

HIGH TEMPERATURE EQUILIBRIA

Thesis by
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CONTENTS

	Page
I. The High Temperature Equilibrium between Silicon Nitride, Silicon and Nitrogen.	
A. Plan of the Investigation	1
B. Apparatus and Procedure	2
C. The Equilibrium Measurements	2
D. Thermodynamic Calculations	4
Summary	5
II. The High Temperature Equilibrium between Titanium Dioxide and Carbon.	
A. Introduction	6
B. Apparatus and Procedure	7
C. Equilibrium Measurements	10
D. The Nature of the Solid Phases	16
E. Determination of the Size of the Unit Cell of TiC	18
F. Thermodynamic Calculations	20
Summary	21
References	22

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THE HIGH-TEMPERATURE EQUILIBRIUM BETWEEN SILICON NITRIDE, SILICON AND NITROGEN

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A. Plan of the Investigation

This investigation is a continuation of the researches in progress in this Laboratory on high-temperature equilibria.¹ The method devised by Prescott and used by Prescott and Hincke^{1d} in studying the equilibrium of the system aluminum carbide, nitrogen, aluminum nitride and carbon was employed. This method consists in heating by an electric current to various temperatures (measured by an optical pyrometer) the solid reaction mixture (in this case the silicon nitride and silicon) within a graphite tube a few millimeters in diameter and a few centimeters long placed within a pyrex bulb, and in measuring the pressures produced. In this article are described measurements made of the dissociation pressures of silicon nitride from 0.27 to 5.49 mm. through a temperature range from 1606 to 1802°K.

¹ (a) Prescott, THIS JOURNAL, 48, 2534 (1926); (b) Prescott and Hincke, *ibid.*, 49, 2744 (1927); (c) Prescott and Hincke, *ibid.*, 49, 2753 (1927); (d) Prescott and Hincke *ibid.*, 50, 3228 (1928); (e) Prescott, *ibid.*, 50, 3237 (1928); (f) Prescott and Hincke, *Phys. Rev.*, 31, 130 (1928).

It has been shown by Weiss and Engelhardt² and by Funk³ that the compound produced, when silicon is heated in nitrogen at 1300 to 1450° as long as the gas continues to be absorbed, is the normal nitride, Si₃N₄. The nitride produced in the experiments here described presumably had this composition, since the conditions of heating were substantially the same.

The authors wish to express their thanks to Dr. C. H. Prescott, Jr., whose suggestions and criticisms have been of great assistance.

B. Apparatus and Procedure

The temperature measurements in this investigation were made by means of an optical pyrometer with a disappearing filament; the details, corrections and limitations of these measurements have already been described.^{1b†} The furnace, the devices for introducing nitrogen and the McLeod gages have also been described.^{1d}

The silicon used was a C. P. Eimer and Amend preparation which had been ground to pass a 200-mesh sieve. The preparation upon treatment with hydrofluoric and nitric acids, evaporation with nitric acid and ignition of the residue yielded 2% of oxides, corresponding to about 1% of metallic impurity.

In the procedure adopted there was placed loosely in the middle zone of the graphite tube a charge of 0.1 g. of finely powdered silicon. After complete evacuation, the apparatus was filled at one atmosphere with (tank) nitrogen that had been passed through a purifying train, and the furnace was heated to 1675°K. for thirty minutes. This converted about 75% of the charge to silicon nitride.⁴ The apparatus was then evacuated, after which it was ready for the equilibrium measurements.

In all of the determinations the temperature of the furnace was held constant, and the equilibrium pressure was found by taking the mean of the final pressures of a forward and a reverse reaction wherein the pressure in the glass bulb containing the graphite furnace increased and decreased, respectively. To hold the furnace at a constant temperature it sufficed to keep the current through it constant, which was done by means of a standard resistance and a potentiometer. A shower of tap water was caused to play continuously over the glass bulb containing the graphite tube while equilibrium measurements were being made. This prevented excessive outgassing of the glass walls and contamination of the nitrogen. A gas micro-analysis apparatus^{1d} was used to determine the partial pressure of nitrogen at the end of each experiment. In all the satisfactory runs the nitrogen formed more than 92% of the gases in the bulb.

For the preliminary formation of silicon nitride the current was drawn from a 1-kilowatt transformer. During the measurements it was taken from storage batteries. To maintain the furnace at 1802°K. about 80 amperes at 10 volts was required.

C. The Equilibrium Measurements

The first equilibrium determination was made at 1675°K. The pressure of the nitrogen in the bulb built up from a vacuum to 0.47 mm. in the course of one hour, the gas then containing 92% of nitrogen. The apparatus was then again evacuated and filled to 0.90 mm. of nitrogen, as measured when the furnace had become hot; in this case the pressure of the gas decreased

² Weiss and Engelhardt, *Z. anorg. Chem.*, **65**, 78 (1910).

³ Funk, *ibid.*, **133**, 67 (1924).

⁴ No silicon carbide was formed at this nitrogen pressure by the reaction of silicon with the graphite furnace; moreover, it was found that silicon carbide is inert to nitrogen under the conditions of these experiments.

in one hour to 0.762 mm., and the gas contained 95% of nitrogen. Two one-hour runs were then made, one at 0.57 mm. and the other at 0.675 mm. of nitrogen, but these showed no measurable change in pressure. Finally a run of two hours with increasing pressure was made, starting from an initial pressure of 0.336 mm. and stopping at 0.553 mm. of nitrogen. The gas analysis showed 100% of nitrogen in this run, which was to be expected because of the pumping off of the outgassed impurities in the previous runs. It was observed that a pellet reacted more slowly after some hours of heating, probably owing to loss of some of the silicon from the charge by volatilization and to sintering of the silicon nitride into a more compact mass.

The pellets removed from the furnaces after each equilibrium determination always gave the characteristic ammonia test on heating with concentrated alkali, and under a low powered microscope showed a white sintered mass speckled with darker particles of silicon.

In each determination the true equilibrium pressure of the nitrogen corresponding to any temperature was assumed to be the average of the two pressures which had been attained in a forward and a reverse run. Each of the two pressures always approached a limiting value that seemed to be as far as the reaction would go within a reasonable time. These pressures, however, did not differ very greatly from one another. At temperatures above 1800°K. sublimation of the silicon and sintering of the silicon nitride were so rapid that a pellet became only slowly reactive after a few runs. This permitted, nevertheless, a range of about 200° over which the equilibrium could be studied.

Table I gives the final pressures (in millimeters) observed at each temperature. There are shown in each case the highest pressures (marked

TABLE I
EQUILIBRIUM PRESSURES OF THE REACTION AT VARIOUS TEMPERATURES AND THE CORRESPONDING FREE ENERGIES

Absolute temp., T	$10^4/T$	Final pressure in mm.			Pressure $\times 10^4$ in atm.	Free energy ΔF
		Increasing	Decreasing	Mean		
1606	6.225	0.179	0.361	0.27	3.5	50,800
1638	6.110	.382	.537	.46	6.0	48,300
1675	5.971	.553	.762	.66	8.7	46,900
1709	5.850	1.110	1.335	1.22	16.1	43,700
1739	5.750	2.215	2.675	2.44	32.0	39,700
1779	5.625	3.560	4.65	4.11	54.0	36,900
1802	5.550	5.05	5.93	5.49	72.0	35,300

“increasing”) which were attained by the forward reaction (decomposition of the nitride) and the lowest pressures (marked “decreasing”) which were attained by the reverse reaction. These pressures are always the partial pressure of the nitrogen in the gas (found by multiplying the total pressure by the fraction of nitrogen present). The mean values of these two pressures for each pair are taken as the equilibrium pressures. The correspond-

ing values expressed in atmospheres are given in an adjoining column. In the last column of the table are given also the values (derived as described below) in calories of the free-energy increase (ΔF) attending the reaction $\text{Si}_3\text{N}_4(\text{s}) = 3\text{Si}(\text{s})$ or $(\text{l}) + 2\text{N}_2(\text{g})$.

In Fig. 1 are plotted as full circles the mean values of $\log_{10} p$ (in mm.) against $10^4/T$. The straight line was drawn so as to fit best the full circles. The corresponding observed "increasing" and "decreasing" values are shown by half-circles.

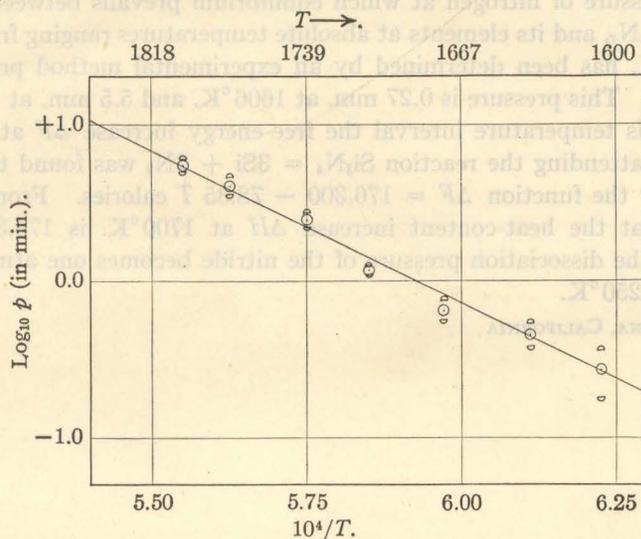


Fig. 1.

The final relation between the equilibrium pressures in atmospheres and the absolute temperature is given by the equation

$$2.3 \log_{10} p \text{ (in atm.)} = 19.75 - \frac{44,500}{T}$$

Since the melting point of silicon is approximately 1687°K., there should be a slight change in slope of the line at this temperature due to the heat of fusion of the silicon, but the data are not accurate enough to show this change in slope.

D. Thermodynamic Calculations

The chemical reaction is $\text{Si}_3\text{N}_4 = 3\text{Si} + 2\text{N}_2$. The free-energy increase (ΔF) attending it when the nitrogen pressure is one atmosphere may then be derived from the equilibrium pressure p in atmospheres by the familiar equation $\Delta F = -RT \ln K$, where $K = p^2$ and $R = 1.987$. From the determinations of the equilibrium pressure p are thus obtained the values of ΔF given in the last column of Table I.

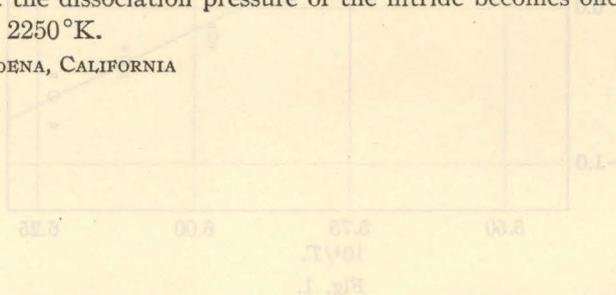
From these values of the free-energy increase one obtains the function

$\Delta F = 176,300 - 78.35T$ for absolute temperatures between 1600 and 1800°. From this it follows that the heat-content increase ΔH is 176,300 calories in this temperature range. The function shows also that at an absolute temperature of 2250° (assuming it to hold up to this temperature) the free-energy increase becomes zero and therefore that the dissociation pressure becomes one atmosphere at this temperature.

Summary

The pressure of nitrogen at which equilibrium prevails between silicon nitride, Si_3N_4 , and its elements at absolute temperatures ranging from 1606 to 1802°K. has been determined by an experimental method previously described. This pressure is 0.27 mm. at 1606°K. and 5.5 mm. at 1802°K. Within this temperature interval the free-energy increase ΔF at one atmosphere attending the reaction $\text{Si}_3\text{N}_4 = 3\text{Si} + 2\text{N}_2$ was found to be expressed by the function $\Delta F = 176,300 - 78.35 T$ calories. From this it follows that the heat-content increase ΔH at 1700°K. is 176,300 cal.; also that the dissociation pressure of the nitride becomes one atmosphere at about 2250°K.

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The final relation between the equilibrium pressure in atmospheres and the absolute temperature is given by the equation

$$2.3 \log p \text{ (in atm.)} = 19.78 - \frac{41,000}{T}$$

Since the melting point of silicon is approximately 1687°K., there should be a slight change in slope of the line at this temperature due to the heat of fusion of the silicon, but the data are not accurate enough to show this change in slope.

Thermodynamic Calculations

The chemical reaction is $\text{Si}_3\text{N}_4 = 3\text{Si} + 2\text{N}_2$. The free-energy increase (ΔF) attending it when the nitrogen pressure is one atmosphere may then be derived from the equilibrium pressure p in atmospheres by the familiar equation $\Delta F = -RT \ln K$, where $K = p^2$ and $R = 1.987$. From the determination of the equilibrium pressure p we thus obtained the values of ΔF given in the last column of Table I. From these values of the free-energy increase one obtains the function

THE HIGH TEMPERATURE EQUILIBRIUM BETWEEN
TITANIUM DIOXIDE AND CARBON

A. INTRODUCTION

This investigation is a continuation of the researches on high temperature equilibria which have been carried out in this Laboratory¹. The high-pressure apparatus previously used in studying the equilibria between zirconium oxide and carbon^{1a}, thorium oxide and carbon^{1c}, and aluminum oxide and carbon^{1b} was employed. The method used consists in electrically heating a small graphite tube furnace which contains the solid reaction mixture, determining the temperature by an optical pyrometer, and measuring the gas pressure on a mercury manometer. The measurements described in this thesis include the pressures of carbon monoxide in equilibrium with the solid phases TiO_2 , TiC and C over the pressure range 0.8 to 2.0 atmospheres and the temperature range 1000° to 1150°C . The composition of the solid reaction mixture was determined by X-ray powder photographs.

The author wishes to express his thanks to Dr. Arnold O. Beckman for his advice and suggestions, to Dr. W.B. Hincke for his interest in this work and to Mr. F.J. Ewing for his assistance in obtaining the X-ray photographs.

B. APPARATUS AND PROCEDURE

The apparatus was substantially the same as that used in the previous high pressure investigations.^{1a,c,d} A more convenient furnace assembly was used, however, which had been developed by Dr. Hincke and the author during the course of an investigation (unpublished) of the calcium oxide-carbon equilibrium. As is shown in Fig. 1A the graphite furnace A was supported by tungsten leads which were in turn connected through flexible copper cables to the water-cooled copper tubes B and C which were held rigidly co-linear by attachment to the heavy rod D. Electrode B was held in place by a micarta insulative support E; electrode C was held by a similar brass support F fitted with a thumbscrew H. The Pyrex furnace bulb was sealed to the electrodes at G with sealing wax. A side-tube with an inverted cup connection also sealed with sealing wax, connected the furnace bulb with the manometer and auxiliary gas apparatus. Since the entire furnace was immersed in a water thermostat it was necessary to protect the exposed sealing wax with paraffin.

To insert a furnace tube, the glass bulb was slipped over the lowered electrode C, which was then raised to allow the insertion of the furnace tube, after which thumbscrew H was tightened and the glass furnace bulb raised and sealed in position. It was found that the sealing wax seals were gas tight even at two atmospheres pressure and a furnace temperature of 2000°K.

The furnace tubes, Fig. 1B, were turned from Acheson graphite with a groove near each end to provide a central region of nearly uniform temperature within which the charge was held by graphite plugs. Two types of charge were used, one consisting of TiC and the other consisting of

Furnace Bulb and Graphite Furnace

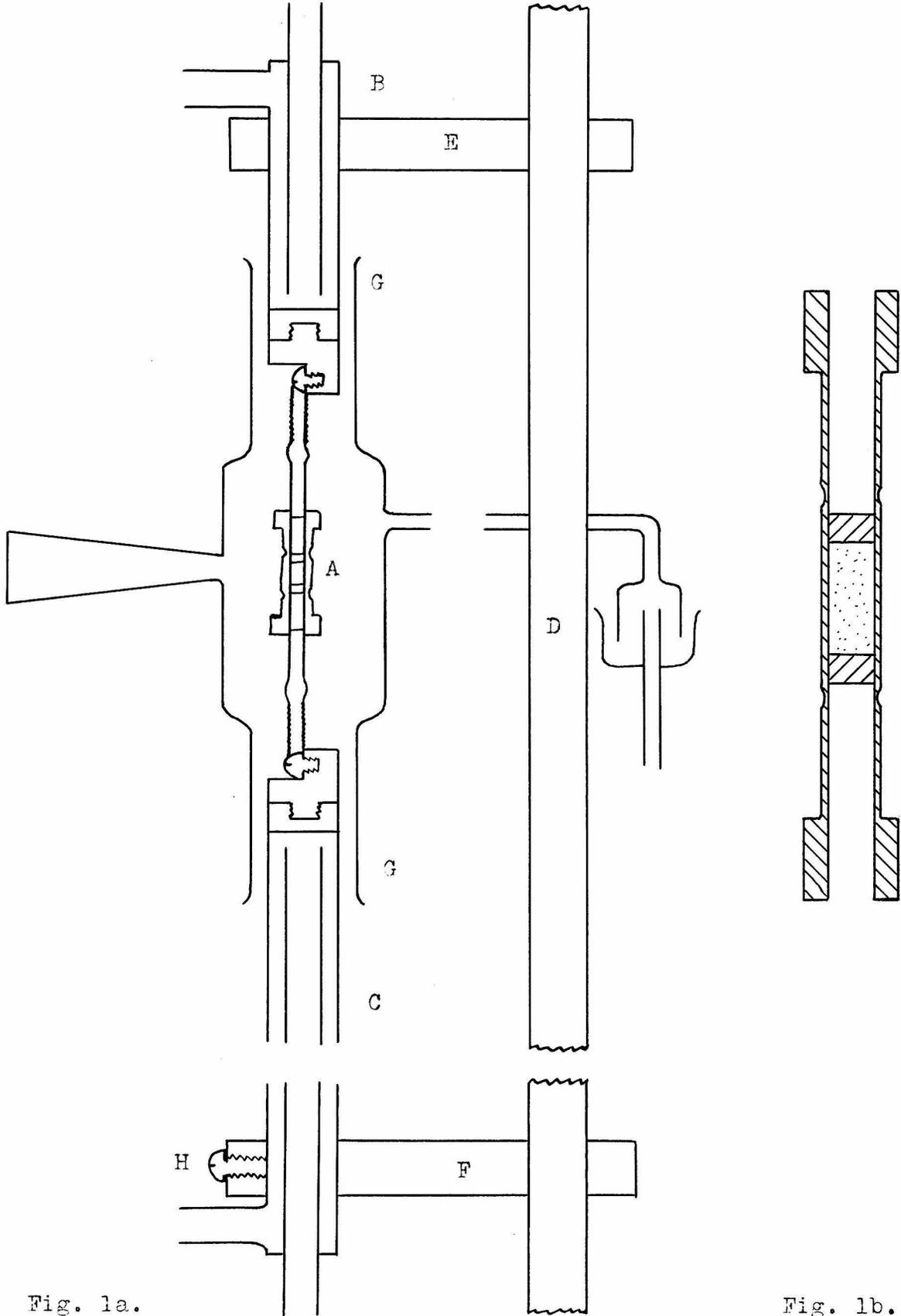


Fig. 1a.

Fig. 1b.

equal quantities of TiO_2 and graphite. In each case the materials were ground to pass through a 200-mesh sieve. The TiC was prepared by heating in vacuo an equimolar mixture of powdered Ti and graphite to a temperature ($1950^\circ K$) sufficiently high to volatilize any uncombined titanium metal. The TiO_2 and Ti metal were Eimer and Amend C.P. preparations.

When the charge consisted of TiC, the furnace was baked out in vacuo at a high temperature after which the temperature was lowered to $1275^\circ - 1350^\circ K$, and the heating continued for 6 to 7 hours with carbon monoxide present at a pressure of about 2 atmospheres. When the charge consisted of TiO_2 and graphite, the furnace was heated in vacuo at a dull red heat for a few seconds. The apparatus was then filled with carbon monoxide at a pressure of about 2 atmospheres and the furnace heated to about $1750^\circ K$ for half an hour, near enough to the equilibrium pressure that the charge would not all be used up, to drive off adsorbed oxygen.

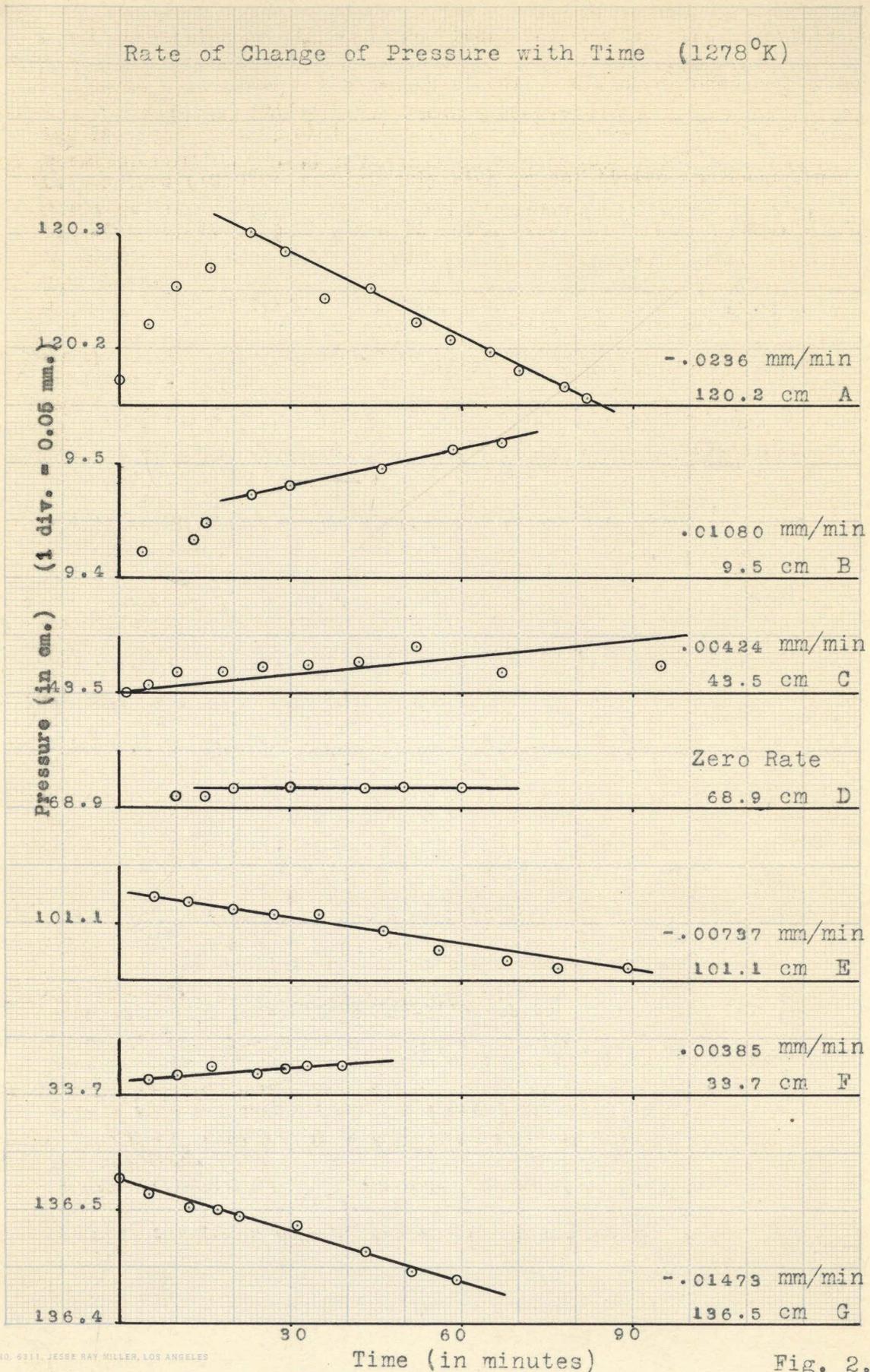
The furnace was then evacuated and refilled with fresh carbon monoxide to the desired pressure for the equilibrium measurements. It was found that under these conditions reaction mixtures were produced which gave satisfactory rates of reaction for the equilibrium measurements.

For preliminary work the furnace was heated by alternating current from a low-voltage one-kilowatt transformer but for the final measurements direct current from storage batteries was used. To maintain a temperature of $1330^\circ K$ a current of about 70 amperes at 6 volts was required.

C. THE EQUILIBRIUM MEASUREMENTS

The equilibrium pressures were determined by measuring the rate of reaction (i.e., rate of change of carbon monoxide pressure) at constant temperature for different pressures of carbon monoxide. By obtaining a series of both forward and reverse rates with the same furnace charge, the equilibrium pressure was found graphically as the pressure corresponding to zero rate. Typical graphs are shown in Figures 2 and 3. In Figure 2 are shown the carbon monoxide pressures plotted as ordinates against the time as abscissae for six successive runs at the temperature 1278°K with different initial carbon monoxide pressures. For each run the average rate of pressure change was determined, rejecting values which were obtained during the first 30-40 minutes of the run when the system was attaining temperature equilibrium. These six rates are shown as ordinates in Figure 3 with the average pressure during the run as abscissae. The intersection with the zero-rate ordinate of the best straight line through these points shows the equilibrium pressure to be 60.5 cm. at this temperature.

Six sets of runs of this kind were made over the temperature range 1278° to 1428°K and pressure range from a few centimeters to two atmospheres. In some cases the initial furnace charge consisted of TiO_2 and C and in other cases of TiC. The equilibrium pressures and corresponding temperatures are given in Table I, where θ is the observed temperature and T is the true temperature after corrections have been made for the transmission of the window and the emissivity of carbon. In Figure 4 the logarithms of the equilibrium pressures are shown plotted



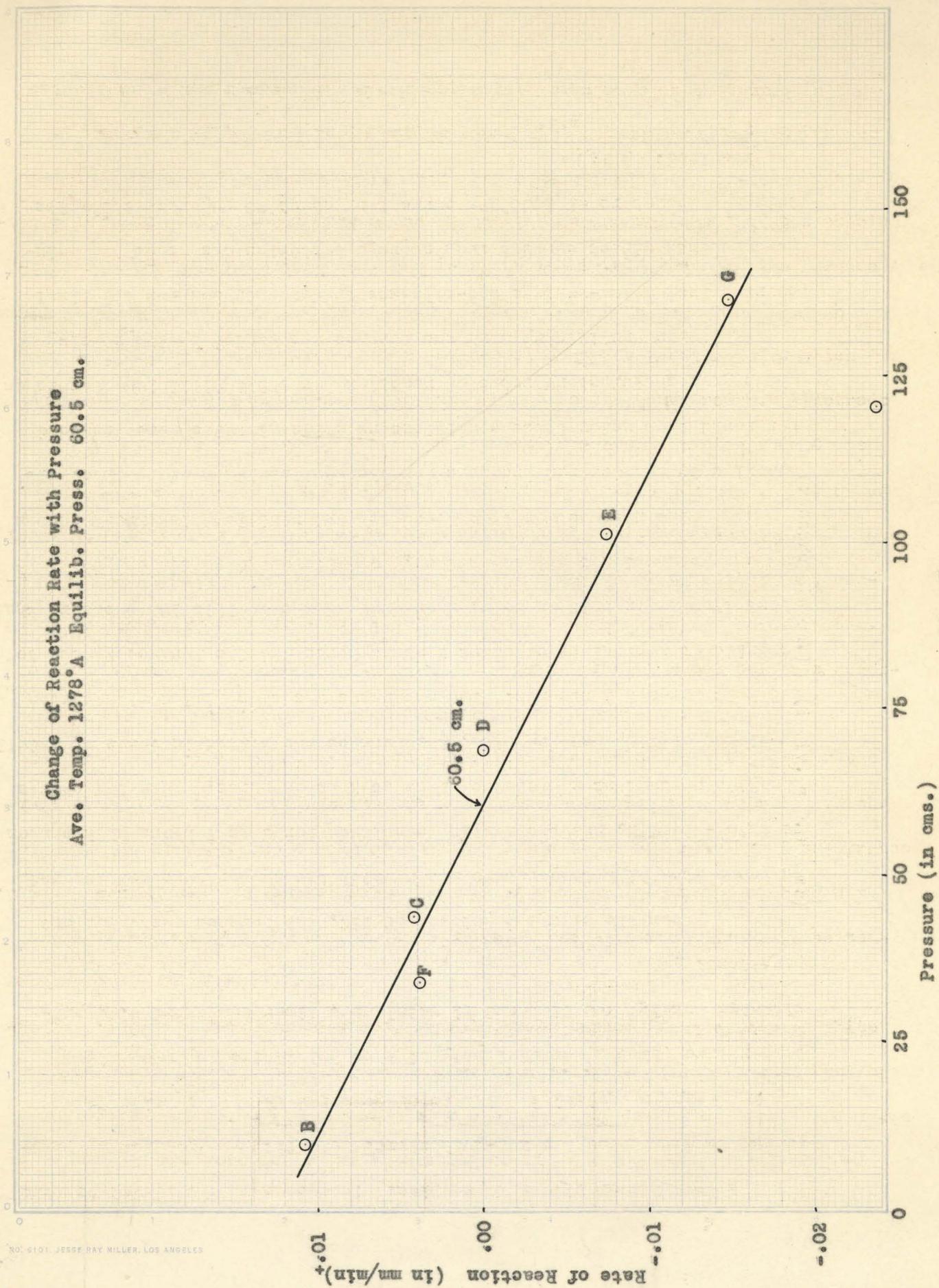


Fig. 3

Relation between Equilib. Press. of CO and Absolute Temperature

Circles - TiO₂-C as original reacting materials

Triangles - TiO-CO as original reacting materials

TiO₂ + 3C = TiC + 2CO Log p = 3.829 - 5,024/T

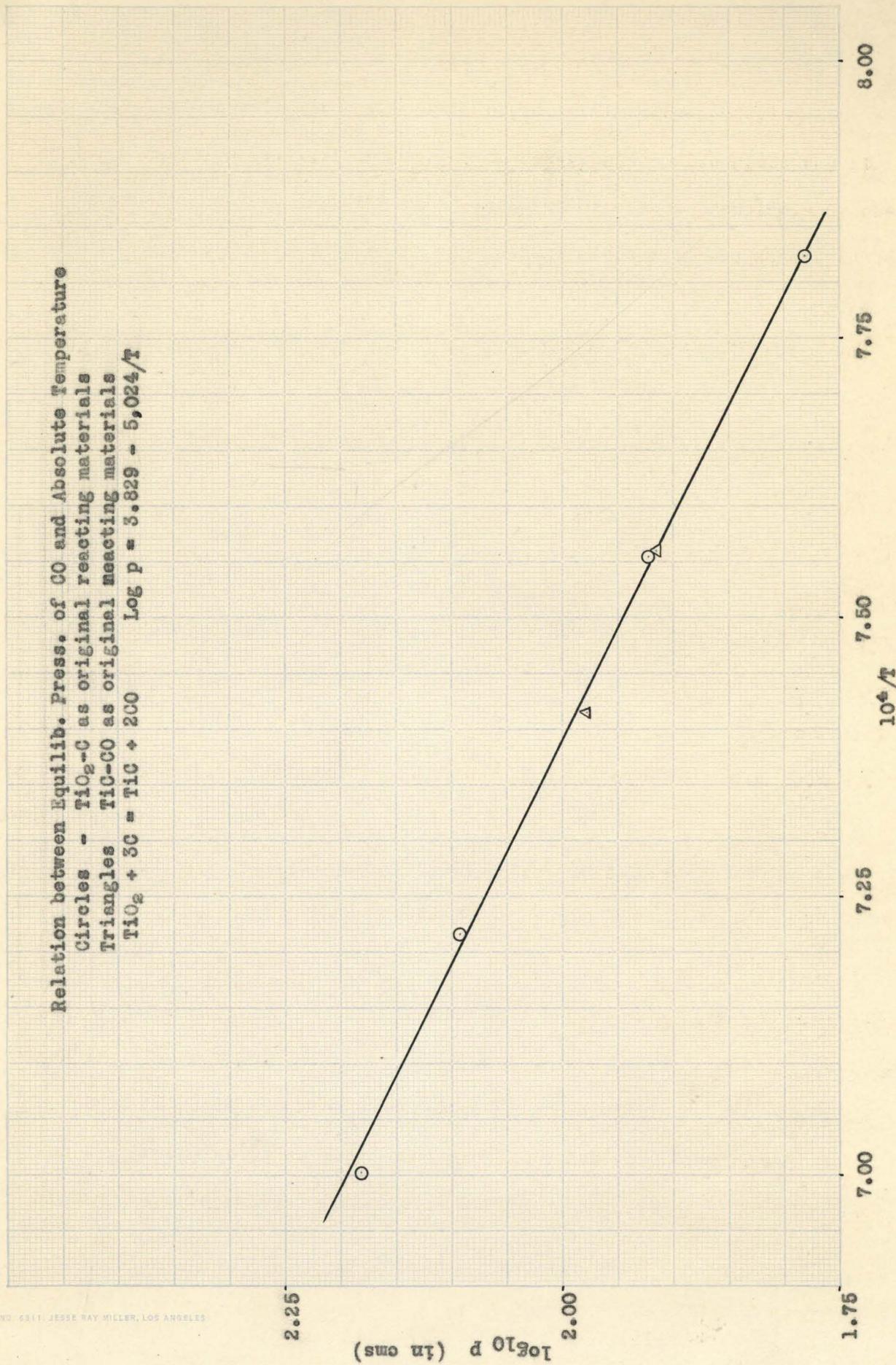


FIG. 4

TABLE I

Equilibrium Pressures and Free Energies at Various Temperatures

θ , °K	T °K	$\frac{1}{T} \times 10^4$	p (atm)	log p (atm)	ΔF (cal)
1250	1278	7.825	0.796	-0.099	+1157
1293	1323	7.559	1.081	0.034	-411
1294	1324	7.553	1.114	.047	-569
1318	1349	7.413	1.216	.085	-1048
1353	1386	7.215	1.634	.213	-2703
1393	1428	7.003	1.995	.300	-3917

against the reciprocal of the absolute temperatures, and it is to be seen that all of the points fall upon a straight line within the experimental error. The relation between the equilibrium pressures and absolute temperature is given by the equation

$$\log_{10} P_{(\text{atm})} = 3.829 - 5024/T.$$

The pellets were never used for more than two equilibrium pressure determinations and usually for only one.

One run was attempted at 1246°K but the reaction rates were too slow to measure accurately.

The dissociation of carbon monoxide into carbon dioxide and carbon is appreciable in this temperature range, being approximately 0.6% at 1278°K and 0.1% at 1428°K. It is well known, however, that the reaction attains equilibrium only very slowly. In blank experiments, using an entirely empty graphite furnace at temperatures, carbon monoxide pressures and over time intervals similar to those used in the equilibrium measurements, no measurable rates were observed, showing that the carbon monoxide dissociation could be entirely neglected.

D. THE NATURE OF THE SOLID PHASES

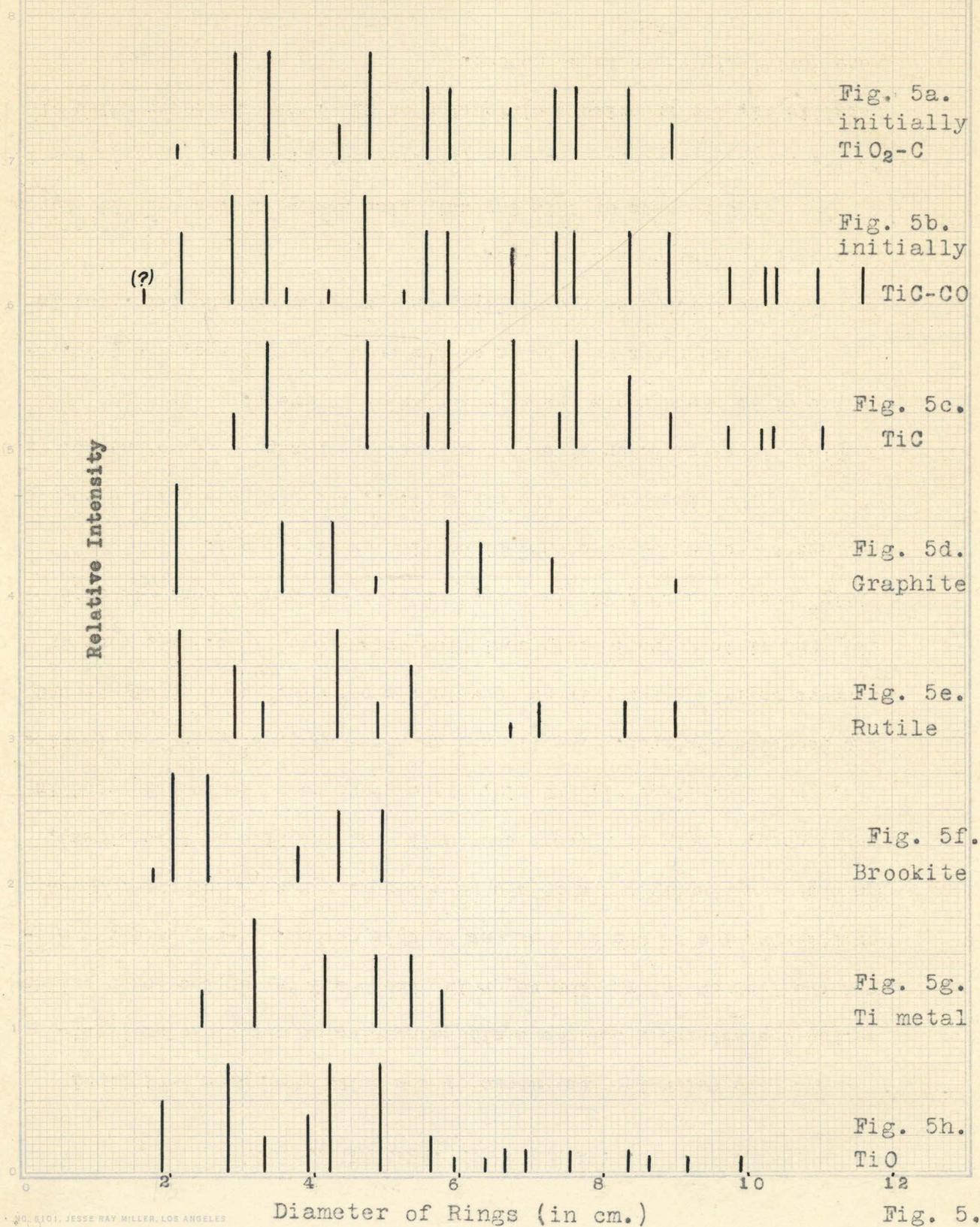
To determine the nature of the solid phases an analytical method was attempted but the small quantities of materials available and the lack of information regarding the chemistry of the lower oxides of titanium led to the abandonment of this method. X-ray powder photographs were finally taken of the reaction mixtures and of the various substances, namely TiO_2 (both the rutile and brookite modifications), TiC , graphite, Ti metal, and TiO , whose presence would be suspected in the reaction mixtures. The TiO was prepared by heating in the graphite furnace to 1775°K for half an hour in vacuo a mixture of finely ground TiO_2 and Ti in approximately stoichiometric proportions. The work of Billy² has shown that TiO is formed under these conditions, although perhaps there may be some uncombined TiO_2 or Ti as well.

The diameters of the rings (i.e., the distance between corresponding lines on either side of the position of zero deflection) obtained on the eight photographs are represented in Figure 5.

Photographs were taken of two reaction mixtures, one (Fig. 5a) in which the initial charge was TiO_2 and graphite and one (Fig. 5b) in which the initial charge was TiC .

The results of this investigation showed that the solid phases in the reaction mixture were TiO_2 (rutile modification), TiC and graphite. Metallic Ti , the brookite modification of TiO_2 , and the lower oxide TiO were definitely shown to be absent.

Results of X-ray Powder Photographs



E. DETERMINATION OF THE SIZE OF THE UNIT CELL
OF TITANIUM CARBIDE

The structure of titanium carbide has been worked out by A.E. van Arkel³ and by K.Becker and F.Ebert.⁴ Both investigators reported the carbide to be cubic but van Arkel reported d_{100} to be 4.29 Å while Bushman and Ebert reported 4.60 Å. During the study of the nature of the solid phases in the titanium oxide-carbon equilibrium, a redetermination of the value for d_{100} for titanium carbide was made.

X-ray powder photographs were taken of a mixture of titanium carbide and sodium chloride. Table II shows the results of the calibration with NaCl. The values of θ in radians for various planes were taken from Wyckoff, "The Structure of Crystals", page 198.

TABLE II

Sodium Chloride Calibration

Plane	Diameter of Ring (cms)	θ in radians	Weight	Distance of Powder to Film (cms)
100 (2)	2.54	.1265	3	5.016
110(2)	3.62	.1794	3	5.046
111(2)	4.43	.2203	1	5.028
100(4)	5.15	.2551	1	5.048
120(2)	5.78	.2860	1	5.053
112(2)	6.30	.3142	2	5.014
			Weighted mean	5.032 cms.

Table III shows the results of TiC measurements

TABLE III

Titanium Carbide Data from NaCl Comparison

Plane	Diameter of ring (in cm)	d_{hkl} (in Å)	Weights	d_{100} (in Å)
111 (1)	2.89	2.479	3	4.294
001 (2)	3.34	2.149	3	4.298
011 (2)	4.71	1.531	3	4.330
113 (1)	5.57	1.299	2	4.308
111 (2)	5.78	1.253	1	4.341
001 (4)	6.78	1.074	1	4.294
133 (1)	7.40	.9875	2	4.304
012 (2)	7.61	.9618	2	4.301
112 (2)	8.35	.8807	2	4.315
111 (3) 115 (1)	8.91	.8289	1	4.307
Weighted mean				4.308 Å

Thus powder photographs have shown the size of the unit cell for titanium carbide to be 4.31 Å, in fair agreement with 4.29 reported by van Arkel and not in agreement with 4.60 reported by Bushman and Ebert.

F. THERMODYNAMIC CALCULATIONS

From the results of the X-ray investigation the equilibrium studied is undoubtedly that expressed by the equation



The value of ΔF , the free energy increase attending this reaction, may be derived from the thermodynamic equation

$\Delta F = -RT \ln K$, where $K = p^2$. The values of ΔF corresponding to the equilibrium pressures at various temperatures are given in the last column of Table I.

From the expression for $\log_{10} p$ given in the previous section, the relation may be obtained

$$\Delta F = 45,930 - 35.01 T$$

for the temperature range 1278 to 1428°K. From this it follows that the increase in heat content, ΔH , is 45,930 calories. At 1312°K the free energy is zero and the equilibrium pressure is one atmosphere.

SUMMARY

Determinations have been made of the equilibrium pressures of CO for the reaction



in the temperature range 1278° to 1428°K. The solid phases were identified by X-ray powder photographs. The length of the unit cube for TiC was found to be 4.31 Å.

With this temperature range the increase in free energy and heat content that attend this reaction at one atmosphere pressure were found to be given by the expressions $\Delta F = 45,930 - 35.01 T$ calories and $\Delta H = 45,930$ calories. The equilibrium pressure is one atmosphere at 1312°K.

References

- 1a. Prescott, J.Am.Chem.Soc., 48, 2534 (1926).
- b. Prescott, *ibid.*, 50, 3237 (1928).
- c. Prescott and Hincke, *ibid.*, 49, 2744 (1927).
- d. Prescott and Hincke, *ibid.*, 49, 2753 (1927).
- e. Prescott and Hincke, *ibid.*, 50, 3228 (1928).
- f. Prescott and Hincke, Phys.Rev., 31, 130 (1928).
- g. Hincke and Erantley, J.Am.Chem.Soc., 52, 48 (1930).
2. Billy, Ann.Chim., 16, 5, (1921).
3. Van Arkel, Physica, 4, 286 (1924).
4. Becker and Ebert, Z.Physik, 31, 286 (1925).