TABLE III

	E^0_m	E^0_N	E^0_c
5% *d*-fructose	0.21900	0.01499	0.21985
10% *d*-fructose	.21502	.01352	.21689

The mean activity coefficients, $y_\pm$, of hydrochloric acid in the two *d*-fructose solutions were computed from the e.m.f. data by the equation

$$\log y_\pm = (E^0_m - E)/0.1183 - \log m \qquad (4)$$

The values so calculated were plotted against m on a large scale and the values at rounded molalities determined. These values are given in Table IV together with the values for pure water listed by Harned and Owen.[2]

The experimental values of the activity coefficients can be reproduced almost exactly by the Debye equation

$$\log y_\pm = -\frac{A\sqrt{c}}{1 + \mathring{a}B\sqrt{c}} - \log(1 + 0.002mM_{xy}) + C'c \qquad (5)$$

in which C' is a constant introduced to account for the "salting out" effect. This constant was not found to be significant in these studies. In only two of the solutions was the deviation between the experimental and theoretical activity coefficients as much as 0.003. It is noted in Table IV that the activity coefficient increases from pure water to 5% *d*-fructose and then decreases for the 10% solution. The same increase and decrease was found for *d*-glucose by Williams, *et al.*[1]

TABLE IV

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN *d*-FRUCTOSE–WATER MIXTURES AT 25°

Molality	$X = 0$	$X = 5\%$	$X = 10\%$
0.005	0.9285	0.931	0.927
.01	.9048	.906	.903
.02	.8755	.877	.874
.03		.858	.853
.05	.8304	.835	.827
.07		.816	.810
.08		.809	.803
.10	.7964	.798	.791
.11		.793	.785

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[2] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 340.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Anhydrous Niobium Tribromide and Trichloride. Preparation and Properties

BY CARL H. BRUBAKER, JR., AND RALPH C. YOUNG

Niobium tribromide has been prepared in a pure state by reduction of the pentabromide with hydrogen at 500°. The substance condensed as a black crust on the tube walls and as black rods on a cold finger-condenser. The rods were much more reactive than the crust. When the tribromide was sublimed *in vacuo* and collected upon a cool surface, the reactivity of the product depended on the temperature gradient. The tribromide decomposes to the metal and $NbBr_5$ at about 925°. Niobium trichloride, which was prepared in essentially the same way as the tribromide, is also obtained as crust and rods. It is more stable than the bromide and less reactive. X-Ray examinations indicated that both rods and crust had the same crystal structure and hence the difference in reactivity is probably a matter of surface. The behavior of both the trichloride and tribromide toward various reagents is given.

Niobium tribromide has not been previously reported but the preparation of anhydrous $NbCl_3$ was first accomplished by Roscoe,[1] in 1878, who led the vapor of $NbCl_5$ through a glass tube heated to redness. He described the trichloride as a black crust, composed of tiny plates "resembling sublimed iodine." Moreover, he reported that these plates were stable in the air, insoluble in water and inert to most aqueous acids and bases. They were oxidized by hot dilute nitric acid to Nb_2O_5. At red heat they reacted with CO_2 and formed $NbOCl_3$ and CO.

Süe[2] also prepared anhydrous $NbCl_3$ by reducing $NbCl_5$ vapor with H_2 at 400°. He too found the compound to be an inert black crust and found that it was attacked by oxygen and air only at temperatures above 270°, at which point it was converted to the pentoxide.

Emeléus and Gutman[3] reduced $NbCl_5$ by subliming it with hydrogen at 500° and obtained a gray-green product, the composition of which corresponded to no definite compound.

Since $TaBr_3$ had been found to be very reactive when prepared by the reduction of the tantalum pentabromide with hydrogen by a method employing the St. Claire–Deville "hot-cold" tube, it was decided to carry out the reduction of the pentabromide of niobium as well as the pentachloride in this same manner.[4,5]

Preparation of Anhydrous $NbBr_3$.—Niobium tribromide was prepared by bromination of 2 g. of granular niobium metal and subsequent reduction of the pentabromide in a continuous train (Fig. 1) to obviate the need of transferring the easily hydrolyzed pentabromide.

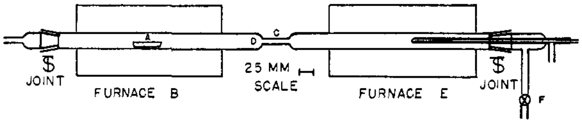

Fig. 1.—Halogenation reduction train.

A boat (A) containing the metal was placed in the tube within furnace (B) and the system was closed and baked out at 200° in a stream of dry nitrogen. When finally dry, furnace (B) was heated to 450° and dry bromine, with nitrogen-carrier, was led through the system at about 90 ml./min. (measured at 26°). When halogenation was complete, furnace (B) was cooled with dry nitrogen flowing through the system.

The $NbBr_5$ was then sublimed across the constriction (C) and through the glass wool plug (D). The constriction and

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[1] H. E. Roscoe, *Chem. News*, **37**, 26 (1878).

[2] P. Süe, *Bull. soc. chim.*, **6**, 830 (1939).

[3] H. J. Emeléus and V. Gutmann, *J. Chem. Soc.*, 2115 (1950).

[4] R. C. Young, *J. Chem. Ed.*, **20**, 378 (1943).

[5] R. C. Young and J. H. Hastings, Jr., THIS JOURNAL, **64**, 1740 (1942).

plug were employed to prevent the gas flow from carrying along any of the powdery and less volatile $NbOBr_3$ which might have been formed. Sublimation was carried out just below the boiling point (270°) of $NbBr_5$.

Furnace (E) was then heated to 500°, the finger being cooled by running water and the pentabromide was slowly sublimed into that furnace in a stream of hydrogen. After about an hour all the $NbBr_5$ had been sublimed and the system was cooled in a stream of nitrogen.

The product was in the form of a shiny black crust (similar to that described for $NbCl_3$ by Roscoe[1]) and as black rods on the finger-condenser.

The apparatus was then sealed off at the constriction (C), stopcock (F) was closed and the tube was transferred to a "dry-box" (filled with dry nitrogen) where it was opened.

The crust was found to be stable in the air and insoluble in water, but the rods from the condenser were found to hydrolyze quickly in air. Analysis of the crust was carried out by fusion with sodium carbonate, acidification with nitric acid, filtration and ignition of niobic acid and precipitation of AgBr. (*Anal.* Calcd. for $NbBr_3$: Nb, 27.93; Br, 72.08. Found: Nb, 27.88; Br, 71.56.)

The rods were hydrolyzed in 1 *N* KOH; silver bromide was precipitated from the acidified solution after removal of the hydrous oxide. The Nb_2O_5 obtained appeared to contain some silica from the alkali digestion in glass vessels and had to be determined from an HNO_3 digestion of another sample. (*Anal.* Found: Nb, 27.63; Br, 71.96.)

It has also been found that if Nb metal is treated with dry HBr at temperatures above 425°, $NbBr_3$ crust is collected on the reaction tube walls and a mixture of $NbBr_3$ and $NbBr_5$ is deposited on the finger-condenser. At lower temperatures $NbBr_5$ was formed and only in small amounts. At about 900° some metal begins to collect on the tube walls, probably due to thermal decomposition of the tribromide. (It will be pointed out later that $NbBr_3$ undergoes thermal decomposition at about this temperature.)

Preparation of Anhydrous $NbCl_3$.—Niobium trichloride was prepared in the same manner as $NbBr_3$ except that chlorination was carried out at 400°. Again both crust and rods were obtained; the rods being more reactive than the crust, and niobium trichloride less reactive than the tribromide. The crust was analyzed by digestion with hot 1 *N* HNO_3. When all the black had disappeared, the Nb_2O_5 was filtered off, ignited and weighed, and the chloride was subsequently determined as AgCl from the filtrate. (*Anal.* Calcd.: Nb, 46.62; Cl, 53.38. Found: Nb, 46.69; Cl, 53.03.)

The same method of analysis was used for the rods, but more rapid and careful manipulation was required due to their greater reactivity. (*Anal.* Found: Nb, 46.83; Cl, 52.99.)

To demonstrate the oxidation state, 75.75 mg. of the rods were oxidized with a known amount of ceric sulfate in sulfuric acid and the excess ceric ion was back titrated with ferrous sulfate. 0.7593 milliequivalent of ceric ion was used. Had the sample been pure $NbCl_3$, 0.7600 milliequivalent should have been required to oxidize the niobium from Nb(III) to Nb(V).

Niobium metal reacts with hydrogen chloride at temperatures above 400°, and the crust of $NbCl_3$ is formed on the walls of the reaction tube and rods of $NbCl_3$ and crystals of $NbCl_5$ are obtained on the cold finger. Some pentachloride was always obtained even at 900° even though hydrogen was mixed with the hydrogen chloride.

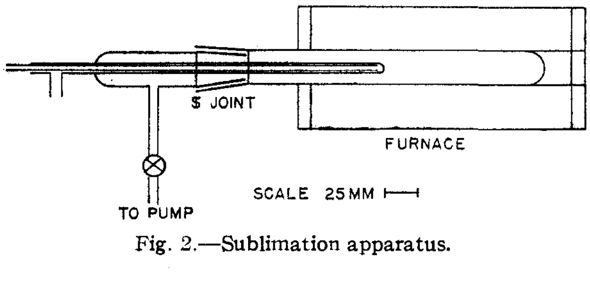

Fig. 2.—Sublimation apparatus.

Properties of $NbBr_3$ and $NbCl_3$

Crystallinity.—Although the properties of the trihalides collected on the tube walls differed greatly from the properties of the halides on the cold element, there was no difference in the crystal structure indicated on the X radiograms of $NbCl_3$, crust and rods having identical patterns. Due to the high fluorescent background, the radiograms have not been analyzed. No single crystals have yet been obtained.

Under a microscope the $NbBr_3$ crust (and also $NbCl_3$) appears to be an aggregation of small plates, while the rods (of both trihalides) seem to be like miniature graphite or carbon electrodes.

Sublimation.—Niobium tribromide was placed in a tube for sublimation *in vacuo* (Fig. 2) and the apparatus was evacuated to about 10^{-4} mm. and the temperature was slowly raised. The first trace of sublimate on the finger-condenser appeared at 390–400°. On the condenser, the sublimate had the form of a black mass and no evidence of chemical change was found. When temperatures slightly above 900° were attained, thermal decomposition of the unsublimed material took place. Niobium metal was deposited on the tube walls and $NbBr_5$ in the cooler regions.

Niobium trichloride behaved similarly except that the first trace of sublimate was detected after the temperature in the tube was about 490–500°. Moreover, the material was thermally stable up to 965°, at which point the Vycor tube collapsed.

A number of sublimation experiments have been carried out on both $NbBr_3$ and $NbCl_3$, and in every case the form of the product was seen to depend on the temperature gradient across which it was collected. If collected upon the tube walls, which are just a bit cooler than the heated section, a black inert crust is formed; when much greater temperature gradients are used, a very finely divided and reactive product is obtained which will take fire in the air. Thus, it would appear that the reactivity of the material is a function of particle size rather than of structure. However, both rods and crust behave in the same way with respect to sublimation.

Reactions.—In Table I certain reactions of the crust-like form of $NbBr_3$ and $NbCl_3$ are described.

TABLE I

ACTION OF CERTAIN REAGENTS ON THE CRUST-LIKE FORM OF $NbBr_3$ AND $NbCl_3$

Reagent	Action on $NbBr_3$	Action on $NbCl_3$
KOH (10%)(100°)	Slow decomp. with evoln. of hydrogen	None visible
Na_2CO_3 (*N*/10)(100°)	Very slow evoln. of H_2	None
NH_3 (48%)(100°)	Slow formn. of Nb_2O_5	Slow formn. of Nb_2O_5
H_2O (100°)	None	None
HCl (3 *N*)(100°)	None	None
HCl (12 *N*)(100°)	None	None
H_2SO_4 (concd.)(300°)	Reacts even at 25°, forming SO_2, Br_2	Slow oxid., forming SO_2
HNO_3 (1–6 *N*)(100°)	Oxid. to Nb_2O_5 with evoln. of Br_2	Oxid. to Nb_2O_5
Acetic acid (glacial) (100°)	None	None
HF (45%)(25°)	None	None
Chlorinated org. solvs. CCl_4, $CHCl_3$, *n*-BuCl at respective b. p.'s	None	None
Benzene, acetone, ether	None	None

The data above indicate that $NbBr_3$ and $NbCl_3$ are quite inert when formed on the heated walls of the reaction tube. When, however, fine subdivision is attained by rapid condensation of the materials from the vapor phase, they decompose quickly in aqueous media and even take fire in the air.

The action of aqueous ammonia upon these compounds is remarkable in view of the fact that other alkalies and water had a very slow effect or none at all. It has been found that they also react with dry ammonia vapor at 25° and this reaction is now being studied.

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