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).

pressure containing about equal parts of aluminum and aluminum carbide. Ruff[8] has also determined the melting point of aluminum oxide as between 1965 and 2065°, stating that the oxide is volatile at about 1900°.

The present investigation has been aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

Apparatus and Procedure

The apparatus and general procedure have already been completely described in references (2) and (3).

Most of the runs were from ten to thirty-five minutes in length; each constituted a determination of the rate of change of pressure in the furnace bulb 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. This procedure was followed on furnaces A to E. In the hope that a different procedure would give better curves for the interpolation, series were made at constant temperature and different pressures on furnaces F to H.

In preliminary experiments it was found that extremely intimate contact was necessary in order to prepare the carbide, so all subsequent work was done on pellets made by thoroughly grinding graphite and an excess of aluminum oxide in ether and just enough Nujol (a pure paraffin oil) to bind the sample when compressed in a pellet press. The excess oxide was to help make up for losses of aluminum by vaporization.

Forward rates with evolution of carbon monoxide were invariably accompanied by a cream-colored deposit on the walls of the glass tube enclosing the furnace, and a black or dark brown deposit at pressures below 5 cm. Reverse rates were frequently terminated by exhaustion of carbide, and more had to be generated by running at higher temperature or lower pressure before another reverse rate could be obtained. Furnaces A, B and C were run till no further reaction could be obtained. The residue of the charge was found to be a small quantity of graphite which ignited completely on a platinum foil. The remaining furnaces were run for but one equilibrium determination apiece; their charges always showed some residue of white oxide on ignition, and in most cases some yellow carbide was to be seen in the charge.

To remove absorbed oxygen from the graphite furnace, each was subjected to a preliminary baking for an hour at about 2050°K. under a pressure of 2.5 atmospheres of carbon monoxide (above the equilibrium pressure of the reaction). During this treatment a slight white deposit appeared which was probably aluminum oxide.

In a preliminary preparation given fifteen minutes at 2000°K., *in vacuo*,

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[8] Ruff, *Ber.*, **43**, 1571 (1910).

a preparation of yellow carbide mixed with graphite was obtained which gave a considerable evolution of hydrocarbon fumes on treatment with sodium hydroxide.

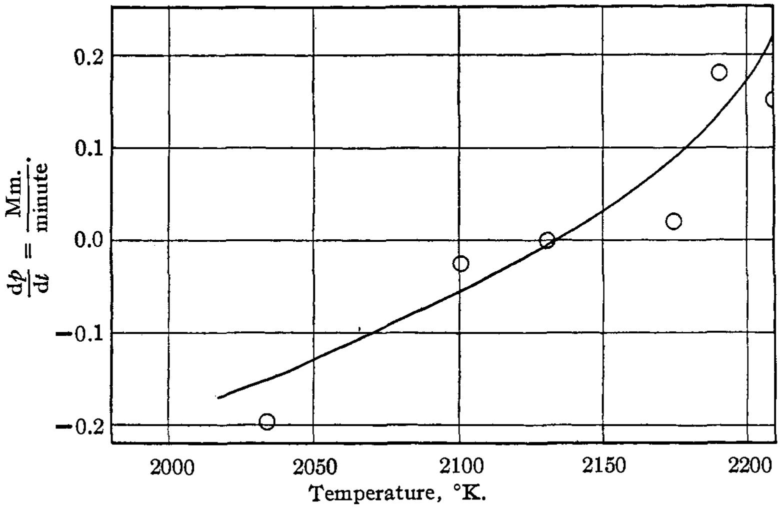


Fig. 1.—Furnace E. $\theta = 2134$. $T = 2224$°K. $p = .4408$ atm.

Both the black and the white material deposited during the carbide formation dissolved completely in both hydrochloric acid and sodium hydroxide and gave characteristic tests for aluminum. On ignition the cream-colored material flashed and turned black. Both deposits

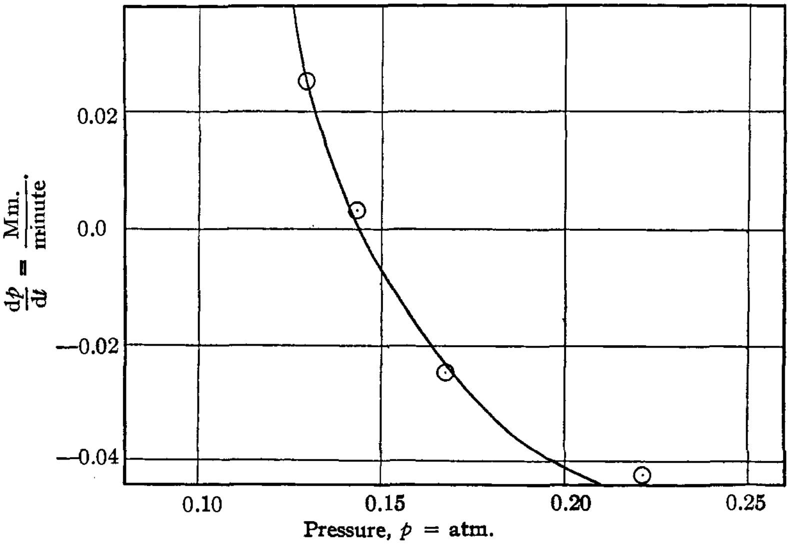
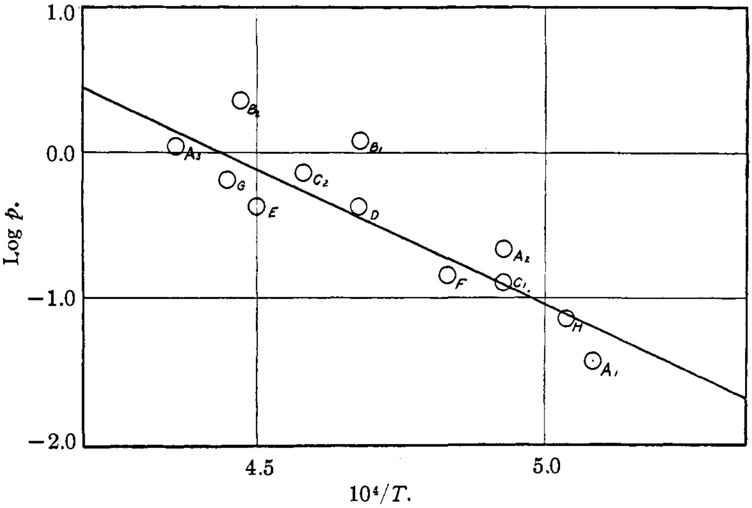


Fig. 2.—Furnace F. $T = 2071$°K. $p = .141$ atm.

gave white oxide on continued ignition. Since it is reported[9] that metallic aluminum reacts with carbon monoxide to give a mixture of carbide and oxide, and the black deposit appeared at low pressures where the rate of reaction was greatest, the black deposit was probably aluminum and the cream-colored aluminum carbide.

Results of the Equilibrium Measurements

The observed rates of change of pressure in the furnace bulb certainly give limits in almost all cases to the possible values of the equilibrium conditions, but due to the radical changes in the pellet and solid interface from one run to the next, the graphical interpolation is attended with considerable uncertainty. Figs. 1 and 2 are given as typical examples of the plots of rate of change of pressure.



$2Al_2O_3 + 9C = Al_4C_3 + 6CO$. $\text{Log } p = 8.21 - 18{,}480/T$.

Fig. 3.

In Fig. 3, the logarithms of the equilibrium pressures in atmospheres are plotted against the reciprocals of the true temperatures. Since the change in the heat of reaction is small, these points should fall on a straight line and a least square solution was made for its constants. As the earlier values were less certain, and, in particular, since determining more than one equilibrium on each furnace was inadvisable, equal weight was given to the values obtained on each furnace, that is, A_1, A_2 and A_3 were weighted $^1/_3$ each, and B_1, B_2, C_1 and C_2, $^1/_2$ each. The final relation between the equilibrium pressure in atmospheres and the true temperature in degrees Kelvin is given in the equation

$$\text{Log } p = 8.21 - 18{,}480/T$$

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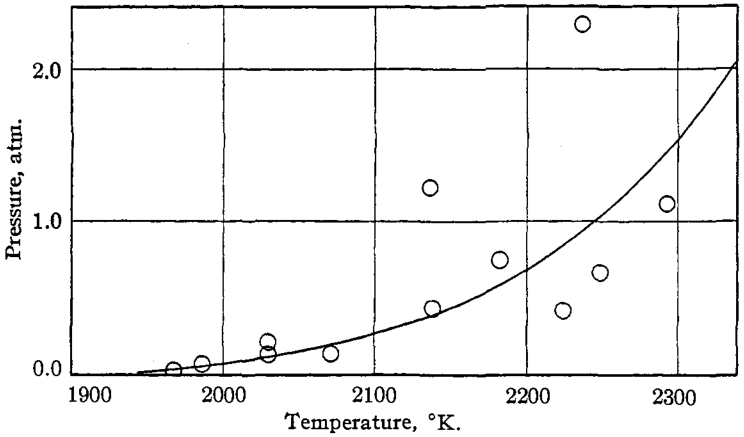
[9] Pring, *J. Chem. Soc.*, **87**, 1530 (1905).

The true temperatures and pressures are plotted in Fig. 4 in the original coördinates where the curve corresponds to the line in Fig. 3. 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.



$2Al_2O_3 + 9C = Al_4C_3 + 6CO.$

Fig. 4.—Equilibrium pressures and temperatures.

TABLE I

EQUILIBRIUM PRESSURES AND TEMPERATURES

Detn.	Θ, °K.	S, °K.	T, °K.	p, atm.
A_1	1898	1938	1967	0.0376
A_2	1956	1999	2030	.2193
A_3	2196	2250	2293	1.122
B_1	2054	2101	2137	1.222
B_2	2145	2197	2237	2.288
C_1	1956	1999	2030	0.1308
C_2	2101	2146	2183	.746
D	2055	2102	2138	.484
E	2134	2185	2224	.441
F	1994	2039	2071	.144
G	2156	2208	2248	.668
H	1908	1956	1987	.0731

Thermodynamic Calculations

The equation expressing the chemical reaction is undoubtedly

$$2Al_2O_3 + 9C = Al_4C_3 + 6CO$$

The value of $\Delta F°$, the free-energy increases attending this reaction, may be derived from the familiar thermodynamic equation, $\Delta F° = -RT \ln K$, where $K = p^6$. 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

Detn.	Temp., T, °K.	ΔF°	Detn.	Temp., T, °K.	ΔF°
A_1	1967	−76,990	C_2	2183	− 7634
A_2	2030	−36,750	D	2138	−21,020
A_3	2293	3150	E	2224	−21,740
B_1	2137	5112	F	2071	−47,880
B_2	2237	22,090	G	2248	−10,808
C_1	2030	−49,270	H	1987	−62,020

From the expression for $\log_{10} p$ derived in the same section we similarly obtain the relations $\Delta F^\circ = 507{,}760 - 225.6T$, and $\Delta H = 507{,}760$ calories. At 2251°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,[10] and those of aluminum oxide and carbide from Kopp's law according to the scheme given in Noyes and Sherrill,[11] as giving a reasonable approximation at high temperatures.

For C $C_p = 1.1 + 0.0048T - 0.0000012T^2$
For CO $C_p = 6.50 + 0.0010T$
For Al_2O_3 $C_p = 24.4$
For Al_4C_3 $C_p = 30.2$

From the above-mentioned heat of reaction and the zero value of the free-energy change at 2251°K., the following equations are obtained and from them by extrapolation the following values at room temperature,

$$\Delta H = 537{,}310 + 10.50T - 0.0186T^2 + 0.0000036T^3$$
$$\Delta F^\circ = 537{,}310 - 10.50T \ln T + 0.0186T^2 - 0.0000018T^3 - 190.39T$$
$$\Delta H_{298} = 538{,}900 \text{ cal.}$$
$$\Delta F^\circ_{298} = 464{,}300$$

Using these values and the values for the formation of aluminum oxide given by Parks and Kelley,[12] and values for the formation of carbon monoxide from Lewis and Randall,[10] values may be calculated for the formation of aluminum carbide from its elements.

$2Al_2O_3 + 9C = Al_4C_3 + 6CO$	$\Delta H_{298} = 538{,}900$	$\Delta F^\circ_{298} = 464{,}300$
$4Al + 3O_2 = 2Al_2O_3$	−756,000	−712,600
$2C + O_2 = 2CO$	−52,280	−65,020
$4Al + 3C = Al_4C_3$	$\Delta H_{298} = -60{,}260$	$\Delta F^\circ_{298} = -53{,}240$

From heats of combustion determined by Berthelot,[13] the heat of reaction for the reduction of aluminum oxide to carbide may be calculated, as well as the heat of formation of aluminum carbide.

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[10] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, pp. 80, 569, 576.

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

[12] Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[13] Berthelot, *Ann. Chim. Phys.*, [7] **22**, 470 (1901); [7] **22**, 479 (1901); Berthelot and Petit, *ibid.*, [6] **18**, 98 (1889); Berthelot and Matignon, *ibid.*, [6] **30**, 555 (1893).

$$\begin{array}{lr}
Al_4C_3 + 6O_2 = 2Al_2O_3 + 3CO_2 & \Delta H = -824{,}000 \\
4Al + 3O_2 = 2Al_2O_3 & -760{,}400 \\
C + O_2 = CO_2 & -\ 94{,}810 \\
2CO + O_2 = 2CO_2 & -136{,}400 \\
2Al_2O_3 + 9C = Al_4C_3 + 6CO & \Delta H = \ 379{,}910 \\
4Al + 3C = Al_4C_3 & -220{,}830
\end{array}$$

The first value is in disagreement with the results of the present work by 160,000 calories. However, the determination of the heat of reaction is not so accurate as those for the free energy, and the slope of the line in Fig. 3 could be reduced by one-third without very serious prejudice to the data; but Berthelot himself remarked that the heat of formation of the carbide seemed abnormally large. The presence of oxide in his carbide might account for the discrepancy.

Summary

Determinations have been made of the chemical equilibrium for the reaction

$$2Al_2O_3 + 9C = Al_4C_3 + 6CO$$

The increases in free energy and heat content that would attend this reaction between 2000 and 2300°K. and one atmosphere pressure were found to be those given by the equations, $\Delta F^\circ = 507{,}760 - 225.6T$ and $\Delta H = 507{,}760$ calories. At 2251°K. the free-energy change is zero and the actual equilibrium pressure is one atmosphere.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-CARBONDISULFIDE. III. BEHAVIOR OF AZIDO-CARBONDISULFIDE TOWARD CHLORINE, BROMINE AND IODINE[1]

BY WM. HOWLETT GARDNER AND A. W. BROWNE

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Azido-carbondisulfide may not inappropriately be designated as a *universal reagent* in the sense in which water has been termed a "universal solvent." Its reactivity toward acids and alkalies, toward oxidizing and reducing agents, toward certain metals and non-metals, toward water and ammonia, and apparently even toward certain organic solvents, together with its tendency to undergo an extremely regular autocatalytic decomposition at room temperature, seems to entitle this substance to characterization as an almost unique reagent.

In connection with the distinctly halogenoid character of azido-carbon-

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[1] For the earlier articles of this series see (a) Browne, Hoel, Smith and Swezey, THIS JOURNAL, **45**, 2541 (1923); (b) Wilcoxon, McKinney and Browne, *ibid.*, **47**, 1916 (1925). The current article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by William Howlett Gardner in partial fulfilment of the requirements for the degree of Doctor of Philosophy.