CONTRIBUTION No. 2321 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

The Vaporization Equilibria of the System Nb$_3$I$_8$(s)–Nb$_6$I$_{11}$(s)[1]

BY MARY ANGELA KUST, JOHN D. CORBETT, AND ROBERT M. FRIEDMAN

The equilibria relating the solids Nb$_3$I$_8$ and Nb$_6$I$_{11}$ have been studied by the transpiration method from 613 to 714° and by a static method with a diaphragm gauge from 611 to 725°. The I/Nb ratio in the gas phase is about 3.9$_5$ and substantially invariant over the range studied. The pressures obtained by the two different methods are in excellent agreement up to about 702° on the basis of a gas phase consisting of NbI$_5$, I$_2$, and I with the indicated constant composition. For the vaporization reaction $^7/_{15}$Nb$_3$I$_8$(s) = $^1/_{15}$Nb$_6$I$_{11}$(s) + NbI$_5$(g), $\Delta H°_{937}$ = 57.1 ± 1.8 kcal, $\Delta S°_{937}$ = 51.6 ± 1.7 eu, and for the reaction $^4/_5$Nb$_3$I$_8$(s) = $^2/_5$Nb$_6$I$_{11}$(s) + I$_2$(g), these quantities are 59.3 ± 2.0 kcal and 52.1 ± 1.7 eu, respectively. An additional unidentified gaseous component begins to contribute to the equilibrium total pressures very far above 700°. At about the same point NbI$_5$(g) begins to attack the Vycor container to form Nb$_5$Si$_3$ while oxide from the glass is transported to the cooler sample where it forms NbOI$_2$. These reactions result in a slow drift of the total pressures to values about one-third higher than for the above equilibria.

Introduction

Thermal decomposition of higher niobium iodides (NbI$_5$, NbI$_4$, NbI$_3$) in sealed tubes at about 600° has been shown to yield Nb$_3$I$_8$. In addition, the phase is readily obtained from the reaction of higher iodides with metal in a sealed tube at about 650–750° after which it may be transported to the cooler zone.[2] The phase has subsequently been shown[3] to contain triangular Nb$_3$ units, formally (Nb$_3$I$_4$)I$_{6/2}$I$_{2/2}$, the latter subscripts designating the sharing of iodine atoms between the core groups. The compound is isotypic with the high-temperature form of Nb$_3$Br$_8$, designated β-Nb$_3$-X$_8$, and it is this form that is of concern here. The related α-Nb$_3$X$_8$ structure[4] pertains to the compounds at the lower limit of a relatively wide homogeneity range with the chloride[5] and bromide[6] and evidently only to a partially substituted phase with a narrow composition range near NbI$_3$.[3,7]

Subsequently a still lower iodide Nb$_6$I$_{11}$ has been prepared and found to have a structural arrangement corresponding to (Nb$_6$I$_8$)I$_{6/2}$. The compound may be obtained by reaction of higher iodides and metal under several different conditions at 800–1000°.[8] Its stoichiometry and crystal structure were also independently established on a sample of the product from the present transpiration studies.[9] The slowness with which Nb$_6$I$_{11}$ is formed in metal–iodide reactions at 800° or below and its contamination with products of side reactions with glass containers at higher temperatures caused its omission in an earlier study.[2]

The gaseous iodides in equilibrium with solid Nb$_3$I$_8$ in its decomposition to Nb$_6$I$_{11}$ are presumably responsible for the transport reaction of the former as well as for the operation of the van Arkel–de Boer or "iodide" process at higher temperatures in the purification of the metal. In order to identify the species and to obtain thermodynamic data on this reaction, the equilibrium pressures above the two lower iodides have been measured in the range of about 610–725°, both with a Vycor diaphragm gauge and by the transpiration technique.

Experimental Section

Materials.—All samples were handled by conventional vacuum and drybox techniques. Niobium(V) iodide was prepared as described earlier[10] from metal and a 10% excess of resublimed iodine heated at 500 and 180°, respectively. Niobium metal shot, a special Du Pont sample obtained through the generosity of Dr. C. A. Swenson of this laboratory, had impurity levels (in ppm) of: Ta, 175; O, 64; N, 1; C, 13, with Fe, Cr, Ni and W each <50.

The Nb$_3$I$_8$ was prepared by heating NbI$_5$ and a 20% excess of metal in a sealed Vycor or niobium tube either at 640° for 3–4 days or at 800° for 2 weeks. After removal of the visible, excess metal by hand, a portion was analyzed and the remainder was stored in an evacuated, sealed container. Samples prepared at the lower temperature had I/Nb ratios of 2.65–2.67, while those obtained under the more extreme conditions had ratios in the range of 2.58–2.67 with one exception, 2.48, and in only the last was Nb$_6$I$_{11}$ found in the powder pattern. The slowness with which metal and Nb$_3$I$_8$ react to form the lowest iodide even at 800° is evident. Samples of Nb$_6$I$_{11}$ were best prepared by carrying out the reaction in sealed niobium tubes at 950–1000° for 1 week. The product is also obtained from the same reaction in silica containers at 850–900° but it may be contaminated by Nb$_5$Si$_3$ and NbOI$_2$ formed by attack of the container. X-Ray identification of the oxyiodide product was accomplished in separate experiments in which Nb$_3$I$_8$–Nb$_6$I$_{11}$ mixtures were heated in sealed Vycor tubes at 800–875° with a 10–20° gradient for 3–7 days and then manually separated in a glove bag with the aid of a microscope.

Analyses.—The I/Nb ratios and the total niobium contents of the solid iodides were obtained as before[2,10] by ignition of weighed samples to Nb$_2$O$_5$. Estimated errors indicate that the I/Nb ratios should be known to ±0.03. Iodide condensed in the transpiration runs was dissolved in KI solution and used to

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) P. W. Seabaugh and J. D. Corbett, *Inorg. Chem.*, **4**, 176 (1965).

(3) A. Simon and H. G. von Schnering, *J. Less-Common Metals*, **11**, 31 (1966).

(4) A. Simon, H. G. von Schnering, H. Wöhrle, and H. Schäfer, *Z. Anorg. Allgem. Chem.*, **339**, 155 (1965).

(5) H. Schäfer and K. D. Dohmann, *ibid.*, **300**, 1 (1959).

(6) H. Schäfer and K. D. Dohmann, *ibid.*, **311**, 134 (1961).

(7) H. Schäfer and A. Simon, unpublished research, cited in ref 3.

(8) (a) H. Schäfer, H. G. von Schnering, A. Simon, D. Giegling, D. Bauer, R. Siepmann, and B. Spreckelmeyer, *J. Less-Common Metals*, **10**, 154 (1965); (b) A. Simon, H. G. von Schnering, and H. Schäfer, *Z. Anorg. Allgem. Chem.*, **355**, 295 (1967).

(9) L. R. Bateman, J. F. Blount, and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1082 (1966).

(10) J. D. Corbett and P. Seabaugh, *J. Inorg. Nucl. Chem.*, **6**, 207 (1958).

titrate a standard As_2O_3 solution with Thiodene (Fisher) as the indicator.

Transpiration Measurements.—The Vycor transpiration cell employed is illustrated in Figure 1. The argon carrier gas entered the outer cell through the side tube, was preheated in the outer part, and then was passed over the sample S at the right end of the cell, back through the center tube where the niobium iodides condensed at C (only), out through the trap at $-80°$ to collect I_2, and onto the gas measuring system. The argon from the cylinder was first passed through a trap at $-80°$, over Linde 4A Molecular Sieve, and over tantalum at 800° to remove traces of water and oxygen. A small manometer teed to this line and filled with dibutyl phthalate was used to measure the pressure difference between the system and the atmosphere. The quantity of argon passed during a run was determined by a simultaneous transpiration run in which the effluent gas passed through two bubblers filled with water and thermostated at 20.0°, the amount vaporized being collected on $Mg(ClO_4)_2$ and weighed. The same final results were obtained when the flow was calibrated by water displacement.
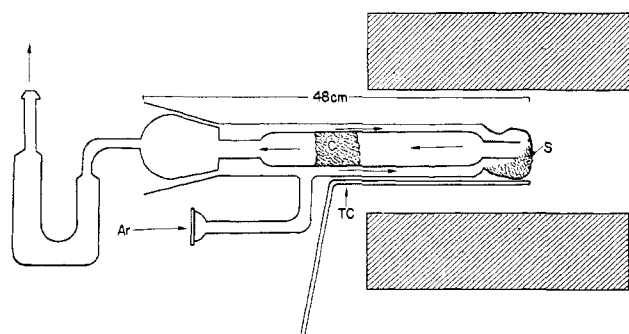

Figure 1.—Vycor transpiration cell: S, sample; C, condensate; TC, thermocouple.

The horizontal, 16-in. Marshall tube furnace which heated the cell contained a 0.25-in. thick Inconel liner to reduce the temperature gradient; shunts on the furnace taps were also used for this purpose. The temperature gradient on the outside of the cell was adjusted to about 3° over the last 3 in. with the end containing the sample cooler. The temperature fluctuation from controller operation was reduced to $\pm 1°$ with a power resistor in series with the furnace and in parallel with the controller switch.

The cell was baked out under dynamic vacuum at 750° for several hours and then loaded in the drybox with about 12 g of powdered Nb_3I_8. (About 2 g of niobium as foil was also added to the narrow neck of the center tube in a number of the early experiments before it was recognized that Nb_6I_{11} and not metal was the product of the decompositon. In any case the metal did not participate in the equilibrium at the temperatures employed ($\leq 713°$) and served mainly to reduce diffusion.) The cell was then cautiously reevacuated and filled with $\sim 3/4$ atm of purified argon. The furnace was heated to about 20° above the desired temperature before the cell was inserted, and thermal equilibrium was established before the preadjusted flow of argon was started. The last step normally took 15–30 min, during which a condensate usually appeared only in the outer and not in the inner tube to any significant extent. The sample temperature was measured with the aid of a calibrated chromel–alumel thermocouple fastened to the outside of the cell with the junction adjacent to the sample, as shown.

After a run, the cell was removed from the furnace to cool and was then evacuated so that any free iodine was transferred from the inner tube into the trap which was then sealed off. The condensed iodides were completely scraped out for analysis in the drybox. At least 0.3 g of the niobium iodide products was collected in each run to ensure a reasonable degree of accuracy.

On the order of 12 g of Nb_3I_8 in the initial loading was necessary in order to obtain consistent results since much smaller amounts

gave substantially lower pressures. With adequate samples a series of pressure measurements fell in a range of about $\pm 10\%$ around the average value of the series. Lower pressures were still obtained if the I/Nb ratio in the sample fell to much less than about 2.2 during a run, corresponding to less than about 45% Nb_3I_8. Accordingly, each sample was used only a few times, and in most cases about 2 g of fresh Nb_3I_8 was added to the sample before the next run.

The effect of flow rate was studied over the temperature range of the measurements. At 623° it was found that the flow rate could be varied from 2 to at least 14 ml (STP) min^{-1} without any appreciable difference in the pressure or the composition obtained. At higher temperatures at least a threefold variation in the flow rate (*e.g.*, 8 to 23+ ml (STP) min^{-1} at 696°) was without effect so pressures obtained at these flow rates were concluded to represent equilibrium values. These results strongly imply that no substantial error arises from inadequate preheating of the incoming argon in the outer tube. This was also directly established at the upper limit of flow rate employed (20–25 ml min^{-1}) by thermocouples within the apparatus in a dummy run. At 702° the incoming gas at the point where the inner tube necked down as an outlet for the saturated vapor was 1° or less below that found within this 9-mm outlet. In the latter region a variation of no more than 0.5° was found from the back wall of the outer tube through the outlet, and these temperatures were at most 1.5° below that measured with the external couple shown.

Diaphragm Gauge Measurements.—Static dissociation pressure measurements were obtained with a Vycor diaphragm gauge[11] as a null-indicating instrument. The gauge used for the equilibrium measurements had a sensitivity of 2 mm of deflection/mm of pressure differential and the null point was invariant to at least 700°. The pointer position was viewed with a 15-power telescope. The pressures were measured on a mercury-filled manometer to ± 0.05 torr by means of a precision cathetometer.

The cell was positioned in a vertical, 12-in. Marshall tube furnace with Transite coverings at the top and bottom of the furnace. The sample temperature was measured with a calibrated chromel–alumel thermocouple placed in a small indentation in the bottom of the cell. A second thermocouple parallel to the cell wall was used to measure the temperature gradient along the cell. A stainless steel liner in the furnace, convection baffles of Transite at both ends of the cell, and shunts on the furnace taps aided in smoothing the temperature profile. The gradient over the 4.7-in. portion containing the cell was adjusted to be about 8–12° in the temperature range 600–750° with the top of the cell being hotter.

Before the cell was filled it was evacuated through a side tube with a diffusion pump and baked out at 500° for approximately 6 hr. After about 3 g of Nb_3I_8 and 1.5 g of metal had been placed in the cell, it was then reevacuated several hours at 500°, cooled to room temperature, and sealed off.

It proved necessary to anneal the sample in the cell at 630–650° for 15–20 hr since the initial pressures obtained otherwise at *ca.* 600° were higher than equilibrium values. For example, on first heating the cell to about 630° the pressures were observed to decrease slowly, but after such an equilibration the pressure at 660° remained constant for 14 hr. Several times, both before and after the pressure drop began, the cell was cooled to room temperature with no indication of a residual pressure. The source of the slow reaction is thought to be traces of higher iodides such as NbI_3 which had not reacted completely with metal during the initial preparation at 640° but which did so when the sample was finely ground and exposed to fresh metal in the cell.

Results

Transpiration Measurements.—The niobium iodide pressures measured above solid Nb_3I_8 from 613 to 714° are shown in Figure 2. These data were calculated

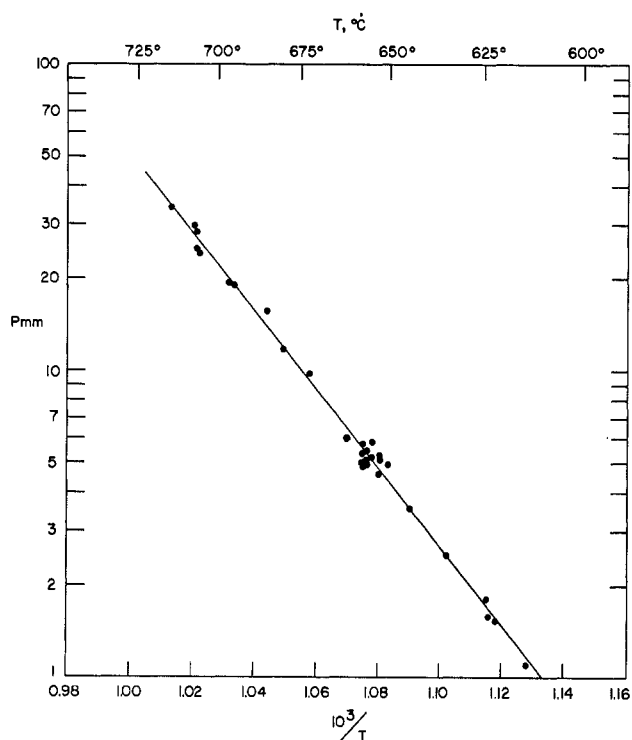(11) R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 54 (1964).

Figure 2.—Niobium iodide pressures over Nb₃I₈–Nb₆I₁₁ from transpiration studies.

Figure 3.—Total iodine to niobium ratios as a function of temperature from transpiration measurements.

from the number of gram-atoms of niobium found in the vapor with the assumption that the gaseous species contained only one niobium atom per molecule. The equation

$$\log P_{\text{torr}} = -[(12.77 \times 10^3)/T] + 14.48 \quad (1)$$

was obtained for the data by the method of least squares. The standard deviation of 0.03 in log P calculated is probably somewhat too large for a fair representation of the data because of the higher scatter of preliminary results near 655°.

The transpiration measurements also yielded the over-all composition of the vapor phase since a sample of the equilibrium gas was removed, condensed, and analyzed. All of the data so obtained are plotted as a function of temperature in Figure 3. The average I/Nb ratio for the 39 determinations is 3.91, with a standard deviation of 0.08₅. There does not seem to be a temperature dependence of the gas composition that is significant with respect to the experimental error. If the data are divided into 30° ranges, those at the lowest temperatures (where the amount of material collected was smallest) average 3.91 ± 0.14, those in the middle (where the largest amount of the early data near 655° is included) average 3.88 ± 0.07, and the most precise data in the upper range average 3.94 ± 0.06. The absence of a significant trend (*i.e.*, > ±0.1 in I/Nb) seems to be borne out further by what are thought to be the best data, the last 14 obtained. These, shown circled in Figure 3, average 3.96 ± 0.05₄.

The average composition of the niobium iodides condensed during the runs was about NbI₃.₂, with the remainder being condensed in the trap as iodine. The
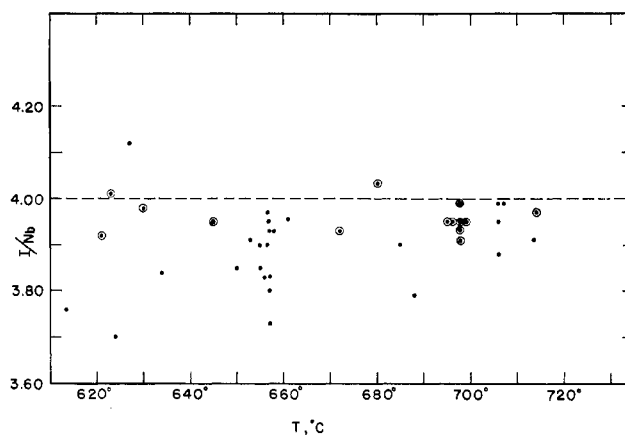
combination of the above data with those from total pressure measurements (below) indicates that the gaseous iodide is NbI₃; however, this readily combines with the free iodine on condensation to give mixtures of NbI₃, α-NbI₄, and NbI₅, as identified by powder patterns.

The product of the decomposition of Nb₃I₈ under the present experimental conditions was shown to be Nb₆-I₁₁, as has also been established in other studies.[8] This phase was observed (by powder patterns) to increase as the decomposition proceeded, and exhaustive transpiration runs near 650° yielded only this product according to X-ray data and analysis (I/Nb = 1.81, 1.83). (Production of this at substantially lower temperatures, as under vacuum, yields a material amorphous to X-rays.[2]) The formation of Nb₆I₁₁ was not recognized in the early part of this study, and so niobium metal as well as Nb₃I₈ was added to the apparatus. However, in the range studied, the rate of reaction of these two to form the equilibrium Nb₆I₁₁ is truly negligible (see Materials in Experimental Section) so that the presence of metal is without effect. This was confirmed by the fact that transpiration runs on Nb₃I₈ between 681 and 713° with no metal present gave the same pressures within experimental error. The magnitude of pressures above the Nb₆I₁₁–Nb system was also briefly investigated. At the same flow rates used previously, the niobium partial pressures obtained at 654 and 707° average 0.07 and 1.10 torr, respectively (each ±10%). The over-all composition obtained was near I/Nb = 4. The pressure at 707° is about 4% of that found at this temperature for the title system; however, the attainment of equilibrium by flow rate variation was not tested so the data may not be too significant.

Total Pressure Measurements.—Initially the measurement of total pressures in a Vycor diaphragm cell was complicated by attack of the glass by NbI₃(g) which led to erratic pressures about one-third higher than subsequent equilibrium values. In such a case the pressure observed very far above 700° within a few hours began to increase gradually toward a "constant" value about which it slowly fluctuated. With increasing time the pressure became increasingly erratic.

Data subsequently measured below 700° with the same cell were also higher than equilibrium values even though the attack of glass here is not significant. No residual pressure was found below 550°. After such experiments a deposit was found on the upper wall of the cell, which had been about 10° warmer than the sample at the bottom. The material had the deceptive appearance of slightly crinkled metal foil of a dark gray to bronze color and was identified as Nb_5Si_3 by its powder pattern.[12] The erratic, and what turned out to be high, pressures were always associated with visible side reactions with the glass to form Nb_5Si_3 (and other products), and successful measurements were subsequently made on the system at lower temperatures where the rate of reaction of the vapor species with silica is negligible. In this case total pressures observed below 700° showed no appreciable change during periods of at least 12–14 hr at constant temperature. In addition, equilibrium was attained sufficiently rapidly with either increasing or decreasing temperature that data could be taken as quickly as the furnace reached thermal equilibrium. Measurements between 702 and 725° were made as rapidly as possible, and those subsequently checked below this range agreed well with data obtained previously so that the troublesome reaction with the container did not appear to be present. Reaction with the wall again became noticeable after about 12 hr above 700°.

The equilibrium total pressures so measured are shown in Figure 4. They are well described up through about 702° by the linear equation

$$\log P_{torr} = -[(12.35_7 \times 10^3)/T] + 14.22_9 \quad (2)$$

with a standard deviation in $\log P$ of 0.01_2, though as will be seen there is no fundamental requirement of a linear relationship. The deviations from this description much above 700° will be considered later.

As seen in Figure 4 the equilibrium pressures over the entire range of the measurements are 50–60% greater than the niobium iodide partial pressures, and the two sets of data also have nearly the same $d(\log P)/d(1/T)$. These factors and the transpiration result that the gas phase has a substantially invariant I/Nb ratio of about 4 strongly suggest that the gas phase actually consists of NbI_3 plus half as much iodine. Accordingly, the partial pressures of NbI_3, I_2, and I were calculated at six temperatures from the total pressures given by eq 2 and known data for the $I_2 = 2I$ equilibrium[13] with the assumption that the I/Nb ratio in the gas was constant and either 4.00 or 3.90. The NbI_3 and I_2 pressures so obtained are listed in Table I where they are compared with the niobium partial pressures given by eq 1 for the transpiration results. The standard deviations listed correspond to only the uncertainty in total pressure; those for the transpiration data are comparable. Clearly the calculated and observed pressures are in agreement within this part of the experimental uncertainties, and although the 3.90 ratio gives results in

(12) E. Parthé, B. Lux, and H. Nowotny, *Monatsh. Chem.*, **86**, 859 (1955).
(13) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1964.
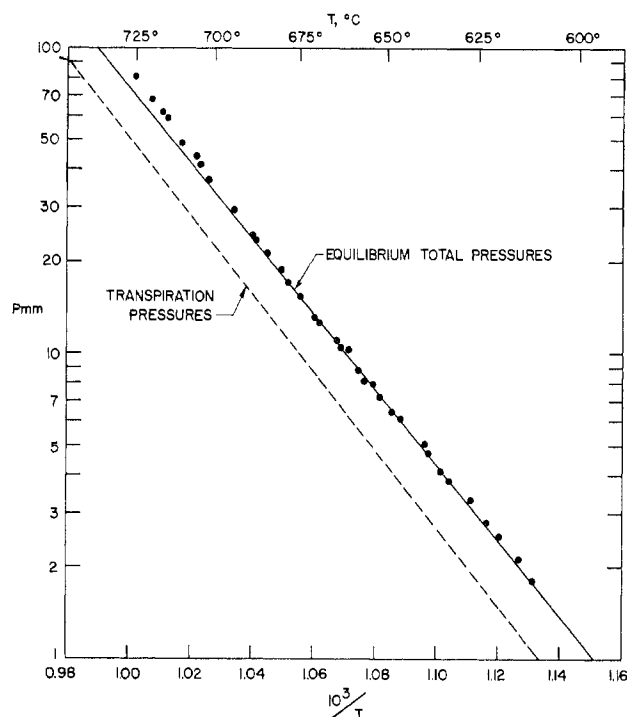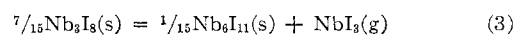

Figure 4.—Equilibrium total pressures over the solid Nb_3I_8–Nb_6I_{11} system.

TABLE I

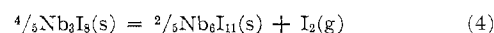COMPARISON OF NbI_3 PRESSURES CALCULATED FROM TOTAL PRESSURES WITH THOSE FROM TRANSPIRATION DATA

| Temp, °C | From total pressures (eq 2), torr | | | | | P_{NbI_3} from transpiration data (eq 1), torr |
| | I/Nb = 4.00 | | I/Nb = 3.90 | | | |
	P_{I_2}	P_{NbI_3}	P_{I_2}	P_{NbI_3}	$\sigma(P_T)$	
614.5	0.46	1.24	0.43	1.29	0.06	1.2_4
627	0.74	1.95	0.69	2.02	0.08	1.9_5
646	1.48	3.78	1.37	3.92	0.17	3.8_5
664	2.77	6.88	2.56	7.14	0.31	7.1_1
678	4.42	10.8	4.10	11.2	0.58	$11._3$
702	9.54	22.7	8.84	23.6	1.0	$24._2$

closer agreement with experiment, either ratio or any trend within their range is consistent within experimental error.[14]

Accordingly it is concluded that the important equilibria between the vapor phase and the condensed Nb_3-I_8–Nb_6I_{11} system are, per mole of the gas product

$$^7/_{15}Nb_3I_8(s) = {}^1/_{15}Nb_6I_{11}(s) + NbI_3(g) \quad (3)$$

and

$$^4/_5Nb_3I_8(s) = {}^2/_5Nb_6I_{11}(s) + I_2(g) \quad (4)$$

with properties such that, with the $I_2 = 2I$ dissociation, the total iodine to niobium metal ratio in the gas phase is substantially constant in the range studied. The difference of these reactions, $3NbI_3(g) = Nb_3I_8(s) +$

(14) Attempts were made to verify directly the presence of $NbI_3(g)$ by mass spectrometric examination of the vapors from a pinhole in a Vycor Knudsen cell. However, the study was complicated by condensation of lower niobium iodides on cooler walls before the vapors reached the ionizing source which made the vapor much richer in iodine and, presumably, higher iodides. As it was, the intensity of NbI_3^+ in the spectra was 4–5 times greater than that of NbI_4^+ in the temperature range of interest, although both were much less than that of iodine. In view of the condensation complication as well as the absence of a study of fragmentation patterns, any conclusions are extremely tenuous.

$^{1}/_{2}$I$_2$, is presumably responsible for the transport reaction of Nb$_3$I$_8$.[2]

The fact that the total pressures much above 700° are somewhat higher than given by eq 2, *e.g.*, by 12.5% at 720°, probably cannot be explained by a ΔC_p term (*ca.* 30 cal deg^{-1} over-all) as it would have the opposite sign from that expected for vaporization and decomposition processes.[15] An additional, more endothermic process, such as further dissociation to NbI$_2$(g) or some side reaction with the silica container, is presumably involved though the pronounced symptoms of substantial glass attack described earlier were not observed during these experiments.

The data in Table I were used to calculate the $\Delta H°_{937}$ and $\Delta S°_{937}$ values for the two reactions given in Table II. The uncertainties cited encompass the results of a

TABLE II

STANDARD ENTHALPY AND ENTROPY
CHANGES FOR REACTIONS 3 AND 4

	$\Delta H°_{937}$, kcal	$\Delta S°_{937}$, eu	$\Delta H°_{298}$, kcal	$\Delta S°_{298}$, eu
Reaction 3 (per mole of NbI$_3$)	57.1 ± 1.8	51.6 ± 1.7	60.5	56.6
Reaction 4 (per mole of I$_2$)	59.3 ± 2.0	52.1 ± 1.7	56.6	45.0

variation of ±0.1 in the I/Nb ratio across the temperature range studied as well as for the vaporization data for NbI$_3$ given directly by eq 1. The values of $H_T - H_{298}$ and $S_T - S_{298}$ necessary to obtain the indicated values at 298°K were obtained from reported estimates[13] for the zirconium iodides, interpolating or extrapolating to the compositions of the solid niobium iodides.
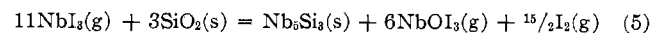
Discussion

The niobium partial pressures, the total pressures, and the gross composition of the gas phase above the solid system Nb$_3$I$_8$–Nb$_6$I$_{11}$ are in good agreement with a gaseous mixture of NbI$_3$, I$_2$, and I with I/Nb = 3.95 ± 0.05 from 610 to about 700°. As the data in Table II show, the apparent invariance of the gas composition in the limited range which could be studied is a somewhat fortuitous result of similar thermodynamic properties of the two independent vaporization reactions 3 and 4 together with the effect of the I$_2$ dissociation equilibrium. A small but significant change in gas composition would be expected if the temperature range could be extended sufficiently.

The entropy changes expected for the two vaporization processes may be estimated if the zirconium iodides are again assumed to be legitimate analogs of the niobium compounds. In this case $\Delta S°_{937}$ for reaction 3 is predicted to be about 44 eu/mol of NbI$_3$ *vs.* 51.6 eu observed, and for reaction 4, $\Delta S°$ is predicted to be 48 eu/mol of I$_2$ compared with 52.1 eu obtained. The only fair agreement is nonetheless judged to be satisfactory considering both the approximate character of the zir-

conium data involved and the fact that they are being applied to rather unusual niobium cluster compounds. In addition, none of the estimates used includes the electronic contributions to the entropy expected for not only NbI$_3$(g) but also the paramagnetic Nb$_3$I$_8$[3] and Nb$_6$I$_{11}$.[8] An uncertainty of at least 5 eu in the estimated values would thus seem very possible.

Entropy estimates alone cannot distinguish the above vaporization reactions from one involving the production of only gaseous NbI$_4$. However, the latter would require a temperature error of about $-13°$ in the transpiration results relative to those from the diaphragm gauge, and we have not been able to find any indication that an essentially constant error of this magnitude could have been present. Transpiration measurements are generally more suspect, but, as detailed in the Experimental Section, the uncertainty in measurement of the sample temperatures here appeared to be no more than about 2°. The attainment of apparent saturation over a three- to sevenfold range of flow rates also seems to deny the existence of a significant error arising from inadequate preheating of the carrier gas. The formation of gaseous NbI$_3$ (plus I$_2$) in the present system compares with the formation of VI$_3$(g) in the presence of excess I$_2$ above about 730°[16] and with TaI$_4$(g) which is thought to be important in the transport reactions of Ta$_6$I$_{14}$.[17] Niobium(IV) chloride appears to be the principal species above Nb$_3$Cl$_8$ and Nb$_6$Cl$_{14}$,[18] reflecting the well-known stability of higher chlorides compared with iodides. In all cases the vaporization reactions are incongruent such that the gaseous metal halides are in a considerably higher oxidation state; this reflects the limited stability of gaseous lower halides which lack strong metal–metal bonding.

The reaction observed between gaseous NbI$_3$ and SiO$_2$ (Vycor) is particularly interesting with regard to the transport reactions involved. The Nb$_5$Si$_3$ product is found only on the hotter walls of the container, well separated from the sample if this is in a cooler zone as in the diaphragm cell. On the other hand, the oxygen from the silica is transported to the cooler part of the cell, presumably as NbOI$_3$(g) as this is evidently the only volatile oxyiodide.[19] Here the oxyiodide reacts to form NbOI$_2$, while NbOI$_3$, NbO$_2$I,[20] and NbO are not detected in any part of the products after the reaction. The reaction at the walls is evidently

$$11\text{NbI}_3(\text{g}) + 3\text{SiO}_2(\text{s}) = \text{Nb}_5\text{Si}_3(\text{s}) + 6\text{NbOI}_3(\text{g}) + {}^{15}/_2\text{I}_2(\text{g}) \quad (5)$$

following which NbOI$_3$ diffuses to the cooler zone where it decomposes according to

$$\text{NbOI}_3(\text{g}) = \text{NbOI}_2(\text{s}) + {}^{1}/_2\text{I}_2(\text{g}) \quad (6)$$

Reaction 6 is known[19] to be exothermic so that transport is to the cooler zone. Although NbO may be the

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(20) The Guinier diagram for NbO$_2$I was kindly provided by Professor Schäfer.

equilibrium product, it is not formed at an appreciable rate at $\leq 875°$. The reactions observed here are somewhat analogous to those found in the Nb_6Cl_{14}–Nb–SiO_2 system where $NbOCl_3$ is the intermediate and the oxygen formed first dissolves in the metal but ultimately produces NbO.[18] In the presence of the condensed lower iodides the net reaction

$$3SiO_2 + {}^{52}/_{15}Nb_6I_{11} = Nb_5Si_3 + 6NbOI_2 + {}^{49}/_{15}Nb_3I_8 \quad (7)$$
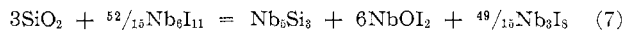
involves only solid phases. Actually still another transport equilibrium is probably involved for Nb_5Si_3 since it is not uniformly distributed on the walls but is more predominant on the hotter parts of the glass. Such presumably involves SiI_4 and might be

$$Nb_5Si_3(s) + {}^{27}/_2I_2(g) = 5NbI_3(g) + 3SiI_4(g) \quad (8)$$
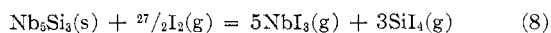
Unfortunately there are insufficient thermodynamic data available for the niobium iodides to judge further the plausibility of these reactions. Presumably the higher pressures that arose in the total-pressure studies once Nb_5Si_3 had been formed resulted from the $NbOI_3$ and SiI_4 contributions, and the erratic character of the pressures observed was caused by irregular contributions of convection to the otherwise steady-state diffusion processes.

According to the present study the vapor species NbI_3 would appear to be of principal importance in the purification of niobium metal by the iodide process. In one study of this method[21] a definite maximum in the

filament growth rate occurred at 450–475° when the temperature of the feed metal was varied at a constant filament temperature of 1250°. On a further increase in the feed temperature the growth rate first decreased up to about 550° and then increased rapidly with increasing temperature up to at least 750°. Rolsten[22] observed a somewhat similar behavior with his growth rate–feed temperature curve, but this was displaced to lower temperatures by about 75–100°, which probably reflects the difficulty in accurately measuring the true feed metal temperature. Since the initial oxidation product of excess metal at 400–500° appears to be NbI_3 rather than a lower iodide,[2] the first increase in the growth rate probably results from the increasing volatility of NbI_3 and this then decreases at higher temperatures as NbI_3 is increasingly reduced and decomposed to the much less volatile Nb_3I_8. However, as the temperature approaches 600° the growth rate rises again as, according to the present study, gaseous NbI_3 is produced by the incongruent vaporization of Nb_3I_8, and this results in the steady increase in the growth rate up to at least 750°. Even at 800–900° the reaction of Nb_3I_8 with metal to produce Nb_6I_{11} is extremely slow, presumably because of the structural complexity of the transformation, so the equilibrium phase is probably not involved in the process at these temperatures.

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CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA 30332

Tetracyano Complexes of Molybdenum(IV)

BY J. VAN DE POEL AND H. M. NEUMANN

Methods are presented for the preparation and identification of the following molybdenum(IV) compounds: red-violet $K_4[MoO_2(CN)_4] \cdot 6H_2O$, tan $K_4[MoO_2(CN)_4]$, blue $K_3[MoO(OH)(CN)_4]$, green $K_2[Mo(OH)_2(CN)_4]$, and black $Mo(OH)_2(CN)_2 \cdot H_2O$. The infrared spectra, which are particularly useful for identification, are discussed. The acid dissociation constants for $MoO(OH)(CN)_4{}^{3-}$ and $Mo(OH)_2(CN)_4{}^{2-}$ at 25° are, respectively, 2.4×10^{-13} and 1.05×10^{-10}. A new compound, $K_6[Mo^{IV}_2Mo^{VI}(CN)_8O_6] \cdot 2H_2O$, is reported.

Tetracyano complexes of molybdenum(IV) have been known for a considerable time. A compound, described as red or red-violet, has been prepared by treating various Mo(V) compounds with KCN and KOH.[1–9] Photochemical decomposition of $Mo(CN)_8{}^{4-}$

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can be made to yield the same product.[10,11] All procedures used have in common the isolation of the compound from a strongly basic solution. Recent crystallographic work[11–13] has demonstrated that this compound contains the *trans*-dioxotetracyanomolybdate(IV) anion and is best formulated as $K_4[MoO_2(CN)_4] \cdot 6H_2O$. The anhydrous compound $K_4[MoO_2(CN)_4]$ was first prepared by Steele.[14]

The red-violet compound dissolves in water to give

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