

1964

The vaporization equilibrium for the system triniobium octaiodide-niobium metal

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KUST, Mary Angela, 1937-
THE VAPORIZATION EQUILIBRIUM FOR
THE SYSTEM TRINIOBIUM OCTAIODIDE—
NIOBIUM METAL.

Iowa State University of Science and
Technology, Ph.D., 1964
Chemistry, inorganic

University Microfilms, Inc., Ann Arbor, Michigan

THE VAPORIZATION EQUILIBRIUM FOR THE SYSTEM
TRINIOBIUM OCTAIODIDE—NIOBIUM METAL

by

Mary Angela Kust

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

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1964

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I. INTRODUCTION

With greater interest in the last few years in the fundamental chemistry of the heavy metals, there has been much interest in the chemistry of niobium, prompted by its far greater availability and its increasingly important uses. Niobium metal has a low neutron cross-section which makes it an excellent candidate for atomic energy applications; also, it is an important constituent in new high-strength, high-temperature alloys.

The chlorides and bromides of niobium have been extensively studied by Schäfer and co-workers (32, 33, 35, 36, 38, 39). Niobium(IV) chloride and bromide disproportionate readily to the corresponding solid trihalide and gaseous pentahalide; the trichlorides and tribromides are homogeneous over a composition range which extends from Nb_3X_8 to beyond NbX_3 . In addition, niobium(II) chloride exists, and niobium(II) bromide has been reported (13). The condensed niobium-iodine system has recently been well characterized (7, 44, 45) including the study of the equilibrium phase diagram; the iodide phases are NbI_5 , NbI_4 , NbI_3 , and Nb_3I_8 . Unlike the trichlorides and tribromides of niobium, the triiodide is a stoichiometric compound, although apparently metastable; at

about 513^{o*} it decomposes to Nb₃I₈ and a liquid phase from which it cannot then be re-formed at lower temperatures. The diiodide is non-existent; the solid iodide in equilibrium with the metal is Nb₃I₈ (NbI_{2.67 ± 0.02}).

It has been suggested (45) that a significant factor in the limited stability of the triiodide and in the absence of a diiodide may be an unusual stability of Nb₃I₈, perhaps a result of a polynuclear structure. Such structures are suggested (50) for the ions Ta₆Cl₁₂²⁺, Ta₆Br₁₂²⁺, and Nb₆Cl₁₂²⁺. These have a hexanuclear metal core, the metal atoms forming an octahedron with the halogens located on the perpendicular bisectors of the edges of the octahedron. A very similar structure is known for Mo₆Cl₈⁴⁺(5). Recent work (19, 22) has shown that the ion Ta₆X₁₂²⁺ (X = Cl, Br, I) has the same structure in aqueous solution and in the solid Ta₆X₁₄. Although there is a dissimilarity in the composition of the lowest tantalum iodide, Ta₆I₁₄, and that of the lowest niobium iodide, Nb₃I₈, it has been found (22) that the cation Ta₆Br₁₂²⁺ undergoes a two-electron oxidation with Fe³⁺ or Ce⁴⁺ in aqueous solution. The tetravalent ion, plus halide

*All temperatures are °C. unless otherwise noted.

anions, would be Ta_6Br_{16} , which, it has been suggested (45), could parallel Nb_3I_8 .

Only a very little information has been available concerning the vaporization of the niobium and tantalum chlorides, bromides, and iodides. All of the early work is summarized by Brewer (3). In a paper (33) concerned with the measurement of the disproportionation pressure of $NbCl_4$ by a dew point method, Schäfer discusses the $NbCl_5$ vapor pressure measurements reported by various authors. These measurements, taken by several methods, indicate that the pentachloride is monomeric and undissociated in the temperature range of the measurements, which extended up to about 240° . Among the measurements discussed were those of Alexander and Fairbrother (2) who determined the pressures of $NbCl_5$, $NbBr_5$, $TaCl_5$, and $TaBr_5$ with a Bourdon-type sickle gauge up to about 360° . There was no evidence for the dissociation of any of these, and at any given temperature the tantalum compounds showed slightly higher pressures than the corresponding niobium compounds. Later, Schäfer and Kahlenberg (39) reported $NbCl_5$ undissociated up to 600° by pressure measurements. Wiseman and Gregory (51) measured the vapor pressure of $TaBr_5$ between 200 and 345° with a glass membrane

manometer; they found no evidence of decomposition to free bromine, or of association of TaBr_5 in the vapor phase.

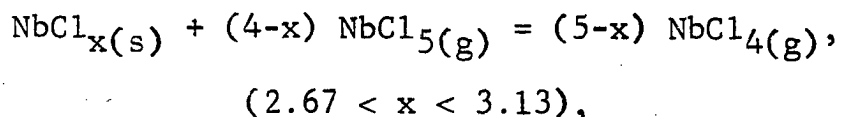
Shchukarev and Kurbanov (46) studied the sublimation and vaporization of TaCl_5 from 152 to 257° by a "membrane" method, and by the same method studied the apparent dissociation of gaseous TaCl_5 beginning at about 500°.

The vapor pressure of TaI_5 was measured by Alexander and Fairbrother (1) up to 540°. They did not observe dissociation of TaI_5 vapor, but reported that vapor pressure measurements of undissociated NbI_5 could not be made, since the solid NbI_5 was observed to give off iodine at a low temperature in a vacuum. Seabaugh (44) measured the total pressures above solid niobium iodide phases with I/Nb ratios between 4.1 and 4.9 at temperatures up to 400°; presumably, the principal contribution to this pressure was that of the dissociated iodine, but the extent of the possible contribution of the NbI_5 vapor pressure is not known.

Less work seems to have been done on the vaporization of the lower halides of niobium and tantalum. After Schäfer, Bayer, and Lehmann (33) measured the disproportionation pressure (NbCl_5) of NbCl_4 by a dew point method, Schäfer and Bayer (32) measured the saturation pressure of NbCl_4 (in the

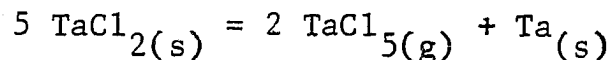
presence of NbCl_5 to suppress the disproportionation) at four temperatures from 304 to 374° by a quenching method.

The NbCl_4 vapor pressure is quite small compared to the NbCl_5 pressure from disproportionation, 44 mm. as compared to 3926 mm. at 374°, for example. Later, Schäfer and Dohmann (35) studied the variation in composition of niobium trichloride prepared by the chemical transport reaction



with varying NbCl_5 pressures. Observations made in the sublimation of lower niobium chlorides by Brubaker and Young (6) indicated that NbCl_4 was produced as the gaseous product of the disproportionation of lower niobium chlorides at about 600°. Frère and Michel (11) studied the decomposition of NbCl_4 in argon by differential thermal and thermogravimetric analysis. These results show that, beginning at 290°, NbCl_4 forms gaseous NbCl_5 and $\text{NbCl}_{3.13}$ as the new solid phase, and at 405°, $\text{NbCl}_{3.13}$ decomposes to $\text{NbCl}_{2.66}$, again with the formation of gaseous NbCl_5 . But at 750°, $\text{NbCl}_{2.66}$ decomposes in two steps, first to NbCl_2 and then to Nb, with the composition of the vapor lost in each step now being NbCl_4 . Frère (10) also studied the decomposition of TaCl_4 by

thermogravimetric analysis. $TaCl_4$ appeared to form gaseous $TaCl_5$ and the solid phase $TaCl_{3.2}$ beginning at about 285° , but little was learned about its decomposition beyond that point. Shchukarev, Smirnova, and Kurbanov (47) reported measurements of the $TaCl_5$ pressure for the reaction



from 660 to 740° . Shchukarev and Kurbanov (46) also reported measurements of the disproportionation pressure of $TaCl_4$ by a "membrane" method. Apparently, no other vaporization studies have been made of the niobium or tantalum chlorides, bromides, or iodides.

High purity niobium metal may be prepared by the van Arkel-de Boer or "iodide" decomposition process, a general technique available for the preparation of high-purity metals involving the use of elemental iodine and crude metal to form a volatile metal iodide and the subsequent thermal decomposition of the iodide into pure metal and gaseous iodine. Although metal chlorides and bromides, including those of niobium, may sometimes be used in this process, the metal iodides are particularly well suited for use since the metal iodides exhibit thermal stabilities lower than those of the corresponding bromides, chlorides, or fluorides. The ready

dissociation of gaseous iodine is an important factor in the thermal decomposition of the iodides, especially those of the higher valence elements, because it provides a large increase in the number of moles of gas formed on dissociation. This leads to a large positive entropy for the dissociation, and even though the heat of formation of the metal iodide has a moderately large negative value, the free energy of dissociation decreases rapidly with increasing temperature (29). The iodide process for the preparation of pure niobium metal has been studied by Rolsten (29, 30) and by McCarley and Tadlock (23, 24).

Because of the importance of the iodide process for niobium special need has developed for thermodynamic data for the niobium iodides, for knowledge of the iodides important in the vapor phase, and for their corresponding vapor pressures. However, no such data have been available.

Probably, the active species in the iodide process is the gaseous species in equilibrium with the solid phases triniobium octaiodide and niobium metal. To obtain information, including thermodynamic data, on such gaseous species, the vaporization of this system has been studied by means of both static pressure measurements with a Vycor diaphragm

gauge and dynamic pressure measurements by the transpiration or gas-saturation technique. Because pressures can only be obtained by the transpiration method if a molecular weight for the vapor species is assumed, the transpiration results may be compared with the actual total pressure of the system measured with the diaphragm gauge in order to deduce the correct species to give the necessary agreement of the pressures measured by the two methods. Thus not only is considerable insight gained as to the identity of the vapor species, but also the data may then be used to calculate the usual thermodynamic quantities.

II. MATERIALS, APPARATUS, AND EXPERIMENTAL PROCEDURES

A. Handling of Materials

Because all of the niobium iodides prepared or produced in this work were at least somewhat sensitive to atmospheric moisture, the work was done in glass systems which were either evacuated or contained an argon atmosphere. All niobium iodide samples were transferred in an argon-filled dry box. The argon used for flushing the box was dried by passing through a trap cooled to -80° and over Linde 4A Molecular Sieve and by maintaining a supply of exposed phosphorus(V) oxide in the dry box.

B. Preparation of Triniobium Octaiodide

As Nb_3I_8 was prepared from NbI_5 , the pentaiodide was prepared first from niobium metal and iodine, as described by Corbett and Seabaugh (7). High purity niobium metal shot, a special DuPont sample, was obtained through the courtesy of Dr. C. A. Swenson of this Laboratory. Principle impurities were: oxygen, 64 ppm; tantalum, 175 ppm; nitrogen, 1 ppm; carbon, 13 ppm; and iron, chromium, nickel, and tungsten, each less than 50 ppm. Iodine (J. T. Baker Reagent) was

purified by subliming in vacuo at ca. 80° . The metal and excess iodine in sufficient quantities to prepare about 40 grams of NbI_5 were heated in opposite ends of an evacuated, V-shaped Pyrex tube at 500 and 180° respectively. After about 40 hours the reaction was complete, and the pentaiodide had sublimed to the junction of the two furnaces. The end of the tube which had contained metal was cooled to within 80° of the iodine end to avoid decomposition; then the tube was cooled uniformly to room temperature.

The NbI_5 was removed in the dry box by breaking the tube and was transferred together with a 15 to 20% excess of niobium metal shot to a short Vycor tube fitted with a ball joint for evacuation for preparation of Nb_3I_8 . The Vycor container was evacuated and flamed before being taken into the dry box because of the sensitivity of NbI_5 to moisture. After being filled, the tube was re-evacuated and sealed off.

The NbI_5 and niobium were heated slowly to 800° and equilibrated at that temperature for periods of three days to two weeks. Two samples were prepared by equilibrating three days at only 640° . After reaction the tube was opened in the dry box, the excess Nb shot removed, the sample finely ground, and then a portion of the sample was removed for analysis.

The remaining sample, including the excess metal, was transferred to a glass tube, evacuated, and sealed off for storage. The I/Nb ratios for the samples equilibrated at 800° fell in the range 2.58 to 2.67 with one exception, 2.48; the ratios for the samples equilibrated at 640° were 2.65 and 2.67. Powder patterns were obtained from all these samples, and from these the presence of the compound Nb₃I₈ (44, 45) was confirmed.

At the start of this work, Nb₃I₈ was prepared by thermal decomposition of NbI₅. First, NbI₅ in one end of a sealed, evacuated Pyrex tube was heated slowly to 400° and held at that temperature two or three days; the iodine evolved was collected in the other end of the tube at about 35° where the iodine vapor pressure is ca. 0.8 mm. The residue of this decomposition, NbI₃, was transferred in the dry box to a Vycor tube which was then evacuated and sealed for further decomposition. Finally, NbI₃ in one end of this tube was heated at temperatures between 500 and 700°, and NbI₄ and NbI₅ together with some NbI₃ condensed in the other end of the tube at room temperature. Powder patterns of the residue identified it as Nb₃I₈, but often the I/Nb ratios determined by analysis were higher than 2.67. Even after long heating

(ca. 40 hrs.) at temperatures less than 600° , the I/Nb ratio of the residue remained near 2.75. However, at temperatures of 650° or greater, NbI_3 decomposed rapidly to niobium metal; after a few hours the I/Nb ratio was often less than 1.00.

For pressure measurements Nb_3I_8 samples were desired which would be free of NbI_3 , but samples produced by the above method often contained some NbI_3 or were too low in Nb_3I_8 . Since it was somewhat difficult to adjust the temperatures and times for the decomposition so that satisfactory Nb_3I_8 samples could be obtained, the first, much more convenient method described above was employed for the preparation of all samples used in this work.

C. Pressure Measurements by the Transpiration Method

In the transpiration or gas-saturation method for measuring vapor pressures, inert gas is saturated with vapor by passing it through or over the sample at a particular temperature. The quantity of material vaporized is obtained either from the loss in weight of the sample or from the weight of the vapor condensed from the gas stream. Assuming Dalton's Law of Partial Pressures and the ideal gas law, the partial pressure of the vapor, P_v , is calculated from the

formula

$$P_v = (n_v)/(n_v + n_a) (P_t)$$

where n_v is the number of moles of material vaporized, n_a is the number of moles of inert gas passed over the sample and P_t is the total pressure over the sample.

This method provides an indirect measurement of the vapor pressure since the molecular weight of the vapor species must be known or assumed. However, the complexity of the vapor may be inferred from a comparison of transpiration and static pressure measurements (25).

The principal problem encountered in the use of this method is that of achieving saturation of the flow gas. To check for saturation at a given temperature, runs must be made at various flow rates to find, hopefully, a range of flow rates for which the ratio n_v/n_a is constant. This ratio may increase rapidly as the flow rate approaches zero due to the increasing importance of the contribution of diffusion to n_v , while it will decrease and approach zero as the flow rate becomes too fast for the carrier gas to be saturated. A plot of (n_v/n_a) vs. flow rate will usually show a plateau for those flow rates where saturation is complete (20, 26). The transpiration method, among other methods for vapor pressure

measurement, is discussed in several reviews on vapor pressure measurements (18, 25, 48).

The Vycor transpiration cell employed in this work is shown in Figure 1. The carrier gas, argon, entered the outer cell through the side tube and was heated in the outer cell before reaching the sample. Then it passed over the sample at the end of the cell, back through the center tube where niobium iodides condensed from the vapor, out through a trap at -80° for iodine, and on to the gas measuring system. Before entering the cell the argon flowed from the cylinder through a n-butyl phthalate pressure regulator, through a trap at -80° , over Linde 4A Molecular Sieve, and over tantalum metal pieces heated to 800° . The latter three removed traces of water and oxygen. This apparatus is shown in Figure 2.

The horizontal 16" Marshall tube furnace heating the cell contained a 0.25"-thick Inconel liner to smooth out the temperature gradient; shunts on the furnace taps were also used for the same purpose. The temperature gradient was about 2 to 4° over the last three inches of the cell with the sample-containing end of the cell being coolest. One end of the furnace was closed with Transite, while Fiberfrax

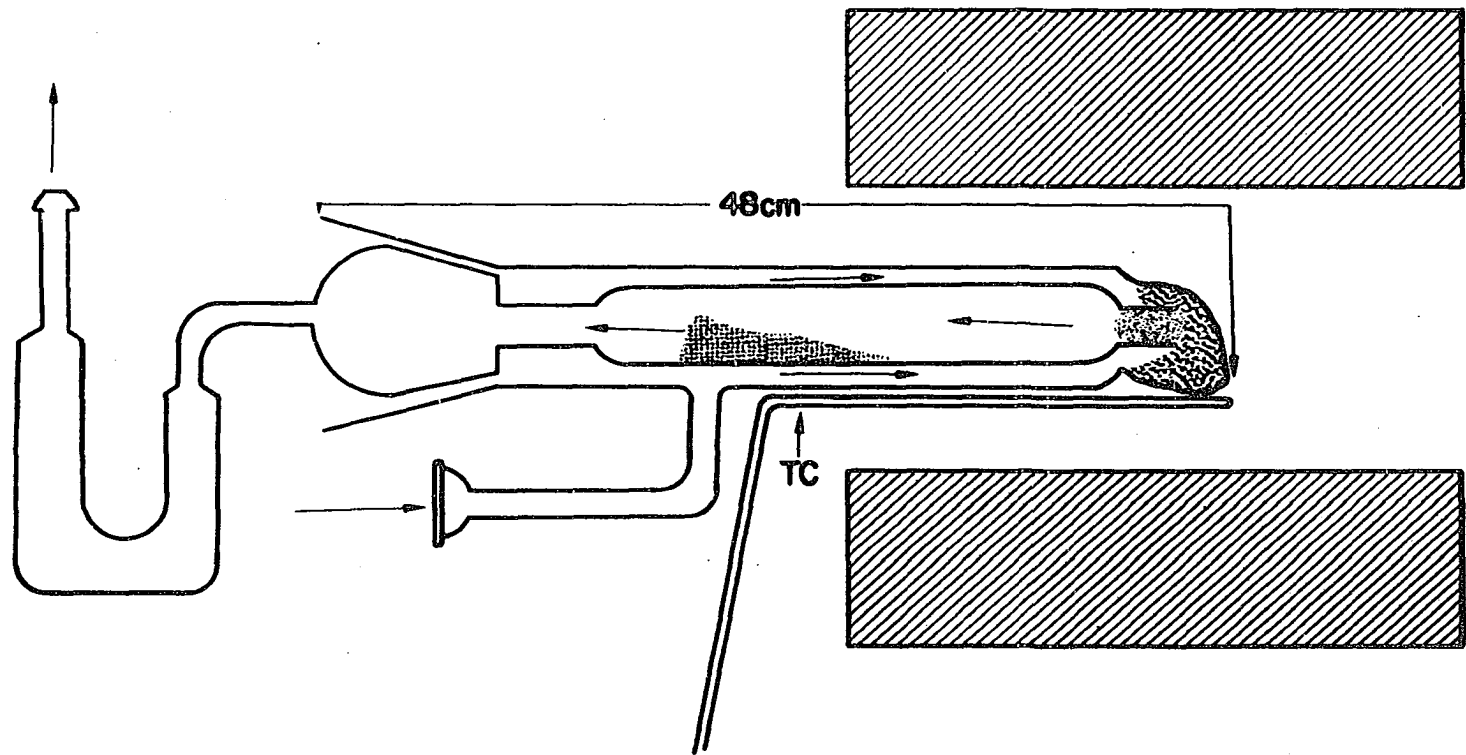


Figure 1. Vycor transpiration cell

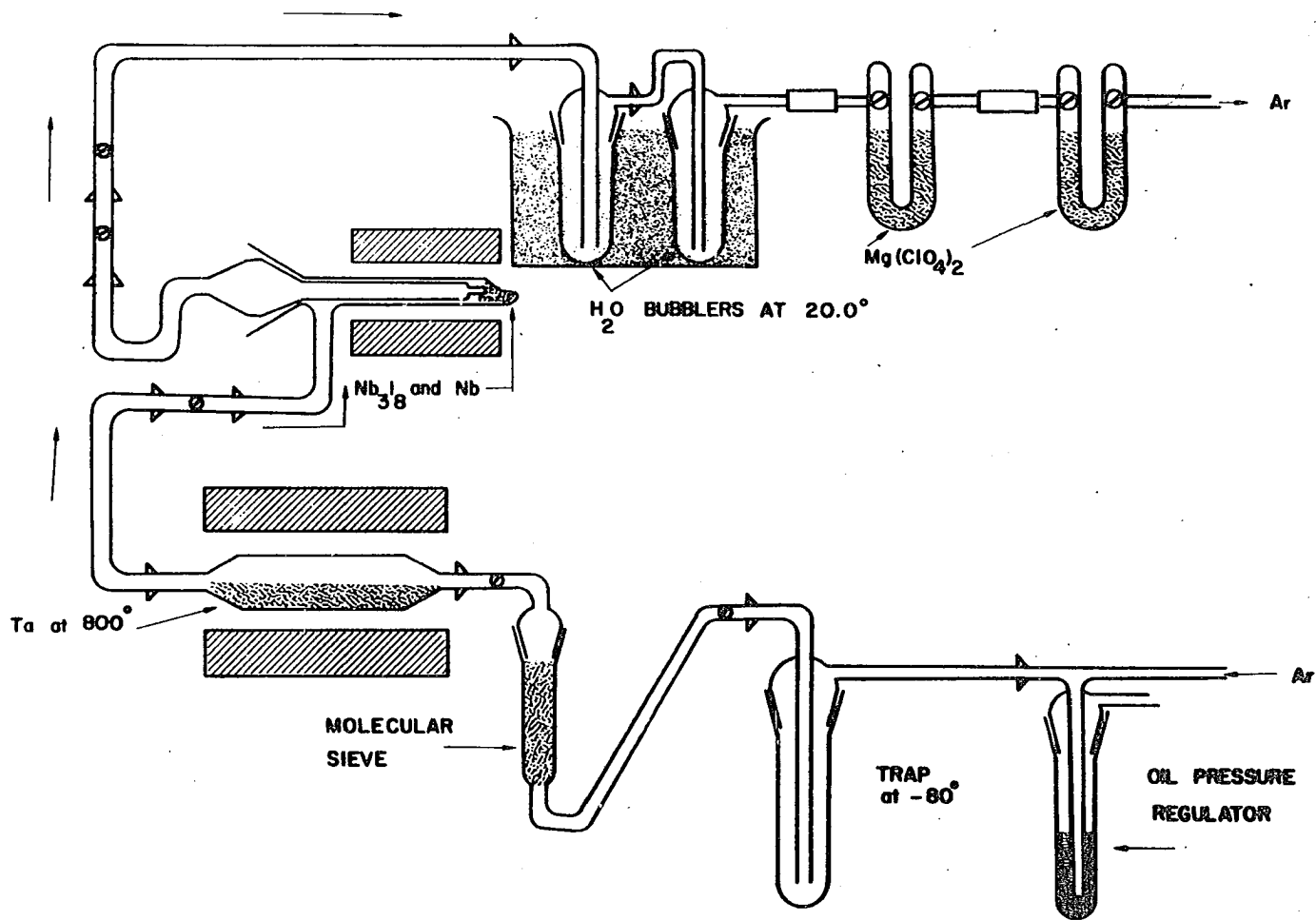


Figure 2. Transpiration apparatus

(Carborundum Co.) insulation was packed around the cell at the other end. The furnace temperature was regulated by a Leeds and Northrup Speedomax Controller with its thermocouple in contact with the inside walls of the furnace. A one-ohm, 25-amp. variable resistor was connected in series with the furnace and parallel with the controller switch so that high or low power, depending on the switch position, was always supplied to the furnace. Careful adjustment of both the resistor and the Powerstat supplying the furnace reduced the temperature cycle caused by the controller operation to $\pm 1^{\circ}$.

Before being filled the cell was baked out under dynamic vacuum at about 750° for several hours. It was then taken in the dry box, and about 12 grams of Nb_3I_8 and 2 grams of niobium metal were placed in the bottom of the outer cell. In most cases, at least two grams of this consisted of an iodide sample that had not been used previously. The narrow (inlet) end of the inner tube was packed with coiled strips of niobium metal to insure good contact of the vapor with the metal and to hinder diffusion of the iodide vapor. In addition, the metal coils were easily removed at the end of the run for access to the condensed iodides. After being removed from the dry box, the cell was re-evacuated, then filled

carefully with argon to about three-fourths atmospheric pressure. The adjustment of the desired flow rate, facilitated by passing the argon through a flowmeter, was made before connecting the cell to the gas flow system. The furnace was heated to about 20° above the desired temperature before placing the cell in the furnace and connecting it to the gas flow system. About 20 to 30 minutes were then required before the cell and furnace again reached the desired temperature; then argon was allowed to pass through the cell, beginning the run. Although at the higher temperatures small amounts of iodine and niobium iodides sublimed to the cool part of the outer cell during this period, none appeared to collect in the inner tube where the vapor was to be condensed.

During the run the total pressure in the cell was read from the level of the n-butyl phthalate regulator. The sample temperature was measured with a chromel-alumel thermocouple fastened to the outside of the cell with the junction even with the sample end of the cell and a Leeds and Northrup Temperature Potentiometer Model 8693. In order to measure the quantity of argon passed through the transpiration cell a second, simultaneous transpiration run was made with water.

The argon, after leaving the cell, was bubbled through water in gas washing bottles immersed in a constant temperature bath, and then it was passed consecutively through two identical tubes filled with anhydrous magnesium perchlorate. At the beginning and again at the end of each run the tubes containing the magnesium perchlorate were weighed to find the weight of the water transported by the argon; the second tube, filled with argon at the same pressure as the first, was used as a counterpoise. From the known vapor pressure of water (15) at the temperature of the bath (20.0°) and the number of moles of water collected, the number of moles of argon which passed through the cell could be easily calculated.

At the end of each run the stopcocks on the cell and on the magnesium perchlorate tubes were closed, stopping the argon flow through the cell, and the cell was removed from the furnace to cool. Niobium iodides had condensed from the carrier gas in a band about half-way up the inner tube, and iodine had condensed both in the inner tube and in the trap at -80° . After the hot end of the cell reached room temperature, the cell was carefully evacuated and the iodine was pumped into the trap. Then the trap was sealed off, and the

amount of iodine determined. The rest of the transpiration cell was taken into the dry box where the inner tube was removed and the metal strips pulled out of the open end. Then the condensed iodides were scraped out onto a weighing paper and transferred to a small weighing bottle for analysis by ignition to Nb_2O_5 . It was possible to scrape out the condensed iodides quite cleanly, losing extremely little in the process and leaving almost nothing behind. At least 0.3 gram of condensed iodides was collected in each run to insure a reasonable degree of accuracy. After each run, the iodine trap was reattached to the cell and the cell rinsed thoroughly with 48% hydrofluoric acid to ready it for the next run.

D. Pressure Measurements with the Vycor Diaphragm Cell

Static dissociation pressure measurements were obtained with the aid of a null-type, Vycor diaphragm gauge (Figure 3) similar to that described by Daniels (8). The most sensitive gauge, which was used for the measurements below 700° where attack of the glass by the niobium iodide is quite slow, had a sensitivity of about two mm. deflection per mm. pressure differential. Two other gauges, used for measurements only

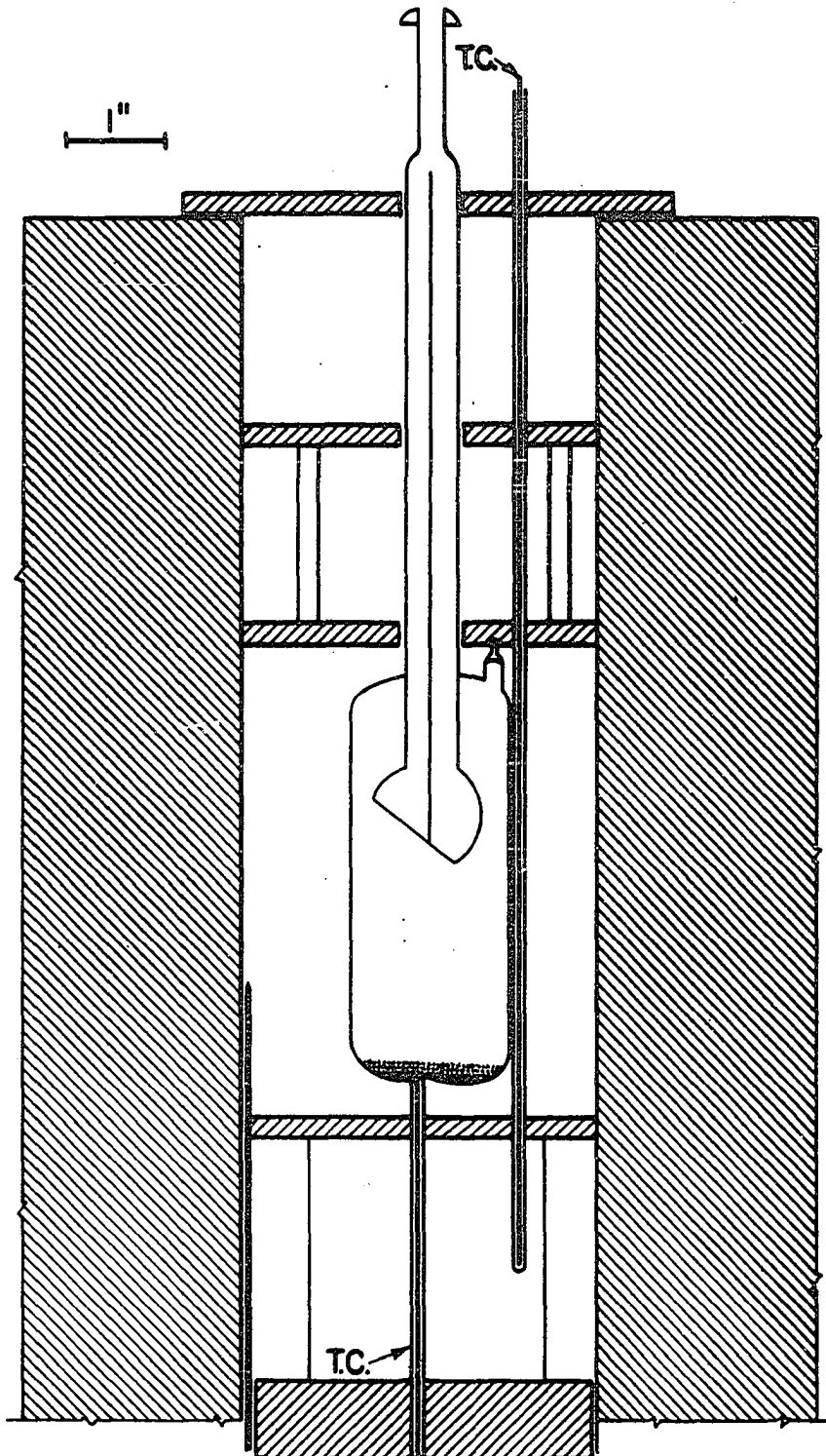


Figure 3. Vycor diaphragm cell

after prolonged heating at temperatures above 700° which resulted in considerable attack of the glass, had sensitivities of about 0.5 mm. deflection per mm. pressure differential. Null points of all gauges were invariant to at least 700° . The pointer position was viewed with a 15X telescope; the pointer of the most sensitive cell responded to pressure changes far smaller than those which could be read from the manometer (0.1 mm.). Pressures indicated on the manometer were read by means of a cathetometer equipped with a 15X telescope. The apparatus used with the diaphragm cell is shown in Figure 4.

The cell was placed in a vertical, 12" Marshall tube furnace with Transite covering at the top and bottom of the furnace. The sample temperature was measured with a chromel-alumel thermocouple placed in a small indentation in the bottom of the cell. The temperature was read with the same Leeds and Northrup Temperature Potentiometer used with the transpiration cell. A second thermocouple parallel to the cell wall, shown in Figure 3, was used to measure the temperature gradient along the cell; the gradient used was about 8 to 12° in the temperature range 600 to 750° with the top of the cell being hottest. A stainless steel liner in the

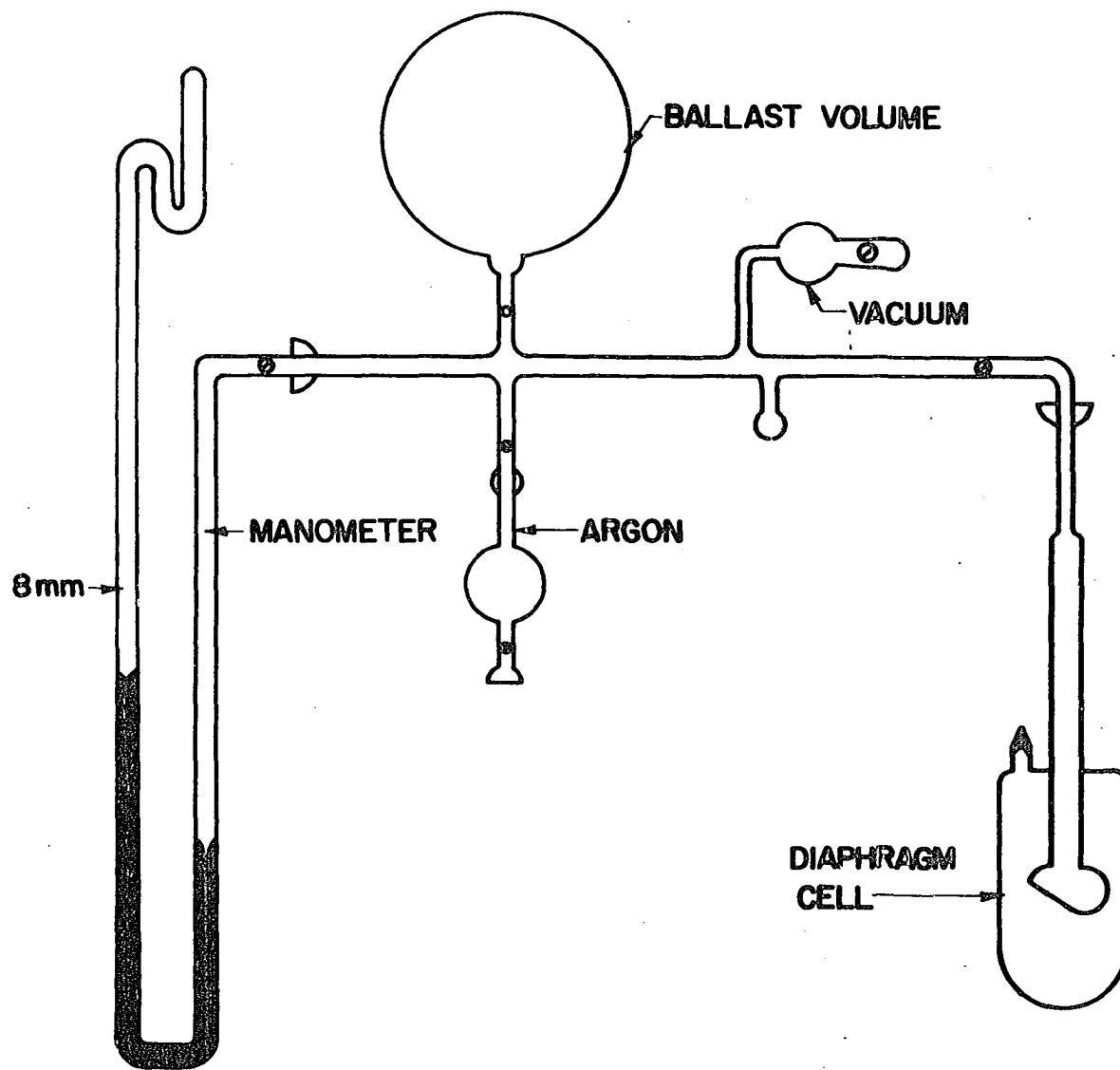


Figure 4. Diaphragm cell apparatus

furnace and convection baffles of Transite at the top and bottom of the cell aided in smoothing the temperature gradient, and this was further reduced by means of shunts on the furnace taps. A Brown proportioning controller with its thermocouple in contact with the inside wall of the furnace regulated the furnace temperature.

Before the cell was filled, it was evacuated with a diffusion pump and baked out approximately six hours at 500° . After being filled with about 3 grams of Nb_3I_8 and 1.5 grams of niobium metal the cell was re-evacuated for 2 hours at 400° , then 2 hours at 500° . A trap immersed in liquid nitrogen condensed a very small amount of iodine which sublimed from the cell during this time; traces of niobium iodides also sublimed from the cell. The cell was then cooled to room temperature, sealed off, and pressure measurements begun.

E. Analyses

I/Nb ratios and total Nb for the solid niobium iodides were obtained by ignition of the weighed samples to Nb_2O_5 , since only niobium and iodine were present. The portion of the sample to be analyzed was transferred in the dry box to

a small weighing bottle which was brought out into the air and weighed both full and empty. A negative buoyancy correction for argon was applied to the sample weight.

The Nb_3I_8 preparation equilibrated at 640° and the niobium iodide condensate from the transpiration runs should have been quite pure because even at 713° , the highest temperature at which a transpiration run was made, the reaction of the niobium iodides with glass (which would have contaminated the condensed samples with NbO_2I) was observed to be quite slow. This reaction is discussed more fully in part B of section III. I/Nb ratios for the above cases are considered to be ± 0.03 based on the estimated errors in the analysis. I/Nb ratios obtained for the Nb_3I_8 preparations equilibrated at 800° were occasionally somewhat low, probably because these almost certainly contained traces of oxyiodide. The lowest I/Nb ratio for any of the preparations, 2.48, was found for the only sample in which the concentration of contaminants was sufficiently high so that lines attributed to NbO_2I appeared in the powder pattern of the bulk sample. (The silicide adhered to the glass tube walls, and its lines were never seen in the sample powder patterns.) For a Nb_3I_8 sample containing 10% (by weight) NbO_2I , the apparent I/Nb

ratio determined from the analysis by ignition would have been 2.44. Since the I/Nb ratios for the other preparations were between 2.58 and 2.67, they probably contained considerably less than 10% NbO₂I.

Iodine condensed in the transpiration runs was dissolved in a potassium iodide solution and used to titrate a standard solution of arsenic(III) oxide (9) using Thiodene (Fisher) as the indicator.

X-ray diffraction patterns were obtained on samples in ca. 0.1 mm. glass capillaries that had been filled in the dry box. The samples were mounted in a 114.6 mm. Debye-Scherrer powder camera and exposed to Ni-filtered Cu K α radiation. NBS tables (50) were used to convert θ to distances where these were needed.

III. EXPERIMENTAL RESULTS

A. Pressure Measurements by the Transpiration Method

The first measurements of the dissociation pressure of triniobium octaiodide were made by the transpiration method. This had the advantage of making possible a determination of the over-all I/Nb ratio for the vapor phase, since a sample of the equilibrium vapor was removed, condensed, and analyzed. With the assumption that any niobium-containing vapor species contained only one niobium atom per molecule, the pressure of this species was calculated from the number of gram-atoms of niobium found in the condensed vapor. Over the temperature range 613 to 714° where transpiration pressure measurements were made, the composition of the vapor phase corresponded closely to that of NbI₄, and the pressure of the niobium-containing species increased from 1.2 mm. at 613° to 34.5 mm. at 714°.

In order to obtain reproducible results, rather large (about 14 grams total) samples of Nb₃I₈ and niobium metal were needed. Apparently, in the transpiration cell used, large amounts of the solid phases were required to obtain saturation of the carrier gas even at the slowest possible

flow rates. At a given temperature and a fairly constant flow rate a series of pressure measurements made on large samples fell in a range of about $\pm 10\%$ around the average value for the series. Smaller samples appeared to give consistently lower results, so all flow rate studies and equilibrium measurements were made on large samples which filled the sample-containing end of the cell. It was also necessary to use samples for which the I/Nb ratio of the salt was greater than about 2.2; if the ratio was less than this, the pressure was again too low, perhaps due to niobium formed on the surface of the salt. Because vaporization of the sample during a transpiration run left it depleted in iodine, each one could be used in only a few transpiration runs, and in most cases about 2 grams of unused salt was added to the sample before each run. However, the addition of fresh sample was not necessary provided that only a small quantity (less than one gram) of the sample had been vaporized, since runs made with samples which had been used in transpiration runs several times but from which comparatively little iodine had been removed gave results in satisfactory agreement with those obtained with fresh samples.

Flow rate studies were made near each end of the

temperature range of the measurements to find out whether the argon carrier gas was being saturated with the vapor so that equilibrium pressures were being measured. The results are shown in Table 1. Since the pressures were measured at temperatures differing by as much as 4° as well as at different flow rates, the pressures in each series were corrected to correspond to pressures at a single temperature for each series with the aid of the rate of change of the equation representing the entire group of transpiration pressure measurements,

$$d \log P_{\text{mm}} = - 12.77 \times 10^3 d(1/T).$$

At 623° the flow rate was increased seven-fold without any appreciable difference in the pressures measured. The lowest flow rate used, about 2 ml./min., was apparently satisfactory up to 656° . At 696° the flow rate 5.40 ml./min. was too low, since the pressures measured at this and lower flow rates were much higher than those measured at 8 to 23 ml./min., which agreed very well. The flow rate 27.8 ml./min. at 696° may have been a little too high, since the pressure measured was a little lower than would have been expected from the usual range of reproducibility (the deviation in $\log P_{\text{mm}}$ at this flow rate and temperature was -0.077

Table 1. Representative transpiration flow rate studies

Temperature, °C	Argon flow rate ml. STP/min.	Pressure ^a mm. Hg	I/Nb ratio of vapor
623	1.94	1.59 ^b	3.76
	1.98	1.76	3.70
	14.7	1.60	4.01
	14.3	1.67	3.92
656	2.17	5.61	3.80
	2.83	5.86	--
	3.44	5.18	3.91
	6.52	5.50	3.83
	6.55	5.50	3.90
	7.58	5.83	--
696	5.40	24.2	3.91
	8.34	19.8	3.95
	22.8	19.3	3.95
	27.8	16.6	3.95
	37.1	14.9	3.99
706	7.75	28.8	3.99
	10.3	24.9	3.95
	15.2	28.3	3.99
	17.9	24.3	3.88

^aThe pressure measured was that of the niobium iodide species in the vapor.

^bThis pressure was corrected from 613°.

whereas the standard deviation in $\log P_{\text{mm}}$ for all data was 0.030). The pressure measured at 37.1 ml./min. at 696° was clearly far too low; this flow rate obviously did not permit

saturation of the argon. At 656° and 706° no effort was made to extend the flow rate ranges beyond those given, although rates up to at least 14 ml./min. at 656° and 23 ml./min. at 706° should have been satisfactory.

At any temperature at least a three-fold variation in flow rates could be made without noticeable effect on the pressures measured, or on the vapor composition (see below). Therefore, it was concluded that the pressures, all of which were obtained with flow rates in the satisfactory ranges, represent equilibrium values.

The I/Nb ratios found for the vapor showed considerable scatter, varying from 3.70 to 4.12; both the lowest and the highest ratios were obtained at the lower end of the temperature range, near 625°. Figure 5 gives a graphical representation of the data for the overall vapor composition. Two of the ratios included are for runs from which no pressure measurement was obtained due to poor temperature control, $\pm 10^\circ$. For three of the runs from which good pressure measurements were obtained it was not possible to obtain I/Nb ratios due to loss of the iodine. The average of the 29 values for the I/Nb ratio is 3.91, and no particular trend with temperature is apparent from Figure 5. (The scatter is

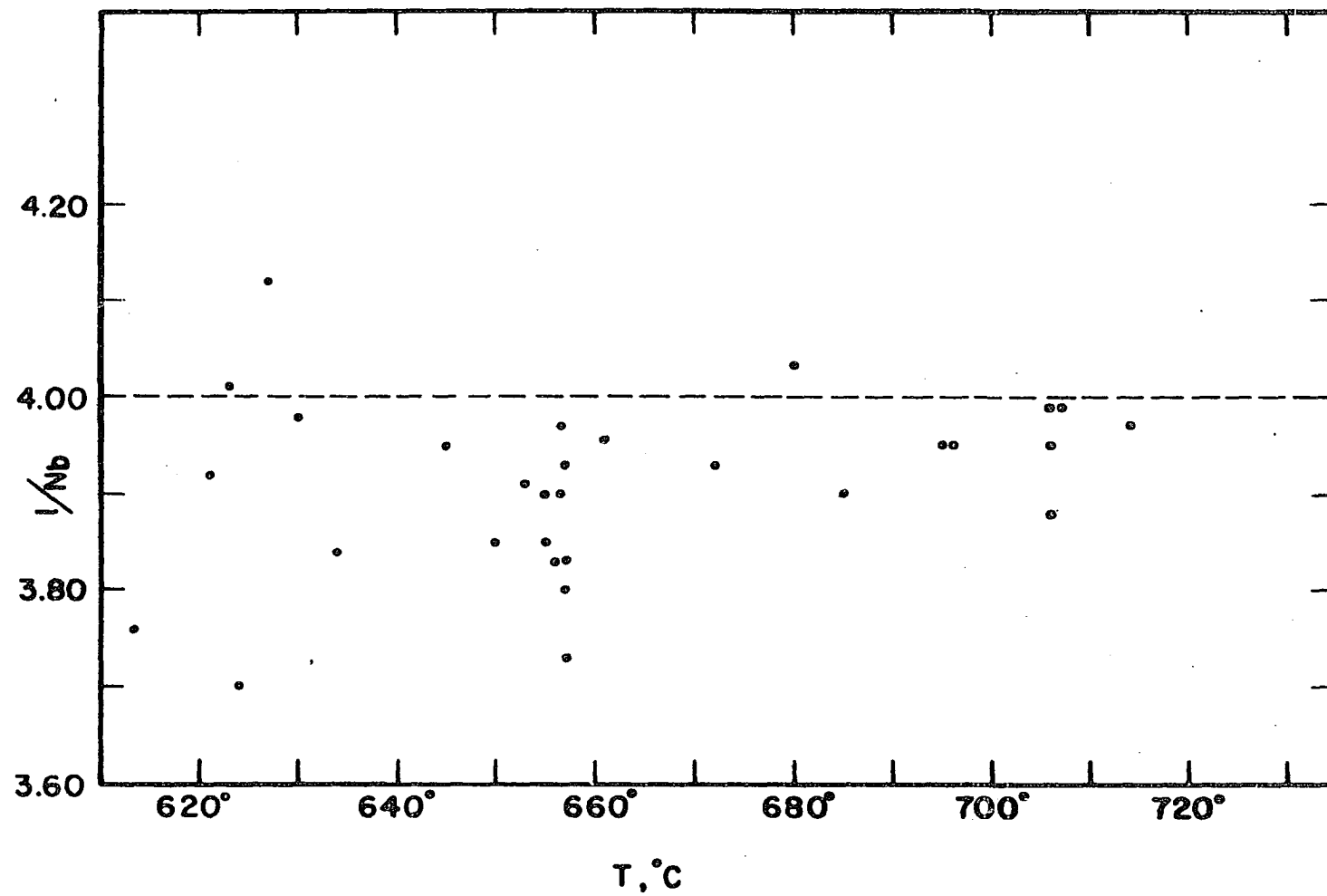


Figure 5. I/Nb ratios for the vapor phase, 613-714°, from transpiration studies

greater at the lower temperatures where the quantity of condensed vapor collected was much smaller.) Although the two lowest flow rates at 613 and 623° also gave two of the lowest I/Nb ratios, this does not appear to be significant as the other very low ratio was obtained at 656° with a flow rate in the middle of the range used, and the lowest ratio found at 706°, 3.88, occurred at one of the higher flow rates.

The presence of a niobium oxyiodide in the vapor would have lowered the ratio since most of the iodine weight was obtained by difference in the ignition. However, such an oxyiodide did not appear to be present in the vapor for several reasons. First, although powder patterns of samples used in three of these runs showed lines attributable to a substance assumed to be NbO_2I (discussed below in part B of this section), pressure measurements made with these samples did not appear significantly different in any way. In fact, in all the transpiration runs no correlation was found between the I/Nb ratio and the corresponding pressure measurement, and no oxyiodide was ever visible in the condensate. The NbO_2I appeared to be quite nonvolatile, as was indicated by the results of a transpiration run made with a

sample whose apparent I/Nb ratio was less than 2.00 and whose powder pattern contained only lines attributable to NbO_2I . (The sample was the residue from the sublimation of Nb_3I_8 from a Nb_3I_8 - NbO_2I mixture.) The pressure measured in this run was exceedingly low, 1.62 mm. at 701° where the usual pressure measured was about 24 mm., and the I/Nb ratio for the gas phase in this case was 4.17. This small pressure can be attributed largely to traces of Nb_3I_8 remaining in the sample.

Finally, the lower I/Nb ratios were found at the lower temperatures, 656° and below, where attack of the glass which might have produced a volatile oxyiodide was judged to be absent, both from observations made with the diaphragm cells and from the appearance of the transpiration cells after these runs. Although at the higher temperatures the inside of the hot end of the transpiration cell was covered with a thin black coating which was perhaps a niobium silicide, this coating was extremely light indeed at temperatures below ca. 680° .

Since the transfer of oxygen from the feed metal to the filament in the iodide process for the preparation of niobium metal indicates the existence of a volatile oxyiodide at

these temperatures, such an oxyiodide may have been present in small quantities which could not be detected. NbOI_3 is suggested by Schäfer and Gerken (37) as the principal oxyiodide vapor species; although their studies of NbOI_3 and NbOI_2 indicated that the NbOI_3 sublimation pressure appeared to reach one atm. at $400\text{-}450^\circ$, they stated that gaseous NbOI_2 could hardly occur in perceptible quantities below 1000° . But 19% (by weight) NbOI_3 , for example, would be necessary to lower the I/Nb ratio of a condensate from 4.00 to 3.80, and it does not seem possible that such a large quantity was present.

The average composition of the niobium iodides condensed during the transpiration runs was about $\text{NbI}_{3.2}$, and sufficient free iodine was collected to bring the average composition of the vapor phase to $\text{NbI}_{3.91}$. The iodides condensed at the edge of the furnace, where the temperature was still fairly high and solid NbI_4 might be expected to have an appreciable iodine dissociation pressure (44). Although the results of the static pressure measurements indicate that the vapor-phase niobium iodide is probably NbI_3 , in condensation it evidently combines very readily with iodine, forming NbI_4 or NbI_5 . The niobium iodides condensed were identified by

powder patterns as mixtures of NbI_3 , $\alpha\text{-NbI}_4$, and NbI_5 .

The temperature range of the transpiration measurements was sharply limited by the rapid change in pressure with temperature, indicating a large heat of vaporization. Near the lower end of the range very long times were required to collect the minimum quantity of solid iodides necessary for analysis, ca. 0.3 gram. For example, at 613° only 0.29 gram was collected in 72 hours at the flow rate 1.98 ml./min. At the highest temperatures the pressures were sufficiently high so that only a small volume of argon could be passed through the cell without seriously depleting the Nb_3I_8 sample in iodine. In turn, the smallest volume of argon which could be measured (ca. 2500 ml. STP) was limited by the minimum weight of water which could be weighed accurately, ca. 0.05 gram.

The niobium iodide pressures above solid Nb_3I_8 and niobium metal from 613 to 714° are shown in Figure 6. The equation

$$\log P_{\text{mm}} = - (12.77 \times 10^3)/(T) + 14.48$$

was obtained for these data by the method of least squares (52); the standard deviation in $\log P_{\text{mm}}$ is 0.03. These pressures were calculated from the experimental data with

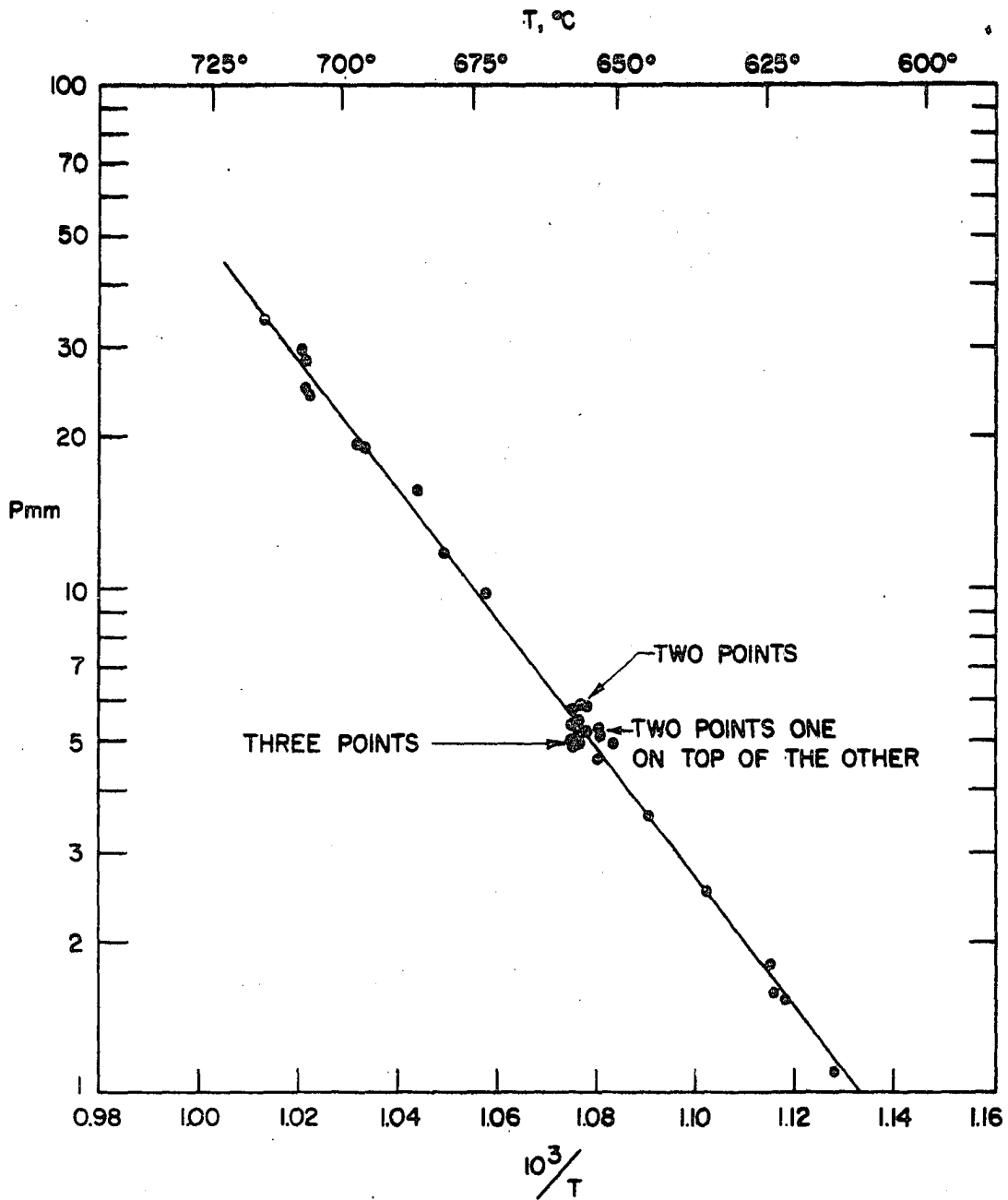


Figure 6. Niobium iodide partial pressures, 613-714^o, from transpiration studies

the assumption that the niobium iodide vapor species contained one niobium atom per molecule.

Although the composition of the vapor was found to correspond to an average of $\text{NbI}_{3.91}$, no inference may be drawn from this alone as to the actual vapor species, which could be associated or dissociated in a variety of ways. No thermodynamic data can be calculated without assuming a molecular weight for the vapor species. However, if there were only one niobium-containing species, the pressures calculated from the transpiration data with the assumption of a monomeric niobium iodide would be equal or directly proportional to the partial pressure of that species.

B. Problems Caused by Reaction with Silica

1. Initial total pressure measurements

In order to investigate the total dissociation pressure above Nb_3I_8 and niobium metal a Vycor diaphragm cell was filled with about three grams of Nb_3I_8 and 0.3 gram of niobium metal, and pressure measurements were begun by heating the cell over a period of about nine hours to 729° . At this temperature a pressure of about 60 mm. (as NbI_4) was expected from the transpiration pressure measurements.

During the heating period the diaphragm gauge indicated that the pressure responded rapidly to changes in the temperature. The pressures were considerably higher than had been expected, 117 mm. at 729° , and it was even more surprising to find that the pressure further increased to 133 mm. after 16 hours.

A number of additional pressure measurements in the temperature range 650 to 770° were made with this cell. In most cases the pressures were approached from lower, but in some cases from higher, values. Although the pressure responded rapidly to changes in temperature, it appeared to reach a constant value extremely slowly, especially at temperatures above 700° . At 739° , for example, the pressure increased for about 60 hours before becoming roughly constant, and at 770° the pressure was still increasing after 26 hours. Below 700° , the pressures became constant much more quickly, but now were always higher than the pressures observed at the corresponding temperatures during the initial heating. For measurements below 700° made on heating the pressure became fairly steady in less than an hour after the desired temperature was reached, and on cooling the pressure appeared to remain more or less constant after four to eight

hours. The cell was cooled to room temperature several times; the pressure dropped very rapidly below 600° , and no residual pressure was observed at room temperature. No particular change in the behavior was found after such a cooling and reheating. However, the pressures measured were only roughly reproducible, even with this one sample, and from time to time especially large (more than $\pm 20\%$) deviations occurred. Moreover, the pressures never really became constant, but fluctuated slowly around the "constant" value. After the cell had been in use for several weeks, the pressures appeared to be becoming extremely erratic, and use of this cell was discontinued.

Another cell was filled with about six grams of Nb_3I_8 and three grams of niobium metal, a proportion of metal much larger than was used at first. The behavior of the sample in the second cell was quite similar to that of the sample in the first cell. The first measurement was at 730° , and the pressures at this and subsequent temperatures showed the same slow climb to a "constant" value and the same oscillation around that value.

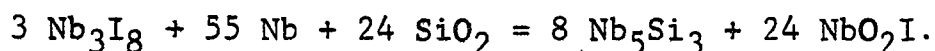
After each of these cells was removed from the furnace, a deposit was found to have formed on the inside upper wall,

which had been about 10° hotter than the bottom part during the run. The deposit had the deceptive appearance of slightly crinkled metal foil, dark grey in color and shading to bronze in some places. The cells were broken open, and the contents were analyzed by means of powder patterns. The metallic-appearing deposit from each cell was identified as Nb_5Si_3 (27, 34). The first sample then consisted of Nb_3I_8 and the material which was assumed to be NbO_2I^* ; none of the niobium metal balls initially added could be found, which perhaps accounts for the extremely erratic behavior observed at the end of the run. The second cell contained Nb_3I_8 and many of the niobium metal balls which had been added with the sample in addition to the niobium silicide on the walls, but no lines attributable to NbO_2I could be detected in the powder patterns. Apparently, the NbO_2I had been well mixed with the large amount of $NbI_{2.67}$ remaining when the cell was broken open, and the percentage of NbO_2I in the resulting

*Schäfer, H., Anorganisch-Chemisches Institut der Universität Münster, Westf., Deutschland. NbO_2I in the residue from the sublimation of $NbOI_3$. Private communication to J. D. Corbett, Ames Laboratory, U. S. Atomic Energy Commission, Iowa State University of Science and Technology, Ames, Iowa. 1964.

mixture was probably too low to permit its detection in the bulk mixture.

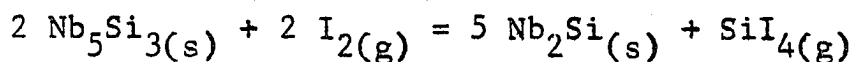
Thus, the measurements with the first two diaphragm cells were not of equilibrium pressures but rather were of steady-state pressures resulting partly from the attack of silica by the gaseous niobium iodide. The net reaction was probably



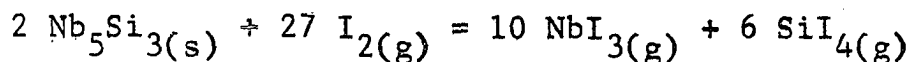
The niobium metal clearly was transported to the Vycor walls for reaction with SiO_2 by means of the gaseous niobium iodide, since the Nb_5Si_3 formed only on the upper (and hotter) part of the diaphragm cell, well away from the Nb_3I_8 -Nb sample. However, the NbO_2I , a loose, powdery material, appeared to have formed at the bottom of the cell. A volatile oxyiodide was presumably formed at the temperatures at which the reaction with SiO_2 occurred. This may have been NbOI_3 , since NbOI_2 is considered to be nonvolatile at these temperatures (37); Schäfer and co-workers (41) suggest that TaOI_3 takes part in the reaction of tantalum with SiO_2 in the presence of iodine.

The steady-state total pressures measured after attack of the glass had begun were about 33% above the total

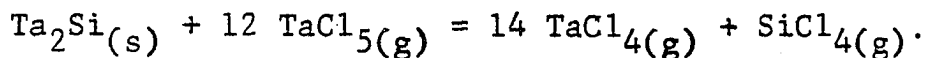
equilibrium pressures over a Nb_3I_8 -Nb sample (measured later, before attack of the glass had begun), suggesting the presence of an additional volatile component. After each of the diaphragm cells had been heated for long periods of time above 700° , and after attack of the glass had been indicated by the pressure drift, pressures as low as the equilibrium pressures could not be obtained again, even in the temperature range 650 - 700° where, judging from the equilibrium measurements later made, initial attack of the glass did not occur. Perhaps SiI_4 is produced by a reaction such as:



or:

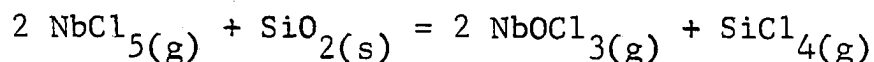


so that after the Nb_5Si_3 has formed the total pressure in the cell is higher than the sum of the equilibrium NbI_3 and I_2 pressures, even below 700° , due to the SiI_4 . Schäfer and co-workers (41) consider that Ta_2Si may be transported by a somewhat similar process:



The reaction of niobium metal with glass in the presence of hydrogen to form Nb_5Si_3 and NbO has been studied by Schäfer and Dohmann (34); the SiO_2 migrates to the niobium as

SiO by means of a chemical transport reaction due to a small hydrogen content of the metal. Schäfer and Kahlenberg (39) also reported that the reaction of niobium with quartz caused difficulties during investigations of the niobium-chlorine system. Beginning at 600° NbCl₅ appeared to react with quartz during pressure measurements, since the pressure increased steadily with time between 600 and 950°. The irreversible reaction appeared to be:



During studies in the titanium-chlorine system, Schäfer and co-workers (42, 43) found that the reaction of titanium with quartz occurs through transport of the metal; at 650° the products are TiOCl and SiCl₄, while at 1100° they are Ti₂O₃ and Ti₅Si₃. Ti₅Si₃ has also been found to form on the walls of a quartz ampoule containing titanium and sulfur heated at 700° (14). In this Laboratory tantalum has been observed to attack glass in the presence of iodine at temperatures above 800° forming Ta₂Si* as a beautiful mirror on glass tube

*Guidotti, R. A., Ames Laboratory, U. S. Atomic Energy Commission, Iowa State University of Science and Technology, Ames, Iowa. The attack of Vycor by tantalum. Private communication. 1964.

walls. This reaction was studied by Schäfer and co-workers (41); they found that it occurred in the presence of tantalum chlorides or iodides or iodine. The products are Ta_2Si and Ta_2O_5 .

During the preparation of Nb_3I_8 for this study by equilibration of higher iodides with niobium metal, some attack of the glass was observed in sample tubes heated several days at 800° or above. Very small amounts of Nb_5Si_3 , identified by powder pattern, were formed next to the glass walls. However, no evidence of such attack was found in sample tubes equilibrated below 700° even after heating for periods of over two weeks.

2. Attempts to quench the vapor species

Because the first diaphragm cell measurements indicated that NbI_4 suggested by the transpiration data must be considerably dissociated in the vapor phase, attempts were made to quench the vapor species in order to identify the niobium iodide. A quenched mixture of iodine and a lower niobium iodide should have been easily separated, since iodine could be pumped off at room temperature where it has a rather high vapor pressure (ca. 0.8 mm.). Although these attempts were not successful, they are described because the results were

surprising.

A small effusion cell was constructed of Vycor, with a sealed capillary drawn from small diameter quartz tubing protruding from one end. A sample of Nb_3I_8 and niobium metal was placed in the cell, and it was then evacuated and sealed. In the dry box, the tip of the capillary was broken off, leaving a small hole through which effusion could occur. The cell was placed in the bottom of a Vycor container fitted with a cold finger cooled by liquid nitrogen which extended over the capillary opening. The container was then placed in a vertical Marshall furnace and evacuated so that the vapors would effuse unhindered through the capillary opening to the cold finger, where they would be quenched.

The capillary was intended to collimate the vapors and to aim them at the cold finger, and its use instead of a thin-walled hole prohibited the measuring of the pressure with this particular effusion cell. In the usual effusion cell, the thickness of the walls of real holes reduces the pressure measured with the cell below the equilibrium pressure because effusing molecules with large sidewise velocities are deflected by the cell walls. To some extent corrections may be made for this channelling effect by use of the Clausing

factor in the ideal Knudsen equation (25). In the present case it was more important to try to collimate the vapor to obtain as directly as possible a sample of the equilibrium vapor than to measure pressures with the effusion cell. The results of the attempts to quench the vapor are shown in Table 2. The diameter of the hole and the length of the capillary were estimated visually. The cell temperature is only approximate, since it was measured by a thermocouple which touched the bottom of the Vycor tube containing the cell.

At the end of each run the cell was removed from the furnace and cooled to room temperature; then the iodine was pumped off the cold finger as the finger warmed to room temperature. The niobium iodide, if any, remained on the cold finger ready to be scraped off and analyzed. At first, the finger was constructed of Vycor. Since better heat transfer could be obtained through metal, it was later altered so that the bottom was stainless steel, soldered to the end of a Kovar glass-to-metal seal.

The first run was made with a rather wide hole directly in the top of the cell. As the pressure was rather high at 720° (41 mm. from the transpiration results), a considerable

Table 2. Attempts to quench the vapors from an effusion cell containing Nb_3I_8 and niobium metal

Run no.	1	2	3	4	5	6
Hole diameter, mm.	0.4	0.1	same as run #2	< 0.1	same as run #4	0.1
Length of capillary, mm.	none	10	same as run #2	12	8	2
Type of cold finger	Vycor	Vycor	Vycor	Steel	Steel	Steel
Distance of finger from capillary tip, cm.	6	5	14	14	14	1
Cell temperature, °C.	720	666	666	692	677	580
Duration of run, min.	90	50	180	210	150	180
Condensate on cold finger	I_2+ $\text{NbI}_{4.54}$	I_2+ thin bronze layer	trace I_2	trace I_2	trace I_2	I_2+ NbI_5

quantity of material was condensed and analyzed by ignition to Nb_2O_5 . Surprisingly, the composition of the niobium iodide which remained on the finger after pumping away the free iodine was much higher in iodine content than the total vapor composition found with the transpiration measurements.

After each run a black deposit appeared on the container walls at the level of the cell hole. This was not unexpected in the first case where no collimator was used; however, it also appeared in every run at the level of the open end of the capillary. Apparently the capillary was not an effective collimator. Attempts to obtain a powder pattern of the deposit were unsuccessful; at best, the pattern showed a broad band and one or two fuzzy lines which could not be identified. This deposit formed at temperatures much lower (e.g. 580°) than those at which silicide formation was observed in the diaphragm cells or in the equilibration tubes; however, the pressure in the container should have been of the order of 10^{-5} mm., much lower than the pressure in the diaphragm cells or equilibration tubes even at 580 or 600° . All that can be concluded is that an unidentified reaction on the container walls must have released a large part of the excess iodine which was condensed on the finger.

The quantity of material condensed in the second attempt was not sufficient for obtaining a powder pattern; nevertheless, the bronze color of the thin layer on the cold finger and its extremely rapid hydrolysis in air suggested that its I/Nb ratio was well above that of NbI_3 . It was thought that the small amount of condensate might be due to insufficient heating of the cell itself. So, for the next three runs the cold finger was raised to permit the tube holding the cell to extend deeper into the furnace, since it was not practical to keep a finger filled with liquid nitrogen actually inside a furnace at these temperatures.

Not only did the long capillaries fail to collimate the vapors, they also seemed to become plugged very readily. Run #3 was made with the same sample and cell at the same temperature as before, but after three hours only a trace of iodine was condensed. Run #4 with a fresh sample and cell yielded again no condensate other than a trace of iodine. An identical result was obtained from run #5, made with the cell from run #4 after breaking off the tip of the capillary which appeared to be plugged. Run #6 was in many ways the most successful quenching attempt; enough condensed material remained after removal of the free iodine for a powder

pattern which identified the material as poorly crystallized NbI_5 .

In the transpiration studies the overall I/Nb ratio of the vapor was found to be close to four, and the total pressures were found to be much greater than the pressures of the niobium-containing species. Consequently, the niobium iodide in the vapor phase above Nb_3I_8 and niobium metal could perhaps be NbI_3 , but it is quite unlikely that NbI_5 would be an important vapor species. A reaction at the container walls probably released additional iodine which was condensed on the finger, and this must then have reacted remarkably easily with a reduced niobium iodide. When it became apparent that such a reaction was interfering with the identification of the niobium iodide vapor species from the quenched vapor, this method was abandoned.

C. Equilibrium Total Pressure Measurements

Although the first attempts to measure the total pressure above Nb_3I_8 and niobium metal in a Vycor diaphragm cell were complicated by attack of the glass, it still seemed possible that successful measurements might be made at lower temperatures where perhaps the reaction of the niobium iodide

vapor species with silica would be sufficiently slight not to interfere. Therefore, a third diaphragm cell was filled with about five grams of Nb_3I_8 and two grams of niobium metal for another attempt.

The initial pressures in this cell were abnormally high. Although a negligible pressure (less than 0.1 mm.) was expected at 518° from extrapolation of the steady-state pressures from the first two cells, the pressure first observed at this temperature in the third cell was a little more than one millimeter. However, at 632° the pressure began to drop very slowly. After the cell was heated for brief periods at higher temperatures (up to 672°) followed by prolonged heating (32 hours) at 632° , the pressure at 661° remained constant for 14 hours. Several times both before and after the pressure began to drop the cell was cooled to room temperature, but no residual pressure was observed. Apparently, traces of a volatile material were present which reacted extremely slowly with the metal at temperatures below 600° . Unlike the samples in the first two cells, which had been prepared at 800° , the Nb_3I_8 sample in this cell had been prepared by equilibration of NbI_5 with niobium metal at temperatures below 640° (to prevent contamination

with Nb_5Si_3 and NbO_2I), and it was then ground to a fine powder in the dry box before being poured into the cell. Perhaps traces of NbI_3 remained which had not been completely reduced by the niobium during the preparation of the sample. (In attempts to prepare Nb_3I_8 by thermal decomposition of NbI_3 it was found that even after prolonged heating below $600\text{-}650^\circ$ the composition of the residue remained somewhat higher than that of Nb_3I_8 .) Or, perhaps a trace of contaminating material was present which reacted slowly with the niobium.

After the initial drop in pressure the total pressures below 700° showed no appreciable changes in periods of 12 to 14 hours at constant temperature. This indicated that the attack of the Vycor had not yet begun, because in all cases when this became a problem the pressures began to drift, and this was quite evident after no more than about five hours. The onset of drifting was particularly easily observed in the third diaphragm cell because of the very great sensitivity of its diaphragm. The behavior of the third run also differed from that of the first two in that equilibrium was attained extremely rapidly with both increasing and decreasing temperature. At any given temperature in the $600\text{-}700^\circ$

range the pressure reached a constant, equilibrium value just as fast as the cell reached that temperature.

The equilibrium total pressures measured on both heating and cooling are shown in Figure 7. As can be seen the system behaved very regularly in the temperature range of these measurements, 611-725°. The lower temperature corresponds to the smallest pressure that could be read from the manometer (about 1.0 mm.), and the upper, to the point beyond which even a very rapid measurement was not reliable due to attack of the Vycor. The measurements from 702 to 725° were made as rapidly as possible; measurements subsequently made below 702° agreed quite well with those previously made. However, the pressures above 702° were found too high to be consistent with those below 702° on the basis of the same gas composition; this is discussed in greater detail below.

Reaction with the cell wall, as indicated by the slow upward drift of the observed pressure, became noticeable at 700°. The pressure remained constant at 680° for 12 hours and at 694° for nearly 7 hours, but an increase of almost two millimeters was noted after 12 hours at 700°. As attack of the glass commenced the pressures in this cell behaved quite similarly to those in the first two cells used in that they

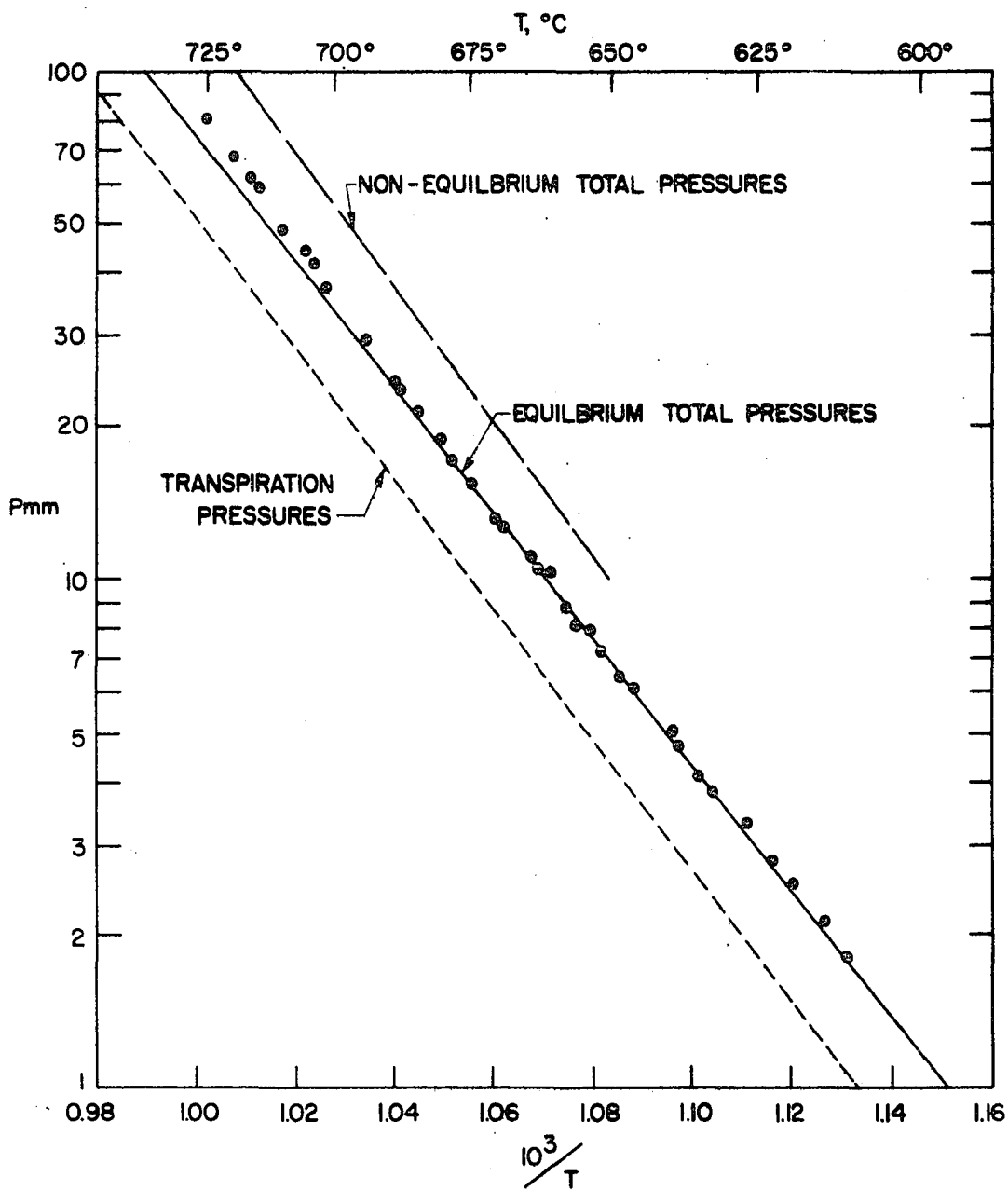


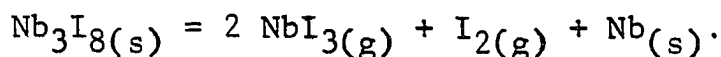
Figure 7. Equilibrium total pressures over solid $\text{Nb}_3\text{I}_8\text{-Nb}$, 611-725°

climbed toward a steady-state value around which they oscillated slowly and rather erratically. After the cell had been held at 729° for 39 hours, the pressures below 700° were higher than the equilibrium values; by that time appreciable amounts of Nb₅Si₃ and NbO₂I must have formed. A line indicating these steady-state pressures is shown in Figure 7 above the equilibrium pressures. At the end of the run Nb₃I₈, Nb, Nb₅Si₃, and NbO₂I were found in the cell.

In Figure 7 the least-squares line representing the niobium iodide partial pressures obtained by the transpiration method lies below the least-squares line representing the equilibrium total pressures from 611 to 702°. It is apparent that $d(\log P)/d(1/T)$ is almost the same for the two lines; also, the equilibrium total pressures for the system are just a little more than one and one-half times as large as the niobium iodide partial pressures over the entire range of the measurements. This suggests that the vapor phase consists of NbI₃ and iodine, with the iodine pressure equal to one-half the NbI₃ pressure, which is the only reasonable gas composition consistent with the observed total and partial pressures and with an I/Nb ratio in the gas phase of 4.00. If this is the case, there will be an

additional contribution to the total pressure from the dissociation of I_2 , which is appreciable at these temperatures and pressures. For example, at 614° and a total iodine pressure of 0.8 mm., I_2 is 25% dissociated, while at 720° and 24 mm. it is 14% dissociated. In all calculations involving the total pressures the iodine dissociation contributions to the pressures were calculated from free-energy values given (21) for $I_2(g)$ and $I(g)$.

With the assumption that the I/Nb ratio in the gas phase is 4.00, the NbI_3 and I_2 pressures were calculated from the total pressures at several temperatures, the data chosen being among those lying on a smooth curve drawn through the equilibrium total pressures from 611 to 725° . The equilibrium constant ($K_p = P_{NbI_3}^2 P_{I_2}$) was then calculated for the vaporization process



As expected, $\log K_p$ varied almost linearly with $1/T$ from 611 to 702° . However, above the latter temperature the $\log K_p$'s were considerably larger than those corresponding to a linear extrapolation of the $\log K_p$'s at lower temperatures.

The increase above 702° could not have been due to the heat-capacity change for the vaporization process. If $\log K_p$

had actually curved between 611 and 725°, the curvature would have corresponded to a ΔC_p of ca. +30 cal./deg. However, ΔC_p for this type of reaction may be expected to be negative from consideration of the usual heat capacity changes for vaporization and decomposition processes (12, 18). Also, ΔC_p can be estimated for the corresponding (hypothetical) vaporization process for Nb_3Cl_8 from data for Nb and Cl_2 (17), the C_p estimated by Schäfer and Kahlenberg (39) for Nb_3Cl_8 , and the estimated C_p (16) of $ZrCl_3(g)$ substituted for that of $NbCl_3(g)$; the resulting ΔC_p at 627° is -18 cal./deg.

With a linear extrapolation for $\log K_p$ (611-702°) the total pressure calculated at 720° was 59.5 mm., but the pressure measured at that temperature was 66.9 mm. The difference is much larger than the experimental error in the pressure measurement. Obviously, the pressures above 702° are much too high to be consistent with those at lower temperatures on the basis of the same gas composition. However, the I/Nb ratio in the gas phase remained close to 4.00 even at 713°, the highest temperature of the transpiration measurements. Perhaps at temperatures above 700° NbI_3 dissociates to NbI_2 and I_2 ; this would increase the total pressures and the sum of the niobium iodide partial

pressures, but would keep the same I/Nb ratio in the gas phase. Alternatively, if a small amount of niobium silicide or oxyiodide had been present in the sample, this might have begun to be volatilized by the iodine or the NbI_3 present by the processes discussed in the preceding part of this section. However, all possible care was used in the preparation of the sample to avoid its contamination.

As Figure 7 shows, $\log P$ varied nearly linearly with $1/T$ below 702° . The total pressures from 611 through 702° may be described by the equation

$$\log P_{\text{mm}} = -(12.357 \times 10^3)/(T) + 14.229$$

for which the constants were obtained by the method of least squares (52). The average deviation for $\log P$ calculated from the equation is 0.01_0 , and the standard deviation, 0.01_2 . The agreement of the pressures represented by this equation with the data can also be seen from Figure 7. Near both 611 and 702° the pressures obtained from the equation are lower than the experimental values, but near 611° the differences are within the error involved in measuring these very small pressures. For example, at 614° the difference is 0.07 mm., and it is 0.05 mm. at 620° , but the levels in the manometer (whose difference measured the pressure) could only

be read from the cathetometer to ± 0.05 mm. The least-squares equation corresponds to a kind of average between one which would give much weight to the very small pressures and one which would give them extremely little.

With the assumption that the I/Nb ratio in the gas phase is 4.00, the NbI_3 , I_2 , and I partial pressures were calculated at six temperatures from the total pressures given by the above equation in order to obtain K_p for the vaporization process. These NbI_3 pressures are listed in Table 3 together with the corresponding NbI_3 pressures obtained from the least-squares equation for the transpiration measurements and the NbI_3 pressures calculated from the total pressures by assuming that the I/Nb ratio in the gas phase is 3.90. The NbI_3 pressures corresponding to the I/Nb ratio 3.90 are also the same as the sum of the NbI_3 and NbI_4 pressures found by assuming an I/Nb of 4.00 and 90% dissociation of NbI_4 .

Plainly, the NbI_3 pressures obtained from the total pressures are in excellent agreement with those measured by the transpiration method. Unfortunately, the NbI_3 pressures cannot be used as a basis for distinguishing between I/Nb ratios of 3.90 and 4.00, as the NbI_3 pressures obtained from both ratios are well within the experimental error of those

Table 3. NbI_3 pressures obtained from total pressure and partial pressure (transpiration) data

T, °C.	P_{NbI_3} , mm., from total P (I/Nb = 4.00)	P_{NbI_3} , mm., from total P (I/Nb = 3.90)	P_{NbI_3} , mm., from transpiration data
614.5	1.25	1.29	1.23
627	1.95	2.02	1.95
646	3.75	3.88	3.78
664	6.88	7.14	7.05
678	10.8	11.2	11.2
702	22.6	23.5	23.9

obtained by the transpiration method. Although the pressures obtained from the ratio 3.90 agree more closely with the transpiration results at the higher temperatures, the difference between the latter and the pressures obtained from 4.00 is quite close to that given by the standard deviation in $\log P$ for the transpiration measurements. Also, the equation for the transpiration pressures was determined by measurements over temperatures up to 714° , and at the upper end of this temperature range the total pressures were too high to be consistent with those at lower temperatures and a

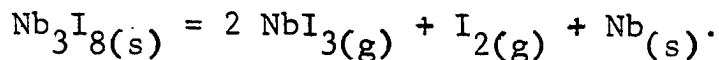
gas phase consisting of only NbI_3 , I_2 , and I over the entire temperature range. Consequently, it is possible that the transpiration pressures calculated from the equation are also a little too high at temperatures approaching 700° .

For the I/Nb ratio 4.00 the equilibrium constant for the vaporization process is described quite closely by the equation

$$\log K_p = -(37.96_4 \times 10^3)/(T) - 33.98_7 ,$$

from 611 to 702° . Apparently, ΔC_p for the vaporization process is negligible over this temperature range. Because of the uncertainty in the I/Nb ratio this equation is based on six values for K_p rather than on the 28 K_p 's which could have been calculated from the 28 pressure measurements at 702° and below. The values chosen were obtained from total pressures given by the least-squares equation for these at 611 - 702° ; the corresponding NbI_3 pressures are shown in Table 3 ($\text{I/Nb} = 4.00$).

From the equation above describing K_p , ΔH° , ΔF° , and ΔS° were obtained for the vaporization process

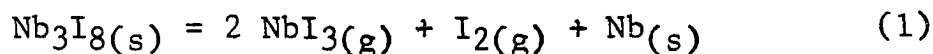


With the usual assumption that ΔH° is constant over the temperature range of the measurements, ΔH_{937}° is found to be

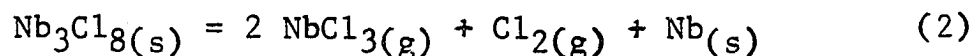
173.7 ± 5 kcal./mole Nb_3I_8 . In addition, ΔF_{937}° is 25.8 ± 1 kcal./mole Nb_3I_8 , which leads to a value of ΔS_{937}° of 155.6 ± 5 e.u./mole Nb_3I_8 . The uncertainties are estimated from the reasonable extremes of the slope of the equation describing the total pressures.

IV. DISCUSSION

Since thermodynamic data are often reported at 298°K., it is convenient to consider the heat and entropy changes for the vaporization process



at this temperature. Fortunately, ΔC_p for a similar (hypothetical) vaporization of Nb_3Cl_8



may be obtained with the use of data for Nb and Cl_2 (17), the C_p estimated by Schäfer and Kahlenberg (39) for Nb_3Cl_8 , and the estimated C_p of $\text{ZrCl}_3(\text{g})$ (16) substituted for that of $\text{NbCl}_3(\text{g})$. The resulting ΔC_p , $-8.8 - 10.0 \times 10^{-3}T + 1.0 \times 10^5 T^{-2}$, should be extremely close to that for the incongruent vaporization of Nb_3I_8 , described by Eq. 1. With the use of this expression for ΔC_p and the values obtained in the preceding section for ΔH_{937}° , 173.7 ± 5 kcal., and for ΔS_{937}° , 155.6 ± 5 e.u., ΔH_{298}° for reaction 1 is found to be 183 kcal., and ΔS_{298}° , 172 e.u.

The entropy change for Eq. 1 may be compared with that for Eq. 2. If Nb_3I_8 and Nb_3Cl_8 are similar compounds, and if the two solid trihalides are similar and also have about the same entropy of sublimation, then the entropy changes for the

two vaporization processes should be approximately the same. But if these differ appreciably, it would suggest that the niobium iodides are not similar to the corresponding chlorides.

From the entropies of Nb and Cl₂ (31), the estimate of Schäfer and Kahlenberg (39) for the entropy of Nb₃Cl₈, and the entropy of NbCl_{3(g)} (the entropy estimated for ZrCl_{3(g)} (16) is substituted for this), ΔS_{298}° for the incongruent vaporization of Nb₃Cl₈, Eq. 2, is 131 ± 21 e.u. This value is quite a bit lower than the experimental value for the vaporization of Nb₃I₈ according to Eq. 1, 172 e.u.; however, at least a part of the difference may be accounted for by the substitution of iodine for chlorine.

The entropy change for reaction 1 may also be approximated by estimating the entropy of Nb₃I₈ from that of Nb₃Cl₈ as described in Lewis and Randall (21), $S_{\text{Nb}_3\text{I}_8}^{\circ} = S_{\text{Nb}_3\text{Cl}_8}^{\circ} + (3)/(2) (R) (8) \ln (126.9)/(35.5)$, and substituting the entropy of ZrI_{4(g)} (16) for that of NbI_{3(g)}. This leads to a value of ΔS_{298}° of 159 e.u., which may be a little high, however, as the entropy of ZrI_{4(g)} is probably somewhat higher than that of NbI_{3(g)}.

Although the ΔS_{298}° obtained from data for the vaporiza-

tion, Eq. 1, 172 e.u., is somewhat higher than those estimated above, the difference (which could reflect a low entropy of Nb_3I_8) may or may not be real, considering the uncertainties of the estimates.

The heat of the vaporization process, Eq. 1, may also be used to obtain a very crude estimate of the heat of formation of Nb_3I_8 , since this heat may be expressed as:

$$\Delta H_v^{\circ} (\text{Nb}_3\text{I}_8) = \quad (3)$$

$$2 \Delta H_f^{\circ} (\text{NbI}_3) + 2 \Delta H_s^{\circ} (\text{NbI}_3) - \Delta H_f^{\circ} (\text{Nb}_3\text{I}_8) + \Delta H_s^{\circ} (\text{I}_2)$$

where v refers to vaporization, f, to formation (solid iodine as the standard state), and s, to sublimation, all these at 298°K. The heat of formation of NbI_3 must be estimated from that obtained by Schäfer and Liedmeir (40) for NbCl_3 , -139.4 kcal./mole NbCl_3 at 298°K. (Schäfer and Kahlenberg (39) considered linear interpolation suitable for obtaining the heat of formation of NbCl_3 from those measured for $\text{NbCl}_{2.67}$ and $\text{NbCl}_{3.13}$.) From the heats of formation known or estimated for YCl_3 and YI_3 (31), ZrCl_3 and ZrI_3 (16), and TiCl_3 and TiI_3 (16), the average difference in the heats of formation of the triiodide from those of the trichloride is -93 kcal./mole (at 298°K.). This, with the heat of formation of NbCl_3 , leads to a value of -46 kcal./mole for the heat of

formation of NbI_3 at 298°K . The most reasonable substitute available for the heat of sublimation of NbI_3 seems to be that estimated (16) for ZrCl_3 at 298°K ., 54 kcal./mole. With the above values, the heat for the vaporization process, Eq. 1, and the heat of sublimation of I_2 at 298°K ., 14.9 kcal./mole (21), the heat of formation of Nb_3I_8 at 298°K . from Eq. 3 is -153 kcal./mole.

This value is rather large (numerically) compared to that used for NbI_3 . From the data of Schäfer and Liedmeir (40) and of Schäfer and Kahlenberg (39), the heat of formation of Nb_3Cl_8 is 2.76 times that of NbCl_3 , and if the same relationship is used for the iodides, the heat of formation of Nb_3I_8 obtained from that estimated for NbI_3 is -128 kcal./mole. Unfortunately, in addition to the uncertainty in the estimation of the heat of sublimation of NbI_3 , a considerable range of choices is possible for its heat of formation. The difference between the heats of formation of the niobium chlorides and the niobium iodides may be much less, which would lead to a larger value for the heat of formation of NbI_3 . The chloride-iodide difference used, -93 kcal./mole NbX_3 , was based on the differences in the heats of formation of the zirconium, titanium, and yttrium trihalides, but the

heats of formation per equivalent of the niobium chlorides are appreciably less than those of the zirconium chlorides (39) (for example, -46.5 kcal. for NbCl_3 compared to -61.0 kcal. for ZrCl_3), and the chloride-iodide difference may be less, also. However, these heats of formation per equivalent are much larger than those of the corresponding molybdenum chlorides (-21.7 kcal. for MoCl_3) (39). The chloride-iodide difference obtained from the (estimated) heats (4) for the molybdenum trihalides is only -50 kcal./mole. If the chloride-iodide difference used to obtain the heat of formation of NbI_3 were -60 kcal., the heats of formation of Nb_3I_8 calculated from Eq. 3 and from 2.76 times the heat of formation of NbI_3 would have been the same (-219 kcal./mole).

So again, due to the enormous difficulties in estimating heats of formation and sublimation, no conclusion can be reached from the heat of vaporization of Nb_3I_8 concerning its heat of formation. However, it is at least possible that the latter is rather large in relation to that of NbI_3 , as is also suggested by the apparent instability of NbI_3 with respect to Nb_3I_8 and NbI_4 (44, 45).

Schäfer and Kahlenberg (39) have suggested that the Nb(III)-state must have little stability in view of the fact

that the stoichiometric trihalides are not distinguished by any special stability within the broad regions of homogeneity of the trichloride and tribromide phases (35, 36) and the fact that Nb_2O_3 does not exist. However, in addition to the existence of NbI_3 as a stoichiometric solid, it becomes quite important in the vapor phase, at least above 600° . No other sensible interpretation is possible for the niobium iodide partial and total pressures measured in this work and an I/Nb ratio for the gas phase of nearly four. On the basis of a gas phase consisting of NbI_3 , I_2 , and I , the total (static) and NbI_3 partial (transpiration) pressures are in excellent agreement up to nearly 700° ; however, it is possible that NbI_2 becomes important above 700° (discussed in the preceding section). Also, a very small proportion of the gas phase could have consisted of undetected NbI_4 , and NbI_4 may be the principal species at lower temperatures, perhaps below 500° .

In comparison to the niobium iodides, NbCl_4 is apparently quite important in the gas phase at high temperatures (ca. 800°) (39), and even NbCl_5 remains undissociated up to 600° (39). There is no evidence for the existence of gaseous VI_3 . Solid TaI_3 is not formed in the tantalum-iodine system,

the stable solid phases being TaI_5 , TaI_4 , and $TaI_{2.33}$ *. Gaseous TaI_5 appears to be undissociated up to 540° (1). ZrI_4 remains undissociated in the vapor phase up to nearly 1000° (28), where it begins to decompose slightly, while both MoI_4 and MoI_3 are unstable in the solid and vapor phases (29).

The vapor species NbI_3 appears to be important in the purification of niobium metal by the iodide process, studied by McCarley and Tadlock (23, 24) and also by Rolsten (29, 30). McCarley and Tadlock found two maxima in the growth rate-feed temperature curve, varying the temperature of the feed metal at a constant filament temperature of $1250 \pm 30^\circ$. A pronounced maximum in the filament growth rate occurred at 450 to 475° ; then the growth rate decreased up to about 550° , but above that point the rate increased rapidly with the temperature up to at least 750° . Rolsten observed a somewhat similar behavior, although his growth rate-feed temperature curve was displaced to lower temperatures by about 75 - 100° , which probably shows the great difficulty in measuring the

*Boatman, J. C., Ames Laboratory, U. S. Atomic Energy Commission, Iowa State University of Science and Technology, Ames, Iowa. The tantalum iodides. Private communication. 1964.

true feed metal temperature with accuracy.

Seabaugh and Corbett (45) found that the initial oxidation product of excess metal at 400-500° is NbI_3 rather than the equilibrium phase Nb_3I_8 . Therefore, the first increase in the growth rate probably reflects the volatility of NbI_3 , which decreases at higher temperatures as NbI_3 is increasingly reduced and decomposes to the much less volatile Nb_3I_8 (45). As the temperature approaches 600°, the growth rate rises again as gaseous NbI_3 is produced by the incongruent vaporization of Nb_3I_8 . Although the NbI_3 pressure is quite low at first, 0.7 mm. at 600°, it increases rapidly as the temperature rises, resulting in the steady increase of the growth rate up to at least 750°.

Additional thermodynamic data are needed to clarify the properties and behavior of NbI_3 and Nb_3I_8 . Studies of the vaporization of solid NbI_3 , which seems to be important at lower temperatures in the iodide process, would be useful in understanding its relationship to Nb_3I_8 . Since NbI_3 can only be sublimed slowly (44, 45) in vacuum below 500°, its sublimation pressure cannot be large, and since it disproportionates in a large temperature gradient (44), the I/Nb ratio for the gas phase may be greater than three. Pressure

measurements by the effusion or the transpiration method at temperatures below 500° where the disproportionation would be extremely slow, might be helpful; more complete information (including identification of all molecules in the vapor) might be obtained from mass spectrographic studies.

If the heat of formation of NbI_4 were known (e.g., from solution calorimetry), and if the heat of its dissociation to NbI_3 and I_2 were obtained by studies of the iodine dissociation pressure, the heat of formation of solid NbI_3 could be obtained from these. Then, with the heat of sublimation of NbI_3 , the heat of formation of Nb_3I_8 could at last be obtained from the heat of vaporization, Eq. 1, measured in this work. Comparison of the heat of formation of NbI_3 to that of Nb_3I_8 would show whether the relation between these is similar to that between the heats for the corresponding niobium chlorides. If NbI_3 is metastable, its heat of formation may be less (numerically) than that for $1/3$ mole Nb_3I_8 .

The results of the determinations of the crystal structures of NbI_3 and Nb_3I_8 may aid considerably in understanding the puzzling differences between the niobium-iodine and niobium-chlorine systems.

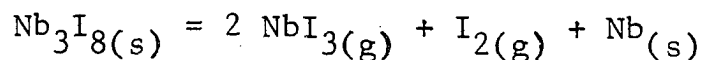
V. SUMMARY

The incongruent vaporization of triniobium octaiodide has been studied by the transpiration method from 613 to 714° and by a static method with a Vycor diaphragm gauge from 611 to 725°. Gaseous NbI_3 was found to attack Vycor readily at temperatures much above 700°, forming Nb_5Si_3 and a niobium oxyiodide tentatively identified as NbO_2I , resulting in a slow upward drift of the total pressures measured toward steady-state values higher than the equilibrium values. Consequently, equilibrium pressure measurements were obtained at lower temperatures where this reaction did not occur.

The I/Nb ratio for the gas phase, obtained by the transpiration technique, is very nearly four (the average is 3.9 with a range of ± 0.2). Since the total pressures for the system are approximately one and one-half times as large as the niobium iodide partial pressures measured by the transpiration method, gaseous NbI_4 suggested by the latter is evidently completely dissociated to NbI_3 and I_2 at these temperatures. This is shown by the excellent agreement up to 702° of the pressures obtained by the two methods on the basis of a gas phase consisting of NbI_3 , I_2 , and I. Above 702°, the total pressures become somewhat too high to be

consistent with those at lower temperatures if the gas composition is to remain the same.

The vaporization process has been identified as



for which

$$\log K_p = -37.96_4 \times 10^3/T - 33.98_7.$$

ΔH_{937}° for the above process is 173.7 ± 5 kcal., and ΔS_{937}° is 155.6 ± 5 e.u. From an estimated ΔC_p , ΔH_{298}° is found to be about 183 kcal., and ΔS_{298}° , 172 e.u.

Gaseous NbI_3 appears to be important in the iodide process for the purification of niobium metal; the rapid increase in the filament growth rate at feed metal temperatures from ca. 550 to at least 750° must be due to NbI_3 produced by the incongruent volatilization of Nb_3I_8 studied in this work.

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VII. ACKNOWLEDGMENTS

The author would like to thank Dr. John D. Corbett for his guidance, helpful criticism, and encouragement which made possible the completion of this work, and for his patience and kindness during her graduate studies.

She thanks the members of Physical and Inorganic Chemistry Group IX for their accommodating cooperation and generous exchange of equipment.

Most of all, she thanks her husband, Roger, for his enthusiastic encouragement, understanding, and extraordinary patience which enabled her to complete her graduate studies.

VIII. APPENDIX

Table 4. Data from transpiration studies for NbI_3 partial pressures over solid Nb_3I_8 -Nb

T, °C.	Argon flow rate, ml. STP/min.	I/Nb for vapor	NbI_3 pressure, mm.
613	1.94	3.76	1.12
621	14.3	3.92	1.56
623	14.7	4.01	1.60
624	1.98	3.70	1.82
634	4.22	3.84	2.54
644	4.98	3.95	3.58
650	3.05	3.85	4.97
653	2.83	--	5.29
653	3.44	3.91	4.67
653	7.58	--	5.26
655	3.59	3.85	5.92
655	6.55	3.90	5.31
656	5.22	3.90	5.16
656	6.20	3.97	5.01
656	6.52	3.83	5.50
657	2.17	3.80	5.80
657	4.29	3.93	4.98
657	4.47	3.73	5.04
657	4.56	3.83	5.42
661	5.40	3.96	5.96
672	17.8	3.93	9.84
680	9.76	4.03	12.8
685	7.88	--	15.7
695	8.34	3.95	19.2
696	22.8	3.95	19.3
706	10.3	3.95	24.9
706	15.2	3.99	28.3
706	17.9	3.88	24.3
707	7.75	3.99	29.7
714	17.5	3.97	34.1

Table 5. Equilibrium total pressures over solid Nb_3I_8 -Nb, in order taken

T, °C.	Pressure, mm.
660.5	10.2
654	7.9
646	6.1
627	3.3
648.5	6.4
663	10.4
635	4.1
664	10.9
639.5	5.0
623	2.8
611	1.8
633	3.8
658	8.7
669	12.5
678	17.0
688	23.7
670	13.1
638.5	4.7
614.5	2.1
656	8.1
674.5	15.3
684	21.1
694	29.2
702	37.0
652	7.2
680	18.7
620	2.5
688	24.4
710	48.2
720	66.9
704.5	41.6
715	58.4
725	79.8
716	61.2
706	44.2

Table 6. X-ray diffraction data for the substance assumed to be NbO₂I

d (obs.), Å.	Relative intensity ^a
3.63	(6)
3.56	(6)
3.33	(1)
3.27	(1)
3.23	(1)
3.19	(1)
2.69	(2)
2.59	(6)
2.49	(3)
2.37	(4)
2.32	(3)
2.28	(1)
2.25	(4)
2.20	(2)
2.17	(4)
2.14	(4)
2.12	(5)
2.08	(3)
2.06	(4)
2.03	(5)
1.998	(4)
1.941	(5)
1.914	(5)
1.836	(5)
1.812	(5)
1.762	(5)
1.686	(4)
1.647	(4)

^a(1) strongest, (6) weakest.