CANADA

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH

RESEARCH REPORT

R 123

Price 25 cents.

Dept. Mines & Technical Surveys
MINES BRANCH
JAN 20 1964
C2
LIBRARY
OTTAWA, CANADA

KINETICS OF THE REACTION OF NIOBIUM PENTACHLORIDE WITH WATER VAPOR

T. R. INGRAHAM & B. J. P. WHALLEY

EXTRACTION METALLURGY DIVISION

REPRINTED FROM THE CANADIAN JOURNAL OF CHEMICAL ENGINEERING, DECEMBER, 1963

DECEMBER 1963

© Crown Copyrights reserved

Available by mail from the Queen's Printer, Ottawa,
and at the following Canadian Government bookshops:

OTTAWA
Daly Building, Corner Mackenzie and Rideau

TORONTO
Mackenzie Building, 36 Adelaide St. East

MONTREAL
Aeterna-Vie Building, 1182 St. Catherine St. West

or through your bookseller

A deposit copy of this publication is also available
for reference in public libraries across Canada

Price 25 cents Catalogue No. M38-1/123

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada
1963

Kinetics of the Reaction of Niobium Pentachloride with Water Vapor[1]

T. R. INGRAHAM[2] *and B. J. P. WHALLEY*[2]

When niobium pentachloride is exposed to moist air, hydrogen chloride is liberated and hydrated niobium pentoxide or niobic acid remains. It is believed that the rate of the reaction is controlled by the rate of diffusion of water across a layer of unidentified intermediate product of constant thickness (about 0.2 mm.). The constant thickness of the layer is maintained by the spalling and cracking of the product after it exceeds a critical thickness. Since the reaction takes place at an interface between the niobium pentachloride and the layer of intermediate, it is necessary to normalize the results for the decrease in interfacial area as the reaction proceeds. When this is done, the rate of the reaction, expressed in terms of grams of niobium pentachloride reacting per square centimetre of interface per hour, is:

$$\text{Rate} = (7.7 \pm 0.4) \times 10^4 (p_s/p) \exp [(-8.1 \pm 0.6) \times 10^3]/RT$$

Lorsque le pentachlorure de niobium est exposé à l'air humide il s'hydrolyse en chlorure d'hydrogène et en acide niobique (pentoxide de niobium hydraté). On croit que le taux de cette réaction est limité par le taux de diffusion de la vapeur d'eau à travers une couche de produit intermédiaire, non-identifié, d'épaisseur constante (environ 0.2 mm). L'épaisseur de cette couche de substance intermédiaire serait maintenue constante par un phénomène de désintégration se produisant lorsqu'une certaine épaisseur critique est atteinte.

Le taux de la réaction a été trouvé égal à:

$$(7.7 \pm 0.4) \times 10^4 (p_s/p) \exp [(-8.1 \pm 0.6) \times 10^3]/RT$$

grammes de pentachlorure de niobium par centimètre carré par heur. Ce taux a été obtenu après correction des résultats expérimentaux pour tenir compte de la diminution de l'aire de l'interface pentachlorure de niobium — produit intermédiaire durant la réaction.

When niobium pentachloride ($NbCl_5$) is exposed to moist air, an overall reaction takes place to produce hydrogen chloride and hydrated niobium pentoxide(1,2). It seems likely that at temperatures near room temperature, the only constituent of moist air involved in the reaction is water. This is because niobium pentachloride is stable in dry oxygen at temperatures up to about 150°C., at which it begins to react slowly to produce niobium oxytrichloride(3).

Because of the generally increasing interest in chlorine metallurgy, and the possibility that niobium pentachloride might prove an interesting source material for reduction to niobium metal, it was decided to investigate the kinetics of the niobium pentachloride-water reaction to enable some of the problems of handling this material to be assessed.

Because of the likelihood that niobium pentachloride would be recovered from a preceding chlorination process as a loose powder, in much the same form as zirconium tetrachloride is recovered, it was decided to make the kinetic study on powdered material, using the pelletizing techniques developed by Warner and Ingraham(4) and Ingraham and Marier(5) for studies of the thermal decomposition of powdered ferric sulphate, aluminum sulphate and calcium carbonate. This technique permits the use of powders without the usual difficulties associated with highly variable surface areas, which are tedious to measure and difficult to reproduce.

Preparation of Materials

Niobium pentachloride was prepared by chlorinating niobium metal (99.7% Nb) with cylinder-grade chlorine gas. This strongly exothermic reaction was controlled by regulating the supply of chlorine in a flow system. During reaction, the metal glowed and the reaction products were evaporated freely from its surface. The solid chlorination product was impure and consisted of yellow niobium pentachloride, white niobium oxytrichloride and some darkly colored material which may have been subchlorides of niobium.

The niobium pentachloride was purified by volatilizing it and passing the vapors through a heated bed of activated charcoal(6) which had previously been flushed with chlorine and niobium pentachloride to desorb contaminants from it. The product recovered by condensation from this operation was a homogeneous, finely crystalline yellow powder. Adsorbed chlorine was removed from the powder by pumping, and the material was stored, under dry nitrogen, in sealed containers. All manipulations involving the pentachloride were made either in a dry box or in a stream of dry nitrogen. The product was analyzed for niobium and chlorine by standard wet methods and for oxygen by neutron activation. The results obtained from the two batches of material were as follows:

	Niobium (%)	Chlorine (%)	Oxygen (%)
Lot No. 1	34.68	64.84	0.15
Lot No. 2	34.45	65.11	0.15
Theoretical	34.39	65.61	0.00

Niobium oxytrichloride ($NbOCl_3$) was prepared by reaction of niobium pentachloride with niobium pentoxide:

$$3NbCl_5 + Nb_2O_5 \rightleftharpoons 5NbOCl_3 \ldots\ldots\ldots\ldots\ldots (1)$$

The niobium pentachloride was heated to 190°C. and entrained in a 150 cc./min. stream of nitrogen. The gases were passed through a vertical bed of −10+65 mesh anhydrous niobium pentoxide which was maintained at a temperature of 300°C. The niobium oxytrichloride was recovered by condensation on a "cold" finger which was maintained at 200°C.

By wet chemical methods, the following analysis of the material was obtained:

---

[1] *Manuscript received June 12, 1963; accepted July 15, 1963*

[2] *Head, Research Subdivision and Senior Scientific Officer, Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ont.*

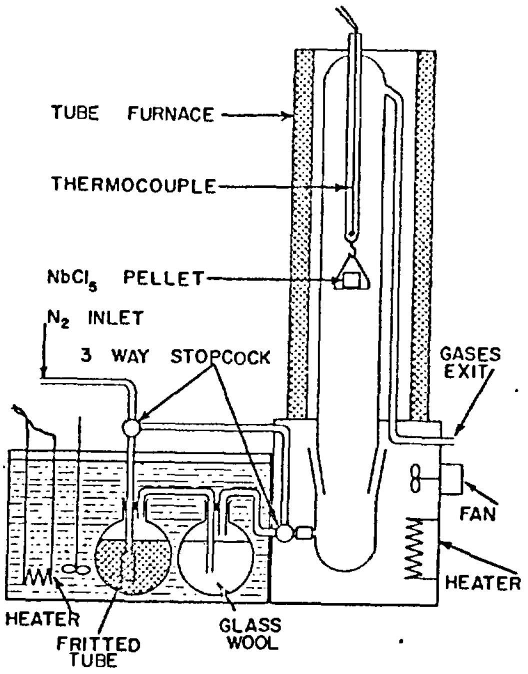

Figure 1—Apparatus.

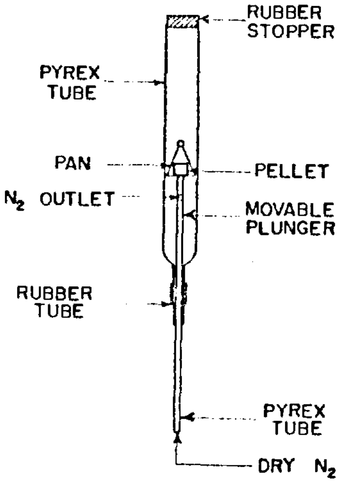

Figure 2—Pellet transfer device.

	Niobium (%)	Chlorine (%)
Lot No. 1	43.29	48.72
Theoretical	43.15	49.41

On the assumption that the overall decomposition reactions for niobium pentachloride and niobium oxytrichloride would be represented by the following equations:

$$2NbCl_5 + (5+x)\,H_2O \rightleftharpoons Nb_2O_5 \,.\, xH_2O + 10\,HCl \ldots\ldots(2)$$

$$2NbOCl_3 + (3+x)\,H_2O \rightleftharpoons Nb_2O_5 \,.\, xH_2O + 6\,HCl, \ldots\ldots(3)$$

a number of preliminary experiments were done to select a satisfactory method for determining the rate of reaction of the pelletized powders in a stream of moist gas. In one group of preliminary experiments, the sample was weighed continuously, using a quartz spring balance, in the expectation that the loss in weight could be used to determine the extent of reaction. This method proved unsatisfactory because of the pronounced and variable retention of water in the reaction products. In a second group of experiments an attempt was made to correlate the rate of reaction with the rate of liberation of hydrogen chloride. This method was only partially satisfactory, because it was found that the hydrogen chloride was quantitatively desorbed only when a very high rate of gas flow was used.

During the preliminary experiments with pellets of niobium pentachloride, it was observed that when the reaction was initiated a dense layer of white product was formed over the yellow pentachloride. As the reaction progressed, the product layer became swollen, cracked, and porous. The product was loose and could be rubbed and scraped off readily to reveal the dense unreacted cylindrical core of niobium pentachloride.

Since the reaction ceased immediately when the flow of water vapor to the pellet was discontinued, it was possible to make an accurate determination of the extent of reaction by weighing the niobium pentachloride core. It was therefore decided to make a series of experiments on identical pellets and to determine the rate of reaction from the fraction of the original weight of material remaining after a series of timed exposures to a flow of moist nitrogen. Nitrogen flow rates of about 1000 cc./min. were used in all experiments because it had been observed in preliminary experiments, that the rate of reaction was unaffected by changes in nitrogen flow rate at flow rates greater than about 500 cc./min.

Apparatus and Procedure

The apparatus used in the niobium pentachloride experiments is shown diagrammatically in Figure 1. It consisted of three parts. In one part, a nitrogen stream of known velocity at atmospheric pressure was saturated with water vapor by being bubbled through water held at a specified temperature in a constant temperature bath. Any entrained spray was removed by passage through packed glass wool. The water-saturated gas was conveyed through the second part of the apparatus, a stirred air bath, which enclosed the port for loading and unloading the sample. The third part of the apparatus consisted of a furnace, which had been wound on pyrex glass to permit observation of the niobium pentachloride pellet, and a sample holder to which a thermocouple was affixed. The pellet was suspended from the sample holder, in a small, perforated pan. It was assumed, because the reaction was slow, that the sample temperature was effectively the same as the ambient temperature which was measured.

To protect the pellet from exposure to atmospheric moisture during loading and unloading, the apparatus shown in Figure 2 was used. By keeping a small positive pressure of nitrogen on this apparatus it was possible to attach or detach the pellet and sample holder from the furnace assembly, and to transfer it to a dry box for weighing and other manipulations.

The pellets used in the experiments were cylindrical in shape and either 0.41 or 0.52 cm. in radius. They were prepared in a cylindrical die at 20,000 psi. pressure, and were cut after extrusion so that the height and diameter of the pellet were identical within ±2%. The density varied slightly from pellet to pellet but was within the range 2.20 to 2.52. The higher density is close to 90% of the density of solid niobium pentachloride.

Results

In the first group of experiments, pellets having an initial radius of 0.52 cm. were subjected to a flow of nitrogen containing water vapor at a partial pressure of 4.02 cm. of mercury. The experiments were done at temperatures of 55, 65, 75, 85 and 95° ±0.5°C.

When the results were analyzed, it was observed that a graph of the residual weight of niobium pentachloride, raised to the two-thirds power, versus reaction time, was linear for any particular reaction temperature and partial pressure of water. This observation suggested that the process was a topochemical one, for which the observed rate of reaction was determined by the area of the interface between the niobium

Figure 3—Weight of $NbCl_5$ reacting per square centimeter of interfacial area as a function of time.

○ = 55°C., △ = 65°C., □ = 75°C., + = 85°C., ▽ = 95°C. P_{H_2O} = 4.02 cm.Hg.

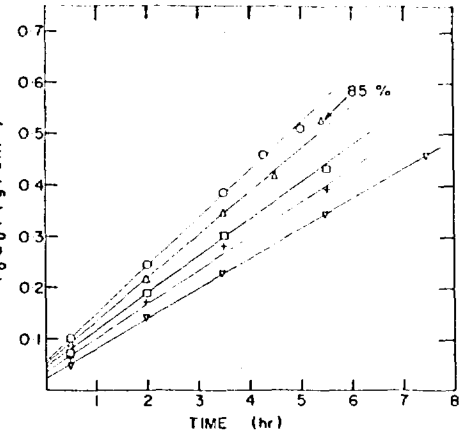

Figure 3.

Figure 4—Rate of reaction c, as a function of relative water vapor pressure, p/p_s. + = 55°C., ▽ = 65°C., ○ = 75°C., △ = 85°C., □ = 95°C.

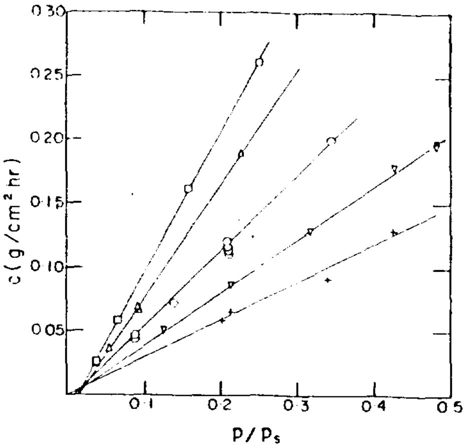

Figure 4.

pentachloride and the reaction products. Since it was anticipated that pellets of different densities and radii would be used, the data were analyzed according to the method of McKewan(7), who has shown that a linear relationship is obtainable for a topochemical reaction with interfacial area rate dependency when the product $r_o d_o f$ is plotted against reaction time. The quantity r_o is the initial radius of a cylindrical pellet of identical height and diameter, d_o is the density of the reactant, and f, for the shape of pellet used in this study(5), is defined by the equation:

$$f = 1 - (1 - \alpha)^{1/3} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

In Equation (4), α is the fraction reacted, which was calculated from the original weight of the pellet and the weight remaining after a specified time of reaction. When the results were plotted according to this procedure, the graph shown in Figure 3 was obtained.

The linearity of the relationships in Figure 3 (shown up to 85% reaction) confirms the topochemical nature of the reaction. It is of interest to note that the slope of the line on the $r_o d_o f$ versus t graph is the reaction rate constant c, expressed in the units of grams per square centimetre per hour. When expressed in this form, it is evident that the reaction rate constant decreases with increasing pellet temperature. This observation, combined with the knowledge that for vapors such as water it is usual to express the partial pressure as a relative pressure(8), led to the re-expression of the results in the form shown in Figure 4.

In Figure 4, the reaction rate constant is shown plotted against the relative pressure term p/p_s for a variety of temperatures. In this graph, p represents the partial pressure of water vapor in the nitrogen stream, and p_s the vapor pressure of water at the temperature of the pellet. All of the lines were fitted by the least squares method. At a constant reaction temperature, p was varied by varying the temperature of the water saturator shown in Figure 1.

It is of interest to note, in Figure 4, that the linearity of the curves for each temperature indicates that the reaction rate constant is related to the relative vapor pressure by an equation of the type:

$$c = kp/p_s$$

The normalized reaction rate constant, k, has the more usual behavior of increasing with increasing temperature.

To obtain the activation energy for the reaction, the logarithm of the water-vapor-pressure normalized rate constant k was plotted against the reciprocal of the experimental temperature. In each instance, the value of k is the slope of the c versus p/p_s graph shown in Figure 4. The graph of log k versus $1/T$ is shown in Figure 5. The slope of the line, as fitted by the least squares method, yields the following equation:

$$\log k = (4.89 \pm 0.02) - (8.1 \pm 0.6) \times 10^3/2.303\,RT \ldots\ldots (5)$$

The constants in the foregoing equation were unchanged when a different batch of niobium pentachloride was used.

Since niobium oxytrichloride has been reported(3) as a possible intermediate in the reaction between niobium pentachloride and water vapor, a brief investigation was made of the rate of decomposition of niobium oxytrichloride in the presence of moisture:

$$2NbOCl_3 + (3+x)\,H_2O \rightleftharpoons Nb_2O_5 \,.\, xH_2O + 6\,HCl, \ldots\ldots (3)$$

The initial experiments showed that the behavior of niobium oxytrichloride toward water vapor was quite different from that of niobium pentachloride under corresponding circumstances. The most obvious difference was that there was no change in color, no swelling, and no visible interface between the reactant and product.

Since the product layer was compact and coherent and there was no visible interface, there was no possibility of using the same method for determining the rate as had been used in the niobium pentachloride experiments. Instead, the rate of reaction was determined from the amount of hydrogen chloride collected from the effluent gases. The results from a typical group of experiments are shown in Figure 6.

In Figure 6, the quantity $(r_o d_o f)^2$ is shown plotted against the time of reaction. Although the correlation with linearity is not particularly good, it is better than correlations obtained when using $r_o d_o f$ versus t or log t. It is significant that when the rate of the reaction as designated in Figure 6 is compared with that for a run done with niobium pentachloride under corresponding conditions, the rates of reaction are about the same: i.e., $NbOCl_3 - H_2O$, 55% in 3.5 hr; and $NbCl_5 - H_2O$, 62% in 3.5 hr.

Discussion

The foregoing hydrolysis experiments have shown that a specimen prepared by compacting powdered niobium pentachloride behaved in essentially the same manner as would be expected of a solid specimen: i.e., the reaction occurred only on the outer surface of the specimen. When the observed rate of reaction was normalized by expression in terms of unit area of interface, it was evident that for constant conditions, the rate of reaction was constant. From this observation it was concluded that the site of reaction rate control was at or near the reactant-product interface. This type of rate control may be caused by a slow chemical reaction in the interface or by a slow process of diffusion through a layer of material of essentially constant thickness in the interface(9). Arguments will be advanced to favour the latter possibility.

When the initial portions of the $r_o d_o f$ versus t graphs were examined, it was evident that the least squares lines, representing the reaction rate constant, did not pass through the origin. Instead, they intersected the $r_o d_o f$ axis at a distance which indicated that the reaction rate was quite rapid at first and then decreased to a somewhat slower linear rate. This suggested a paralinear process, in which the initial parabolic portion of the curve was relatively short and represented the formation of a partially protective layer(10). The presence of such a layer was observed on examination of partially reacted specimens. A very thin, tightly adherent layer was present on the surface of the residual niobium pentachloride. The product outside

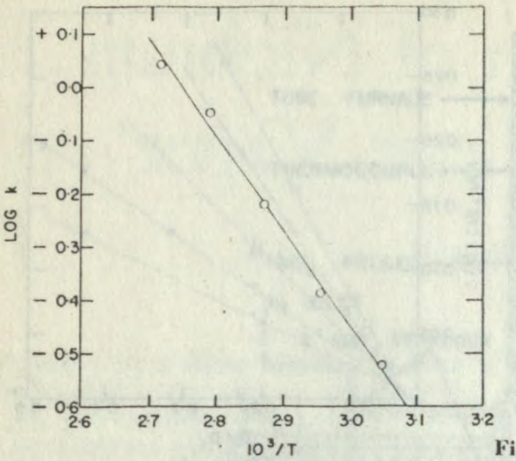

Figure 5 — Graph of logarithm of normalized rate constant, versus reciprocal temperature.

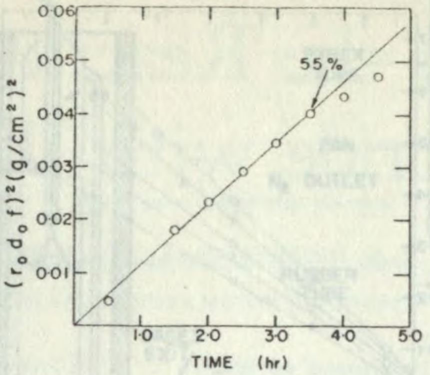

Figure 6—The parabolic rate of disappearance of $NbOCl_3$ in the $NbOCl_3$-H_2O reaction at 75°C.

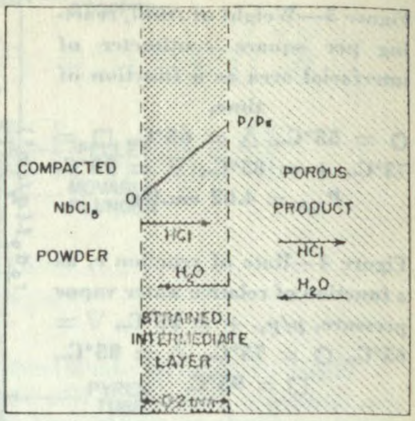

Figure 7—Schematic representation of reaction mechanism.

this layer was loose and porous, suggesting that the layer was probably under substantial strain as it was formed, and that its maintenance at a constant thickness was probably due to splitting and cracking when some critical thickness had been exceeded. By assuming continued linearity, and extrapolating some of the $r\,d\,f$ versus t lines back to the t axis, it was estimated that the critical thickness of the protective product layer was about 0.2 mm. This concept is in accord with the oxidation behavior of some metals[11,12].

From experiments done to determine the reaction rate from the difference in weight caused by the adsorption of water and the liberation of hydrogen chloride, it was evident that both water and hydrogen chloride were retained in the product layers in substantial amounts. The amount of water available on the product side of the protective layer is determined by the ratio p/p_s. Since the amount of water available on the pentachloride side of the protective layer may reasonably be assumed to be zero, then the driving force for the diffusion of water across the layer is $(p/p_s - 0)$, or p/p_s. This is in accord with the finding that the reaction rate constant is a function of the ratio p/p_s. The small activation energy for the reaction (8 kcal.) is consistent with a diffusion process[13].

The part, if any, played by niobium oxytrichloride in the hydrolysis of niobium pentachloride is not clear. However, it seems reasonable to argue that since the rates of hydrolysis per unit area of both materials are about the same, and since it is entirely likely that any niobium oxytrichloride formed from niobium pentachloride would present a much larger surface area than the original material, any niobium oxytrichloride formed should hydrolyze very rapidly. If this were true, then niobium oxytrichloride would not be observed as a reaction intermediate during the hydrolysis of niobium pentachloride. It has not been possible to confirm this premiss by X-ray identification because all of the reaction products are amorphous. However, it is significant that all attempts to recover niobium oxytrichloride by distillation from the residues were unsuccessful.

The final evidence suggesting that niobium oxytrichloride is probably not involved in the niobium pentachloride-water reaction, is based on the difference in behavior of niobium pentachloride and niobium oxytrichloride. The oxytrichloride builds up a partially protective layer which continues to increase in thickness as the reaction proceeds. At no time has this layer been observed to crack or spall. For these reasons, it seems plausible to argue that niobium oxytrichloride is not directly involved in the hydrolysis of niobium pentachloride. The exact nature of the partly protective product layer has not been resolved, but it may be that some of the compounds characterized in hydrochloric acid solutions, e.g., $Nb(OH)_2Cl_3$[14], might be involved. The presence of hydroxychlorides of the type mentioned would be consistent with the formation of niobic acid as the final product of reaction.

The mechanism of the reaction process as deduced on the basis of the foregoing experiments, is illustrated in Figure 7.

Conclusions

When niobium pentachloride is exposed to moist air at temperatures up to near 100°C., the pentachloride reacts with the moisture to produce a hydrated niobium pentoxide, or niobic acid, and hydrogen chloride. The rate of the reaction is probably controlled by the rate of diffusion of water across a layer of product which is maintained at a constant thickness by cracking when the stresses in the layer exceed a critical limit. When the observed reaction rate is normalized for the area of the interface between the reactant and product, the results can be correlated by the linear relationships applicable to a topochemical process.

The rate of the reaction may be estimated from the following equation:

$$\text{Rate} = (7.7 \pm 0.4) \times 10^4\,(p_s/p)\exp[(-8.1 \pm 0.6) \times 10^3]/RT$$

Acknowledgments

The authors are pleased to acknowledge the following contributions by other members of the Mines Branch staff: J. Brannen, assembly and operation of apparatus; H. P. Dibbs, neutron activation analyses; and L. G. Ripley, chemical analyses.

References

(1) Remy, H., "Treatise on Inorganic Chemistry", Vol. 2, Elsevier Publishing Company, Amsterdam, p. 108, (1956).
(2) Friend, J. N., "A Text Book of Inorganic Chemistry" Vol. VI, Charles Griffin and Co., London, Pt. III, p. 150, (1929).
(3) Fairbrother, F., Cowley, A. H. and Scott, N., J. Less Common Metals, **1**, 206 (1959).
(4) Warner, N. A. and Ingraham, T. R., Can. J. Chem. Eng., **40**, 263 (1962).
(5) Ingraham, T. R. and Marier, P., Can. J. Chem. Eng., **41**, 170 (1963).
(6) Lind, R. and Ingles, T. A., "The Chlorination of Niobium Ores and Oxides", Technical Note 106, Research and Development Branch (C), UKAEA, (1954).
(7) McKewan, W. M., Trans. Am. Inst. Mining Met. Engrs., **212**, 791 (1958).
(8) Weiser, H. B., "Colloid Chemistry", John Wiley and Sons, Inc., New York, p. 30, (1946).
(9) Farrer, R. L. Jr. and Smith, H. A., J. Phys. Chem., **59**, 763 (1955).
(10) Massoth, F. E. and Hensel, W. E., Jr., J. Phys. Chem., **63**, 697 (1959).
(11) Cubicciotti, D., J. Am. Chem. Soc., **74**, 1200 (1952).
(12) Vernon, W. H. J., Akeroyd, E. I. and Stroud, E. G., J. Inst. Metals, **65**, 301 (1939).
(13) Glasstone, S., Laidler, K. J. and Eyring, H., "The Theory of Rate Processes", McGraw-Hill Book Company Inc., New York, p. 544 (1944).
(14) Kanzelmeyer, J. H., Ryan, J., and Freund, H., J. Am. Chem. Soc., **78**, 3020 (1956).

* * *