

A New Process for the Separation of Tantalum from Niobium

D. R. SADOWAY AND S. N. FLENGAS

A new process for the separation of tantalum from niobium (Cb) has been developed: This process consists of repeatedly reacting the mixed pentachloride vapors of niobium and tantalum with an alkali-metal chloride powder to form complex compounds of the type, $AMCl_6$, where A is an alkali metal, and M is Nb or Ta. Tantalum tends to concentrate in the condensed $AMCl_6$ phase leaving a vapor enriched in niobium. The results of tests conducted with NaCl, KCl, RbCl, and CsCl are presented along with a discussion of the thermodynamics of the process. The best separation was achieved with KCl, where the molar ratio of pentachloride to KCl was 2:1, the pentachlorides were heated to 229°C, and the KCl was heated to 342°C. Under these conditions the concentration of tantalum was reduced by a factor of almost three in one separation step.

HIGH purity niobium metal is a necessary component for the production of the zirconium alloys which are used in nuclear reactors. Niobium used for these purposes must contain extremely small amounts of tantalum as the latter has a thermal neutron capture cross-section of 21.3 barns per atom,¹ which is twenty times that of niobium. However, niobium and tantalum are found together in nature, and their strong chemical similarity makes it difficult to refine either metal free from the other.

The first industrial process for separating niobium and tantalum from each other was developed by Marignac² and involved the crystallization of K_2TaF_7 from dilute hydrofluoric acid solutions. However, in this method the niobium and all other impurities accumulate in the aqueous phase making the production of high purity niobium difficult.

This procedure has been superseded by liquid-liquid extraction. About 200 different combinations of solvent and extractant were tested by the U.S. Bureau of Mines with the purpose of developing an industrial separation process.³ Suitable aqueous phases were mixtures containing HF, HF-HCl, and HF-H₂SO₄. Excellent separations were achieved with the organic solvent methyl isobutyl ketone (MIBK). However, MIBK is a relatively volatile substance with a flash point of 24°C and requires the use of flame proof equipment. In addition, MIBK is a consumable reagent, dissolving in the aqueous phase (~2 pct), and contributes substantially to the cost. Perhaps the most significant disadvantage of the solvent extraction separation method is that it introduces a separate hydrometallurgical step into the flow-sheet for niobium production which, otherwise is entirely pyrometallurgical.

Other methods include separation with microbiological collectors,⁴ electrolytic separation,⁵ and selective reaction of the pentachlorides of niobium and tantalum with various reagents such as CaO and CaF₂,⁶ molten NaAlCl₄,⁷ alkali-metal chlorides in the presence of excess hydrogen,⁸ and even niobium metal itself.⁹

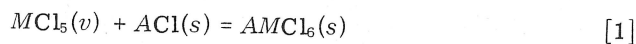
Fractional distillation of the pentachlorides has been proposed by Nisel'son¹⁰ and Steele and Geldart¹¹ and is found in processes developed by Ugué Kuhlmann in France¹² and duPont in the USA.²⁵ However, an independent study¹³ has concluded that this last method is suitable for the elimination of Si, Ti, Sn, Al, Fe, Sb, Bi, and Mo, but that a different technique should be used to separate Ta from Nb.

The separation method described herein consists of reacting the mixed pentachloride vapors of niobium and tantalum with an alkali-metal chloride to form complex compounds of the type, $AMCl_6$, where A is an alkali metal and M is Nb or Ta. Previous work in this laboratory has shown that for a given alkali metal the hexachlorotantalate is stabler than the hexachloroniobate.¹⁴ Also, TaCl₅ is known to be more volatile than NbCl₅.¹⁵ The present method simultaneously exploits both these effects to achieve a separation efficiency superior to that possible by the simple fractional distillation of TaCl₅-NbCl₅ mixtures.¹⁰

It should be noted that HfCl₄ present in ZrCl₄-HfCl₄ vapor is also separated by a similar process^{16,17} based on the formation of the A_2ZrCl_6 and A_2HfCl_6 complex compounds.

EXPERIMENTAL PROCEDURE

NbCl₅ and TaCl₅ vapors react with alkali-metal chlorides according to the following reaction:



In this laboratory the vapor pressures of NbCl₅ and TaCl₅ in equilibrium with the $AMCl_6$ compounds, where A is Na, K, Rb, or Cs, and M is Nb or Ta,¹⁴ were previously measured, and the order of thermal stability of these compounds was established.

The separation process is based on the selective reactivity of a solid alkali chloride with the TaCl₅ present in a gaseous mixture consisting of NbCl₅ and TaCl₅. When the reaction is conducted in a closed container, the equilibrated gas phase becomes richer in NbCl₅, which may be recovered through condensation.

The apparatus for the separation experiments is shown in Fig. 1.

The separation reactor was constructed of borosilicate glass and was divided into two compartments,

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Manuscript submitted November 7, 1978.

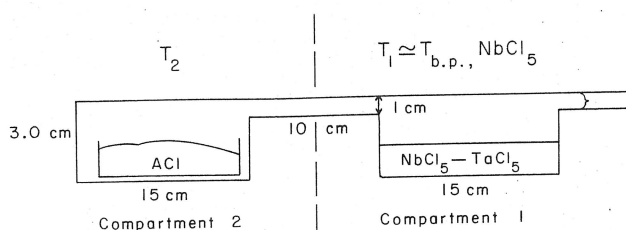


Fig. 1—Apparatus for separation experiments.

each regulated at a different temperature to within 1 K by independently controlled tubular resistance furnaces.

Separation experiments were performed by reacting a TaCl_5 - NbCl_5 mixture of nominal impurity 1.56 mol pct TaCl_5 with each of NaCl , KCl , RbCl , and CsCl . This impurity level corresponds to the average Ta content in Canadian pyrochlore ore.

All chemicals used in this work were of "reagent grade" purity.

Before reaction the salts were further purified and dehydrated by previously described methods.¹⁸ The TaCl_5 - NbCl_5 mixture which was the starting material for all experiments was prepared in lots of 50 g by weighing the appropriate amount of each salt, comelting, and storing in evacuated flame sealed glass vials. The alkali chlorides were ground to a particle size of less than 80 microns for use in the reactor.

In a typical experiment the alkali-metal chlorides and the NbCl_5 - TaCl_5 mixture were weighed in a dry box filled with helium and transferred to their respective compartments in the separation cell, as shown in Fig. 1.

The alkali chloride powder in compartment 2 was

degassed by heating under vacuum at 500°C for about 12 h, after which time the reactor was flame sealed while under vacuum.

During reaction compartment 1, which contained the $\text{Nb}(\text{Ta})\text{Cl}_5$ mixture was heated to a temperature T_1 close to the normal boiling point of NbCl_5 (~248°C),¹⁵ while compartment 2 which contained the alkali chloride powder, was heated to a temperature T_2 which was always greater than T_1 and lower than the eutectic temperature of the respective ACl - AMCl_6 subsystem.

After reacting for approximately 3 days the reaction tube was cooled by first decreasing T_2 to about 10 K greater than T_1 and then allowing both compartments to cool simultaneously to room temperature.

At this stage of the reaction the $\text{Nb}(\text{Ta})\text{Cl}_5$ mixture, now enriched in NbCl_5 , had condensed in compartment 1, while most of the ACl in compartment 2 had reacted to form a solid solution of ANbCl_6 and ATaCl_6 . The reaction tube was opened in a glove box under a helium atmosphere. The boat containing ACl and the reacted ANbCl_6 - ATaCl_6 solid solution was weighed. Then the material was hydrolyzed and converted to the anhydrous pentoxides for subsequent determination of Nb and Ta by neutron activation analysis. The analytical technique and the method of preparing representative niobium and tantalum pentoxide samples and standards are given elsewhere.¹⁹ Ta in Nb was determined with an absolute error of estimate of less than 0.1 wt pct.

RESULTS AND DISCUSSION

The results of the separation experiments are summarized in Table I.

Table I. Results of Separation Experiments

Separating Agent, ACl	Run No.	Before Reaction		After Reaction		T_1 , °C	T_2 , °C	Degree of Reaction, ξ	Reaction Time, h.	Mole Ratio a/b		Separation Efficiency η Pct		Comments
		Compartment 1	Compartment 1	Compartment 2						Initial ¹	Effective ²	Experimental	Calculated	
		X_{TaCl_5}	X_{TaCl_5}	X_{ATaCl_6}										
NaCl	1	0.0161	0.0082	0.0348		245	350	0.912	72	3.12	3.42	48.6	45.3	Condensed phases in compartment 2 at T_2 consist of solid ACl and a solid solution of ANbCl_6 - ATaCl_6
KCl	1	0.0157	0.0055	0.0309		229	342	0.786	72	2.00	2.54	64.5	58.7	"
	2	0.0153	0.0059	0.0303		229	342	0.723	216	2.06	2.85	61.1	57.0	"
	3	0.0161	0.0107	0.0374		229	342	0.724	72	4.01	5.54	33.0	36.8	"
	4	0.0161	0.0123	0.0381		229	342	0.786	72	6.00	7.63	23.1	28.8	"
KCl	1	0.0164	0.0115	0.0211		229	438	1.00	4	2.06	—	29.6	—	Condensed phase in compartment 2 at T_2 consists of a liquid solution of KCl - NbCl_5 - TaCl_5
CsCl	1	0.0151	0.0088	0.0239		237	425	0.700	72	2.02	2.89	41.4	40.6	Condensed phases in compartment 2 at T_2 consist of solid ACl and a solid solution of ANbCl_6 - ATaCl_6
	2	0.0156	0.0108	0.0271		246	422	0.545	72	2.81	5.16	30.4	25.2	"
	3	0.0154	0.0118	0.0255		237	425	0.783	72	4.24	5.42	22.9	25.2	"
	4	0.0165	0.0139	0.0290		237	425	0.816	72	6.09	7.46	15.3	13.5	"
RbCl	1	0.0157	0.0083	0.0238		237	335	0.668	72	1.99	2.98	46.6	—	"

*Balance 1 - X represents NbCl_5 content.

†Balance 1 - X_{ATaCl_6} represents ANbCl_6 content in reacted solid solution phase.

¹"Initial a/b " represents the mole ratio of ACl to $\text{Nb}(\text{Ta})\text{Cl}_5$ in the material which is charged into the reactor.

²"Effective a/b " represents the mole ratio of ACl to $\text{Nb}(\text{Ta})\text{Cl}_5$ based on the degree of reaction ξ .

In this table the quantity a/b is the molar ratio of pentachloride mixture in compartment 1 to the alkali-metal chloride in compartment 2 at the beginning of a separation experiment. The feed and product compositions are specified by the mole fraction of each component. The variable ξ represents the degree of reaction to form the complex mixture and is defined by:

$$\xi = (n_{\text{ACl, initial}} - n_{\text{ACl, final}}) / n_{\text{ACl, initial}} \quad [2]$$

where n_{ACl} is the mass of ACl in moles. If all the ACl in compartment 2 reacts to form ANbCl_6 - ATaCl_6 , $\xi = 1$.

The variable η is the efficiency of the experiment to reduce the concentration of Ta in the $\text{Nb}(\text{Ta})\text{Cl}_5$ mixture and is defined as,

$$\eta = \frac{(\text{Initial wt pct Ta}) - (\text{Final wt pct Ta})}{(\text{Initial wt pct Ta})} 100 \text{ pct} \quad [3]$$

where wt pct Ta represents the weight fraction of Ta in a Nb-Ta solution prepared by completely reducing the corresponding pentachloride mixture to metal. Thus, if all the Ta in the feed is removed so that at the end of the experiment the material in compartment 1 contains no Ta, $\eta = 100$ pct.

The reaction with ACl significantly reduces the Ta concentration of the NbCl_5 - TaCl_5 mixture in compartment 1. Using a ratio of MCl_5 : $\text{ACl} = 2:1$, the pentachloride mixture of initial composition corresponding to 3 wt pct Ta on a metal-metal basis with Nb, was refined by reaction with CsCl to 1.7 wt pct Ta, and, by reaction with KCl to 1.1 wt pct Ta.

The separation efficiency decreases as the ratio of MCl_5 : ACl increases. For example, with MCl_5 : $\text{CsCl} = 2:1$ the efficiency was 40 pct whereas with MCl_5 : $\text{CsCl} = 6:1$ the efficiency was only 15 pct. This simply reflects that in a closed reactor with a fixed amount of reagent, in this case ACl, one has the option of either refining small amounts of material very efficiently or refining large amounts of material to a lesser degree. From the data in Table I, efficiency plots were constructed and are shown in Fig. 2. The points plotted were determined by experiment, while the solid curves are those generated by the thermodynamic model to be discussed subsequently.

Most of the results in Table I were obtained at reaction temperatures T_2 which were always below the corresponding eutectic temperatures of the ANbCl_6 - ACl subsystems.¹⁴ Accordingly, the condensed phases found in compartment 2 during reaction were solids. However, as seen by the values for ξ which are always less than unity, some unreacted ACl remained. Examination of the samples in compartment 2 after reaction revealed that some sintering had occurred. It appears, therefore, that the gas-solid reaction is impeded by the presence of this sintered material, and 100 pct conversion of the ACl could not be obtained within the duration of these experiments when the alkali chloride was in the form of a static bed of finely divided powder.

Powders coarser than 200 mesh were also tested. While sintering was not as pronounced, the degree of reaction ξ was even lower, presumably because of the greater reliance on solid state diffusion through the actual ACl particles to complete the reaction.

To eliminate the deleterious effects of sintering a separation experiment was conducted with KCl at a temperature at which the product KNbCl_6 - KTaCl_6 solu-

Simulation :		Experimental Data :	
— — —	KCl , using $K_{\text{ex}} = 3.45$	∇	NaCl
- · - · -	CsCl , using $K_{\text{ex}} = 2.11$	\square	KCl
+	NaCl , using $K_{\text{ex}} = 3.04$	\triangle	RbCl
		\circ	CsCl

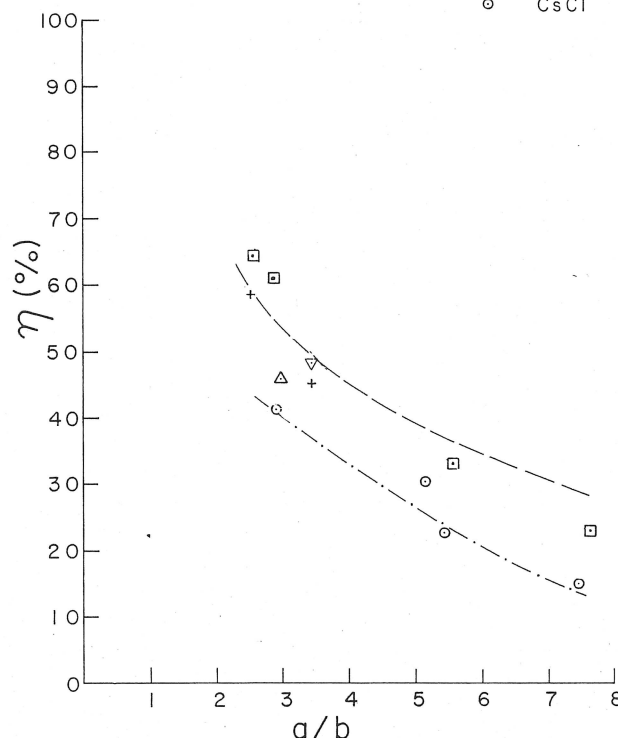


Fig. 2—Experimental and calculated separation efficiencies as a function of the "effective" mole ratio a/b . Lines represent values calculated from the thermodynamic model, while points are experimental. The characteristic temperatures for the various separation experiments are given in Table I.

tion was molten. These results are also shown in Table I. In this case the separation of Ta from Nb was less efficient than those conducted at solid state temperatures. As seen in Table I, the separation efficiency of the solid-gas reaction at 342°C and for $a/b = 2.00$ is 64.5 pct and this should be compared with 29.6 pct for the gas-liquid reaction at 438°C for the same a/b ratio. However, to the advantage of this latter experiment, the consumption of alkali-metal chloride was complete; in contrast to the experiments involving gas-solid reactions where ξ was usually 0.7 to 0.8, even after 3 days, the gas-liquid reaction gave $\xi = 1.0$ after only 4 h.

It should be noted that the reaction times shown in Table I were selected on the basis of previous experience acquired during the measurement of the vapor pressures of NbCl_5 or TaCl_5 in equilibrium with the solid and liquid condensed phases in question.¹⁴ The reaction times used for separation far exceeded the observed equilibration times.

To confirm these observations a prolonged experiment was conducted with KCl as the separation agent at a a/b ratio of 2.06. The reaction was allowed to proceed for 216 h instead of 72. It is readily seen in Table I that both the ξ and η values do not change significantly.

With regard to choosing a gas-solid vs a gas-liquid type separation, it appears that gas-solid reactions achieve higher separation efficiencies at the expense of time. However, the present experiments were con-

ducted in closed containers where the alkali chlorides lay as packed powder beds. If the separation were to be performed under conditions of particle isolation as in a fluidized bed, the kinetics of the reaction could be greatly enhanced.

A comparison of all the separations by gas-solid reaction reveals that the efficiency, η , appears to decrease as the mass of the alkali-metal chloride increases. Comparing values for experiments for which $a/b = 2$, it is readily seen that η drops from approximately 65 pct in the case of KCl, to 46 pct for RbCl, and to 40 pct for CsCl. The results for NaCl at $a/b = 3.12$, $\eta = 48.6$ pct should be compared with the results for KCl at the same a/b ratio which yield $\eta_{KCl} = 48$ pct (Fig. 2). Thus, NaCl and KCl solids are equally effective as separating agents and are far better than either RbCl or CsCl.

It is important to note that despite the fact that RbCl and CsCl form stabler complexes with $NbCl_5$ and $TaCl_5$.¹⁴ NaCl and KCl appear to act more efficiently to separate Ta from Nb. It seems that what is critical in determining the efficiency of separation is not the absolute value of the vapor pressures of $NbCl_5$ and $TaCl_5$, but rather the relative volatility of the two pentachlorides in relation to the $AMCl_6$ compounds formed with a given ACl. These data show that in equilibrium with $KNbCl_6$ and $KTaCl_6$ the vapor pressures of $NbCl_5$ and $TaCl_5$ differ more than they do when the pentachlorides are in equilibrium with $CsNbCl_6$ and $CsTaCl_6$; hence, the process works better with KCl, even though CsCl is a more effective complexing agent, as the dissociation temperatures illustrate. One atm pressure is measured over $KNbCl_6$ at 468°C and over $CsNbCl_6$ at 547 K.¹⁴

THERMODYNAMIC MODEL FOR THE SEPARATION PROCESS

Considering the nonisothermal closed separation cell shown in Fig. 1, the theoretical reaction efficiency η may be calculated from available thermodynamic data.

In compartment 1, at T_1 the $NbCl_5$ - $TaCl_5$ mixture is initially present as a molten solution having mole fractions, X and $1 - X$, respectively. These change as the reaction with the alkali chloride present in compartment 2 proceeds. In compartment 2, which initially contains pure alkali chloride ACl, the reaction produces a mixture of the complex compounds, $ANbCl_6$ and $ATaCl_6$, which are known²⁰ to form a solid solution.

Because the two compartments are connected, equilibrium is established when the dissociation vapor pressures of $NbCl_5$ and $TaCl_5$ above the solid solution in compartment 2 are equal to those of the $NbCl_5$ - $TaCl_5$ melt in compartment 1. At equilibrium all of the alkali chloride initially present in compartment 2 has been converted to the aforementioned solid solution.

The overall reaction which governs the separation process may be written as:



where the underline signifies the solid solution.

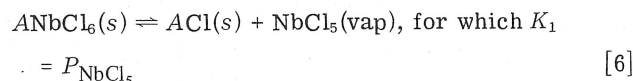
The equilibrium constant for this exchange reaction is then:

$$K_{ex} \text{ (at } T_2) = \left(\frac{a_{ATaCl_6}}{a_{ANbCl_6}} \right) \frac{f_{NbCl_5}}{f_{TaCl_5}} \quad [4]$$

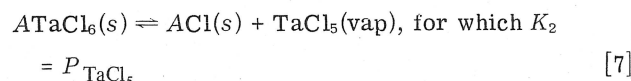
Density measurements^{21,22} have shown that the vapors of $NbCl_5$ and $TaCl_5$ closely approximate the behavior of monomeric ideal gases in the temperature and pressure ranges under study; hence, fugacities in Eq. [4] may be replaced by partial pressures. Phase diagram studies have shown that both the $ATaCl_6$ - $ANbCl_6$ solid solutions²⁰ and the $NbCl_5$ - $TaCl_5$ molten solutions²³ may be considered as ideal. Thus, in Eq. [4] one can make the substitution $f_{MCl_5} = X_{MCl_5} \cdot P_{MCl_5}^0$, where $P_{MCl_5}^0$ is the vapor pressure of pure MCl_5 at the temperature T_1 of the mixed pentachloride melt. Furthermore, when the $AMCl_6$ solution is solid, $a_{AMCl_6} = X_{AMCl_6}$. Under these circumstances Eq. [4] simplifies to:

$$K_{ex} \text{ (at } T_2) = \frac{X_{ATaCl_6}}{X_{ANbCl_6}} \frac{X_{NbCl_5}}{X_{TaCl_5}} \left(\frac{P_{NbCl_5}^0}{P_{TaCl_5}^0} \right) \text{ at } T_1 \quad [5]$$

Values of K_{ex} may be calculated from previously measured dissociation vapor pressures of the pure solid complex compounds representing the reactions,



and,



For this calculation the standard states for the solids are chosen as the pure solids at all temperatures, and for the gaseous components the pure gases at 1 atm pressure at all temperatures. It follows that,

$$K_{ex} = \frac{K_1}{K_2}$$

The available equilibrium data for the NaCl and CsCl systems are summarized in Table II which also includes the calculated temperature dependence of K_{ex} for these two systems.

The mass balance shown in Table III may be described as follows. During the separation initially a moles of $Nb(Ta)Cl_5$ mixture of composition, $X_{NbCl_5} = x$, $X_{TaCl_5} = 1 - x$ are placed into compartment 1, and b moles of ACl are placed into compartment 2. At equilibrium the amount of $ANbCl_6$ formed is y moles and of $ATaCl_6$ is z moles. The $ANbCl_6$ - $ATaCl_6$ solid solution is immiscible with solid ACl; hence, the activity of ACl, $a_{ACl} = 1.0$, both initially and finally. The partial pressures of $NbCl_5$ and $TaCl_5$ are constant throughout the reactor and are determined by the equilibrium with molten $NbCl_5$ - $TaCl_5$ in compartment 1 at temperature T_1 .

The stoichiometry of the compounds $ANbCl_6$ and $ATaCl_6$ requires that the mole ratio $ACl/Nb(Ta)Cl_5$ always be unity. Hence, in the case of complete reaction of ACl with the $Nb(Ta)Cl_5$ vapor the sum of the moles of $ANbCl_6$ and $ATaCl_6$ in the solid solution is b irrespective of composition, or,

$$y + z = b \quad [8]$$

Table II. Equilibrium Constants

Reaction	Temperature Range of Measurement, T/K	$\ln P_{MCl_5} = a_0 + \frac{a_1}{T}$		$\ln K_{ex} = b_0 + \frac{b_1}{T}$	
		a_0	a_1	b_0	b_1
$\text{NaNbCl}_6 (\beta\text{-solid}) \rightarrow \text{NaCl (s)} + \text{NbCl}_5 (\text{vap})$	518 to 561	8.075	-4,750	—	—
$\text{NaTaCl}_6 (\beta\text{-solid}) \rightarrow \text{NaCl (s)} + \text{TaCl}_5 (\text{vap})$	497 to 650	10.8930 ± 0.2883	$-7,131.3 \pm 163.5$	—	—
$\text{CsNbCl}_6 (\beta\text{-solid}) \rightarrow \text{CsCl (s)} + \text{NbCl}_5 (\text{vap})$	670 to 708	0.4815 ± 0.6533	$-2,354.9 \pm 457.5$	—	—
$\text{CsTaCl}_6 (\beta\text{-solid}) \rightarrow \text{CsCl (s)} + \text{TaCl}_5 (\text{vap})$	675 to 732	0.7937 ± 0.1453	$-3,095.6 \pm 102.2$	—	—
$\text{TaCl}_5 (\text{vap}) + \text{NaNbCl}_6 \rightarrow \text{NbCl}_5 (\text{vap}) + \text{NaTaCl}_6$	up to 721*	—	—	-2.82	2380
$\text{TaCl}_5 (\text{vap}) + \text{CsNbCl}_6 \rightarrow \text{NbCl}_5 (\text{vap}) + \text{CsTaCl}_6$	up to 808*	—	—	-0.31	740

*Melting point of lower melting compound.

Table III. Mass Balance for Separation of Ta from Nb by Reaction in a Closed System With ACl

Material	Amount of Material, Moles			Mole Fraction at Equilibrium
	Initial	Change	Final	
NbCl_5 Compartment 1	ax	$-y$	$ax - y$	$\frac{ax - b + z}{a - b}$
TaCl_5 Compartment 1	$a(1 - x)$	$-z$	$a(1 - x) - z$	$\frac{a(1 - x) - z}{a - b}$
ANbCl_6 Compartment 2	0	$+y$	y	$\frac{b - z}{b}$
ATaCl_6 Compartment 2	0	$+z$	z	$\frac{z}{b}$
ACl (immiscible component) Compartment 2	b	$-(y + z)$	$b - y - z$	1.0

Substitution from Table III into Eq. [5] gives the following relationship:

$$K_{ex} \text{ (at } T_2) = \frac{b}{b - z} \cdot \frac{ax - b + z}{a - ax - z} \left(\frac{P_{\text{NbCl}_5}^0}{P_{\text{TaCl}_5}^0} \right)_{T_1} \quad [9]$$

where P^0 values are the evaporation pressures for the pure liquids, NbCl_5 and TaCl_5 , at T_1 . These pressures are given by the expressions:¹⁵

$$\begin{aligned} \ln(P/\text{atm}) &= 103.801 - 12,344T^{-1} - 12.8474 \ln T \\ &\quad - 6.738 \times 10^4 T^{-2} + 1.8468 \times 10^{-6} T^2 \\ &\quad \pm 0.004 \end{aligned} \quad [10]$$

for $\text{NbCl}_5(\text{liq}) \rightleftharpoons \text{NbCl}_5(\text{vap})$ and,

$$\ln(P/\text{atm}) = 12.710 - 6.4478 \times 10^3 T^{-1} \pm 0.005 \quad [11]$$

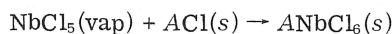
for $\text{TaCl}_5(\text{liq}) \rightleftharpoons \text{TaCl}_5(\text{vap})$. For given a and b values Eq. [9] can be solved for z and the composition of the pentachloride mixture after reaction calculated.

Calculated separation efficiencies are compared with those measured experimentally, and the results are included in Table I. It should be noted that Eq. [9] predicts the experimentally observed dependence of the separation efficiency η on the mole ratio a/b . This mole ratio is calculated from the initial mole ratio a/b after accounting for the degree of reaction ξ , and, in effect, " b " in a/b represents the amount of alkali

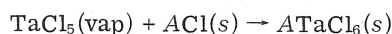
chloride which has reacted during an experiment. The thermodynamic model gives the correct values for the Ta concentration in the product.

The value of K_{ex} calculated from Eq. [9] using values of z determined by neutron activation analysis following a separation experiment is the same as that calculated from the equations for pure NaNbCl_6 and NaTaCl_6 , given in Table III. This demonstrates that separation experiments can be used to determine the complete temperature dependence of the thermodynamic properties of the exchange reaction. The restrictions are that the solutions of the condensed phases conform to Raoult's law and that the gas phase be ideal.

It should be noted that although $\xi < 1$ in the experiments, the model correctly simulated the separation process. This suggests that both the gas-solid reactions,



and,



must be taking place at similar rates.

Niobium metal produced from typical Canadian pyrochlore concentrate would contain 1 wt pct Ta if some method of separation were not employed. By repeated reaction with KCl, for example, a pentachloride mixture of composition corresponding to 1 wt pct Ta on a metal-metal basis of Nb should be refined to <300 ppm Ta in 3 steps or <100 ppm Ta in 4 steps. This compares favorably with the fractional distillation of NbCl_5 - TaCl_5 melts. Indeed, in cases where extremely high purity Nb is required e.g. 10 ppm Ta, the process described herein could be used following a fractional distillation treatment to make Nb containing 1000 ppm Ta.

Although the experiments of the present study were performed as batch-type operations, separation should also be achieved either in a fluidized bed reactor, in which the pentachloride gas mixture is made to flow through a bed of solid alkali chloride particles, or in a simple counter-current reactor, in which the pentachloride gas mixture and alkali chloride flow counter-currently. In either reactor rapid reaction should occur. After its reaction with ACl the pentachloride gas mixture would have to be collected in a condenser. The alkali chloride reagent could be regenerated by heating the ANbCl_6 - ATaCl_6 mixture in a distillation column to liberate the pentachlorides as vapors which could then be added in limited quantity to the feed. Ugine Aciers

has been issued a patent²⁴ for the continuous separation of hafnium from zirconium by selective absorption of their tetrachloride vapors by molten potassium chloroaluminate or molten potassium chloro-ferrate in a counter-current reactor. This technology could be adapted to separate tantalum from niobium by reaction with potassium chloride with excellent results.

The research of this study was directed at the separation of tantalum from niobium, primarily because of the desire to meet nuclear specifications. However, there is also a demand for high purity tantalum free of niobium, and the separation process developed herein could be modified to make such material. To this end, compartment 1 should be charged with the pentachloride feed, consisting mainly of $TaCl_5$ with a small amount of $NbCl_5$, the latter being the impurity in this case. Compartment 2 should be charged with alkali chloride. The reaction products should be a pentachloride mixture enriched with niobium in compartment 1, and a mixture of $ATaCl_6$ - $ANbCl_6$ enriched in tantalum in compartment 2. Heating the latter would vaporize enriched $TaCl_5$ which could then be either reduced to Ta metal or reacted with fresh $AlCl_3$.

CONCLUSIONS

The feasibility of a process for the separation of tantalum from niobium has been demonstrated. Every experiment without exception succeeded in refining the feed material to lower tantalum concentrations. The best results were obtained with potassium chloride where the ratio of pentachloride to potassium chloride was 2:1. The low cost of potassium chloride or sodium chloride plus the fact that they are not consumable reagents make this new process worthy of further consideration as a commercial operation.

REFERENCES

1. C. A. Hampel, ed.: *Rare Metals Handbook*, 2nd ed., p. 480, Reinhold, London, 1961.
2. M. C. Marignac: *Ann. Chim. (Paris)*, 1866, vol. 8, pp. 5-21; *ibid.*, 1866, vol. 9, pp. 249-61.
3. K. B. Higbie and J. R. Werning: U.S. Bur. Mines Rep. Invest., RI 5239, 1956.
4. S. Fisel, N. Topala, and V. Tintaru: *Lucr. Conf. Nat. Chim. Anal.*, 1971, vol. 4, pp. 425-30.
5. R. Monnier, P. Grandjean, and J. Zahler: *Helv. Chim. Acta*, 1963, vol. 46, pp. 2966-70.
6. F. D. Stevenson and J. E. Conway: U.S. patent 3508862, April 28, 1970.
7. I. S. Morozov and V. A. Krokhn: U.S.S.R. patent 152873, June 20, 1969 (*Chem. Abs.*, 1969, vol. 71, no. 126656).
8. CIBA Ltd., W. Scheller and J. Renard, Inventors: German patent 1144489, Feb. 28, 1963 (*Chem. Abs.*, 1963, vol. 58, no. 12264).
9. Manufactures de Produits Chimiques du Nord, Etablissements Kuhlmann, P. Frere, and A. Michel, inventors: French patent 1303630, Sept. 14, 1962 (*Chem. Abs.*, 1963, vol. 58, no. 3177).
10. L. A. Nisels' son: *Zh. Neorg. Khim.*, 1958, vol. 3, pp. 2603-17; Eng. translation: *Russ. J. Inorg. Chem.*, 1958, vol. 3, no. 12, pp. 14-32.
11. B. R. Steele and D. Geldart: *Extr. Ref. Rarer Metals, Proc. Symp.*, London, pp. 287-309, Inst. Mining Metall., London, 1956.
12. M. Vanlaer and R. Durand: *Rev. Phys. Appl.*, 1970, vol. 5, pp. 487-94.
13. T. Ishiyama and T. Kuroda: *Denki Kagaku*, 1960, vol. 28, pp. 261-67.
14. D. R. Sadoway and S. N. Flengas: *Can. J. Chem.*, 1978, vol. 56, pp. 2538-45.
15. D. R. Sadoway and S. N. Flengas: *Can. J. Chem.*, 1976, vol. 54, pp. 1692-99.
16. J. E. Dutrizac and S. N. Flengas: Canadian patent 863258, Feb. 9, 1971.
17. S. N. Flengas and J. E. Dutrizac: *Met. Trans. B*, 1977, vol. 8B, pp. 377-85.
18. D. R. Sadoway and S. N. Flengas: *Can. J. Chem.*, 1978, vol. 56, pp. 2013-18.
19. D. R. Sadoway: Ph.D. Thesis, University of Toronto, Toronto, Ontario, 1977.
20. A. P. Palkin and N. D. Chikanov: *Zh. Neorg. Khim.*, 1962, vol. 7, pp. 2394-99; English translation: *Russ. J. Inorg. Chem.*, 1962, vol. 7, pp. 1242-45.
21. J. W. Johnson and D. Cubicciotti: *High Temp. Sci.*, 1970, vol. 2, pp. 2-19.
22. L. A. Nisels' son, A. I. Pustil'nik, and T. D. Sokolova: *Zh. Neorg. Khim.*, 1964, vol. 9, pp. 1049-52; English translation: *Russ. J. Inorg. Chem.*, 1964, vol. 9, pp. 574-96.
23. H. Schaefer and C. Pietruck: *Z. Anorg. Allg. Chem.*, 1951, vol. 267, pp. 174-80.
24. Ugine Aciers, P. Besson, J. Guerin, P. Brun, and M. Bakes, inventors: German patent 2453864, May 28, 1975.
25. C. H. Muendel and R. A. Rowe: *The Design of Metal Producing Processes*, R. M. Kibby, ed., pp. 284-99, AIME, New York, 1969.