rate of complex formation or the energy release did not produce differential equations capable of solution. The alternative is to introduce an arbitrary step function to describe the force solely in the vicinity of the interface.

Since this work was completed in early 1954, Lewis has published[9] results obtained with stirring in essentially the same system. No interfacial barrier was observed initially. However, a barrier did appear in later stages of the extraction. The latter fact in no way contradicts the present work. It is quite reasonable that the eddy diffusion coefficients be larger than those for molecular diffusion with the interfacial barrier providing a resistance intermediate to these extremes. The lack of an immediate barrier in the stirred system suggests that even here the energy of reaction is sufficiently great to prevent its formation.

Acknowledgment.—The author is indebted to the Laboratory Analytical group under E. W. Christopherson for analyses, and to Dr. L. L. Burger for helpful discussion.

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[9] J. B. Lewis, *Nature*, **178**, 274 (1956).

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Preparation of Tungsten Carbide

BY ARTHUR E. NEWKIRK AND IFIGENIA ALIFERIS

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The tungsten carbide, WC, may be prepared by heating tungstic acid, a blue oxide of tungsten or ammonium paratungstate in a mixture of hydrogen and methane at 850 to 1000°. The effects of time, temperature and methane concentration are given. With tungstic acid, the reduction to tungsten metal is shown to be complete before carburization begins.

As a part of a general investigation of reactions forming tungsten carbide, the reactions of tungstic acid, a blue oxide of tungsten and of ammonium paratungstate with a gaseous mixture of hydrogen and methane were examined. The only reference to these specific reactions is by Hilpert and Ornstein[1] who reported they succeeded one time in preparing tungsten carbide by heating tungsten trioxide at 1000° in a 1:1 mixture of methane and hydrogen. In general, the rate of carbon formation was so rapid at this temperature that a reasonably pure product could not be obtained, and it was necessary to use lower temperatures. No details of such experiments were reported. There are numerous references to the carburization of metallic tungsten by carbon or carburizing gases and of the formation of tungsten carbides by reaction of tungsten oxides with carbon.[2]

The tungsten trioxide–hydrogen–methane reaction was first tried in this Laboratory by E. H. Winslow and E. L. Brady[3] who showed that tungsten carbide could be obtained in quantitative yield by heating tungsten oxide between 2 and 5 hours at 1000° in hydrogen containing 0.85% methane by volume. The gas composition was selected as containing slightly less methane than that which would deposit carbon, 0.95% at this temperature.[4] Using the data of Kubaschewski and Evans[5] it can be shown that the free energy of the over-all reaction

$$WO_3 + CH_4 + H_2 = WC + 3H_2O \qquad (1)$$

is favorable to the formation of tungsten carbide under these conditions, and that the equilibrium pressure of methane for the reaction

$$W + CH_4 = WC + 2H_2 \qquad (2)$$

is less than that for the decomposition of methane to carbon and hydrogen. The effect of time, temperature and methane concentration were therefore studied for reactions similar to the one shown in eq. 1.

Experimental

Materials.—Tungsten compounds were obtained from the Lamp Wire and Phosphors Department of the General Electric Company and their tungsten content determined by measuring the loss in weight after firing in hydrogen for three hours at 1000°. In each case the product gave an X-ray diffraction pattern showing only the presence of elemental tungsten. Tungstic acid, residue weight 74.06%, theory for H_2WO_4 73.59%, for WO_3 79.30%; ammonium paratungstate, residue weight 70.50%, theory for $5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$, 70.43%; blue oxide residue weight 79.35%, theory for WO_3 79.30%, for $W_{20}O_{58}$ 79.85%. The ammonium paratungstate gave variable results until samples were equilibrated and weighed in a room at constant temperature and humidity. This material was also difficult to handle due to static charges. The difficulty was overcome by holding the active element of a "Static master" brush near the boat while loading it into the quartz tube.

Laboratory line hydrogen was passed through a "Deoxo" unit and a liquid nitrogen trap to obtain hydrogen with a dew point below −100°. Commercial methane was used directly from a cylinder.

Apparatus and Procedure.—The hydrogen and methane were separately metered to a mixing bulb provided with a fritted filter on the outlet. This led to the inlet of a quartz combustion tube 2 cm. dia. by 75 cm. long which was heated by an electric furnace over a 55 cm. length. Semicylindrical boats of fused quartz or nickel were used. For the parallel boat runs, a special boat was made which held two quartz liners each having a quarter-circle cross section. In this way both tungsten and the oxide could be exposed under the same conditions. The temperature was measured by a chromel–alumel thermocouple in a quartz well centered above the sample. The outlet of the combustion tube was drawn to a jet. Samples were inserted through the inlet end which had been fitted with a ground joint for the purpose.

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[1] S. Hilpert and M. Ornstein, *Ber.*, **46**, 1669 (1913).

[2] P. Schwarzkopf and R. Kieffer, "Refractory Hard Metals," The Macmillan Co., New York, N. Y., 1953, Ch. 13.

[3] E. H. Winslow and E. L. Brady, private communication.

[4] National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Series 3, Table 3, 1947.

[5] O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

The usual procedure was to insert the boat containing 0.6 to 1.0 g. of sample into the combustion tube, flush with the methane–hydrogen mixture for 25 minutes, light the escaping gas at the outlet, heat to 1000° in approximately one hour, heat at temperature for the desired time, remove the furnace, cool the tube with jets of air on the outside and transfer the boats to a desiccator.

The products were analyzed for carbon by combustion using the method of Simons, Fagel and Balis[6] which has confidence limits of ±0.1%. X-Ray diffraction patterns were obtained by mixing a portion of the products with "Lubriseal," spreading in a thin film on a microscope slide, and recording the pattern with an X-ray spectrometer using filtered copper radiation. Examination of known mixtures made from tungsten and tungsten carbide powders showed that 1% tungsten could be detected in tungsten carbide.

The thermobalance runs were made with a Chevenard pen-recording thermobalance manufactured by Société A.D.A.M.E.L., Paris, France. The instrument and its operation have been described previously.[7]

Results and Discussion

The results are shown in Table I. It is not possible to calculate a yield of WC from the data available. The presence of free carbon might be counterbalanced by the presence of W or W_2C to yield experimentally both the theoretical weight change and theoretical carbon content. However, the results of the X-ray diffraction examination indicate that the yield of WC is essentially quantitative in all three cases.

Table I

Carburization of Tungsten Compounds

3 hr. at 1000°, H_2 = 350 cc./min., CH_4 = 3 cc./min.[a]

Compound	Sample, g.	Product Grams	Product % C[b]	Product X-Ray identification
Tungstic acid	0.9059	0.7146	6.07	WC
Ammonium paratungstate	.9535	.7161	6.07	WC
	.9538	.7186	6.05	WC
Blue oxide	.8459	.7159	6.11	WC
Parallel boat runs				
Tungstic acid[c]	0.8543	0.6700	5.77	WC, W_2C
Tungsten	.6327	.6704	5.90	WC, W_2C
Ammonium paratungstate	.8946	.6731	6.12	WC
Tungsten	.6301	.6663	6.15	WC
Blue oxide	.7568	.6394	6.02	WC
Tungsten	.6008	.6386	6.19	WC

[a] Ratio of methane used to methane required was 5.9 for the first four runs, and 3.2 for the last two runs. [b] Theory for WC = 6.13%. [c] Concentration of methane low during part of the run.

The tungsten used for the parallel boat runs was prepared by reducing the related tungsten compound separately in hydrogen, and allowing the powder thus obtained to stand in air at room temperature for a few days to a week before carburizing. There appears to be no difference in reactivity between the tungsten thus prepared and the starting compounds. This is shown most strikingly by the parallel boat run with tungstic acid in which the methane concentration was low for an indeterminate part of the run, resulting in less than the theoretical carbon content in both samples.

Several runs were made with excess methane present to determine whether the expected formation of free carbon would occur. These runs were made with 0.846 g. of blue oxide heated at 1000° for three hours, a hydrogen flow rate of 350 cc./min., and a methane flow rate of 3, 6, 12, or 24 cc./min. The carbon contents of the product were 6.11, 6.49, 7.88 and 8.02%, respectively. Free carbon was also noted on the walls of the combustion tube in all but the first run. Samples of WC containing initially 5.80% C after firing one hour under similar conditions and methane flow rates of 6, 12, or 24 cc./min. gave products containing 6.24, 7.86 and 8.34% carbon, respectively.

Similar experiments showed that tungsten carbide could be decarburized in hydrogen or at low methane concentrations. Thus a product containing only 4.44% C was obtained by heating tungsten carbide (5.80% C) for 3 hours at 1000° in a hydrogen stream flowing at 350 cc./min. A run with another sample resulted in an insignificant reduction to 5.76% C, when the hydrogen rate was doubled and 3 cc./min. of methane added.

Successful carburizations also were obtained at lower temperatures by increasing the methane concentration. Thus blue oxide was carburized at 900° in 3 hours with a gas mixture of 350 cc. of hydrogen per minute and 7 cc. of methane per minute to yield a product analyzing 5.98% C, and at 850° and 10 cc. of methane per minute to yield a product analyzing 6.00% C. In each case the methane concentrations were selected to be slightly less than would result in the formation of free carbon.

Changes in procedure were necessary to prepare larger samples successfully. Increasing the concentration of methane and the time was not sufficient, compare the first two runs of Table II *vs.* the fourth run of Table I, but an increase in time and total gas flow without excess methane gave satisfactory results, Table II. Three duplicates of the 7 hour run gave products in which the presence of tungsten could not be detected by X-ray diffraction. The tungsten content of the other samples was estimated from the peak height ratio of the 40.4° peak of tungsten and the 64.7° peak of tungsten carbide.

Table II

Carburization of Blue Oxide[a]

Sample weight 10.00 g.

Time at 1000°, hr.	H_2 flow rate, cc./min.	CH_4 flow rate, cc./min.	% C	Product X-ray identification
6.7	350	6	5.12	WC,W(>10%)
10	350	6	5.77	WC,W(7%)
6	1050	9	6.15	WC,W(2%)
7	1050	9	6.19	WC,W(1%)
8	1050	9	6.34	W,W_2C,W(1%)

[a] Boat size (length × diameter) was 102 × 19 mm. in the runs listed in Table I, 92 × 16 mm. in the first run above, and 203 × 24 mm. in the other runs.

The course of the drying, reduction and carburization of tungstic acid in hydrogen plus methane is clearly shown by the thermobalance curve, Fig. 1,

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(6) E. L. Simons, J. E. Fagel and E. W. Balis, *Anal. Chem.*, **27**, 1123 (1955).

(7) E. L. Simons, A. E. Newkirk and I. Aliferis, *ibid.*, **29**, 48 (1957).

made at a heating rate of 300° per hour. The tungstic acid first loses water to form tungsten trioxide. This reaction overlaps the stepwise reduction to metallic tungsten. The details of the reduction have been reported recently by Hegedus and co-workers.[8] The metallic tungsten is then relatively inert in the temperature range 780 to 920° after which it carburizes slowly to tungsten carbide over a period of 4.5 hours at 1025°. The slower reaction in the thermobalance crucible compared to the combustion boat is probably due to the deeper vessel and greater bed-depth in the former. This run was made with a sample of tungstic acid that gave a residue weight of 73.35% when fired in hydrogen. The following data were derived from the thermobalance curve: sample weight = 0.9000 g.; minimum weight = 0.6619 g., theory for W = 0.6602 g.; final weight = 0.7032 g., theory for WC = 0.7005 g. The product contained 6.21% C by analysis, and gave an X-ray diffraction pattern showing only WC.

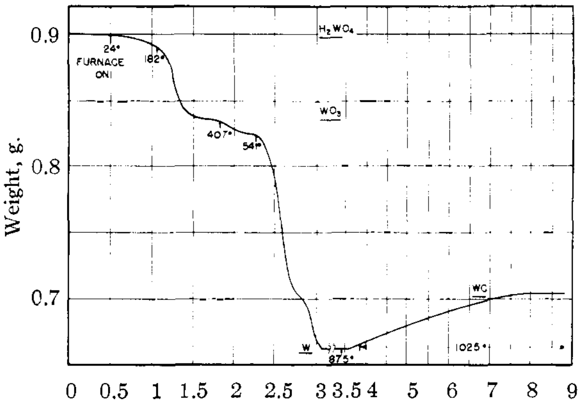

Fig. 1.—Thermobalance curve from heating H_2WO_4 in $H_2 + CH_4$.

Acknowledgment.—We wish to thank Drs. E. H. Winslow and E. L. Brady for helpful advice.

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[8] A. J. Hegedus, T. Millner, J. Neugebauer and K. Sasvari, *Z. anorg. allgem. Chem.*, **281**, 64 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Polarographic Characteristics of Osmium. I. The +8 State

BY LOUIS MEITES

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Information is presented concerning the reduction of +8 osmium from a number of common supporting electrolytes at both dropping mercury electrodes and large stirred mercury electrodes.

Introduction

Osmium tetroxide is widely used both as a catalyst for oxidation–reduction titrations and as a powerful oxidizing agent in its own right for various purposes of organic chemistry. Though the elucidation and further development of such procedures would doubtless be greatly aided by a detailed understanding of the oxidation–reduction chemistry of osmium, and in spite of the growing interest in the analytical chemistry of the platinum metals, our present fund of information relating to the electrochemistry of the numerous oxidation states of osmium is exceedingly meagre. The present series will describe the results of a systematic effort to elucidate the oxidation–reduction equilibria which interrelate the oxidation states of this element in aqueous solutions, beginning in this paper with those processes which are involved in the reduction of +8 osmium.

The available information concerning the electrochemistry of osmium has been briefly summarized by Latimer.[1] Crowell, Heyrovsky and Engelkemeir[2] were the first to investigate the polarographic characteristics of osmium(VIII). They found it impossible to obtain polarograms in acid media because of the reduction of the osmium by their mercury pool "reference" electrode. Nor could they secure "consistent and well-defined" waves in solutions of lithium, sodium, potassium or tetramethylammonium hydroxide. In saturated (*ca.* 0.02 *M*) calcium hydroxide, however, they observed a well-defined triple wave which they attributed to stepwise reduction to the +6, +4 and +3 states on the basis of the relative heights of the waves.

Zuman[3] reported that osmium(VIII) in neutral or acidic media gives a wave which rises from zero applied e.m.f. and represents reduction to the +6 state. Kolthoff and Parry[4] found a double wave in an 0.5 *M* acetate buffer of *p*H 4.7 and attributed it to stepwise reduction to the +6 and +2 states. Breda, Meites, Reddy and West[5] secured no wave for osmium(VIII) in an 0.5 *M* malonate buffer, which doubtless merely reflects a rapid chemical reduction of osmium(VIII) by excess malonate.

Experimental

All polarograms were secured with an automatically recording polarograph designed and constructed by the author. The cell used was of the modified H-type[6] equipped with a sintered-Pyrex gas-dispersion cylinder to permit rapid de-

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[1] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., Second Edition, 1952, pp. 230–233.

[2] W. R. Crowell, J. Heyrovsky and D. W. Engelkemeir, THIS JOURNAL, **63**, 2888 (1941).

[3] P. Zuman, *Collection Czechoslov. Chem. Communs.*, **15**, 1107 (1950).

[4] I. M. Kolthoff and E. P. Parry, *Anal. Chem.*, **25**, 188 (1953).

[5] E. J. Breda, L. Meites, T. B. Reddy and P. W. West, *Anal. Chim. Acta*, **14**, 390 (1956).

[6] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 504 (1939).