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Estimation of the Entropy of Formation at 298°K. for Some Refractory Metal Carbides[1]

by Wayne L. Worrell

Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California
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Although their heats of formation are fairly well known, few entropies of formation at 298°K. ($\Delta S°_{298}$) of refractory metal carbides have been determined. Until such data become available, any estimation of $\Delta S°_{298}$ should be very useful. By combining the estimated $\Delta S°_{298}$ with the measured $\Delta H°_{298}$, one can obtain a free energy of formation equation for the carbide at 298°K. Because Kopp's rule ($\Delta Cp \approx 0$) is usually a good approximation for carbides,[2] this equation is also applicable at elevated temperatures.

Krikorian[3] has estimated values for $\Delta S°_{298}$ for some refractory metal carbides by correlating the entropy of formation of the carbides from the gaseous elements. In his calculations, the electronic contributions to the entropies of the gaseous atoms were neglected and only their translational entropies were considered. By comparing the results of similar calculations for the oxides and for some nitrides with the tabulated entropies of Kelley,[4] Krikorian[3] demonstrated that quite reasonable entropy values were obtained for the refractory metal carbides, nitrides, and oxides.

In 1949, Richardson[5] attempted to correlate the sign of $\Delta S°_{298}$ with the structure and melting point of the carbide. He noted that a face-centered-cubic carbide had a melting temperature significantly higher than that of its parent metal and a negative $\Delta S°_{298}$, but that a hexagonal-close-packed carbide usually melted at a comparable or lower temperature than its parent metal and had a positive $\Delta S°_{298}$.

However, further research[6] has indicated that the vanadium group metals form a hexagonal-close-packed carbide (M_2C) which melts at a higher temperature than its parent metal and probably has a negative $\Delta S°_{298}$. Although this indicates that the sign of $\Delta S°_{298}$ of a carbide probably is not linked to its crystal structure, a correlation should be possible between its melting temperature and its value for $\Delta S°_{298}$.

Recent melting point data for the titanium group, the vanadium group, and the chromium group metal–carbide systems[6] have been used to calculate t_M/t_C values where t_M and t_C are the melting points of the metal and the carbide, respectively. The melting points, the calculated t_M/t_C values, and the available entropy data[7] for these metal–carbide systems are tabulated in Table I. If the melting temperature varies with the composition of the carbide, its maximum value, which is not necessarily that at the stoichiometric composition, is tabulated. The peritectic temperature is used to calculate t_M/t_C for those carbides which peritectically decompose.

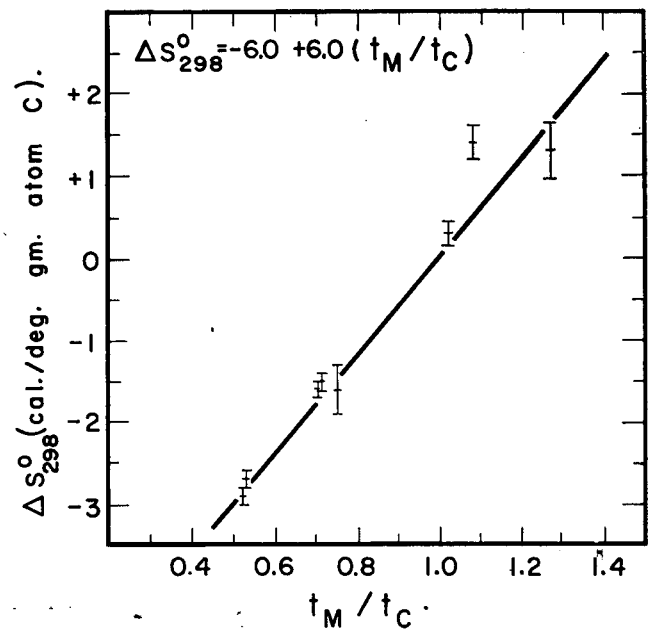

Figure 1. Variation of $\Delta S°_{298}$ with t_M/t_C for some refractory metal carbides.

A qualitative correlation between the melting point quotient (t_M/t_C) and $\Delta S°_{298}$ can be expected.[8] The main contribution to the entropy of formation

(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) O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, N. Y., 1958.

(3) O. H. Krikorian, Lawrence Radiation Lab Report UCRL-2888 1955.

(4) K. K. Kelley, U. S. Bur. Mines Bull. 477, U. S. Govt. Printing Office, Washington, D. C., 1950.

(5) F. D. Richardson, *J. Iron Steel Inst.* (London), **163**, 382 (1949).

(6) E. K. Storms, Los Alamos Scientific Lab Report LAMS-2674' 1962.

(7) K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, U. S. Govt. Printing Office, Washington, D. C., 1961.

(8) See L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, Paper 6, "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," Vol. 19 B, National Nuclear Energy Series, ed. by L. L. Quill, 1950. They have estimated entropy values for some halides by considering $S°_{298}$ to be a linear function of the melting temperature.

Table I: Melting Point Data[6] and Entropy Data[7] for Some Refractory Metal Carbides

Substance	Melting point, °C.	t_M/t_C	$\Delta S°_{298}$, cal./deg. g.-atom C
Ti	1660		
TiC (fcc)	3180	0.52	-2.9 ± 0.07
Zr	1855		
ZrC (fcc)	3480	0.53	-2.69 ± 0.1[a]
Hf	2222		
HfC (fcc)	3890	0.57	...
V	1888		
V_2C (hcp)	2165	0.87	...
VC (fcc)	2650	0.71	-1.5 ± 0.1[b]
Nb	2467		
Nb_2C (hcp)	3090	0.80	...
NbC (fcc)	3500	0.71	-1.6 ± 0.1[b]
Ta	3000		
Ta_2C (hcp)	3500	0.86	...
TaC (fcc)	4000	0.75	-1.6 ± 0.3[b]
Cr	1915		
$Cr_{23}C_6$ (fcc)	1520	1.27	1.32 ± 0.35
Cr_7C_3 (hcp)	1780	1.08	1.39 ± 0.19
Cr_3C_2 (orth)	1895	1.01	0.30 ± 0.12
Mo	2620		
Mo_2C (hcp)	2410	1.09	...
MoC (hcp)	2575	1.02	...
W	3407		
W_2C (hcp)	2800	1.22	...
WC (hcp)	2720	1.25	...

[a] Obtained from the low temperature heat capacity data of E. F. Westrum, Jr., and G. Feick reported in Tech. Doc. Rept. No. ASD-TDR-62-204, part II, May, 1963. [b] Obtained from W. L. Worrell and J. Chipman, *J. Phys. Chem.*, **68**, 860 (1964).

of the refractory metal carbides would be from vibrational effects because changes in the electronic and configurational entropies are very small. A carbon atom is more loosely bonded in the carbide than in pure graphite; hence the lattice vibrations and the vibrational entropy of a carbon atom should be greater in the carbide. However, $\Delta S°_{298}$ of a carbide is probably influenced more by the entropy changes of the metal atom because the vibrational entropy of a pure metal at 298°K. is five to seven times that of carbon.

A metal should be more rigidly bonded in a carbide whose melting point quotient (t_M/t_C) is less than one. The lattice vibrations and the vibrational entropy of the metal in this carbide would be less than that in the pure metal, and $\Delta S°_{298}$ is probably negative. A similar argument would predict a positive $\Delta S°_{298}$ for a carbide which has a lower melting point than that of its parent metal ($t_M/t_C > 1$).

The linear variation of $\Delta S°_{298}$ with the melting point quotient (t_M/t_C) is shown in Fig. 1 and can be represented by the equation

$$\Delta S°_{298} = -6.0 + 6.0(t_M/t_C) \text{ cal./deg. g.-atom of C} \quad (1)$$

This expression has been used to calculate values of $\Delta S°_{298}$ tabulated in Table II. Krikorian's estimates[3] and recommended values are also presented in Table II.

Table II: Estimated Values of $\Delta S°_{298}$ for Some Refractory Metal Carbides

Carbide	t_M/t_C	$\Delta S°_{298}$, cal./deg. g.-atom C: This study	Krikorian[3]	Recommended
HfC	0.57	-2.6	-4.0 ± 1.0	-3.0 ± 1.5
Nb_2C	0.80	-1.2	-1.0 ± 1.5	-1.0 ± 1.0
V_2C	0.87	-0.8	-2.0 ± 1.0	-1.0 ± 1.0
Ta_2C	0.86	-0.8	-0.4 ± 1.0	-0.5 ± 1.0
MoC	1.02	0.1	0.0 ± 1.0	0.0 ± 1.0
Mo_2C	1.09	0.6	2.1 ± 1.0	1.5 ± 1.0
W_2C	1.22	1.3	2.5 ± 1.5	2.0 ± 1.5
WC	1.25	1.5	0.6 ± 1.0	1.0 ± 1.0

A precision of ±100° in the melting points of the carbides would result in a variation of approximately ±10% in the calculated values of $\Delta S°_{298}$. However, because of the empirical nature of eq. 1, no quantitative estimate of the uncertainties associated with the values of $\Delta S°_{298}$ calculated in this study has been made. The uncertainties quoted for the recommended values in the last column of Table II are based arbitrarily on those of Krikorian[3] and on the agreement between his estimates and those of this study.

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