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THE FREE ENERGY OF FORMATION OF NIOBIUM DIOXIDE BETWEEN 1100 AND 1700° K

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The Free Energy of Formation of Niobium Dioxide between 1100 and 1700°K.[1]

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The free energy of formation of NbO_2 has been determined by measuring the carbon monoxide equilibrium pressure of reaction 1 between 1050 and 1200°K.

$$Nb_2O_5(s) + C(gr) \rightleftharpoons 2NbO_2(s) + CO(g) \quad (1)$$

Combining these results with recent thermal data[2] and with another equilibrium study[3] yields free energy of formation values for NbO_2 which are more precise than those tabulated by Elliott and Gleiser[4] and by Coughlin.[5]

To obtain an expression for the free energy of formation of NbO_2 between 1100 and 1700°K., the standard free energy change of the reaction

$$Nb_2O_5(s) \rightleftharpoons 2NbO_2(s) + 0.5O_2(g) \quad (2)$$

was calculated from the results of the three investigations.

In this study a solid pellet of NbO_2–Nb_2O_5–C was equilibrated with a carbon monoxide atmosphere at elevated temperatures. The experimental apparatus and procedures are described elsewhere.[6,7] The amount of CO (usually >94%) was determined by Orsat analysis,[8] and an X-ray diffraction pattern of the remaining pellet indicated that only the initially charged phases were present. The results are summarized in Table I, in which $\Delta F^\circ_{(1)}$ and $\Delta F^\circ_{(2)}$ are the standard free energy changes of reactions 1 and 2,

(1) This note is based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology, May, 1963. The work was supported principally by the National Science Foundation and the U. S. Atomic Energy Commission.
(2) E. G. King and A. O. Christensen, U. S. Bur. Mines Rept. Invest. 5789, U. S. Govt. Printing Office, Washington, D. C., 1961.
(3) V. I. Lavrent'ev, Y. I. Gerasimov, and T. N. Rezakhina, *Dokl. Akad. Nauk SSSR*, **136**, 1372 (1961).
(4) J. F. Elliott and M. Gleiser, "Thermochemistry of Steelmaking," Vol. I, Addison-Wesley Publishing Co., Inc., Reading, Mass., 1960.
(5) J. P. Coughlin, U. S. Bur. Mines Bull. 542, U. S. Govt. Printing Office, Washington, D. C., 1954.
(6) W. L. Worrell and J. Chipman, *J. Phys. Chem.*, **68**, 860 (1964).
(7) M. Gleiser and J. Chipman, *ibid.*, **66**, 1539 (1962).
(8) "Manual for Gas Analysis," Catalog No. 80, Burrell Technical Supply Co., Pittsburgh, Pa.

respectively; values for $\Delta F^\circ_{(2)}$ are obtained by subtracting the free energy of formation of CO(g)[4,5] from $\Delta F^\circ_{(1)}$ and are shown in Fig. 1.

Table I: Standard Free Energy Changes of Reactions 1 and 2

T, °K.	P_{CO}, mm.	$\Delta F^\circ_{(1)}$, cal.	$\Delta F^\circ_{(2)}$, cal.
1175	662	323	51,948
1143	452	1182	52,132
1074	135	3682	53,182
1090	205	2341	52,681
1172	754	25	51,585
1127	302	2062	52,682

Lavrent'ev, Gerasimov, and Rezakhina[3] have measured the steam-to-hydrogen equilibrium pressure ratios between 1473 and 1673°K. for reaction 3.

$$Nb_2O_5(s) + H_2(g) \rightleftharpoons 2NbO_2(s) + H_2O(g) \quad (3)$$

Their data for reaction 2 are shown in Fig. 1.

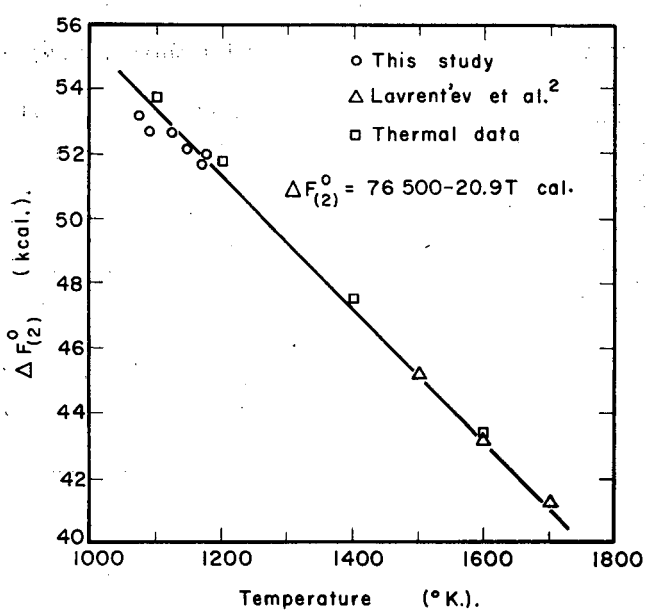

Figure 1. Standard free energy change of the reaction $Nb_2O_5(s) \rightleftharpoons 2NbO_2(s) + 0.5O_2(g)$.

The standard free energy change of reaction 2 at 298°K. can be calculated from Mah's measured heat of reaction[9] and the available entropy data.[10] Combining this value with high-temperature thermal data for Nb_2O_5,[11] $O_2(g)$,[11] and NbO_2,[2] one obtains the thermal values for the standard free energy change of reaction 2 shown in Fig. 1.

The results presented in Fig. 1 agree within the experimental uncertainties. However, the two low temperature values from this study appear not to have been at equilibrium, possibly due to the inertness of graphite below 1100°K.[12] Hence, these two values were disregarded in the subsequent calculations.

Using available thermal data,[2,10,11] one obtains 20.9 cal./deg. for the temperature variation of $\Delta F^\circ_{(2)}$ between 1100 and 1700°K. Combining this value with the results shown in Fig. 1 yields the following equation for $\Delta F^\circ_{(2)}$ between 1100 and 1700°K.

$$\Delta F^\circ_{(2)} (\pm 600) = 76{,}500 - 20.9T \text{ cal.} \quad (4)$$

With this equation and the free energy of formation values for Nb_2O_5,[4,5] one obtains the following equation for the free energy of formation of NbO_2 between 1100 and 1700°K.

$$\Delta F^\circ_{NbO_2} (\pm 500) = -185{,}600 + 38.9T \text{ cal./mole} \quad (5)$$

The uncertainty in $\Delta F^\circ_{(2)}$ was calculated by the usual method[13] of assessing the deviation of the individual points from the straight line variation shown in Fig. 1. The uncertainty in $\Delta F^\circ_{NbO_2}$ of ±500 cal. was obtained by applying the usual technique[13] for combining the independent uncertainties in $\Delta F^\circ_{(2)}$ and $\Delta F^\circ_{Nb_2O_5}$.[14]

Using eq. 5 and recent thermal data,[2] one obtains an average value of −190.7 kcal./mole for the standard heat of formation at 298°K. of NbO_2, which is in good agreement with Mah's value[9] of −190.9 (±0.4) kcal./mole determined from combustion calorimetry.

Acknowledgment. The author wishes to express his appreciation to Professor John Chipman for many helpful discussions.

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