Contrails

Thermodynamics of the Interaction of Niobium and Tantalum with Oxygen and Nitrogeı at Temperatures Near the Melting Point

J. Paul Pemsler

Nuclear Metals, Inc.

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FOREWORD

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ABSTRACT

The concentration of nitrogen and oxygen present in niobium and tantalum in equilibrium with the pure gas has been determined as a function of pressure at each of three temperatures near the melting point, and in the liquid phase at the melting point. The solubility of nitrogen in niobium is directly proportional to the square root of the pressure (Sievert's Law) up to the solubility limit, where the saturated solution is in equilibrium with Nb_2N. The solubility of nitrogen in tantalum shows a negative deviation from Sievert's Law at nitrogen concentrations above 5 atomic percent; beyond the solubility limit saturated solution is converted to Ta_2N. The niobium-oxygen and tantalum-oxygen systems obey Sievert's Law up to the solidus point. The temperatures investigated were above the melting points of the metal oxides and no oxide scales were obtained. A curious solubility inversion was noted in the tantalum-oxygen system where the oxygen concentration in equilibrium with a specified pressure of oxygen is lower at 2850 than at 2960°C. Data were used to calculate the partial molar and integral values of the free energy, enthalpy, and entropy of dissociation of solutions of nitrogen in niobium and tantalum and partial molar free energy and enthalpy of dissociation of solutions of oxygen in niobium and tantalum. It was shown that the concentration of hydrogen in equilibrium with metal at high temperature is very low.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

FREEMAN F. BENTLEY
Chief, Analytical Branch
Physics Laboratory
Materials Central

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I. INTRODUCTION

Niobium and tantalum are becoming increasingly important as structural materials for use at high temperatures. The mechanical properties on which such use is based are known to be greatly affected by the presence of small amounts of impurity atoms in the lattice. These properties are particularly sensitive to the presence of the gaseous elements oxygen, nitrogen, and hydrogen. It is therefore important to evaluate quantitatively the affinity of the metal for these gases. Thermodynamic data concerning the solution of gases at very high temperatures up to the melting point and in the liquid phase would help define the conditions both wherein the metals absorb gases and wherein the gaseous impurities can be removed.

The present work seeks to provide such data by studying the equilibrium reactions of niobium and tantalum with oxygen and nitrogen at very high temperatures.

II. LITERATURE SURVEY

A literature survey on gases in niobium and tantalum was prepared to aid in planning the experimental parts of this program and has been issued as a separate report. This document, (NMI-9800), covers (1) structure and phase diagrams; (2) thermodynamic data; (3) disposition of gases in the metals and effect of gases on physical properties; (4) gas removal by vacuum annealing and (5) selected oxidation - reduction reactions.

III. EXPERIMENTS AND RESULTS

A. Materials

A double electron-beam vacuum-melted niobium rod 1 inch in diameter and 21 inches long was obtained from the Wah Chang Corp. of Albany, Oregon, and a 3.4 pound electron-beam vacuum-melted tantalum ingot was obtained from the National Research Corp. of Cambridge, Mass. The analyses reported by the suppliers are given in Table 1.

The gases used were purified according to the following schemes:

Oxygen

Tank oxygen $\longrightarrow$ Anhydrone $\longrightarrow$ platinum asbestos at $300^{\circ}C$ $\longrightarrow$ Anhydrone $\longrightarrow$ Ascarite $\longrightarrow$ liquid nitrogen trap $\longrightarrow$ system.

Nitrogen

Tank dry nitrogen $\longrightarrow$ copper turnings at $600^{\circ}C$ $\longrightarrow$ Anhydrone $\longrightarrow$ Ascarite $\longrightarrow$ liquid nitrogen trap $\longrightarrow$ system.

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Table 1

Chemical Analysis of Niobium and Tantalum

Niobium		Tantalum	
Element	ppm	Element	ppm
O	150	C	< 10
N	45	O	10
H	< 5	H	---
C	< 30	N	10
Al	< 20	Fe	< 20
B	< 1	Cr	< 10
Cd	< 1	Ni	< 10
Cr	< 20	Si	< 30
Cu	< 40	Nb	< 25
Fe	< 100	Al	< 50
Mg	< 20	Cu	< 50
Mn	< 20	Ti	< 10
Mo	< 20	Mo	150
Ni	< 20		
Pb	< 20		
Si	< 100		
Sn	< 20		
Ta	520		
Ti	< 150		
V	< 20		
W	< 150		
Zn	< 20		

Hydrogen

Tank hydrogen $\longrightarrow$ Anhydrone $\longrightarrow$ Ascarite $\longrightarrow$ liquid nitrogen trap $\longrightarrow$ system.

B. Analytical Procedure

Nitrogen was determined by means of the micro-Kjeldahl procedure developed at the MIT Metallurgical Project.[1] Samples were dissolved in platinum dishes with concentrated hydrofluoric acid and hydrogen peroxide.

Oxygen was determined with the aid of a National Research Corp. vacuum fusion unit. Samples were melted in a graphite crucible and the carbon monoxide evolved converted to CO_2. The difference in pressure before and after freezing out the CO_2 was used as a measure of the oxygen content.

Hydrogen was determined by warm extraction at $1000^{\circ}C$. A National Research Corp. vacuum fusion unit was used and the pressure of hydrogen collected was read on a McLeod gage.

C.   Apparatus

Thermodynamic data were obtained by equilibration of the gas at various pressures with metal at elevated temperature. The apparatus used for the equilibration is shown schematically in Fig. 1 and in a photograph in Fig. 2. The sample consisting of a rectangular parallelepiped about 2 mm x 3 mm x 40 mm long was resistance heated to the test temperature between water-cooled copper electrodes. The silica reaction chamber which held the sample is shown schematically in Fig. 3. Samples were given a preliminary outgassing at 10^{-6} mm Hg for 5 minutes at a temperature near the melting point. The temperature of the sample was then adjusted to the value required and purified gas admitted to the system.

D.   Pressure Measurement and Control

A temperature gradient existed in the sample, since it was heated between water-cooled electrodes, the ends being much cooler than the uniform central zone. Portions of the sample near the ends were often in a temperature range where nitriding or oxidation converted that area to the nitride or oxide while the center zone, at a uniform higher temperature, may have been dissolving gas to form a solid solution. Thus, even after equilibrium was established in the uniform temperature zone, areas forming nitride or oxide continually absorbed gas so that a slow bleed of gas into the system was needed to maintain constant pressure. This was achieved by the use of tapered stopcocks equipped with a fine control adjustment.

Data were obtained by approaching the composition in equilibrium with gas at a given pressure from compositions both above and below the equilibrium composition. In some experiments gas was bled in until the pressure reached the desired value and then was held constant for the duration of the run. In other experiments the gas pressure was brought to a value considerably above (often a factor of 10 above) the final equilibrium pressure. The high pressure was maintained for a sufficient period of time to reach a steady state. Gas was then removed from the system, lowering the pressure to the equilibrium value being investigated. This latter pressure was then maintained for an additional period of time in order to establish the final equilibrium. Chemical analysis indicated that the final concentration of gas in the metal was identical whether approached from above or below, and hence a true equilibrium was attained.

Pressure was measured by a means of Pirani vacuum gage with 0 to 2 mm-Hg range, a McLeod gage with a 0 to 5 mm-Hg range, a Hastings vacuum gage with a 0 to 30 mm-Hg range, or a mercury manometer with a 0 to 760 mm-Hg range, depending upon the pressure.
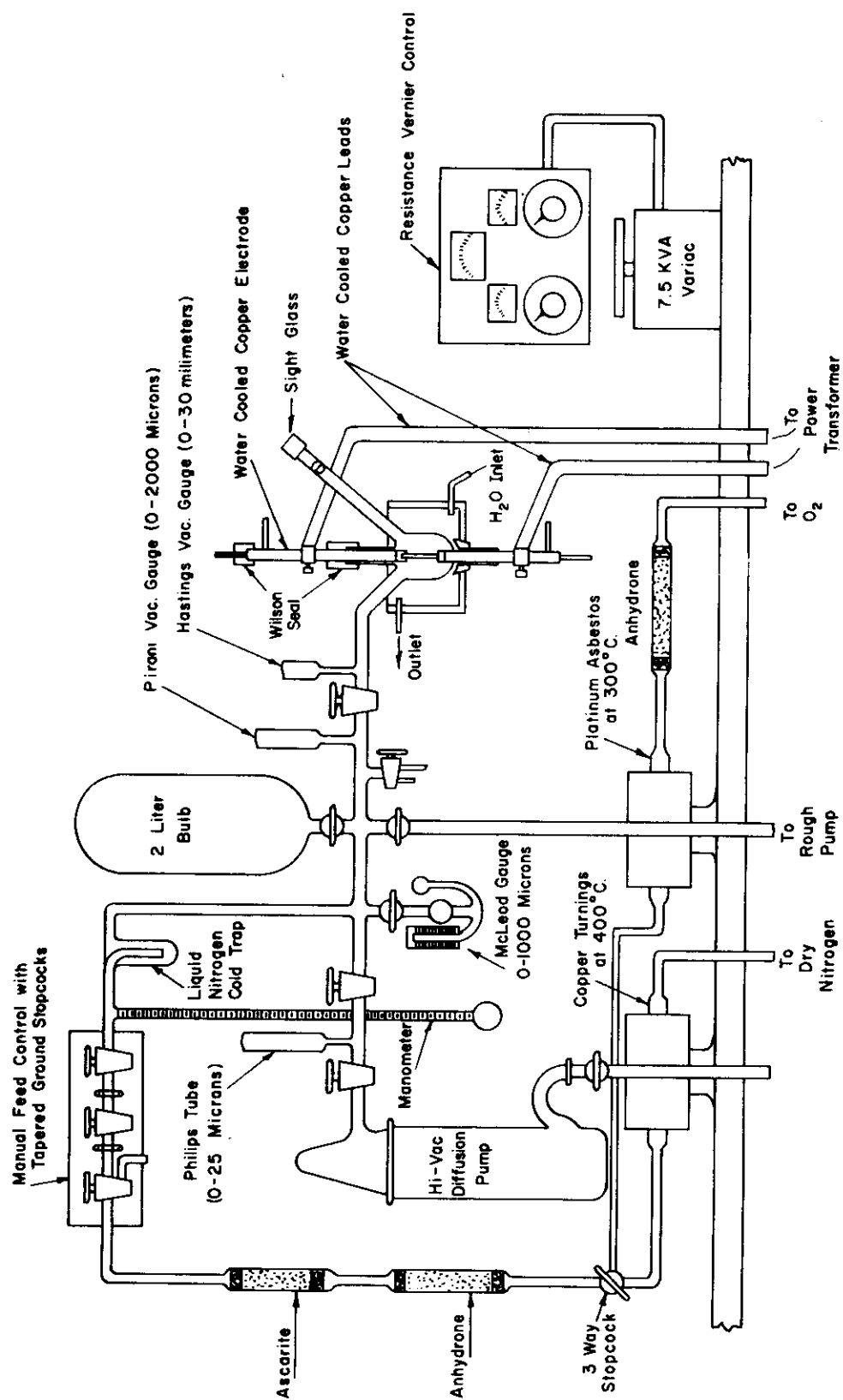
Fig. 1 - Apparatus for equilibration of gas with solid metal.

RF-7531

Fig. 2 - Vacuum system used to equilibrate gases
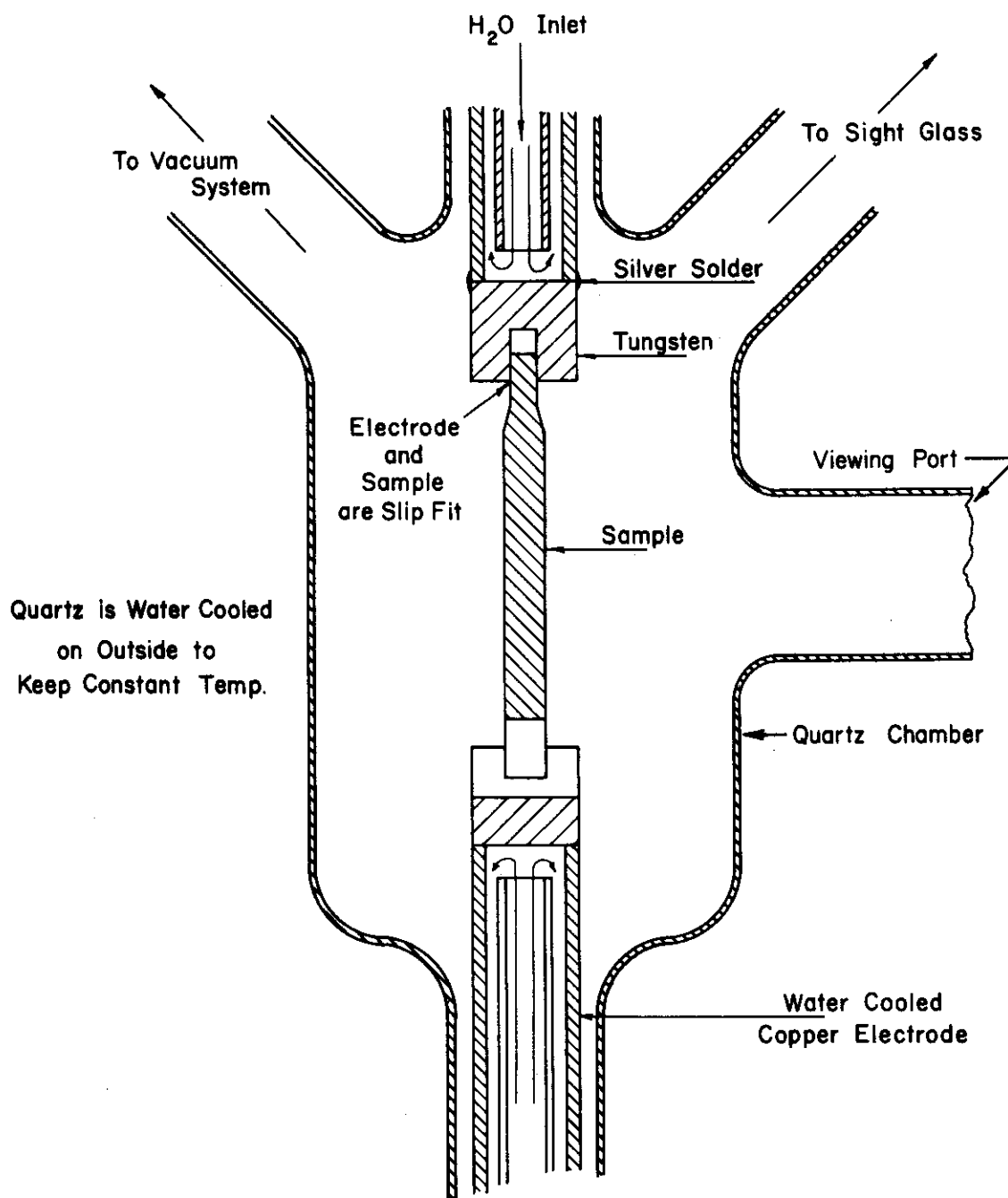with niobium and tantalum.

Fig. 3 - Reaction chamber and electrode assembly.

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E. **Temperature Measurement**

The temperature of the sample was maintained constant during the experiment by adjusting a vernier attached to a variable transformer which controlled the current through the sample. Temperatures were measured with an optical pyrometer calibrated at a wave length of 0.65 micron. An emissivity calibration correction was made by observing the temperature of a sample with a small hole drilled into it to a depth sufficient to approximate blackbody conditions (depth-to-breadth ratio of eight). The apparent temperature read from the surface of the specimen is plotted in Figs. 4 and 5 as a function of the black-body temperature read from the black-body hole. The emissivities near the melting points were calculated from the above data. The value of 0.362 for niobium is substantially different from the older value of 0.49.[2] The value of 0.352 for tantalum is in excellent agreement with the value of 0.350 reported by Glazier et al.[3] The melting point of niobium was determined as $2740^{\circ}K$, in agreement with a value of $2740^{\circ}K$ reported by Schofield[4] and higher than the value of $2690^{\circ}K$ reported by Wilhelm et al.[5] The melting point of tantalum observed here was $3290^{\circ}K$, in agreement within experimental error of the value $3270^{\circ}K$ reported by Langmuir and Malter.[6] During equilibration no attempt was made to correct emissivity values for changes due to the dissolution of nitrogen or oxygen in the metal or the appearance of a shiny subnitride layer on the surface. All samples were shiny upon examination after the conclusion of an experiment and it is believed that emissivity changes occurring during the course of equilibration, corresponding to temperature errors, were fairly small.

F. **Liquid Drop**

Equilibration of the liquid phase was accomplished by suspending a liquid drop vertically in the center of the metal sample attached to the electrodes. Specimens were similar to those used in the solid phase studies but portions of the center were ground away so that the sample had the appearance of a flat tensile specimen. The tension between the electrodes had to be carefully controlled to offset the thermal expansion of the sample. This control was accomplished by a series of reduction gears attached to the electrode and to a coarse and fine adjustment dial. In this way very small vertical adjustments of the top electrode relative to the fixed bottom electrode could be made. It was also found possible, by adjusting the inter-electrode distance, to achieve fine adjustment of the temperature and to control instabilities developing in the drop due to vibration. Forcing the electrodes together would increase the drop diameter and decrease its length. The corresponding reduction in electrical resistivity of the compressed sample would decrease the over-all size of the drop. A photograph of a suspended molten drop is shown in Fig. 6. The temperature of the drop was taken as the melting point. This value may be slightly in error due to superheating of the drop and to the change in melting point of the metal with dissolved nitrogen or oxygen. However, the thermodynamic data obtained from the solid phase experiments extrapolate smoothly to the liquid region, indicating that the temperature of the drop was probably not very different from the melting point of the pure metal.
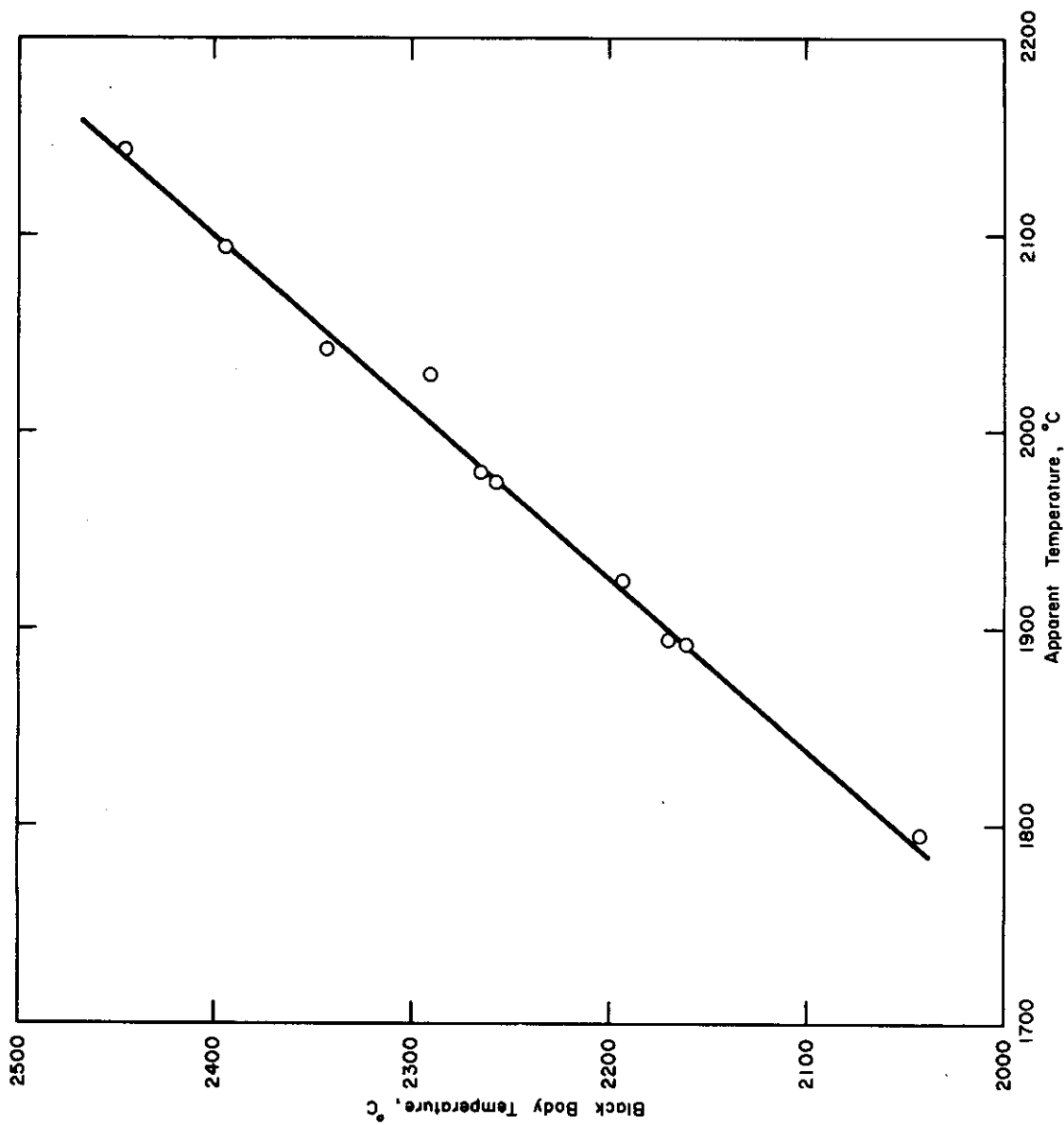
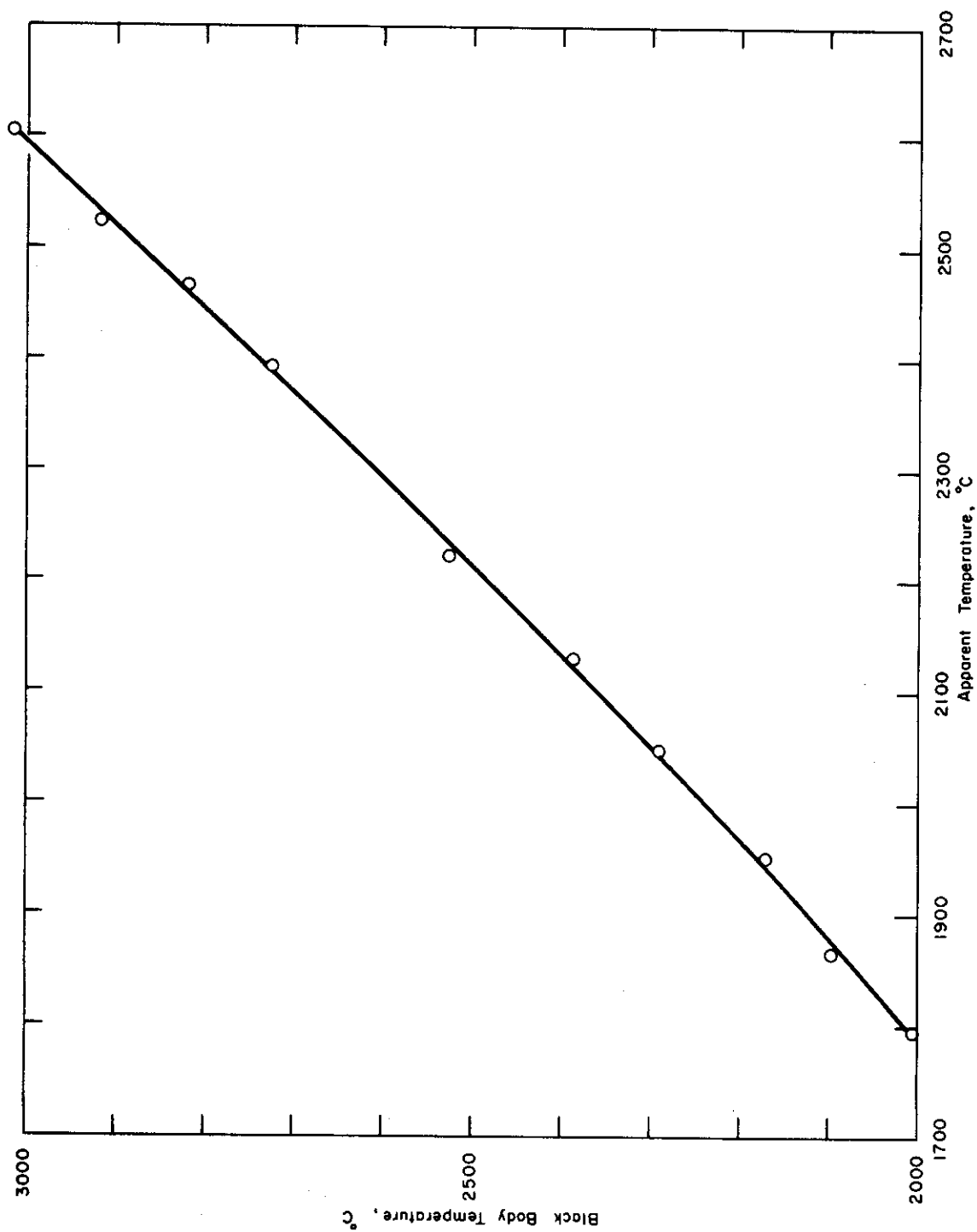Fig. 4 - Determination of the emissivity correction for niobium.

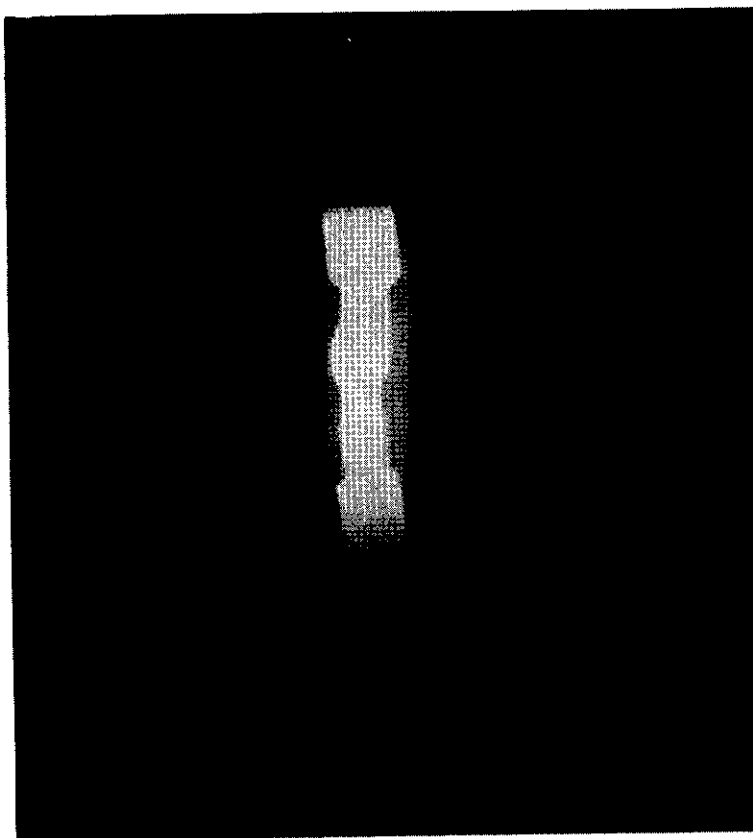Fig. 5 - Determination of the emissivity correction for tantalum.

Fig. 6 - Photograph of a molten tantalum drop in
the center of a tantalum specimen.

G.   Examination of Samples

Samples were examined metallographically after each experiment, and micro-hardness traverses were made on selected samples to insure the absence of a concentration gradient within the metal.

IV.   RESULTS

A.   Equilibrium Data

1.   Nitrogen

Data for the niobium-nitrogen and tantalum-nitrogen systems are summarized in Tables 2 and 3. The nitrogen pressures and times at temperature during equilibration are shown in columns 5 and 6 of the Tables. In some cases preliminary gassings were made at pressures higher than the final equilibrium value so that the equilibrium concentration of nitrogen in the sample was approached from above, i.e., the sample expelled nitrogen as it approached equilibrium. Data for the preliminary high-pressure gassings are presented in columns 3 and 4.

Sievert's Law (which is a modification of Henry's Law) states that at constant temperature the solubility of a diatomic gas in a metal is propor- . tional to the square root of the pressure:

$$S = kP^{1/2} \tag{1}$$

This law should hold at low concentrations of gas in the metal, where an ideal solid solution may exist. A Sievert's Law plot for niobium-nitrogen is shown in Fig. 7. The nitrogen solubility is a linear function of the square root of the pressure within the solubility range. There is a slight curvature of the line depicting the liquid drop data. The terminal solubility of nitrogen in niobium in equilibrium with Nb_2N as determined by Elliott and Komjathy[7] is shown on the graph. Points to the right of this line are not equilibrium values but represent partially nitrided samples as discussed below. Terminal solubilities in the liquid phase have not been determined.

Metallographic examination revealed that the niobium samples quenched from high temperature and containing up to about 0.5 atomic percent nitrogen were homogeneous throughout with no evidence of a second-phase precipitate. Albrecht and Goode[8] report the terminal solubility of nitrogen in niobium as 1.2 atomic percent at $1100^{\circ}C$ and 0.28 atomic percent at $800^{\circ}C$.

Samples containing between about 0.5 atomic percent nitrogen and the saturation values indicated in Fig. 7 consist of a dispersion of second-phase particles in the niobium matrix as shown in Fig. 8. The second phase is presumed to be Nb_2N.[7] Since isothermal diffusion in binary alloys cannot produce such a dispersed two-phase structure, the Nb_2N must have precipitated upon quenching. Thus, all the nitrogen was present in solution at the elevated temperatures.

Table 2

Equilibrium Solubility of Nitrogen in Niobium at Various Pressures

Sample No.	Temp. (°C)	Preliminary Gassing Pressure (mm-Hg)	Time (min)	Equilibration Pressure (mm-Hg)	Time (min)	Nitrogen Concentration (at. %)
250				0.01	5	0.40
245				0.1	6.5	1.15
247				1.0	6	3.10
156	2470			1.0	8	2.75
311	(liquid)			9.0	10	7.62
248				• 10	3.5	8.85
307				48	12	14.15
159				100	5.5	16.30
184				0.010	30	0.38
186		0.1	21	0.010	30	0.38
91				0.10	60	0.82
188		1	16	0.10	26	0.90
92				1.0	60	3.22
190		10	16	1.0	45	2.75
304				4.8	45	7.10
268	2420			5.0	45	7.74
269		10	15	5.0	45	8.40
93				10.0	60	10.1
101		100	50	10.0	30	10.3
306				19.5	45	18.5
94				100	60	29.3
197		700	45	100	60	30.1
185				0.010	30	0.37
187		0.1	22	0.010	30	0.64
208				0.010	45	0.57
189		1	20	0.10	30	1.45
125				0.10	60	1.50
126				1.0	60	4.70
192	2280	10	19	1.0	30	4.75
267				5.0	45	14.3
305				5.3	45	14.4
193		100	18	10.0	60	23.6
194				10.0	60	18.0
195				100	60	21.7
199		700	16	100	60	31.6
201				0.010	30	0.90
202		0.1	15	0.010	30	1.05
200				0.10	45	2.73
203	2170	1	16	0.10	45	2.45
198				1.0	45	8.12
205		10	15	1.0	45	8.17
266				3.0	45	15.3
204				10.0	120	19.7
209		100	16	10.0	120	22.6

Table 3

Equilibrium Solubility of Nitrogen in Tantalum at Various Pressures

| Sample No.	Temp. (°C)	Preliminary Gassing		Equilibration		Nitrogen Concentration (at. %)
		Pressure (mm-Hg)	Time (min)	Pressure (mm-Hg)	Time (min)	
253	3020 (liquid)			0.10	4.5	0.55
259				1.0	5.5	1.50
256				10.0	5	3.65
257				100	7	9.25
157				100	10	9.25
310				360	9	14.1
260				700	7	17.5
96	2960			0.10	60	0.41
211		1.0	15	0.10	30	0.47
97				1.0	60	1.08
212		10	16	1.0	60	1.40
98				10.0	60	3.86
100		100	50	10.0	26	3.96
99				100	60	9.75
213		700	17	100	60	10.2
274				360	120	14.5
275		600	18	360	112	14.6
217				700	120	24.7
308				700	90	24.4
132	2850			0.10	60	0.72
220		1	15	0.10	30	0.47
131				1.0	60	1.65
215		10	15	1.0	30	1.55
134				10.0	60	4.94
216		100	15	10.0	60	4.8
133				100	60	12.0
218		700	15	100	60	11.52
273				100	90	11.75
309				225	90	14.5
272				360	105	23.75
219				700	120	26.25
221	2390	1	16	0.10	45	1.80
222				0.10	30	1.68
223		10	17	1.0	60	4.95
224				1.0	45	5.05
225				10.0	60	11.63
226		100	15	10.0	60	12.41
270				35.0	45	20.0
227		700	17	100	120	26.35
228				100	120	28.8
271				360	120	29.0
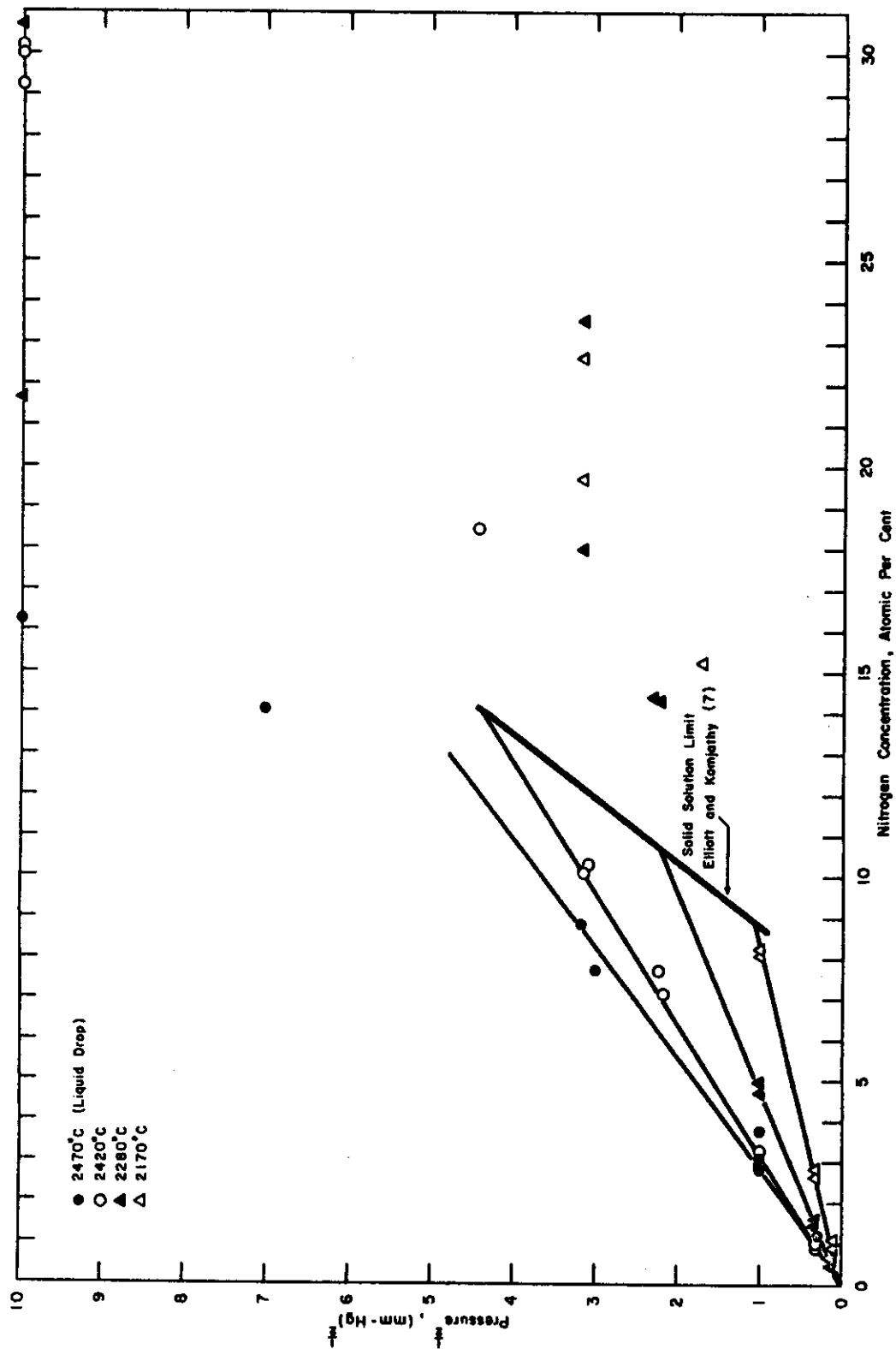
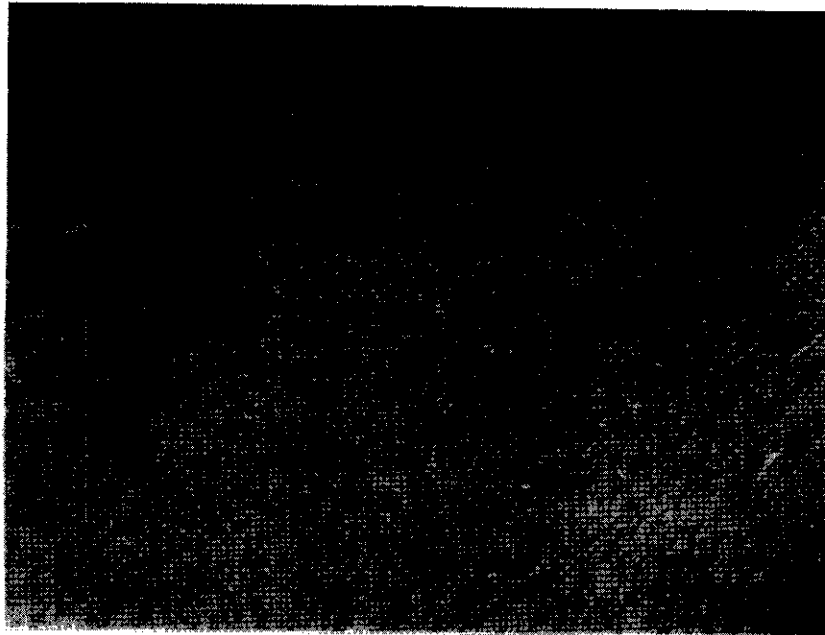Fig. 7 - Sievert's Law plot of the solubility of nitrogen in niobium.

150X Bt.Lt.   A-2686-9a

Fig. 8 - Dispersion of Nb_2N in niobium matrix. The
         sample was equilibrated for 10 minutes at
         $2420^{\circ}C$ in nitrogen at a pressure of 10 mm-Hg.
         Edge of sample is shown at top, and micro-
   hardness indentations are visible.

Samples containing more than the solution limit of nitrogen were observed to consist of a scale of varying thickness surrounding a zone containing a dispersion of Nb_2N in a matrix of niobium saturated with nitrogen (see Fig. 9). The scale was identified by x-ray diffraction as Nb_2N. The extent of nitriding is probably controlled by the rate of diffusion of nitrogen ions, niobium ions, or both through the Nb_2N layer. Thus, the extent of conversion of the sample to Nb_2N depends on the dimensions of the sample, the temperature, and the time of the reaction. Nitriding for long times completely converts the niobium to Nb_2N. The pressure of nitrogen necessary to form an Nb_2N scale varies from about 1 mm at $2170^{\circ}C$ to about 20 mm at $2420^{\circ}C$.

A Sievert's law plot for tantalum-nitrogen is shown in Fig. 10. No high-temperature solubility values of nitrogen in tantalum are available in the literature. On the basis of metallographic examination of the alloys, an approximate terminal solubility line is sketched in Fig. 10. At the lowest temperature, $2390^{\circ}C$, the concentration varies linearly with the square root of pressure. At higher temperatures there is appreciable curvature beyond 6 atomic percent. Above the solid-solubility limit the data scatter widely, reflecting the extent to which Ta_2N was formed on a particular sample.

Samples quenched from high temperature and containing up to about 11 atomic percent nitrogen exhibited no second-phase precipitate when examined metallographically. The room temperature solubility of nitrogen in tantalum may, therefore, be as high as 11 atomic percent, or tantalum may be capable of retaining large amounts of nitrogen in supersaturated solution when quenched from high temperature. Gebhardt et al.[9] fix the room temperature solubility as less than 5 atomic percent. In the composition range of about 11 atomic percent nitrogen to the solid solution limit, a dispersion of second-phase particles in the tantalum matrix is observed at room temperature, as shown in Fig. 11. Beyond the solid-solution limit a nitride layer is present as shown in Fig. 12. Quenched alloys containing from 25 to 28 atomic percent nitrogen exhibit complete nitriding of the tantalum. Brauer and Zapp[10] report a structure, referred to as Ta_2N, with a homogeneity range of 29 to 33 atomic percent nitrogen, while Schonberg[11] reports the homogeneity range from 28 to 31 atomic percent nitrogen. Ta_2N is, thus, nonstoichiometric and its composition depends on the temperature and external nitrogen pressure.

2. Oxygen

Data for the niobium-oxygen and tantalum-oxygen systems are summarized in Tables 4 and 5, and Sievert's law plots are shown in Figs. 13 and 14. The scatter of data in the oxygen-metal systems is much larger than that obtained in the nitrogen-metal systems. This may be due in part to the necessity of working at low pressures in the oxygen systems, where the error in reading the pressure may be appreciable. The temperatures used in this investigation are above the melting points of the metal oxides, so no oxide scale can form on the sample. The maximum concentration of oxygen which can be obtained in a metal-oxygen alloy at a particular temperature is limited to a value corresponding to the composition of the solidus point at that temperature.
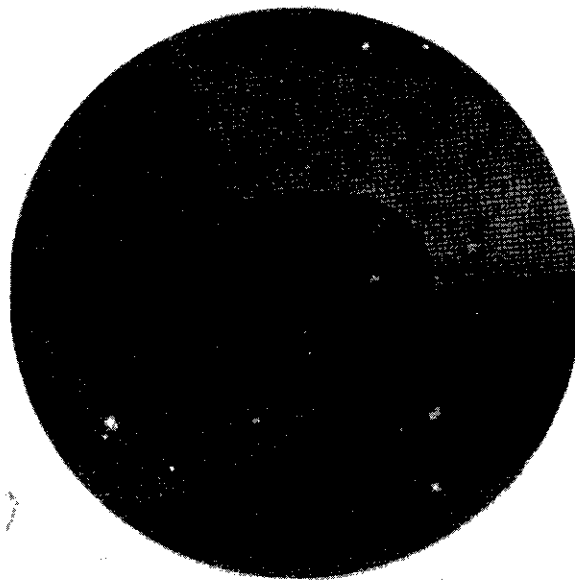
50X Pd.Lt.   A-2696-4a

Fig. 9 - Central zone of Nb_2N dispersed in a niobium
matrix surrounded by three large grains of
Nb_2N. Sample was equilibrated for 1 hour at
$2420^{\circ}C$ in nitrogen at a pressure of 100 mm-Hg.
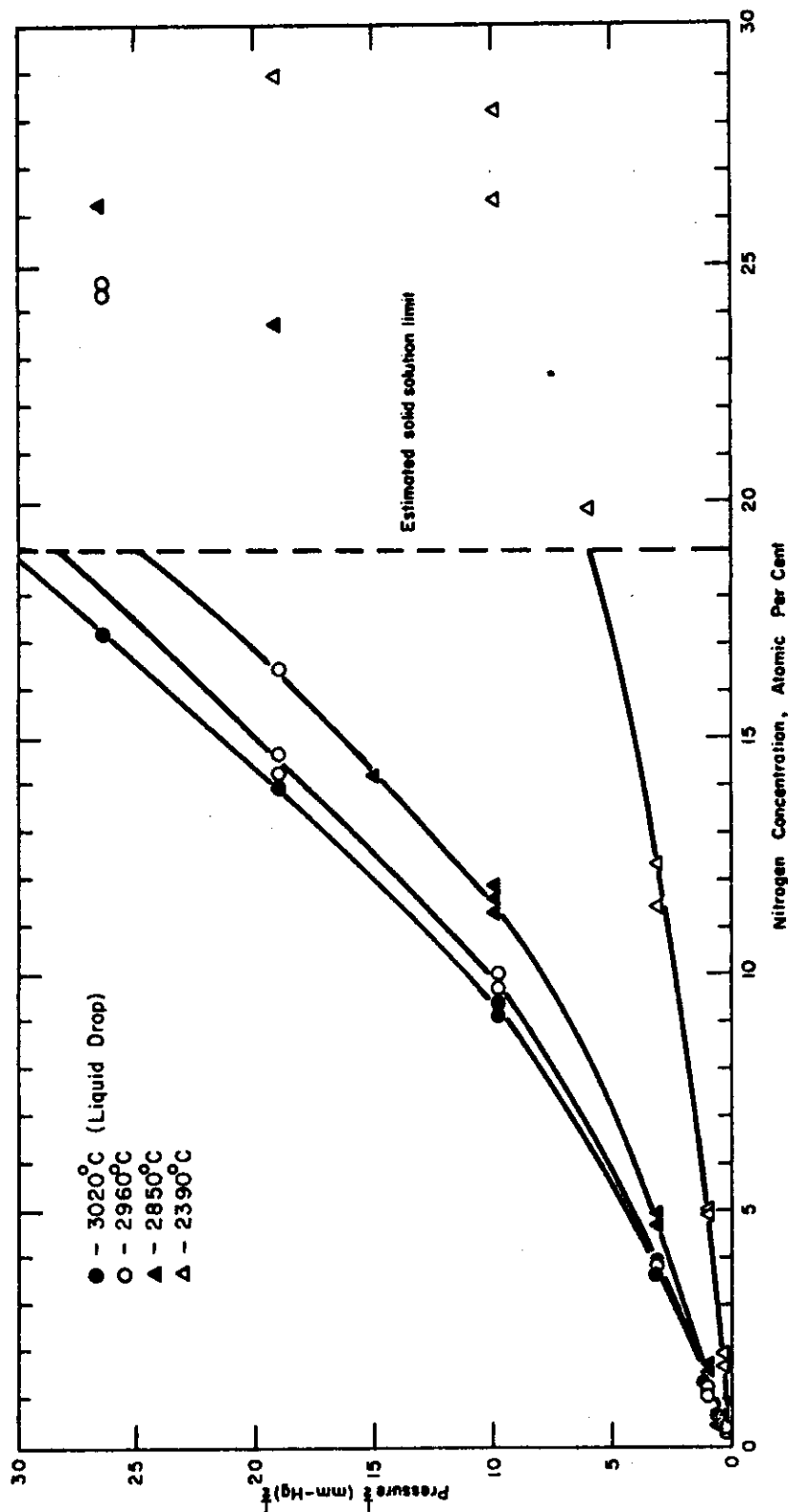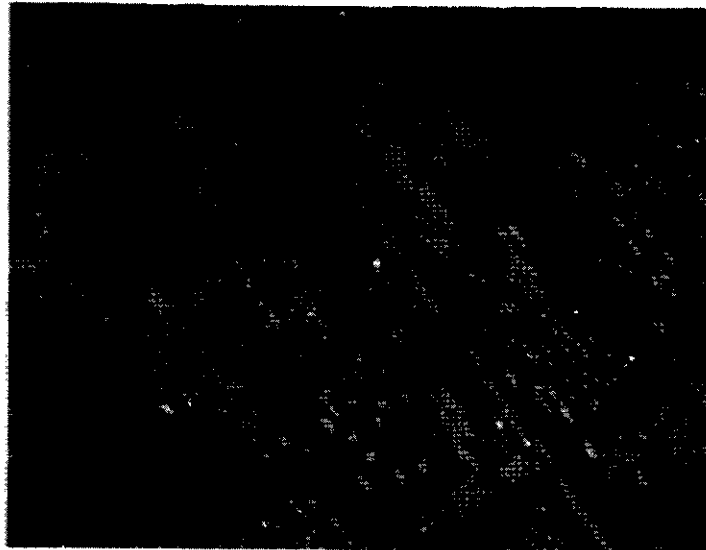
Fig. 10 - Sievert's Law plot of the solubility of nitrogen in tantalum.

150X Pd.Lt.   A-2856-8

Fig. 11 - Dispersion of Ta$_2$N in tantalum matrix.
         The sample was equilibrated for 2
         hours at 2960°C in nitrogen at a pres-
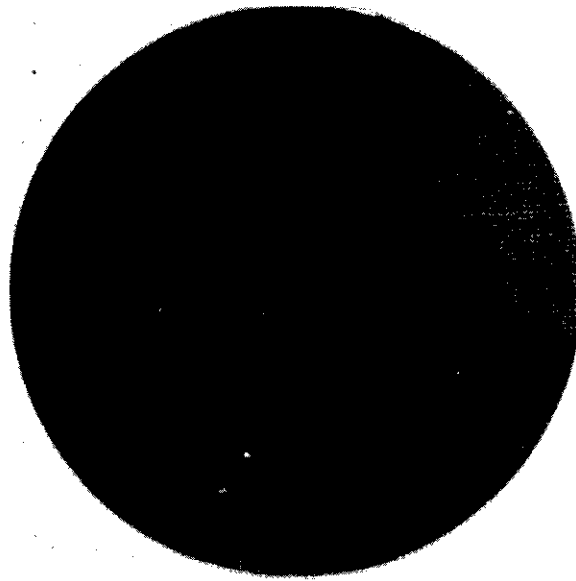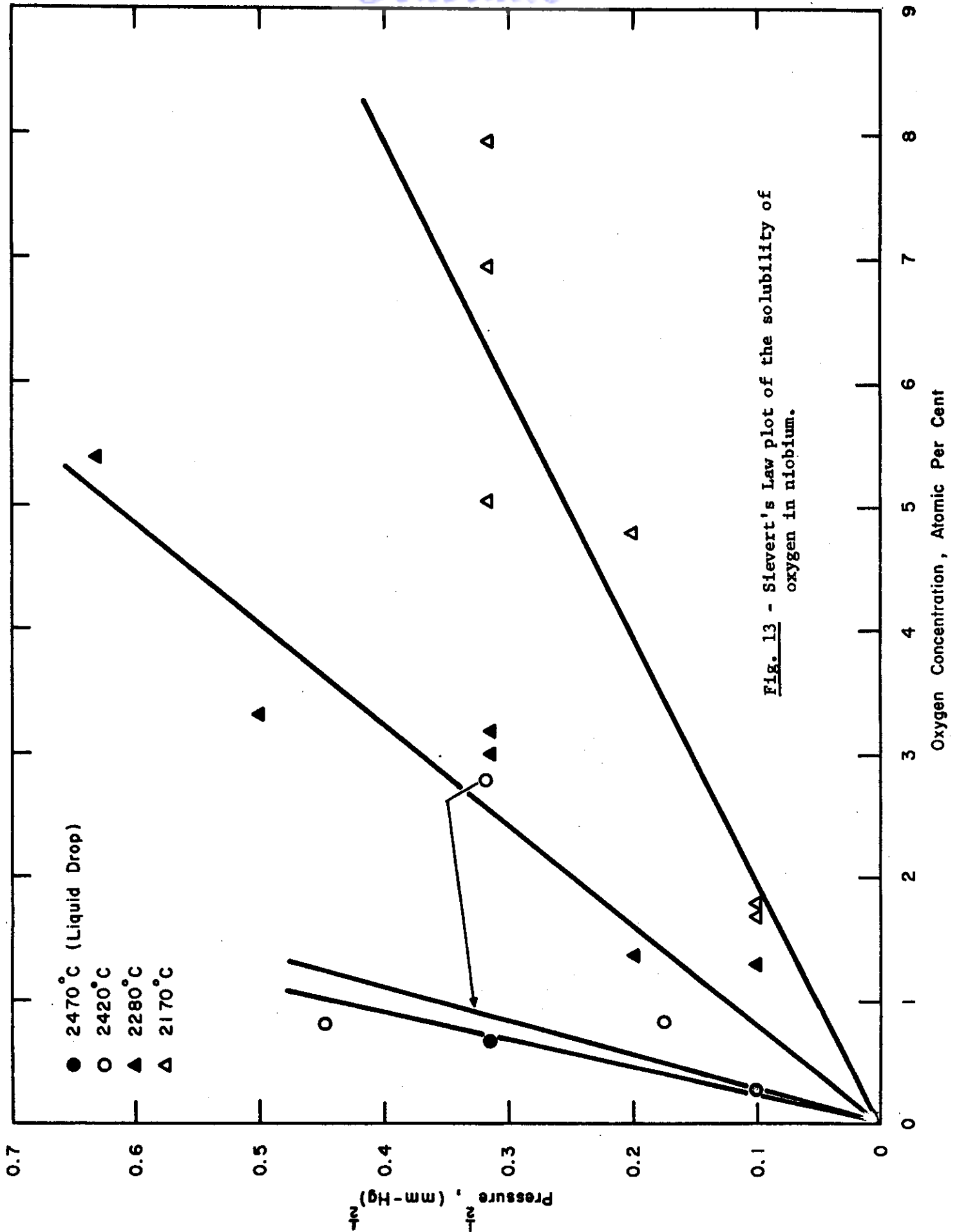   sure of 360 mm-Hg.

Fig. 12 - Central zone of Ta_2N dispersed in a tanta-
lum matrix surrounded by three large grains
of Ta_2N. Sample was equilibrated for 45
minutes at 2390°C in nitrogen at a pressure
of 35 mm-Hg.

Table 4

Equilibrium Solubility of Oxygen in Niobium at Various Pressures

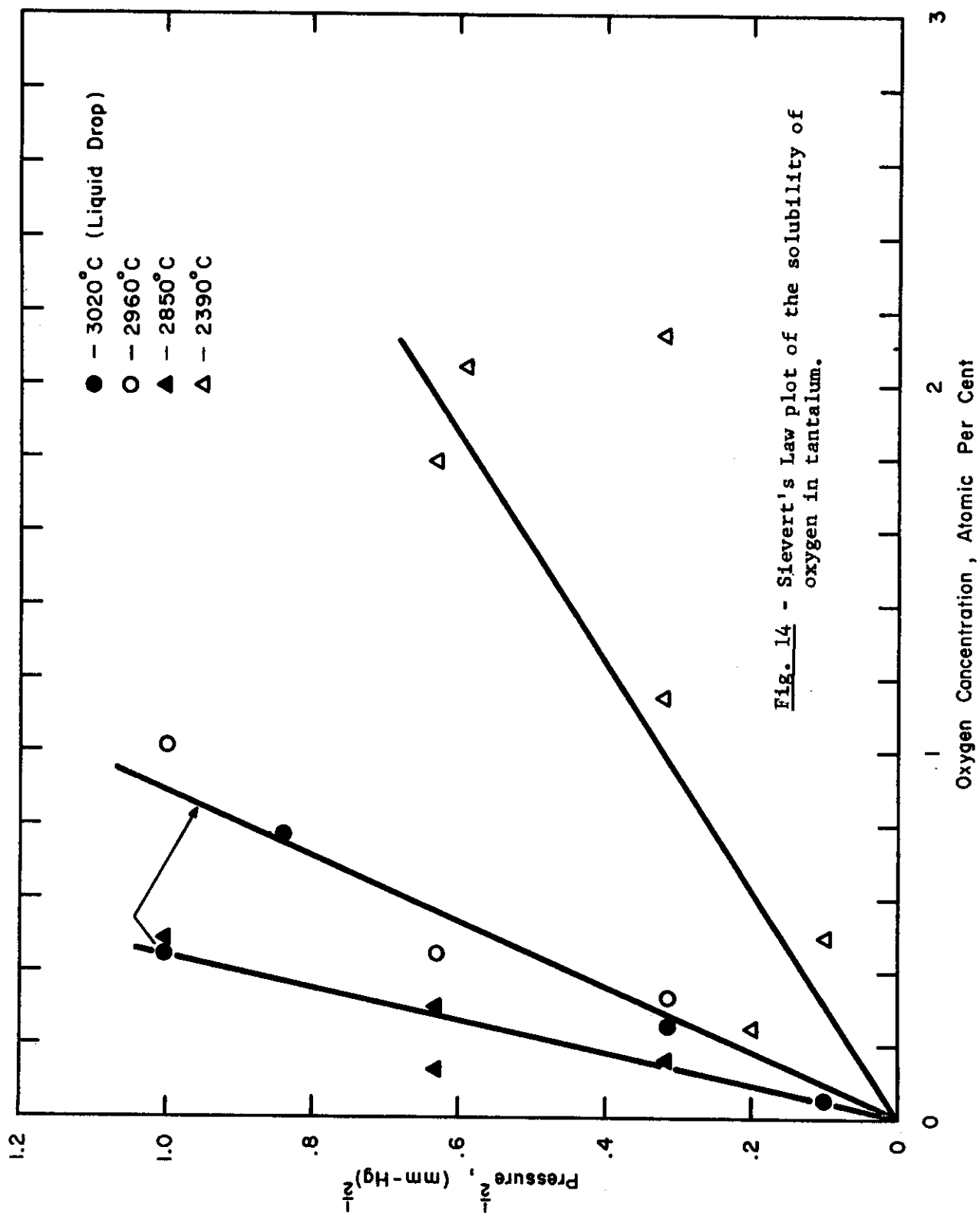| Sample No.	Temp. ($^{\circ}$C)	Equilibration		Oxygen Concentration (at. %)
		Pressure (mm-Hg)	Time (min)	
300	2467	0.010	7	0.24
301	(liquid)	0.10	5.5	0.68
276		0.030	30	0.48
277	2420	0.10	30	2.824
320		0.20	30	0.81
279		0.010	30	1.30
280		0.040	30	1.37
281	2280	0.10	30	3.02
229		0.10	30	3.19
315		0.25	30	2.84
282		0.40	30	5.40
230		0.01	30	1.74
283		0.01	30	1.80
284	2170	0.04	30	4.80
231		0.10	30	6.91
285		0.10	30	7.87
313		0.10	30	5.12

Table 5

Equilibrium Solubility of Oxygen in Tantalum
at Various Pressures

Sample No.	Temp. (°C)	Equilibration		Oxygen Concentration (at. %)
		Pressure (mm-Hg)	Time (min)	
295	3020 (liquid)	0.01	6	0.045
297		0.10	7	0.25
323		0.70	4	0.79
299		1.0	6	0.45
286	2960	0.10	30	0.33
318		0.40	18	0.45
287		1.0	21	1.02
289	2850	0.10	30	0.15
290		0.40	30	0.32
316		0.40	30	0.12
291		1.0	30	0.49
236	2390	0.01	30	0.49
292		0.04	30	0.25
293		0.10	30	1.15
234		0.10	30	2.12
317		0.35	30	2.05
294		0.40	30	1.79

Fig. 13 - Sievert's Law plot of the solubility of oxygen in niobium.

Fig. 14 - Sievert's Law plot of the solubility of oxygen in tantalum.

The niobium-oxygen data, as shown in Fig. 13, resembles the niobium-nitrogen data as shown in Fig. 7, but a curious solubility inversion exists in the tantalum-oxygen system. Tantalum-oxygen solutions are less stable at 2850°C than they are at 2960°C, or in the liquid; a given pressure of oxygen will result in a more concentrated solution at 2960°C than at 2850°C. If these data can be extrapolated to lower pressures, it would suggest that vacuum degassing at high temperatures in the solid phase can result in a lower ultimate oxygen concentration than can be obtained by electron-beam vacuum-melting. The rate of oxygen removal of the liquid will undoubtedly be more rapid than in the solid, but the ultimate attainable oxygen concentration is lowest at some temperature below the melting point. Additional work is needed in this area to confirm these results and to establish the optimum temperature for gas removal.

Metallographic examination at room temperature revealed that niobium alloys containing more than about 7 atomic percent oxygen exhibited a second-phase precipitate, probably NbO (see Fig. 15). All tantalum alloys examined were uniform.

3. Hydrogen

Niobium and tantalum are known to absorb hydrogen exothermally into solid solution. Systems such as these are characterized by the decreasing solubility of hydrogen with increasing temperature. Consequently, it was anticipated that the solubility of hydrogen in niobium and tantalum at temperatures near their respective melting points would be very small.

Measurement of the equilibrium solubility of hydrogen in niobium and tantalum at temperatures near the melting point is complicated by the very rapid rate of diffusion of hydrogen in the metals at high temperature. The metals may rapidly absorb appreciable quantities of hydrogen while cooling in the hydrogen atmosphere from the test temperature to room temperature, even with cooling rates of the order of 200°C per second as obtained in the apparatus used in this study. Since at the conclusion of an experiment the sample would contain both hydrogen absorbed during equilibration with the hydrogen atmosphere at the test temperature, and hydrogen absorbed during cooling, an experiment was performed in order to evaluate the contribution of the hydrogen absorbed on cooling to the total hydrogen content of the sample. The pressure drop on cooling was measured using first niobium and tantalum samples which had been equilibrated with hydrogen and, second, tungsten "dummy" samples identical in size to the niobium and tantalum samples. Tungsten does not absorb a significant quantity of hydrogen. The pressure drop on cooling using a tungsten sample is due only to the change in temperature of the gas, while the pressure decrease using a niobium or tantalum sample is due both to the cooling of the sample and to the absorption of hydrogen during cooling.

Experiments with tantalum at 2850°C and niobium at 2280°C in hydrogen at 700 mg-Hg indicate that, within experimental error, all the hydrogen absorbed by the samples was absorbed during cooling. The solubility of hydrogen in niobium and tantalum at temperatures near their respective melting points is estimated as 0 to 100 ppm.

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Fig. 15 - Dispersion of NbO in niobium matrix. The
sample was equilibrated for 30 minutes at
2170°C in oxygen at a pressure of 0.10 mm-Hg.

B. Thermodynamic Data

The partial molar free energy ($\Delta \bar{F}$) of dissociation of a solid solution of a gas in a metal is given by the expression

$$- \Delta \bar{F} = RT \ln P \tag{2}$$

where R is the gas constant, T is the absolute temperature, and P is the equilibrium pressure.

The variation of the partial molar free energy of dissociation of solid solutions of nitrogen in niobium and tantalum with concentration are depicted in Figs. 16 and 17. Values of $\Delta \bar{F}$ are for one mole of nitrogen, i.e., for the reaction $\frac{y NbN_2}{y} = yNb + N_2$. According to the fundamental nature of the free energy of solution, the affinity of the metal for nitrogen increases with decreasing concentration. Partial molar free energies are observed to increase with decreasing temperature, indicating that the increased stability of the solid solution at lower temperature. Throughout the region beyond the solution limit where the reaction $(Nb \text{ or } Ta)N_{sat} + N_2 \longrightarrow (Nb \text{ or } Ta)_2 N$ is occurring, the partial molar free energy becomes invariant, and would be represented by a horizontal line out to the lower limit of composition of $(Nb \text{ or } Ta)_2 N$.

The relation between the partial molar and integral values of the free energy of dissociation is given by the equation

$$\Delta F = N \int_{0}^{x} \Delta \bar{F} \, dx \tag{3}$$

where N is the atom fraction of niobium or tantalum and x is the ratio of the atom fractions, $x = \dfrac{N_{N_2}}{N_{metal}}$. ΔF is expressed as the integral free energy of dissociation per gram atom, i.e., for the reaction $\dfrac{1}{2+y} (\frac{y NbN_2}{y} = yNb + N_2)$.

Thus, the integral free energy of dissociation may be evaluated by measuring the area under the curves in Figs. 16 and 17, with the abscissa expressed as atomic fraction, x.[12] Values of the partial and integral free energies of dissociation near at the melting points are given in columns 2 and 3 of Tables 6 and 7. The values at 33 atomic percent nitrogen represent the free energies of dissociation of Nb_2N and Ta_2N near at the respective melting points of the metal.

The partial molar enthalpy ($\Delta \bar{H}$) and entropy ($\Delta \bar{S}$) for the reaction $\frac{y NbN_2}{y} = yNb + N_2$ are related to the partial molar free energy by the equation

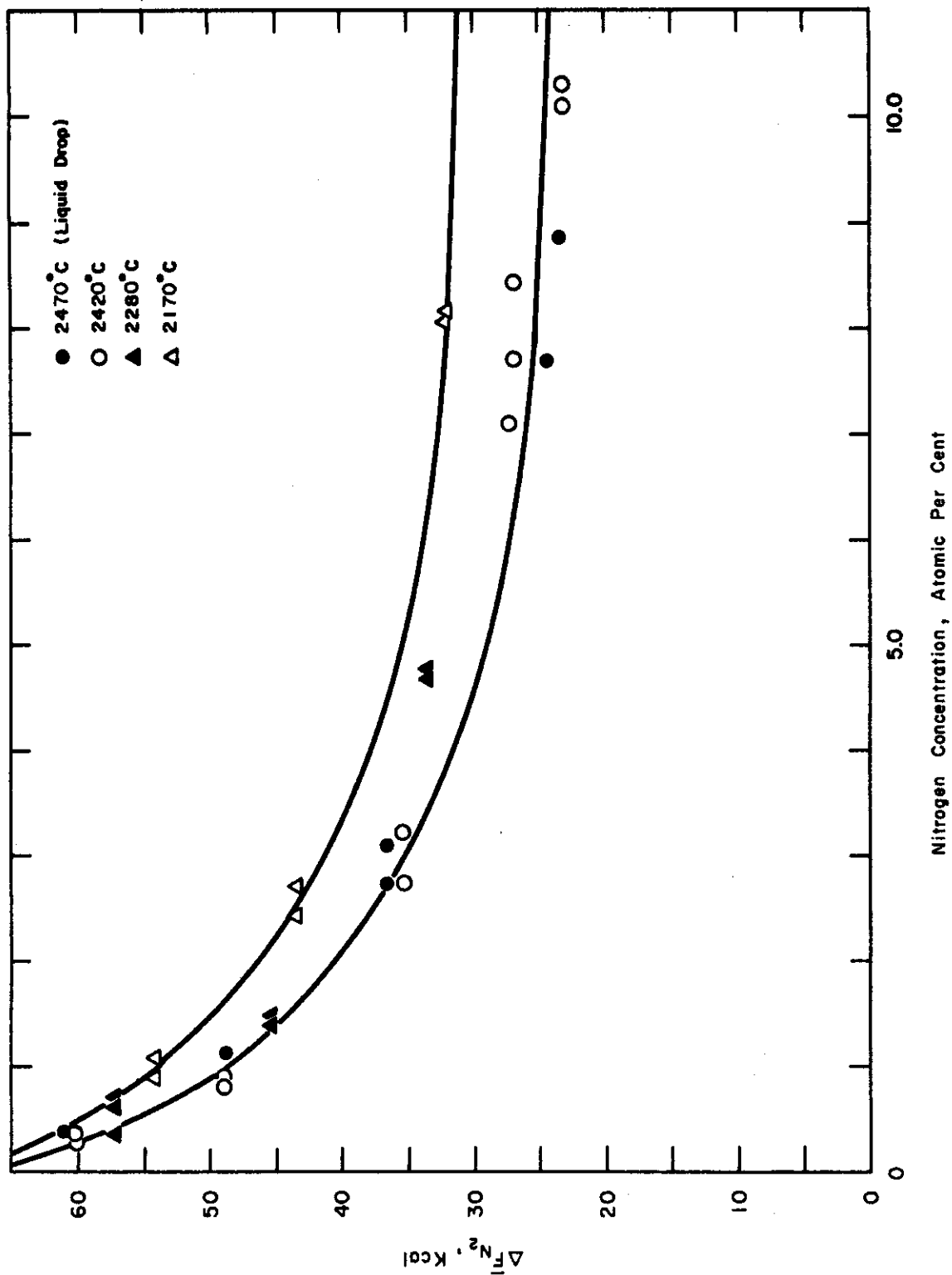$$\Delta \bar{F} = \Delta \bar{H} - T \Delta \bar{S} \tag{4}$$

Fig. 16 - Partial molar free energy of dissociation of
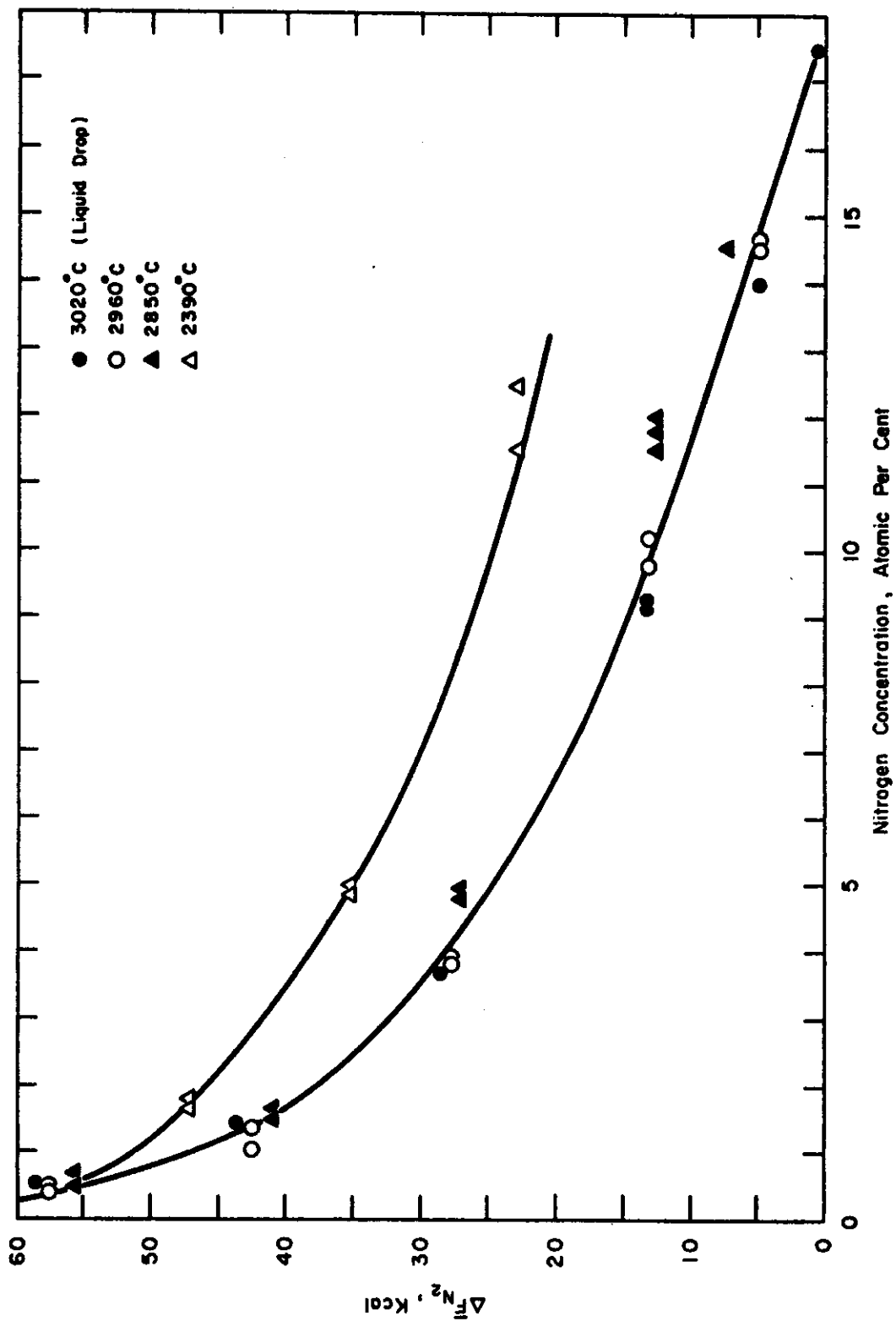niobium-nitrogen solid solution.

Fig. 17 - Partial molar free energy of dissociation of tantalum-nitrogen solid solution.

Table 6

Thermodynamic Properties of Niobium-Nitrogen at the Melting Point

Nitrogen (at. %)	$\Delta \bar{F}$ Kcal/mole N_2	ΔF Kcal/g-atom	$\Delta \bar{H}$ Kcal/mole N_2	ΔH Kcal/g-atom	$\Delta \bar{S}$ cal/degree/mole	ΔS cal/degree/g-atom
2	40	1.0	81	1.6	−15.5	−0.18
4	32	1.7	83	3.3	−18.5	−0.53
6	27	2.3	84	5.0	−20.4	−0.89
8	25	2.9	85	6.8	−21.6	−1.35
10	24	3.2	87	8.7	−22.9	−1.82
33	24	8.3		27.7	−22.9	−7.35

Table 7

Thermodynamic Properties of Tantalum-Nitrogen at the Melting Point

Nitrogen (at. %)	$\Delta \bar{F}$ Kcal/mole N_2	ΔF Kcal/g-atom	$\Delta \bar{H}$ Kcal/mole N_2	ΔH Kcal/g-atom	$\Delta \bar{S}$ cal/degree/mole	ΔS cal/degree/g-atom
3	32	0.9	86	2.6	−17.5	−0.35
6	22	1.2	86	5.2	−20.6	−0.76
9	14	2.4	86	7.7	−22.5	−1.42
12	9	2.7	90	10.8	−24.4	−2.23
15	5	2.8	93	14.0	−25.8	−2.92
33	0	2.4		29.3	−27	−8.0

Combining with Equation 2,

$$2.303 \ \log P = \frac{-\Delta \bar{H}}{RT} + \frac{\Delta \bar{S}}{R} \tag{5}$$

Therefore, at constant composition, if $\Delta \bar{H}$ is temperature independent, a plot of $\log P$ vs $\frac{1}{T}$ will be linear. The slope of the line will be equal to $\frac{-\Delta \bar{H}}{2.303 \ R}$ and the intercept at $T = \infty$ to $\frac{\Delta \bar{S}}{2.303 \ R}$.

Plots of $\log P$ vs $\frac{1}{T}$ for the compositions indicated are shown in Figs. 18 and 19. For niobium, the data can be represented as falling on two straight lines. The partial molar enthalpy of dissociation can thus be considered constant in each of the two temperature ranges studied, and has values of $\Delta H = 84$ Kcal/mole N_2 in the range 2280 to 2470°C, and $\Delta H = 121$ Kcal/mole N_2 in the range 2170 to 2280°C. Values of the integral enthalpy of dissociation and the partial molar and integral entropies of dissociation of niobium-nitrogen at the melting point are given in columns 4 to 7 of Table 6.

In the tantalum-nitrogen system, the plot of $\log P$ vs $\frac{1}{T}$ can be considered linear throughout the temperature range studies. The partial molar enthalpy of dissociation is therefore a constant and has the value $\Delta H = 88$ Kcal/mole N_2. Values of the integral enthalpy of dissociation and the partial molar and integral entropies of dissociation of tantalum-nitrogen at the melting point are given in columns 4 to 7 of Table 7.

The partial molar free energies of dissociation of niobium and tantalum-oxygen alloys are plotted in Figs. 20 and 21. Data for the tantalum-oxygen system indicate the anomalous behavior of the tantalum-oxygen system at 2850°C where alloys are less stable than at the melting points.

Plots of $\log P$ vs $\frac{1}{T}$ are shown in Figs. 22 and 23. The partial molar enthalpy of dissociation of niobium-oxygen alloys, ΔH, is constant in the temperature range investigated and has the value 198 Kcal/mole. The solubility inversion in the tantalum-oxygen system is reflected in Fig. 23 by a change in the sign of the slope of the $\log P$ vs $\frac{1}{T}$ curve (and hence a change in the sign of $\Delta \bar{H}$).
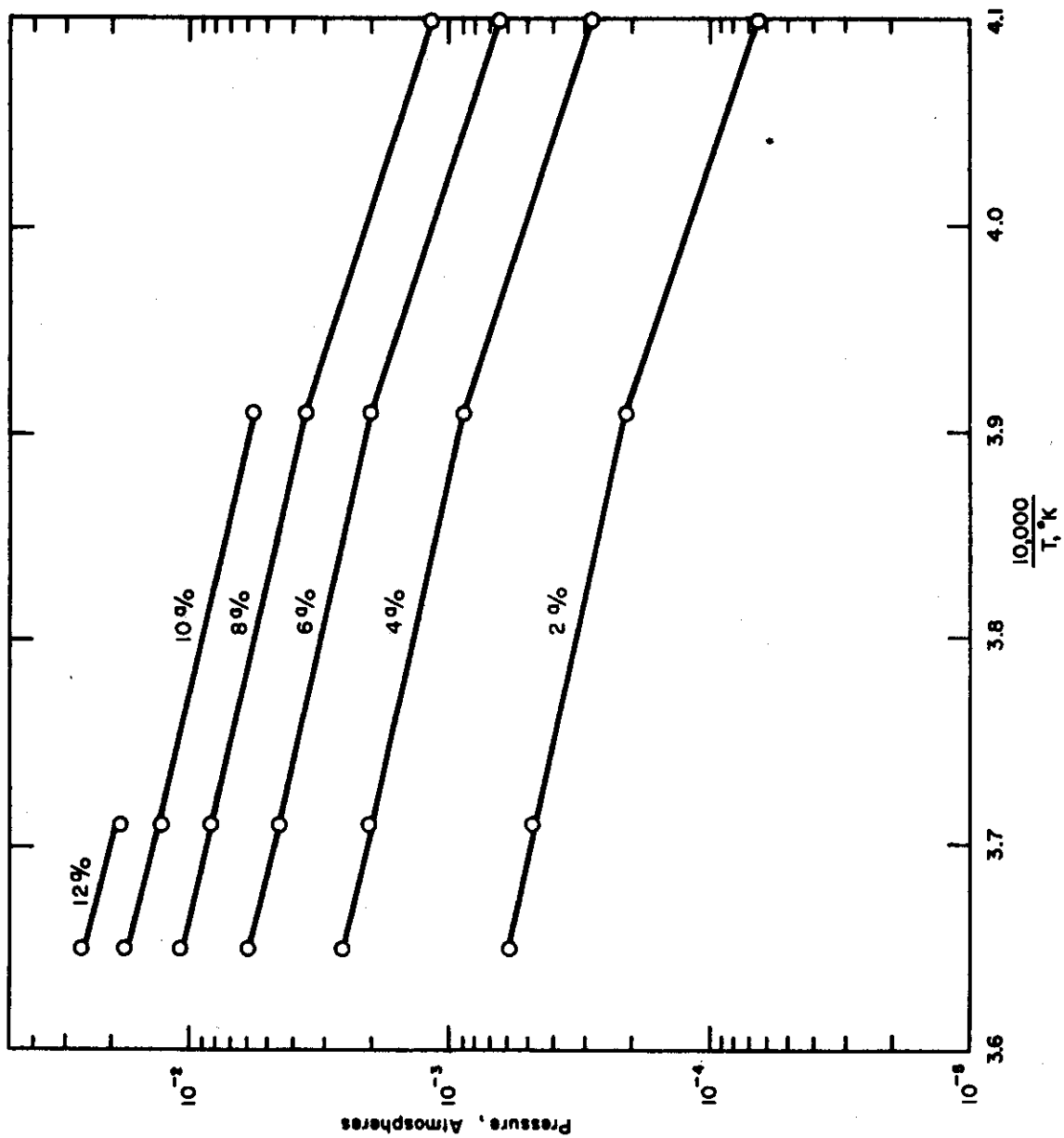
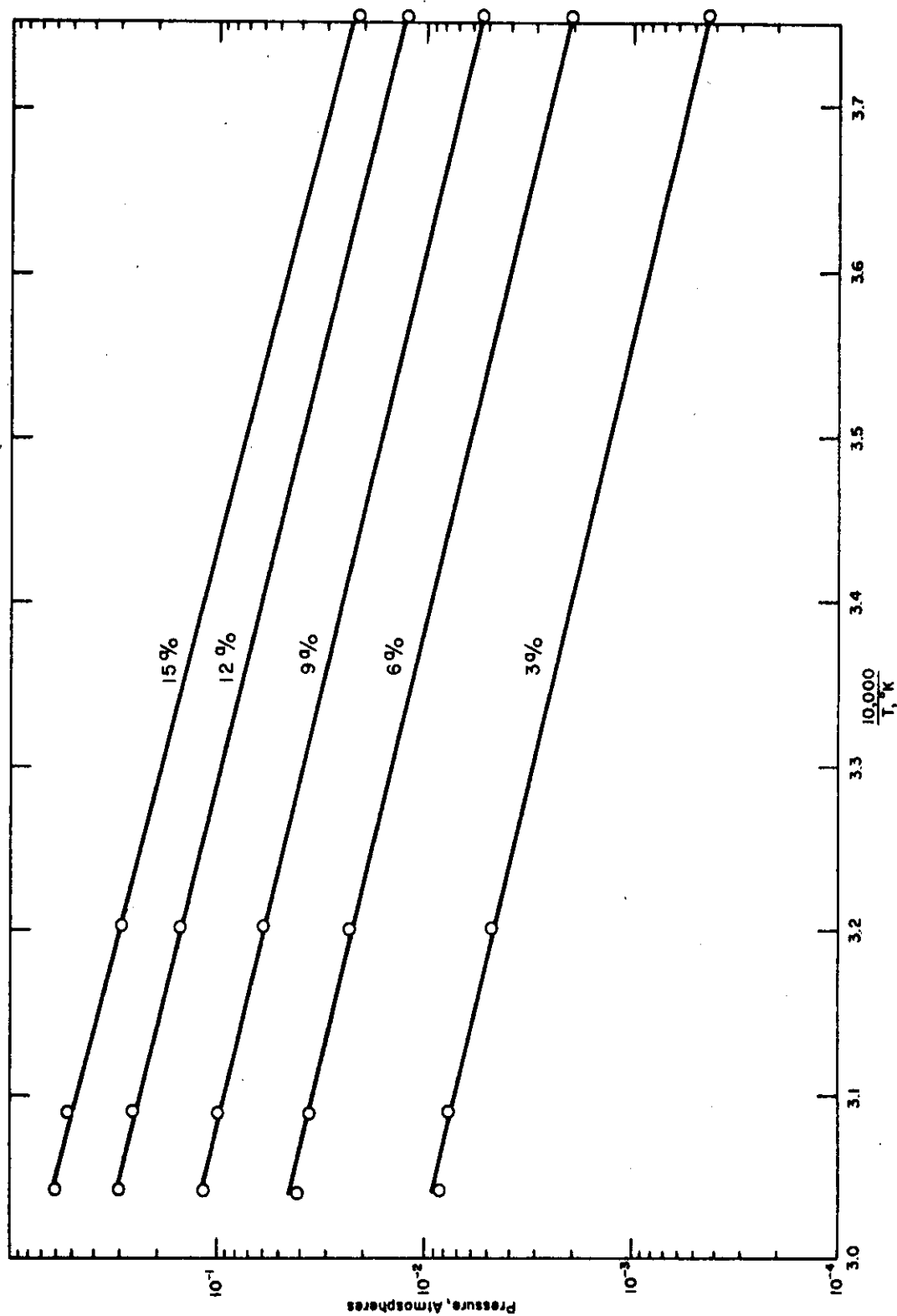Fig. 18 - Equilibrium pressure of nitrogen over niobium containing various amounts of nitrogen.

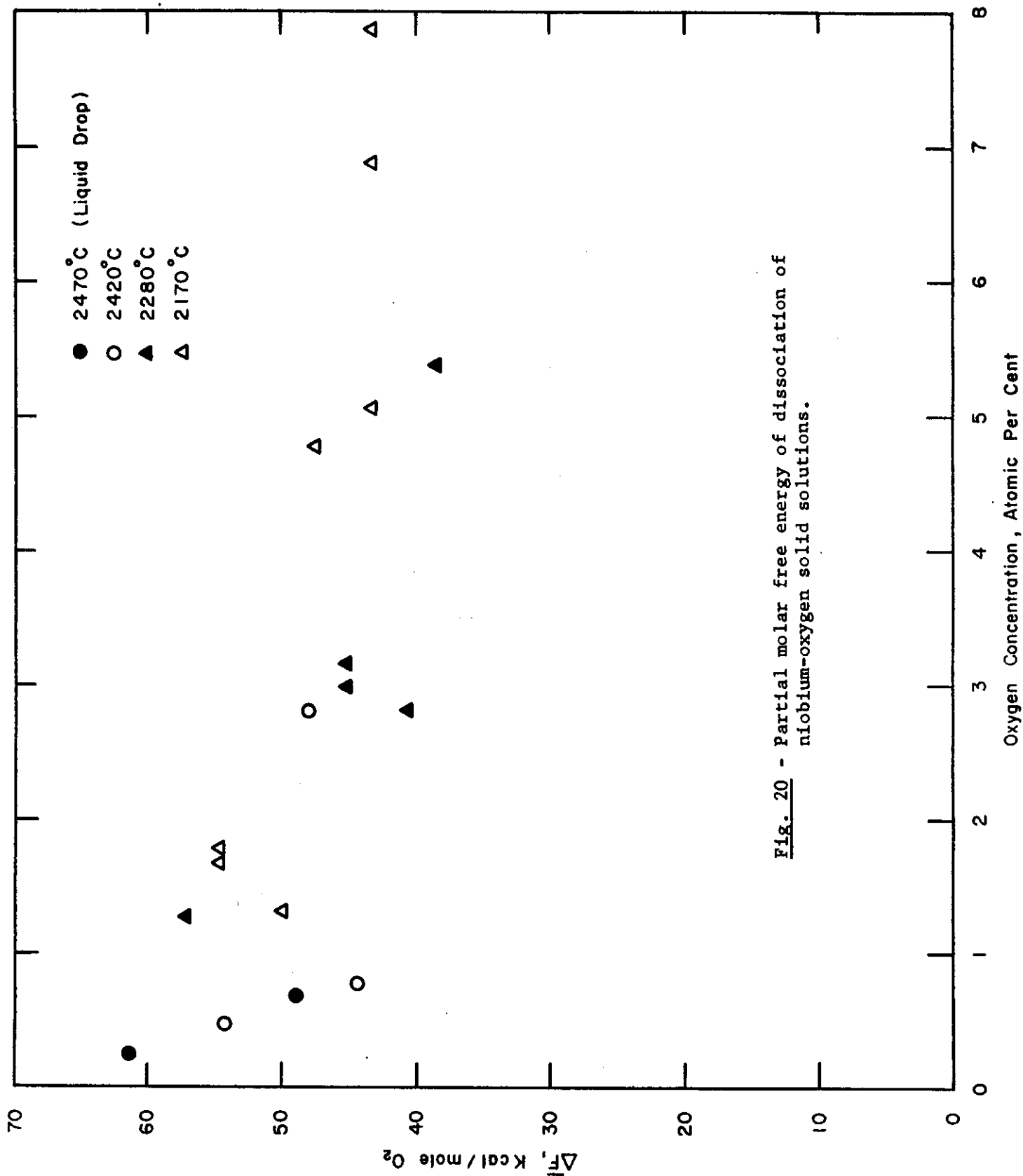Fig. 19 - Equilibrium pressure of nitrogen over tantalum containing various amounts of nitrogen.

Fig. 20 - Partial molar free energy of dissociation of niobium-oxygen solid solutions.

Legend:
● 2470°C (Liquid Drop)
○ 2420°C
▲ 2280°C
△ 2170°C

x-axis: Oxygen Concentration, Atomic Per Cent
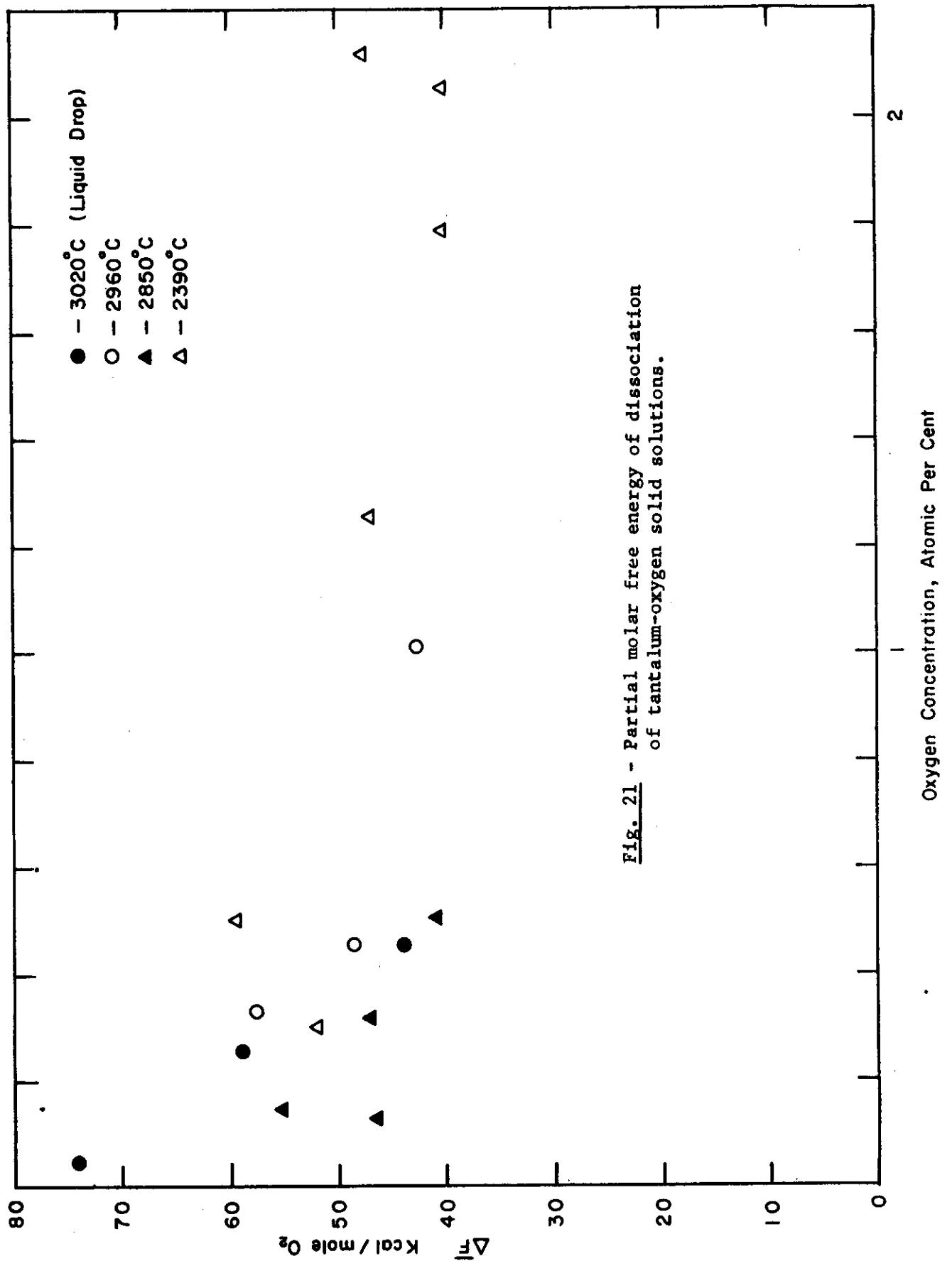
y-axis: $\Delta \bar{F}$, kcal/mole O_2

Fig. 21 - Partial molar free energy of dissociation of tantalum-oxygen solid solutions.
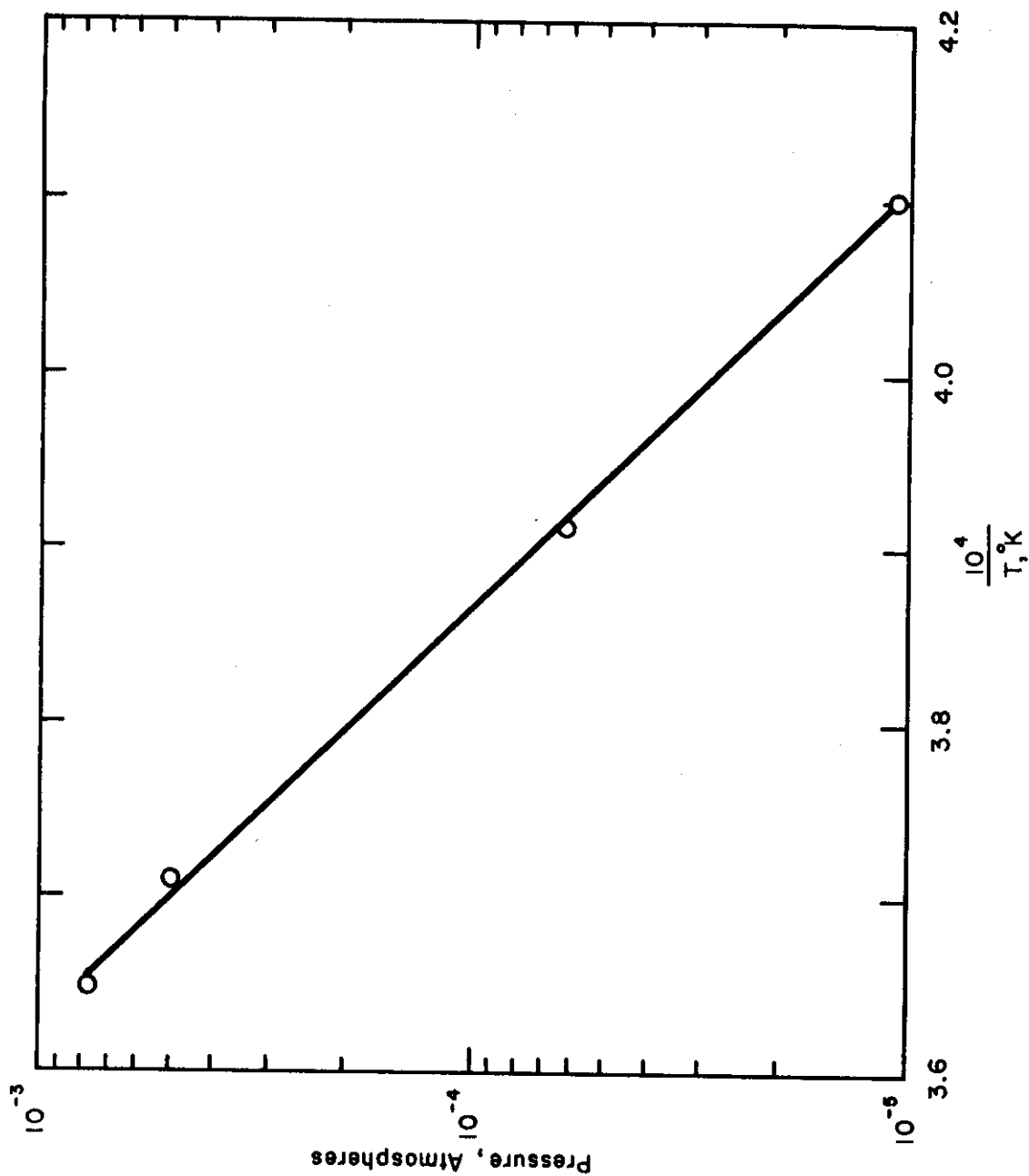
Fig. 22 - Equilibrium pressure of oxygen over niobium containing 1.75 atomic percent oxygen.
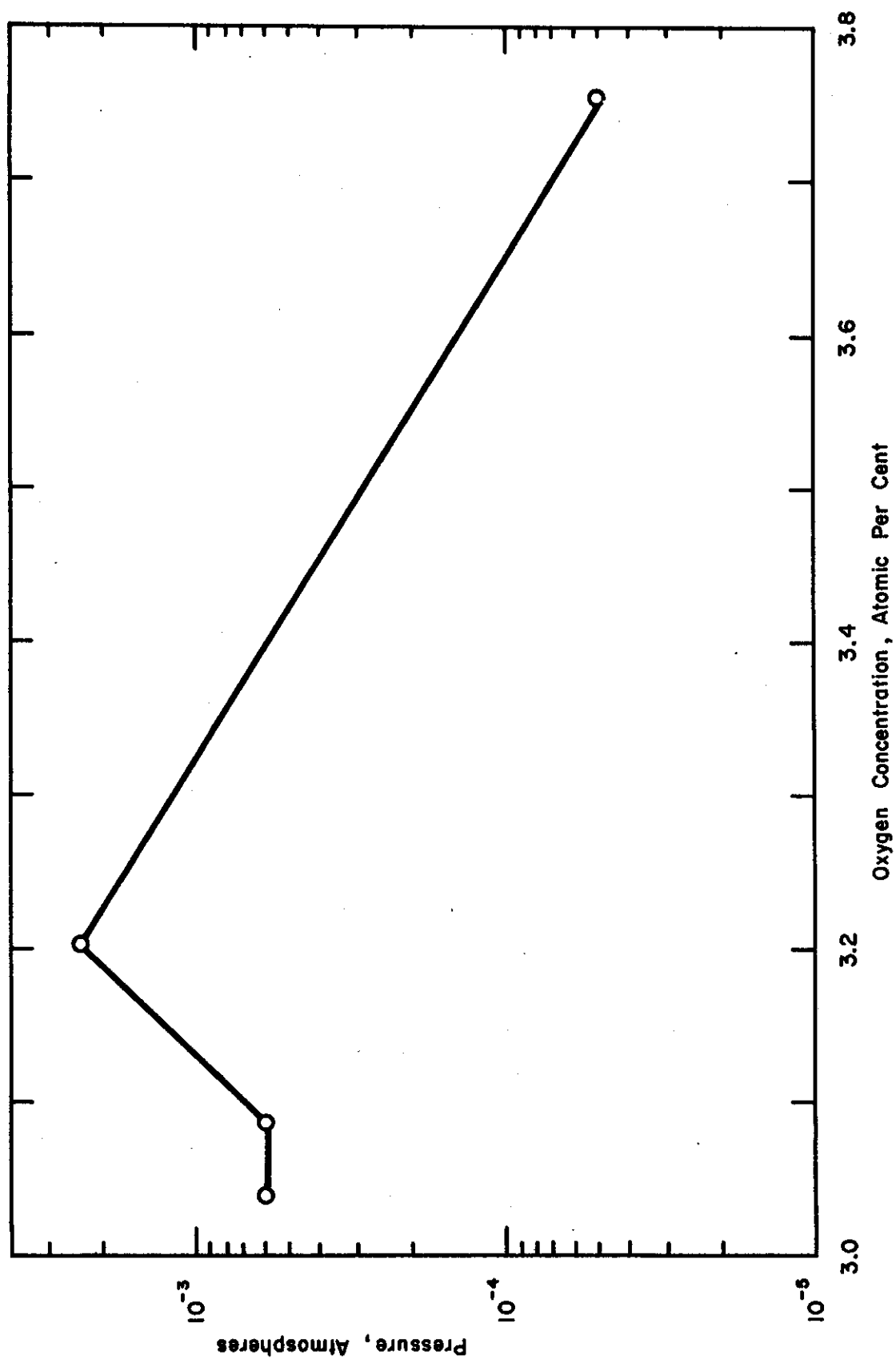
Fig. 23 - Equilibrium pressure of oxygen over tantalum containing 0.3 atomic percent oxygen.

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