according to Louw, VanDenBerg, Ferreira and Pienaar[26] contains two chemically distinct forms of carbon. This suggests the simple hypothesis that the carbon atoms in excess of the ratio of one carbon atom to three iron atoms donate no electrons at all. This would mean, for FeC, that $^2/_3$ of the carbon atoms are in a form that has not donated electrons. This reasoning is readily extended to postulate that the carbides of the composition Fe_2C also have two forms of carbon, and for this case $^1/_3$ of the carbon atoms donate no electrons.

Paramagnetism of Carbides.—The intercepts with the ordinate in Fig. 2 are the products of paramagnetic susceptibility and f (equation 1). Paramagnetic susceptibilities for χ-iron carbide and cementite are indicated in Table VIII. Their reciprocals, plotted as a function of temperature in Fig. 4, give paramagnetic Curie points for χ-iron carbide and cementite of 246 and 233°, respectively. The slopes of the functions as approximated by the indicated straight lines substituted into the equation

$$\chi M = N(n\beta)^2/3k(T - \theta) \qquad (11)$$

were used to evaluate "n" for these carbides, resulting in values of 5.55 Bohr magnetons per iron atom for χ-iron carbide and 3.89 for cementite. These values are larger than the corresponding ferromagnetic ones by factors of 3.2 and 2.2, respectively. This situation is usual for ferromagnetics; in the case of nickel, the ratio is 3.14. The lower points in Fig. 4 do not fall on the straight line because there is still some ferromagnetic effect just above the Curie point.

TABLE VIII

PARAMAGNETIC SUSCEPTIBILITIES OF IRON CARBIDES, 10^{-6} CC. GRAM^{-1}

Temp., °C.	χ-Iron carbide	Cementite
217.5	..	2640
232	..	2170
246	..	1480
260	2766	1065
274	2156	835
287.5	1604	647
302	1180	500
316	999	..
329.5	814	..
343	714	..
356.5	630	..

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[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Heats of Formation of Tungsten Trioxide and Tungsten Dioxide

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Combustion calorimetry was used to find the standard heats of formation of tungsten trioxide, −201.46 ± 0.20 kcal./mole, and tungsten dioxide, −140.94 ± 0.21 kcal./mole.

The only previous direct measurement of the heat of combustion of tungsten dioxide is that of Delépine and Hallopeau,[2] who obtained −135 kcal./mole. Calculations from equilibrium data[3] give −137 ± 2 kcal./mole, which has a large uncertainty and is in poor agreement with the direct result. Although the work of Huff, Squitieri and Snyder[4] furnishes an accurate value for the heat of formation of tungsten trioxide (−200.84 ± 0.10 kcal./mole), it was decided to redetermine this value so that the heat of formation of the dioxide would be based entirely upon results from our calorimeter.

Materials

Two samples of metallic tungsten, both finely divided powders, were used. Sample A was made by reducing tungstic acid (C.A.F. Kahlbaum) with purified and dried hydrogen at 900°. Spectrographic analysis, together with the weight increase upon complete oxidation, indicated the following composition: 99.86% tungsten, 0.014% iron, 0.012% silicon, 0.06% molybdenum, 0.011% magnesium, 0.005% calcium and 0.04% oxygen. Sample B was obtained from Professor A. W. Searcy of the Division of Mineral Technology, University of California, Berkeley, California. This sample was treated with dried, purified hydrogen at 900° before use. Analysis as above showed 99.95% tungsten, 0.004% iron, 0.012% silicon, 0.02% molybdenum, 0.004% magnesium, 0.003% calcium and 0.01% oxygen.

Tungsten dioxide was prepared by oxidizing a portion of tungsten sample B to the trioxide and then reducing batches of it with purified hydrogen at 600° to near the dioxide composition. After analysis, batches with slight oxygen excess were mixed with batches slightly deficient in oxygen to ascertain the correct oxygen-to-tungsten ratio, and the mixture was homogenized by prolonged heating at 1000° in

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[2] M. Delépine and L. A. Hallopeau, *Compt. rend.*, **131**, 186 (1900).

[3] J. P. Coughlin, U. S. Bureau of Mines Bulletin 542, 1954.

[4] G. Huff, E. Squitieri and P. E. Snyder, THIS JOURNAL, **70**, 3380, 4279 (1948).

helium. Two samples prepared in this manner had oxygen-to-tungsten ratios of 1.9993 and 1.9988. The X-ray diffraction patterns agreed with that in the A.S.T.M. catalog. There was no evidence of the presence of either tungsten metal or tungsten trioxide.

Experimental

The combustion calorimeter has been described previously.[5] Calibration with National Bureau of Standards benzoic acid sample 39 g. gave 32495.3 ± 0.01% cal./ohm. All weights were corrected to vacuum, and heat values are in terms of the defined calorie (1 cal. = 4.1840 abs. joules). Ignition was by means of a platinum spiral and a filter-paper fuse. The combustions were made under 30 atm. of oxygen. Oxides of nitrogen were in negligible amounts after combustion. The tungsten metal and dioxide showed no oxidation upon prolonged standing at 30° under 30 atm. oxygen.

Shallow silica dishes, lined with tungsten trioxide, held the samples for combustion. About 15% of the tungsten combustion product and 0.5% of the dioxide combustion product deposited on the walls of the bomb, and the rest remained in the dish. The X-ray diffraction patterns for wall deposits, combustion products and liner all agreed with that in the A.S.T.M. catalog for tungsten trioxide.

The percentages of completion of combustion were obtained from the additional weights gained by the combustion products upon ignition at 700°. This ranged from 97.37 to 99.94% for the tungsten combustions and 99.69 to 100.00% for the dioxide combustions.

Results

The combustion data are in Table I. The successive columns show the mass of substance burned, the total energy evolved, the correction for ignition, the correction for incomplete combustion, the corrected energy evolved and, finally, the corrected energy of combustion per gram. The assigned uncertainties were calculated by the method of Rossini and Deming.[6]

To correct for impurities in the tungsten-metal samples, iron and molybdenum were assumed to be metallic and silicon, magnesium and calcium in the form of oxides. The impurities originally present in tungsten sample B were assumed to be oxidized under the conditions of preparation of the dioxide and amounted to about 0.06% of the dioxide samples. The correction for impurities in the dioxide samples includes the necessary adjustment to exact stoichiometric composition.

The combined mean value for the combustion of the tungsten samples, corrected for impurities, corresponds to $\Delta E_{303.15}$ = −200.41 kcal./mole under bomb conditions. Corrections to unit fugacity of oxygen (−135 cal.), to a constant pressure process (−904 cal.) and to 298.15°K.(−15 cal.) results in $\Delta H_{298.15} = -201.46 \pm 0.20$ kcal./mole for the heat of formation of tungsten trioxide.

TABLE I

COMBUSTION DATA AT 30°

Mass of substance, g.	Total energy evolved, cal.	Energy from *EIt*, fuse, cal.	Cor. incomp. comb., cal.	Net energy, cal.	$-\Delta U_B$, cal./g.
		Tungsten A			
2.00026	2177.48	5.55	6.84	2178.77	1089.2
1.99984	2181.02	5.04	1.31	2177.29	1088.7
2.00009	2126.09	5.04	57.33	2178.38	1089.1
			Mean		1089.0 ± 0.3
			Cor. for impurities		+1.1 ± .4
					1090.1 ± .5
		Tungsten B			
1.99986	2182.46	7.84	4.93	2179.55	1089.9
2.00015	2152.93	5.73	33.67	2180.87	1090.4
1.00059	1087.59	4.27	6.55	1089.87	1089.2
			Mean		1089.8 ± 0.7
			Cor. for impurities		+0.1 ± .1
					1089.9 ± .8
		Tungsten dioxide, $WO_{1.9993}$			
3.00122	838.87	5.23	2.58	836.22	278.63
3.99958	1122.44	6.68	0.00	1115.76	278.97
4.00193	1118.70	5.92	1.73	1114.51	278.49
3.99971	1118.20	5.09	1.08	1114.19	278.57
			Mean		278.66 ± 0.21
			Cor. for impurities		−0.03 ± .01
					278.63 ± .21
		Tungsten dioxide, $WO_{1.9988}$			
4.00490	1119.64	4.02	2.10	1117.22	279.09
3.99993	1119.69	4.10	0.00	1115.59	278.90
			Mean		279.00 ± 0.20
			Cor. for impurities		−0.17 ± .05
					278.83 ± .21

Similarly, the mean value for the combustion of the tungsten dioxide samples corresponds to $\Delta E_{303.15}$ = −60.16 kcal./mole. Corrections to unit fugacity (−46 cal.), to a constant pressure process (−301 cal.), and to 298.15° (−8 cal.), give the heat of combustion, $\Delta H_{298.15} = -60.52 \pm 0.05$ kcal./mole. Combining with the above value for tungsten trioxide leads to −140.94 ± 0.21 kcal./mole as the heat of formation of tungsten dioxide from the elements.

The heat of formation of tungsten trioxide obtained by this work does not differ greatly from that of Huff, Squitieri and Snyder.[4] The heat of formation of the dioxide, however, is several (4–6) kcal. more negative than those previously found.[2,3]

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