and to contain indium and ferrocyanide in the ratio $5In:4Fe(CN)_6$ (within 0.2%). The formula of the precipitate is therefore presumably $In_5K(Fe(CN)_6)_4$. The determination of the ratio of indium to ferrocyanide in this compound permits using metallic zinc for standardizing the ferrocyanide solution, since the composition of the zinc ferrocyanide precipitate has been determined.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 150]

THE HIGH-TEMPERATURE EQUILIBRIUM BETWEEN THORIUM OXIDE AND CARBON

BY C. H. PRESCOTT, JR. AND W. B. HINCKE

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Plan of the Investigation

The present work is a continuation of a program of research in the field of high-temperature equilibria, using the same general methods and apparatus that have been more completely described in an article on zirconium oxide and carbon.[1] Many facilities have been added to increase the precision and improve the physical conditions of the work. The equilibrium measurements have been carried on up to a temperature of 2500°K. As a result of the higher temperatures now employed many new sources of difficulty and error have been encountered, necessitating a complete study of the temperature corrections for the deviations in behavior of the carbon furnace from that of an ideal black body. It has not been possible to make the carbon elements strictly reproducible but, in spite of the elevated temperature, results have been obtained comparable in precision to the previous work under more moderate conditions.

Previous work on the reduction of thorium oxide by carbon is that of Troost[2] and of Moissan and Étard.[3] Impure thorium metal can be obtained, but with excess of carbon the carbide, ThC_2, is formed. This is a yellow, crystalline compound that yields a wide variety of hydrocarbons on hydrolysis with water. These have been studied in detail by Lebeau and Damiens.[4]

Acknowledgment is due to Dr. W. E. Forsythe of the Nela Research Laboratory for assistance with the pyrometry.

This investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

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[1] C. H. Prescott, Jr., THIS JOURNAL, **48**, 2534 (1926).

[2] Troost, *Compt. rend.*, **116**, 1229 (1893).

[3] Moissan and Étard, *ibid.*, **122**, 576 (1896).

[4] Lebeau and Damiens, *Compt. rend.*, **156**, 1987 (1913).

The Temperature Measurements

The temperature was measured with an optical pyrometer of the disappearing filament type made in the laboratory shop after a design by Forsythe.[5] Two thicknesses of Corning red glass were used for a monochromatic screen and absorption screens were used of noviweld glass, shade six and shade eight. These were calibrated through the courtesy of the Nela Research Laboratory. The effective wave length of the red screen was approximately 0.660μ. The pyrometer was calibrated against a standard ribbon filament tungsten lamp, also obtained from the Nela Research Laboratory.

Corrections for the emissive power of carbon were obtained on six different furnaces mounted in furnace bulb No. 1.[1] Each had three holes 0.38 mm. in diameter in its wall, 120° apart around its circumference, and 1.6 mm. apart along its axis at the center where the temperature was most uniform. The hole served as an experimental black body and a comparison of the temperature (T) measured there with the apparent temperature (S) of the adjacent wall afforded a determination of the effective emissive power (ϵ) of the carbon. This is calculated from the Wien radiation law by the formula

$$\frac{1}{T} - \frac{1}{S} = \frac{\lambda \ln \epsilon}{c_2}$$

Here λ is the effective wave length of the red screen and c_2 is $14{,}330\mu$ degrees. This effective emissive power is the quantity giving the actual correction between true and observed temperature as required for the equilibrium determinations. The data obtained on the emissive power from 1250 to 2700°K. are best summarized by the relation $\epsilon = 0.930 - 4.17 \cdot 10^{-5}T$.

It was found that the inside and outside surfaces of several of the furnaces were not quite concentric; there was considerable temperature gradient along the furnace except at the exact center; there were progressive changes in the surface due to volatilization, especially at the higher temperatures. As a result there were errors in the calculated emissive power, increasing with the temperature, corresponding to a variation in the temperature as great as 25° from the mean at 2700°K. To balance the errors as much as possible, equal numbers of determinations were made on each of the three holes on each furnace, and a mean square solution made of all the data.

Apparatus and Procedure

The main features of the apparatus and general procedure are the same as already described in connection with the work on zirconium. The furnace is a small tube of Acheson graphite 0.318 cm. in diameter at the central section, with a 0.05cm. wall.

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[5] Forsythe, *Astrophys. J.*, **43,** 295 (1916).

The detail of the furnace and its mounting in furnace bulb No. 2 are shown in Fig. 1. For the equilibrium measurements the furnace was loaded with a small pellet of compressed thorium dioxide and graphite and connected to the apparatus in a thermostat at 35° as shown in Fig. 2. The pressure of carbon monoxide was measured on a mercury manometer and the temperature measured by sighting the pyrometer at the center of the furnace through a window in the thermostat. The transmission of this system of two windows with water between was measured and found to be 78.7%.

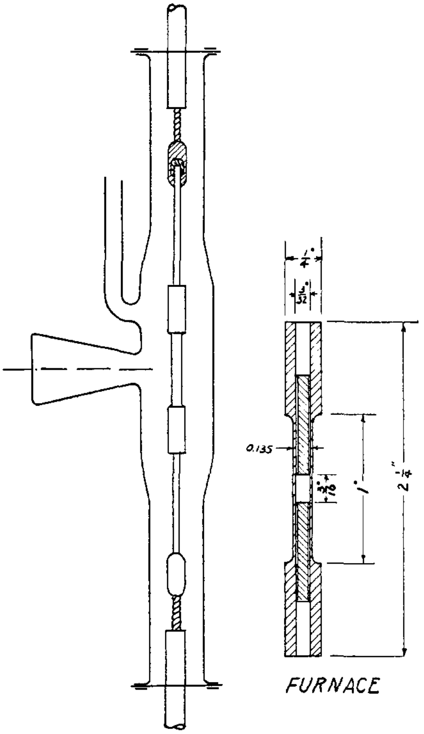


Fig. 1.—Furnace bulb No. 2.

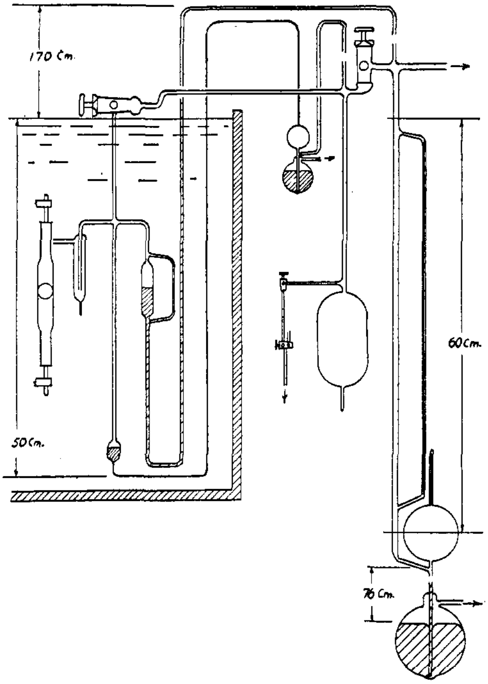


Fig. 2.—Diagram of apparatus for high temperature equilibria.

The power was drawn from a battery of sixty 150-ampere-hour storage cells. At 2500°K. six cells were connected in series and ten in parallel, the current being about 110 amperes. The current was measured and controlled by a Leeds and Northrup Type K potentiometer, using the potential drop across a 0.0034-ohm resistance. At constant current the temperature was very steady throughout a run, so only a few measurements were necessary. The pyrometer current was measured on the same potentiometer from the potential drop across a 1-ohm standard resistance.

Two observers were required, one to make pyrometer settings, read the manometer and perform manipulations, the other to read the potentiometer, regulate the furnace current and record data.

Most of the runs were from fifteen to forty minutes in length; each constituted a determination of the rate of change of pressure at a definite temperature and pressure. As it was more convenient to vary the temperature, a series of runs was made at approximately the same pressure, from which the equilibrium temperature could be estimated by interpolation.

It was found advisable to subject each furnace to a preliminary baking out at 2400°K. under a pressure of two atmospheres (above the equilibrium pressure of the reaction) to drive off adsorbed oxygen.

The product of the reaction was a yellow, microcrystalline aggregate smelling strongly of acetylene immediately upon removal from the furnace. Within a few hours it hydrolyzed to a buff-colored powder, with considerable increase in volume, even when kept over phosphorus pentoxide.

$\frac{dp}{dt} = \frac{\text{Mm.}}{\text{minute}}$	p = Mm.	θ, °K.
−0.13	65.0	1903
−0.127	68.2	2018
−0.03	66.6	2031
−0.019	66.4	1740
0.0	66.0	2038
0.082	63.5	2043
0.14	67.5	2063
0.21	68.3	2054

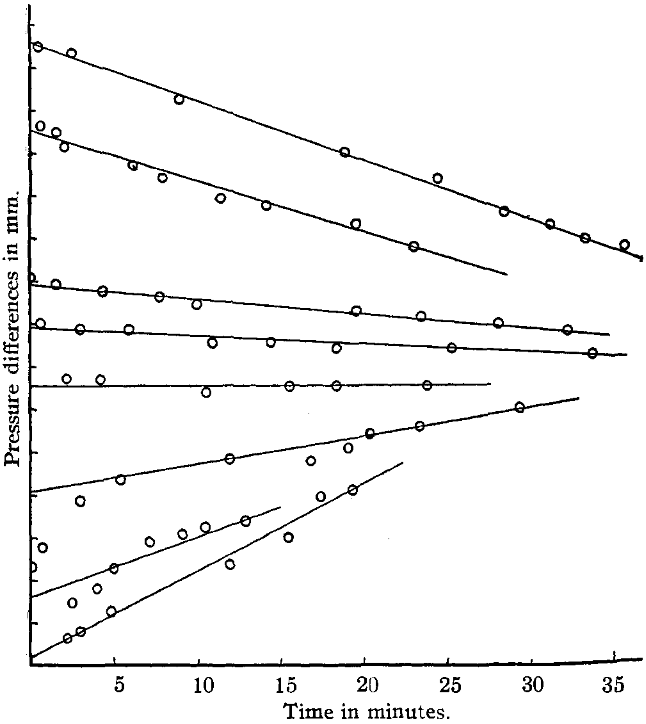
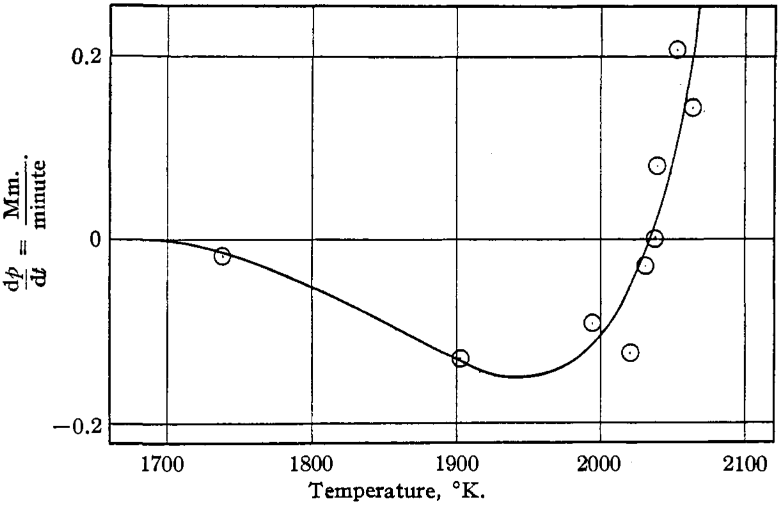


Fig. 3.—Original data at 6.54 cm.

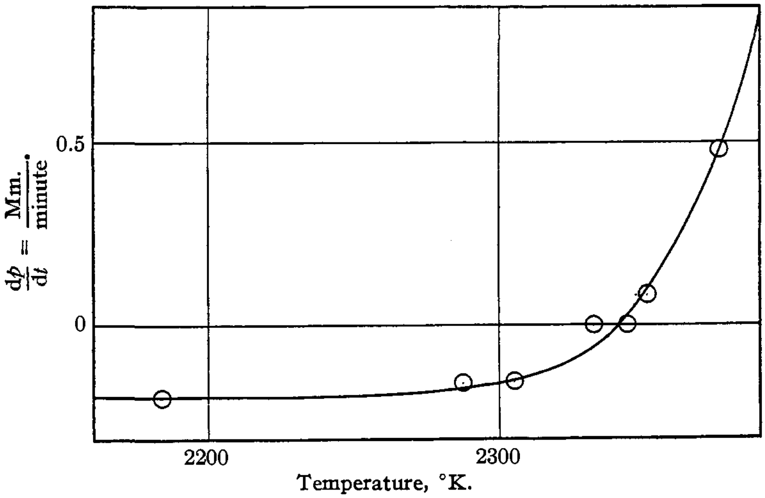
Results of the Equilibrium Measurements

In working up the data the pressures during a run were plotted against the time. The slope of the best straight line gave the rate for the run. Rates at the same pressure were then plotted against the observed temperature (uncorrected). Each of the family of curves so obtained shows the combined influence of two factors, the deviation from equilibrium conditions and an exponential rise in the rate of reaction with temperature. The rate of pressure increase rises enormously with temperature above the equilibrium conditions, decreases to zero at equilibrium and becomes negative as the temperature is reduced, returning to zero as the temperature falls below 1800°K. The intercept of this curve was taken as the observed equilibrium temperature (Figs. 3, 4 and 5 are given as typical examples). To this were added corrections for the transmission of the window and for the emissivity of graphite to give the true temperature. The logarithms of the pressures in atmospheres were then plotted against the reciprocals of the true equilibrium temperatures (Fig. 6). Since the change in the heat of reaction is small, these should fall on a straight



θ = 2035°K.; p = 6.54 cm. = .0861 atm.

Fig. 4.



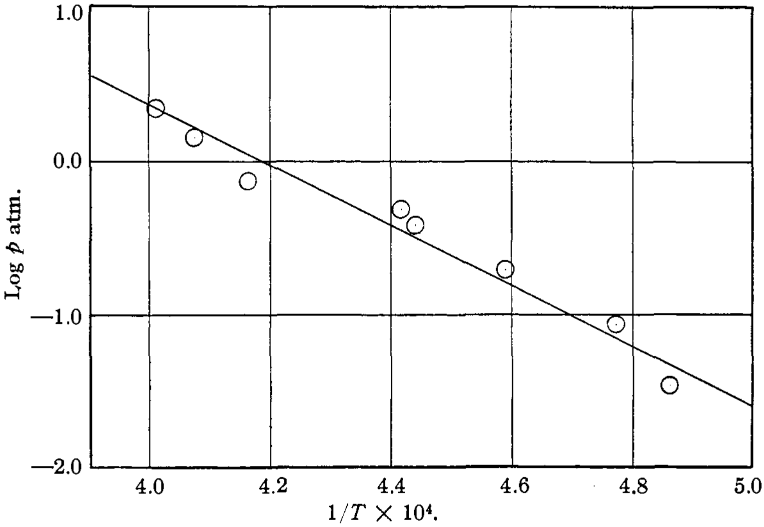
θ = 2341°K.; p = 105.9 cm. = 1.393 atm.

Fig. 5.

line and a least square solution was made for the most probable values of its constants. The largest deviation corresponds to an error of 40% in the pressure, which is easily accounted for by the imperfections of the furnace described in connection with the emissivity measurements. The final relation between equilibrium pressure in atmospheres and the true temperature in degrees Kelvin is given by the equation,

$$\text{Log } p = 8.069 - 19,325/T$$

The true temperatures and pressures are plotted in Fig. 7 in the original coördinates where the curve corresponds to the line in Fig. 6. These values are tabulated in Table I where Θ is the observed temperature, S is the brightness temperature of carbon (corrected for the transmission of the window), T is the true temperature (corrected for the emissivity of carbon) and p is the pressure.



$ThO_2 + 4C = ThC_2 + 2CO$. Log p atm. = 8.069 − 19,325/T. $\Delta F° = 176,970 - 73.892\ T$. $\Delta H = 176,970$.

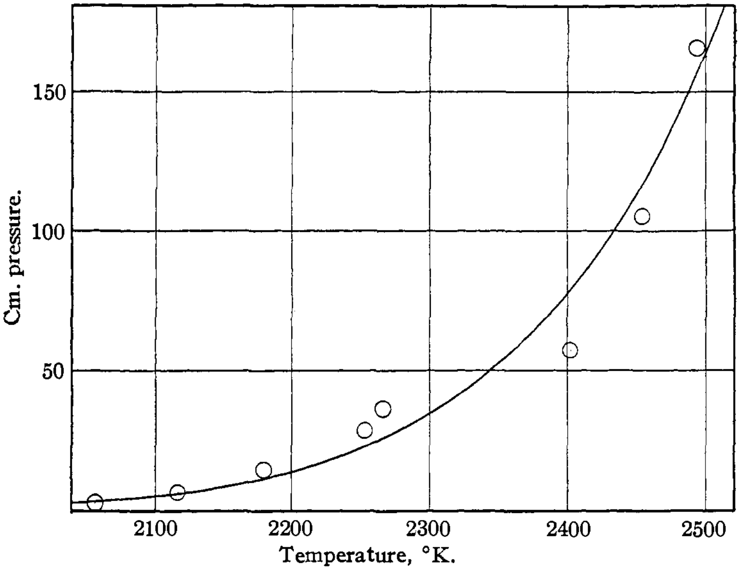
Fig. 6.

TABLE I

EQUILIBRIUM PRESSURES AND TEMPERATURES

Θ, °K.	S, °K.	T, °K.	p, atm.
2377	2441	2494	2.17
2341	2403	2454	1.39
2293	2352	2402	0.752
2170	2223	2265	.480
2158	2210	2252	.380
2092	2141	2179	.192
2035	2082	2117	.0861
1980	2024	2057	.0345

The reaction was so rapid, especially at the higher temperatures, that the interface was not closely comparable from one run to the next, producing considerable variation in the rates. Also, when near equilibrium, the rate would fall off after a couple of runs, probably due to a sintering effect increasing the particle size. It was particularly noticeable that on the reversal of the reaction after a large rate the initial rate was larger than anticipated until the newly formed material was exhausted. There were two very striking observations leading to the above explanations. While determining the equilibrium at 2500°K. the current was momentarily raised enough to fuse the pellet. No further reaction was detectable. One series of runs at low temperature was made on a pellet of exact proportions to produce ThC_2. The forward rates were normal, but no reverse rates were obtained until the pressure was increased many fold, when an extremely slow reverse rate was observed under conditions where previously the reverse reaction went to completion before any readings could be taken. The published data were obtained on pellets containing an excess of oxide to separate the particles of carbide formed, the proportions corresponding to the hypothetical formation of ThC.



$ThO_2 + 4C = ThC_2 + 2CO$. Log p cm. $= 9.950 - 19{,}325/T$. $\Delta F^\circ = 176{,}970 - 73.892\,T$.

Fig. 7.

Besides the preliminary data which were not so correlated that an equilibrium temperature could be interpolated, one complete series of runs was discarded in which the rates were very small and erratic. It was found that the reverse reaction had gone to completion before the readings were taken. On running the reaction ahead for a pressure increase of two centimeters a normal series of runs was obtained with no other change.

The Melting Point of Thorium Carbide

The behavior of a melted pellet has been partly described in the preceding paragraph. Besides the cessation of reaction, it was remarked that the furnace current had increased at the same setting of the control resistances. After regulating the current it was found that the temperature had dropped greatly. On removal it was seen that the pellet had wet the furnace wall and presumably short circuited the central segment. This suggested a method of determining the melting point of the carbide.

A pellet of proportions to yield ThC_2 was mounted in furnace bulb No. 1. It was run. *in vacuo,* at 2100°K. for an hour and a half so as to form the carbide. Carbon monoxide was then admitted to one atmosphere pressure and the temperature raised to 2500°K. The temperature was raised by approximately ten degree steps. At each setting the current was held constant and voltage read across the furnace bulb terminals before and after a series of pyrometer readings. The voltage increased slightly due to the volatilization of the furnace.

At a current of 120.5 amperes the true temperature was 2773°K. The voltage dropped from 7.783 volts to 7.772. Another series of readings showed that the temperature was dropping, and in a few minutes the temperature had dropped 50°, the potential 0.1 volt, and both were changing rapidly.

Upon removal, one-half of the pellet was found melted and the other was a microcrystalline aggregate as in previous preparations at lower temperatures. The preparation was probably reasonably pure at the moment of fusion, so the above value of 2773°K. is not far off.

Thermodynamic Calculations

The chemical reaction is undoubtedly

$$ThO_2 + 4C = ThC_2 + 2CO$$

We may now proceed to calculate the free-energy increase (ΔF) and the heat-content increase (ΔH) attending this reaction when the carbon monoxide pressure is one atmosphere.

The value of ΔF may be derived from the equilibrium pressure p by the familiar thermodynamic equation $\Delta F^\circ = -RT \ln K$, where $K = p^2$. From the determinations of the equilibrium pressure p tabulated in Table I we thus obtain the values given in Table II.

TABLE II

FREE-ENERGY INCREASE ATTENDING THE REACTION

Temp., T, °K.	2494	2454	2402	2265	2252	2179	2117	2057
ΔF°, cal.	−7685	−3224	2723	6612	8666	14301	20660	27543

From the expression for $\log_{10} p$ derived in the same section we similarly obtain the relations, $\Delta F^\circ = 176{,}970 - 73.89\ T$, and $\Delta H = 176{,}970$ calories. At 2395°K. the free-energy change is zero and the actual equilibrium pressure is one atmosphere.

The molal heat capacities, C_p, of graphite and carbon monoxide were taken from Lewis and Randall,[6] and those of thorium oxide and carbide estimated from Kopp's law according to the scheme given in Noyes and Sherrill.[7]

For C $C_p = 1.1 + 0.0048T - 0.0000012T^2$
For CO $C_p = 6.50 + 0.0010T$
For ThO_2 $C_p = 14.2$
For ThC_2 $C_p = 9.8$

From the above-mentioned heat of reaction and the zero value of the free-energy change at 2395°K. the following equations are obtained and from them by extrapolation the following values at room temperature.

$$\Delta H = 194{,}261 + 4.2T - 0.0086T^2 + 0.0000016T^3$$
$$\Delta F^\circ = 194{,}261 - 4.2T \ln T + 0.0086T^2 - 0.0000008T^3 - 64.438T$$
$$\Delta H_{298} = 194{,}790 \text{ cal.};\ \Delta F^\circ_{298} = 168{,}660 \text{ cal.}$$

Combining this heat of reaction with the heat of formation of carbon monoxide,[6] and the heat of formation of thorium oxide,[8] permits a calculation of the heat of formation of thorium carbide.

$ThO_2 + 4C = ThC_2 + 2CO$	$\Delta H = 194{,}790$
$2CO = 2C + O_2$	$52{,}280$
$Th + O_2 = ThO_2$	$-326{,}000$
$Th + 2C = ThC_2$	$\Delta H = -78{,}930$

Summary

The chemical equilibrium between thorium oxide, graphite, thorium carbide and carbon monoxide has been determined at temperatures from 2000 to 2500°K., and at pressures from two centimeters to two atmospheres.

Temperatures were measured with an optical pyrometer. The furnace was a graphite tube 0.318 cm. in diameter with a 0.05cm. wall supported on tungsten rods and enclosed in Pyrex glass. The pressures were read on a mercury manometer. The enclosed gas space was about 100 cc. and was all below the water level of a thermostat at 35°.

Experiments were made on compressed pellets of thorium oxide and graphite. The procedure was to determine at a series of temperatures and pressures the rate of change of pressure with the time. From a series of such experiments at a single pressure and different temperatures the equilibrium temperature was estimated.

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, pp. 89, 569, 576.

[7] Noyes and Sherrill, "Chemical Principles," Macmillan Co., New York, **1922**, p. 93.

[8] Von Wartenberg, *Z. Elektrochem.*, **15**, 869 (1909).

The increases in free-energy and heat-content that would attend this reaction between 2000 and 2500°K. at one atmosphere were found to be those given by the equations $\Delta F^\circ = 176{,}970 - 73.89T$, and $\Delta H = 176{,}970$ calories.

At 2395°K. the free-energy change becomes zero and the actual equilibrium pressure is one atmosphere.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 151]

THE HIGH-TEMPERATURE EQUILIBRIUM BETWEEN ALUMINUM OXIDE AND CARBON

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Plan of the Investigation

The present work is a continuation of a program of research in the field of high-temperature equilibria, using the same apparatus and procedure that have already been applied to reactions between zirconium oxide and carbon,[2] and thorium oxide and carbon.[3] The extraordinary stability of the oxides and carbides of zirconium and thorium at incandescent temperatures has rendered them very fortunate objects of study. Though the results are no less definite, the volatility of aluminum carbide and its consequent tendency to depart from the reaction area have limited the precision attainable in the study of the equilibrium between aluminum oxide and carbon.

The first reliable study of aluminum carbide is that of Moissan[4] who prepared it from its elements in the electric furnace. He found it to be a yellow, crystalline compound of composition corresponding to the formula Al_4C_3, yielding methane on hydrolysis. Askenasy[5] and his associates have shown that mixtures of carbide and metallic aluminum may be obtained by reduction of the oxide with carbon. Fraenkel[6] has shown that the carbide is formed at more moderate temperatures. Ruff[7] has made approximate measurements on the vapor pressure of aluminum carbide, finding that at 2200° the carbide melts and is in equilibrium with liquid aluminum and carbon and with a vapor at 400 mm.

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[1] National Research Fellow in Chemistry.

[2] C. H. Prescott, Jr., THIS JOURNAL, **48**, 2534 (1926).

[3] Prescott and Hincke, *ibid.*, **49**, 2744 (1927).

[4] Moissan, *Compt. rend.*, (II) **119**, 15 (1894).

[5] Askenasy, Jarkowsky and Waniczek, *Z. Electrochem.*, **14**, 811 (1908). Askenasy and Lebedeff, *Z. Elektrochem.*, **16**, 559 (1910).

[6] Fraenkel, *ibid.*, **19**, 362 (1913).

[7] Ruff, *ibid.*, **24**, 157 (1918).