It has been calculated that the entropy effect due to the existence of the two forms of hydrogen would be 4.39 ± 0.06 cal./deg. per mole. This amount must be added to that given by the Sackur equation or to that given by the ordinary application of the third law of thermodynamics. It does not appear possible to reconcile this addition with third law data unless a similar consideration, not necessarily leading to the same amount, is applied to molecules containing hydrogen. These effects may be expected in many, if not most, of the other elements.

We believe that any system approaches zero entropy as the absolute zero of temperature is approached when true equilibrium exists in the distribution of energy between such energy states as are actually occupied by the system. As a particular example, the cooling of a solution of isotopes is considered. Our conclusions are in complete agreement with the third law of thermodynamics as stated by Lewis and Gibson, although we recognize additional difficulties in the application of this law.

We wish to emphasize the distinction between the exactness of the third law of thermodynamics and our experimental inadequacy in using it directly.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 182]

EQUILIBRIUM BETWEEN ALUMINUM CARBIDE AND NITROGEN AT HIGH TEMPERATURES

BY C. H. PRESCOTT, JR.[1] 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 involving the extension of our previous methods to cover a region of very low pressures. Measurements have been made of equilibrium pressures from 0.0016 mm. to 0.017 mm. at temperatures from 1774°K. to 1909°K. The McLeod gages now in use would cover the range up to 5 mm. The manometer technique previously devised has been used at pressures from 3 cm. to 2.3 atmospheres and at temperatures up to 2500°K. So the combined methods seem applicable to pressures differing by a factor of a million and at temperatures from 1000°K. to 2500°K. The most significant region probably lies above 1500°K. where more conventional technique is inapplicable.

The subject of the present work is the equilibrium of the system aluminum carbide, nitrogen, aluminum nitride and carbon. The equilibrium pressure of nitrogen may be approximately predicted by combining the

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results of Fraenkel[2] on the system aluminum oxide, carbon, nitrogen, aluminum nitride, with those of our own experiments on the system aluminum oxide, carbon, aluminum carbide and carbon monoxide.[3] These values have been verified by the present experiments. According to Fichter and Oesterheld[4] the sublimation of aluminum nitride accompanied by decomposition begins at 1870° under about 14 mm. of nitrogen. The chemistry of aluminum nitride has been thoroughly reviewed by Krase, Thompson and Yee.[5]

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

Apparatus and Procedure

The temperature measurements were made with an optical pyrometer. The details and corrections have already been described.[6]

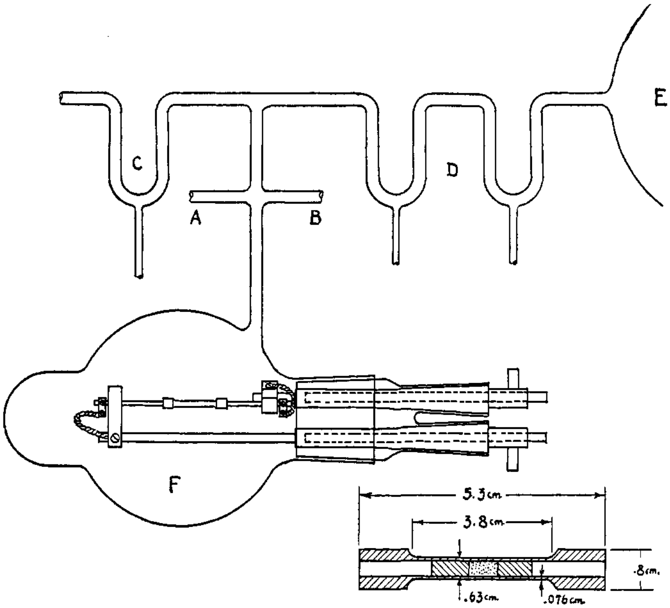

Fig. 1.—Apparatus for low pressure equilibria.

The furnace, shown in Fig. 1, was a tube of Acheson graphite 5.3 cm. long, 0.8 cm. in diameter at the ends, and 0.53 cm. in the central section for a length of 3.8 cm., with a 0.076 cm. wall. In the preliminary experiments a smaller furnace was used whose center was 0.032 cm. in diameter with a 0.04 cm. wall. A pellet of compressed aluminum and graphite powder about 0.4 cm. long was held in the center of the furnace by graphite

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[2] Fraenkel, *Z. Elektrochem.*, **19**, 362 (1913).

[3] Prescott and Hincke, This Journal, **49**, 2753 (1927).

[4] Fichter and Oesterheld, *Z. Elektrochem.*, **21**, 50 (1915).

[5] Krase, Thompson and Yee, *Ind. Eng. Chem.*, **18**, 1287 (1926).

[6] Prescott and Hincke, This Journal, **49**, 2744 (1927); *Phys. Rev.*, **31**, 130 (1928).

plugs. In the later experiments a groove was cut on either side of the center centimeter of the furnace to equalize the temperature gradient.

This furnace was supported horizontally on tungsten rods pressed into its ends, which rested on steel guides clamped to water-cooled copper leads. Electrical connection was made by flexible copper wire fastened to steel clamps on the ends of the tungsten rods. The outer ends of the water-cooled leads were tapered to fit ground-glass seals in a Pyrex plug which in turn was ground to fit a 1-liter Pyrex flask. Seals were made with Dennison's banker's specie sealing wax. A plane glass window was waxed to the end of a 2.5-cm. tube which projected 16 cm. from the side of the flask, as the flask itself became clouded with a mirror of metallic aluminum. This was developed from apparatus used in preliminary studies on zirconium oxide and carbon.[7]

The flask (F) was connected through a mercury cut-off (C) to a single-stage mercury diffusion pump backed by a Hyvac oil pump. Two mercury cut-offs (D) connected to a 3-liter flask (E) which served as a nitrogen reservoir. Small amounts of nitrogen were introduced by alternately opening the two cut-offs. Tube A led to a Toepler pump which withdrew samples of gas for analysis.[8] Tube B led to two McLeod gages with a combined range from 10^{-4} to 5 mm. Their volumes were as small as possible, 50 and 7 cc., to minimize dead space.

In the procedure finally adopted the whole apparatus was evacuated and the furnace run for a moment at 1500°K. to drive off a part of the adsorbed gases. Hydrogen was next introduced to one atmosphere and the furnace run at 1880°K. for one hour. This baked off the remaining gases, formed the aluminum carbide and partially sintered it, reducing the amount of metallic aluminum which vaporized later. It also helped bake out the Pyrex flask. The apparatus was next evacuated and filled to 6 cm. of nitrogen and the furnace run at 1880°K. for from thirty minutes to three hours to change some of the carbide to nitride. It was again evacuated and a stream of tap water turned on at the top of the flask which completely enveloped it and kept it cold while equilibrium measurements were taken. After this treatment the evolved gases were from 97 to 101% nitrogen as compared to 10% without the stream of water. The gases evolved from the walls were chiefly hydrogen and carbon monoxide. The carbon monoxide probably came from water vapor which reacted with the carbon furnace. The hydrogen was too much in proportion to be accounted for in this way unless the water vapor also reacted with the aluminum on the walls.

For the preliminary baking the current was drawn from a 1-kw. transformer. During the measurements it was drawn from a storage battery. To maintain the larger size of furnace at 1880°K. required 100 amps. at 10 volts, though most of the power was lost in the leads.

The Equilibrium Measurements

The reacting material was in each case a pellet of Baker's analyzed metallic aluminum and Acheson graphite, each ground to pass 200 mesh, and mixed in proportions to form Al_4C_3 with a 10% excess of carbon to reduce any oxide which might be in the finely divided aluminum.

In the first significant experiment such a pellet was run for an hour at 1880°K. in one atmosphere of nitrogen. It was then removed and tested for combined nitrogen. A sample was digested in sodium hydroxide and vapors caught in 0.02 *N* hydrochloric acid as in a standard

[7] Prescott, This Journal, **48**, 2534 (1926).

[8] Prescott, *ibid.*, **50**, 3237 (1928).

Kjeldahl determination. Further samples were run under reduced pressures of nitrogen down to 1 mm. All showed a considerable proportion of combined nitrogen.

The first equilibrium measurements were made on small furnaces with no cooling water on the flask. Ten times as much interfering gases were evolved as of the nitrogen under consideration. At each temperature several runs were made of an hour's duration, starting each at a different pressure of nitrogen. The final nitrogen pressure was obtained by an analysis of the gases. From the several values of the change of pressure it was possible roughly to interpolate for the equilibrium pressure. The values obtained with two different furnaces are plotted as points in triangles in Fig. 2, a graph where one scale is proportional to the logarithm of the equilibrium pressure in millimeters, and the other is proportional to the reciprocal temperature. A blank run, however, indicated that some nitrogen was also evolved from an empty furnace, of the same order of magnitude as the former pressure changes, so the results are rather dubious. To get sufficient material the pellets were made about 0.6 cm. long and at the conclusion of each series little aluminum remained except at the ends of the original pellet, a region probably at lower temperature than the maximum temperature where the pyrometer was sighted. In view of such uncertainties these measurements are of little weight in comparison with later determinations under better conditions.

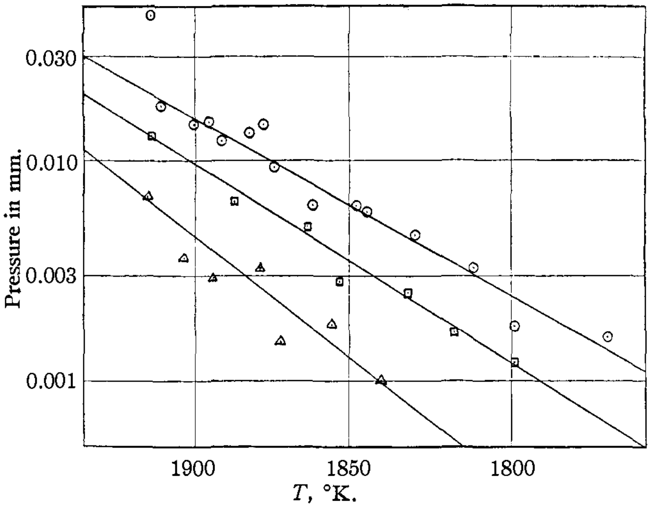

Fig. 2.—Preliminary and final results. Log $P_{\text{mm.}} = 12.772 - 27697/T$.

The next measurements were a series of runs on a single large furnace after preliminary baking in hydrogen and with cooling water on the flask.

The interfering gases dropped to a few per cent. and it was possible at once to follow the changes in nitrogen pressure on the McLeod gages, so that two runs of one hour each were sufficient to determine an equilibrium pressure. The results are plotted as points in squares in Fig. 2. It was noticed in assembling that the contact between one tungsten rod and the furnace was quite loose. It was also noticed that this contact ran rather hotter than the other. Unfortunately the pyrometer was still sighted at the maximum of temperature, which, due to the unsymmetrical heating, probably did not coincide with the geometrical center of the furnace where the charge was located. The discrepancy between these and the later results would be equivalent to a temperature error of 36°.

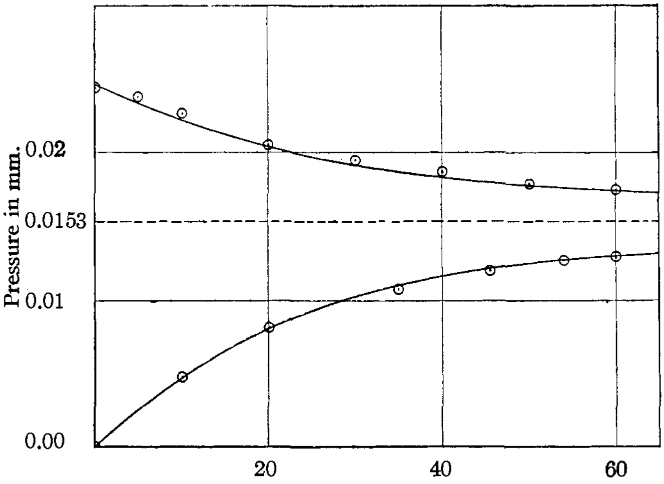

Fig. 3.

With the next furnace the loose contact was eliminated and in two later furnaces grooves were cut to equalize the temperature gradient along the middle portion of the furnace. The pyrometer was sighted at the geometrical center where the charge was definitely located. Fig. 3 is a typical example of two runs which determined an equilibrium pressure. The furnace was run for ten minutes on the pumps. The mercury cut-off C was then released and the pressure rose as shown in the lower curve of the figure. After an hour the current was turned off and the gas pumped off for analysis.[8] Cut-off C was (Fig. 1) lowered and the flask evacuated. It was again raised and nitrogen introduced from the reservoir E to twice the final pressure of the previous run. The furnace was then run for an hour, the pressure falling as shown in the upper curve of the figure. This gas was also pumped off for analysis. In this case both contained 98.5% nitrogen. The two final pressures were corrected and their average taken as the equilibrium pressure: 0.0150 mm.· at 1895°K. The broken line on the figure is the average of the uncorrected pressures. The equilibrium values obtained from these three furnaces are plotted as points in circles in Fig. 2 and also in Fig. 4 by themselves.

Anomalous results were obtained from two furnaces in cases where mercury was spilled into the furnace flask before the baking in nitrogen. Nitrogen was evolved at pressures up to one-half millimeter. In the one case which was thoroughly studied reverse rates were at first obtained above this pressure, but later no absorption of nitrogen occurred. Upon removal and analysis of the pellet the nitrogen content was found to be just slightly less than that corresponding to the formation of AlN. This indicated the absence of any aluminum compound higher in nitrogen content. On keeping mercury out of the furnace flask no further trouble resulted. The formation of a nitride of mercury is improbable, so the effect is probably due to adsorption on the finely divided material which distilled around. This gave off gas during the runs, the absorption of nitrogen going on until all of the aluminum carbide present was converted to nitride. It should be noted that mercury vapor was always present at about 10^{-3} mm. from the various traps and gages but never figured in any of the McLeod gage readings of gas pressure.

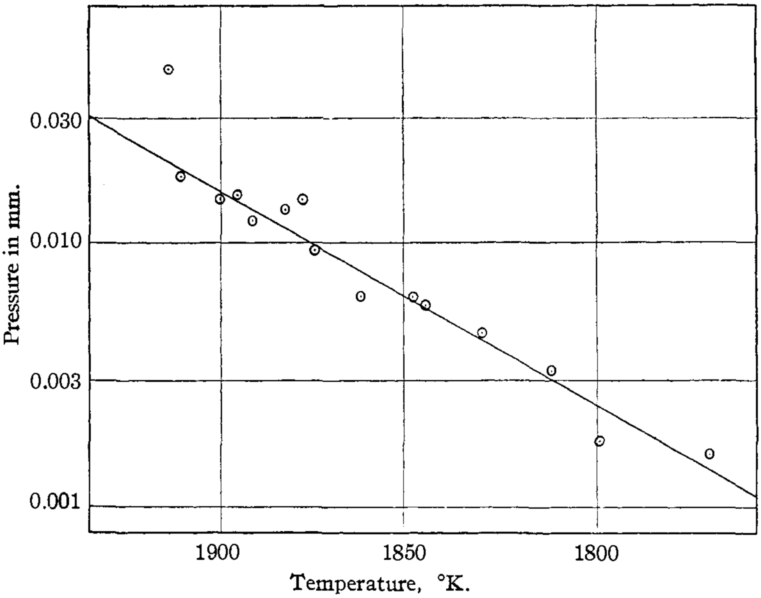

Fig. 4.—$4AlN + 3C = Al_4C_3 + 2N_2$. Log $P_{mm.} = 12.772 - 27697/T$.

Results of the Measurements

The most certain and reproducible results are those plotted in Fig. 4.

The same data are recorded in Table I, together with the duration of the initial baking in nitrogen.

TABLE I

EQUILIBRIUM PRESSURES AND TEMPERATURES

Furnace	Detn.	Temp., °K.	Press., mm.	Time of nitrification
A	1	1895	0.01503	145 minutes
	2	1874	.00954	
	3	1850	.00622	
	4	1829	.00458	
	5	1877	.01453	
B	1	1884	.01334	60 minutes
	2	1845	.00582	
	3	1813	.00325	
	4	1774	.00158	
	5[a]	1915	.0455	
C	1	1891	.01215	30 minutes
	2	1901	.01461	
	3	1909	.01732	
	4	1799	.00176	
	5	1862	.00612	

[a] Discarded.

According to the times of nitrification furnace A should have had the highest nitrogen content and C the lowest. This accords with the fact that the final determinations on furnaces A and B fell high, and on furnace C low, although the initial determinations are in very excellent agreement. As material volatilized from the pellet, either carbide or nitride would tend to be exhausted as both were appreciably volatile. The trend of the equilibrium pressures might indicate a slight dependence on concentration effects due to mutual solubility of the solid phases, but is more probably a dynamic effect depending on the methods of measurement. In a true equilibrium state forward and reverse reaction velocities must be equal, and both will occur simultaneously at the same solid interface. When an observable reaction occurs, however, the interface will spread into the reacting material, so the area of the interface and the net over-all velocity of reaction will depend to some extent on the mass of the reacting material. This dependence will decrease the closer approach is made to equilibrium conditions, but will always influence equilibrium measurements derived from the interpolation of finite velocities of reaction, particularly when materials become exhausted.

This might be a valid reason for rejecting such a determination as B 5, the last of its series. A least-square solution of the data in Table I gave a probable error corresponding to an 18% deviation in the pressure. On account of its large deviation the point B 5 could be rejected in accordance with established principles from the laws of probability.[9] A least square solution of the remaining data for the constants of the linear relation shown in Fig. 4 gave the result where log p is the common logarithm of the pressure in millimeters and T the absolute temperature

$$\text{Log } p_{\text{mm.}} = 12.772 - 27697/T$$

Or for the pressure in atmospheres

$$\text{Log } p_{\text{atm.}} = 9.891 - 27697/T$$

with a probable error corresponding to an 11% deviation in the pressure, which is equivalent to 5.8° in the temperature measurements.

In reading pressures, particularly with a McLeod gage, the errors to be expected will be roughly proportional to the pressure, so the weights of observations will be most nearly equal when expressed on a logarithmic scale. Also, in matching light intensities, by Weber's law a difference in visual sensation corresponds to a change in the logarithm of the energy intensity. By the Wien radiation law

$$\frac{1}{T} - \frac{1}{T'} = \frac{\lambda \ln \epsilon}{c_2}$$

Here ϵ would correspond to the ratio of intensities, the logarithm of the ratio of intensities being proportional to the difference in the reciprocal temperature. So the weights of observations should be most nearly equal in the scale adopted, that of the logarithm of the pressure against the reciprocal temperature. Also, since the van't Hoff equation predicts a linear relation for small changes of the heat of reaction, this is the most convenient scale for the adjustment of observations.

$$2.303 \log K = -\frac{\Delta H}{RT} + \text{const.}$$

Thermodynamic Calculations

The equation expressing the chemical reaction involved is

$$4\text{AlN} + 3\text{C} = \text{Al}_4\text{C}_3 + 2\text{N}_2$$

We may now proceed to calculate the free-energy increase (ΔF) and the heat-content increase (ΔH) attending this reaction when the nitrogen 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 determination of the equilibrium pressure p tabulated in Table I, we thus obtained the values given in Table II.

From the expressions for $\log_{10} p$ derived in the same section we similarly obtain the relations, $\Delta F^\circ = 253{,}630 - 90.58\ T$, and $\Delta H = 253{,}630$ calories. At 1875°K. the equilibrium pressure is 0.0100 mm. and the free-energy change is 83,800 calories.

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[9] Merriman, "Method of Least Squares," John Wiley and Sons, Inc., New York, **1911**, p. 166.

TABLE II

FREE-ENERGY INCREASE ATTENDING THE REACTION

Temp., T, °K.	1909	1901	1895	1891	1884	1877	1874
$\Delta F°$, cal.	81150	82150	81700	83100	82100	81200	84100
Temp., T, °K.	1862	1850	1845	1829	1813	1799	1774
$\Delta F°$, cal.	86900	86300	86500	87500	89100	92800	92400

The molal heat capacities, (C_p), of graphite and nitrogen were taken from Lewis and Randall,[10] and those for aluminum carbide and nitride estimated from Kopp's law according to the scheme given in Noyes and Sherrill,[11] taking the atomic heat of nitrogen as 2.9, the mean of carbon and oxygen.

For C $C_p = 1.1 + 0.0048T - 0.0000012T^2$
For N_2 $C_p = 6.50 + 0.0010T$
For Al_4C_3 $C_p = 30.2$
For AlN $C_p = 9.1$

From the above-mentioned heat of reaction and the value of the free-energy change at 1875°K., the following equations are obtained and from them by extrapolation the following values at room temperature

$$\Delta H = 260{,}954 + 3.5T - 0.0062T^2 + 0.0000012T^3$$
$$\Delta F° = 260{,}954 - 3.5T \ln T + 0.0062T^2 - 0.0000006T^3 - 77.621T$$
$$\Delta H_{298} = 261{,}478 \text{ cal.} \qquad \Delta F°_{298} = 232{,}406 \text{ cal.}$$

From these values and the values for the formation of aluminum carbide given by Prescott and Hincke[12] values may be calculated for the formation of aluminum nitride from its elements.

$$2N_2 + Al_4C_3 = 4AlN + 3C \qquad \Delta H_{298} = -261{,}478 \qquad \Delta F°_{298} = -232{,}406$$
$$4Al + 3C = Al_4C_3 \qquad = -\ 60{,}260 \qquad = -\ 53{,}240$$
$$Al + {}^1/_2N_2 = AlN \qquad = -\ 80{,}434 \qquad = -\ 71{,}411$$

By combining equations for the oxide–carbide equilibrium[12] with those for the carbide–nitride equilibrium given above, the following relations are obtained for the reaction involving the simultaneous reduction and nitrification of aluminum oxide

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$$
$$\log K = 14.74 - 27743T \qquad K = p^3_{CO}/p_{N_2}$$
$$\Delta F° = 127{,}065 - 67.5T \qquad \Delta H = 127{,}065 \text{ cal.}$$
$$\Delta H = 138{,}178 + 3.5T - 0.0062T^2 + 0.0000012T^3$$
$$\Delta F° = 138{,}178 - 3.5T \ln T + 0.0062T^2 - 0.0000006T^3 - 56.385T$$
$$\Delta H_{298} = 138{,}711 \text{ cal.} \qquad \Delta F°_{298} = 115{,}947 \text{ cal.}$$

From the above equation the values of the equilibrium constant at 1500 and 1600° are, respectively, 0.123 and 0.851. For a total pressure of one

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[10] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," 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] Prescott and Hincke, THIS JOURNAL, **49**, 2753 (1927).

atmosphere the fraction of carbon monoxide in an equilibrium mixture would be 41.6 and 66.0%. These values are on the upper limits which Fraenkel[2] assigned from his study of this reaction: 25 – 40% at 1500° and 50 – 65% at 1600°.

Summary

Apparatus has been devised and methods have been extended for the study of chemical equilibria at incandescent temperatures at pressures of 0.01 mm. Determinations were made for the reaction $4AlN + 3C = Al_4C_3 + 2N_2$. The increases in free energy and heat content that would attend this reaction between 1775°K. and 1910°K. at one atmosphere pressure were found to be those given by the equations $\Delta F^\circ = 253{,}630 - 90.58T$, and $\Delta H = 253{,}630$ cal. At 1875°K. the equilibrium pressure is 0.0100 mm. and the free-energy change is 83,800 calories.

Calculations have been made for the reaction $Al_2O_3 + 3C + N_2 = 2AlN + 3CO$. The corresponding equations are $\Delta F^\circ = 127{,}065 - 67.5T$ and $\Delta H = 127{,}065$ cal. These values are in agreement with the observations of Fraenkel on this reaction.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 183]

APPARATUS FOR MICRO GAS ANALYSIS

BY C. H. PRESCOTT, JR.[1]

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In connection with measurements on the equilibrium between aluminum carbide and nitrogen[2] it was necessary to analyze quite small quantities of gas to determine the partial pressure of nitrogen. Langmuir[3] has briefly described methods by which quantities of gas as small as one cubic millimeter at atmospheric pressure may be subjected to quantitative analysis. The author has seen this apparatus through the courtesy of Dr. Langmuir and recalls that the methods consisted in treating very small volumes of gas with aqueous reagents at atmospheric pressure.

In the present technique the gases are handled at low pressure over mercury using solid reagents. The volumes are of reasonable size and no gases need be introduced but those actually undergoing analysis. The methods would seem capable of a sensitivity at least as great as that indicated by Langmuir, though this has not been necessary for our present work. The apparatus was developed during one phase of the work on

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[1] National Research Fellow in Chemistry.

[2] Prescott and Hincke, THIS JOURNAL, **50**, 3228 (1928).

[3] Langmuir, *ibid.*, **40**, 1378 (1918); *Ind. Eng. Chem.*, **20**, 333 (1928).