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AFML ltr dtd 16 Mar 1972

AFML-TR-65-299
PART I

EQUILIBRIUM STUDIES OF REFRACTORY NITRIDES

Part I. Details of the Apparatus and Studies of the Ti-N System

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TECHNICAL REPORT AFML-TR-65-299, Part I

SEPTEMBER 1965

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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EQUILIBRIUM STUDIES OF REFRACTORY NITRIDES

Part I. Details of the Apparatus and Studies of the Ti-N System

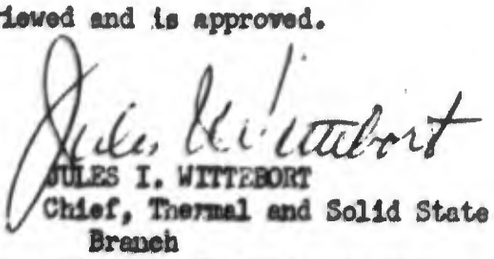
L. A. McClaine
C. P. Coppel

FOREWORD

This report was prepared by Arthur D. Little, Inc., Cambridge, Massachusetts, under USAF Contract No. AF 33(615)-1713. The contract was initiated under Project No. 7360, "The Chemistry and Physics of Materials," Task No. 736001, "Thermodynamics and Heat Transfer." The work was administered under the direction of the Materials Physics Division, Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Mr. Paul W. Dimiduk, Project Engineer.

This report covers work conducted from 1 June 1964 through May 1965. The manuscript was released by the authors in September 1965 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.



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ABSTRACT

This report describes an apparatus assembled specifically for studies on refractory nitrides. The apparatus provides for measurement of nitrogen pressure as a function of temperature and composition of the nitride sample by a static technique.

The titanium nitride phase was studied. Equilibrium nitrogen pressures were determined for nitride compositions ranging from about $Ti_{.54}N_{.46}$ to $Ti_{.5}N_{.5}$. Equilibrium titanium pressures over pure titanium, the α-titanium-titanium nitride two phase mixture and a nitride composition of about $Ti_{.55}N_{.45}$ were determined by a Knudsen technique. These pressure data are related and extended across the titanium nitride phase region utilizing thermodynamic theory.

Previous work on titanium nitride is reviewed and a consistent account of all the available data is developed.

TABLE OF CONTENTS

ILLUSTRATIONS

LIST OF TABLES

I. INTRODUCTION

It is recognized that the refractory metals of groups IV, V, and VI B (Ti, Zr, Hf; V, Nb, Ta; and Cr, Mo, W respectively) form several nitrides which exist over wide ranges of stoichiometry. Detailed thermodynamic data for these metal-nitrogen systems as a function of composition and temperature can be extremely valuable to the materials engineer or scientist concerned with using or explaining the behavior of a specific metal nitride. Such data are also valuable when considering the possible reactions of the refractory metal or its compounds with nitrogen or nitrogen containing systems.

It is generally recognized that only elements are in the vapor over the refractory metal nitride phases and that there is a wide variation in the activities of the individual elements as stoichiometry varies within a given nitride phase. Low evaporation coefficients are recognized for some nitrides such as BN and AlN[1] and recent work[2] has indicated that equilibrium conditions are often not attained in the Knudsen technique for vapor pressure determination over the refractory metal nitrides.

It became apparent that further study of the nitrides should utilize a technique which permits a nitrogen pressure measurement under equilibrium conditions as a function of temperature and nitride composition. In addition to providing thermodynamic data within a given nitride phase these measurements together with X-ray diffraction and metallographic studies of specific samples can also provide information on phase boundaries and phase relationships within the metal-nitrogen systems.

Our objective under Contract AF 33(615)-1713 was to develop a technique for such studies and to apply it initially to the study of titanium nitride.

II. EXPERIMENTAL

A. APPARATUS

To achieve the purposes of this study one must determine the nitrogen pressure in equilibrium with a sample of known temperature and composition. The apparatus was designed to provide a capability for work with samples on the order of one gram in weight over a temperature range of 1000-2500°C and a pressure range of 10^{-3} - 10^{-6} torr. Provision was made for equilibrium measurements using either a static or a flow system. To make it easier to achieve low pressures and to minimize sample contamination due to outgassing from the sample chamber walls while heating the sample, the apparatus was designed to permit the baking out at 350°C of the sample chamber portion of the system. This portion of the system will be at low pressure during studies in the 10^{-3} - 10^{-6} torr range.

A schematic drawing of the apparatus is presented in Figure 1. The heart of the apparatus is the bakeable section within the dotted lines of Figure 1. A photograph of this section is presented in Figure 2. Figure 3 presents a close-up of the sample chamber within the bakeable section and shows clearly the sample suspended from a quartz spiral. Weight changes from one equilibrium to another can be determined by using a micrometer microscope to read the changes in the extension of the quartz spiral. Knowing the weight change history of the sample together with chemical analyses of the initial and/or final sample composition permits the calculation of sample compositions for each set of equilibrium conditions. The micrometer microscope which is used to follow the quartz spring extensions can be seen in position in front of the sample chamber in the overall view of the apparatus presented in Figure 4. In Figure 3 the sample is in weighing position.

The quartz springs used during this study had sensitivities of 0.052 mm/mg for the first two samples reported on and 0.200 mm/mg for the rest of the samples. The micrometer microscope was read to 0.001 mm; however, vibrations, temperature fluctuations, etc., resulted in an uncertainty of ± 0.01 mm which for most of the work reported represents an uncertainty of ± 0.05 mg. An internal reference consisting of a quartz fiber suspended from a hook at the top of the quartz spring eliminated any error in absolute positioning of either the system or the microscope. A level on the microscope eliminated any possible vertical alignment anomalies.

The sample is heated inductively using an eddy current concentrator sealed within the sample chamber. The concentrator is taken from a

Sylvania RF lamp* and the corresponding power supply (Model RFS-2)* is used as a power unit for this apparatus. The sample must be lowered to place it within the concentrator field. This is accomplished by pulling it down from below. A needle is suspended below the sample and extends into a capillary tube at the bottom of the sample chamber. An electromagnetic field is used to pull the needle to the bottom of this capillary. The suspension from the sample is of a length such that when the needle is at the bottom of the capillary the sample is positioned in the center of the RF field. Some experiments prior to final design of the apparatus showed that the sample cannot be heated with the concentrator when it is freely suspended. The field gradients are so great that the sample moves up or down and away from the correct position for optimum heating. In some exploratory experiments we did heat a ZrN_{1-x} sample to about 2200°C in an atmosphere of nitrogen and were still far from using full power. The experiment was discontinued because of marked sample interaction with impurities in the atmosphere, but it did show the capabilities of this power supply to be more than adequate for our needs.

A McLeod gauge as well as mercury and butyl phthalate manometers are attached to the sample chamber. For the studies in the 10^{-3} to 10^{3} torr range the manometer train is open to the sample chamber and directly measures pressure at equilibrium. An ion gauge (Veeco Type RF 75p) is attached directly to the sample chamber for pressure measurement in the 10^{-3} to 10^{-6} torr range. This ion gauge was separately calibrated against the McLeod gauge in the manometer train. When working at low pressures (10^{-3} - 10^{-6} torr) the manometer train is not open to the sample chamber system.

Also attached to the sample chamber through a variable leak valve is a train for the purification and drying of nitrogen gas. This provides the source of pure nitrogen for the equilibrium studies using either a static or a flow technique. The train consists of a tube containing copper turnings heated to 500°C, a drying tube containing drierite, and a cold trap cooled with a dry ice-acetone mixture.

Temperature of the sample is measured with a pyrometer by sighting through a window above the sample chamber. The position of the pyrometer and mirror can be seen in Figure 4. The pyrometer was sighted on a 1 mm hole in the molybdenum crucible used for the titanium nitride studies.

The Pyrometer (Pyro Micro Optical Pyrometer) was calibrated using a General Electric Lamp No. 431-P-247 (Type T/24) ribbon filament lamp designed for pyrometer calibration. Our pyrometer was also compared with a Leeds & Northrup Optical Pyrometer 8622-C which had recently been calibrated and set against a National Bureau of Standards secondary standard by Leeds & Northrup. The two instruments agree within the ability to read the scales.

* Supplied by Sylvania Electric Products Inc., Lighting Division, 60 Boston Street, Salem, Massachusetts.

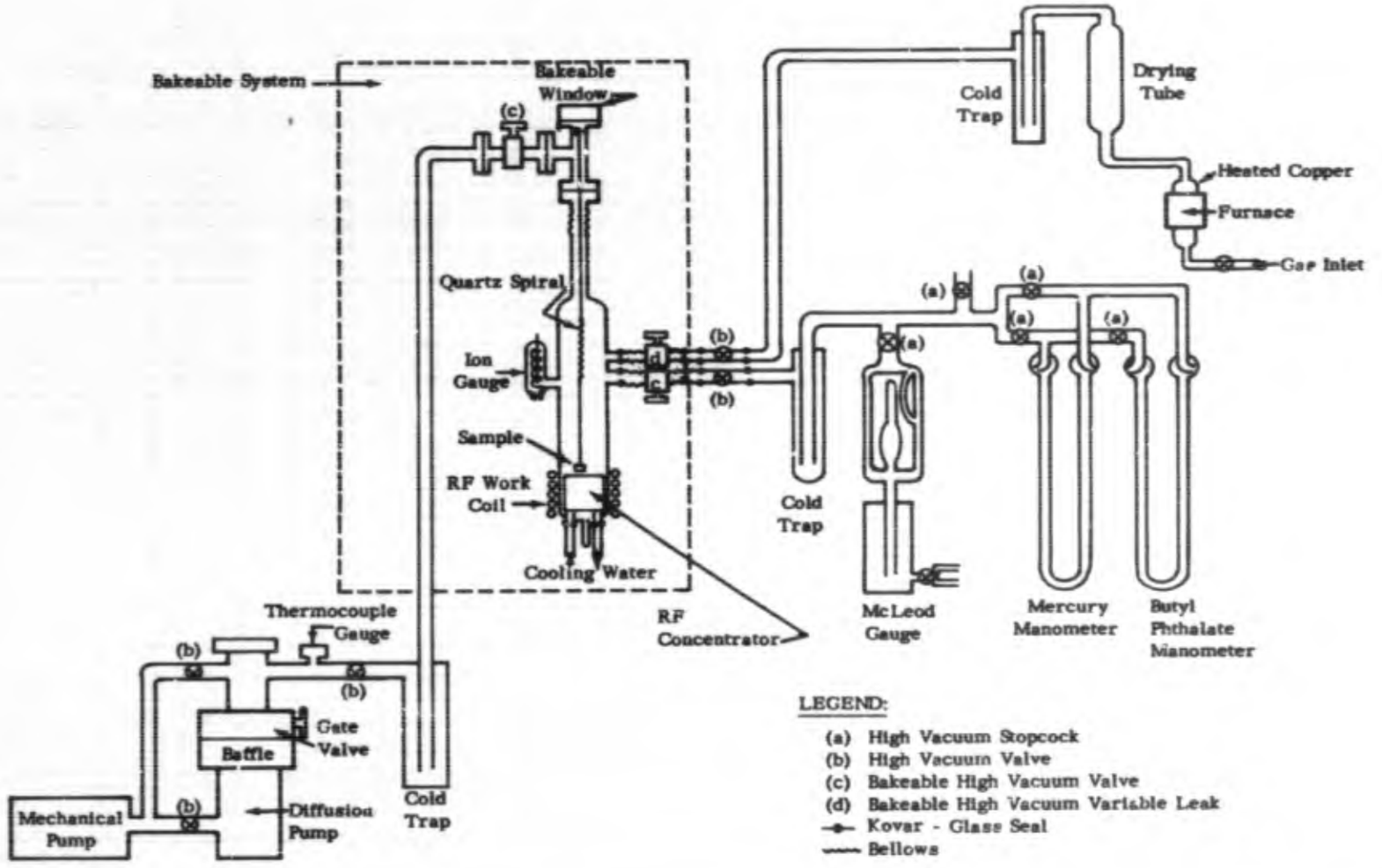

FIGURE 1 NITRIDE VAPOR PRESSURE - COMPOSITION APPARATUS

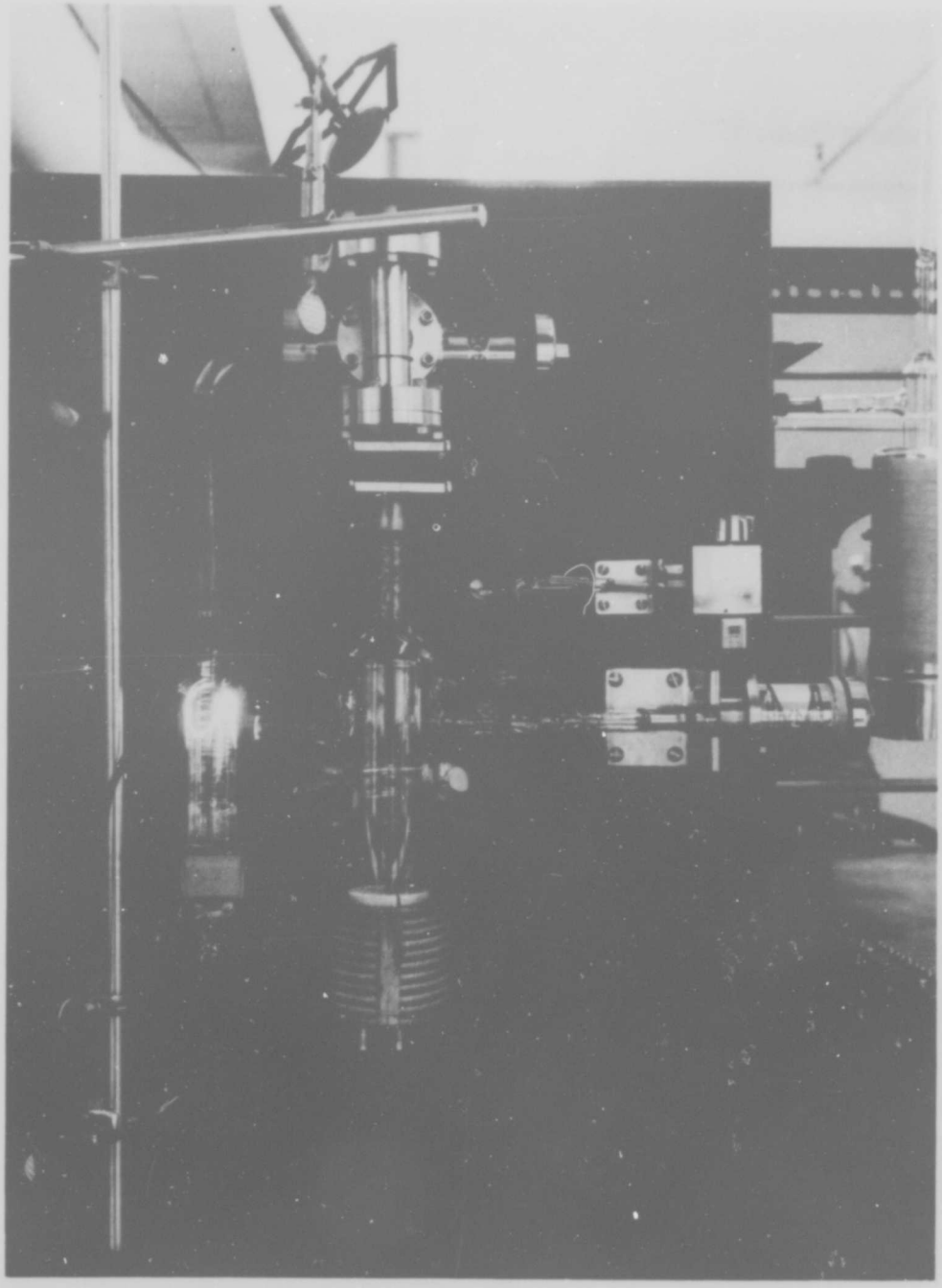

FIGURE 2 BAKEABLE SECTION OF APPARATUS

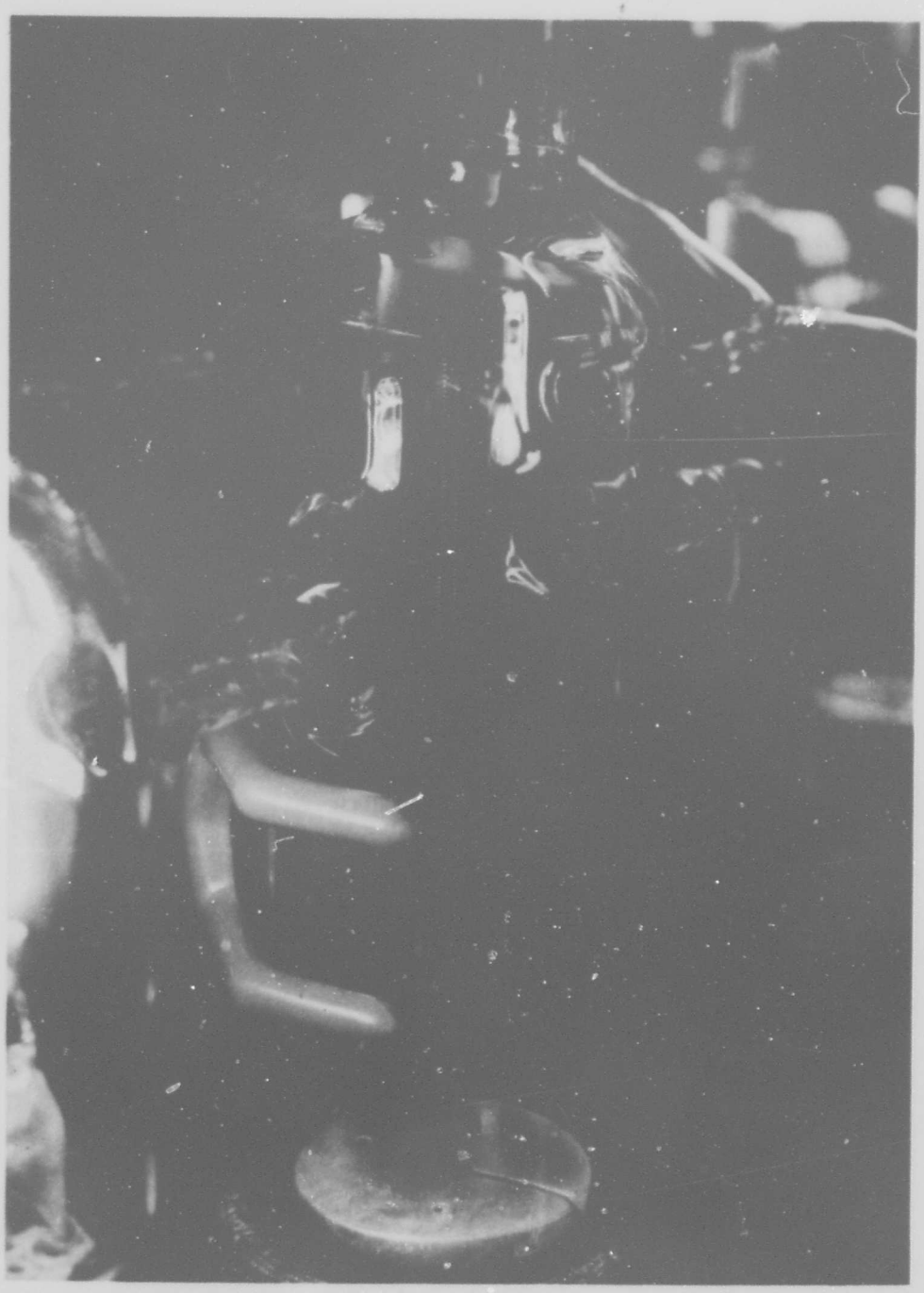

FIGURE 3 CLOSE-UP OF SAMPLE CHAMBER SHOWING SAMPLE IN POSITION FOR WEIGHING

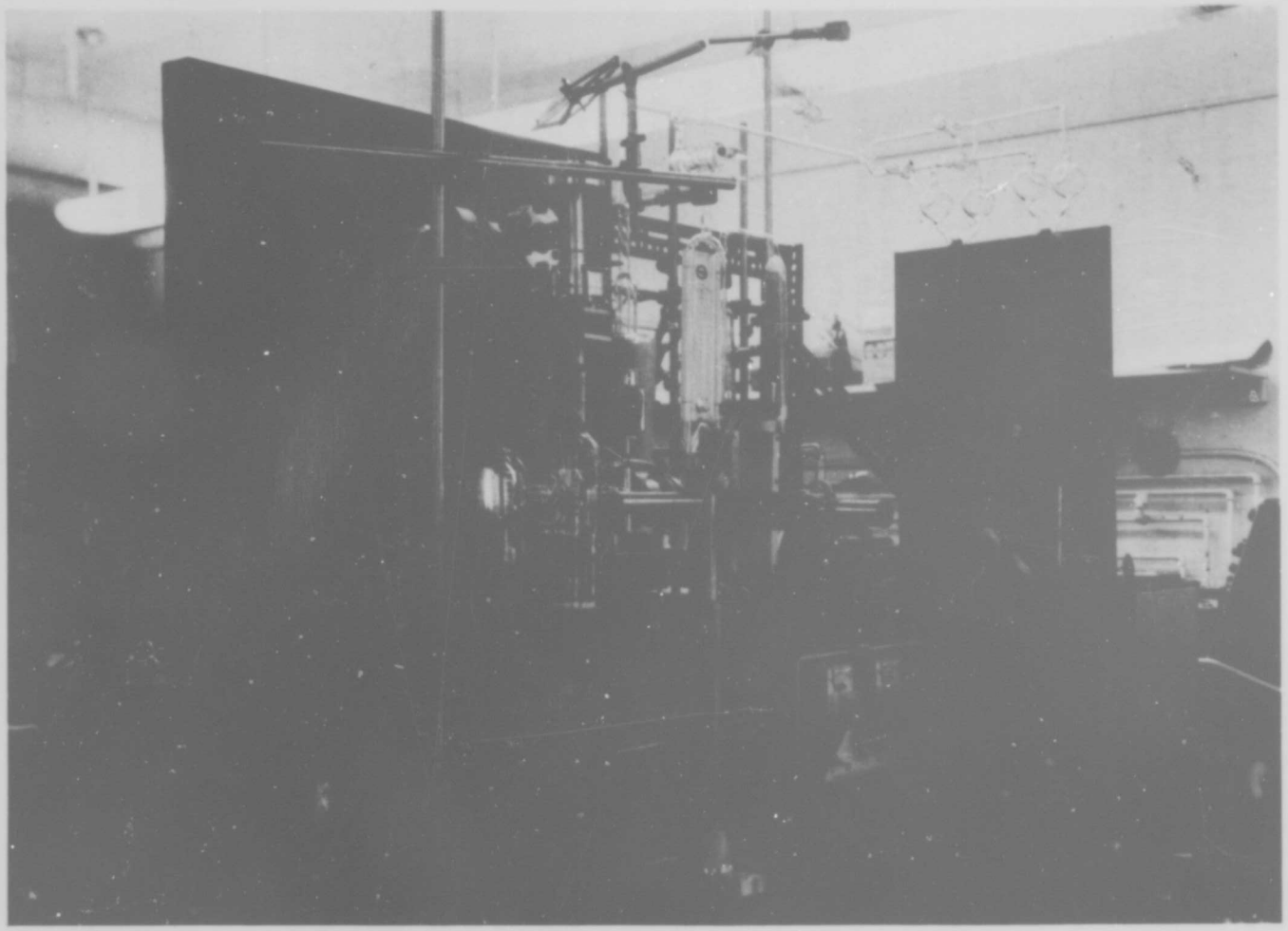

FIGURE 4 GENERAL VIEW OF APPARATUS FOR STUDY OF NITRIDES

A window correction for our system was established by determining the ribbon filament lamp temperatures with and without our window in the optical path. The window correction varied from 11° at 1330°C to 19° at 1700°C. All temperatures reported here have been corrected for the window effect on the pyrometer reading.

An oven was constructed to fit over the bakeable section shown in Figure 2. This permits baking out the high vacuum section at 350°C prior to studies in the low pressure range. The baking out process increases our ability to achieve low pressures; it also minimizes contamination of the sample by gases released from the sample chamber walls and components during the heating cycles.

The vacuum system consists of a 4 inch oil diffusion pump (Consolidated Vacuum Corp. PMC-720) backed by a Welch duo-seal roughing pump coupled to the sample chamber through a cold trap.

B. MATERIALS

It was our intention to prepare a bar of titanium nitride using the zone melting apparatus which has been described previously[3] in connection with the preparation of borides and carbides. In this technique a hot or molten zone is passed along a rod of material maintained in a controlled atmosphere. Our work was directed towards the direct nitridation of titanium metal rods. Thus a nitrogen atmosphere was maintained. Rods of crystal bar "iodide" titanium as well as high purity commercial titanium were procured. All initial test work which developed the preparative technique was with the commercial titanium rods.

We found immediately that if a molten zone above the melting point of TiN was passed along the bar that we did not obtain a titanium nitride phase. The nitride at this temperature must be completely dissociated. However, after further experimentation we found that if the temperature of the hot zone was maintained below the melting point of the nitride but above that of the titanium metal a good sample for our purposes can be obtained. The bar prepared in this manner had a yellow skin and a silver interior. The interior is shown to be single phase by X-ray diffraction study and analyzes 13.76% nitrogen. This corresponds to 35 atom percent nitrogen which is well within the homogeneity range of 28-53 atom percent reported in Hansen[4]. We believe that the material was molten within a skin of TiN. We spark machined the bar removing the yellow skin leaving a sample bar 5/16 inches in diameter and about 4 inches long. Samples for the initial test work were sliced from this bar.

Initial test work was carried out using as sample material some disks cut from the bar which had been prepared as described. The disks were 5/16 inch diameter by 1/8 inch thickness and were suspended in the field of the concentrator using tungsten wire.

It quickly became evident that significant loss of titanium occurred above 1500°C. We also observed that at 1500°C only a surface coating of higher nitride was formed after a several hour period of heating in 200 torr nitrogen.

These test results indicated that we must work at 1500°C or lower to avoid measurable titanium losses if weight changes of the sample were to be used as a measure of nitrogen content of the sample. To work in this temperature range available diffusion data[5] indicate that we must use much smaller particle size material if we are to achieve uniform sample composition within reasonable equilibration times.

Therefore the titanium nitride bar was crushed and screened and the fraction measuring 88 to 149 microns in diameter was taken for sample use. To contain this sample material crucibles were drawn from 2 mil molybdenum sheet stock. The crucibles measure 5/16 inches in diameter and 3/16 inches deep and have a lid containing three 1 mm diameter holes. We attempted to draw crucibles from tungsten sheet but the molybdenum proved easier to work. Tungsten and molybdenum were chosen as possible crucible materials since they form relatively unstable nitrides. Data quoted in "Vacuum Technique" by S. Dushman[6] indicate that weight changes due to nitrogen solubility in molybdenum will be negligible in our system. This was also confirmed experimentally.

After a run with this granular sample material we tried lathe turnings from an "iodide" titanium crystal bar as sample material. The lathe turnings do not pack as densely as the granules thus providing a greater porosity. We had observed marked sintering of the granules and felt that we were experiencing increased difficulty in nitridation after a period of working with the granular sample which might be attributable to an increase in particle size and/or a decrease in porosity. The majority of the work reported here was on titanium nitride prepared directly in our system by the nitridation of the "iodide" titanium turnings. One of the samples reported on (No. 895a-2) was the granular material obtained from the "zone melted" bar.

The lathe turnings used for most of this study were cut from an "iodide" titanium crystal bar obtained from Foote Mineral Company. The major impurity according to their representative analysis was .05% Zr. The next highest impurities were reported to be Al and Si at .005%. These claimed impurity levels agreed well with later analysis of a titanium nitride sample (see Table IV). Oxygen analysis of the lathe turnings gave values of 300 and 340 ppm compared with a representative value of 10 ppm claimed by the producer for the crystal bars.

C. RESULTS

1. Nitrogen Pressure Studies

Briefly the technique consists of heating a titanium nitride sample of known composition in a closed system and observing the

equilibrium nitrogen pressure. The nitrogen content is adjusted initially by adding a measured volume of nitrogen to a closed system containing a sample of pure titanium. The titanium sample is then heated over a period of several hours to absorb the nitrogen and to achieve equilibrium. One measure of equilibration was the reproducibility of observed pressure measurements as temperature was cycled. Frequently initial measurements were high compared to the final "equilibrium" data. Following a series of pressure measurements as a function of temperature with a sample of a given nitrogen content we have frequently increased the nitrogen content by repeating the dosing process. Nitrogen content of the samples may be calculated from observed weight changes of the sample within the system or by analysis of the sample after it is removed from the experimental system.

The results obtained are presented in Figure 5 and Table I. Titanium nitride samples have ranged in composition from $Ti_{.551}N_{.449}$ ($\sim TiN_{.82}$) to $Ti_{.499}N_{.501}$ ($\sim$ TiN). These sample compositions represent equilibrium nitrogen pressures ranging from about 10^{-7} to 300 torr. The data used in plotting Figure 5 are tabulated in Appendix I.

It may be observed on Figure 5 that the pressure-temperature slopes are essentially parallel except at the very low nitrogen content end where we observed sharply increased slopes. As discussed later in Section III, pressure measurements below 5×10^{-6} torr appear to be subject to some systematic error.

We found that equilibration of the samples was extremely slow and difficult. Because of this equilibration problem there are certain sample data points which we now consider to be "better" than others because of longer periods of time at temperature. Also because of this problem we will tend to favor the "lower" equilibrium pressure data in our discussion of these experimental results.

Table I shows the data for a titanium nitride sample close to stoichiometry. Because of the long equilibration times required it was not possible to make pressure measurements as a function of temperature as had been done with previous samples. The most sensitive measure of change in our samples under pressures on the order of a torr or greater is the weight change of the sample. We followed the weight changes of the sample as a function of time at selected pressures and temperature. Table I shows that times on the order of 1-3 days of heating at temperatures of about 1660°C are required before we feel confident that samples in this composition range are equilibrated. Over the long heating periods the temperature would vary due to power line fluctuation. Power was adjusted periodically during the day to maintain temperatures of about 1660°C. The ranges given in Table I represent fluctuation limits and from a consideration of the temperature histories we feel that a temperature uncertainty of ± 20°C must be applied to the nominal temperature of 1657°C. We conclude that at a temperature of 1657°C ± 20°C sample compositions of $Ti_{.504}N_{.496}$ and $Ti_{.499}N_{.501}$ will be found in equilibrium with nitrogen pressures of 31 and 330 torr respectively.

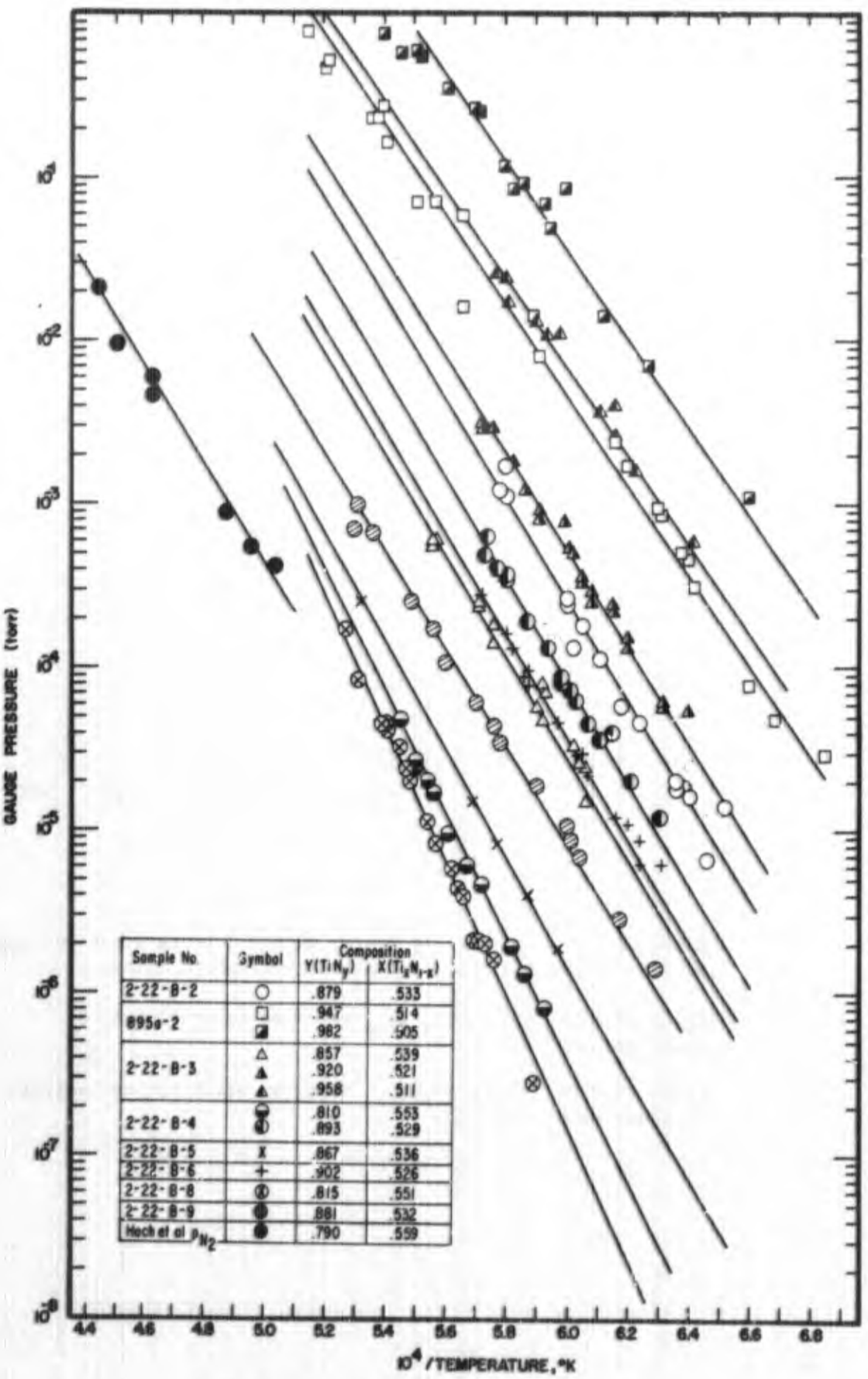

FIGURE 5. NITROGEN PRESSURE vs TEMPERATURE

TABLE I

HISTORY OF SAMPLE NO. 2-22-B-10

Pressure (torr)	Temp. (°C)	Time (min)	W_s (mg)	W_{Ti} (mg)	W_N (mg)	X **	X ***
			90.4	90.4	-----	1.0	
31.2	1210 - 1688	357	115.74	90.4	25.34	.511	
31.2	1688 - 1703	250	116.28	90.4	25.88	.506	
30.9	1658 - 1668	420	116.34	90.4	25.94	.505	.504
330	1627 - 1663	1232	116.51*				
329	1653	1051	116.56*				
330	1653	270	116.56*				
330	1688 - 1658	1007	116.54*				
			116.82	90.4	26.42	.500	.499

* Based on weighing taken at approximately 3 hours after cooling sample. Other weighings are after overnight cooling.

** Value of x in formula $Ti_x N_{1-x}$ based on internal weight measurements.

*** Value of x in formula $Ti_x N_{1-x}$ based on quantitative analysis of final sample material.

2. Titanium Pressure Studies

The data obtained from studies discussed under 1, above, will permit determination of the activity of nitrogen versus nitrogen content of the samples at a given temperature. From such data one may calculate titanium activity versus composition if one knows a single activity value for titanium in the composition range studied. It seemed worthwhile to attempt to obtain a measure of the titanium activity in our system using the crucibles as Knudsen cells.

Weight loss measurements were made on three types of samples: first on samples in the $Ti_{.55}N_{.45}$ composition range, where both nitrogen and titanium pressures were directly measureable in our system. These samples were No. 2-22-B-5 and No. 2-22-B-8. In these experiments the samples were first equilibrated to the desired nitrogen content of about $Ti_{.55}N_{.45}$ at temperatures where titanium losses were negligible. The samples were then raised into a temperature range where measurable weight losses could be observed during a 6 to 7 hour period. The weight loss experiments were carried out under conditions such that nitrogen pressure remained essentially constant; this insures that sample composition does not change. The data for these three measurements are given in Table II. Under conditions of the experiment the mean free path was about 500 centimeters and thus Knudsen effusion conditions were met. To calculate the actual nitrogen pressure within the Knudsen cell we assume that the nitrogen within the cell is at the temperature of the cell and that the nitrogen outside of the cell is at the temperature of the walls of the closed system which is about 300° Kelvin. Considering the thermomolecular pressure correction for nitrogen and the weight losses of the system, the titanium and nitrogen pressures were calculated as given in Table II. From these data we calculated the standard free energy of formation for the observed composition of the titanium nitride sample. To indicate the variation to be expected due to the temperature differences for the three experiments we have also listed in the final column of Table II the free energy of formation for stoichiometric titanium nitride. The agreement between the three experiments is quite good.

Second, samples were prepared which fell within the (α-Ti)-TiN two phase region. Initial X-ray diffraction patterns of the samples showed Ti, TiN, and Ti_2N phases present. Based on the phase diagram we would expect at least some conversion of TiN phase to Ti_2N on cooling.

The titanium pressures over these samples (No. 2-22-B-11) and (No. 2-22-B-15) were measured by a Knudsen technique over the temperature range 1575 - 1760°C and the results are shown in Figure 6. The data for the experimental points are tabulated in Appendix II.

X-ray lattice parameter measurements on these samples made after the Knudsen experiments showed only titanium nitride phase present. Calculations showed that titanium volatilization from the "two phase" sample within the crucible coupled with alloying at the molybdenum crucible walls could have removed enough titanium to explain the shift to the final single phase composition as indicated by the lattice parameter.

TABLE II

TITANIUM ACTIVITY MEASUREMENTS

Sample	Composition	Temp. (°K)	Gauge Pressure (atm)	Time (min)	Weight Loss (mg)	P_{N_2} (atm)	P_{Ti} (atm)	$\Delta G^{\circ}_{Ti_xN_{1-x}}$ (1) (cals/gm-atm)	ΔG°_{TiN} (2) (cals/gm-atm)
2-22-B-5	$Ti_{.536}N_{.464}$	1885	3.29×10^{-7}	385	1.045	8.24×10^{-7}	2.18×10^{-7}	-16,200	-19060
		1896	3.68×10^{-7}	420	1.075	9.21×10^{-7}	2.06×10^{-7}	-16,700	-18930
2-22-B-8	$Ti_{.551}N_{.449}$	1930	9.2×10^{-8}	431	3.10	2.3×10^{-7}	5.85×10^{-7}	-16,700	-18540

(1) Calculated from experimental data.

(2) Taken from JANAF tables.

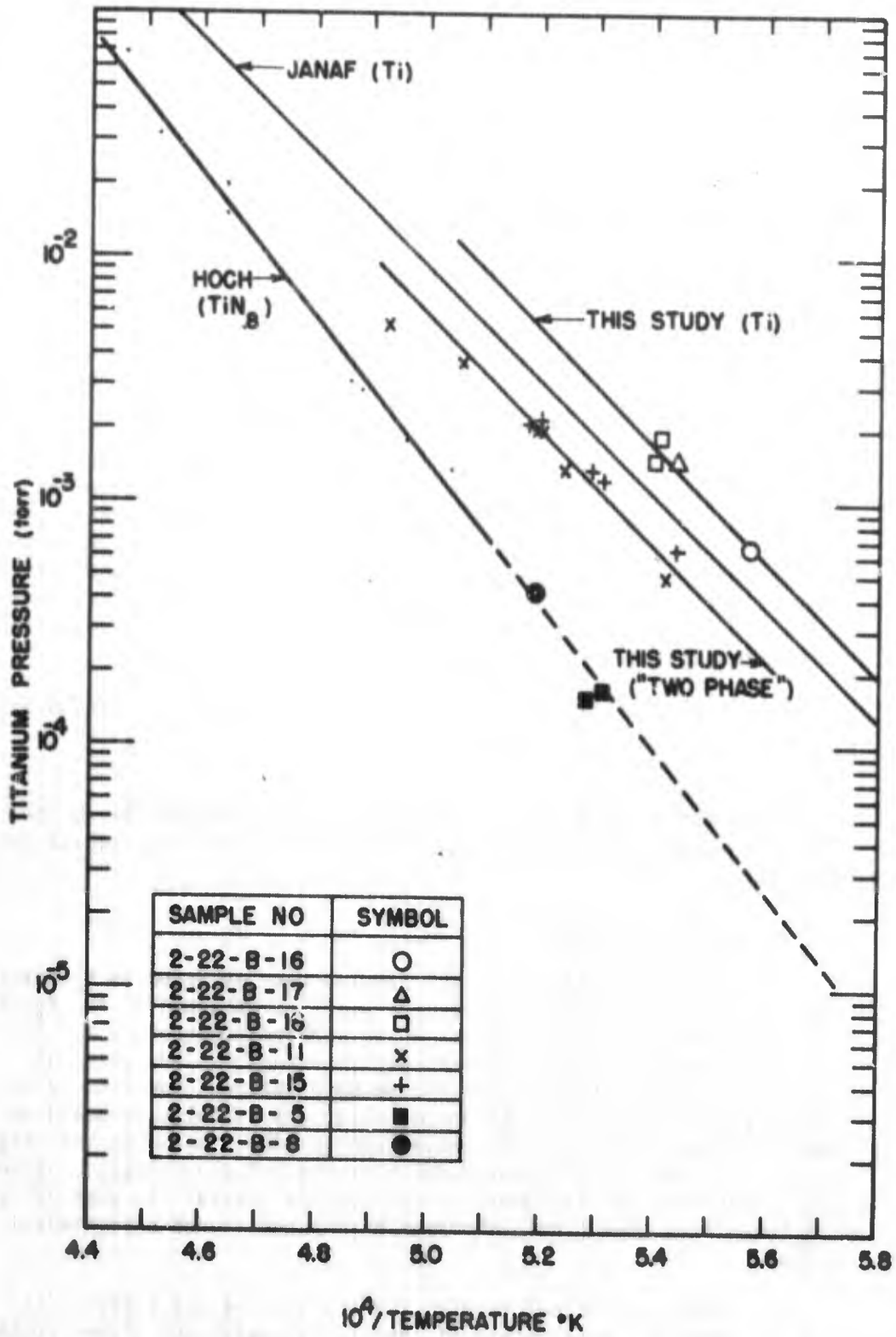

FIGURE 6. TITANIUM PPESSURE vs. TEMPERATURE

We do believe that the initial titanium activity points determined for each of these samples represent a good measure of titanium pressure over the "two phase" material. This value is used in the discussion later.

Third, Knudsen experiments were run on pure titanium samples. These are Samples No. 2-22-B-16, No. 2-22-B-17, No. 2-22-B-18, and are shown on Figure 6. Again the data for these experimental points are tabulated in Appendix II. The titanium pressures calculated from these runs were 50-60% higher than those previously reported[16] and used in developing the JANAF Tables. Samples No. 2-22-B-16 and No. 2-22-B-17 were run in crucibles having three 1 mm orifices. Sample No. 2-22-B-18 was run in a crucible with a single 2 mm orifice. The change in orifice size was made as an attempt to eliminate surface diffusion as a possible cause for our observed pressures being higher than those reported. The agreement achieved seems to indicate that the results are real. These experiments were also run for minimum times at temperature to minimize interaction with the crucible which could lead to marked composition changes and/or diffusion through the cell walls. Heating periods were on the order of one hour and no evidence of interaction was observed between the crucible and the titanium sample.

The equation used to calculate all Knudsen cell pressures was

$$P = 17.14 \; G\sqrt{\frac{T}{M}}$$

where P is the pressure in torr, T the absolute temperature, M the molecular weight, and G the evaporation rate in grams per square centimeter per second.

3. Analytical Data

Nitrogen analyses on the samples were obtained by Kjeldahl, Dumas and direct oxidation. Nitrogen analyses obtained by the Kjeldahl and Dumas techniques gave results which appeared impossibly low based on observed weight changes of the samples within our experimental system. To resolve this difficulty we have oxidized portions of our samples and determined the titanium content by calculation based on sample weights after complete conversion to TiO_2. Assuming the original sample to contain only titanium and nitrogen, we can calculate nitrogen content for the various samples which are, in general, in good agreement with the weight change data observed within the closed experimental system.

These analytical results for our samples are reported in Table III together with values of lattice parameter and oxygen content determined for each sample. For some of these samples our nitrogen contents as calculated from weight changes within the closed system are somewhat uncertain because of possible titanium losses during the experiment. However, even with this uncertainty we were obtaining nitrogen contents from Kjeldahl and Dumas techniques which were impossibly low. As an

TABLE III

SAMPLE DATA SUMMARY

Sample No. (a)	Composition as y in TiN_y		as x in Ti_xN_{1-x}	Lattice Parameter	Oxygen Content (ppm)
	Oxidation	Gravimetric	Oxidation		
2-22-B-2	.879	.799	.533	4.2365	4302
895a-2	.982	.981	.505	4.2401	2384
2-22-B-3	.958	.969	.511	4.2396	4618
2-22-B-4	.893	.909	.524	4.2364	794
2-22-B-5	.867	.854	.536	4.2345	499
2-22-B-6	.902	.899	.526	4.2364	3183
2-22-B-7	.897	.884	.527	4.2363	
2-22-B-8	.815	.829	.551	4.2326	367
895a	.606		.624	4.2219	
2-22-B-9	.881	.879	.532	4.2354	11
2-22-B-10	1.003	1.001	.499	4.2403	0
2-22-B-11	.732		.578	4.2279	0
2-22-B-13	.511	.496	.662	4.2166	0
2-22-B-15				4.2251	

(a) Samples not reported (Nos. 895a-1, 2-22-B-1, -12, and -14) were omitted because they were either early samples and were considered developmental or because extreme conditions led to sample - crucible interaction.

example let's consider the first sample listed in Table III (2-22-B-2). In our experiments with this sample we did lose titanium and considered that our weight loss calculation which gave $TiN_{.799}$ was quite uncertain. However, the Kjeldahl method gave $TiN_{.55}$ and the Dumas method gave $TiN_{.31}$. Both results were impossibly low. The oxidation technique gave a value of $TiN_{.879}$ which placed this sample in good relationship with respect to other samples which had been studied and in which our weight change data had a much smaller uncertainty. Several later samples, for which extreme care was taken to prevent any uncertainty due to titanium losses, showed excellent agreement between the nitrogen content determined by the oxidation technique and that determined by weight changes within the closed system.

From a comparison of the results for various samples as determined by Kjeldahl and Dumas techniques we observe that the Dumas values are more in error the larger the particle size of our sample. Apparently the standard technique being used does not allow for the longer reaction times required by larger particle material. We have also found mention in the literature that some nitrogen evolution has been observed during the dissolving of metal nitrides in acids. This behavior could account for low Kjeldahl values. Because of these problems of incomplete reaction and the release of some free nitrogen rather than complete conversion to ammonia some workers concerned with the analyses of boron and silicon nitrides recommend the use of an oxidizing alkaline fusion followed by measurement of the nitrogen gas evolved as in the Dumas technique. For the purposes of this study the direct oxidation technique has proven very satisfactory.

We have obtained precision X-ray lattice spacing measurements on each of our samples. The analysis was performed with a Norelco High Angle Automatic Recording Diffractometer utilizing Ni filtered Cu radiation and scintillation detector. The accuracy of these values was determined using a Si powder standard as a comparison and reproducibility checks were run. These lattice spacing values are plotted in Figure 7 versus our assigned compositions. A straight line can be drawn through all of our points within the uncertainty in composition and lattice spacing measurements. We believe that the good agreement of the data indicated by this plot tends to confirm our composition assignments. Vainshtein et al.[7] have also observed from a study of samples ranging from 11.7 to 22.4 weight percent nitrogen that lattice spacing varies linearly across the titanium nitride homogeneity range.

A spectrographic analysis was obtained for one of our samples. The results are presented in Table IV. This indicates some slight pickup of molybdenum by the sample from the crucible. However, we do not consider that this amount of molybdenum will measureable affect the results.

In Table III we also present data for the oxygen content of the samples. Several of the earlier samples were an order of magnitude higher in oxygen content than we expected based on the oxygen content of

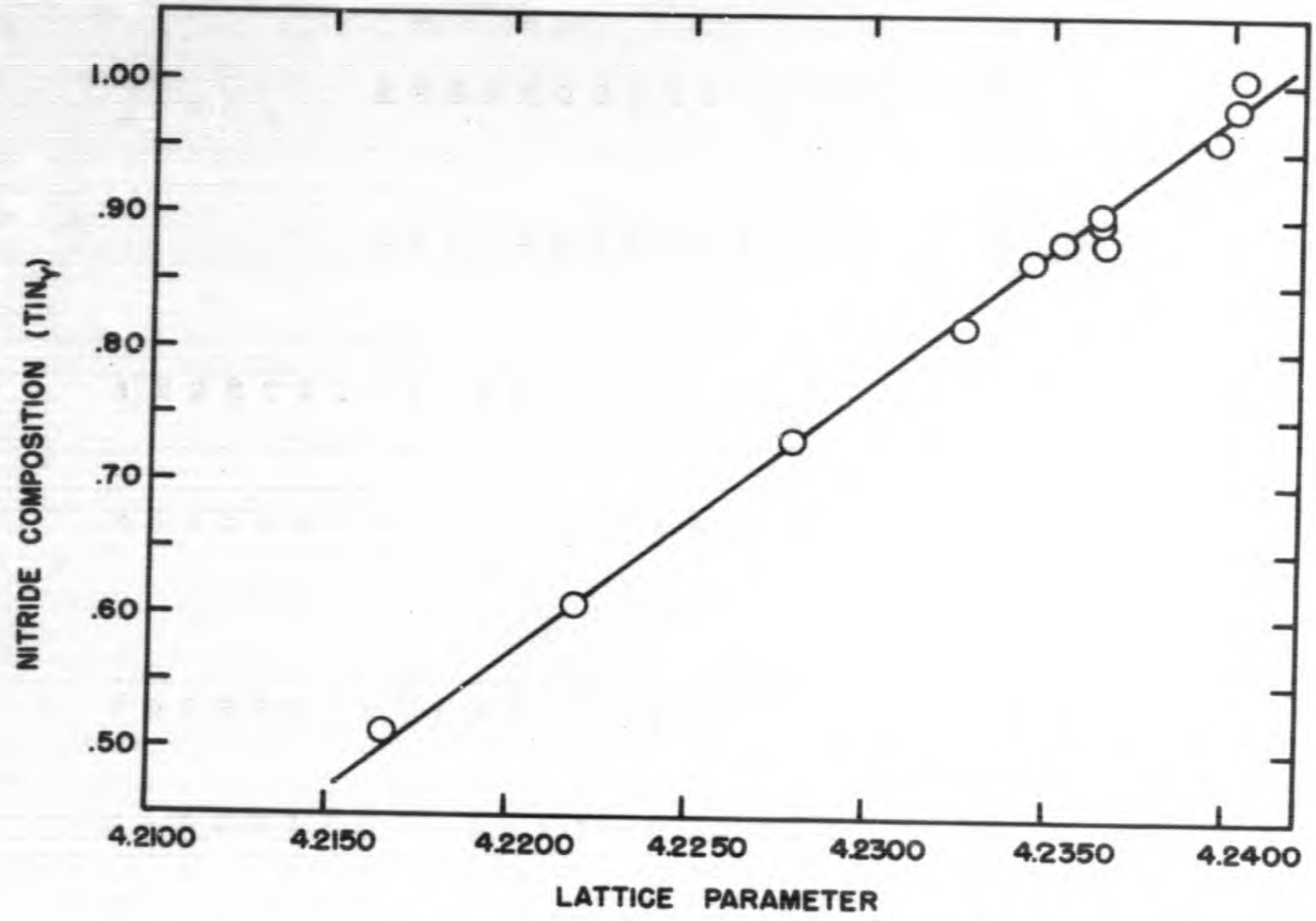

FIGURE 7. NITRIDE COMPOSITION vs X-RAY LATTICE PARAMETERS

TABLE IV

SPECTROSCOPIC ANALYSIS - (SAMPLE NO. 2-22-B-5)

Impurity	Percentage	Impurity	Percentage	Impurity	Percentage
Li	ND	Nb	ND	Tm	ND
Be	ND	Mo	.01-.1	Yb	ND
B	ND	Ru	ND	Lu	ND
Na	.0001-.001	Rh	ND	Hf	ND
Mg	.0001-.001	Pd	ND	Ta	ND
Al	<.0001	Ag	ND	W	ND
Si	.001-.01	Cd	ND	Re	ND
K	ND	In	ND	Os	ND
Ca	ND	Sn	ND	Ir	ND
V	ND	Sb	ND	Pt	ND
Cr	<.0001	Te	ND	Au	ND
Mn	.0001-.001	Cs	ND	Hg	ND
Fe	.0001-.001	Ba	ND	Tl	ND
Co	ND	La	ND	Pb	ND
Ni	ND	Ce	ND	Bi	ND
Cu	<.0001	Pr	ND	Th	ND
Zn	ND	Nd	ND	U	ND
Ga	ND	Sm	ND		
Ge	ND	Eu	ND		
As	ND	Gd	ND		
Rb	ND	Tb	ND		
Sr	ND	Dy	ND		
Y	ND	Ho	ND		
Zr	.01-.1	Er	ND		

the starting material. Oxygen analysis of the molybdenum crucibles indicated that this was not the source. Thus the oxygen must have been picked up in the system. We revised our gas handling techniques in an effort to further minimize any introduction of oxygen. The major changes were to thoroughly outgas the gas purification train and the manometer train and then to always maintain these under nitrogen pressure and vacuum respectively when not in use. Following these changes and with care taken to maintain a closed system of minimum volume in so far as possible, we obtained for later samples a much lower oxygen content. We believe that the source of oxygen was related to the use of the manometer train and difficulties in completely outgassing the mercury. In no case do we consider these oxygen contents high enough to significantly affect the experimental results. The last four samples which showed essentially no oxygen content are somewhat unexpected, since the starting material had an oxygen content of approximately 300 ppm. It is, however, conceivable that the oxygen activity in these titanium nitride systems is high enough to lead to "purification" of the system with respect to oxygen by the volatilization of a species such as TiO.

III. DISCUSSION

A. PHASE RELATIONSHIPS

Before proceeding to the derivation of thermodynamic data from the experimental work we will first review the available phase information on the titanium-nitrogen system.

The most detailed phase study to date was that of Palty, Margolin and Nielsen[8]. They developed a phase diagram on the basis of metallographic, X-ray diffraction, and melting point data. The diagram presented in Figure 8 is that of these workers modified as discussed in the following paragraphs.

The melting point of titanium was corrected to 1950°K to agree with the value adopted in the JANAF Thermochemical Data Tables.

Nowotny, Benesovsky, Brukl and Schob[9] reported that the α-titanium solution range extends to 25 atom percent nitrogen. Now Palty et al.[8] reported uncertainties in composition for their α + δ samples of about one weight percent nitrogen. Thus we choose in Figure 8 to increase the solution range of α-titanium over that originally indicated by Palty et al. the equivalent of one weight percent nitrogen while maintaining the same relative width of the α + δ region. This gives weight to the Nowotny et al. measurement while maintaining the relative behavior observed by Palty et al.

Holmburg[10] has recently made a careful study on samples annealed at 900°C. He reports a solubility limit in α-titanium at 17 atom percent nitrogen. He had identified the ε-phase as Ti_2N (Nowotny et al. had suggested this as the composition) with a very narrow range of composition and an upper limit at $TiN_{.5}$. He finds the lower limit of the δ-TiN phase at $TiN_{.6}$. Vainshtein et al.[7] have prepared homogeneous δ-TiN phase samples ranging from 11.7 to 22.4 weight percent at 1200°C which indicates that the lower limit of the δ-TiN phase is less than 31 atom percent nitrogen at this temperature. Ehrlich[11] in his studies fixed this boundary at 29.5 atom percent. On the basis of these data we place the α + δ/δ boundary at 1200°C at 30% and we show the ε-phase with a maximum at about 1100°C. We give a greater slope to the α/α + ε boundary to obtain the best fit to the Holmburg and Palty et al. data. The original Palty et al. boundaries are shown as dotted lines to make clearer the changes we have made in their diagram.

We show the high nitrogen boundary of the δ-TiN phase at $Ti_{.5}N_{.5}$. Our experimental data do not indicate any significant composition range beyond $Ti_{.5}N_{.5}$. Extrapolation of our nitrogen pressure data as presented in Figure 9 to a pressure of 1 atmosphere nitrogen would indicate a composition limit of $Ti_{.498}N_{.502}$ ($TiN_{1.01}$) at 1930°K.

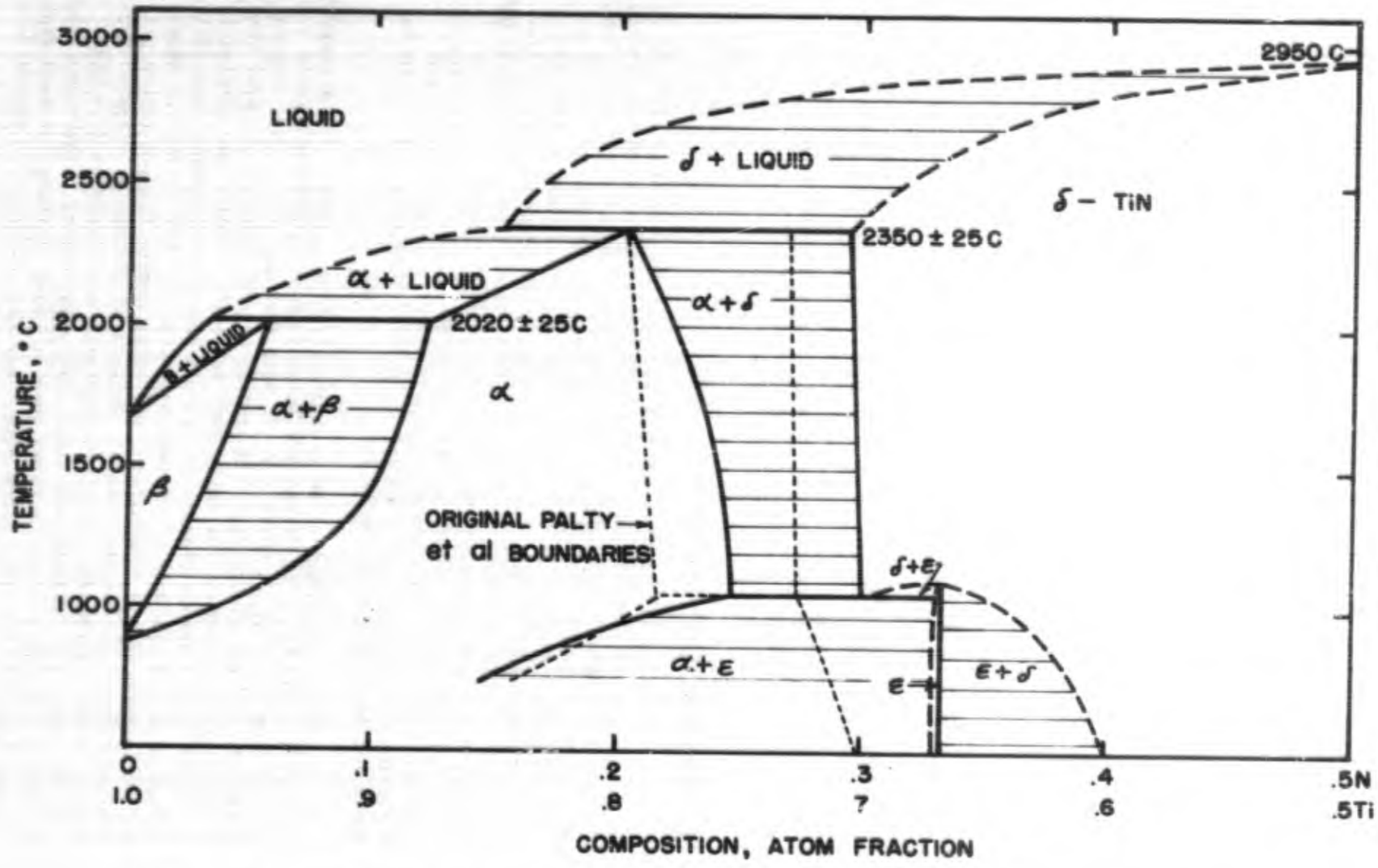

FIGURE 8. APPARENT PHASE RELATIONSHIPS FOR THE TITANIUM - NITROGEN SYSTEM

The phase diagram presented in Figure 8 represents our current understanding of the phase relationships in the titanium-nitrogen system. Our experimental work was concerned with developing thermodynamic data for the δ-TiN phase over its range of composition.

The vapor species over the titanium nitride phase have been studied by mass spectrometry using a Knudsen cell source by Akishin and Klodeev[12]. They found no evidence for the existence of undissociated TiN over solid nitride. Based on the sensitivity of their apparatus they report the upper pressure limit possible at 1800°C for the species TiN as 2×10^{-8} atm. which they report is many orders of magnitude lower than the observed nitrogen pressure. Some spectral evidence for the existence of TiN and ZrN species have been obtained by mass spectrographic analysis in an RF spark source instrument.[13] However since the conditions of RF spark and the vapors it produces are not well understood, partial pressures are not calculable. We conclude on the basis of the data obtained under the Knudsen conditions which are most applicable to our studies that only the gaseous elements are found in appreciable concentration over solid titanium nitride.

B. THERMODYNAMIC CALCULATIONS

We have presented in section II C the experimental nitrogen and titanium pressure data obtained as a function of temperature and stoichiometry of the δ-TiN phase. These data are summarized in Figures 5 and 6. They cover only a limited portion of the total range of composition of the nitride phase. Because of the wide variation in the partial pressures it is impractical to experimentally measure these pressures across the complete range of homogeneity for the δ-TiN phase. However thermodynamic relationships can be derived which relate the nitrogen and titanium properties within this phase and make it possible to derive the partial pressure curves for the complete range of nitride composition. The necessary thermodynamic relationships for the titanium nitride solution phase are developed in Appendix III.

We plot pressure data vs composition in Figure 9 for a temperature of 1930°K. The P_{N_2} data points are taken from the curves of Figure 5 and extend from $Ti_{.55}N_{.45}$ to $Ti_{.5}N_{.5}$. Note that the points for samples 2-22-B-2, -3 and -4 are high compared to points obtained on later samples. These samples represent the early runs in which titanium was completely nitrided in the sample chamber to produce the desired sample composition. As our experimental work progressed we recognized how slowly the sample became homogeneous in composition, and consequently allowed longer periods for equilibrium in our later work. Because of the way we prepared these samples, lack of complete sample homogeneity would tend to give high results such as we observe for these early sample runs. Therefore, since we believe the data from the later runs are more accurate, we have drawn the smooth curve to favor these data. For the low pressure points, a

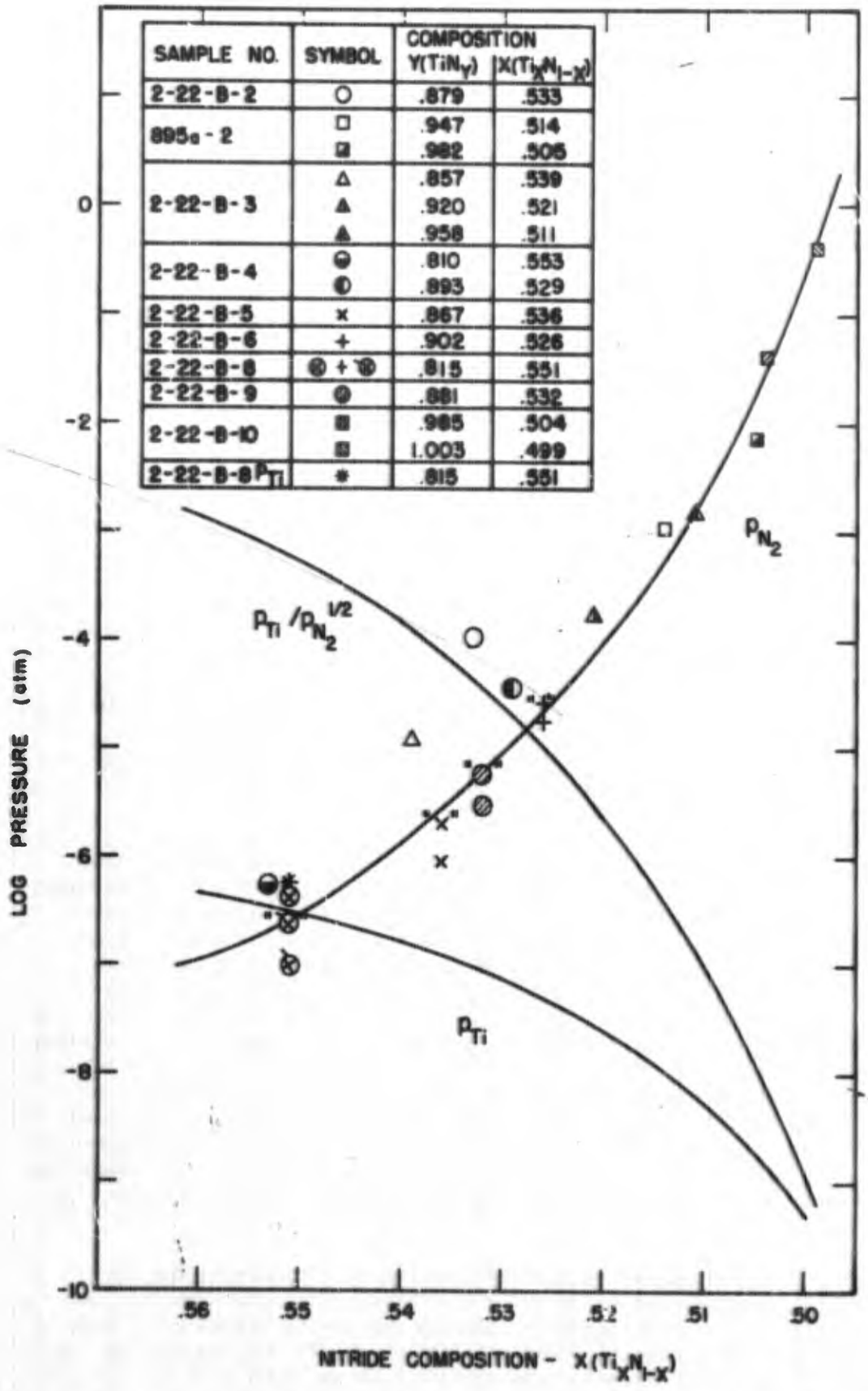

FIGURE 9. NITROGEN AND TITANIUM PRESSURE vs NITRIDE COMPOSITION (1930°K)

pressure correction must be made since in our study we heat only the sample cell and consequently the temperature of the gas inside the sample cell is not equal to the temperature of the gas in the chamber in which the pressure gauge is located.

When the mean free path of the molecules is large with respect to the orifice between the sample and the gauge, the relationship between the pressure inside and outside is given by

$$\frac{P \text{ inside}}{P \text{ outside}} = \sqrt{\frac{T \text{ inside}}{T \text{ outside}}}$$

Thus at the low pressure end of our studies where pressures on the order of 10^{-7} atm are obtained at equilibrium the actual pressure inside the sample cell at a temperature of 1930°K is about 2.5 times that outside where the pressure is measured by our ionization gauge at a temperature of about 300°K. At the high pressure end of the curve where equilibrium pressures are on the order of 10^{-1} atm, the mean free path is very small compared to the orifice and thus the pressures can be expected to be equal inside and outside the sample cell. As a result of this thermomolecular effect, we draw our curve giving a full correction to the experimental gauge measurements at the low pressure end and no correction at the high pressure end. Points to which we have applied a thermomolecular correction are shown in parenthesis as "x" on Figure 9 to indicate the relative magnitudes of the correction we have allowed at various pressures.

The change in P_{Ti} with change in P_{N_2} as composition changes in the nitride phase is given by the Gibbs-Duhem equation as developed in Appendix III. The partial pressure of titanium may be calculated as a function of composition based on the experimental pressures of nitrogen as a function of composition providing the partial pressure of titanium is known at a single composition. We have measured a titanium pressure over $Ti_{.551}N_{.449}$ and this may be used as a basis for calculating titanium pressures as a function of composition or, alternatively, as discussed in Appendix III, we may use the thermodynamic data tabulated for stoichiometric TiN as the basis for determining the pressure of titanium over stoichiometric titanium nitride which may then be used as a basis for deriving P_{Ti} as a function of composition. We choose the latter approach as a basis for drawing the curve for P_{Ti} vs composition on Figure 9. The curve checks the measured pressure over $Ti_{.551}N_{.449}$ within a factor of two which we consider as good agreement.

In Figure 10 we plot P_{Ti} and P_{N_2} vs composition for the Ti_xN_{1-x} system from pure titanium at x equal 1 to stoichiometric nitride at x = 0.5. On this figure we indicate the partial pressure of pure titanium as given in the JANAF tabulations and in our experiments. We also indicate the titanium pressure which we measured near the $\alpha + \delta/\delta$ phase boundary. It is evident that the possible behavior of the P_{Ti}

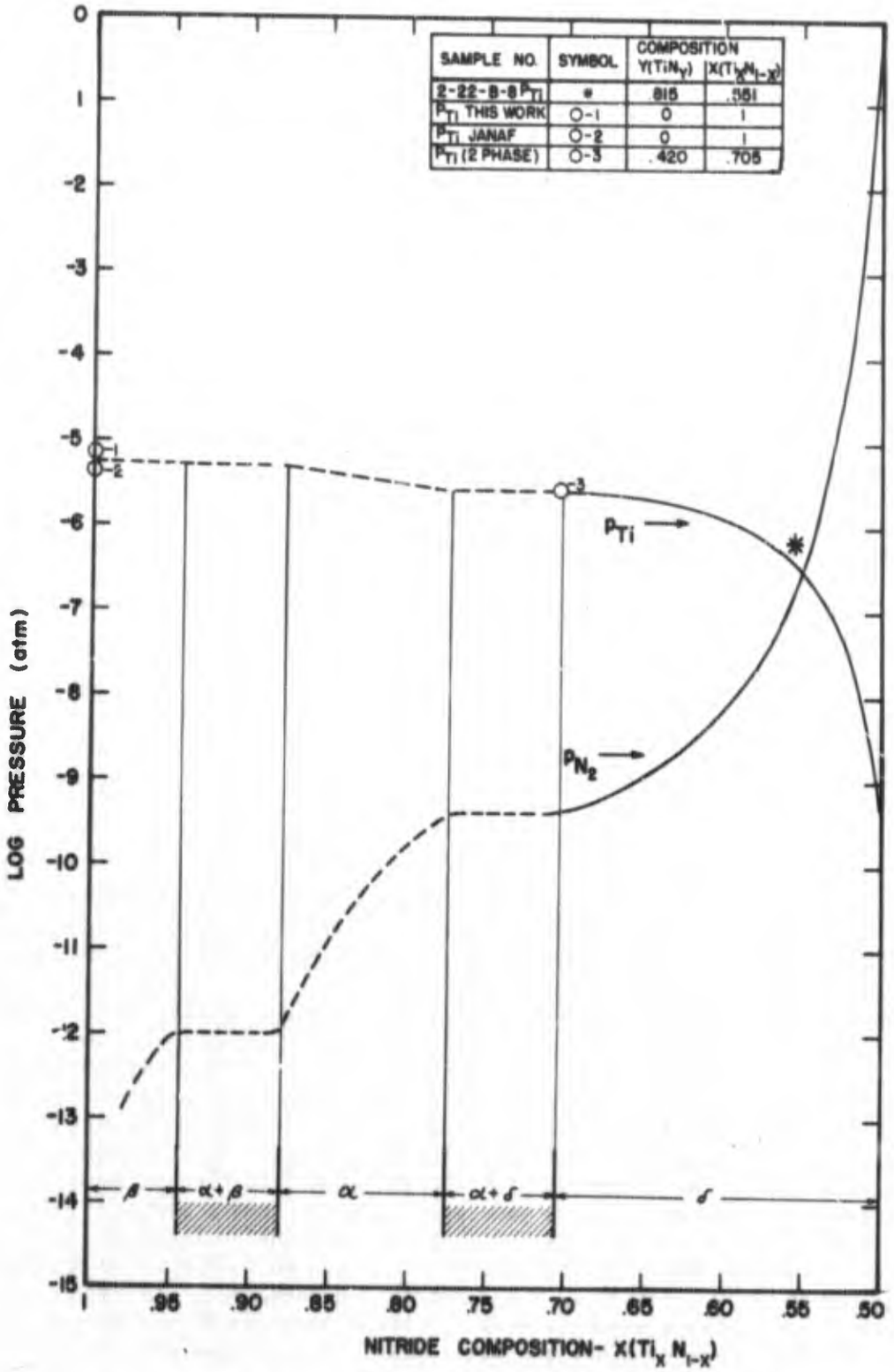

FIGURE 10. NITROGEN AND TITANIUM PRESSURE vs. NITRIDE COMPOSITION (1930°K)

curve is severely restricted between $Ti_{.55}N_{.45}$ and the lower nitrogen content boundary of the δ-TiN phase and that we can extend therefore the P_{Ti} curve to the lower boundary of the phase without much uncertainty. Applying the Gibbs-Duhem relationship between P_{Ti} and P_{N_2} we next extend the P_{N_2} curve to the lower phase boundary. These two curves now satisfy the thermodynamic relationship required for the nitride solution phase and agree well with all the experimental data we have available.

We can approximate in Figure 10 the behavior of the P_{Ti} and P_{N_2} curves extending beyond the nitride phase to pure titanium on the following basis. We know that in solutions of oxygen in titanium metal Raoult's law is applicable up to concentrations of approximately 2 weight percent oxygen.[14] Therefore, assuming similar behavior for nitrogen, we apply Raoult's law to determine the P_{Ti} curve in the β-Ti phase. After this calculation the P_{Ti} value is now fixed at the upper and lower boundary of the α-Ti phase and we join these points with a straight line. The P_{N_2} curve may now be calculated for the α- and β-Ti phases using the Gibbs-Duhem relationship.

The change in P_{N_2} and P_{Ti} with temperature in the δ-TiN phase are given by the expressions

$$\frac{Rd(\ln P_{N_2}^{1/2})}{d(1/T)} = \bar{H}_N \quad \text{and} \quad \frac{Rd(\ln P_{Ti})}{d(1/T)} = \bar{H}_{Ti}$$ derived in Appendix III. From the slopes of pressure vs reciprocal temperature curves such as those presented in Figures 5 and 6, we can calculate the partial enthalpies for titanium and nitrogen for the specific nitride compositions which we have studied. If we knew these quantities for the entire δ-TiN composition range, they could be used to calculate the integral enthalpies across the δ-TiN phase range. One method of obtaining these data for compositions other than those studied would be to calculate the $\bar{H}$ values for titanium and nitrogen pressure data taken from smoothed pressure vs. composition curves (such as those presented in Figure 9) for different temperatures. We have chosen however to use the "least square" slopes taken from the original pressure vs temperature data tabulated in Appendixes I and II. This method allows us to "best fit" all the known enthalpy information, i.e., it allows us to fit the partial nitrogen enthalpies from the data for the $Ti_{.54}N_{.46}$ to $Ti_{.50}N_{.50}$ composition range with the partial titanium enthalpies taken from the titanium pressure data obtained at the $\alpha + \delta/\delta$ phase boundary and with titanium enthalpies derived for pure titanium and for $Ti_{.5}N_{.5}$.

In Table V we present the enthalpy values obtained by least squares treatment of our experimental data as shown on Figures 5 and 6 and tabulated in Appendixes I and II. These partial enthalpy data are

TABLE V

ENTHALPY VALUES DERIVED FROM EXPERIMENTAL DATA

Sample No.	X (Ti_xN_{1-x})	m[a] (slope)	b[a] (intercept)	$\bar{H}_N$[b] (kcal/gm.atom)	$\bar{H}_{Ti}$[c] (kcal/gm.atom)
2-22-B-2	0.533	-30.118	14.453	68.92	
895a-2	0.514	-26.514	13.578	60.67	
895a-2	0.505	-25.922	14.133	59.32	
2-22-B-3	0.539	-28.723	12.738	65.72	
2-22-B-3	0.521	-27.536	13.228	63.01	
2-22-B-3	0.511	-25.265	13.006	57.82	
2-22-B-4	0.553	-35.234	14.768	80.62	
2-22-B-4	0.529	-29.103	13.371	66.60	
2-22-B-5	0.536	-32.054	13.404	73.35	
2-22-B-6	0.526	-28.491	12.651	65.20	
2-22-B-8	0.551	-43.330	19.025	99.16	
2-22-B-9	0.532	-28.097	11.799	64.30	
2-22-B-11	"Two phase"	-25.067	10.279		114.72
2-22-B-15	"Two phase"	-20.734	8.084		94.89

(a) Values derived for equation $\log {}^{P}N_2 = m(1000/T^{\circ}K) + b$ (${}^{P}N_2$ in torr.) by least squares treatment of experimental data which is tabulated in Appendixes I and II for each sample

(b) $\bar{H}_N = -2.288\ m$ ($\bar{H}$ in kcal/gm.atom)

(c) $\bar{H}_{Ti} = -4.576\ m$ ($\bar{H}$ in kcal/gm.atom)

plotted on Figure 11 and a smooth curve is drawn through the $\bar{H}_N$ data points so that a value of $\bar{H}_N$ can be derived from the curve for a composition of $Ti_{.5}N_{.5}$.

Now since

$$H = \Sigma n_i \bar{H}_i$$

we can use the thermodynamic data tabulations (JANAF) for stoichiometric TiN as the basis for determining the partial enthalpy of titanium in stoichiometric titanium nitride. From this calculation we derive a value of $\bar{H}_{Ti} = -94$ kcal for $Ti_{.5}N_{.5}$. We also know that changes in the partial enthalpies across the δ-TiN solution range are related by an expression analogous to the Gibbs-Duhem equation relating partial molal free energies. This expression is:

$$x \frac{\partial \bar{H}_{Ti}}{\partial x} + (1-x) \frac{\partial \bar{H}_N}{\partial x} = 0$$

Using this relationship together with $\bar{H}_{Ti}$ for $Ti_{.5}N_{.5}$ and $\bar{H}_N$ data taken from the smooth curve of Figure 11 in the composition range $Ti_{.5}N_{.5}$ to $Ti_{.54}N_{.46}$, partial titanium enthalpies were calculated for the same composition region. The $\bar{H}_{Ti}$ curve was then extrapolated to the two phase boundary composition on the following basis. From our two studies of titanium pressure over an (α Ti) - (δ TiN) mixture, we have derived values as summarized in Table V for $\bar{H}_{Ti}$ at the two phase boundary. These values differ widely and cannot fix $\bar{H}_{Ti}$ very accurately at the two phase boundary. However, as the nitrogen content decreases we can expect that $\bar{H}_{Ti}$ will approach very close to the known value of -108 kcal for the heat of sublimation of β-titanium. Allowing for the differences in structure between β-titanium and δ-TiN, we would expect the limiting value to be about -109.5 kcal per gram atom which value falls within the two experimental points. We will assume that this value is essentially attained at the low nitrogen boundary of the δ-TiN phase and extrapolate the $\bar{H}_{Ti}$ curve accordingly.

Using $\bar{H}_{Ti}$ values from this extrapolated curve, nitrogen enthalpy values were calculated and the $\bar{H}_N$ curve was extended to the two phase boundry. It is evident from considering the available data points and the relationships which must be obeyed within the solution phase that the $\bar{H}_{Ti}$ and $\bar{H}_N$ curves are severely restricted in behavior. The smooth curve for the nitrogen enthalpy data in the range $Ti_{.5}N_{.5}$ to $Ti_{.54}N_{.46}$ was "fitted" so as to allow for the necessary smooth transition in titanium enthalpy from stoichiometric TiN to the two phase boundary. It would appear that the $\bar{H}_N$ slopes obtained on the two low nitrogen content samples must be too high. If they are not taken to be in error, the behavior of the $\bar{H}_N$ and $\bar{H}_{Ti}$ curves will not vary smoothly and unidirectionally across the δ-TiN phase as we would expect in such compounds. This behavior may be due to errors caused by adsorption on the sample chamber walls at very low pressures. The $\bar{H}_{Ti}$ and $\bar{H}_N$ curves of Figure 11 permit the calculation of the integral heat for the formation of Ti_xN_{1-x} from the gaseous elements. The behavior of the curves of Figure 11 are consistent with what we now know about Ti_xN_{1-x} and the values of $\bar{H}_{Ti}$ and $\bar{H}_N$ given in Figure 11 can be used together with the data of Figure 9 or 10 and the relationships given previously to calculate P_{Ti} or P_N data for the δ-TiN phase at temperatures other than 1930°K.

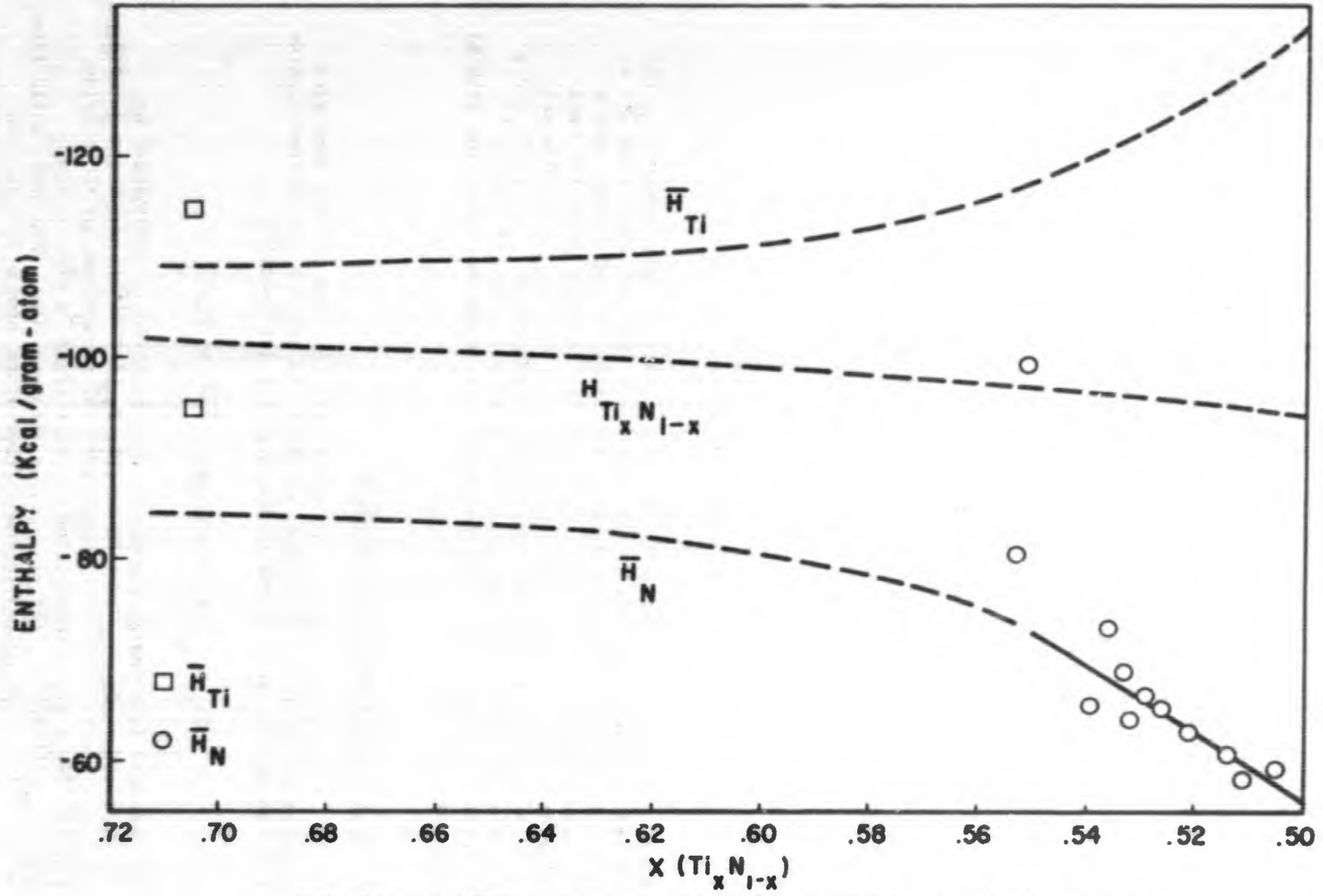

FIGURE II. PARTIAL AND INTEGRAL ENTHALPIES vs. COMPOSITION

Figure 12 shows the partial and integral free energy values for titanium, nitrogen, and titanium nitride. The partial and integral free energies in this Figure were calculated for the reaction

$$x\ Ti(s) + \frac{1 - x}{2}\ N_2(g) = Ti_x\ N_{1-x}\ (s)$$

using the relationships

$$\mu_N^s = 1/2\ R\ T\ \ln P_{N_2}$$

$$\mu_{Ti}^s = R\ T\ \ln \frac{P_{Ti}}{P_{Ti}^o}$$

and

$$\Delta G_{Ti_x\ N_{1-x}} = x\ \mu_{Ti}^s + (1-x)\ \mu_N^s$$

where μ is the partial free energy, G the integral free energy, P_{N_2} the nitrogen pressure, P_{Ti} the titanium pressure, P_{Ti}^o the vapor pressure of pure titanium, R the gas constant, T the absolute temperature, and x the mole fraction of titanium. Nitrogen and titanium pressures were taken from the smoothed curves of Figure 9. The $\Delta G_{Ti_x\ N_{1-x}}$ obtained (at x = .5) is the integral free energy of formation of $Ti_{.5}\ N_{.5}$ from the standard reference states of solid titanium and gaseous nitrogen. The minimum in the free energy of formation curve (for 1930°K) comes at about $Ti_{.52}\ N_{.48}$ ($TiN_{.92}$).

C. RELATED WORK ON TITANIUM NITRIDE

Since the experimental quantities obtained in this work were titanium and nitrogen pressures, we choose to compare the related studies on titanium nitride in terms of the vaporization reaction

$$Ti_x\ N_{1-x}\ (s) = x\ Ti\ (g) + \frac{1-x}{2}\ N_2\ (g)$$

The standard free energy change for this reaction is represented by the expression $\Delta G^o_{Ti_x\ N_{1-x}} = -RT\ \ln (P_{Ti}^x\ P_{N_2}^{(1-x)/2})$ in which the quantity $\Delta G^o_{Ti_x\ N_{1-x}}$ will change with the composition of the nitride. However, for a given composition of the nitride, a plot of log $(P_{Ti}^x \cdot P_{N_2}^{(1-x)/2})$ vs 1/T will give a straight line. The upper solid line on Figure 13 (Curve A) represents such a plot for the vaporization reaction derived from data in the JANAF Thermochemical Data Tabulations for stoichiometric titanium nitride ($Ti_{.5}\ N_{.5}$).

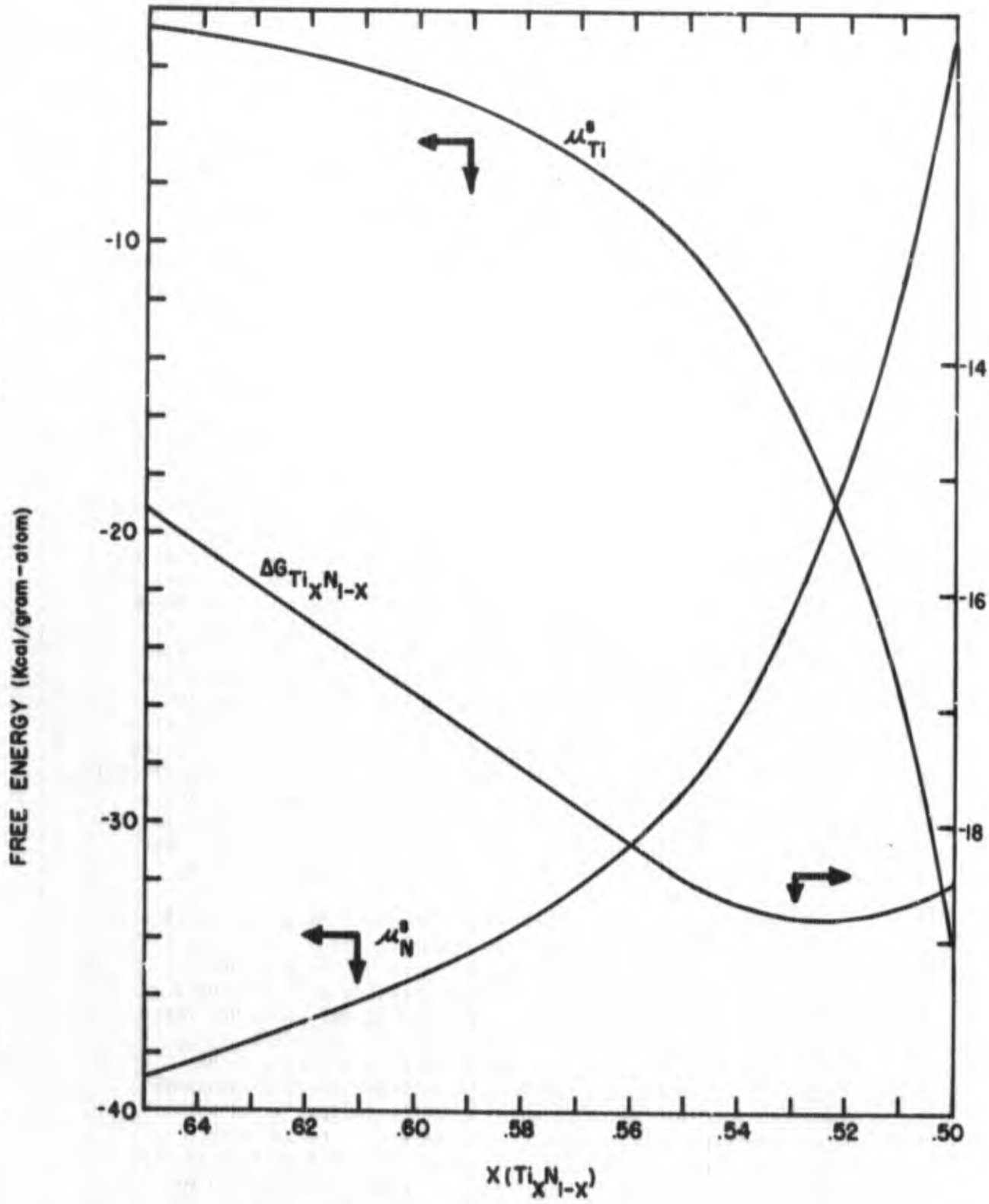

FIGURE 12. PARTIAL AND INTEGRAL FREE ENERIES vs COMPOSITION (1930°K)

Very recently Linevsky[15] has studied essentially stoichiometric titanium by an atomic resonance line absorption technique at 2120°K. Basically this study measured the equilibrium titanium activity while the nitrogen pressure was maintained constant. The results are represented as a single point on Figure 13. This technique depends on use of the JANAF data for the process Ti(s) = Ti(g) to calibrate the apparatus. Thus the agreement with curve A tends to confirm the JANAF data for the standard free energy of formation of TiN at 2120°K rather than for the vaporization process to gaseous elements as we have written it.

Hoch, Dingledy, and Johnston[16] studied the vaporization of a nitride sample using a Knudsen technique. Our work indicates that they were studying a sample approximately equivalent to $TiN_{.8}$. Their original sample was reportedly $TiN_{.79}$. Their weight loss data as recalculated by us for the process of congruent vaporization of $TiN_{.8}$ are presented in Figure 13. These data indicate a slope of -113 kcal which is significantly greater than that indicated by the JANAF data for TiN and appears unreasonably high based on our Figure 11. Our own Knudsen cell studies are at somewhat lower temperatures than the study of Hoch et al. and fall above the line (Curve B) representing an extrapolation of their work although they do not differ greatly in stoichiometry from that assigned to the Hoch et al. material. On further examination of the Hoch et al. data, one finds that the lower temperature set of points was obtained with a much larger orifice to area ratio than the higher temperature set and thus would be more subject to error due to a low evaporation coefficient for nitrogen. Note that in our studies the nitrogen pressure was fixed and thus the results would not be affected by a low evaporation coefficient. We conclude therefore that the correct Knudsen equilibrium curve for a stoichiometry near $TiN_{.8}$ is more likely to be very nearly parallel to the JANAF curve and somewhat lower passing through the average of the high temperature Hoch et al. data and our low temperature data (Curve C).

Margrave and Dreger[17] studied the Langmuir vaporization of a nitride sample. We plot their data taken from the Ph.D. Thesis of Dreger. These data were calculated on the basis of the process $Ti_{.5}N_{.5}$ (s) = .5 Ti(g) + .25 N_2(g). Their pressure data are quite low compared to ours. We conclude on the basis of our work that their sample probably had a composition corresponding to about $TiN_{.85-.90}$. We reach this conclusion in the following manner. Except for the initial runs, their data do not show any consistent shift in pressure up or down with continued heating which would be indicative of a continuously changing sample composition. Thus we conclude they effectively had congruent vaporization during the major portion of their study. By a congruent vaporization process, we mean that the vapor composition leaving the system has the same composition as the solid sample; thus it is evident that an effective $P_{Ti} : P_{N_2}$ ratio of vapor loss equal to or greater than two is required over any composition of the TiN phase. For a closed system (or one nearly closed such as a Knudsen cell) in which equilibrium pressures are obtained, our P_{N_2} and

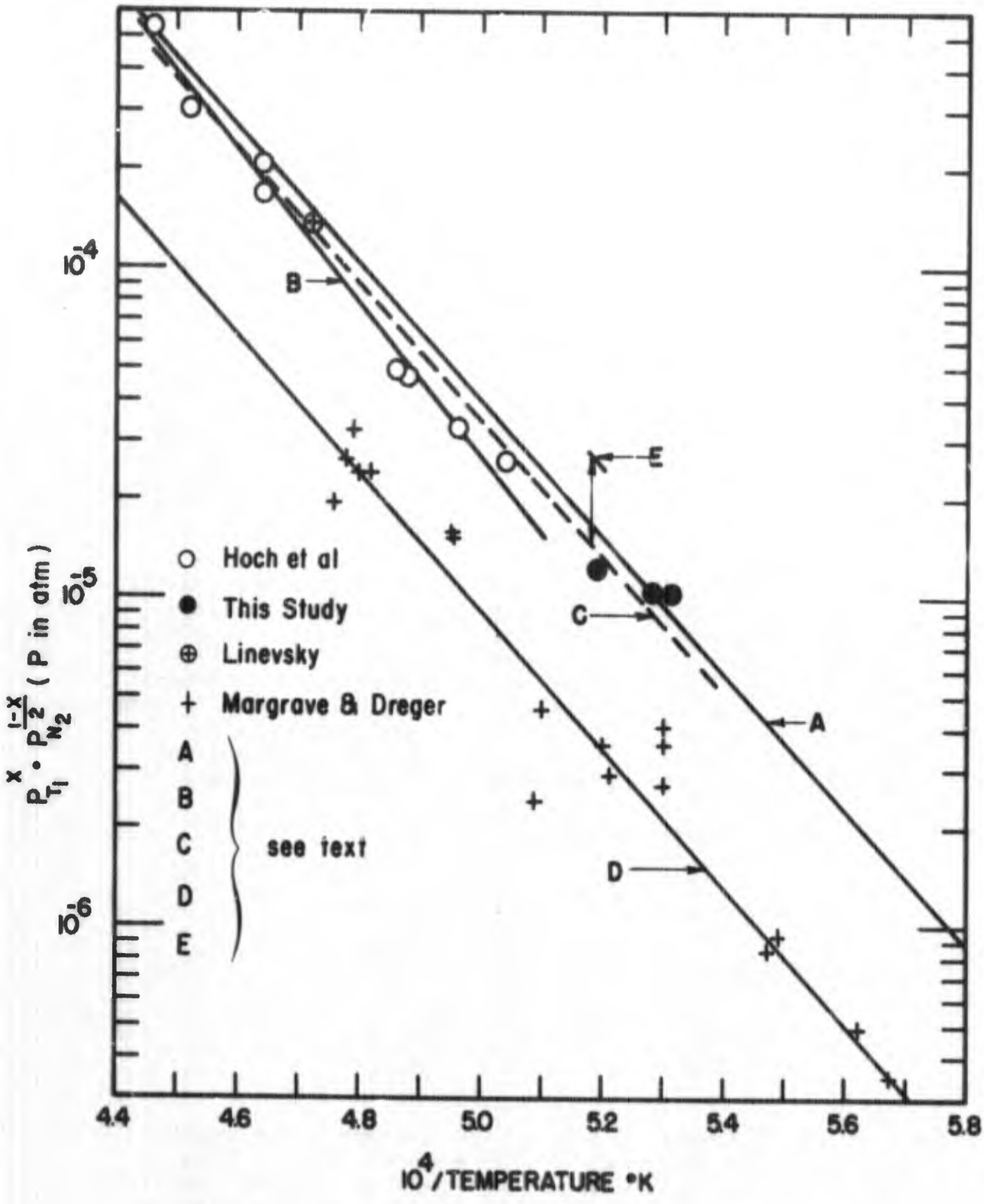

FIGURE 13. PRESSURE PRODUCT vs TEMPERATURE

P_{Ti} curves in Figures 9 and 10 indicate that congruent vaporization occurs at a composition of about $Ti_{.555}N_{.445}$. For this composition at T = 1930°K, our data predict an equilibrium pressure of about 10^{-6} atm. But Margrave and Dreger in their Langmuir study calculated a pressure of about 10^{-7} atm. This lower pressure obtained from their Langmuir experiments is attributed to a low evaporation coefficient; the data of Margrave and Dreger when considered in relation to our equilibrium pressure data provide the opportunity for some estimates of evaporation coefficients. It seems most reasonable at this stage of our knowledge to expect that the evaporation coefficient (α) for nitrogen will be very small compared to that for titanium, and we will assume that α for titanium is one. With this assumption, it is apparent from an examination of Figure 9 that if the total pressure calculated from the Langmuir experiment is on the order of 10^{-7} atm then the composition for a congruent vaporization process in this study must be near $Ti_{.53}N_{.47}$ ($TiN_{.89}$) and that for this composition (if α for titanium is one) α for nitrogen must be in the range of 0.01 to 0.001.

The indication of such a low evaporation coefficient tends to support our contention made earlier that Curve C in Figure 13 is the most likely representation of the pressure product vs 1/T for a sample composition of about $TiN_{.8}$. Thus we conclude that our points are in agreement with the high temperature data of Hoch et al. It is possible from our experimental partial pressure vs composition data such as given in Figure 9 to calculate how far apart on Figure 13 the curves for $TiN_{.8}$ and TiN should fall and thus to determine whether the relative positions of curves A and C are compatible with our measurements.

Recall that for the reaction

$$Ti_x N_{1-x}\,(s) = x\,Ti\,(g) + \frac{1-x}{2}\,N_2\,(g)$$

we can write $\Delta G^{o}_{Ti_x N_{1-x}} = -RT \ln \left(P^{x}_{Ti} \cdot P_{N_2}^{\frac{1-x}{2}}\right)$

or $$\log \left(P^{x}_{Ti} \cdot P_{N_2}^{\frac{1-x}{2}}\right) = -\frac{\Delta G^{o}_{Ti_x N_{1-x}}}{2.3\,RT}$$

Now, at constant temperature $\Delta G^{o}_{Ti_x N_{1-x}}$ for the vaporization reaction varies with composition and an expression for this change related to the experimental equilibrium titanium and nitrogen pressures and nitrogen pressures can be obtained as follows. On differentiation

and recombining of terms, we have

$$\frac{d\left(-\frac{\Delta G_{Ti_x N_{1-x}}}{2.3\ RT}\right)}{dx} = \left(\log P_{Ti} - \frac{1}{2}\log P_{N_2}\right) + \left(x\ \frac{d \log P_{Ti}}{dx} + \frac{1-x}{2}\ \frac{d \log P_{N_2}}{dx}\right)$$

According to the Gibbs-Duhem equation (as shown in Appendix III), the last term in brackets is equal to zero. Thus, we can write

$$\frac{-\Delta G^{o}_{Ti_{.5} N_{.5}}}{2.3\ RT} - \frac{-\Delta G^{o}_{Ti_x N_{1-x}}}{2.3\ RT} = \int_x^{.5} \log \frac{P_{Ti}}{P_{N_2}^{1/2}}\ dx$$

or $$\log (P_{Ti}^{.5}\ P_{N_2}^{.25}) - \log (P_{Ti}^{x}\ P_{N_2}^{\frac{1-x}{2}}) = \int_x^{.5} \log \frac{P_{Ti}}{P_{N_2}^{1/2}}\ dx$$

This can be integrated graphically if we plot $\log (P_{Ti} / P_{N_2}^{1/2})$ vs x from our experimental data. This curve is plotted in Figure 9, and it is evident upon examination that it will be little affected by the possible experimental errors in P_{Ti} and P_{N_2}. Thus the integration based on the experimental data will give a reliable measure of the changes in $\log (P_{Ti}^{x}\ P_{N_2}^{(1-x)/2})$ with stoichiometry. When carried out, the integration indicates a decrease in $\log (P_{Ti}^{x}\ P_{N_2}^{(1-x)/2})$ of .27 units in going from a stoichiometry of $TiN_{.8}$ to TiN. This distance from curve C is indicated by the point E on Figure 13, which is considerably above the JANAF data for stoichiometric nitride represented by curve A. The same result could have been calculated directly from the partial pressure data for the two stoichiometries taken from Figure 9, but we believe the approach adopted here emphasizes that the change with composition for this pressure product is known quite accurately even though some uncertainty may exist as to the absolute value for a given stoichiometry.

In the previous paragraph, we have shown that curves A and C are not as far apart as our experimental pressure data indicates should be the case. Thus either the JANAF tabulations represented by curve A or our experimental points and the high temperature data of Hoch et al. represented by curve C must be in error. An error in the JANAF tabulation is consistent with our measurements on pure titanium. The vapor pressures over pure titanium measured in this study using a Knudsen technique are higher by a factor slightly less than two then those determined

previously[18] by Langmuir studies. The Langmuir data were used in developing the JANAF tables and could be low if the evaporation coefficient for titanium is not one. Allowance for a factor of two increase in the vapor pressure data used in the JANAF tables would raise curve A on Figure 13 by about .15 units in log K_p improving the overall consistency of the several studies. It should be noted that any change made in the vapor pressure data used in developing the JANAF tabulations would produce a corresponding change in the point determined by Lanevsky.

We conclude that a reasonably consistent picture for the several studies can be developed. It does indicate that the vapor pressure data for pure titanium determined by the Langmuir technique may be low by a factor approaching two. It would be of great interest to carry out a measurement of the evaporation coefficient for pure titanium to check this point.

IV. CONCLUSION

The apparatus designed and assembled specifically for studies of the refractory nitrides has proven very satisfactory in the study of the titanium-nitrogen system. It was utilized in four different ways in this study.

1. Samples of titanium nitride of desired composition were prepared by direct combination of nitrogen and titanium metal within the sample chamber.

2. For nitride compositions with equilibrium nitrogen pressure in the 10^{-1} - 5×10^{-6} torr range, equilibrium nitrogen pressure vs temperature was determined for a given nitride composition. In this pressure range the most sensitive measure of change in the closed system is the pressure, thus direct measurement is possible.

3. For nitride compositions with equilibrium nitrogen pressure in the 1 to 700 torr range, the most sensitive measure of change in the system is the weight of the system. Thus equilibrium nitrogen pressure vs composition data were determined by observing weight changes as a function of time at constant nitrogen pressure and temperature.

4. Titanium pressure measurements were carried out in the apparatus using the Knudsen technique. When nitrogen pressures were comparable to the titanium pressures being measured, the nitrogen pressure was held constant during the period of the experiment.

The apparatus is capable of reaching much higher temperatures than those required in the study of titanium nitride. We believe that temperatures of 2500°C can be readily achieved with existing apparatus. We believe that the lower pressure limit for reliable measurements is about 5×10^{-6} torr. We frequently achieve gauge pressures as low as 1×10^{-8} torr but now believe that at pressures below 5×10^{-6} torr the sample is no longer the major factor controlling the pressure of the system. It is now believed that in the very low pressure region adsorption changes due to varying temperature of the sample chamber walls produces changes in the gauge pressure.

Equilibrium nitrogen pressures have been determined for nitride compositions ranging from about $Ti_{.54}N_{.46}$ to $Ti_{.5}N_{.5}$ by a static technique. Equilibrium titanium pressures over pure titanium, the $\alpha + \delta/\delta$ two phase mixture, and a nitride composition of about $Ti_{.55}N_{.45}$ were determined by a Knudsen technique. These pressure data are related and extended across the δ-TiN phase region utilizing thermodynamic theory.

Other studies on titanium nitride are reviewed and a consistent account of all the available data is developed. This account indicates

that pure titanium may have an evaporation coefficient less than one so that Langmuir data should not be used directly in developing tables of thermodynamic functions.

We recommend that this program be continued with primary emphasis during the next year on the zirconium-nitrogen and niobium-nitrogen systems. An experimental effort on these systems such as described in this report can check existing data and provide additional information as required to extend our knowledge of phase relationships and vaporization behavior and to further define the thermodynamics of these systems.

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APPENDIX I.

NITROGEN PRESSURE DATA TABULATIONS

SAMPLE No. 2-22-B-2

COMPOSITION: $Ti_{.533}N_{.467}$

T (°C)	T (°K)	$10^4/T$ ($°K^{-1}$)	P (ion gauge) (torr)
1453	1726	5.80	1.7×10^{-3}
1382	1655	6.05	1.8×10^{-4}
1330	1603	6.24	4.6×10^{-5}
1259	1532	6.53	1.4×10^{-5}
1346	1619	6.18	5.8×10^{-5}
1397	1670	5.99	2.4×10^{-4}
1453	1726	5.80	1.1×10^{-3}
1390	1663	6.01	1.3×10^{-4}
1298	1571	6.36	1.8×10^{-5}
1397	1670	5.99	2.6×10^{-4}
1292	1565	6.39	1.6×10^{-5}
1300	1573	6.36	2.0×10^{-5}
1301	1574	6.35	2.0×10^{-5}
1295	1568	6.39	1.8×10^{-5}
1365	1638	6.11	1.1×10^{-4}
1459	1732	5.77	1.2×10^{-3}
1276	1549	6.46	6.5×10^{-6}

SAMPLE NO. 895a-2

COMPOSITION: $Ti_{.514}N_{.486}$

T (°C)	T (°K)	$10^4/T$ ($°K^{-1}$)	P (ion gauge) (torr)	P (McLeod) (torr)	P (manometer) (torr)
1244	1517	6.60	7.7×10^{-5}		
1185	1459	6.86	2.9×10^{-5}		
1222	1495	6.69	4.8×10^{-5}		
1295	1568	6.38	5.0×10^{-4}		
1314	1587	6.31	8.7×10^{-4}		
1353	1626	6.16	2.4×10^{-3}		
1315	1588	6.30	9.4×10^{-4}		
1293	1566	6.39	4.6×10^{-4}		
1284	1557	6.43	3.1×10^{-4}		
1342	1615	6.20	1.7×10^{-3}		
1348	1621	6.17	2.4×10^{-3}		
1589	1862	5.37			2.31×10^{-1}
1673	1946	5.14			7.70×10^{-1} (a)
1652	1925	5.20			4.62×10^{-1} (a)
1583	1856	5.40			2.70×10^{-1}
1525	1798	5.56			7×10^{-2}
1428	1701	5.88			1.4×10^{-2}
1499	1772	5.65			5.39×10^{-2}
1595	1868	5.36			2.31×10^{-1}
1646	1919	5.21			5.15×10^{-1} (a)
1581	1854	5.40			1.62×10^{-1}
1543	1816	5.51			6.93×10^{-2}
1494	1767	5.66		1.6×10^{-2}	
1419	1692	5.91		$\delta \times 10^{-3}$	

(a) Omitted in least squares analysis; high pressures resulted in change of stoichiometry.

SAMPLE NO. 895a-2

COMPOSITION: $Ti_{.505}N_{.495}$

T (°C)	T (°K)	$10^4/T$ ($°K^{-1}$)	P (McLeod) (torr)	P (manometer) (torr)
1416	1689	5.93		6.93×10^{-2}
1479	1752	5.71		2.54×10^{-1}
1546	1819	5.50		6.00×10^{-1} (a)
1400	1673	5.98		8.47×10^{-2}
1485	1758	5.69		2.62×10^{-1}
1542	1815	5.51		5.77×10^{-1} (a)
1582	1855	5.39		7.46×10^{-1} (a)
1513	1786	5.61		3.46×10^{-1}
1443	1716	5.83		8.47×10^{-2}
1361	1634	6.12		1.4×10^{-2}
1244	1517	6.60	1.1×10^{-3}	
1321	1594	6.28	7×10^{-3}	
1410	1683	5.94	4.9×10^{-2}	
1561	1834	5.45		5.77×10^{-1} (a)
1437	1710	5.85		9.24×10^{-2}
1453	1726	5.80		1.15×10^{-1}

(a) Omitted in least squares analysis; high pressures resulted in change of stoichiometry.

SAMPLE # 2-22-B-3

COMPOSITION: $Ti_{.539}N_{.461}$

T (°C)	T (°K)	$10^4/T$ ($°K^{-1}$)	P(ion gauge) (torr)	P (McLeod) (torr)
1466	1739	5.75	1.4×10^{-4}	1.4×10^{-4}
1387	1660	6.03	2.6×10^{-5}	3×10^{-5}
1378	1651	.06	2.4×10^{-5}	1.5×10^{-5}
1414	1687	5.93	4.8×10^{-5}	7×10^{-5}
1480	1753	5.71	2.3×10^{-4}	2.5×10^{-4}
1524	1797	5.57	6.0×10^{-4}	6×10^{-4}
1526	1799	5.56	5.5×10^{-4}	6×10^{-4}
1417	1690	5.92	4.8×10^{-5}	8×10^{-5}
1467	1740	5.75	1.8×10^{-4}	
1390	1663	6.01	3.3×10^{-5}	
1426	1699	5.89	5.7×10^{-5}	
1525	1798	5.56	5.5×10^{-4}	6×10^{-4}

SAMPLE #2-22-B-3

COMPOSITION: $Ti_{.521}N_{.479}$

T (°C)	T (°K)	$10^4/T$ (°K^{-1})	P(ion gauge) (torr)	P(McLeod) (torr)
1476	1749	5.72		3.1×10^{-3}
1404	1677	5.97	7.8×10^{-4}	8×10^{-4}
1371	1644	6.09	2.9×10^{-4}	2.5×10^{-4}
1290	1563	6.40	5.4×10^{-5}	
1342	1615	6.20	1.5×10^{-4}	1.3×10^{-4}
1390	1663	6.01	5.4×10^{-4}	5×10^{-4}
1435	1708	5.86		1.2×10^{-3}
1466	1739	5.76		2.9×10^{-3}
1482	1755	5.70		2.9×10^{-3}
1421	1694	5.91	8.0×10^{-4}	9×10^{-4}
1380	1653	6.05	3.3×10^{-4}	3.5×10^{-4}
1309	1582	6.32	5.7×10^{-5}	
1310	1583	6.32	6.0×10^{-5}	
1392	1665	6.01	5.3×10^{-4}	
1396	1669	6.00	5.2×10^{-4}	5×10^{-4}
1447	1720	5.82		1.8×10^{-3}
1356	1629	6.14	2.2×10^{-4}	2.4×10^{-4}

SAMPLE #2-22-B-3

COMPOSITION: $Ti_{.511}N_{.489}$

T (°C)	T (°K)	$10^4/T$ (°K^{-1})	P (ion gauge) (torr)	P (McLeod) (torr)
1353	1626	6.15		4.0×10^{-3}
1400	1673	5.98		1.1×10^{-2}
1454	1727	5.80		2.4×10^{-2}
1422	1695	5.90		1.3×10^{-2}
1363	1636	6.11		3.7×10^{-3}
1451	1724	5.80		1.7×10^{-2}
1365	1638	6.11		3.7×10^{-3}
1332	1605	6.23		1.6×10^{-3}
1462	1735	5.77		2.6×10^{-2}
1412	1685	5.94		1.1×10^{-2}
1351	1624	6.16		2.6×10^{-3}
1284	1557	6.43	5.8×10^{-4}	5.5×10^{-4}

SAMPLE #2-22-B-4

COMPOSITION: $Ti_{.553}N_{.447}$

T (°C)	T (°K)	$10^4/T$ (°K^{-1})	P (ion gauge) (torr)
1435	1708	5.86	1.3×10^{-6}
1492	1765	5.67	6.1×10^{-6}
1550	1823	5.49	2.7×10^{-5}
1513	1786	5.61	9.5×10^{-6}
1446	1719	5.82	1.9×10^{-6}
1534	1807	5.54	2.0×10^{-5}
1530	1803	5.55	1.7×10^{-5}
1566	1839	5.44	4.8×10^{-5}
1550	1823	5.49	2.4×10^{-5}
1476	1749	5.72	4.7×10^{-6}
1414	1687	5.93	8.0×10^{-7}

SAMPLE #2-22-B-4

COMPOSITION: $Ti_{.529}N_{.471}$

T (°C)	T (°K)	$10^4/T$ (°K^{-1})	P (ion gauge) (torr)
1472	1745	5.75	6.3×10^{-4}
1455	1726	5.80	3.6×10^{-4}
1394	1667	6.00	7.2×10^{-5}
1400	1673	5.98	8.3×10^{-5}
1473	1746	5.73	4.8×10^{-4}
1356	1629	6.14	4.0×10^{-5}
1400	1673	5.98	8.6×10^{-5}
1460	1733	5.77	4.0×10^{-4}
1431	1704	5.87	1.9×10^{-4}
1397	1670	5.99	7.6×10^{-5}
1366	1639	6.11	3.6×10^{-5}
1335	1608	6.22	2.0×10^{-5}
1387	1660	6.03	6.1×10^{-5}
1454	1727	5.80	3.5×10^{-4}
1412	1685	5.94	1.3×10^{-4}
1374	1647	6.07	4.5×10^{-5}
1310	1583	6.31	1.2×10^{-5}

SAMPLE #2-22-B-5

COMPOSITION: $Ti_{.536}N_{.464}$

T (^{o}C)	T (^{o}K)	$10^4/T$ ($^{o}K^{-1}$)	P (ion gauge) (torr)
1611	1884	5.31	2.5×10^{-4}
1432	1705	5.87	4.0×10^{-6}
1487	1760	5.69	1.5×10^{-5}
1461	1734	5.77	8.3×10^{-6}
1402	1675	5.97	1.9×10^{-6}

SAMPLE #2-22-B-6

COMPOSITION: $Ti_{.526}N_{.474}$

T (°C)	T (°K)	$10^4/T$ ($°K^{-1}$)	P (ion gauge) (torr)
1382	1655	6.05	3.0×10^{-5}
1314	1587	6.31	6.2×10^{-6}
1342	1615	6.20	1.1×10^{-5}
1332	1605	6.24	8.7×10^{-6}
1375	1648	6.07	2.2×10^{-5}
1404	1677	5.97	4.6×10^{-5}
1439	1712	5.84	8.7×10^{-5}
1478	1751	5.71	2.8×10^{-4}
1453	1726	5.80	1.6×10^{-4}
1424	1697	5.90	6.5×10^{-5}
1387	1660	6.03	2.9×10^{-5}
1353	1626	6.16	1.2×10^{-5}
1330	1603	6.24	6.2×10^{-6}
1446	1719	5.82	1.3×10^{-4}
1431	1704	5.87	6.8×10^{-5}
1431	1704	5.87	9.5×10^{-5}

SAMPLE #2-22-B-8

COMPOSITION: $Ti_{.551}N_{.449}$

T (°C)	T (°K)	$10^4/T$ ($°K^{-1}$)	P (ion gauge) (torr)
1580	1853	5.40	4.6×10^{-5}
1625	1898	5.27	1.7×10^{-4}
1567	1840	5.44	3.2×10^{-5}
1466	1739	5.76	1.6×10^{-6}
1511	1784	5.61	5.8×10^{-6}
1558	1831	5.46	2.4×10^{-5}
1584	1857	5.39	4.5×10^{-5}
1535	1808	5.54	1.1×10^{-5}
1482	1755	5.70	2.1×10^{-6}
1502	1775	5.64	4.3×10^{-6}
1554	1827	5.48	2.0×10^{-5}
1581	1854	5.40	4.1×10^{-5}
1607	1880	5.32	8.3×10^{-5}
1524	1797	5.57	8.3×10^{-6}
1496	1769	5.66	3.9×10^{-6}
1475	1748	5.72	2.0×10^{-6}
1429	1702	5.88	2.8×10^{-7}
1485	1758	5.69	2.1×10^{-6}
1650	1923	5.20	5.5×10^{-5} (a)
1498	1771	5.65	9.3×10^{-8} (a)

(a) Omitted in least squares analysis.

SAMPLE #2-22-B-9

COMPOSITION: $Ti_{.532}N_{.468}$

T (°C)	T (°K)	$10^4/T$ (°K^{-1})	P (ion gauge) (torr)
1615	1888	5.30	6.9×10^{-4}
1613	1886	5.31	9.7×10^{-4}
1459	1732	5.78	3.4×10^{-5}
1386	1659	6.04	6.9×10^{-6}
1394	1667	6.00	8.7×10^{-6}
1468	1741	5.75	4.4×10^{-5}
1515	1788	5.60	1.04×10^{-4}
1422	1695	5.90	1.9×10^{-5}
1484	1757	5.70	6.1×10^{-5}
1552	1825	5.48	2.5×10^{-4}
1527	1300	5.56	1.7×10^{-4}
1466	1739	5.76	4.4×10^{-5}
1396	1669	6.00	1.07×10^{-5}
1317	1590	6.29	1.4×10^{-6}
1597	1870	5.35	6.5×10^{-4}
1349	1622	6.17	7.8×10^{-6}

APPENDIX II.

TITANIUM PRESSURE DATA TABULATION

Sample No.	Composition	Temperature (°K)	Time (min.)	Weight Loss (mg.)	Orifice Area (cm^2)	P_{Ti} (torr)	
2-22-B-5	$Ti_{.536}N_{.464}$	1885	385	1.045	.024	1.66×10^{-4}	
		1896	420	1.075		1.57×10^{-4}	
2-22-B-8	$Ti_{.551}N_{.449}$	1930	431	3.10	.024	4.27×10^{-4}	
2-22-B-11	"Two phase"	1929	460	0.901	.00176	2.05×10^{-3}	
		1926	420	0.826		2.06×10^{-3}	
		1979	240	0.850		3.76×10^{-3}	
		2028	150	0.747		5.36×10^{-3}	(a)
		1910	460	0.603		1.36×10^{-3}	
		1847	1677	0.798		4.89×10^{-4}	
2-22-B-15	"Two phase"	1925	60	1.70	.024	2.14×10^{-3}	
		1891	60	1.08		1.34×10^{-3}	
		1840	180	1.54		6.29×10^{-4}	
		1881	60	0.988		1.22×10^{-3}	
		1932	40	1.11		2.10×10^{-3}	
2-22-B-16	Titanium	1795	60	0.545	0245	6.50×10^{-4}	
2-22-B-17	Titanium	1839	60	1.20	.024	1.48×10^{-3}	
2-22-B-18	Titanium	1847	120	4.05	.034	1.84×10^{-3}	
		1851	60	1.64		1.49×10^{-3}	

(a) Omitted in least squares analysis.

APPENDIX III.

THERMODYNAMIC RELATIONSHIPS FOR THE TITANIUM NITRIDE SOLUTION PHASE

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THERMODYNAMIC RELATIONSHIPS FOR THE TITANIUM NITRIDE SOLUTION PHASE

Recall the following relationships. By definition in a gas phase

$$\mu_i^g = \mu_i^{og} + R\,T\,\ln P_i$$

and in a solution phase

$$\mu_i^s = \mu_i^{os} + R\,T\,\ln a_i .$$

Also in a solution phase the integral free energy and enthalpy quantities are related to the partial molal quantities by the relationships

$$G = \sum n_i\,\mu_i$$

$$H = \sum n_i\,\bar{H}_i .$$

The condition for equilibrium within a homogeneous phase may be written

$$\sum \mu_i\,dn_i = 0$$

and in a multi-phase system equilibrium is represented by the relationship

$$\mu_i^{\alpha} = \mu_i^{\beta} .$$

Now consider the reaction

$$x\,Ti(g) + \frac{1-x}{2}\,N_2(g) = Ti_x N_{1-x}\,(s) \qquad (1)$$

representing the formation from the gaseous elements of one gram-atom of titanium nitride solution phase with x atom fraction of Ti and (1-x) atom fraction of N. In the gas phase the components are Ti atoms and N_2 molecules and in the solution phase the components are Ti and N atoms.

Relate the μ_i^s to the p_i. In the gas phase

$$\mu_{Ti}^g = \mu_{Ti}^o + RT \ln p_{Ti}$$

and

$$\mu_{N_2}^g = \mu_{N_2}^o + RT \ln p_{N_2} .$$

We arbitrarily choose the reference state for μ_{Ti}^g and $\mu_{N_2}^g$ as one atmosphere at all temperatures and set

$$\mu_{Ti}^o = \mu_{N_2}^o = 0.$$

Thus

$$\mu_{Ti}^g = RT \ln p_{Ti}$$

$$\mu_{N_2}^g = RT \ln p_{N_2} .$$

This reference state for titanium rather than the element in its stable state at temperature T permits us to work with our data without introducing at this point experimental vapor pressure data for pure titanium.

In the solution phase we recognize the dissociation of nitrogen

$$N_2 = 2N$$

thus

$$\mu_{N_2}^s = 2\mu_N^s$$

or

$$\mu_N^s = \frac{\mu_{N_2}^s}{2}$$

Since at equilibrium $\mu_i^s = \mu_i^g$ we can now write

$$\mu_{Ti}^s = \mu_{Ti}^g$$

and

$$\mu_N^s = \frac{\mu_{N_2}^s}{2} = \frac{\mu_{N_2}^g}{2}$$

Therefore

$$\mu_{Ti}^{s} = RT \ln p_{Ti}$$

$$\mu_{N}^{s} = RT \ln p_{N_2}^{1/2}$$

Experimentally we have measured p_{N_2} as a function of temperature and composition of $Ti_x N_{1-x}$. Thus μ_N^s as a function of temperature and composition can be plotted. Now within the solution phase a relationship does exist between $d\mu_N^s$ and $d\mu_{Ti}^s$.

Relate $d \ln p_{Ti}$ to $d \ln p_{N_2}$ over $Ti_x N_{1-x}$. The Gibbs-Duhem equation as applied to such a solution phase at constant temperature simplifies with neglible error to

$$\sum n_i \, d\mu_i = 0.$$

In terms of the atom fractions in $Ti_x N_{1-x}$ this can be written $X \, d\mu_{Ti}^s + (1-x) d\mu_N^s = 0$. In terms of the relationships between μ_i^s and p_i derived above, this expression at constant temperature can be written as

$$x \, d \ln p_{Ti} + (1-x) \, d \ln p_{N_2}^{1/2} = 0$$

or

$$\ln p_{Ti}^{B} - \ln p_{Ti}^{A} = - \frac{1-x}{2x} \int_{A}^{B} d \ln p_{N_2} .$$

This indicates that if p_{N_2} as a function of composition is known as well as one value for p_{Ti} within this range of composition then p_{Ti} as a function of composition can be derived.

In our work we have obtained a value for p_{Ti} in two ways. One method is by direct measurement over a low nitrogen content sample for which p_{Ti} becomes significant compared to p_{N_2}. The second method is to derive the value from our knowledge of the integral free energy of formation of stoichiometric titanium nitride as derived from calorimetric studies combined with a measured value of p_{N_2} over stoichiometric titanium nitride. That is to say, for the formation of one gram atom $Ti_{.5} N_{.5}$ from the gaseous elements according to equation (1) we can write

$$\Delta G^{o} = - RT \ln p_{Ti}^{.5} \, p_{N_2}^{.25}$$

Now ΔG^o per gram-atom can be calculated from existing data tabulations. The p_{N_2} over stoichiometric nitride has been determined experimentally and thus p_{Ti} can be calculated for this nitride composition. The use of both methods in our work provides a basis for relating our measurements to those of other workers on titanium nitride samples since the derived curve of ln p_{Ti} vs composition should satisfy the experimental results obtained at different compositions.

It is evident from the above discussion that we now know μ_N^s and μ_{Ti}^s as a function of composition. Thus we can also plot the integral free energy for the formation of $Ti_x N_{1-x}$ since

$$G = \sum n_i \mu_i$$

$$G_{Ti_x N_{1-x}} = x \mu_{Ti}^s + (1-x) \mu_N^s$$

Consider variation of μ_i with T. The next question is the relationship of μ_i^s (or p_i over $Ti_x N_{1-x}$) to a temperature variation. In a solution phase the partial molal free energy and enthalpy quantities are related by

$$\frac{\partial \frac{\mu_i^s}{T}}{\partial \frac{1}{T}} = \bar{H}_i^s$$

thus at constant composition

$$\frac{d(\frac{\mu_{Ti}^s}{T})}{d(\frac{1}{T})} = \frac{R d(\ln p_{Ti})}{d(\frac{1}{T})} = \bar{H}_{Ti}$$

and

$$\frac{d(\frac{\mu_N^s}{T})}{d(\frac{1}{T})} = \frac{R d(\ln p_{N_2}^{1/2})}{d(\frac{1}{T})} = \bar{H}_N$$

where $\bar{H}_{Ti}$ may be thought of as the enthalpy change for the reaction

$$Ti(g) + y\ Ti_x N_{1-x}\ (s) = y\ Ti_{x + 1/y}\ N_{1-x}\ (s)$$

where $y \gg 1$

similarly for $\bar{H}_N$

$$\frac{1}{2} N_2(g) + y\ Ti_x N_{1-x}\ (s) = y\ Ti_x N_{1-x + 1/y}\ (s)$$

where $y \gg 1$

From the experimental data for $\ln p_{N_2}$ as a function of temperature and composition we can thus calculate $\bar{H}_N$ for the range of $Ti_x N_{1-x}$ compositions studied. Since the integral heats for the solution phase are related to the partial heats by the expression

$$H = \sum n_i \bar{H}_i \quad \text{we see that}$$

$$H_{Ti_x N_{1-x}} = x \bar{H}_{Ti} + (1-x) \bar{H}_N.$$

From the experimental values of $\bar{H}_N$ as a function of composition and the integral enthalpy of formation of stoichiometric nitride one can calculae $\bar{H}_{Ti}$ for the stoichiometric nitride. Within the solution phase the $\bar{H}_{Ti}$ and $\bar{H}_N$ are related by an expression

$$x \frac{\partial \bar{H}_{Ti}}{\partial x} + (1-x) \frac{\partial \bar{H}_N}{\partial x} = 0$$

which is analogous to the Gibbs-Duhem relationship applied earlier to the partial molal free energies. Thus from knowledge of $\bar{H}_{Ti}$ for $Ti_{.5} N_{.5}$ and $\bar{H}_N$ as a function of composition one can derive H_{Ti} as a function of composition.

UNCLASSIFIED
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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)*
ARTHUR D. LITTLE, INC.
CAMBRIDGE, MASSACHUSETTS

2a REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b GROUP

3 REPORT TITLE
EQUILIBRIUM STUDIES OF REFRACTORY NITRIDES

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Summary Technical Report 1 June 1964 to 31 May 1965

5 AUTHOR(S) *(Last name, first name, initial)*
McClaine, Leslie A.
Coppel, Claude P.

6 REPORT DATE	7a TOTAL NO. OF PAGES	7b NO. OF REFS
September, 1965	63	18

8a CONTRACT OR GRANT NO.	9a ORIGINATOR'S REPORT NUMBER(S)
AF 33(615)-1713 b. PROJECT NO. 7360 Task No. 736001 c. d.	AFML-TR-65-299 PART I 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10 AVAILABILITY/LIMITATION NOTICES
Qualified requestors may obtain copies of this report from DDC.

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	AF Materials Laboratory Materials Physics Division (MAYT) Wright-Patterson AFB, Ohio 45433

13 ABSTRACT

This report describes an apparatus assembled specifically for studies on refractory nitrides. The apparatus provides for measurement of nitrogen pressure as a function of temperature and composition of the nitride sample by a static technique.

The titanium nitride phase was studied. Equilibrium nitrogen pressures were determined for nitride compositions ranging from about $Ti_{.54}N_{.46}$ to $TiN_{.5}$. Equilibrium titanium pressures over pure titanium, the α-titanium-titanium nitride two phase mixture and a nitride composition of about $Ti_{.55}N_{.45}$ were determined by a Knudsen technique. These pressure data are related and extended across titanium nitride phase region utilizing thermodynamic theory.

Previous work on titanium nitride is reviewed and a consistant account of all the available data is developed.

DD FORM 1 JAN 64 1473

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Titanium Nitride Titanium-Nitrogen System gas-solid equilibria Thermochemical Data Vapor Pressure Measurement						

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