

Thermodynamic properties of the alkali metal hexachloroniobate and hexachlorotantalate compounds by vapour pressure measurements

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The vapour pressures for the decomposition of the solid and liquid compounds $AMCl_6$ where $A = Na, K, Rb, \text{ or } Cs$, and $M = Nb \text{ or } Ta$, were measured by a fused quartz Bourdon spiral pressure gauge. The hexachlorotantalates were found to be more stable thermally than the hexachloroniobates. Enthalpies of decomposition were calculated. The dissociation temperatures of each sequence of compounds increase with increasing size of the radius of the alkali-metal cation. Partial pressures of $NbCl_5$ or $TaCl_5$ vapour in equilibrium with solutions representing the binary systems $KCl-KNbCl_6$ and $KCl-KTaCl_6$, respectively, are also reported.

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Faisant appel à une jauge de Bourdon en silice, on a mesuré les tensions de vapeur accompagnant les décompositions des composés solides et liquides $AMCl_6$ où $A = Na, K, Rb$ ou Cs et $M = Nb$ ou Ta . On a trouvé que les hexachlorotantalates sont plus stables du point de vue thermique que les hexachloroniobates. On a calculé les enthalpies de décomposition. Les températures de dissociation pour chaque série de composés augmentent avec une augmentation du diamètre du cation du métal-alkalin. On rapporte aussi les tensions de vapeur partielles du $NbCl_5$ ou du $TaCl_5$ en équilibres respectivement avec des solutions représentant des systèmes binaires $KCl-KNbCl_6$ et $KCl-KTaCl_6$.

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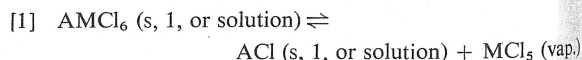
Introduction

Niobium and tantalum pentachloride vapours react with alkali-metal chlorides to form compounds of the type $[A^+][MCl_6^-]$, where A represents an alkali metal and M represents Nb or Ta . These compounds can melt congruently, as does $KNbCl_6$ (1), or incongruently, as does $NaNbCl_6$ (1). Covalently bonded $NbCl_5$ and $TaCl_5$ melts behave as molecular liquids (2-5); in contrast, solutions of these pentachlorides in molten alkali-metal chlorides are ionic in character, as their electrical conductivities show (6, 7), and thermodynamically stabler than the former, as vapour pressure measurements demonstrate. For example, at $450^\circ C$ pure $NbCl_5$ has a vapour pressure of 22 atm (8), whilst the partial pressure of $NbCl_5$ over molten $KNbCl_6$ at the same temperature is reported as 0.15 atm (9). These changes in behaviour may be explained by the presence of complex species in the MCl_5 - ACl solutions (4, 10, 11).

The compounds $NaNbCl_6$, $NaTaCl_6$, $KNbCl_6$, $KTaCl_6$, $RbNbCl_6$, $RbTaCl_6$, $CsNbCl_6$, and $CsTaCl_6$ were synthesized in this laboratory by the reaction of $NbCl_5$ or $TaCl_5$ vapour with solid alkali-metal chloride under controlled pressure and temperature

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conditions. The preparation has been described elsewhere (12). The thermodynamic properties of the aforementioned compounds and of solutions of $KCl-KNbCl_6$ and $KCl-KTaCl_6$ were determined by vapour pressure measurements of the following equilibrium:



Experimental

The vapour pressure of $NbCl_5$ or $TaCl_5$ in equilibrium with the compounds $AMCl_6$ or with $AMCl_6$ - ACl solutions have been measured by a fused quartz Bourdon spiral pressure gauge contained in a closed apparatus which has been described elsewhere (13).

For these measurements the temperature of the sample container was varied between 190 and $660^\circ C$ while the upper part of the apparatus containing the Bourdon spiral was maintained at temperatures about $50^\circ C$ higher than the corresponding normal boiling points of pure $NbCl_5$ and $TaCl_5$.

Samples of the $AMCl_6$ compounds and of their mixtures with alkali-metal chlorides were prepared by methods previously described (12). Materials were handled in a glove box filled with dehydrated helium. Specimens were introduced into the sample container of the apparatus in the form of powders. The part of the cell consisting of the sample container and the Bourdon spiral were sealed under vacuum. It was found that large quantities of adsorbed gas were released from the salt upon heating. This introduced a systematic error into the measurements. Accordingly, an elaborate degassing procedure was employed in which the cell was repeatedly

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heated, cooled, reopened, and evacuated. When residual gas was no longer present upon cooling, a proper experiment was conducted to measure the vapour pressure of the sample.

Results and Discussion

1. Properties of the $AMCl_6$ Compounds

Figures 1-4 display the experimental results for the vapour pressures of the decomposition of the compounds $AMCl_6$, where A is Na, K, Rb, or Cs. Each figure shows the results for both the hexachloroniobate and the hexachlorotantalate of a given alkali metal. The figures also show the results of other investigators. Least-squares lines are given in Table 1.

The shape of the curve of $\ln P_{MCl_5}$ vs. $1/T$ may be understood in terms of the equilibrium constant for the decomposition reaction in eq. [1] (14-19). For this reaction

$$[2] \quad K = P_{MCl_5} \cdot a_{ACl} / a_{AMCl_6}$$

where the standard state for the compounds ACl and $AMCl_6$ is the pure solid at all temperatures, and for MCl_5 is the vapour at a pressure of 1 atm.

In the ACl- $AMCl_6$ subsystem, below the eutectic temperature three phases are present: the pure solids, ACl, and $AMCl_6$, whose activities are unity, and MCl_5 vapour. Therefore, in this region, $K = P_{MCl_5}$.

In the temperature and composition range where molten ACl- $AMCl_6$ solutions are saturated with either ACl or $AMCl_6$ solid, the expression for the equilibrium constant is written as $K = P_{MCl_5} / a_{AMCl_6}$ or $K = P_{MCl_5} a_{ACl}$, respectively. Accordingly, as the activity terms are always less than unity the pressure curves of these solutions are expected to inflect at the eutectic and liquidus temperatures of the corresponding ACl- $AMCl_6$ systems.

The $\ln P_{MCl_5}$ vs. $1/T$ plot is also expected to change slope at temperatures below the eutectic points when the solids present undergo solid-solid transitions.

This is particularly significant for the hexachloroniobate and hexachlorotantalate compounds in which several phase changes in the solid state have been observed.

In connection with this last comment Table 2 is presented as a summary of previously reported results from this laboratory (12). Thus in the present work measurements were taken within temperature ranges for which well defined phases were present.

Figure 1 shows the results for the decomposition of both β -NaNbCl₆ and β -NaTaCl₆ along with the results of other investigations for these two compounds. It is of interest to note that their decomposition pressures reach 1 atm at temperatures lower than their melting points. Accordingly a plot of $\ln P_{MCl_5}$ vs. $1/T$ should be linear.

TABLE I. Summary of vapour pressure measurements

Reactions	Temperature range of measurement (T/K)	$\ln P_{MCl_5}$ (atm) = $a_0 + a_1/T$		Standard error of estimate S	ΔH_R^{0*} (K cal/mol)	ΔS_R^{0*} (e. u)
		a_0	a_1			
NaNbCl ₆ (β-solid) → NaCl(s) + NbCl ₅ (vap.)	518-561	(8.075)	(-4750)	—	—	—
NaTaCl ₆ (β-solid) → NaCl(s) + TaCl ₅ (vap.)	497-650	10.8930 ± 0.2883	-7131.3 ± 163.5	0.0552	14.17 ± 0.32	21.72 ± 0.56
KNbCl ₆ (β-solid) → KCl(s) + NbCl ₅ (vap.)	568-643	7.3969 ± 1.7530	-7015.6 ± 1078.7	0.0455	13.94 ± 2.14	14.74 ± 3.50
KNbCl ₆ (l) → KCl (in soln) + NbCl ₅ (vap.)	673-735	8.1329 ± 0.2019	-6040.1 ± 140.1	0.0238	12.00 ± 0.28	—
KTaCl ₆ (l) → KCl (in soln) + TaCl ₅ (vap.)	673-805	11.688 ± 0.145	-9316.8 ± 104.8	0.0302	—	—
RbNbCl ₆ (β-solid) → RbCl(s) + NbCl ₅ (vap.)	583-632	4.7581 ± 0.0640	-4991.3 ± 38.8	0.0037	9.92 ± 0.08	9.52 ± 0.12
RbNbCl ₆ (l) → RbCl (in soln) + NbCl ₅ (vap.)	672-852	9.8853 ± 0.3480	-8304.1 ± 261.1	0.0775	—	—
RbTaCl ₆ (l) → RbCl (in soln) + TaCl ₅ (vap.)	693-848	10.4041 ± 0.2553	-8856.1 ± 192.4	0.0596	—	—
CsNbCl ₆ (β-solid) → CsCl(s) + NbCl ₅ (vap.)	670-708	8.4815 ± 0.6533	-2354.9 ± 457.5	0.0290	4.68 ± 0.90	9.63 ± 1.30
CsNbCl ₆ (l) → CsCl (in soln) + NbCl ₅ (vap.)	822-843	9.9450 ± 0.8453	-8286.2 ± 701.2	0.0176	—	—
CsTaCl ₆ (β-solid) → CsCl(s) + TaCl ₅ (vap.)	675-732	0.7937 ± 0.1453	-3095.6 ± 102.2	0.0087	6.15 ± 0.20	1.59 ± 0.29
CsTaCl ₆ (l) → CsCl (in soln) + TaCl ₅ (vap.)	828-1106	12.8243 ± 0.2572	-11881.6 ± 225.8	0.0320	—	—

Where $\Delta H_R^{0} = a_1 R$ and $\Delta S_R^{0*} = a_0 R$, where $R = 1.98716$ cal/mol K.

TABLE 2. Characteristic temperatures (12)

Compound	Melting point (K)	Eutectic temperature† (K)	Solid-solid transformation‡ (K)		Comments
			$\alpha \rightarrow \beta$	$\beta \rightarrow \gamma$	
NaNbCl ₆	(721)*	—	518	572	Incongruently melting
NaTaCl ₆	(748)*	—	498	—	Incongruently melting
KNbCl ₆	673	643	572	—	Congruently melting
KTaCl ₆	674	646	411	584	Congruently melting
RbNbCl ₆	653	—	578	—	—
RbTaCl ₆	690	655	534	586	Congruently melting
CsNbCl ₆	808	(712)*	563	—	—
CsTaCl ₆	823	(717)*	569	—	Congruently melting

*Average values from several investigations (6, 7, 20, 22, 23, 30).

†Eutectic temperatures corresponding to the ACl-AMCl₆ type sub-systems.

‡Systems not yet fully known crystallographically. Solids α , β , and γ simply describe solid-solid transformations observed cryoscopically with increasing temperature. It should be noted that other authors used different symbolism (23, 24, 30).

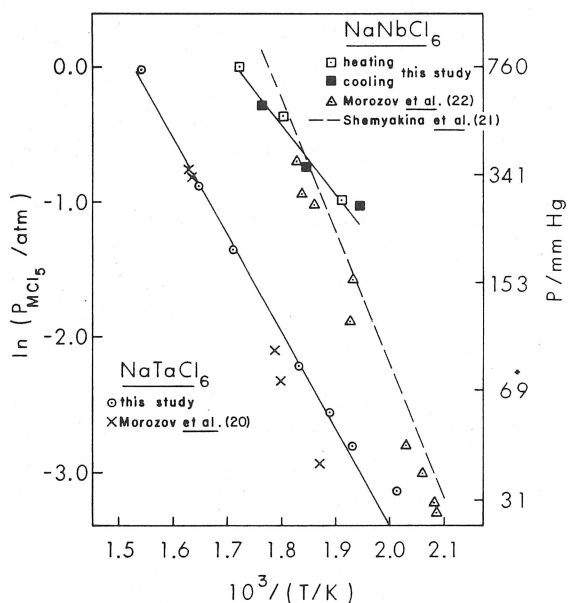


FIG. 1. $\ln P_{MCl_5}$ vs. $1/T$ plots for the systems NaNbCl₆ and NaTaCl₆. Solid lines represent best fit of present data.

In comparison with other vapour pressure studies the results of this work agree well with that of Morozov, Korshunov, and Simonich (20) for the α -NaTaCl₆ system. Shemyakina *et al.* (21) and Morozov and Korshunov (22) have measured the decomposition of NaNbCl₆ at temperatures lower than that in this investigation, and their values tend to converge at about 518 K which is the transition temperature for its $\alpha \rightarrow \beta$ transformation.

Figure 2 shows the results of both β -KNbCl₆ and molten KTaCl₆. Data for the decomposition of solid KTaCl₆ are not given as the pressures were too low to be measured by the apparatus. Figure 2 also shows the results of other investigations.

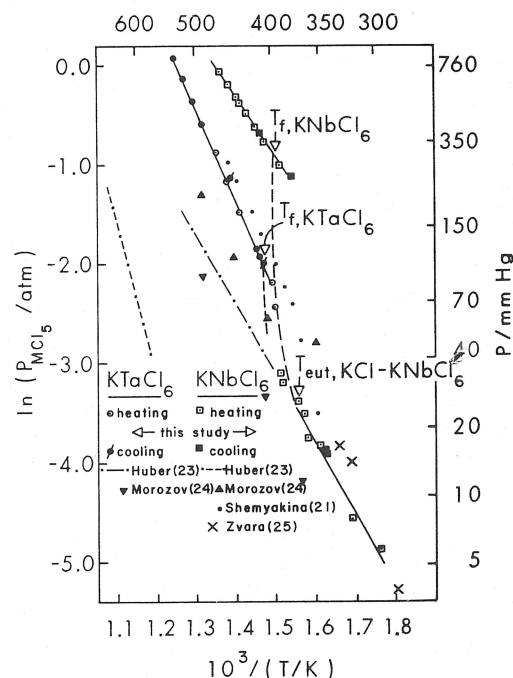


FIG. 2. $\ln P_{MCl_5}$ vs. $1/T$ plots for the systems KNbCl₆ and KTaCl₆. Solid lines represent best fit of present data. Dashed line is simply drawn to link the solid and liquid regions.

The thermal decomposition of KNbCl₆ has been studied by Huber *et al.* (23), Morozov and Simonich (24), Shemyakina *et al.* (21), and Zvara and Tarasov (25). The results of the present study for low temperatures agree best with those of Zvara and Tarasov (25), who measured vapour pressures in equilibrium with both α - and β -KNbCl₆ solids using a radioactive tracer technique. These authors, however, did not make any comments on the solid-solid transformations occurring during their measurements.

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Figure 3 sho measurements fo RbNbCl₆ and reportedly melts Attempts to r RbTaCl₆ at ten were unsuccessful low, and despite enough inert gas Huber *et al.* vapour pressure molten state. I

Equilibrium pressures reported by both Morozov and Simonich (24) and by Shemyakina *et al.* (21) are not in agreement with values measured in the present study. The former used a transportation technique, while the latter used a null membrane type manometer. Both authors plotted their measured pressures of NbCl_5 as a single least-squares line crossing solid-solid transition temperatures and extending into the temperature range for molten KNbCl_6 . Huber *et al.* (23) measured vapour pressures of NbCl_5 in equilibrium with molten KNbCl_6 by a transportation method. The results are much lower than those recorded herein. In reports of vapour pressures measured by the transportation technique (23, 24) the authors failed to mention that consideration was given to the problem of depletion of NbCl_5 from the KNbCl_6 condensed phase as the experiment progressed.

The thermal decomposition of KTaCl_6 has been studied by Huber *et al.* (23), Morozov and Simonich (24), and Zvara and Tarasov (25). The results of Huber *et al.* (23) and Morozov and Simonich (24) for molten KTaCl_6 , both studies having employed transportation techniques, are much lower than those of the present study. No mention was made of the problem of depletion of TaCl_5 from the condensed KTaCl_6 phase during the course of the experiment. Furthermore, the data of Morozov and Simonich (24), which span the temperature range from solid KTaCl_6 to molten KTaCl_6 , have been represented by a single least-squares line (26).

In Fig. 2 the plot of the $\ln P_{\text{NbCl}_5}$ vs. $1/T$ for $\beta\text{-KNbCl}_6$ from the results obtained in the present work shows inflections at the eutectic temperature of the KCl-KNbCl_6 subsystem and at the melting point of KNbCl_6 . The curvature of the dotted line joining these two temperatures results from the changing activity of KCl in the melt whose composition varies along the liquidus tie line as temperature is increased. Pressure curves of a similar shape have been recorded in this laboratory for P_{ZrCl_4} and P_{HfCl_4} in equilibrium with K_2ZrCl_6 and K_2HfCl_6 , respectively (19).

Figure 3 shows equilibrium vapour pressure measurements for the decomposition of the molten RbNbCl_6 and RbTaCl_6 compounds. The former reportedly melts incongruently.

Attempts to measure the decomposition of solid RbTaCl_6 at temperatures below the melting point were unsuccessful. The equilibrium pressures were low, and despite elaborate degassing there was still enough inert gas present to confound the data.

Huber *et al.* (23) have measured decomposition vapour pressures for both these compounds in the molten state. Figure 3 shows their results for

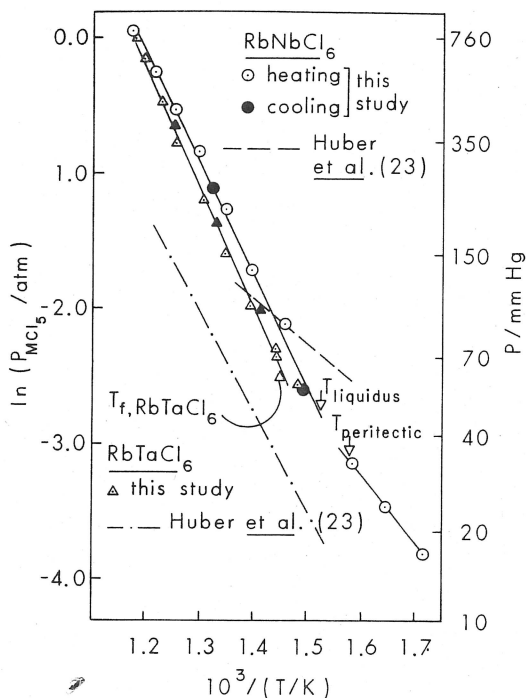


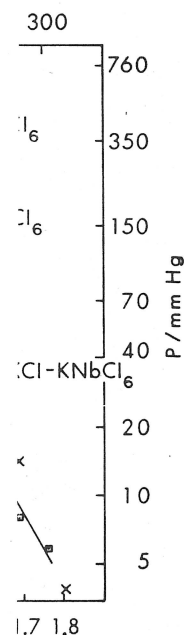
FIG. 3. $\ln P_{\text{MCl}_5}$ vs. $1/T$ plots for the systems RbNbCl_6 and RbTaCl_6 . Solid lines represent best fit of present data.

RbNbCl_6 to be of the same order of magnitude as the results of this study. Their results for RbTaCl_6 are lower than in this study. Huber *et al.* (23) employed a transportation technique but did not discuss the effect of the depletion of the volatile pentachloride from the condensed phase during the course of an experiment.

Figure 4 shows the vapour pressures measured for the decomposition of CsNbCl_6 and CsTaCl_6 . Both compounds melt congruently and the $\text{CsMCl}_6\text{-CsCl}$ type phase diagrams indicate simple eutectic melting (23). Therefore, according to the thermodynamic analysis presented earlier, the partial pressure of the pentachloride should be represented on a plot of $\ln P_{\text{MCl}_5}$ vs. $1/T$ by two linear segments joined by a region of curvature.

These two compounds were extremely difficult to degas, particularly CsNbCl_6 . This was true both for compounds prepared by precipitation from $\text{SOCl}_2\text{-ICl}$ solutions and for those made by gas-solid reaction. Accordingly the reported vapour pressures over the solid compounds are approximate values and are presented here only for the sake of completeness. Many samples were prepared and studied. The results quoted below were selected as the best because they represent the lowest reproducible pressures measured.

Figure 4 also shows the results of Morozov and



systems KNbCl_6 and present data. Dashed and solid lines represent liquid regions.

KNbCl_6 has been reported by Morozov and Simonich (24) and Zvara and Tarasov (25). The former used a transportation technique, while the latter used a null membrane type manometer. Both authors plotted their measured pressures of NbCl_5 as a single least-squares line crossing solid-solid transition temperatures and extending into the temperature range for molten KNbCl_6 . Huber *et al.* (23) measured vapour pressures of NbCl_5 in equilibrium with molten KNbCl_6 by a transportation method. The results are much lower than those recorded herein. In reports of vapour pressures measured by the transportation technique (23, 24) the authors failed to mention that consideration was given to the problem of depletion of NbCl_5 from the KNbCl_6 condensed phase as the experiment progressed.

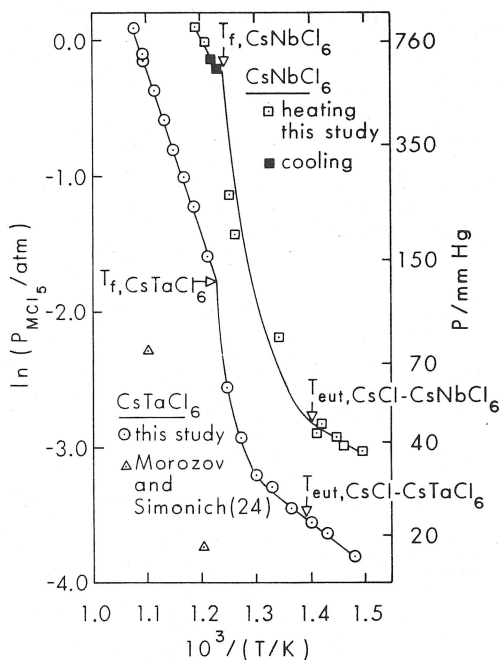


FIG. 4. $\ln P_{MCl_5}$ vs. $1/T$ plots for the systems $CsNbCl_6$ and $CsTaCl_6$. Solid lines represent best fit of present data.

Simonich (24) for $CsTaCl_6$. Their equilibrium pressures are lower in magnitude, but the slope of the $\ln P_{TaCl_5}$ vs. $1/T$ plot is similar to that recorded herein. Again a transportation technique was used and no explanation was given of effects of depleting $TaCl_5$ from the condensed phase during an experiment.

It appears that this study is the first to report decomposition vapour pressures for $CsNbCl_6$.

2. Properties of the Solutions of $NbCl_5$ -KCl and $TaCl_5$ -KCl

Figures 5 and 6 show the equilibrium vapour pressure measurements for the $NbCl_5$ -KCl and $TaCl_5$ -KCl systems, respectively. It should be noted that the corresponding phase diagrams show that the composition range of liquid solubility is very narrow. Although the liquid range widens at higher temperatures, the partial pressure of $NbCl_5$ or $TaCl_5$ above these solutions exceeds the upper limit of the pressure gauge used in this investigation. Accordingly, measurements herein were restricted to a narrow range of composition and temperature.

The results for the system $NbCl_5$ -KCl shown in Fig. 5 span the concentration range, $0.401 < X_{NbCl_5} < 0.502$. The solution of composition, X_{NbCl_5}

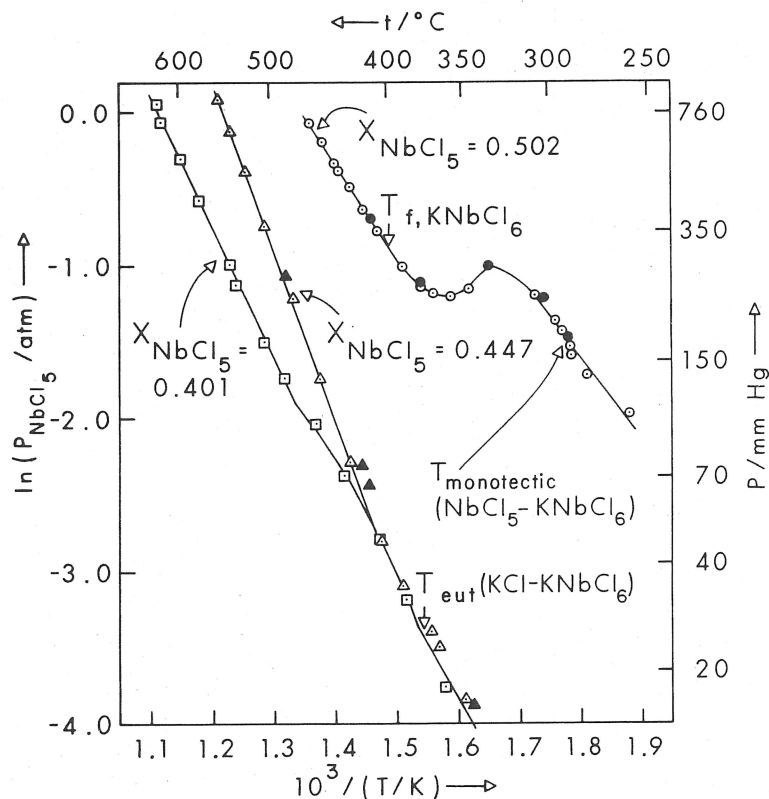


FIG. 5. $\ln P_{NbCl_5}$ vs. $1/T$ plots for the binary subsystem $KCl-KNbCl_6$. Solid lines represent best fit of present data. The pressure curve at $X_{NbCl_5} = 0.502$ represents solutions in the $NbCl_5$ - $KNbCl_6$ subsystem.

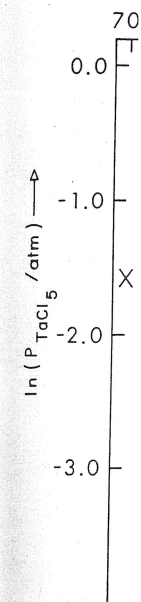


FIG. 6. $\ln P_{TaCl_5}$ vs. $1/T$ plot for the $KCl-KTaCl_6$ system.

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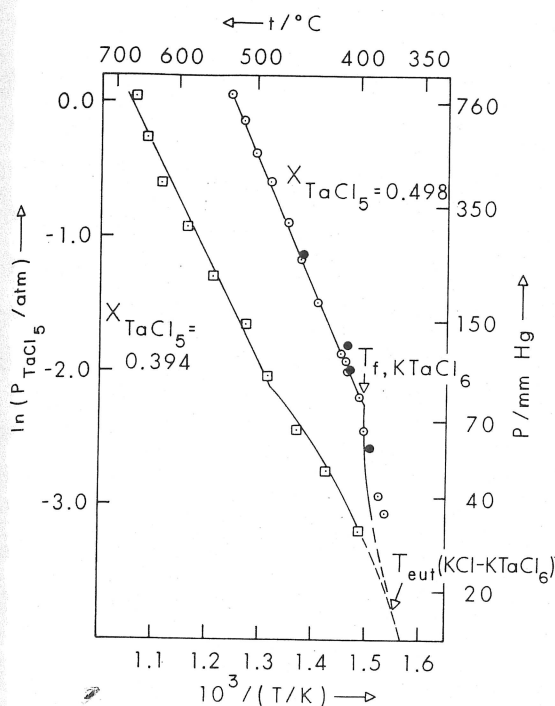


FIG. 6. $\ln P_{\text{TaCl}_5}$ vs. $1/T$ plots for the binary subsystem KCl-KTaCl₆. Solid lines represent best fit of present data.

$X_{\text{NbCl}_5} = 0.502$, is part of the KNbCl₆-NbCl₅ subsystem. As such, its pressure curve is expected to inflect at the monotectic temperature, 285°C (27), and at the liquidus temperature, which in this case is close to the melting point of KNbCl₆, which is about 400°C. The solutions of composition, $X_{\text{NbCl}_5} = 0.401$ and $X_{\text{NbCl}_5} = 0.447$ are part of the KCl-KNbCl₆ subsystem. Their pressure curves reveal a common segment at temperatures below the KCl-KNbCl₆ eutectic at 370°C (12, 27), as expected. Figure 5 shows a comparison of decomposition pressures between the KCl-rich solutions and the NbCl₅-rich solutions. Pressures recorded over the former are much lower and are evidence of the stabilizing effect of the formation of the complex compound KNbCl₆.

The results displayed in Fig. 6 are restricted to the KCl-KTaCl₆ subsystem. It is interesting to compare the shapes of the curves for the two solutions, as they are found on opposite sides of the KCl-KTaCl₆ eutectic composition. Both inflect at the KCl-KTaCl₆ eutectic temperature of 370°C (7, 12), and at the corresponding liquidus temperature, which for $X_{\text{TaCl}_5} = 0.498$ is almost identical with the melting point of KTaCl₆, 401°C (12).

Conclusions

The results of the present study indicate that the thermal stability of the complex compounds ANbCl₆

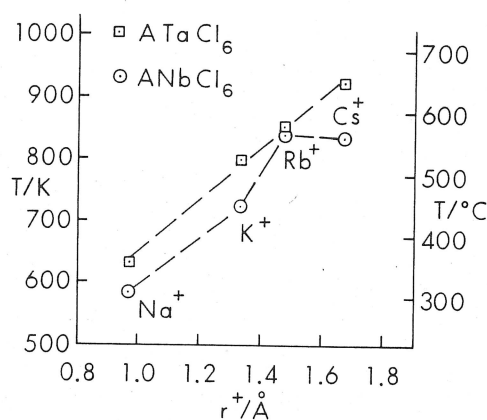


FIG. 7. Dependence of the decomposition temperature of the alkali hexachlorotantalate and hexachloroniobate compounds on the ionic radii of the alkali metal cations.

and ATaCl₆ is dependent upon the size of the alkali metal cation present.

Figure 7 shows the dependence of the dissociation temperature of the AMCl₆ compounds on the alkali-metal cation radius. The dissociation temperature is defined as the temperature at which the equilibrium pressure P_{MCl_5} becomes 1 atm and, therefore, can be taken as a measure of thermal stability of the AMCl₆ compound.

With the exception of RbNbCl₆, the results lie on two lines, one for the hexachloroniobates and one for the hexachlorotantalates. The latter have higher dissociation temperatures than their congeners, indicating the greater thermal stability of the hexachlorotantalate compound to the hexachloroniobate alkali-metal compounds. In general complexing for either NbCl₅ or TaCl₅ results in a dramatic reduction in the pressure of MCl₅ in equilibrium with a compound. For example, at 500°C pure NbCl₅ has a vapour pressure of 36 atm (8); in contrast, the partial pressure of NbCl₅ over KNbCl₆ is 1.43 atm and over CsNbCl₆ is 0.37 atm at that temperature.

Secondly, there is a reversal in stability. Pure TaCl₅ is more volatile than NbCl₅ (13). However, this changes upon formation of the AMCl₆ compounds. The partial pressure of NbCl₅ over the hexachloroniobate, ANbCl₆, is greater than that of TaCl₅ over the hexachlorotantalate of the same alkali metal. Nisel'son (28) has reported similar behaviour when NbCl₅ and TaCl₅ were complexed with POCl₃. In this laboratory the same reversal has been observed with ZrCl₄, HfCl₄, and the complex compounds which they form with the alkali-metal chlorides (14-19).

It is of interest to note that the relative volatility of the two pentachloride vapours is greater over the

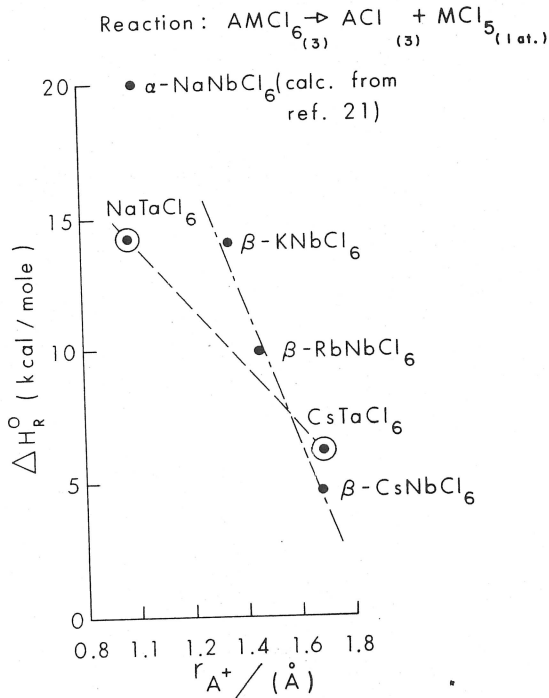


FIG. 8. Plot of ΔH_R^0 vs. the ionic-radii of the alkali metal cations.

complex compounds than over the pure pentachloride. At 230°C, $P_{TaCl_5}^0/P_{NbCl_5}^0 = 1.42$ (13), while at 500°C over the corresponding potassium complexes, $P_{NbCl_5}^0/P_{TaCl_5}^0 = 2.10$.

Interesting trends are also seen in the standard enthalpy changes for the decomposition reactions given in Table 1. The data shown in this table provide the temperature dependence of $\ln P_{MCl_5}$ and may be used for calculating standard enthalpies in temperature ranges in which the $AMCl_6$ type-compounds are present as single phase solids. The results of these calculations for ΔH_R^0 and ΔS_R^0 are also included in Table 1. A plot of ΔH_R^0 vs. the alkali metal cation radius, shown in Fig. 8, indicates that reaction enthalpies increase as the size of the alkali metal cation present in the complex compound decreases. The point for NaTaCl₆ was calculated from results on α -NaTaCl₆ obtained by Shemyakina *et al.* (21) and is expected to deviate from trends followed by the β -phase compounds.

Activity data for MCl_5 calculated from the results on the binary molten solutions of KCl-KNbCl₆ and KCl-KTaCl₆ indicate a further stabilization for MCl_5 in the presence of excess KCl. Figure 9 shows a plot of the concentration dependence of a_{MCl_5} in molten NbCl₅-KCl and TaCl₅-KCl solutions at 496°C, where $a_{MCl_5} = P_{MCl_5}/P_{MCl_5}^0$. Values for $P_{MCl_5}^0$ at 496°C were found in the literature: 34.8 atm for

□ TaCl₅ - KCl System
○ NbCl₅ - KCl System

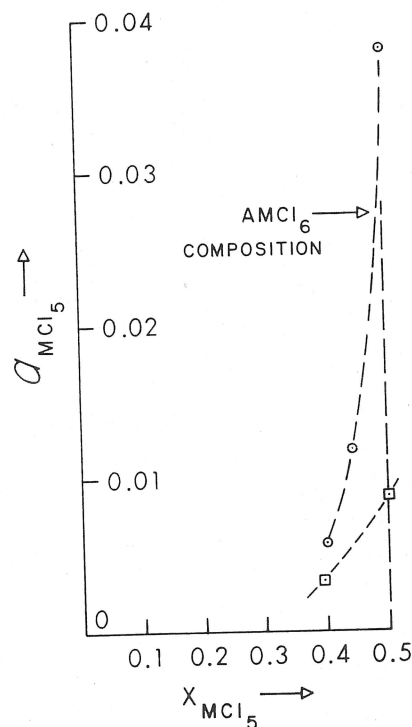


FIG. 9. Activity isotherms for a_{MCl_5} at 496°C for the molten KCl-KNbCl₆ and KCl-KTaCl₆ solutions.

NbCl₅ (8) and 43.0 atm for TaCl₅ (29). As in the case of the pure $AMCl_5$ compounds, the molten hexachlorotantalate solutions are chemically more stable than the molten hexachloroniobates. Figure 9 also illustrates the significantly higher pentachloride activity in solutions whose pentachloride content exceeds the complex composition of 50 mol%.

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1. A. P. PALKIN and N. D. CHIKANOV. Zh. Neorg. Khim. 4, 898 (1959); Russ. J. Inorg. Chem. 4, 407 (1959).
2. W. BILTZ and A. VOIGT. Z. Anorg. Allg. Chem. 120, 71 (1922).
3. I. R. BEATTIE, T. R. GILSON, and G. A. OZIN. J. Chem. Soc. A, 2765 (1968).
4. W. BUES, F. DEMIRAY, and H. A. ØYE. Z. Phys. Chem. Frankfurt am Main, 84, 18 (1973).
5. J. W. JOHNSON and D. CUBICCIOTTI. High Temp. Sci. 2, 9 (1970).
6. A. P. PALKIN and N. D. CHIKANOV. Zh. Neorg. Khim. 7, 1370 (1962); Russ. J. Inorg. Chem. 7, 705 (1962).

7. A. P. PALKIN 2388 (1962); Russ. J. Inorg. Chem. 7, 705 (1962).
8. J. W. JOHNSON Temp. Sci. 2, 9 (1970).
9. I. S. MOROZOV 1907 (1957); Russ. J. Inorg. Chem. 2, 1907 (1957).
10. R. GUT. Helv. Chim. Acta, 41, 103 (1958).
11. C. M. COOK, J. Chem. Phys. 46, 1203 (1967).
12. D. R. SADOW 2013 (1978).
13. D. R. SADOW 1692 (1976).
14. R. L. LISTER (1965).
15. J. E. DUTRIZATE Metallurg. Trans. A, 1, 103 (1970).
16. S. N. FLENGAS Chem. 46, 495 (1978).
17. S. N. FLENGAS Chem. 55, 115 (1978).
18. D. A. ASVESTI Chem. 55, 115 (1978).
19. G. J. KIPOURO (1978).
20. L. S. MOROZOV Zh. Neorg. Khim. (7), 203 (1956).

7. A. P. PALKIN and N. D. CHIKANOV. *Zh. Neorg. Khim.* **7**, 2388 (1962); *Russ. J. Inorg. Chem.* **7**, 1239 (1962).
8. J. W. JOHNSON, W. J. SILVA, and D. CUBICCIOTTI. *High Temp. Sci.* **2**, 20 (1970).
9. I. S. MOROZOV and A. T. SIMONICH. *Zh. Neorg. Khim.* **2**, 1907 (1957); *Russ. J. Inorg. Chem.* **2**(8), 311 (1957).
10. R. GUT. *Helv. Chim. Acta*, **43**, 830 (1960).
11. C. M. COOK, JR. *J. Am. Chem. Soc.* **81**, 535 (1959).
12. D. R. SADOWAY and S. N. FLENGAS. *Can. J. Chem.* **56**, 2013 (1978).
13. D. R. SADOWAY and S. N. FLENGAS. *Can. J. Chem.* **54**, 1692 (1976).
14. R. L. LISTER and S. N. FLENGAS. *Can. J. Chem.* **43**, 2947, (1965).
15. J. E. DUTRIZAC and S. N. FLENGAS. *Advances in Extractive Metallurgy Symposium*, April 17-20, 1967, The Institution of Mining and Metallurgy, London, England.
16. S. N. FLENGAS, J. E. DUTRIZAC, and R. L. LISTER. *Can. J. Chem.* **46**, 495 (1968).
17. S. N. FLENGAS and P. PINT. *Can. Metall. Q.* **8**, 151 (1969).
18. D. A. ASVESTAS, P. PINT, and S. N. FLENGAS. *Can. J. Chem.* **55**, 1154 (1977).
19. G. J. KIPOUROS and S. N. FLENGAS. *Can. J. Chem.* **56**, 1549 (1978).
20. L. S. MOROZOV, B. G. KORSHUNOV, and A. T. SIMONICH. *Zh. Neorg. Khim.* **1**, 1646 (1956); *Russ. J. Inorg. Chem.* **1**, (7), 203 (1956).
21. T. S. SHEMAKINA, E. K. SMIRNOVA, T. I. POPOVA, and V. M. KUPTSOVA. *Zh. Neorg. Khim.* **9**, 2387 (1964); *Russ. J. Inorg. Chem.* **9**, 1291 (1964).
22. I. S. MOROZOV and B. G. KORSHUNOV. *Zh. Neorg. Khim.* **1**, 145 (1956); *Russ. J. Inorg. Chem.* **1**(1), 150 (1956).
23. K. HUBER, E. JOST, E. NEUENSCHWANDER, M. STUDER, and B. ROTH. *Helv. Chim. Acta*, **41**, 2411 (1958).
24. I. S. MOROZOV and A. T. SIMONICH. *Zh. Neorg. Khim.* **2**, 1907 (1957); *Russ. J. Inorg. Chem.* **2**(8), 311 (1957).
25. I. ZVARA and L. K. TARASOV. *Zh. Neorg. Khim.* **7**, 2665 (1962); *Russ. J. Inorg. Chem.* **7**, 1388 (1962).
26. I. S. MOROZOV and D. YA. TOPTYGIN. *Izv. Akad. Nauk SSSR Ser. Khim.* 1920 (1959); *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1832 (1959).
27. O. R. GAVRILOV and L. A. NISEL'SON. *Zh. Neorg. Khim.* **11**, 209 (1966); *Russ. J. Inorg. Chem.* **11**, 114 (1966).
28. L. A. NISEL'SON. *Zh. Neorg. Khim.* **2**, 816 (1957); *Russ. J. Inorg. Chem.* **2**(4), 162 (1957).
29. L. A. NISEL'SON, A. D. PUSTIL'NIK, and T. D. SOKOLOVA. *Zh. Neorg. Khim.* **9**, 1049 (1964); *Russ. J. Inorg. Chem.* **9**, 574 (1964).
30. *Gmelins Handbuch der anorganischen Chemie*, Verlag Chemie GmbH, Weinheim, Fed. Repub. Germany, Tantal, System-Nummer 50, Teil B2, 1971.



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(29). As in the ds, the molten chemically more niobates. Figure higher pentachloride ion of 50 mol%.

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Council of Ca-

1. *Neorg. Khim.* **4**, (1959).
Illeg. Chem. **120**, 71

A. OZIN. *J. Chem.*

E. Z. *Phys. Chem.*

High Temp. Sci. **2**, 9

1. *Neorg. Khim.* **7**, 5 (1962).