is not operating in the absence of chloride. The volatile acid in pure ammonium nitrate melts is HNO_3. In the chloride-containing melts, volatilization of HCl and of Cl_2 also occurs, the rate depending on the respective Henry's law coefficients and on the melt concentrations. Although the loss of chloride was not detectable analytically, it may be sufficient to account for the fact that in Table II the pH of the 0.10 mole ratio melts at the termination of flushing (t_0) is uniformly about 0.1 unit higher at each t_f than for the 0.05 melts.

The t_i values in the *B* columns of Table I are independent of R_f within experimental error, in marked contrast to the data in the *A* columns. When chloride is added to the melt after flushing, it is added to a melt of constant acidity, irrespective of R_f, since the data in Table II show that the acidity produced by flushing pure ammonium nitrate is independent of R_f and t_f. The dependence of the induction period on both acidity and chloride concentration undoubtedly accounts for the inability of Guiochon[3] to find any consistent variation of his induction periods with chloride concentration alone.

The complete mechanism for decomposition under steady-state conditions[1] is rather complex, but the important features for the present discussion may be summarized very briefly as follows. The key step is the reaction

$$NO_2^+ + Cl^- \longrightarrow NO_2 + Cl$$

where the NO_2^+ is generated by the autoprotolysis of the HNO_3 resulting from the dissociation of the ammonium nitrate. The radicals NO_2 and Cl then initiate a set of cage reactions which lead to N_2O through nitramide as a precursor, and to N_2 by two paths with nitrosamine and chloramine as precursors. The mechanism therefore requires an initial excess of acidity to allow formation of NO_2^+.

It has been shown subsequently[5] that the mass balance is such that the N_2-producing reactions generate more acidity than they consume. The reaction is therefore potentially acid autocatalytic, except that volatilization of acid may produce a steady state at various levels of acidity depending on the conditions. In fact, the observed unsymmetrical bell-shaped rate curve has further been shown[5] to be characteristic of a second-order autocatalytic reaction in which the concentration of the reactants attains a constant value after the rate maximum. In Table II, the pH values at t_i, which represents the rate maximum R_m, and at t_i + 15 min., which is well into the region of spontaneous steady-state decomposition, are all constant at 2.30 ± 0.02 pH units irrespective of prior R_f or t_f. The present data, therefore, in addition to providing a mechanistic explanation for the induction period, also confirm the arguments used earlier[1] to justify an important assumption in the mechanism, namely, that the freely decomposing melts spontaneously develop a constant steady-state acidity.

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(5) C. I. Colvin, Ph.D. Thesis, University of Miami, 1963.

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The Niobium Iodides. Characterization of Niobium(IV) Iodide, Niobium(III) Iodide, and Triniobium Octaiodide[1]

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The condensed niobium–niobium(V) iodide system contains three intermediate phases, NbI_4, NbI_3, and Nb_3I_8, all qualitatively diamagnetic at room temperature. Niobium tetraiodide is evidently trimorphic. The weakly endothermic $\alpha \rightarrow \beta$ transition observed at *ca.* 348° only on heating is without effect in the powder pattern data. A more substantial $\beta \rightarrow \gamma$ transition occurs at 417°, and γ-NbI_4 melts incongruently at 503° to form an iodide-rich liquid and solid Nb_3I_8. Niobium(III) iodide may be obtained by thermal decomposition of NbI_4, as a sublimate from mixtures with Nb_3I_8, or as the initial product of oxidation of excess metal. The phase is apparently not an equilibrium compound in the system since it decomposes slowly and irreversibly at about 513° into iodide-rich liquid and Nb_3I_8. The phase in equilibrium with the metal is Nb_3I_8 ($NbI_{2.67\pm0.02}$), which may also be obtained by thermal decomposition of higher iodides or as the phase transported from mixtures with metal. The two lower niobium iodides show only a limited correspondence with those reported in the niobium chloride and bromide and tantalum iodide systems.

Introduction

Although several investigators[2-7] have reported synthesis of niobium(V) iodide samples of varying purity,

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Commission.

(2) F. Körösy, *J. Am. Chem. Soc.*, **61**, 838 (1939).

(3) K. M. Alexander and F. Fairbrother, *J. Chem. Soc.*, 2472 (1949).

(4) R. F. Rolsten, *J. Am. Chem. Soc.*, **79**, 5409 (1957).

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

(6) L. A. Nisel'son and I. V. Petrusevich, *Zh. Neorgan. Khim.*, **5**, 249 (1960).

(7) D. M. Chizhikov and A. M. Grin'ko, *ibid.*, **4**, 979 (1959).

information on the lower iodides has been somewhat fragmentary. Körösy[2] first noted that NbI_5 decomposed at 300 to 400° under vacuum to give compositions in the range of $NbI_{2.33}$ to $NbI_{2.5}$, not further characterized. Chaigneau[8] treated Nb_2O_5 with Al_2I_6 to give a mixture of NbI_5, $NbOI_3$,[9] and Al_2O_3, and, on separation of the mixture by fractional sublimation, observed that the NbI_5 decomposed to iodine and the less-volatile NbI_3 ($NbI_{2.91}$ by analysis). He later reported[11] that the hydrogen reduction of NbI_3 at 300 to 400° gave the limiting composition NbI_2, although no physical evidence was cited to support its identification as a single phase.

Chizhikov and Grin'ko[7] allowed a stream of I_2 vapor to react with niobium metal at 600 to 1300° and obtained a number of compositions, evidently admixed with free iodine, on the water condenser. The products NbI_5, NbI_4, and $NbI_{3.2}$ were mentioned, although additional information was given only for the last. Different preparations, apparently in the neighborhood of $NbI_{3.2}$, were reported to give powder patterns with lines of the same intensities but with their positions displaced, from which the presence of solid solutions was inferred. Similar compositions ($3.0 < I/Nb < 3.25$, 98 to 99% recovery as $Nb + I$) were also obtained by reaction of iodine with excess metal in sealed, fused silica containers at 600°. The triiodide obtained by either method was stated to sublime under vacuum at 600° and to give green solutions in aqueous HCl.

Finally, the present authors earlier described[5] the synthesis of NbI_4 and NbI_3 by thermal decomposition of previously-sublimed NbI_5 in a sealed, "hot-cold" tube wherein the evolved I_2 (and higher iodides) condensed in the cooler part. The pure tetraiodide was obtained as a residue at 270°, and as a sublimate at 300°, while a residue of NbI_3 resulted from further decomposition at 425°. The latter was found to sublime with a small amount of decomposition at 450 to 500° and to be insoluble in concentrated HCl, in contrast to the above citation. At that time it was noted that a still lower iodide was evidently also formed. The present paper presents further characterization of all three lower iodides as well as some of their unusual properties.

Experimental

Synthesis.—Except where noted all samples were handled by conventional vacuum and drybox techniques. Sublimed niobium(V) iodide was prepared as before[5] by the reaction of the metal with a 10 to 15% excess of resublimed iodine. The components were heated to 500 and 180°, respectively, in an evacuated, V-shaped tube so that the product sublimed to the central portion of the container. The niobium metal, obtained through the generosity of Dr. R. E. McCarley of this laboratory, had representative impurity levels (p.p.m.) of Ta, 500–1000; O, 610; N, 400; C, 950; H, 5. Analysis of NbI_5 as prepared indicated iodine to niobium ratios of 4.95 or greater. Resublimation of this in an iodine atmosphere (salt at 450°, I_2 at 180°) was employed where a higher purity was desired, *e.g.*, $I/Nb = 5.00 \pm 0.01$. The tetra- and triiodide were generally prepared as previously described[5] (see Introduction). The lowest iodide is obtained from a similar but more exhaustive decomposition at still higher temperatures (525–600°) where condensation of NbI_4 in the cooler part of the container becomes increasingly important. Of course, a residue of almost any intermediate composition can also be obtained from such a nonequilibrium method of synthesis by suitable adjustment of time and temperature. However, the stabilities of the various phases are sufficiently different with respect to I_2 dissociation or to disproportionation that the limiting compositions obtained under appropriate conditions are very close to those of the pure phases isolated under equilibrium conditions.

Analysis.—Nearly all samples were analyzed by ignition of weighed samples to Nb_2O_5[5] since only niobium and iodine were present in most cases. The method was checked on aqueous solutions of samples with $4 < I/Nb < 5$ by precipitation of niobium with aqueous NH_3, filtration, and ignition to Nb_2O_5. Iodide was determined by the standard titration with silver using Eosin Y in a 50% solution of polyethylene glycol 400[12] as the indicator. Material balances were $100.0 \pm 0.2\%$. Ignition alone was considered adequate for lower iodides since they were prepared directly from such high-purity, higher iodides, and the reaction with glass is very slow below 700°.[13] Iodine to niobium ratios reported are considered to be ±0.02 unless otherwise noted.

Phase Studies.—Thermal analysis, differential thermal analysis, and isothermal equilibrations were employed for the construction of the equilibrium phase diagram. Samples were contained in small Pyrex or Vycor ampoules inasmuch as all of the iodides have iodine or iodide pressures above them at least at some of the temperatures employed. For thermal studies a small length of 3-mm. tubing was sealed through the side of the container and fused to the inside bottom to serve as a thermocouple well. Because of the sensitivity of the iodides to moisture, especially those with $I/Nb > 3$, the containers were evacuated and flamed before being taken into the drybox where they were loaded with 20 to 25 mmoles of salt *via* the attached ball joint, evacuated, and sealed off. Since the method of preparation may give mixtures that are not at equilibrium, the contained material was usually equilibrated for several hours before running the first heating or cooling curve.

The thermal analyses were carried out with the sample suspended axially in a 16-in. Marshall tube furnace and bracketed by convection baffles. Temperature was regulated by a proportioning controller with its thermocouple in contact with the inside wall of the furnace. Cooling and heating rates were usually about 5° $min.^{-1}$ although in specific cases these were $<1°$ $min.^{-1}$. Temperature and the differential result relative to an Al_2O_3 sample just below the iodide were registered on a two-pen recorder equipped with a variable span and suppression on the temperature record.

Powder Patterns.—X-Ray powder diffraction data given earlier[5] for $NbI_4(\alpha)$ and NbI_3 would be improved by the addition of 2.35 Å. (4) and 1.858 Å. (5) to the former. Better data for the stronger lines (Å.) from NbI_5, with relative intensities in parentheses, are: 3.24 (10), 3.07 (7), 3.04 (6), 2.39 (3), 2.34 (3), 2.01 (5), 1.862 (4), 1.850 (4), 1.826 (5), 1.625 (8). The more prominent lines for the other phases are as follows. γ-NbI_4: 3.07 (10), 2.36 (6), 2.03 (7), 1.81 (6), 1.714 (5), 1.693 (5), 1.542 (3), 1.355 (3), 1.304 (6), 1.255 (5), 1.229 (4), 1.200 (3). Nb_3I_8: 3.43 (10), 3.04 (4), 2.86 (10), 2.57 (3), 2.29 (4), 1.959 (8), 1.895 (4), 1.816 (4), 1.731 (8), 1.663 (5), 1.639 (3), 1.609 (3), 1.581 (5), 1.277 (4), 1.243, (4).

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(8) M. Chaigneau, *Compt. rend.*, **242**, 263 (1956).

(9) The $NbOI_3$ was reported[8] to be ruby-red, although other sources[5,10] have found it to be black. We have observed that ruby-red crystals form when NbI_5 is heated in the presence of a small amount of moist air.

(10) H. Schäfer and R. Gerken, *Z. anorg. allgem. Chem.*, **317**, 105 (1962).

(11) M. Chaigneau, *Compt. rend.*, **245**, 1805 (1957).

(12) R. B. Dean, W. C. Wiser, G. E. Martin, and D. W. Barnum, *Anal. Chem.*, **24**, 1638 (1952).

(13) M. A. Kust and J. D. Corbett, to be published.

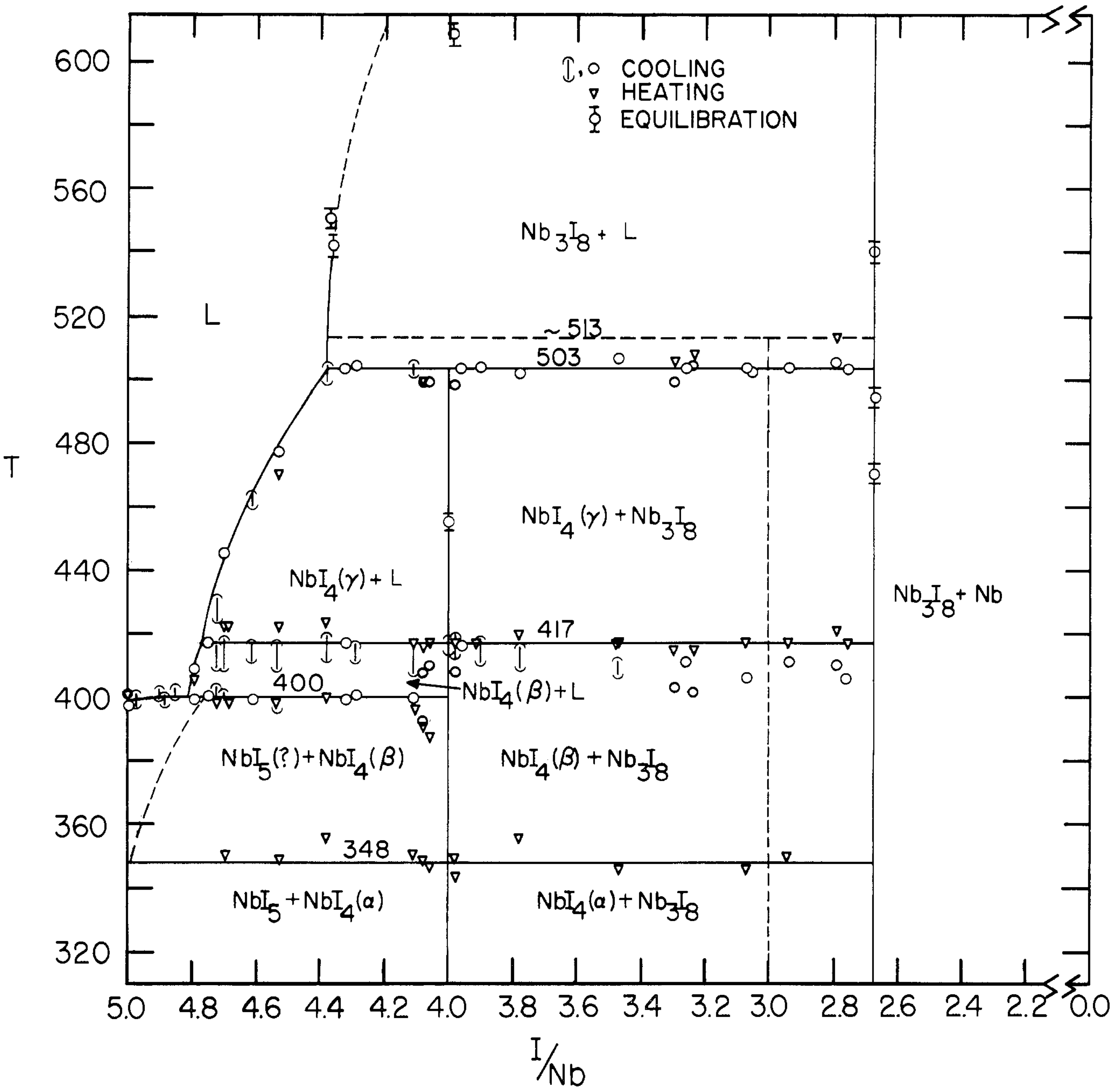

Figure 1.—The NbI$_5$–Nb phase diagram. Thermal analysis according to O, cooling (⟟ range observed on repetition); ∇, heating; Φ, equilibration (and filtration for liquidus points).

Results

The phase diagram of the niobium(V) iodide–niobium system (Figure 1) concisely summarizes the behavior of the individual phases as well as much of the chemistry of the condensed system. The evidence leading to this construction will be detailed, first for the stable lower phases NbI$_4$ and Nb$_3$I$_8$, then for the unusual NbI$_3$ as it is in a sense metastable in the system, and finally, for the region near NbI$_5$ where some problems of phase composition exist.

Niobium(IV) Iodide.—Samples near NbI$_4$ give prominent thermal effects near 503 and 417°. The higher is readily identified as the incongruent "melting" to a liquid *ca.* NbI$_{4.4}$ and what is subsequently shown to be Nb$_3$I$_8$. The decomposition on heating is sluggish and not well defined, but is clearly evident on cooling. The 417° transition persists over the same range and is certainly due to a fairly energetic phase transformation designated as $\beta \rightarrow \gamma$ on heating. Although the change is readily reversible in either direction, the high temperature γ form may be quenched to room temperature as judged by powder pattern results (see Experimental section). The change at 400° for samples with I/Nb > 4.0 is probably associated with a peritectic reaction with NbI$_5$ that will be considered later.

One of the observations that precipitated the present phase study was the occurrence of a distinct thermal effect near 320 to 340° in the I$_2$ dissociation pressures of the solid NbI$_5$–NbI$_4$ system,[14] and yet such was not observed in the preliminary thermal analysis. It sub-

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(14) P. W. Seabaugh and J. D. Corbett, unpublished research.

sequently developed that a small, endothermic effect was found at *ca.* 348° only on heating, and then only for samples that had been equilibrated 10–12 hr. near 300°. Shorter equilibration times or cooling analysis were without result. This change is assigned to an $\alpha \rightarrow \beta$ transition in NbI_4 since it persists over the range $2.94 < I/Nb < 4.70$. Evidently the reverse change is particularly slow. Powder patterns taken of samples equilibrated above or below 348° and either quenched or cooled in air exhibited no discernible difference.

As noted earlier, α-NbI_4 may be sublimed in a hot-cold tube at about 300°. Pure γ-NbI_4 may also be sublimed from mixtures with lower iodides provided these are first heated to about 520° to decompose NbI_3 (see below). A crystalline product, $NbI_{4.00\pm0.01}$, is obtained in a sealed tube with the sample at 430–490° and the condensate 3–10° cooler. The metallic-gray to brassy crystals are diamagnetic at room temperature according to a qualitative, Gouy measurement, as is α- (and β-) NbI_4.[15]

Triniobium Octaiodide.—Residues resulting from exhaustive thermal decomposition of higher iodides (see Experimental section) were typically found to have I/Nb ratios of 2.67–2.70. The results of transport, equilibration, and thermal analysis experiments verify that this is the correct composition of the phase and that it is the lowest stable iodide in the system. In the first method, a 3:1 mixture of metal and the composition $NbI_{2.26}$, for example, was heated in a sealed, evacuated, fused silica tube for 1 day at 600° to ensure equilibrium and then in a gradient 750–650° for 4 days to give a sample analyzing $NbI_{2.67}$ in the cooler end. (The vaporization of Nb_3I_8 is incongruent such that the solid transported separates from a more oxidized gas composition; a quantitative study of the equilibrium vaporization has been completed.[13]) The product of equilibration of higher iodides with excess metal shot or foil at 650–700° for several days yields the analysis ($I/Nb = 2.67$–2.65[13]) and the powder pattern of Nb_3I_8. In addition, nothing new is observed either in powder patterns or on thermal analysis up to 790° of mixtures in the range $2.2 < I/Nb < 2.6$ obtained through decomposition of Nb_3I_8.[17] The black Nb_3I_8 is visually stable in air for several days at room temperature, thus being similar to the corresponding chloride and bromide.[18,19] It reacts slowly with hot HCl or dilute HNO_3 and is qualitatively diamagnetic. The phase is sufficiently inert that it may also be recovered from mixtures with NbI_4 by solution of the latter in cold water, followed by drying the residue under vacuum at 200° (*e.g.*, $I/Nb = 2.64$, 2.67). The washing step probably should not exceed 10 min. Although this simple method provides a quick and easy means for the separation of Nb_3I_8 in reasonable purity, equilibration of NbI_5 with excess metal or thermal decomposition of higher iodides is preferable for a high-purity product.

Niobium(III) Iodide.—Pure NbI_3 can be obtained as a residue in the thermal decomposition of higher iodides[5] or as a sublimate from more reduced compositions ($2.67 < I/Nb < 3.0$), for example, after 48 hr. at 400 to 490° in a sealed, evacuated tube with the sample 9–14° hotter. All such products were in the range of $I/Nb = 3.00 \pm 0.05$. No significant trend or variation in X-ray data for NbI_3 was noted in diverse mixtures with NbI_4 or Nb_3I_8, supporting the analytical conclusion that there is no substantial homogeneity range in this phase. The triiodide also appears to be the principal product of the reaction of higher iodides or iodine with excess metal in a sealed tube up to ~500°, although the equilibrium phase would, of course, be the limiting Nb_3I_8. In one case analysis indicated that about 60% of the added NbI_4 had been reduced to NbI_3 after 8 hr. at 410°, as evident visually and confirmed by the powder pattern.

In spite of the identification of NbI_3 as an intermediate phase in the system, normal thermal analysis of a number of preparations in which it was present according to X-ray analysis failed to reveal any unique thermal effects attributable to it. Instead, as shown in Figure 1, the NbI_4 transformations were observed down to the composition $NbI_{2.75}$. It was finally established that NbI_3 decomposes substantially irreversibly near 513° and that only thermal effects for NbI_4 were found in the region $2.67 < I/Nb < 3.0$ because the first measurements had been made on cooling from above the NbI_3 decomposition point. In a few of many mixtures subsequently studied some evidence was found for the respective peritectic decomposition of NbI_4 and NbI_3 at 511–517° and 526–535°, and at 526° alone for NbI_3–Nb_3I_8 mixtures, but only on the first heating. However, the thermal effect for γ-NbI_4 is particularly poorly defined on first heating, probably because of the low density of the initial powder, so that this approach is not especially useful. The decomposition of NbI_3 was characterized better from powder patterns of samples that had been equilibrated at specified temperatures for 3 hr. and then quenched. These showed that NbI_3 persists at 500°, disproportionates completely at 522°, and only partially decomposes in this time at 513° (γ-NbI_4, NbI_3, and Nb_3I_8 evident after cooling). Furthermore, once NbI_3 decomposes it apparently does not re-form from the γ-NbI_4 and Nb_3I_8 obtained on cooling in reasonable periods of time at lower temperatures, *e.g.*, in 24 hr. at 510° for the composition $NbI_{2.94}$, in 46 hr. at 310° for $NbI_{3.07}$, and in 15 days at 400 or 450° for $NbI_{2.92}$. Since the decomposition appears to be slow in contrast to normal peritectic reactions, and its reversal difficult if not impossible, the phase is considered to be metastable and not a normal equilibrium product of the system, although unusual kinetic factors alone could be responsible.

The NbI_5–NbI_4 System.—This portion of the phase diagram, although not directly connected with the identification of lower iodides, contains some unusual

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[15] A previous report[5] to the contrary was in error, as noted elsewhere.[16]

[16] L. F. Dahl and D. Wampler, *J. Am. Chem. Soc.*, **81**, 3150 (1959).

[17] The diffractions due to metal do not appear until well below $I/Nb = 2.0$, doubtlessly a result of the refractory nature of the metal, so this alone is not an adequate test for the pure phase character of these compositions.

[18] H. Schäfer and K.-D. Dohmann, *Z. anorg. allgem. Chem.*, **300**, 1 (1959).

[19] H. Schäfer and K.-D. Dohmann, *ibid.*, **311**, 134 (1961).

effects that are not completely understood. Between the compositions NbI_5 and $NbI_{4.82}$ only a thermal effect at 400 ± 3° could be found on careful determination of differential heating and cooling curves (at $\leq 2°$ min.$^{-1}$; higher rates tended to give lower temperatures). A melting point of 400 ± 2° was repeatedly found for NbI_5 by thermal analysis. The same resulted with a sample to which excess iodine had been added to repress the dissociation and from a visual determination in a melting point block. Although the absence of the small effect of the transition in NbI_4 at 348 ± ° is not unusual in this range, the constancy of the principal thermal halt and absence of a higher liquidus effect are well established. Furthermore, powder patterns of mixtures in the same range that had been quenched to ice temperature from ~250 to 380° failed to give any indication of the formation of either solid solutions in NbI_5 or an intermediate compound not otherwise evidenced. Nonetheless, it still seems probable that significant solid solutions of at least β-NbI_4 in NbI_5 are formed and that these must revert to something close to the pure components relatively rapidly at room temperature. The inability to detect solidus transformations by thermal analysis is not particularly unusual. Thus the more or less constant halt from NbI_5 to $NbI_{4.82}$, perhaps increasing by a couple of degrees, is taken to represent the two unresolved loops for melting of this solution, and the 400° halt thereafter, its peritectic decomposition. The dashed solidus shown in Figure 1 is consistent with the observables as well as with one additional observation. Preliminary study of the iodine dissociation pressures of the compositions $NbI_{4.12}$ and $NbI_{4.55}$ in diaphragm cells gave concordant and well-behaved results below about 340°.[20] Above here, after some sluggishness, the log P–$1/T$ function changed slope, as expected, but to that corresponding to a process with a *lower* enthalpy change (by 3.0 kcal./mole of NbI_5). Since the heat of the presumed $\alpha \rightarrow \beta$ transition in NbI_4 must be positive, though evidently small (*vide supra*), this can be explained only if a more endothermic process in the reactant phase is overriding. The latter may be the solution of β-NbI_4 in NbI_5 if this is large with respect to that of α-NbI_4, as shown.

Discussion

Niobium–niobium bonding is apparently present in all of the diamagnetic niobium(IV) iodides. Dahl and Wampler[16,21] found that the α phase contains chains of iodine octahedra sharing opposite edges, with niobium atoms therein shifted from the centers in alternate directions so as to form niobium–niobium bonds at 3.31 Å. The β form is distinguished solely by a weakly endothermic transition at ~348° on heating but is not discernibly different from α-NbI_4 according to powder pattern results. These effects, and the fact that only the $\alpha \rightarrow \beta$ transition is rapid, suggest that such a subtle change as an order–disorder transition is involved.

The more endothermic $\beta \rightarrow \gamma$ change in NbI_4 at 417° accompanies more substantial rearrangement. According to Seabaugh and Dahl,[22] the structure of γ-NbI_4 is remarkable in that it is derived from the β-$TiCl_3$ (ZrX_3) structure with the 1:4 metal to iodide ratio accommodated by disordering the metal atoms over three-quarters of the usual cation sites. Center-to-center distances between neighboring cation sites appear to be somewhat shorter than in α-NbI_4.

Niobium(III) iodide is unusual in that it "melts" or decomposes slowly rather than sharply at *ca.* 513° to give Nb_3I_8 and $NbI_{4.4}$(l), and thereafter it cannot be re-formed from these products at lower temperatures in a period of more than 2 weeks. Analytical data for this phase as isolated from either metal- or iodide-rich compositions as well as X-ray data for these mixtures give no indication that the compound has a substantial variability in its composition. In particular, we were not able to verify our previous report to the contrary[5] as being significant. A substantial comparison with the NbI_3 composition reported by Chaigneau[8] is not possible since he reported little more than an analysis. However, the further reduction of this material to NbI_2 by hydrogen[11] is in conflict with the present results. Perhaps Chaigneau's product was a mixed compound such as NbI_2H since the reported gray-black NbI_2 seems somewhat more reactive toward water and acids than is Nb_3I_8.

Products in the neighborhood of NbI_3 obtained by Chizhikov and Grin'ko[7] (see the Introduction) by passage of iodine over the heated metal probably were not equilibrium phases since free iodine was mixed with them on the condenser. Although shifts in the powder line data and the absence of a product of definite composition were taken to indicate a range of solid solutions near $NbI_{3.2}$, the X-ray data given appear to be those for a mixture of γ-NbI_4, NbI_3, and Nb_3I_8 plus an unknown phase. The reported sublimation of NbI_3 under vacuum at 600–630° and its decomposition to metal on the walls of the container above 700° would be well above the disproportionation temperature of solid NbI_3 as well as the temperature at which we were able to (slowly) sublime the material in an evacuated, sealed tube. Furthermore, the metallic-appearing Nb_5Si_3 that forms from reaction of gaseous NbI_3 with glass above 700°[13] may have been mistaken for the metal.

It was noted in the previous section that the initial oxidation product of excess metal at ~400–500° is NbI_3 and not the equilibrium phase Nb_3I_8. A recent study[23] of niobium metal production by the hot wire or iodide process suggests that a similar effect may be important there. In this case variation of the temperature of the feed metal was found to give a pronounced maximum in the filament growth rate at 450–475°, and thereafter a smooth increase in rate as temperature was increased from 500 to at least 750°. The first increase in rate could result from the larger volatility of the triiodide as the initial product, with a subsequent decrease because of increased reduction to Nb_3I_8 and the ulti-

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[20] log $P_{mm} = (-3.836 \times 10^3)/T + 8.071$.[14]

[21] L. F. Dahl and D. Wampler, *Acta Cryst.*, **15**, 903 (1963).

[22] P. W. Seabaugh and L. F. Dahl, to be published.

[23] R. E. McCarley and W. Tadlock, U.S.A.E.C. Rept. IS-17 (1959), p. 40.

mate decomposition of NbI_3 above about 513°. Thereafter the incongruent volatilization of Nb_3I_8 would be controlling.

The lowest equilibrium phase in the iodide system is doubtlessly the "line" phase Nb_3I_8 ($NbI_{2.67}$), and it may be obtained from the thermal decomposition or metal reduction of higher iodides or as a "sublimate" transported from metal mixtures to the cooler end of a sealed tube at about 700°. This result is in distinct contrast with the reported preparation of niobium(II) chloride[18,23a] and bromide.[24] It can be speculated that an unusual stability of Nb_3I_8, perhaps a result of a polynuclear structure, may be a significant factor in the limited stability of the triiodide and in the absence of a lower iodide.

In addition, a striking dissimilarity exists between the composition invariability of the present triiodide and the character of the niobium trichloride and tribromide phases. Schäfer and Dohmann[18,19] have clearly shown that the stoichiometric trichloride and bromide are only incidental compositions in homogeneous phases of remarkable breath, $2.69 \pm 0.02 < Cl/Nb < 3.13 \pm 0.02$ and $2.67 < Br/Nb < 3.03$, respectively, with Nb_3X_8 as the lower limit in each. Both phases are reported to have the same hexagonal, layer structure, derived from the CdI_2 prototype with three-fourths of the metal positions occupied.[25] As a result Schäfer and Dohmann have suggested that the niobium(III) oxidation state may not exist as such and that these homogeneous phases can perhaps be better considered in terms of a variability in the relative amounts of, formally, niobium(IV) and niobium(II). Niobium(III) oxide is also unknown,[26] although the trifluoride has been reported.[27] In contrast, $NbI_{2.67}$ and NbI_3 appear as separate "line" phases in the iodide system with no significant variability in the composition of either, let alone a single phase region connecting them.

The powder diffraction data for NbI_3 can be indexed on a hexagonal basis (a = 6.61, c = 6.82 Å.),[28] with indices of the prominent reflections the same as observed for γ-NbI_4 but with a c/a ratio (1.03) notably greater than in γ-NbI_4[22] and the closely related triiodides of the group IV elements[29] (0.90–0.92). Although there thus may be some similarity between the structures of NbI_3 and γ-NbI_4, there is no suggestion of solid solutions between them. It is also interesting to note that the d^1 ZrX_3 phases show only what may be a suggestion of antiferromagnetic ordering at room temperature,[30] whereas NbI_3, with one more 5d electron per metal atom, is qualitatively diamagnetic at room temperature. Although the NbI_3 powder pattern[5] is reported to agree well in line sequence with the (unpublished) data for the $NbBr_3$ composition,[19] the latter has the Nb_3Cl_8 structure, where c/a is 1.82 or 2(0.91). On the other hand, Nb_3I_8 can be indexed with an orthorhombic cell, a = 7.57, b = 7.86, c = 14.61 Å.[28]

More work will obviously be necessary in order to understand the relationship of the niobium iodide phases to those in chloride and bromide systems, although at present the correspondence does not appear particularly direct. It is also interesting to note that although tantalum(IV) iodide is isostructural with the (α) niobium analog,[21] there is a definite dissimilarity in the composition of the lowest tantalum iodide, which is Ta_6I_{14} or $TaI_{2.33}$.[31] Some relationship may still be present, however, since the cation obtained in aqueous solution, $Ta_6X_{12}^{2+}$, can be oxidized to the tetrapositive ion, which then corresponds to $TaX_{2.67}$ with halide anions.[32]

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(23a) NOTE ADDED IN PROOF.—A recent report indicates the phase is more probably $NbCl_{2.33}$ [H. Schäfer and H. G. Schnering. *Angew. Chem.*, **76**, 833 (1964)].

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