶⁾, is the use of galvanic cells utilizing fused salt solutions containing Ca C_2 as the electrolyte. Electrolytic conduction via the $\text{C}_2^=$ acetylide ion occurs in such electrolytes, and a cell of this type was used successfully to determine the activity of carbon in austenite up to 1000°C . With suitable choice of fused salt it is possible that such cells could be used at even higher temperatures.

In a cell of the type:



a possible side reaction is:



The severity of this reaction may be judged from the data of Table 5, which gives the Ca (g) pressures over a mixture of metal, metal carbide, and calcium carbide. It is obvious that this side reaction would be very serious and probably preclude the use of cells in which elemental Nb or Ta were in contact with Ca C_2 in any form. such cells with Mo or W might be feasible, however, up to quite high temperatures.

C. Other Methods: Komareck and associates ⁽⁷⁾ have determined the activities of oxygen in Ti, Zr, and Hf by equilibrating samples with Mg O (s) and Mg (g) in a gradient furnace. This suggests determination of the activities of carbon in the refractory metals by equilibration with $\text{Ca C}_2 (\text{s})$

and Ca (g). The feasibility of the method depends upon the magnitude of calcium vapor pressures developed. Limiting values of these vapor pressures may be estimated from the free energies of formation of Ca C₂ and the refractory metal subcarbides. The pertinent equations are:



$$K = P_{\text{Ca}} = \exp \left(- \frac{\Delta G_8^{\circ}}{RT} \right) \quad (8)$$

Values of Ca Pressures over mixtures of metal, metal carbide, and calcium carbide, as well as Ba pressures over mixtures of metal, metal carbide, and barium carbide, calculated as indicated above, are given in Table 4. The Ca and, without a doubt, also the Ba pressures over the Nb and Ta systems are much too high for this to be a feasible method for C in Nb or Ta. However, the Ca and Ba pressures over the Mo and W systems are reasonable over much of the temperature scale.

As a final possibility, the effusion method may be mentioned as a technique for measuring the vapor pressures of carbon and/or metal at very high temperatures in these metal-carbon systems. This technique has been used to study the thermodynamic properties of a number of refractory metal carbides, as reviewed by Storms⁽⁸⁾. The details of the method depend upon the system under consideration, since evaporation of metal as well as carbon occurs.

TABLE 5: VAPOR PRESSURES OF Ca AND Ba OVER MIXTURES OF METAL, Me_2C , AND CaC_2 OR BaC_2

Temp. °K	Pressure, atm.					
	Mo		W		Nb	Ta
	P_{Ca}	P_{Ba}	P_{Ca}	P_{Ba}	P_{Ca}	P_{Ca}
1000	3.2×10^{-3}	1.5×10^{-4}	3.1×10^{-5}	1.5×10^{-6}	5.7×10^{12}	1.1×10^{11}
1200	3.3×10^{-2}	---	6.5×10^{-4}	---	3.0×10^{11}	3.2×10^9
1300	---	9.2×10^{-3}	---	2.4×10^{-4}	---	---
1400	2.6×10^{-1}	---	5.7×10^{-3}	---	2.0×10^{10}	3.1×10^8
1600	9.8×10^{-1}	1.9×10^{-1}	3.0×10^{-2}	5.6×10^{-3}	2.7×10^9	5.3×10^7
1800	2.8	---	1.1×10^{-1}	---	5.7×10^8	1.4×10^7
1900	---	1.2	---	4.8×10^{-2}	---	---
2000	6.6	---	3.0×10^{-1}	---	1.7×10^8	4.6×10^6
2200	13.1	4.5	6.8×10^{-1}	2.1×10^{-1}	5.5×10^7	1.9×10^6
2300	17.6	---	9.8×10^{-1}	---	3.5×10^7	4.8×10^5

Due to the low carbon concentrations and high temperatures involved, it was felt that the effusion method might be difficult to put into effect for our purposes, and it has not been given serious consideration at this point.

III. CONCLUSIONS

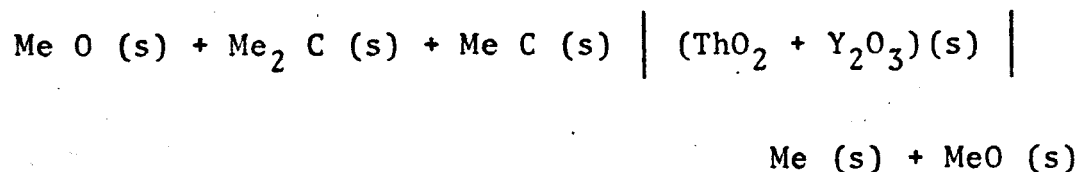
It is evident that there is a variety of possibilities for the experimental determination of the thermodynamic properties of C in these systems, certain techniques being

more suitable for some systems than others. For C in Mo or W, equilibration with mixtures of CO_2 and CO appears feasible up to about 1600°K . A disadvantage of this method under certain circumstances, is the known solubility of oxygen in the metal carbides. Equilibration with CH_4/H_2 mixtures appears also to be a possibility for the Mo-C and W-C systems at lower temperatures, although the CH_4 concentrations are quite low. Again, the emf method using fused salt solutions containing Ca C_2 is theoretically feasible for investigations of C activities in the Mo-C and W-C systems at temperatures in the vicinity of 1000°C . Finally, equilibration of mixtures of metal, metal carbide, calcium (barium) carbide, with gaseous calcium (barium) might be a useful technique in these two systems over a wide temperature range.

It is felt at this time that there are some points in favor of the latter technique. The solubility of Ca or Ba in Mo and W and their carbides is probably very low. The free energies of formation of Ca C_2 and Ba C_2 have recently been accurately determined by measurement of Ca or Ba vapor pressures over the carbide⁽⁹⁾ (10). It is felt that a measurement of the Ca or Ba vapor pressure over a mixture of Me, Me_2C , and $(\text{Ca or Ba})_2\text{C}$ would, in view of the fact that the solubilities of C in Mo and W are very low, permit an accurate determination of the activity of C in the terminal solutions at the compositions of the solvus lines.

These measurements would in addition provide an interesting check of the data of Gleiser and Chipman⁽²⁾ for the free energy of formation of Mo_2C , where the presence of oxygen in the system introduced an uncertainty. Techniques for measurement of the Ca or Ba vapor pressures are being examined, in further exploration of this possibility.

In the Nb-C and Ta-C systems, the measurement of CO pressures over mixtures of $\text{Me} + \text{C}$ and Me O_n offer a possibility of determining C activities at higher temperatures in view of the fact that the free energies of formation of NbO and Ta_2O_5 are well known. The appreciable solubility of oxygen in the terminal solid solutions would introduce an uncertainty into the accuracy of this method. Some assistance in determination of the free energies of formation of Nb and Ta subcarbides might be obtained by the emf method using a solid Th O_2 electrolyte, as previously mentioned, although the variable composition of these carbides would introduce complications into the interpretation of data from a cell of the type discussed, namely:



The possibilities here are still being appraised.

In the future, experimental methods for the oxygen-metal systems will also be carefully studied, since further data are required for particularly the Mo-O and W-O solutions.

REFERENCES

1. S. C. Srivastava and L. Seigle, Fifth semiannual report, 6/1/68 - 12/1/68, NASA Grant NGR - 33-015-035.
2. M. Gleiser, J. Chipman, J. Phys. Chem. 66, (1962) 1539.
3. See particularly R. Singh and L. Seigle, First semi-annual report 6/1/66 - 12/1/66, and the Fifth semi-annual report (ref. 1), under NASA Grant NGR-33-015-035.
4. T. Ellis, I. M. Davidson, and C. Bodsworth, J. Iron and Steel Inst. 201 (1963) 582.
5. Egon and S. Aronson, "Nuclear Metallurgy" Vol. 10 p. 255, AIME-IMD Special Report #13 (1964).
6. G. L. Hawkes, and D. R. Morris, Tr. AIME, 242 (1968)1083.
7. M. D. Silver, P. A. Farrar, K. L. Komarek, TR. AIME, 227 (1963) 876.
8. E. K. Storms, "The Refractory Carbides" Academic Press, New York, (1967).
9. R. L. Faircloth, R. H. Flowers, F. C. W. Pummery, J. Inorg.Nucl. Chem. 29 (1967) 311.
10. R. H. Flowers, E. G. Rauh, J. Inorg.Nucl. Chem. 28 (1966) 1355.