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The Thermochemistry of Transition Metal Carbides

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A general survey is made of the available data for the standard Gibbs energies of formation of solid carbides of transition metals. The results are plotted as standard Gibbs energy vs. temperature diagrams. The equations and the estimated accuracy when available are given for each substance.

KEY WORDS: standard Gibbs energy of formation; transition metal carbides; Ellingham diagrams.

INTRODUCTION

A review of the equilibrium and thermodynamic data of the transition metal carbides is presented with particular emphasis on the Gibbs energy of formation. This work reviews, updates, and extends the earlier surveys performed by Richardson[1] and Kubaschewski *et al.*,[2] and the more recent ones by Reed[3] and Wicks and Block.[4] Much of Reed's compilation of carbide thermochemical data was gathered from Richardson.[1] Data for the Gibbs energies of formation for carbides as a function of temperature are presented as Ellingham plots as shown in Figs. 1 and 2. In this paper, the Gibbs energies are normalized with respect to 1 mole of C. The general reaction considered is:

$$xM + C \rightarrow M_xC$$

For these reactions the standard states are as follows†: (1) for solid or liquid metal, a coexistence with its lowest carbide, (2) for C, a solid of unit activity, and (3) for carbides, the solid and liquid carbide in coexistence

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†Many of the existing data are based on coexistence standard states, not pure standard states.

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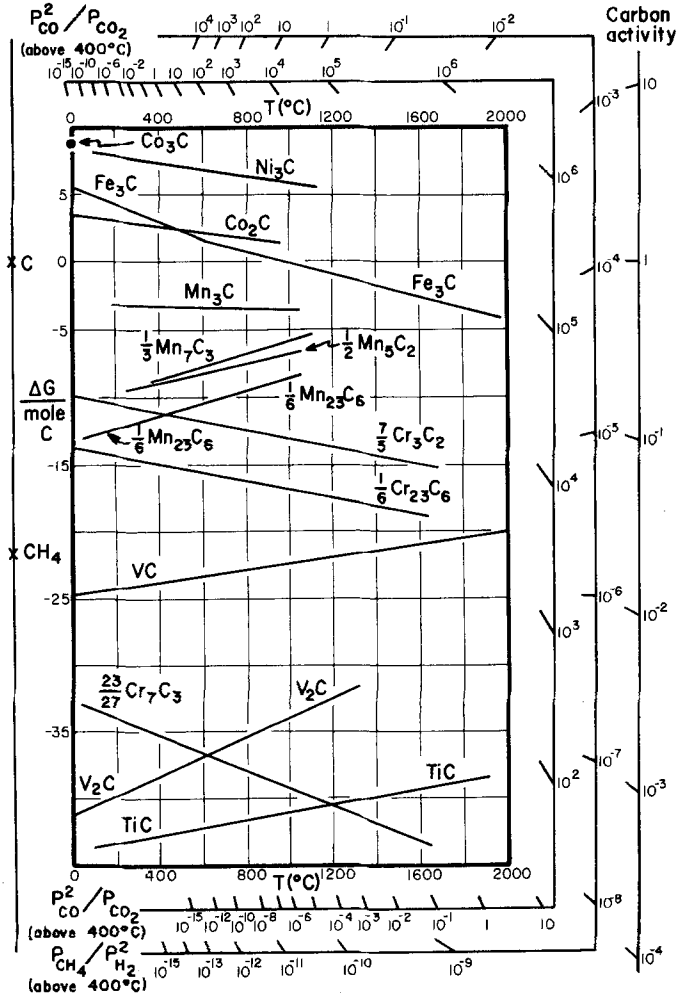

Fig. 1. Ellingham diagram for the first transition series carbides. The formation of the lowest compound formed from the metal upon reaction with 1 mole of C is denoted only by the compound M_xC. (Note: all Gibbs energy values are reported in calories and are normalized to 1 mole of carbon and since many of the existing data are based on coexistence standard states, the unit activity for the metal is the metal saturated with respect to the carbide and likewise unit activity for the carbide is the carbide saturated with its respective metal.)

equilibrium with the other condensed phase of the reaction. Many transition metals form several carbides, and an effort is made to report their existence and stabilities. Examination of the available phase diagrams notes the large deviation from stoichiometry of many of the transition metal carbides. An

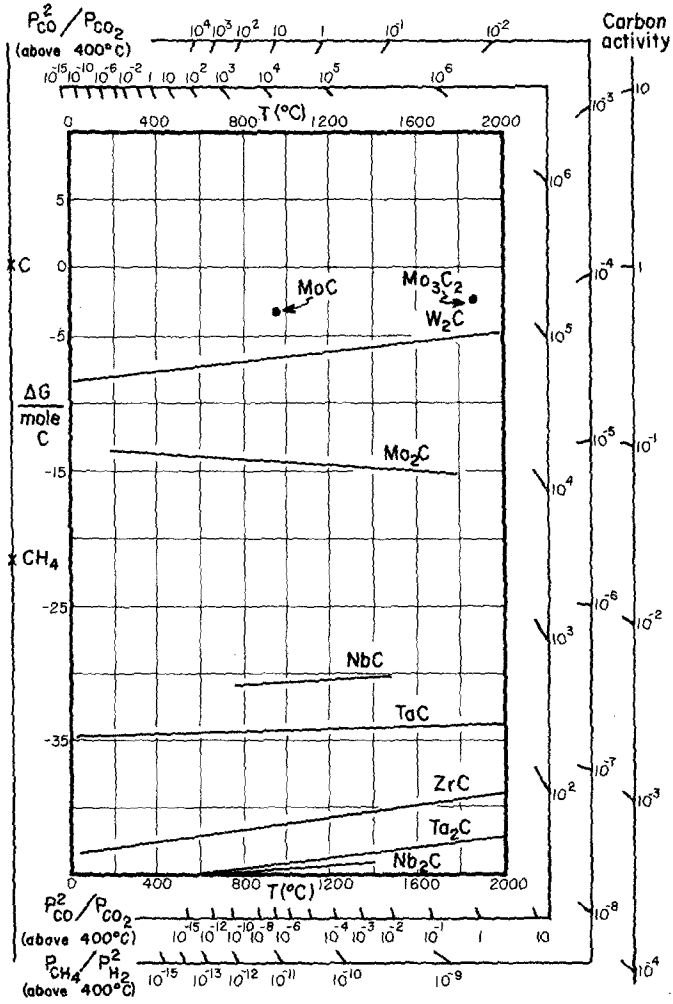

Fig. 2. Ellingham diagram for the second and third transition series carbides. The formation of the lowest compound formed from the metal upon reaction with 1 mole of C is denoted only by the compound M_xC.

effort has been made to note this deviation from stoichiometry. Generally a carbon deficit is observed. The influence of the nonstoichiometry upon the thermochemistry has not generally been examined.

The standard free energy change for each reaction (ΔG_f^0) is related to the standard enthalpy change (ΔH_f^0) and the standard entropy change (ΔS_f^0) by the following equation:

$$\Delta G_f^0 = \Delta H_f^0 - T\Delta S_f^0$$

Many of the reported data appear in this form. Since the change in enthalpy and entropy can be expressed directly in terms of heat capacity and temperature, an empirical equation may be written for the standard free energy change:

$$\Delta G_f^0 = \left[\Delta H_f^0(298) + \int_{298}^{T} \Delta C_p\, dT\right] - T\left[\Delta S_f^0(298) + \int_{298}^{T} \frac{\Delta C_p\, dT}{T}\right]$$

Since C_p is normally expressed as

$$C_p = a + bT + cT^{-2}$$

the above expression can be readily integrated to yield ΔG_f^0 as a function of temperature.

CARBIDES OF THE FIRST TRANSITION SERIES

Titanium

Only one carbide of Ti is known to exist,[5–8] TiC (melting point 3340°K). "TiC" is generally considered to have a considerable deficit of carbon and thus may vary continuously from $Ti_{1.8}C$ to TiC. Richardson[1] first reported the Gibbs energy of formation of TiC corresponding to the reaction

$$Ti + C \rightarrow TiC$$

to be:

$$\Delta G_f^0(TiC) = -43{,}750 + 2.41T \text{ cal/mole C } (\pm 3000 \text{ cal})$$

in the temperature range 298–1150°K. At higher temperatures (1150–2000°K), Richardson[1] reported:

$$\Delta G_f^0(TiC) = -44{,}600 + 3.16T \ (\pm 3000 \text{ cal})$$

These early measurements are found to be in good agreement with more recent data of Wicks and Block[4] and Kelley and Mah.[10] Wicks and Block[4] report for the above reaction

$$\Delta G_f^0(TiC) = -45{,}100 - 2.48T \ln T + 1.37 \times 10^{-3} T^2 + 0.74 \times 10^5 T^{-1} + 19.4T$$

for the temperature range of 298–1150°K and

$$\Delta G_f^0(TiC) = -45{,}200 - 0.23T \ln T + 0.11 \times 10^{-3} T^2 + 0.74 \times 10^5 T^{-1} + 4.96T$$

for the temperature range 1150–1800°K. Fujishiro and Gokcen,[11] using a Knudsen cell equilibrium pressure measurement, have found the ΔG_f^0(TiC) for the temperature range 2383–2593°K to be

$$\Delta G_f^0(\text{TiC}) = -141{,}064 + 35.0T \ (\pm 2000 \text{ cal}).$$

Vanadium

Numerous carbides of vanadium have been reported[5,9,12]: V_2C (melting point 2460°K), V_3C_2 (stable below 1800°K), V_6C_5, V_8C_7, and VC (melting point 2921°K). A large degree of nonstoichiometry is present in both V_2C and VC. Storms *et al.*[12] report that VC exists between $VC_{0.74}$ and $VC_{0.91}$ at 1700°K. At the upper composition, the vacancies apparently order at 1403°K to give V_8C_7 and C. V_2C in a similar manner extends from $VC_{0.45}$ to $VC_{0.58}$ at 1700°K.[12] Pillai and Sundaresan,[13] using EMF techniques, have measured $\Delta G_f^0(V_2C)$ to be

$$\Delta G_f^0(V_2C) = -41{,}970 + 21.26 \times 10^{-3} T \text{ cal/mole C } (\pm 1800 \text{ cal})$$

for the reaction

$$2V + C \rightarrow V_2C$$

within the temperature range 770–850°K. These results are in good agreement with the previous work of Worrell and Chipman[14] and Kireev and Karapetyantes,[15] but not with the earlier work of Volkova and Gel'd[16] and Alekseev and Shavartsman.[17] Apparently difficulties due to mixed vanadium carbides can account for the lack of agreement, which thus discounts the earlier work. For the above reaction Worrell and Chipman[18] report

$$\Delta G_f^0(V_2C) = -35{,}200 + 1.0T \text{ cal/mole C } (\pm 2000 \text{ cal})$$

for the temperature range 1200–1350°K. For the reaction

$$V + C \rightarrow VC$$

Worrell and Chipman[14] report

$$\Delta G_f^0(\text{VC}) = -24{,}100 + 1.5T \text{ cal/mole C } (\pm 850 \text{ cal})$$

for the temperature range 1180–1370°K. This result is in good agreement with those reported by Wicks and Block,[4] while this work supercedes that reported by Richardson.[1] Fujishiro[19] used a Knudsen cell to obtain high-temperature data for the above reaction. For the temperature range 2350–2550°K he reports

$$\Delta G_f^0(\text{VC}) = -23{,}300 + 2.0T$$

which is in good agreement with the results of Mah.[20]

Chromium

Three carbides of Cr have been reported[9]: $Cr_{23}C_6$ (melting point 1848°K), Cr_7C_3 (melting point 2038°K), and Cr_3C_2 (melting point 2083°K). Kulkarni and Worrell[21] have recently remeasured the reaction

$$\tfrac{23}{6}Cr + C \rightarrow \tfrac{1}{6}Cr_{23}C_6$$

and obtained

$$\tfrac{1}{6}\Delta G_f^0(Cr_{23}C_6) = -12{,}833 - 3.05T \text{ cal/mole C } (\pm 1200 \text{ cal})$$

for the temperature range of 1150–1300°K. Although in disagreement with the previous data reported by Wicks and Block[4] and Richardson,[1] the torsion effusion experiments performed by Kulkarni and Worrell[21] are believed to be more reliable.

Kulkarni and Worrell[21] also studied the reaction

$$\tfrac{7}{27}Cr_{23}C_6 + C \rightarrow \tfrac{23}{27}Cr_7C_3$$

and obtained for the temperature range 1100–1720°K

$$\Delta G_f^0(\tfrac{7}{27}Cr_{23}C_6 \rightarrow \tfrac{23}{27}Cr_7C_3) = -29{,}985 - 7.41T \ (\pm 400 \text{ cal})$$

This is also in conflict with the previously reported data.[1,2,4] In addition, they studied[21] the reaction

$$\tfrac{3}{5}Cr_7C_3 + C \rightarrow \tfrac{7}{5}Cr_3C_2$$

in the temperature range 1300–1500°K and obtained

$$\Delta G_f^0(\tfrac{3}{5}Cr_7C_3 \rightarrow \tfrac{7}{5}Cr_3C_2) = -9840 - 2.64T \text{ cal/mole } (\pm 400 \text{ cal}).$$

These results are in good agreement with the previous results of Mabuchi and Matsushita,[22] Storms,[23] and Tanaka *et al.*[24] They are in fair agreement with the previous results of Kleykamp,[25] and Vintaikin[26] and are in poor agreement with the results of Kelley *et al.*,[27] Gleiser,[28] Wicks and Block,[4] and Richardson.[1] Again mixed carbides appear to account for the poor agreement of earlier results.

Manganese

Numerous carbides of Mn have been reported[9,29]: $Mn_{23}C_6$ (melting point 123°K), $Mn_{15}C_4$ (stability range 1123–1293°K), Mn_3C (stability range 1243–1323°K), Mn_5C_2 (melting point 1360°K), and Mn_7C_3 (melting point 1423°K). Moattar and Anderson[29] have studied the reaction

$$\tfrac{23}{6}Mn + C \rightarrow \tfrac{1}{6}Mn_{23}C_6$$

and have determined $\frac{1}{6}\Delta G_f^0(Mn_{23}C_6)$ for the temperature range 900–

1100°K:

$$\tfrac{1}{6}\Delta G_f^0(Mn_{23}C_6) = -15{,}359 + 5.6T \text{ cal/mole C } (\pm 1200 \text{ cal})$$

For the compound $Mn_{15}C_4$ there are no reported thermodynamic data. The compound Mn_3C has been extensively studied. Frad[30] notes that Mn_3C is thermodynamically unstable below 1123°K. Richardson[1] and Wicks and Block[4] report data for Mn_3C for 298–1010 and 1500°K, respectively. For the reaction

$$3Mn + C \rightarrow Mn_3C$$

Richardson[1] reports $\Delta G_f^0(Mn_3C) = -3330 - 0.26T$ cal/mole C (±3000 cal) for the temperature range 298–1010°K. This result is in good agreement with the results of Wicks and Block.[4] Moattar and Anderson[29] also have studied the reaction

$$\tfrac{5}{2}Mn + C \rightarrow \tfrac{1}{2}Mn_5C_2$$

and have determined the $\frac{1}{2}\Delta G_f^0(Mn_5C_2)$ for the temperature range 900–1100°K:

$$\tfrac{1}{2}\Delta G_f^0(Mn_5C_2) = -10{,}780 + 3.2T \text{ cal/mole C } (\pm 300 \text{ cal})$$

for the reaction

$$\tfrac{7}{3}Mn + C \rightarrow \tfrac{1}{3}Mn_7C_3$$

Moattar and Anderson[29] obtained

$$\tfrac{1}{3}\Delta G_f^0(Mn_7C_3) = -10{,}130 + 3T \text{ cal/mole C } (\pm 440 \text{ cal})$$

for the temperature range 900–1100°K. This is in good agreement with the previous results of McCabe and Hudson[31] but in poor agreement with Gokcen and Fujishiro.[32]

Iron

Numerous carbides of Fe have been reported, ranging in composition from Fe_4C to Fe_2C. There are few data concerning most of the carbides except for the great wealth of data available concerning Fe_3C. It is generally agreed upon that the compounds Fe_4C, Fe_3C (melting point 1500°K), Fe_5C_2 (melting point greater than 503°K), Fe_7C_3, $Fe_{20}C_9$, and Fe_2C exist. Fe_2C was first suggested by Glud *et al.*[33] Hagg[34] noted that above 498°K mixtures of Fe_2C and Fe_3C were found, whereas above 673°K only Fe_3C was noted. Hultgren *et al.*[35] note that Fe_2C can better be described as $Fe_{20}C_9$. For the reaction

$$3Fe + C \rightarrow Fe_3C$$

Wicks and Block[4] report for the temperature range of 298–463°K:

$$\Delta G_f^0(Fe_3C) = +4530 - 5.43T \ln T + 1.16\times10^{-3}T^2 - 0.40\times10^5T^{-1} + 31.98T$$

for the temperature range 463–1033°K:

$$\Delta G_f^0(Fe_3C) = +3850 - 11.41T \ln T + 9.66\times10^{-3}T^2 - 0.40\times10^5T^{-1} + 66.2T$$

for the temperature range 1033–1179°K:

$$\Delta G_f^0(Fe_3C) = 13{,}130 + 9.68T \ln T - 0.99\times10^{-3}T^2 - 1.05\times10^5T^{-1} - 78.14T$$

for the temperature range 1179–1500°K:

$$\Delta G_f^0(Fe_3C) = -1000 - 7.00T \ln T + 3.5\times10^{-3}T^2 - 1.05\times10^5T^{-1} + 46.45T$$

for the temperature range 1500–1674°K:

$$\Delta G_f^0(Fe_3C) = 7340 - 11.95T \ln T + 5.01\times10^{-3}T^2 - 1.05\times10^5T^{-1} + 74.62T$$

for the temperature range 1674–1803°K:

$$\Delta G_f^0(Fe_3C) = 21{,}700 + 4.4T \ln T + 0.5\times10^{-3}T^2 - 1.05\times10^5T^{-1} - 47.48T$$

while for the temperature range 1803–1900°K:

$$\Delta G_f^0(Fe_3C) = 8980 + 3.50T \ln T + 0.51\times10^{-3}T^2 - 1.05\times10^5T^{-1} - 33.8T$$

Hultgren *et al.*[35] have reported $\Delta G_f^0(Fe_2C) = 373$ cal/mole C at 600°K.

Cobalt

Two rather unstable carbides of Co have been reported, Co_2C (range of stability between 773 and 1073°K) and Co_3C. Richardson[1] reports for the reaction

$$2Co + C \rightarrow Co_2C$$

that the free energy of formation of Co_2C is

$$\Delta G_f^0(Co_2C) = +3950 - 2.08T \text{ cal/mole C } (\pm 500 \text{ cal})$$

for the temperature range 298–1200°K. Wicks and Block[4] note

$$\Delta G_f^0(Co_3C) = +9000 \text{ cal/mole C at } 298°K.$$

Nickel

One carbide of Ni has been reported, Ni_3C. Ni_3C has been reported to be unstable even under a pressure of 60 kbar.[8] Richardson[1] had reported for the reaction

$$3Ni + C \rightarrow Ni_3C$$

$$\Delta G_f^0(Ni_3C) = +8110 - 1.70T \text{ cal/mole C } (\pm 3000 \text{ cal})$$

for the temperature range 298–1000°K. This is in good agreement with the results reported by Wicks and Block.[4]

Copper

Only the explosive carbide Cu_2C_2 has been reported.[8]

Zinc

The compound ZnC_2 has been reported but no further work has been reported.[8]

CARBIDES OF THE SECOND TRANSITION SERIES

Zirconium

Only one carbide of Zr has been reported: ZrC[4,5] (melting point 3718°K). Kubaschewski *et al.*[2] report the $\Delta G_f^0(ZrC)$ for the reaction

$$Zr + C \rightarrow ZrC$$

to be

$$\Delta G_f^0(ZrC) = -44{,}100 + 2.2T \text{ cal/mole C } (\pm 3000 \text{ cal})$$

within the temperature range 298–2220°K. These results are in good agreement with the later results of Wicks and Block[4] at 298°K and Pollock[36] at 2675°K.

Niobium

Two carbides of Nb have been identified: Nb_2C (melting point 2777°K)[5,9] and NbC (melting point 3881°K).[5,9] Worrell and Chipman[14,18] studied the ΔG_f^0 of both Nb_2C and NbC. They determined the $\Delta G_f^0(NbC)$ for the reaction

$$Nb + C \rightarrow NbC$$

to be

$$\Delta G_f^0(\text{NbC}) = -31{,}100 + 0.4T \text{ cal/mole } (\pm 600 \text{ cal})$$

for the temperature range 1180–1370°K. These results are in excellent agreement with the data obtained by Pankratz *et al.*[37] In a similar manner, Worrell and Chipman[14,18] measured the $\Delta G_f^0(\text{Nb}_2\text{C})$ for the reaction

$$2\text{Nb} + \text{C} \rightarrow \text{Nb}_2\text{C}$$

to be

$$\Delta G_f^0(\text{Ng}_2\text{C}) = -46{,}000 + 1.0T \text{ cal/mole C } (\pm 900 \text{ cal})$$

for the temperature range 1180–1370°K.

Molybdenum

There appears to be some conflict concerning the number and composition of molybdenum carbides. Gleiser and Chipman[38] report measurements on "Mo_2C" where the composition varies from $Mo_{2.21}C$ to $Mo_{1.98}C$. Wallace *et al.*[39] report values for $MoC_{.61}$ which is approximately $\frac{1}{3}Mo_3C_2$. Rudy,[5] in his phase diagram, illustrates only two compounds, Mo_2C and MoC_{1-x}. Storms,[23] however, notes the formation of three carbides, MoC (melting point 2800°K), α-Mo_3C_2 (melting point 2823°K), and Mo_2C (melting point 2978°K). The apparent discrepancies are most probably related to the high degree of deviation from stoichiometry that is exhibited in the Mo–C system. For the reaction

$$2\text{Mo} + \text{C} \rightarrow \text{Mo}_2\text{C}$$

Solbakken and Emmett[40] report

$$\Delta G_f^0(\text{Mo}_2\text{C}) = -12{,}030 - 1.44T \text{ cal/mole C } (\pm 1000 \text{ cal})$$

for the temperature range 600–900°K. These results are in good agreement with the previous results of Gleiser and Chipman,[38] who report

$$\Delta G_f^0(\text{Mo}_2\text{C}) = -11{,}710 - 1.83T \text{ cal/mole C } (\pm 1000 \text{ cal})$$

for the temperature range 1200–1340°K. These results are also in good agreement with the vaporization studies of Fries.[41] The standard free energy of formation of Mo_3C_2 at 2100°K was reported by Wallace *et al.*[39] to be

$$\Delta G_f^0(\text{Mo}_3\text{C}_2) = -2600 \text{ cal/mole C } (\pm 1500 \text{ cal})$$

Browning and Emmett[42] report the ΔG_f^0 of MoC at 950° to be $\Delta G_f^0(\text{MoC}) = -3211$ cal/mole of C.

Ruthenium

A eutectic phase diagram with no compound formation has been reported.[8] Gingerich,[43] however, has identified RuC as a gas phase compound.

Rhodium

A eutectic phase diagram with no compound formation has been reported.[8]

Palladium

A eutectic phase diagram with no compound formation has been reported.[8]

Silver

Sneed and Brasted[44] and Sidgewick[45] report the existence of the highly unstable Ag_2C_2.

Cadmium

There is no reported compound formation in the Cd–C system.

CARBIDES OF THE THIRD TRANSITION SERIES

Hafnium

There is little information concerning the carbides of Hf. One carbide, HfC (melting point 4201°K), has been reported.[5–9]

Tantalum

Two carbides of Ta have been identified: TaC (melting point 3603°K) and TiC (melting point 4256°K). Using the torsion-effusion technique, Kulkarni and Worrell[46] obtained for the reaction

$$2Ta + C \rightarrow Ta_2C$$

$$\Delta G_f^0(Ta_2C) = -47{,}000 + 2.1T \text{ cal/mole C } (\pm 300 \text{ cal})$$

for the temperature range 1740–1900°K. Worrell and Chipman[14,18] obtained thermodynamic data for the reaction

$$Ta + C \rightarrow TaC$$

For the temperature range of 1250–1400°K, they obtained

$$\Delta G_f^0(\text{TaC}) = -34{,}900 + 0.5T \text{ cal/mole C } (\pm 600 \text{ cal}).$$

This result is in good agreement with previous results of Pankratz *et al.*[47] but not with the reported values of Wicks and Block.[4]

Tungsten

Two compounds of W have been identified: W_2C (melting point 3049°K) and WC (melting point 3049°K). Gupta and Seigle[48] have recently reinvestigated the W–C system. For the reaction

$$2W + C \rightarrow W_2C$$

They obtained $\Delta G_f^0(W_2C) = -7300 - 0.5T$ cal/mole C (± 100 cal) for the temperature range 1150–1575°K. These results are in good agreement with previously reported data by Kubaschewski *et al.*,[2] but in poor agreement with the data reported by Wicks and Block.[4]

Rhenium

No carbide compounds have been reported.[8]

Osmium

A eutectic system with the compound OsC has been reported.[8] No further data are known.

Iridium

There are no reported Ir compounds.[8]

Platinum

There are no reported Pt carbides; a simple eutectic phase diagram has been proposed.[8]

Gold

The highly explosive Au_2C_2 compound has been reported.[45]

Mercury

There are no reported Hg carbides.[8]

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