Chloro Complexes in Molten Salts. VII. Potentiometric, Spectrophotometric, and Raman Spectroscopic Study of the System $\text{KCl}-\text{AlCl}_3-\text{NbCl}_5$ at 300 °C

JENS H. von BARNER, NIELS J. BJERRUM* and G. PEDRO SMITH**

Chemistry Department A, The Technical University of Denmark, DK-2800 Lyngby, Denmark

Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Potentiometric, spectrophotometric and Raman spectroscopic measurements on the molten system $\text{KCl}-\text{AlCl}_3-\text{NbCl}_5$ at 300 °C indicate the presence of an equilibrium between Nb(V) species as follows: $\text{NbCl}_6^- \rightleftharpoons \text{NbCl}_5 + \text{Cl}^-$. For an Nb(V) concentration of 0.1 F this equilibrium holds over the pCl^- range 0.42–5.44 with pK of 4.49 ± 0.05 (in molar units) while at 0.3 F it holds over 0.42–4.72 with a pK of 4.19 ± 0.03 . Further support for this interpretation is provided by measurements of the vapor-phase concentration of NbCl_5 in equilibrium with the melt. The vapor-liquid distribution coefficient of NbCl_5 is independent of other compositional variables and has a value of 0.133 ± 0.011 at 300 °C.

As part of a general study of the acid-base properties of molten salts,^{1–5} an investigation was made of the chloroniobium(V) species in the $\text{KCl}-\text{AlCl}_3-\text{NbCl}_5$ system.

It is well-known that NbCl_5 is a Lewis acid and, therefore, has a strong affinity for chloride ions. Examination^{6,7} of the $\text{MCl}-\text{NbCl}_5$ systems ($\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) shows that the NbCl_6^- ion is present (except in the $\text{LiCl}-\text{NbCl}_5$ system) and in cases where structural data are available this complex is found to have an octahedral configuration.^{8,9} Bues, Demiray and Øye⁹ found that the equilibrium

$\text{Nb}_2\text{Cl}_{10} \rightleftharpoons 2\text{NbCl}_5$ probably occurs in liquid niobium(V) chloride and that at temperatures above 320 °C almost all niobium(V) chloride is present as NbCl_5 .

An interesting problem for salt systems containing chlorocomplexes of Nb(V) is whether or not a dinuclear ion such as $\text{Nb}_2\text{Cl}_{11}^-$ may form under special conditions. Such dinuclear ions are well-known for other Lewis acid chlorides. For example, Al_2Cl_7^- and Fe_2Cl_7^- occur in $\text{MCl}-\text{AlCl}_3$ ^{1,10–12} and $\text{KCl}-\text{FeCl}_3$ ⁴ melts. Such a dinuclear ion for Nb(V) should be favored at high Nb(V) concentrations but, unfortunately, the NbCl_5 vapor pressure over $\text{MCl}-\text{NbCl}_5$ melts at high Nb(V) concentrations is very substantial.⁶ For this reason we found it necessary to work with melts that are relatively dilute in Nb(V) and, under these conditions, did not find dinuclear complexes.

EXPERIMENTAL

Aluminium trichloride was made from pure metal (99.999 %) and HCl gas (made by reaction between concentrated hydrochloric acid and concentrated sulfuric acid), and further purified by sublimation. Potassium chloride (analytical reagent from Riedel-de Haën) was purified by first passing HCl gas (electronic grade from Matheson) over the solid and then through the melt, then flushing with pure N_2 , and finally filtering the melt. Niobium(V) chloride (analytical reagent from Schuchardt) was further purified by 5 distillations under a chlorine pressure of 1/3 atm. An analysis of the material

* To whom correspondence should be addressed.

** Permanent address: Oak Ridge National Laboratory, Post Office Box X, Oak Ridge, Tennessee 37830, U.S.A.

gave a chlorine content of 65.25 ± 0.51 % (theoretical value 65.61 %). The materials that made up a melt were weighed in a nitrogen-filled glove-box with a measured water content of about 5 ppm and continuous gas purification by forced recirculation through external molecular sieves. The oxygen content of the box was not monitored but the box was filled and flushed with nitrogen containing less than 40 ppm of O_2 plus H_2O . In order to minimize the formation of oxychloride, $NbCl_5$ was kept in sealed ampoules until used. The experimental techniques and equipment used in this investigation were almost the same as those used in previous work.¹⁻⁵ The densities of the melts used were calculated from the assumption that mixtures of $NbCl_5$ and $KCl-AlCl_3$ behave ideally. This assumption can give rise to only a small error because the amounts of $NbCl_5$ were small compared to the amounts of $KCl-AlCl_3$. The densities of $NbCl_5$ and $KCl-AlCl_3$ were obtained from the work of Nisel'son *et al.*¹³ and Morrey and Carter,¹⁴ respectively.

The electrochemical cells were made of Pyrex with glassy carbon rods (Carbone-Lorraine) fused into the bottom and had a shape similar to that of the cells used earlier.^{1,2,4,5} The cells were filled with chlorine (Fluka >99.9 %) at 0.5 atm and then sealed vacuum-tight. Because of the fairly high vapor pressure above the melt the tube connecting the two cell compartment was sealed after chlorine had been added. This could cause an error due to different chlorine pressures in the two cell compartments. Experiments performed at compositions with high chloride activity (and low vapor pressure) showed that there was only a small difference between the results obtained with open and sealed connecting tubes. The same is also probably true at low chloride activity (and high vapor pressure) because the solubility of chlorine in chloride melts is rather low and seems to increase with increasing chloride activity.¹⁵

The optical cells were of fused quartz. Short pathlengths (less than 0.1 mm) were obtained by placing precision-ground fused-silica inserts into 5 mm cells. The spectra were measured with a Cary 14R spectrophotometer equipped with a Datex digital system for punching out spectral data on paper tape.

The optical cells used for the Raman spectra were the same as those used for the UV-Vis spectra but without inserts. The Raman spectra were recorded using a Coderg PH1 laser spectrometer with 632.8 nm (60–80 mW) excitation and a cooled photomultiplier. A 90° scattering was used and the polarization of the laser beam was kept fixed. The depolarization measurements were made by the conventional method of two different analyzer orientations in the scattered beam ($\rho=0.75$ for

depolarized lines). The uncertainty in the measured Raman shifts due to the instrument was ± 2 cm^{-1} .

When $NbCl_5$ was added to molten $KCl-AlCl_3$, small amounts of Nb(V) oxychlorides were formed, largely from oxide impurities in the solvent. These contributed to the absorption spectrum and it was necessary to take the following steps to minimize this contribution. First, the highest practical concentration of Nb(V) was used. The limitation on this concentration was set by the high molar absorptivities (up to 26×10^3 $M^{-1} cm^{-1}$) of the chlorocomplexes of Nb(V) formed in the melt in combination with the shortest pathlengths that were practical to use. In order to obtain reproducible results, it was necessary to place the insert in the cell in exactly the same way each time, and to handle the cell in the same manner in each experiment. Finally, measurements were made with two different concentrations of Nb(V), one with the highest concentration at which spectra could be measured and one with 1/3 to 1/2 of this concentration. Since $AlCl_3$ from the same batch was used in both experiments subtraction of these two spectra gave a spectrum with almost no contribution from oxychloride complexes.

The vapour pressure of $NbCl_5$ over acidic melts was so high that a correction was necessary. It was measured spectrophotometrically with a special cell made from a normal cell with a fixed pathlength of 0.5 mm. Fused to the end of this cell was a compartment of about 1.5 cm^3 which contained the melt under examination.

GENERAL CONSIDERATIONS

The nomenclature used in this work is the same as that used in previous publications.¹⁻⁴ The initial molar amount of one of the added substances (in the present work KCl , $AlCl_3$, and $NbCl_5$) dissolved in 1 l of melt is defined as its formality, C' . The values used for the self-dissociation reactions of the solvent at 300 °C were 7.78 ± 0.02 and 6.86 ± 0.11 for the reaction $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$ and $Al_2Cl_7^- \rightleftharpoons Al_2Cl_6 + Cl^-$, respectively.¹⁶ From other measurements^{10,12,16} we realize that the equilibria in the chloroaluminate melts are described better by including a third reaction. However, in the present case two parameters describe the chloride activity of the solvent almost as well as three parameters. The pCl^- value for the $KCl-AlCl_3$ system saturated with KCl at 300 °C was taken to be 0.255 ± 0.03 .¹⁶ From what has been said above and as we shall see later, it is clear that at low pCl^- we are dealing with $NbCl_6^-$ in solution. The average experimental coordination number, $\bar{n}$, for Nb(V) is defined as

$(C'_{\text{KCl}} + 3C'_{\text{AlCl}_3} + 5C'_{\text{NbCl}_5} - [\text{Cl}^-] - 4[\text{AlCl}_4^-] - 7[\text{Al}_2\text{Cl}_7^-] - 6[\text{Al}_2\text{Cl}_6]) / C'_{\text{NbCl}_5}$. Since $\bar{n}$ decreases as we increase pCl^- , chloride ions are simultaneously taken away from Nb(V). This can be described by a set of general equations or models where the ratio Cl:Nb for each successive complex becomes smaller and smaller.

It has previously been shown² that close to the 1:1 composition in the KCl–AlCl₃ system (from 47 to about 52 mol % KCl), the potential of a concentration cell is within experimental uncertainty given by

$$\text{pCl}^- = -(F/RT \ln 10)\Delta E + \text{pCl}^-_{\text{II}} \quad (1)$$

where pCl^-_{I} and pCl^-_{II} are the negative logarithms of the chloride concentration in cell compartments I and II, respectively, and II usually refers to the reference compartment saturated with KCl. From the measured pCl^- of the melt and from the formality of Nb(V), $\bar{n}$ can be calculated. For each of the models mentioned above (to explain the variation of $\bar{n}$ versus the pCl^- -values) and from arbitrarily chosen equilibrium constants the concentrations of each of the proposed complexes can be calculated. These concentrations can be used to calculate a new $\bar{n}$ -value. By varying systematically the values for the equilibrium constants a minimum value for the deviation (least squares) between measured and the calculated $\bar{n}$ -values can be found. By looking at different models, the minimum variance for each model can be obtained in this way. The ratio between the minimum variances obtained in this way and the experimental variances (for example obtained in a concentration range where there is only one species present) can then be compared. Based on an *F*-test the distinction can be made between models with a probability of greater or less than 90 %. Models with higher than 90 % probability are then marked with asterisks in the tables. To obtain $F_\alpha(\phi_N, \phi_D)$ (where $(1 - \alpha) \times 100\%$ is the probability and ϕ_N and ϕ_D are the numbers of degrees of freedom in the nominator and denominator, respectively) in connection with the potentiometric method, it was assumed that ϕ_N was equal to the number of melt compositions minus the number of equilibrium constants in the equilibria and ϕ_D equal to the number of measurements necessary to determine the average of $\bar{n}$ in the basic region (where the experimental variance is obtained) minus one.

The spectrophotometric measurements are used

in this connection to obtain the number of different Nb(V) complexes present in the melt. The Bourger-Beer law and the law of additive absorbances were assumed to be valid.

The variation in the activity coefficients was neglected in all the calculations. This can be justified by the fact that the solvent was KAlCl₄ and that the concentrations of solute species were small compared to the concentrations of K⁺ and AlCl₄⁻.

RESULTS AND DISCUSSION

Measurements and calculations for cell potentials in the KCl–AlCl₃–NbCl₅ system. In Table 1 are shown the values of $-\Delta E$ at given mol fractions of KCl and AlCl₃ for 0.1 and 0.3 F NbCl₅ with the composition corrected for the presence of NbCl₅ in the gaseous phase. The measurements for 0.3 F NbCl₅ could not be performed accurately at pCl^- values much higher than ca. 4.7 (corresponding to a $-\Delta E$ of ca. 500 mV). Plots of the average experimental coordination number ($\bar{n}$) as a function of the pCl^- values calculated from Table 1 are shown in Fig. 1. From this figure it is clearly indicated by an $\bar{n}$ -value close to 6.0 that NbCl₆⁻ is the only stable species at pCl^- values below 2.1. In this connection it is interesting to examine more accurately the value of $\bar{n}$ at low pCl^- values. In Table 2 the average $\bar{n}$ -values for a number of measurements are given. From this table it is clear that the values of $\bar{n}$ for both 0.1 and 0.3 F Nb(V) solutions are very close to 6.00. The variances given in this table are based on the deviation from the average given in $\bar{n}$ -units.

From Fig. 1 it can also be seen that the lowest measured value of $\bar{n}$ is around 5.0. More important is to notice that there seems to be a levelling off of the curve around 5.0. Due to the high vapor pressure of the melt at high pCl^- values and even at fairly low Nb(V) concentrations (which makes the potentiometric measurements impossible with the present cells) this effect is only observed for the approx. 0.1 F Nb(V) solutions. In the present case it is furthermore very unlikely that we are dealing with complexes with more than two niobium atoms linked together. This is primarily based upon the fact that we have a fairly dilute solution and that Nb₂Cl₁₀ is the highest known polymer for liquid niobium(V) chloride. Together these restrictions give the five models shown in Table 3. Here the data given in Table 1 for pCl^- values higher than

Table 1. Values of cell potential and composition^a of NbCl₅ in molten KCl–AlCl₃ at 300 °C.

0.1 F NbCl ₅			0.3 F NbCl ₅		
–Δ <i>E</i> mV	Mol fraction KCl	AlCl ₃	–Δ <i>E</i> mV	Mol fraction KCl	AlCl ₃
586.2	0.4898 ₂	0.5047 ₀	508.0	0.4917 ₆	0.4912 ₀
553.5	0.4936 ₃	0.5008 ₄	462.2	0.4945 ₃	0.4874 ₉
531.5	0.4953 ₄	0.4990 ₂	410.2	0.4965 ₇	0.4842 ₆
519.8	0.4958 ₉	0.4984 ₃	365.5	0.4981 ₅	0.4820 ₃
507.8	0.4969 ₂	0.4971 ₃	346.0	0.4987 ₅	0.4817 ₁
483.8	0.4977 ₇	0.4961 ₈	244.0	0.5002 ₅	0.4794 ₈
476.4	0.4975 ₇	0.4966 ₂	109.9	0.5023 ₂	0.4775 ₆
414.3	0.4989 ₁	0.4948 ₀	55.5 ₈	0.5061 ₃	0.4739 ₁
395.9	0.4991 ₈	0.4940 ₅	44.4 ₂	0.5076 ₂	0.4725 ₁
298.2	0.5000 ₃	0.4933 ₄	34.2 ₀	0.5091 ₉	0.4709 ₇
203.5	0.5005 ₀	0.4928 ₀	18.4 ₁	0.5124 ₆	0.4678 ₄
127.7	0.5016 ₄	0.4917 ₀			
87.8 ₀	0.5032 ₃	0.4901 ₈			
55.8 ₅	0.5059 ₀	0.4874 ₇			
54.3 ₁	0.5061 ₁	0.4872 ₉			
32.3 ₃	0.5094 ₇	0.4839 ₅			
29.9 ₈	0.5096 ₄	0.4837 ₅			
18.8 ₈	0.5124 ₇	0.4809 ₃			

^a Corrected for the presence of NbCl₅ in the gaseous phase.Table 2. Average values of $\bar{n}$ for Nb(V) in the basic region.

Concentration of NbCl ₅ , M	Number of measurements	pCl [–] region	$\bar{n}$	Variance × 10 ⁴
0.1	8	0.42–2.04	6.006 ± 0.055	29.7
0.3	5	0.42–1.22	6.006 ± 0.020	4.1

Table 3. Comparison between different models for 0.1 F and 0.3 F NbCl₅ in KCl–AlCl₃ at 300 °C. Based on potentiometric measurements.^a

Equilibria	Model No.	0.1 F NbCl ₅ ^b pK	Variance × 10 ⁴	0.3 F NbCl ₅ ^c pK	Variance × 10 ⁴
NbCl ₆ [–] ⇌ NbCl ₅ + Cl [–]	(1)	4.49 ± 0.05	48.8 *	4.19 ± 0.03	5.6 *
2NbCl ₆ [–] ⇌ Nb ₂ Cl ₁₀ + 2Cl [–]	(2)	7.95 ± 0.13	99.6	7.70 ± 0.13	54.3
NbCl ₆ [–] ⇌ NbCl ₅ + Cl [–]	(3)	4.49 ± 0.05		4.19 ± 0.03	
2NbCl ₅ ⇌ Nb ₂ Cl ₁₀		^d	48.8	^d	5.6 *
2NbCl ₆ [–] ⇌ Nb ₂ Cl ₁₁ [–] + Cl [–]	(4)	3.24 ± 0.28		3.57 ± 0.10	
Nb ₂ Cl ₁₁ [–] ⇌ Nb ₂ Cl ₁₀ + Cl [–]		4.51 ± 0.20	51.9 *	4.11 ± 0.10	5.9 *
2NbCl ₆ [–] ⇌ Nb ₂ Cl ₁₁ [–] + Cl [–]	(5)	4.05 ± 0.80		4.56 ± 0.60	
Nb ₂ Cl ₁₁ [–] ⇌ 2NbCl ₅ + Cl [–]		4.91 ± 0.77	52.1 *	3.82 ± 0.60	6.0 *

^a Number of measurements, 10 and 6 for 0.1 and 0.3 F NbCl₅, respectively. ^b Asterisks based on $F_{0.10}(9.7)=2.72$ or $F_{0.10}(8.7)=2.75$ with experimental variance taken from Table 2. ^c Asterisks based on $F_{0.10}(5.4)=4.05$ or $F_{0.10}(4.4)=4.11$ with experimental variance taken from Table 2. ^d No minima found here.

Fig. 1. Average experimental coordination number ($\bar{n}$) for Nb(V) at 300 °C as a function of pCl^- : A, 0.1 F Nb(V), B, 0.3 F Nb(V), compared with calculated lines for the reaction $NbCl_6^- \rightleftharpoons NbCl_5 + Cl^-$ (full lines). The vertical dashed lines show the limiting pCl^- , due to saturation with KCl. The half-filled circle represents a coincidence between two open circles. The measurements have been corrected for $NbCl_5$ present in the gaseous phases above the melts.

2.1 ($-\Delta E$ higher than 210 mV) are used in the calculations. As discussed under General Considerations, models marked with asterisks indicate those for which the probability is higher than 90 % as compared with the experimental variances. A problem one should be aware of here is that the experimental variance could be a function of pCl^- .

One way of solving this problem would be to assume that the lowest variance is in fact the correct experimental variance for the examined range. However, this assumption will still give the same picture as shown in Table 3 (*i.e.* none of the asterisks are moved). This leaves us with four possible models, namely: models (1), (3), (4), and

(5). It is not possible to distinguish among these models on the basis of potentiometric measurements alone.

It will be seen from Table 3 that model (1) involves only two chromophoric species, whereas models (3), (4) and (5) involve three chromophoric species. In order to distinguish between these possibilities spectrophotometric measurements are needed.

Spectrophotometric measurements on $NbCl_5$ in $KCl-AlCl_3$. The problem with oxychloride formation was partly solved as described in the Experimental Section by subtracting spectra for high and low concentrations of $NbCl_5$. A set of spectra

Fig. 2. Spectra of NbCl_5 in $\text{KCl}-\text{AlCl}_3$ at 300°C . Mol fractions of KCl , AlCl_3 , and formal concentration of NbCl_5 , respectively, for the two sets of melts which form the basis for each calculated spectrum; the low concentrations are given in parentheses: A, 0.510₅ (0.510₇), 0.486₆ (0.488₁), 0.042₄ (0.017₄); B, 499₄ (0.499₆), 0.497₈ (0.499₃), 0.040₀ (0.014₂); C, 0.498₈ (0.499₁), 0.499₃ (0.499₈), 0.027₇ (0.015₈); D, 0.491₁ (0.491₇), 0.506₁ (0.506₂), 0.040₈ (0.019₄). Based on a pK -value for the reaction $\text{NbCl}_6^- \rightleftharpoons \text{NbCl}_5 + \text{Cl}^-$ of 4.49 and the self-dissociation constants for the solvent (given in the text) the average experimental coordination number ($\bar{n}$) for the niobium complex and the pCl^- for the melt could be calculated to be (values for the low concentrations are given in parentheses): A, 6.00₀ (6.00₀), 4.93 (4.88); B, 5.80₈ (5.82₄), 3.85 (3.80); C, 5.59₂ (5.62₇), 4.31 (4.25); D, 5.11₆ (5.11₇), 5.35 (5.35), respectively. All measurements have been corrected for NbCl_5 present in the gaseous phase above the melt.

obtained in this way is shown in Fig. 2. An examination of these spectra shows that even if we are not dealing with a perfect two-species system (due to the influence of some oxychloride) the best way to describe the spectra is probably by a two-species model. If only two species are present there is only one model left of the models given in Table 3, namely model (1) ($\text{NbCl}_6^- \rightleftharpoons \text{NbCl}_5 + \text{Cl}^-$). Under these circumstances, what we observe as we increase the pCl^- value for the melt is a change from NbCl_6^- ions to NbCl_5 molecules. Based on the equilibrium constant given in Table 3 for 0.1 F Nb(V) and the self-dissociation constant for the solvent given under General Considerations, pCl^- and the average experimental coordination number can be calculated for the composition corresponding to each spectrum. These values are given in the caption to Fig. 2. It can be seen that spectrum A represents the spectrum of pure NbCl_6^- , whereas spectrum D

represents a mixture of 88.4 % NbCl_5 and 11.6 % NbCl_6^- . In Fig. 3 are shown the spectrum of pure NbCl_5 in the melt (calculated from the spectra in Fig. 2) and the spectrum of pure NbCl_6^- . It will be seen from these figures that NbCl_6^- has two band maxima located at 34.4×10^3 and $41.3 \times 10^3 \text{ cm}^{-1}$. NbCl_5 also has two band maxima located at 33.7×10^3 and $43.8 \times 10^3 \text{ cm}^{-1}$, with molar extinction coefficient that are smaller than those of the NbCl_6^- bands.

Spectrophotometric measurements on NbCl_5 in the gas phase. Fig. 4 shows the spectrum of NbCl_5 in the gas phase at 300°C compared with the calculated spectrum of NbCl_5 in the melt. It can be seen that in the gas phase two bands are found at 34.8×10^3 and $43.4 \times 10^3 \text{ cm}^{-1}$, respectively. These band positions are close to those of NbCl_5 in the $\text{KCl}-\text{AlCl}_3$ melt, but molar extinction coefficients for NbCl_5 in the melt are much smaller than those of NbCl_5 in the gas.

Fig. 3. Comparison between the calculated spectra of NbCl_6^- , A, and NbCl_5 , B, in $\text{KCl}-\text{AlCl}_3$ at 300°C .

Fig. 4. Comparison between spectra of NbCl_5 at 300°C : A, in the gas phase (concentration of Nb(V) , $1.707 \times 10^{-3} \text{ M}$); B, in $\text{KCl}-\text{AlCl}_3$ (calculated).

Fig. 5. Measured concentrations of NbCl_5 in the gas phase above $\text{KCl}-\text{AlCl}_3-\text{NbCl}_5$ melts at 300°C versus the calculated concentrations of NbCl_5 in the melt (based on a pK -value of 4.49 for the reaction $\text{NbCl}_6^- \rightleftharpoons \text{NbCl}_5 + \text{Cl}^-$ and the self-dissociation constants for the solvent given in the text). The calculated concentrations of NbCl_5 in the melt, the calculated pCl^- values, and calculated $\bar{n}$ -values were: 7.75×10^{-3} M, 4.24, 5.63₃; 1.57×10^{-2} M, 4.27, 5.61₅; 1.79×10^{-2} M, 5.36, 5.11₅; 3.03×10^{-2} M, 5.31, 5.12₇; 4.59×10^{-2} M, 5.39, 5.10₈, respectively.

Since we know that at high pCl^- values there is a fairly high vapor pressure of Al_2Cl_6 above the melt, it is important to determine whether there is any interference between Al_2Cl_6 and NbCl_5 in the gas phase. Addition of Al_2Cl_6 to the gas cell had no influence on the gas spectrum of NbCl_5 . This we consider to be an indication that no gaseous complexes are formed between NbCl_5 and Al_2Cl_6 at the given temperature in contrast to what is usually found between chlorides of transition metals and aluminum chloride.^{17,18} A further consequence of this observation is that it is unlikely that NbCl_5 is solvated by AlCl_4^- in the melt.

If we now examine the gaseous phase above different $\text{KCl}-\text{AlCl}_3-\text{NbCl}_5$ melts, the measurements show as expected that there is no NbCl_5 present if the melt is basic and a fairly high con-

centration if the melt is acidic. If we take a series of different melts with different pCl^- values and measure the concentration of NbCl_5 above the melt and plot this concentration against the concentration of NbCl_5 present in the melt calculated from the equilibrium constant given in Table 3 model (1) a plot as shown in Fig. 5 is obtained. There is a very good linear correlation here between the concentration in the gas phase and the concentration in the melt phase independent of the pCl^- of the melt. This is, of course, a further reason to believe that we have obtained the right model for the system. From the slope of this curve the vapor/liquid distribution coefficient is calculated to be 0.133 ± 0.011 at 300°C . This distribution coefficient can be used to make accurate corrections for the NbCl_5 present in the gas phase above a given melt.

Raman spectra of NbCl_5 in $\text{KCl}-\text{AlCl}_3$ melt at 300°C . In Fig. 6 are shown a series of spectra of 0.2 to 0.3 F NbCl_5 dissolved in different $\text{KCl}-\text{AlCl}_3$ melts (with different pCl^- values). Most of the bands shown are due to the AlCl_4^- complex but a comparison with the spectrum of pure KAlCl_4 ^{10,19} reveals that the band around 376 cm^{-1} must be

Fig. 6. Series of Raman spectra (parallel and perpendicular polarizations) of NbCl_5 dissolved in molten $\text{KCl}-\text{AlCl}_3$ at 300°C . The mol fractions of KCl , AlCl_3 , and the formal concentration of NbCl_5 as well as the calculated pCl^- and $\bar{n}$ (based on a pK -value of 4.19 for the reaction $\text{NbCl}_6^- \rightleftharpoons \text{NbCl}_5 + \text{Cl}^-$) were: A, 0.5135₁, 0.4668₉, 0.2963, 3.89, 6.00₀; B, 0.4964₅, 0.4864₂, 0.2558, 3.97, 5.62₃; C, 0.4884₁, 0.4972₄, 0.2134, 5.18, 5.09₃; D, 0.4824₂, 0.5035₈, 0.2072, 5.54, 5.04₂, respectively.

due to Nb(V). In order to obtain the correct position for this band, the background due to the AlCl_4^- band has been subtracted in the vicinity of 376 cm^{-1} . The band at 376 cm^{-1} must be the ν_1 vibration of the octahedral NbCl_6^- ion (the band position in liquid CsNbCl_6 at 600°C is found⁹ at 373 cm^{-1} in complete agreement with our proposed model). In this connection it is interesting to look for the other bands found in CsNbCl_6 at 600°C , i.e. at 281 cm^{-1} (E_g) and at $181, 173\text{ cm}^{-1}$ (T_{2g}). The band at 281 cm^{-1} is weak and this is probably the reason why it is not seen. The bands at 181 and 173 cm^{-1} are stronger but they are concealed by the 182 cm^{-1} band due to AlCl_4^- .

As the melt is made increasingly acidic a change occurs so that the band at 376 cm^{-1} disappears and a new, weaker band appears. This band, which is also strongly polarized, is located around 397 cm^{-1} . In this connection it is very important to subtract the background due to AlCl_4^- before the band maximum is determined. A comparison with the spectrum of liquid NbCl_5 at 300°C (where the main part of the liquid consists of NbCl_5 molecules⁹) shows that the strongest band is located at 397 cm^{-1} and this band is also polarized. According to the work of Bues, Demiray and Øye⁹ $\text{Nb}_2\text{Cl}_{10}$ is characterized by a band at 415 cm^{-1} . Unfortunately, the present spectra are not good enough to reject the possibility of the presence of a smaller band at 415 cm^{-1} in addition to the band at 397 cm^{-1} . However, the observed behavior agrees well with the other types of measurements we performed. As in the case of the NbCl_6^- complex the other bands due to NbCl_5 are obscured by bands due to AlCl_4^- , i.e. the bands at 182 and 122 cm^{-1} .

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