

Ternary Chlorides in the Systems $ACl/TbCl_3$ ($A = K, Rb, Cs$)

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The phase diagrams of the pseudobinary systems $ACl/TbCl_3$ ($A = K, Rb, Cs$) were investigated by DTA. Powder diffractograms of the existing ternary compounds were indexed in analogy to known structure families. By solution calorimetry and measurements of $emf = f(T)$ in galvanic cells for solid electrolytes, the enthalpies ΔH° and free enthalpies ΔG° for the formation of the ternary chlorides from the compounds adjacent in the systems were determined. In all systems the compounds A_3TbCl_6 and ATb_2Cl_7 exist. Furthermore, compounds A_2TbCl_5 exist with $A = Cs, K$, but not with $A = Rb$, in contrast to the system $RbCl/GdCl_3$. The crystal structures are analogous to those of the Gd compounds (Cs_3BiCl_6 and K_3MoCl_6 type; Cs_2DyCl_5 and K_2PrCl_5 type; $RbDy_2Cl_7$ and KDy_2Cl_7 type). The coordination number is 7 in the K_2PrCl_5 structure; in all other structures, octahedra exist. Two compounds are stable only above temperatures >0 K, K_3TbCl_6 (≥ 394 K) and KTb_2Cl_7 (≥ 93 K). All other compounds have exothermic synproportionation enthalpies and therefore are stable at 0 K. The main difference from the systems of $GdCl_3$ is the nonexistence of the compound Rb_2TbCl_5 . © 1995 Academic Press, Inc.

1. INTRODUCTION

Since 1985 we have investigated the systems $ACl/LnCl_3$ ($A = Na-Cs$), starting with lanthanum (1) and completing the early lanthanide group with the systems of gadolinium (2). We reinvestigated the phase diagrams, determined the crystal structures of the existing double chlorides, and measured their thermodynamic stabilities by solution calorimetry and emf measurements in galvanic cells for solid electrolytes. The properties of the K, Rb, and Cs compounds vary systematically with the size of the Ln^{3+} ions; we have recently surveyed this group (3, 4). The

sodium compounds have another feature: beginning with europium (5), the compounds $NaLnCl_4$ become dominant.

This paper reports the results of investigations on the systems $ACl/TbCl_3$ ($A = Cs, Rb, K$). Korshunov *et al.* (6) found three compounds when elucidating the phase diagram of the system $KCl/TbCl_3$ by DTA: K_3TbCl_6 , K_2TbCl_5 , and KTb_2Cl_7 . Meyer (7, 8) has determined the lattice parameters for some of the ternary chlorides from powder patterns (Table 1).

2. EXPERIMENTAL

Materials

$TbCl_3$ was prepared by dehydration of $TbCl_3 \cdot 6H_2O$ (99.99%; Johnson-Matthey, Karlsruhe), first by heating at $90^\circ C$ in a drying oven, then by heating in an HCl stream. To avoid hydrolysis, the temperature was slowly raised to $320^\circ C$ over 2 days. $TbCl_3$ is strongly hygroscopic. The hygroscopy of the ternary chlorides increases with increasing content of terbium and with decreasing size of the alkali metal ions. Tb^{3+} compounds are colorless. The alkali metal halides were dried at $500^\circ C$.

Differential Thermal Analysis (DTA)

The DTA measurements were performed in a home-built device for samples (0.5 g) in vacuum-sealed quartz ampoules. If necessary the material could be annealed after melting with a gas flame and homogenizing by shaking and quenching. In general, heating curves were measured (heating rate $2^\circ C \text{ min}^{-1}$).

X-Ray Powder Patterns

Powder patterns were taken at ambient temperature with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During

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exposure ($CuK\alpha$ radiation) the samples were kept under a helium atmosphere. For dynamic high-temperature photographs, the Simon–Guinier method was applied. Corundum ($a = 475.92$ pm; $c = 1299.00$ pm) was used as an internal standard.

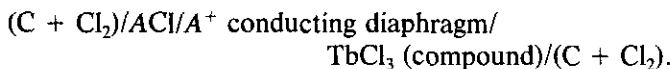
Solution Calorimetry

The device for solution calorimetry was a homebuilt calorimeter. Samples of 2–4 g were dissolved in 1.1 liter H_2O , which is a good approximation of an infinitely diluted system. From the enthalpies of solution, $\Delta_{sol}H_{298}^\circ$, the enthalpies for the formation from $nACl + TbCl_3$, Δ_fH° , were calculated:

$$\Delta_fH_{298}^\circ = \{\Delta_{sol}H_{298}^\circ (TbCl_3) + n\Delta_{sol}H_{298}^\circ (ACl)\} - \Delta_{sol}H_{298}^\circ (A_nTbCl_{n+3}).$$

emf Measurements

A detailed description of the galvanic cell was given previously (9). For the formation of the most $TbCl_3$ -rich compound in a system $ACl/TbCl_3$ the setup was



The solid electrolytes (compressed disks) were separated by an A^+ -conducting sintered glass powder, containing only one alkali metal, A . The collected emf vs T values could be subjected to a linear regression analysis. The temperature range was 300–480°C.

3. RESULTS

The Polymorphism of $TbCl_3$

The most comprehensive investigations of the modifications of $TbCl_3$ were conducted by Simon and Umland (see 10). They prepared the compound by a transport reaction with $AlCl_3$. At $\sim 400^\circ C$ they obtained a deposit of an orthorhombic phase (PuBr₃-type); at $\sim 210^\circ C$, a hexagonal phase UCl_3 -type) was formed. At 370–400°C the hexagonal modification was irreversibly transformed to the PuBr₃ modification, which at 517°C undergoes a reversible phase transition to H- $TbCl_3$ (orthorhombic trirutile structure). By slow cooling a re-formation of the UCl_3 structure does not occur. The authors concluded that the UCl_3 modification must be metastable at all temperatures.

Our investigations essentially confirm these findings. We obtained the UCl_3 phase by dehydrating $TbCl_3 \cdot xH_2O$ at a temperature of $\sim 320^\circ C$.

When a melt is quenched, a strongly distorted phase is formed; its X-ray pattern contains only one broad peak. During heating in the DTA cell a strong exothermic peak

was found at 180–200°C: the metastable phase was transformed to the UCl_3 -type modification. By continued heating at $\sim 360^\circ C$ the PuBr₃-type modification was formed with a small endothermic enthalpy. Finally, at 509°C H- $TbCl_3$ was produced with a large endothermic enthalpy, comparable to that of melting. Russian scientists (11) measured a transition enthalpy of 23.1 ± 4.6 kJ mol⁻¹ at 793 K, while the melting enthalpy at 857 K is 31.6 ± 6.3 kJ mol⁻¹.

Thus, one must conclude that the UCl_3 type is the genuine modification stable at ambient temperature. It is transformed to the PuBr₃-type structure at $\sim 360^\circ C$. When the PuBr₃-type modification is cooled and annealed at temperatures below 360°C, the re-formation of the UCl_3 modification is so strongly hindered that it does not occur. Therefore, it is not difficult to keep the PuBr₃ modification metastable at ambient temperature. The only possibility of obtaining the UCl_3 modification is to prepare it directly at a temperature where it is stable ($< 360^\circ C$), either from the vapor or by dehydration of $TbCl_3 \cdot xH_2O$.

The lattice parameters for $TbCl_3$ (UCl_3 type) given by Umland (see 10) are space group $P6_3/m$, $Z = 2$, $a = 737.63$ (2) pm, and $c = 405.71$ (2). We were able to confirm these values.

For $TbCl_3$ (PuBr₃ type) Umland and co-workers found, in good agreement with previous measurements of Templeton *et al.* (12) and with neutron-diffraction values of Fischer *et al.* (13), space group $Cmcm$, $Z = 4$, $a = 384.71$ (6) pm, $b = 1177.37$ (7) pm, and $c = 851.77$ (4) pm.

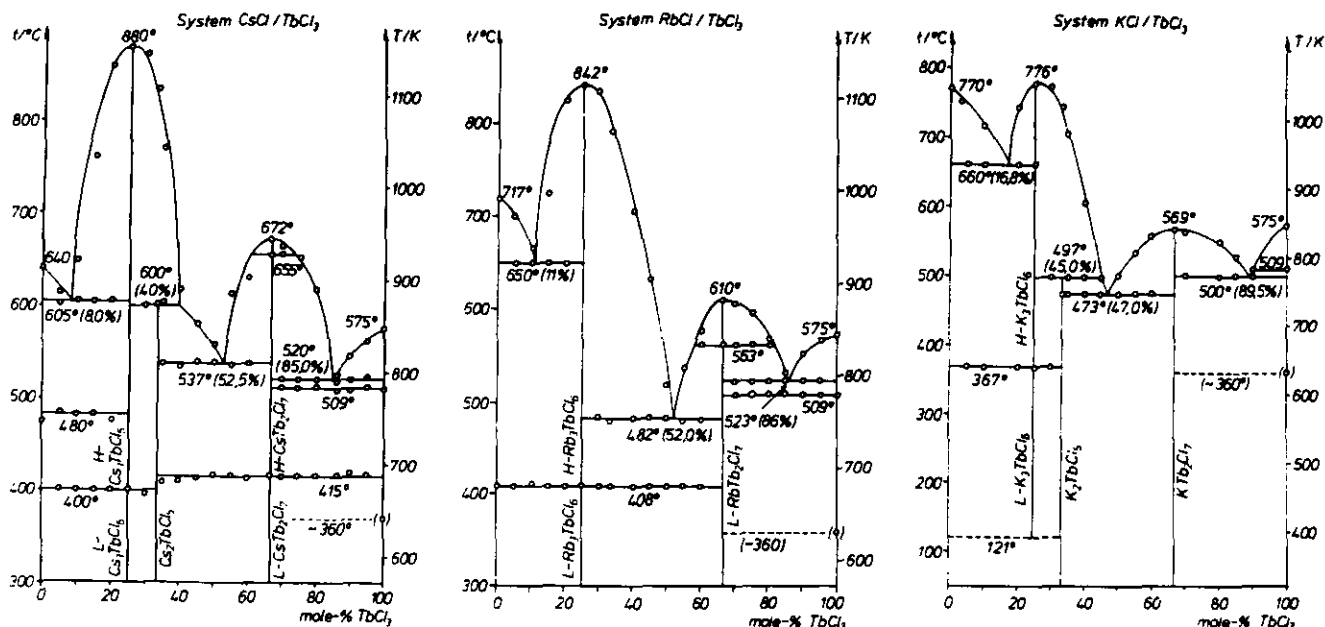
The molar volumes are 57.57 and 58.09 cm³ mole⁻¹, respectively. The transformation from the UCl_3 type to the PuBr₃ type occurs with an expansion of 0.52 cm³ mole⁻¹. This correlates with an endothermic transition enthalpy of 1.2 kJ mol⁻¹ (see below).

The Phase Diagrams

Figure 1 illustrates the results of the DTA investigations. Congruently melting compounds A_3TbCl_6 and ATb_2Cl_7 exist in all systems. All these compounds, KTb_2Cl_7 excepted, undergo reversible phase transitions. The decomposition of K_3TbCl_6 at 121°C could not be detected by DTA, but was extrapolated from emf measurements. In the systems with $A = Cs$ and K , additional 2:1 compounds A_2TbCl_5 exist, both with incongruent melting points. The system $KCl/TbCl_3$ agrees well with the findings of Korshunov *et al.* (6).

Crystal Structures

Table 1 shows the results of our X-ray diffraction measurements on powders together with the unit cell parameters found by Meyer and co-workers for the compounds ATb_2Cl_7 and K_2TbCl_5 . Intensities were calculated using the site parameters for the elpasolite type ($Fm\bar{3}m$) and

FIG. 1. Phase diagrams of systems ACI/TbCl₃.

for Cs₃LaCl₆ (C2/c) (4). For L-K₃TbCl₆ the site positions were taken from K₃MoCl₆ (15) and for Cs₂DyCl₅ (16). The ΔV_m values were calculated using experimental molar volumes for the binary compounds (in cm³ mole⁻¹): LaCl₃ = 57.6; CsCl (NaCl-type modification) = 52.4; RbCl = 42.3; KCl = 37.3.

The compounds A₃TbCl₆ contain isolated [TbCl₆] octahedra. The high-temperature modifications have the cubic pseudoelpasolite structure. At low temperatures, the octahedra are distorted, so that monoclinic unit cells result either with the Cs₃BiCl₆ structure (14) or with the K₃MoCl₆ structure (15) for L-K₃TbCl₆. For the last compound only

poor X-ray photographs could be obtained, so that the cell parameters could be calculated only approximately.

In the compounds CsTb₂Cl₇ and RbTb₂Cl₇ (RbDy₂Cl₇ type), KTb₂Cl₇ (KDy₂Cl₇ type), and K₂TbCl₅ (K₂PrCl₅ type) the CN for Tb is 7. According to our findings, Cs₂TbCl₅ belongs to the Cs₂DyCl₅ type (16) with connected Tb-Cl octahedra.

Solution Calorimetry

The solution enthalpies of the two modifications of TbCl₃ were determined by three measurements each:

TABLE 1
Unit-Cell Parameters for Ternary Chlorides of Tb (III)

Compound	Space group	a (pm)	b (pm)	c (pm)	β (°)	V_m (cm ³ mole ⁻¹)	ΔV_m
H-Cs ₃ TbCl ₆ ^a	<i>Fm</i> 3 <i>m</i>	1159.7(2)				234.9	+20.1
H-Rb ₃ TbCl ₆ ^a	<i>Fm</i> 3 <i>m</i>	1125.9(2)				214.9	+30.4
H-K ₃ TbCl ₆ ^a	<i>Fm</i> 3 <i>m</i>	1101.8(2)				201.4	+21.9
L-Cs ₃ TbCl ₆	C2/c	2704.3(8)	816.7(2)	1324.6(3)	100.17(2)	216.8	+ 2.0
L-Rb ₃ TbCl ₆	C2/c	2598.6(9)	788.5(2)	1295.2(4)	99.60(3)	197.0	+12.5
L-K ₃ TbCl ₆	<i>P</i> 2 ₁ / <i>c</i>	1300	761	1302	109.2	183.0	+ 3.5
Cs ₂ TbCl ₅	<i>Pnma</i>	956.9(2)	750.9(7)	1525.8(5)		165.1	+ 2.7
From the work of Meyer							
K ₂ TbCl ₅ (12)	<i>Pnma</i>	1262.7(2)	859.2(2)	792.5(1)		129.5	- 2.7
CsTb ₂ Cl ₇ (13)	<i>Pnma</i>	1329.1(2)	701.5(1)	1274.7(3)		178.9	+11.4
RbTb ₂ Cl ₇ (13)	<i>Pnma</i>	1288.5(2)	694.0(2)	1269.2(4)		170.9	+13.4
KTb ₂ Cl ₇ (13)	<i>P</i> 2 ₁ / <i>a</i>	1277.0(2)	689.0(2)	1264.9(2)	89.52(2)	167.6	+15.0

^a Measured at 500°C.

TABLE 2
Thermodynamic Properties of Ternary Terbium Chlorides
(Enthalpies in kJ mole^{-1}) Entropies in $\text{J K}^{-1} \text{mole}^{-1}$

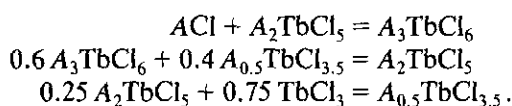
Compound	$\Delta_{\text{sol}}H^\circ$	Δ_fH°	$\Delta_{\text{syn}}H^\circ$ (cal)	$\Delta_{\text{syn}}H^\circ$ (emf)
Cs_3TbCl_6	-61.0(3)	-73.5	-16.0	-17.0
Cs_2TbCl_5	-95.1(4)	-57.5	-2.1	-1.9
$Cs_{0.5}TbCl_{3.5}$	-151.4(7)	-28.3	-13.9	-13.7
Rb_3TbCl_6	-74.3(4)	-61.7	-39.2	-37.7
$Rb_{0.5}TbCl_{3.5}$	-157.5(5)	-22.5	-12.2	-8.9
K_3TbCl_6	-98.1(2)	-37.0	+15.7	18.4
K_2TbCl_5	-100.3(4)	-52.7	-25.6	-26.7
$K_{0.5}TbCl_{3.5}$	-167.6(2)	-12.2	+1.0	1.2

$\Delta_{\text{sol}}H^\circ$ ($TbCl_3$, UCl_3 type) = $-188.8(4) \text{ kJ mole}^{-1}$; $\Delta_{\text{sol}}H^\circ$ ($TbCl_3$, $PuBr_3$ type) = $-190.0(6) \text{ kJ mole}^{-1}$; literature values range from 187 to 192 kJ mole^{-1} without any specification of the modification.

The $PuBr_3$ modification that is metastable at ambient temperature was prepared by annealing a $TbCl_3$ sample for 2 days at $\sim 400^\circ\text{C}$. The transition enthalpy (UCl_3 modification) \rightarrow ($PuBr_3$ modification) is 1.2 kJ mole^{-1} . For all further calculations the value for the UCl_3 modification was used.

The solution enthalpies for the alkali metal chlorides were taken from previous investigations; they are: $CsCl = 18.1(2)$, $RbCl = 17.6(2)$, and $KCl = 17.9(1) \text{ kJ mole}^{-1}$.

The solution enthalpies for all compounds and their formation enthalpies, Δ_fH° , from the binary compound $nACl$ and $TbCl_3$ are compiled in Table 2. In the fifth column enthalpies $\Delta_{\text{syn}}H^\circ$ are given; they relate to the following synproportionation reactions:



emf Measurements

A comprehensive description of the method was given recently in this journal (4). The emf values were measured for the formation of each compound from ACl and the adjacent $TbCl_3$ -richer compound in the temperature range ~ 300 – 500°C . In this range the dependence of emf on T was linear. Thus, the equations for the regression lines could be transformed to the Gibbs–Helmholtz equation $\Delta_fG^\circ = \Delta_fH^\circ - T\Delta_fS^\circ$ by multiplication by $-nF$. By means of thermodynamic cycles these functions were transformed to those for the reactions $nACl + TbCl_3 = A_nTbCl_{3+n}$, denoted Δ_fG° , Δ_fH° , and Δ_fS° , and further to the free enthalpies of synproportionation, $\Delta_{\text{syn}}G^\circ$, from the two neighboring compounds. For high-temperature modifications the temperatures of formation (decomposition) were calculated by the condition $\Delta_{\text{syn}}G^\circ = 0$ and

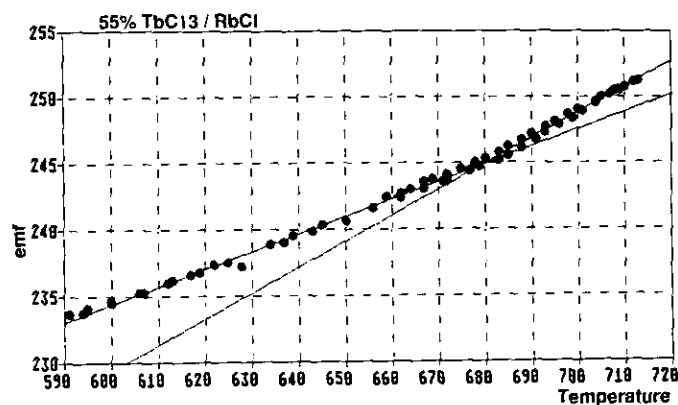


FIG. 2. Computer plot emf vs T for the reaction $2.5 RbCl + Rb_{0.5}TbCl_{3.5} = Rb_3TbCl_6$.

transformation temperatures from low- to high-temperature modifications by Δ_fG° (H -modification) = Δ_fG° (L -modification). For the compound Rb_3TbCl_6 , which is formed according to $2.5 RbCl + Rb_{0.5}TbCl_{3.5} = (H \text{ or } L)Rb_3TbCl_6$, a computer plot is shown as an example in Fig. 2.

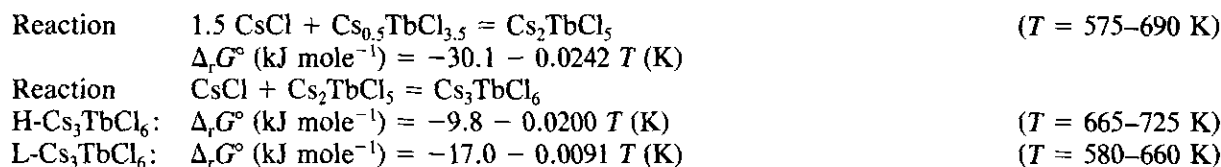
emf Measurements could be performed for all K and Rb compounds, but only for two Cs compounds, Cs_3TbCl_6 and Cs_2TbCl_5 . According to our present experiences, the emf cells break down for emf values higher than ~ 500 mV. For $Cs_{0.5}TbCl_{3.5}$ the Δ_fH° value from solution calorimetry is $-28.3 \text{ kJ mole}^{-1}$. Assuming the most favorable case, that $\Delta_fS^\circ = 0$, so that $\Delta_fG^\circ = -28.3 \text{ kJ mole}^{-1}$, we have to expect emf values for at least 586 mV. Thus, no constant results were obtained for this compound.

The Gibbs–Helmholtz equations for the reaction in the cell and for formation from ACl and $TbCl_3$ are listed below, together with the temperature ranges of the measurements.

The range of error was smaller than 1 kJ mole^{-1} for the energy values and $0.8 \text{ J K}^{-1} \text{ mole}^{-1}$ for the entropies.

TABLE 3
Synproportionation Enthalpies and Entropies for Ternary Terbium Chlorides Together with Decomposition Temperatures and Differences of Mole-Volumina

Compound	$\Delta_{\text{syn}}H^\circ$ (kJ mole^{-1})	$\Delta_{\text{syn}}S^\circ$ (kJ mole^{-1})	T_D (K)	ΔV_m ($\text{cm}^3 \text{mole}^{-1}$)
Cs_3TbCl_6	-17.0	9.1		+2.0
Cs_2TbCl_5	-1.9	4.2		+2.7
$Cs_{0.5}TbCl_{3.5}$	-13.7	0 (estim)		+5.7
Rb_3TbCl_6	-37.7	31.0		+12.5
$Rb_{0.5}TbCl_{3.5}$	-8.9	8.5		+6.7
K_3TbCl_6	18.4	46.6	394	+13.5
K_2TbCl_5	-26.7	31.9		-2.7
$K_{0.5}TbCl_{3.5}$	1.2	14.6	79	+7.5



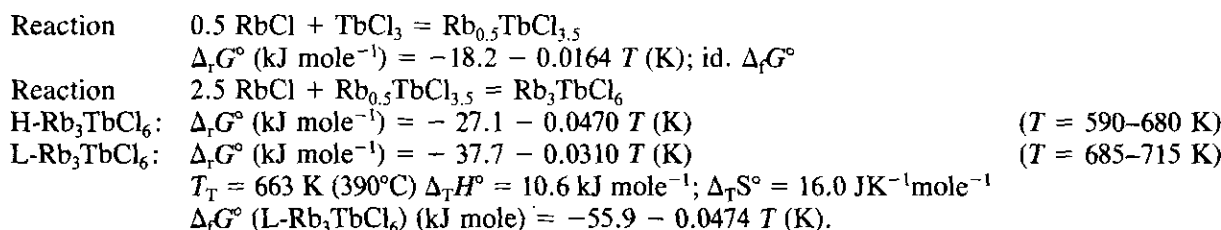
Transformation temperature $T_T = 661 \text{ K}$ (388°C); $\Delta_T H^\circ = 7.2 \text{ kJ mole}^{-1}$; $\Delta_T S^\circ = 10.9 \text{ kJ mole}^{-1}$.

Together with the estimated $\Delta_r G^\circ$ value for $\text{Cs}_{0.5}\text{TbCl}_{3.5}$ the following equations for the formation reactions result:

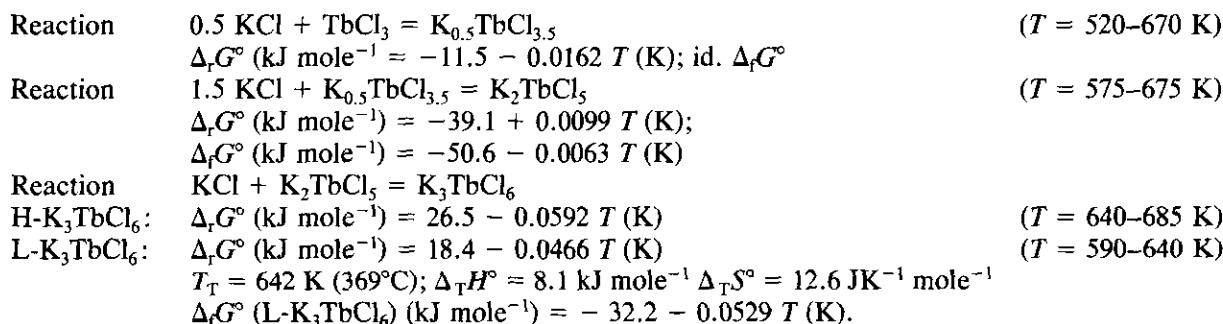
$$\Delta_r G^\circ (\text{Cs}_2\text{TbCl}_5) (\text{kJ mole}^{-1}) = -58.4 - 0.0242 T (\text{K})$$

$$\Delta_r G^\circ (\text{L-Cs}_3\text{TbCl}_6) (\text{kJ mole}^{-1}) = -75.4 - 0.0333 T (\text{K})$$

Rb Compounds



K Compounds



4. DISCUSSION

A ternary compound is stable when the free enthalpy for the formation from the two adjacent compounds in its pseudobinary system, the free synproportionation enthalpy, is negative. If $\Delta_{\text{syn}} G^\circ$ becomes 0, the compound decomposes to these neighbors. Since the reaction entropies in general are positive, this occurs when the enthalpies $\Delta_{\text{syn}} H^\circ$ are positive. The condition for the decomposition temperature T_D is $\Delta_{\text{syn}} H^\circ = T_D \cdot \Delta_{\text{syn}} S^\circ$ which means that a loss in lattice enthalpy must be compensated for by a sufficiently large gain in entropy. In Table 2 these synproportionation properties are compiled. Only two compounds, K_3TbCl_6 and KTb_2Cl_7 , are unstable at $T = 0$, and K_2TbCl_5 is the only compound formed with a volume contraction.

This feature can be explained by considering the coordi-

nation numbers for the Tb^{3+} and the A^+ ions. In all 3:1 compounds and in Cs_2TbCl_5 the Tb^{3+} ion is in an octahedral environment, while in the compounds ATb_2Cl_7 and K_2TbCl_5 (K_2PrCl_5 Typ) its CN is 7. In the elpasolite structure A_2AMCl_6 of $\text{H-A}_3\text{TbCl}_6$ the CN for two A^+ is 12, and for the third A^+ it is 6. In Cs_2TbCl_5 the CN for Cs^+ is (10 + 1), in K_2TbCl_5 for K^+ (8 + 1), and in the compounds ATb_2Cl_7 it is approximately 12 for the A^+ .

For the three potassium compounds the CN 7 for Tb^{3+} and (8 + 1) for K^+ are more favorable than the combination 6/12 for K_3TbCl_6 and 7/12 for KTb_2Cl_7 . With the bigger Rb^+ the higher CN becomes more favorable: the formation enthalpies from AlCl and TbCl_3 , $\Delta_r H^\circ$ (Table 2), become more exothermic; the compound Rb_2TbCl_5 no longer exists. This is the main difference from the GdCl_3 system (2), where Rb_2GdCl_5 still exists. This tendency continues when advancing to the Cs compounds, but now

a 2:1 compound exists, crystallizing in the Cs_2DyCl_5 structure type with the coordination numbers 6/10. The specific ternary chlorides that are produced seem to be those in which the A^+ ions have the most suitable surroundings.

Considering the effect of entropy, a high synproportionation entropy is found for the compounds A_3TbCl_6 with isolated octahedra. This issue was discussed in detail in a previous paper (4).

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