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REDUCTION OF NIOBIUM PENTACHLORIDE AND TANTALUM PENTACHLORIDE WITH NIOBIUM METAL IN A GAS CHROMATOGRAPH

by

David John Lorine

M.S. Thesis, May 1967

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REDUCTION OF NIOBIUM PENTACHLORIDE
AND TANTALUM PENTACHLORIDE WITH NIOBIUM METAL
IN A GAS CHROMATOGRAPH

by

David John Lorine

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REDUCTION OF NIOBIUM PENTACHLORIDE AND
TANTALUM PENTACHLORIDE WITH NIOBIUM METAL IN A
GAS CHROMATOGRAPH*

David John Lorine

ABSTRACT

A dual column gas chromatograph was used to study the separate reactions of TaCl_5 and NbCl_5 with niobium metal. The results of a preliminary reduction study confirmed that NbCl_5 could be completely reduced by niobium metal to the nonvolatile NbCl_3 at a temperature of about 450°C . It was also verified that there is essentially no reduction of TaCl_5 by niobium metal under similar conditions.

In the studies using the gas chromatograph, ratios of the amount of pentachloride leaving the niobium reduction bed to the amount of pentachloride entering the reduction bed (response ratios) were measured as a function of temperature at a given space time for both NbCl_5 and TaCl_5 . From response ratios measured at 500°C and at different space times, it was concluded that the reduction of NbCl_5 with niobium metal is essentially first order. The reaction rate constant was estimated to be 3.14 sec^{-1} .

Reaction of both NbCl_5 and TaCl_5 with the stainless steel components of the chromatograph system complicated the study of the reactions of NbCl_5 and TaCl_5 with niobium metal. Because of this difficulty, the chromatograph was found unsuitable for actual separation studies using mixtures of NbCl_5 and TaCl_5 .

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Contamination of the NbCl_5 samples with niobium oxychloride also complicated the study. However, complete separation of NbCl_5 from NbOCl_3 was achieved by fractional sublimation. This separation was accomplished by temperature programming from 70° to 220°C .

INTRODUCTION

A rapidly growing interest in the technology of niobium and tantalum has developed due to their attractive properties and importance in modern industry. Because of its high-temperature strength and low neutron cross section, niobium alloys are used extensively in nuclear reactors, gas turbines, and missiles as well as in many other such related applications. Interest in tantalum stems mainly from its high resistance to corrosive media. It is, therefore, used extensively in equipment in the chemical industry, particularly in alloys.

Because niobium and tantalum almost always appear together in nature, a great deal of work has been done on the separation of the two metals. The first separation method to be used industrially was the Marignac process (10, p. 38). This process involves the crystallization of potassium fluotantalate from a dilute solution of hydrofluoric acid. In the same solution, the niobium salt is more soluble. Other separation methods have been developed but up until the past few years have not been commercially employed.

Interest in the separation of the pentachlorides of niobium and tantalum has developed from the chlorination

process for the extraction of niobium and tantalum from their ores. In this process the ores are first chlorinated and then a crude distillation of the resulting chlorides yields a relatively pure mixture of niobium pentachloride and tantalum pentachloride. Because the thermodynamic properties of tantalum pentachloride and niobium pentachloride are very similar, separation methods for these two compounds have been limited to difficult distillation and selective reduction methods. A number of investigations have shown that niobium pentachloride can be selectively reduced by a number of reducing agents whereas tantalum pentachloride is left unaffected.

It was the primary purpose of this investigation to determine if mixtures of niobium pentachloride and tantalum pentachloride could be quantitatively separated by the selective reduction of niobium pentachloride to niobium trichloride with niobium metal. A dual column gas chromatograph was incorporated to study the reduction reactions.

REVIEW OF LITERATURE

A great deal of interest in the separation of the pentachlorides of niobium and tantalum has developed from the chlorination process for the extraction of niobium and tantalum from their ores. It has been shown by Ainscough, Holt, and Trowse (1) that mixtures of TaCl_5 (b.p., 234°C) and NbCl_5 (b.p., 247°C) form nearly ideal liquid solutions which closely follow Raoult's Law. As a result, distillation has been used as a separation technique although it is complicated by the presence of tungsten and iron.

Schafer, Goser, and Bayer (5) investigated the formation of NbCl_4 by the reduction of NbCl_5 using hydrogen, iron, niobium, and aluminum as the reducing agents. When a mixture of NbCl_5 and hydrogen was passed through a tube at 450°C , black NbCl_3 deposited in the hottest portion of the tube. Brown NbCl_4 deposited at an intermediate temperature and the yellow NbCl_5 deposited in the coldest part of the tube. Niobium pentachloride was also reduced by aluminum at about 270°C . The process left a residue in the cold part of the tube containing NbCl_4 and aluminum trichloride. When using iron as the reducing agent, the NbCl_5 was reduced to NbCl_4 at 400°C . The ferrous chloride formed in the reaction

was not volatilized. When niobium powder at 400° C was used as the reducing agent, gaseous NbCl_4 was formed. In addition to these experiments, it was found that the reduction of TaCl_5 by the above reducing agents was more difficult than was the reduction of NbCl_5 . It was surmised that a separation of TaCl_5 and NbCl_5 might be accomplished by using a selective reduction process which would incorporate hydrogen, iron, niobium, or aluminum as the reducing agent.

In a similar investigation, Schafer and Pietruck (9) studied the reduction of NbCl_5 with niobium, NbCl_5 with tantalum, TaCl_5 with niobium, and TaCl_5 with tantalum. It was found that at 400° C, NbCl_5 could be reduced with either niobium or tantalum according to the following reactions:

The reduction of TaCl_5 could not be accomplished with either niobium or tantalum at a temperature of 400° C.

The results of Brubaker and Young (2) are tabulated in Table 1. It was shown that NbCl_4 is stable in the presence of NbCl_5 at 350 to 400° C. However, at temperatures ranging from 400 to 500° C, it was shown that NbCl_5 is quantitatively reduced to NbCl_3 when greater amounts of niobium are used.

Table 1. The results of Brubaker and Young (2) for the reaction between niobium pentachloride and niobium metal

Experiment	NbCl ₅ /Nb ^a	Temperature °C	Products
1	5/1	350	Large needles of NbCl ₄ with NbCl ₅
2	5/1	400	Large needles of NbCl ₄ with NbCl ₅
3	4/1	400	NbCl ₄ needles with NbCl ₃ , some NbCl ₅
4	2/1	450 - 500	Inert NbCl ₃ and Nb
5	3/2	400 - 450	Inert NbCl ₃ and Nb
6	1/1	475 - 500	Inert NbCl ₃ and Nb

^aMole ratio.

The separation of NbCl₅ and TaCl₅ by the selective reduction of NbCl₅ has been studied by the Union Carbide Metals Company (10, p. 605). A mixture of the pentachloride vapors was passed through a bed containing enough niobium to quantitatively reduce the NbCl₅ to NbCl₃. The reduction bed temperature ranged from 350 to 400° C. The NbCl₅ was reduced, whereas the TaCl₅ was not affected. It was surmised that the

reduction bed could be rejuvenated by the disproportionation of the NbCl_3 into NbCl_5 and niobium metal at a higher temperature. According to Brubaker and Young (2), this temperature should be approximately 950°C .

Schafer and Pietruck (9) found that when hydrogen was used as the reducing agent, NbCl_5 was converted to NbCl_3 in a temperature zone of 400 to 450°C . At 500°C , it was found that TaCl_5 remained unchanged. McIntosh and Broadley (3) found that with a five-fold excess of hydrogen at 500°C , only 74 percent of the initial amount of NbCl_5 could be reduced.

Schafer et al. (5) studied the disproportionation of NbCl_4 into NbCl_5 and NbCl_3 . It was found that the reaction was reversible:

At 280°C , it was found that the equilibrium was dependent upon the pressure of NbCl_5 . If the pressure was low, the NbCl_4 decomposed to NbCl_3 and NbCl_5 . At high NbCl_5 pressures, the NbCl_4 was stable.

THEORY

Possible Mechanisms for the Reduction
of NbCl_5 to NbCl_3 with Niobium Metal

In view of the discussion in the previous section, it is evident that at least three general reaction mechanisms exist for the reduction of NbCl_5 to NbCl_3 with niobium metal:

Mechanism	K_{P500°
A. $\frac{2\text{Nb(s)}}{3} + \text{NbCl}_5(\text{g}) = \frac{5\text{NbCl}_3(\text{s})}{3}$	1.7×10^9
B. $\frac{1\text{Nb(s)}}{4} + \text{NbCl}_5(\text{g}) = \frac{5\text{NbCl}_4(\text{g})}{4}$	511
$2\text{NbCl}_4(\text{g}) = \text{NbCl}_5(\text{g}) + \text{NbCl}_3$	16.2
C. $\frac{1\text{Nb(s)}}{4} + \text{NbCl}_5(\text{g}) = \frac{5\text{NbCl}_4(\text{g})}{4}$	511
$\frac{1\text{Nb(s)}}{3} + \text{NbCl}_4(\text{g}) = \frac{4\text{NbCl}_3(\text{s})}{3}$	1.7×10^5

The equilibrium conditions for these reactions are shown in Figure 1 for a temperature range of 200 to 550° C. The thermodynamic properties which were used to derive these conditions are shown in Table 2.

Figure 1. The effect of temperature upon equilibrium conditions for the reactions

$$\log K_p = -7.55 + 12,980/T$$

$$\log K_p = 2.42 + 223/T$$

$$\log K_p = -8.25 + 7390/T$$

$$\log K_p = -7.95 + 10,180/T$$

Table 2: The thermodynamic properties of the tantalum and niobium chlorides
as compiled from Schafer and Kahlenberg (6,8)

Compound	$\Delta H_f^\circ_{298}$ kcal/g-mole	S°_{298} cal/g-mole $^\circ$ K	C_p	Melting point $^\circ$ C	Boiling point $^\circ$ C
NbCl ₅ (s)	-190.5	54	$38 - (3)10^5 T^{-2}$	204.7	
TaCl ₅ (s)	-205.0	56	$38 - (3)10^5 T^{-2}$	215.0 ^a	
NbCl ₅ (l)					247.4
TaCl ₅ (l)					232.9 ^a
NbCl ₅ (g)	-169.9	93	$31.6 - (3.7)10^5 T^{-2}$		
TaCl ₅ (g)	-182.7	100	$31.6 - (3.7)10^5 T^{-2}$		
NbCl ₄ (s)	-166.0	44	$31.9 - (2.9)10^5 T^{-2}$	sublimes 350 - 400	
NbCl ₄ (g)	-136.6	85	$25.8 - (2)10^5 T^{-2}$		
NbCl ₃ (s)	-139.0	35.2	$23 + (3.9)10^{-3} T -$ $(1.7)10^5 T^{-2}$	disproportionates 900 - 1000	

^aMelting point and boiling point of TaCl₅ from Ainscough et al. (1)

By observing the equilibrium data at 500° C, it is concluded that equilibrium conditions for all three mechanisms favor a complete reduction if the niobium metal is present in excess of the amount needed to entirely reduce the NbCl_5 to NbCl_3 .

In mechanism A, complete irreversibility is indicated by the high value of the equilibrium constant ($K_p = 1.7 \times 10^9$). In mechanism B, the first reaction is essentially irreversible ($K_p = 511$) while the second reaction may be considered reversible ($K_p = 16.2$). (The reversibility of the latter reaction conforms with the conclusions of Schafer et al. (5) and Brubaker and Young (2)). In the first reaction, complete reduction of NbCl_5 to NbCl_4 is evident. Since NbCl_4 will only be stable in the presence of NbCl_5 , complete conversion to NbCl_3 should result. For the overall mechanism, the equilibrium pressures of NbCl_5 and NbCl_4 are, respectively, 5.8×10^{-10} atm and 6.0×10^{-6} atm. In mechanism C, both reactions are irreversible. The equilibrium pressures of NbCl_5 and NbCl_4 are the same as for mechanism B.

Since no investigations on the reaction rates of these reactions have been published, it is difficult to predict

the results which might be obtained if NbCl_5 is reduced with niobium metal in a tubular flow reactor.

The Study of a First Order Reaction

Using a Dual Column Gas Chromatograph

Consider the following irreversible reaction:

Assuming this reaction to be first order with respect to B, the equation for the rate of disappearance of B may be written as

$$-r = -\frac{dc}{dt} = k_1 C \quad (1)$$

where C is the concentration of B and k_1 is the first order reaction rate constant.

Consider a tubular reactor containing a bed of solid component D. The net change in the number of moles of B with time within a differential void volume element of the bed, viz. dV , will be

$$vC|_{l+d\ell} - vC|_l = r dV \quad (2)$$

where v is the volumetric flow rate. Taking the limit as dV approaches zero (i.e., as $d\ell$ approaches zero) gives

$$\frac{d(vC)}{dv} = r = -k_1 C. \quad (3)$$

If it can be shown that v is constant throughout the bed, i.e., that negligible variation in the residence time t results from the substitution of V/v_0 for t (see Appendix A), equation (3) may be rearranged to give

$$\frac{dC}{C} = -k_1 \frac{dV}{v_0} \quad (4)$$

where v_0 is the constant volumetric flow rate. Integration between the inlet and outlet of the reactor yields

$$\int_{C_1}^{C_2} \frac{dC}{C} = - \frac{k_1}{v_0} \int_0^V dV \quad (5)$$

$$\ln \frac{C_2}{C_1} = - k_1 \frac{V}{v_0} = - k_1 \tau \quad (6)$$

where C_1 and C_2 are, respectively, the concentrations of B at the inlet and outlet of the reactor, V , the void volume of the reaction bed, and τ , the residence time in the reaction bed. From this result, it is noted that for a constant residence time, the concentration ratio C_2/C_1 is also constant and is independent of the concentration at the beginning of the reaction bed.

Consider the case where a sample of B is injected as a pulse into a carrier gas which flows at a constant rate through a reaction bed. In Figure 2, the concentration profile of B resulting from this pulse injection is shown at

Figure 2. Illustration of concentration profiles at inlet and outlet of reduction bed for a first order reaction

the beginning and at the end of the reaction bed as B passes through the bed. For a first order reaction, it is noted that the instantaneous concentration of B at the end of the reaction bed at a time $t = \tau$ is proportional to the instantaneous concentration of B at the beginning of the bed at a time $t = 0$.

With the assumption of negligible dispersion of the concentration through the reaction bed (see Appendix B), the resulting concentration profiles can be represented as in Figure 3. The curve $C_1 = f_1(l)$ represents the concentration of B as it passes into the reaction bed and the curve $C_2 = f_2(l)$ represents the concentration of B as it passes out of the reaction bed.

The area under the curve $C_1 = f_1(l)$ can be expressed as

$$A_1 = \int_0^{l_0} f_1(l) \, dl \quad (7)$$

and the area under the curve $C_2 = f_2(l)$ can be expressed as

$$A_2 = \int_0^{l_0} f_2(l) \, dl. \quad (8)$$

It has been established that for a first order reaction and for a constant residence time

$$\frac{C_2}{C_1} = k_0 = \text{constant} = \frac{f_2(l)}{f_1(l)}. \quad (9)$$

Figure 3. Comparison of concentration profiles at inlet and outlet of reduction bed for a first order reaction

Therefore, since $f_2(l) = k_0 f_1(l)$, the area under the curve $C_2 = f_2(l)$ can be represented as

$$A_2 = k_0 \int_0^{l_0} f_1(l) dl. \quad (10)$$

It is observed then that the area ratio can be expressed as

$$\frac{A_2}{A_1} = \frac{k_0 \int_0^{l_0} f_1(l) dl}{\int_0^{l_0} f_1(l) dl} = k_0 = \frac{C_2}{C_1}. \quad (11)$$

From this result, it is concluded that the area ratios are equal to the concentration ratios for a constant residence time and negligible dispersion. Equation (6) may then be expressed as

$$\ln \frac{A_2}{A_1} = - k_1 \frac{V}{V_0} = - k_1 \tau. \quad (12)$$

In view of the result obtained in equation (12), it is evident that a first order reaction of the type

may be studied with a dual column gas chromatograph. A jumper tube is used to connect the exit port of the first analytical column to the injection port of the second analytical column. The first column is left empty and a bed of D is placed in the second column. If a sample of B is

injected as a pulse into the injection port of the first column, a response representing B before it has passed into the reaction bed will be obtained from the first side of the detector. Another response representing B after it has passed out of the reaction bed will be obtained from the second side of the detector. The ratio of the area under the second response to the area under the first response then represents the ratio of the amount of B leaving the reaction bed to the amount of B entering the reaction bed. By injecting pulse samples of B at a constant bed temperature and at varying carrier gas flow rates, the first order reaction rate constant k_1 in equation (12) can then be determined.

This type of study may be applied to the reaction

if the overall reduction of NbCl_5 to NbCl_3 with niobium metal is first order. In this case, components B, D, and E represent, respectively, NbCl_5 , niobium metal, and NbCl_3 . The corresponding rate expression would be

$$-\frac{d(\text{NbCl}_5)}{dt} = k_1(\text{NbCl}_5)$$

where (NbCl_5) represents the concentration of NbCl_5 .

EXPERIMENTAL

The experimental work consisted of two parts. The first part consisted of a preliminary investigation in which the reduction of NbCl_5 to NbCl_3 by niobium metal was qualitatively and quantitatively observed. In addition, the effect of niobium metal upon TaCl_5 was also observed. The results and operating variables of this investigation were then used as a basis for the second part which consisted of applying the reduction process to a dual column gas chromatograph.

Preliminary Reduction Studies

To qualitatively and quantitatively observe the reduction reaction between niobium pentachloride and niobium metal, a two-step process was incorporated. In the first step, niobium metal was chlorinated to form the pentachloride. In the second step, the pentachloride was reduced by subliming it through a heated bed of niobium metal.

Figures 4 and 5 show, respectively, the entire system and the design of the tubular reactors. To eliminate any chlorine reactions with the system, the entire system was constructed from Pyrex glass tubing. All connections were made with polyethylene tubing which at room temperature does

Figure 4. Flow diagram of apparatus used in preliminary reduction studies

Figure 5. Illustration of tubular reactors used in preliminary reduction studies

not react with chlorine. A movable furnace was constructed in order to heat the reactor in the necessary positions. Chlorine was made available to the system by condensing gaseous chlorine into a glass tube which was inserted into a dry ice-acetone bath. When the chlorine was fed into the reactor, the tube containing the liquid chlorine was lifted out of the bath and the chlorine was vaporized into the system. In this way, the amount of chlorine fed into the system could be easily determined.

The tubular reactors were constructed from 10 mm. OD Pyrex glass tubing with a length of about five feet. The metal which was chlorinated was first weighed and then placed in a glass boat which was then inserted into the reactor. The metal used as the reduction bed was first weighed and then poured into the reactor at the desired position. Both reactants were kept in place by small plugs of glass wool.

In the chlorination process, the section of the tube which contained the glass boat with the niobium was heated to about 470° C. Chlorine was fed into the system along with the nitrogen carrier gas until the niobium was completely converted to the pentachloride. The pentachloride

was deposited at the end of the furnace. While the oven was cooling, the system was purged with nitrogen to remove absorbed chlorine.

In the reduction process, the oven was moved to the initial position as shown in Figure 5. After the reduction temperature had come to equilibrium, the oven was moved slowly over the pentachloride until the final oven position was reached. In this way, the pentachloride was vaporized and carried into the reduction bed by the flow of nitrogen.

To find the weight gain in the reduction bed, the section of the tube containing the reduction bed was removed and weighed. This section was then cleaned and reweighed. Since the weights of the two glass wool plugs and the weight of the reduction bed were known prior to the reaction, the weight gain in the reduction bed was then calculated. From the stoichiometry of the reaction, the amount of niobium pentachloride reduced to niobium trichloride was determined.

Reduction Studies Using the Gas Chromatograph

An F & M Model 720 Dual Column Gas Chromatograph was used in this investigation. The chromatograph was equipped with a Honeywell ElectroniK 15 Chromatograph Recorder. For the measurement of areas, the recorder was equipped with a

Model 201-B Disc Chart Integrator. The detector cells and injection ports were constructed from stainless steel 316. Nickel filaments were used as the thermal conductivity detection units.

To eliminate decomposition of the pentachlorides, all columns were constructed from 1/4 inch OD Pyrex glass tubing. A twelve inch uncoiled glass tube was used as the first column and a fourteen foot coiled glass tube was used as the second column. One-quarter inch OD Kovar glass-to-metal seals were connected to the leads of the columns. These seals were used to enable the fitting of the columns to the leads from the injection block with 1/4 inch Swagelok fittings.

The exit port of the first column and the injection port of the second column were connected with a coiled, fourteen foot, 1/4 inch OD Pyrex glass tube. The coil was heated in a well insulated Transite box which was internally heated with a coil of 18 gage Chromel A furnace wire. The leads of the jumper tube were covered with pieces of graphite and wrapped with heating tapes.

Argon was used as the carrier gas. Before entering the system, the argon was sent through a bed of molecular sieves

and then through a dry ice-acetone cold trap. The tubing in the cold trap was filled with granules of anhydrous calcium chloride in order to increase the internal surface area. The argon flow was controlled with a Moore Flow Controller (constant differential type) in conjunction with a fine-taper needle valve. The flow rate was measured with a soap-film flow meter. A flow sheet of the chromatograph system is shown in Figure 6.

In order to incorporate a gas chromatograph for the study of the reduction of niobium pentachloride, a method of injection had to be used in which the only detector response would be due to the presence of the pentachloride. This requirement eliminated the use of liquid injection -- a method in which the material to be studied is dissolved in a solvent and then injected with a syringe. Moreover, this method was found unsuitable because of the hygroscopic and reactive nature of niobium pentachloride and tantalum pentachloride.

An injection method was adopted which allows the sample to be vaporized in the injection port and then, when equilibrium is attained, to be injected into the system as a vapor. To incorporate this method, the material is sealed in a small

Figure 6. Flow diagram of gas chromatograph system

capillary tube (see Appendix C for sample preparation details) which is then inserted into the stem of a solid sample injector (Figure 7) near the handle. The stem of the injector is then inserted into the injection port of the chromatograph and the sample capsule allowed to reach thermal equilibrium. The capillary is then broken by pushing the plunger and the vaporized sample is carried into the system by the carrier gas.

Figure 7. Illustration of solid sample injector (actual size)

RESULTS

Preliminary Reduction Studies

The results of three quantitative runs and one qualitative run are represented in Table 3. The last column (percent MCl_5 accounted for) includes the amount of pentachloride reduced to NbCl_3 plus any unreduced pentachloride or pentachloride reduced to NbCl_4 . These values were used to roughly check the analytical procedure incorporated.

In Run No. 1-3, 95.5 percent of the pentachloride was reduced to NbCl_3 . However, a slight amount of NbCl_4 was observed at the end of the furnace. Qualitatively, the NbCl_4 possessed a brown color. It later appeared to slowly disproportionate to NbCl_5 and non-volatile black NbCl_3 while the system was being purged with nitrogen.

In Run No. 3-3, using a smaller initial amount of pentachloride and a lower flow rate, it was found that the NbCl_5 was completely reduced to NbCl_3 . After the reaction, the tube was completely void of any residue except for the black NbCl_3 in the reduction bed.

In Run No. 61-2, approximately fifteen grams of -40+80 mesh niobium metal were used in the reduction bed. It was found that at a reduction bed temperature of 450°C and a

Table 3. Results from the reduction of NbCl₅ and TaCl₅ with niobium metal

Run No.	Metal converted to pentachloride grams	Weight of reduction bed grams	Metal mesh size	Reduction bed temperature °C	Carrier gas flow rate ml/min	Theoretical ^a weight gain in reduction bed grams	Actual weight gain in reduction bed grams	% MCl ₅ reduced	% MCl ₅ accounted for
1-3 ^b	niobium 0.2072	15.0270	-100+140	448	16.2	0.6026	0.5752	95.5	98.0
3-3	niobium 0.1451	15.0680	-100+140	455	13.8	0.4220	0.3985	94.4	94.4 ^c
61-2 ^d	niobium	15	-40+80	450	15.0				
5-3	tantalum 0.1983	14.9495	-100+140	465	15.8	0.3926	0.0012	0.3	101.2

^aBased on the amount of TaCl₅ or NbCl₅ fed into the reduction bed.

^bSlight NbCl₄ formation.

^cDue to unidentified random errors.

^dLittle NbCl₃ formation and much NbCl₄ formation.

flow rate of 15.0 ml/min, brown NbCl_4 was deposited at the end of the furnace. Only a slight amount of black NbCl_3 was present in the reduction bed.

In Run No. 5-3, TaCl_5 was sublimed through the reduction bed. After the reduction process, the reduction bed appeared to be void of any reduced chloride and a large amount of white TaCl_5 was deposited at the end of the furnace.

The results of seven runs in which mixtures of TaCl_5 and NbCl_5 were sublimed through a niobium reduction bed are represented in Table 4. These results are plotted in Figure 8. In all runs except in Run No. 12, a yellow tint indicating the presence of NbCl_5 was observed in the residue at the end of the furnace. The conversion of NbCl_5 to NbCl_3 obtained in Run No. 12-3 is not shown in Figure 8 because of analytical uncertainties (footnote c, Table 4).

Table 4. The effect of temperature upon the conversion of NbCl_5 to NbCl_3 using mixtures of NbCl_5 and TaCl_5

Run No.	Niobium converted to pentachloride grams	Tantalum converted to pentachloride grams	Reduction bed temperature °C	Carrier gas flow rate ml/min	Weight of reduction bed ^a grams	Theoretical weight gain in reduction bed grams	Actual weight gain in reduction bed grams	% NbCl_5 reduced
6-3	0.1014	0.1931	453.5	15.8	15.0388	0.2949	0.2485	84.3
7-3	0.0797	0.1534	475	15.4	15.0478	0.2318	0.2072	89.4
8-3 ^b	0.0531	0.0982	455	11.5	11.9783	0.1544	0.1286	83.3
9-3	0.0322	0.0690	445	15.9	14.8857	0.0936	0.0742	79.3
10-3	0.0348	0.0705	380	13.8	14.8645	0.1012	0.0037	3.7
11-3	0.0780	0.0892	413	13.7	13.9796	0.2268	0.0993	43.8
12-3 ^c	0.0809	0.0566	490	14.0	15.0620	0.1646	0.1458	88.6

^aExcept for Run No. 8-3, the reduction bed contained a 50-50 mixture of -40+80 mesh and -140+finer mesh niobium metal. In Run 8, -40+80 mesh metal was used.

^bA considerable amount of NbCl_4 was formed in this run.

^cThe weight of the residue at the end of the furnace was only 89.9 percent of the weight of TaCl_5 passed into the reduction bed. If the value for the conversion of NbCl_5 to NbCl_3 (88.6 percent) was correct, the weight of the residue at the end of the furnace should have been over 100 percent of the weight of TaCl_5 passed into the reduction bed. Unidentified random errors are indicated in the results of this run.

Figure 8. The effect of temperature upon the conversion of NbCl_5 to NbCl_3 using mixtures of NbCl_5 and TaCl_5

Reduction Studies Using the Gas Chromatograph

Figures 9 and 10 show typical responses for TaCl_5 and NbCl_5 which were observed at detector and injection port temperatures where response tailing and sample reaction within the chromatographic system, as will be discussed later, were reduced to a minimum. These responses were obtained by injecting samples through two empty columns connected in series. The operation variables for these responses are given in Table 5. A nitrogen response is included which shows that both sides of the detector yielded responses of equal areas for an inert sample. Figure 9 also shows the method of area measurement which was incorporated in this work.

Table 5. Operation variables for the responses shown in Figures 9 and 10

Sample response	Detector temperature °C	Injection port temperature °C	Argon flow rate ml/min	Oven temperature °C
1 TaCl_5	170	195	90	200
2 N_2	240	230	90	193
3 TaCl_5	166	216	90	204
4 NbCl_5	166	216	90	204

Figure 9. Detector responses due to injections of pure TaCl₅ and nitrogen with two empty columns connected in series

Figure 10. Detector responses due to injections of pure TaCl₅ and NbCl₅ with two empty columns connected in series

Reduction of NbCl₅ and TaCl₅ versus reduction bed temperature

In Run No. 86-4, a small heating coil was wrapped around the portion of the second chromatograph column which contained 4.4 grams of -100+140 mesh niobium metal. The oven was maintained at 172° C and the detector and injection port temperatures were held at 162 and 201° C, respectively. The response ratios (the ratio of the amount of NbCl₅ passed through the second side of the detector to the amount passed through the first side of the detector) are tabulated in Table 6. The relative sample size is also included to show the effect of the initial amount of pentachloride upon the extent of reduction.

In Run No. 83-4, using the same operating variables except that the reduction bed contained 3.2 grams of niobium metal, the effect of temperature upon the reduction of TaCl₅ was observed at 350 and 400° C. The measurable responses which were obtained are tabulated in Table 7. The results of Tables 6 and 7 are shown graphically in Figure 11.

Table 6. The effect of temperature upon the reduction of NbCl_5 and TaCl_5 by niobium metal^a (Run No. 86-4)

Compound	Reduction bed temperature °C	Relative sample size ^b	A_2/A_1	A_2/A_1 (avg)
NbCl_5	172	1.22	0.812	
	172	1.27	0.839	0.830
	172	0.98	0.836	
NbCl_5	350	1.07	0.412	
	350	1.43	0.391	0.405
	350	1.31	0.412	
NbCl_5	500	1.32	0.338	
	500	0.99	0.313	0.316
	500	1.20	0.297	
TaCl_5	172	1.86	0.938	
	172	1.77	0.958	0.948
TaCl_5	500	1.03	0.890	
	500	2.07	0.950	0.920

^aThe argon flow rate was 68.6 ml/min.

^bThis value is the number of counts given by the integrator for the first response divided by 1000.

Table 7. The reduction of TaCl_5 by niobium metal at 350 and 400° C^a (Run No. 83-4)

Reduction bed temperature °C	Relative sample size	A_2/A_1	A_2/A_1 (ave)
350	2.01	0.934	0.934
400	1.49	0.917	
400	1.47	0.953	
400	0.99	0.999	0.947
400	1.23	0.921	

^aThe argon flow rate was 68.6 ml/min.

Rate of reduction of NbCl_5

In Table 8, the response ratio A_2/A_1 is tabulated as a function of the argon flow rate measured at 25° C. The last four data points were taken as the flow rate was decreasing due to plugging in the 1/8 inch OD stainless steel tubing leading to the first side of the detector. The reduction bed contained 5.2 grams of -100+140 mesh niobium metal which was held at a constant temperature of approximately 500° C. The detector and injection port temperatures were maintained at 157 and 199°C, respectively.

Figure 11. The effect of temperature upon the reduction of $NbCl_5$ to $NbCl_3$ and upon the reduction of $TaCl_5$

Table 8. The effect of the argon flow rate upon the reduction of NbCl_5 at 500°C (Run No. 90-4)

Argon flow rate ml/min	Relative sample size ^a	A_2/A_1 ^b	Residence time sec	$\ln A_2/A_1$
68.6	1.05	0.278	0.364	-1.280
68.6	1.66	0.274	0.364	-1.295
68.6	1.21	0.267	0.364	-1.321
68.6	0.85	<u>0.273</u>	0.364	<u>-1.298</u>
		0.273 (ave)		-1.298 (ave)
51.9	0.58	0.188	0.481	-1.672
48.5	2.12	0.170	0.515	-1.772
46.7	2.35	0.157	0.535	-1.852
44.7	1.61	0.148	0.559	-1.911

^aThe last four values of the relative sample size are corrected to 68.6 ml/min since peak area is inversely proportional to the flow rate.

^bThese values are corrected because of interference from the unknown impurity responses which will be discussed later.

A result of Run No. 90-4 was to assume a first order reaction with respect to the disappearance of NbCl_5 . The value of the $\ln A_2/A_1$ is tabulated as a function of the residence time in the bed (the ratio of the void volume of the reduction bed to the argon flow rate corrected to 500°C) in the last two columns of Table 8. These data are correlated in Figure 12. It is noted that the data appear to follow a straight line. The first order rate constant was calculated from the slope of this straight line to be 3.14 sec^{-1} at 500°C .

Sample reduction within the chromatograph system

Figure 13 shows the effect of the detector temperature upon the response ratio A_2/A_1 (the ratio of the amount of pentachloride passed through the second side of the detector to the amount of pentachloride passed through the first side of the detector) for two empty glass columns connected in series. The higher curve represents pure TaCl_5 samples and the lower curve represents pure NbCl_5 samples. The data are also shown in Table 9 along with the argon flow rate, the injection port temperature, and the oven temperature incorporated for each detector temperature.

Figure 12. The data in Table 8 applied to a first order reaction hypothesis

Figure 13. The effect of detector temperature upon the response ratio A_2/A_1 using two empty columns connected in series

Table 9. The effect of detector temperature upon the response ratio A_2/A_1 using two empty columns connected in series. (Operating variables are also shown.)

Run no.	Oven temperature °C	Argon flow rate ml/min	Injection port temperature °C	Detector temperature °C	TaCl ₅ A_2/A_1 ratio	NbCl ₅ A_2/A_1 ratio
69-3	194	52.9	193	157		0.717 0.753 0.810 0.828 0.788
59-3	204	90.0	216	166	0.965 0.985	0.802 0.738 0.831 0.725 0.785 0.823
57-3	193	90.0	230	243	0.692 0.798 0.757 0.775 0.814	0.669 0.651 0.649 0.578
51-3	262	90.0	240	282	0.532 0.552	0.362 0.395

Unknown impurity contamination

An impurity in the NbCl_5 samples (suspected to be TiCl_4) was observed in Run No. 90-4 because of a bad injection. When the sample was injected, the capillary was evidently just slightly cracked. As a result, a gaseous component in the heated sample yielded positive responses of approximately equal areas from both sides of the detector. Because of the nature of the injection, a late and broadened response was obtained for the pentachloride allowing detection of the gaseous impurity. After the injector was withdrawn from the injection port, a large amount of NbCl_5 was still present in the cracked capillary. The chromatogram resulting from this bad injection is represented in Figure 14.

Separation of NbOCl_3 and NbCl_5

In Table 10 an experiment is described in which a sample of NbCl_5 was injected into the first column at room temperature; the sample condensing in the column just past the heated injection port. The column temperature was then raised in intervals. The response was noted during each interval. System variables were: injection port temperature, 292°C , detector temperature, 308°C , and helium flow rate, 75 ml/min.

Figure 14. Chromatogram showing response due to unidentified impurity in NbCl₅ samples (2 x actual size) (Run No. 90-4)

Table 10. A qualitative experiment on the separation of NbCl_5 and NbOCl_3 (Run No. 33-3)

Temperature interval °C	Description
70-100	No response.
101-117	No response.
118-138	A symmetrical response was obtained. After this response, the oven was opened and the column was inspected. The yellow NbCl_5 had disappeared. However, a white residue remained.
139-164	No response.
165-184	A broadened response was obtained.
185-196	No response.
197-298	No response. The oven was then opened. The column was void of any substance.

In a similar experiment, at the same detector and injection port temperatures, the oven was temperature programmed from 70° C at 7.5° C/min. The helium flow rate was 159 ml/min. The chromatogram represented in Figure 15 shows two responses, the first apparently representing NbCl_5 and the second apparently representing NbOCl_3 .

Figure 15. The effect of temperature programming upon the separation of NbCl_5 and NbOCl_3 (Run No. 34-3)

A slight amount of white residue indicating the presence of NbOCl_3 was visually observed in the NbCl_5 samples used in Run No. 33-3 and Run No. 34-3. An attempt was made to purify the NbCl_5 from which these samples were prepared by vacuum sublimation at 160°C . An analysis of the resulting preparation yielded a chlorine to niobium mole ratio of 5.02. However, very slight traces of NbOCl_3 were, nevertheless, still noted in the first column of the chromatograph upon injection of these previously purified NbCl_5 samples.

DISCUSSION

Preliminary Reduction Studies

The primary purpose of this preliminary investigation was to determine if NbCl_5 could be completely reduced to NbCl_3 in a flow process such as was used in this work. The results of Run No. 3-3 in Table 3 show that all of the NbCl_5 that could be accounted for was reduced to NbCl_3 . In Run No. 5-3, it is apparent that TaCl_5 is not significantly reduced by niobium metal. The 0.3 percent conversion reported is well within the limits of experimental error. It should then be possible to separate NbCl_5 and TaCl_5 in a tubular reactor containing a packed bed of niobium metal provided that NbCl_5 can be completely reduced to NbCl_3 . The feasibility of the process would depend upon the kinetics of the reduction of NbCl_5 to NbCl_3 .

In the second set of experiments using mixtures of NbCl_5 and TaCl_5 it is noted that higher temperatures were required to convert the NbCl_5 to NbCl_3 . The reason for this difference appears to be due to the reduced retention time resulting from an increased mesh size of the metal. A rough weight-volume analysis of this metal revealed that the void volume in a 15 gram bed was approximately 2.14 cc whereas in

a -100+140 mesh bed of the same weight, the void volume was 3.47 cc. The retention time was, therefore, decreased by a factor of about 38 percent for identical flow rates. There was not any significant change in the bed surface area.

The formation of NbCl_4 in Run No. 61-2 when -40+80 mesh metal was used in the reduction bed suggests that the direct reduction of NbCl_5 to NbCl_3 (mechanism A, theory section) may be unlikely. After reduction of NbCl_5 to NbCl_4 , either disproportionation (mechanism B) or reduction (mechanism C) or a combination of both would cause the formation of NbCl_3 from NbCl_4 . If disproportionation was the mechanism, the low conversion to NbCl_3 in Run No. 61-2 could have been due to a high NbCl_5 pressure throughout the bed. This conclusion is consistent with the observations of Schafer et al. (5). If reduction of NbCl_4 to NbCl_3 was the mechanism, the low conversion of NbCl_3 could be due to the decrease in bed surface area which was approximately 50 percent.

The low value for the conversion of NbCl_5 to NbCl_3 (94.4 percent) in Run No. 3-3 reveals some random errors in the type of analysis used. These errors are unidentified. Therefore, depending upon the nature of these errors, the conversion percentages given in Tables 3 and 4 are probably reliable to only about 6 percent.

Reduction Studies Using the Gas Chromatograph

It was found that while using the chromatograph, reduction studies could not be undertaken until irregularities occurring within the chromatograph system were thoroughly understood. For this reason, these irregularities will be discussed beforehand to enable a better understanding of later topics.

Sample reduction within the chromatograph system

In order to incorporate a gas chromatograph as an effective analytical tool, there are two requirements which are necessary for reliable analyses:

- 1) no reaction of the injected samples with the chromatographic system and
- 2) well-defined responses from which reliable peak heights or peak areas can be measured.

In respect to the first requirement, it was found that both niobium pentachloride and tantalum pentachloride appeared to be reduced by the iron in the stainless steel 316 from which the detector and injection ports were constructed. A brown-black scaling was observed in the injection ports and in the stainless steel columns which were used prior to glass columns. Both the columns and injection ports were rinsed

with absolute alcohol and the resulting solutions tested with silver nitrate and potassium thiocyanate. Both tests were positive suggesting the presence of FeCl_3 . It is presumed that further reduction to FeCl_2 may have also occurred. If sample reaction with the internal chromatograph system had not occurred, the A_2/A_1 ratios in Figure 13 should have been equal to unity and temperature independent.

This conclusion seems to agree with the observations of Schafer et al. (5). It was found that NbCl_5 was reduced by iron at 400°C with the formation of ferrous chloride. Schafer and Kahlenberg (8) reported a standard free energy of $-10 \text{ kcal/mole NbCl}_4$ at 400°C for the reaction:

This reaction is then essentially irreversible at 400°C .

It is observed in Figure 13 that the response ratio A_2/A_1 for NbCl_5 levels off to a value of approximately 0.8 at a detector temperature of about 160°C . After the NbCl_5 sample leaves the first side of the detector, it passes through the injection port to the second column before reaching the other side of the detector. It appears then to be partially reduced in the injection port at temperatures of 190 to 220°C while not being significantly reduced in the

detector at a temperature of about 160° C. If the injection port temperature could be lowered to about 160° C (see next paragraph), it is suspected that the response ratio would approach a value of unity.

In respect to the second requirement, it was found that at injection port temperatures below 190° C, well-defined responses could not be obtained due to response broadening and tailing. This response characteristic made quantitative measurements unreliable.

The effect of this apparent sample reduction is then that quantitative studies involving the separation of mixtures of NbCl_5 and TaCl_5 cannot be accomplished in the existing system since sample reaction with the internal system of the chromatograph can be eliminated only at low detector and injection port temperatures (somewhere between 150 and 170° C). If, however, the injection port temperature is lowered to a point which is too distant from the boiling points of TaCl_5 and NbCl_5 (233 and 247° C, respectively), quantitative measurements become difficult and, therefore, unreliable due to response broadening and tailing.

Reduction of NbCl₅ and TaCl₅ versus reduction bed temperature

From Figure 11, it is noted that the A_2/A_1 ratios for TaCl₅ remain essentially constant for all reduction bed temperatures studied. Furthermore, it is recalled from Figure 13 that at a detector temperature of 166° C and with two empty columns connected series, an average of 97.5 percent of the TaCl₅ was passed through the system. In Figure 11, the average A_2/A_1 ratios obtained over the temperature range studied varied between 0.948 and 0.920 (at a detector temperature of 162° C) for TaCl₅ injections. The variation here is only about three percent. From these observations drawn from Figures 11 and 13, it is evident then that TaCl₅ is essentially not reduced by niobium metal up to 500° C.

On the other hand, it is noted that there is a definite increase in the rate of reduction of NbCl₅ with temperature. This observation is consistent with the evidence shown in the preliminary reduction studies.

It is noted that the temperatures necessary for reduction in Figure 8 are much higher than those indicated in Figure 11. In the preliminary investigation, the reduction bed temperature was recorded with thermocouples inserted into a graphite cylinder in which the reactor was placed. A high

resistance to heat transfer to the reduction bed probably resulted due to the air space between the graphite cylinder and the reactor. On the other hand, the temperature of the reduction bed in the chromatograph column was recorded at the glass surface allowing the observance of a more representative reduction bed temperature.

Rate of reduction of NbCl₅

From Tables 6 and 8, it is noted that the observed A_2/A_1 ratios obtained for injections of NbCl₅ appear to be independent of the relative sample size. This characteristic appears to support the conclusion of a first order overall reaction for the reduction of NbCl₅ to NbCl₃ with niobium metal. From the integrated rate equation for a first order reaction (see theory section),

$$\ln \frac{A_2}{A_1} = -k_1\tau,$$

it is observed that for a constant residence time, the A_2/A_1 ratio must remain constant regardless of the magnitude of A_1 .

From the calculation of the rate constant, rough predictions can be made as to the amount of -100+140 mesh niobium metal which would be needed to acquire certain conversions of NbCl₅ to NbCl₃ at 500° C. For example, at an

argon flow rate of 68.6 ml/min measured at 25° C, a 99 percent conversion ($A_2/A_1 = 0.01$) would require approximately 21 grams of metal. A 99.9 percent conversion ($A_2/A_1 = 0.001$) would require approximately 31 grams of metal.

Experimental error In view of the error analysis (see Appendix D), the uncertainty of the last four A_2/A_1 values given in Table 8 is estimated to be ± 13 percent. This value leads to an uncertainty in the reaction rate constant of about ± 27 percent. That is, $k_1 = 3.14 \pm 0.85 \text{ sec}^{-1}$ for the rate expression

$$-\frac{d(\text{NbCl}_5)}{dt} = k_1(\text{NbCl}_5).$$

Unknown impurity contamination

The impurity from which the response in Figure 14 was obtained was not positively identified. Since the response was positive, the impurity had to have a thermal conductivity which is less than the thermal conductivity of argon. According to the approximate relationship between thermal conductivity and molecular weight (4, p. 196),

$$k_1/k_2 = (M_2/M_1)^{1/2},$$

the molecular weight of the impurity should be greater than the molecular weight of argon.

A remote possibility for the identification of this impurity arises from a remark made by Schafer et al. (8). It was noted that when NbCl_5 was heated to 600°C in a quartz silica vessel, the number of moles of gas in the vessel remained the same. However, when the vessel was heated from 600 to 950°C , an unduly sharp increase of pressure was noted and equilibrium was not attained. This phenomenon was attributed to the following irreversible reaction:

The boiling point of SiCl_4 is approximately 58°C .

When the capillaries containing the pentachloride were sealed in the dry box and then sealed at the desired length outside of the dry box, it is possible that the above reaction may have occurred. It was estimated that the temperature necessary for sealing the capillaries was in the vicinity of 1100°C .

Before the chromatogram in Figure 14 was obtained, previous NbCl_5 injections had given a similar response from the second side of the detector immediately before the response due to NbCl_5 . Only one response, however, was obtained from the first side of the detector. It is apparent

then that a separation of the impurity and NbCl_5 occurred between the first and second sides of the detector. After the nature of this impurity was understood, response ratios for NbCl_5 were corrected when the response due to this impurity was not negligible.

Separation of NbOCl_3 and NbCl_5

There was at first some question as to whether the second response shown in Figure 15 was due to NbOCl_3 (sublimation point: 335 to 350° C). It is noted that the temperatures at which the two responses started were approximately 96 and 157° C, respectively. The temperatures where the responses exhibited a maximum were at approximately 116 and 197° C, respectively. If the empirical vapor pressure equations reported by Schafer and Kahlenberg (7, 8) are used to calculate the vapor pressures of NbCl_5 and NbOCl_3 at the above temperatures, the following results are obtained:

$$P(\text{NbCl}_5, 96^\circ \text{ C}) = 0.48 \text{ mm Hg}$$

$$P(\text{NbOCl}_3, 157^\circ \text{ C}) = 0.17 \text{ mm Hg}$$

$$P(\text{NbCl}_5, 116^\circ \text{ C}) = 1.9 \text{ mm Hg}$$

$$P(\text{NbOCl}_3, 197^\circ \text{ C}) = 2.0 \text{ mm Hg}$$

The close proximity of these values at the corresponding

response beginnings and maximums indicate that the second response was almost certainly due to NbOCl_3 .

During the course of many injections, small amounts of NbOCl_3 condensed in the first column and slowly sublimed into the 1/8 inch OD stainless steel tubing leading to the first side of the detector. As a result, this tubing would become plugged at detector temperatures below approximately 165°C . Because of this difficulty, the carrier gas flow rate would then decrease. The system could be cleared by heating the detector to temperatures ranging from 200 to 250°C .

The reason for the apparent contamination problem with NbOCl_3 is not altogether clear. If moisture was present in the carrier gas, it seems as though NbOCl_3 would have formed in the second chromatograph column and the jumper tube as well as in the first chromatograph column. Inspection of the second chromatograph column and the jumper tube revealed, however, that this was not the case.

Another possible source of NbOCl_3 could be that the NbCl_5 samples were partially contaminated with NbOCl_3 . It was noted that NbCl_5 samples which had been previously purified still gave a slight white residue in the first chromatograph column. The NbOCl_3 would then have had to be formed

when the NbCl_5 was inserted into the capillaries in the dry box. A small amount of moisture could react with the NbCl_5 according to the reaction:

A detector response would not be noted for HCl because of its high reactivity with the internal system of the chromatograph. Any hydrogen evolved (from the reaction of HCl with iron) would yield negative responses. No significant responses of this nature were observed.

It is recalled from the discussion of the unknown impurity contamination that when NbCl_5 reacts with SiO_2 , not only SiCl_4 is formed, but also NbOCl_3 . It is possible then that NbOCl_3 could have been present in the samples because of this reaction.

NbOCl_3 contamination had no effect upon other results of this study. Because the sublimation of NbOCl_3 into the detector system was slow, no responses were obtained indicating its presence.

CONCLUSIONS AND RECOMMENDATIONS

An analysis of the results of this study lead to the following conclusions.

1. There is essentially no reduction of TaCl_5 by niobium metal at temperatures up to 500°C .
2. The rate of reduction of NbCl_5 to NbCl_3 increases with temperature with the maximum conversion being obtained at the highest reduction temperature incorporated, i.e., 500°C . Furthermore, NbCl_5 can be completely reduced in a flow process.
3. A reaction rate equation was obtained which represents the rate of reaction of NbCl_5 with niobium metal at 500°C . The overall reduction of NbCl_5 to NbCl_3 with niobium metal appears to follow a first order reaction rate expression with respect to NbCl_5 .
4. Although the separation of TaCl_5 and NbCl_5 by the selective reduction of NbCl_5 with niobium metal appears to be promising, the gas chromatograph was not suitable for analytical separation studies using mixtures of TaCl_5 and NbCl_5 due to internal corrosion.

5. Qualitative experiments arising from the apparent contamination of the NbCl_5 samples with NbOCl_3 showed evidence of a possible chromatographic separation of NbCl_5 and NbOCl_3 . Since NbOCl_3 is a major impurity in NbCl_5 , it is recommended that a thorough investigation be undertaken to study this separation. A temperature programming approach seems to be best suited for this study.

It is recommended that the chromatographic system be fabricated entirely from glass to eliminate corrosion. The effect of any reactions with SiO_2 would, however, need to be considered.

NOMENCLATURE

A	area under recorder response, counts
A_2/A_1	ratio of the area under the second response to the area under the first response
C	concentration, moles/cc or grams/cc
C_p	heat capacity at constant pressure, cal/mole °K
H_f°	standard enthalpy, kcal/mole
ID	inside diameter
k_1	reaction rate constant, sec^{-1}
k_o	constant
K_p	equilibrium constant
l	distance along base of concentration profile
l_o	length of base of concentration profile
OD	outside diameter
P	pressure, atm or mm Hg
S°	standard entropy, cal/mole °K
t	time
v_o	volumetric flow rate of carrier gas, ml/min
V_o	void volume of reduction bed, cc
	residence time or space time in reduction bed

Subscripts

g	gaseous component
l	liquid component
s	solid component

LITERATURE CITED

1. Ainscough, J. B., Holt, R. J. W. and Trowse, F. W. Niobium and tantalum pentachlorides and their binary system. J. Chem. Soc. (London) 1957: 1034-1037. 1957.
2. Brubaker, C. H. and Young, R. C. Anhydrous niobium tribromide and trichloride. Preparation and properties. J. Am. Chem. Soc. 73: 4179-4180. 1951.
3. McIntosh, A. B. and Broadley, J. S. The extraction of pure niobium by a chlorination process. Extraction and refining of the rarer metals symposium. Institution of Mining and Metallurgy, London 1957: 272-286. 1957.
4. Nogare, S. D. and Juvet, R. S. Gas-liquid chromatography. New York, N. Y., John Wiley and Sons, Inc. 1962.
5. Schafer, H., Goser, C. and Bayer, L. Das Niobtetrachlorid und sein Zerfall in Trichloride and Penta-chlorid. Z. anorg. Chem. 265: 258-272. 1951.
6. Schafer, H. and Kahlenberg, F. Die Bildungsenthalpie des Tantal(IV)-chlorids und die Thermochemie der Chloride $TaCl_5$, $TaCl_4$, und $TaCl_3$. Z. anorg. Chem. 305: 178-189. 1960.
7. Schafer, H. and Kahlenberg, F. Bildungsenthalpie, Sättigungsdruck und thermochemisches Verhalten des Nioboxydchlorides $NbOCl_3$. Z. anorg. Chem. 305: 327-340. 1960.
8. Schafer, H. and Kahlenberg, F. Die Thermochemie der Niobchloride. Z. anorg. Chem. 305: 291-326. 1960.
9. Schafer, H. and Pietruck, C. Die Trennung der Elemente Niob und Tantal durch Reduktion des Niobpentachlorids. Z. anorg. Chem. 266: 151-160. 1951.
10. Sisco, Frank T. and Epremian, Edward. Columbium and tantalum. New York, N. Y., John Wiley and Sons, Inc. 1963.

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APPENDIX A

The validity of the first order integrated equation used in describing the results of Figure 12 depends upon the variation of the actual residence time (or space time) τ from V/v_0 where V is the void volume in the reduction bed and v_0 is the volumetric flow rate of argon at 500°C. The maximum value of the mole fraction of NbCl_5 entering the reduction bed would be approximately 0.03. This value was obtained from the vapor pressure of NbCl_5 at the detector temperature of 157° C and a total pressure of one atmosphere. With the assumption of a negligible pressure drop across the bed, the maximum variation in τ from V/v_0 was found to be three percent. If a pressure drop was taken into account (calculated from empirical relations for packed beds (4, p. 133)), the maximum variation in τ was again found to be three percent. These estimates are, however, possibly higher than in reality. The pressure in the reduction bed was only slightly higher than one atmosphere being equivalent to the pressure drop in the exit system. A higher pressure would decrease the maximum mole fraction of NbCl_5 in the carrier gas causing a lower variation in τ . In addition, these calculations were based upon complete

conversion of NbCl_5 to NbCl_3 . It is concluded then that the use of V/v_0 as the residence time introduces negligible error when used in the equation

$$\ln \frac{A_2}{A_1} = -k_1 \tau$$

for calculation of the rate constant.

APPENDIX B

By examining symmetrical nitrogen responses, it was found that the sample dispersion between the first side of the detector and the second side of the detector had a value of 1.35 (1.00 for no dispersion) when the second column contained 5.2 grams of -100+140 mesh niobium metal. With the second column empty, the dispersion was 0.7 percent less, i.e., 1.34, which indicates that dispersion due to the presence of the reduction bed was negligible. By comparing the residence time in the reduction bed to the residence time between the two sides of the detector, the dispersion was found to be 1.002 through the reduction bed which is negligible for this work.

APPENDIX C

Commercially obtained niobium pentachloride and tantalum pentachloride (specified purity: 99.95%) were used for the preparation of samples. The capillary tubes had an inside diameter of about 1.5 mm. and a length of 10 cm. The samples were prepared in a dry box under an argon atmosphere. Before entering the dry box, the capillary tubes were sealed at one end with a gas-oxygen torch. All materials were then put into the dry box. Enough pentachloride was inserted into a capillary to give a gas volume (reduced to room temperature) of about 0.5 to 1.0 cc. (approximately 5 to 10 mg. of niobium pentachloride and 7 to 14 mg. of tantalum pentachloride). The capillary was then sealed at the other end by contacting it with a stainless steel heating core which had previously been heated to about 1200° C (Figure 16). The sealed capillaries were then removed from the dry box. Each capillary was dipped into liquid nitrogen in order to condense the argon and, therefore, create a partial vacuum in the capillary. The capillary was then sealed at the desired length (about 0.75 in.) with a gas-oxygen flame. If a leak existed in a capillary, a seal could not be made since the glass would not collapse upon

contact with the flame. It was found that with practice, about 75 samples could be prepared in one hour by this method.

- K-26 FIREBRICK INSULATION
- POWDERED ALUMINUM OXIDE INSULATION
- METAL SEALING CORE
- 26 GAUGE KANTHAL WIRE
HELICAL COIL: 1/16 INCH ID
- ASBESTOS SHEET INSULATION
- ALUMINUM TUBING, INNER: 1/2" THREADED;
OUTER: 5/4" ID

Figure 16. Sealing device for capillary tubes

APPENDIX D

In Table 6, it is noted that the maximum deviation between the response ratios for NbCl_5 occurs at 500°C . This deviation amounts to:

$$\frac{(0.338 - 0.297)}{0.316} 100 = 13 \text{ percent.}$$

Since the response ratios in Table 8 were calculated in the same manner as those in Table 6, it is assumed that the maximum deviation of the last four response ratios in Table 8 is also 13 percent. However, since only one value of the response ratio exists for each flow rate, a maximum deviation of ± 13 percent must be applied to each value. The deviation from the average response ratio for the flow rate, 68.6 ml/min, is taken as:

$$\frac{(0.278 - 0.267)100}{0.273 (2)} = \pm 2 \text{ percent}$$

Figure 17 shows these deviations when applied to Figure 12. It is noted that the slope between these deviations may vary from a value of 3.99 sec^{-1} to a value of 2.42 sec^{-1} . This observation yields an experimental error of approximately ± 27 percent from the calculated value in Figure 12 of 3.14 sec^{-1} .

Figure 17. Experimental error limits of first order reaction rate constant found in Figure 12