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THERMOCHEMICAL STUDIES ON THE SYSTEM $KCl/CeCl_3$

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ABSTRACT

The system $KCl/CeCl_3$ has been reinvestigated by DTA and X-ray analysis. For the existing compounds the crystal structures were determined. Their thermodynamic functions were yielded by solution calorimetry and e.m.f. measurements in a galvanic cell with solid electrolytes.

INTRODUCTION

Our method to get thermodynamic functions for the formation of ternary chlorides in a galvanic cell with solid electrolytes [1] can be applied for tervalent metals too. In this paper our findings concerning the system $KCl/CeCl_3$ are given

$$KCl + CeCl_3 = K_nCeCl_{n+3}$$

For the formation of the Ce-richest compound the set-up of the cell is: $(C+Cl_2)/KCl_{(s)}/K^+$-conduct.diaphragm $/LaCl_3(+K_nCeCl_{n+3})/(C+Cl_2)$. The measured e.m.f. E can be transformed into the free enthalpy of reaction ΔG_R using the relation $\Delta G_R=-n\cdot F\cdot E$ (n=transported charge, F=Faraday constant). The temperature dependence of the e.m.f. was found to be linear in the range of measurements; thus $\Delta G_R=a+b\cdot T$ with $a=\Delta H_R$ and $b=-\Delta S_R$ according to the Gibbs-Helmholtz relation. Additionally, ΔH_R(298K) was measured by solution calorimetry.

RESULTS

The system $KCl/CeCl_3$

In an older investigation [2] two compounds are described: K_3CeCl_6 with a phase transition at 512°C and K_2CeCl_5. A reinvestigation by means of DTA and crystal-powder-X-rax-photographs yielded two corrections (fig. 1):

1) The compound K_3CeCl_6 is stable only at high temperature.
2) A new incongruently melting compound $K_3Ce_5Cl_{18}\equiv KCe_{1.67}Cl_6$.

The crystal structures

K_3CeCl_6: With a high-temperature Guinier-camera a powder pattern

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was taken at 560°C using Al_2O_3 as inner standard. It could be indexed with a cubic cell of the elpasolite type of structure: a=11.241±0.002 Å.

$\underline{K_2CeCl_5}$: The structure determination of Meyer [3] could be confirmed (orthorhombic K_2PrCl_5-type).

$\underline{KCe_{1.67}Cl_6}$: This compound has a hexagonal unit cell which is related to the $LaCl_3$-structure [4]: one third of the La^{3+}-sites is occupied by K^+-ions; $2/3K^+$ are occupying the position 2b: 0,0,0; 0,0,1/2 of the space group 176-$P6_3/m$. (For the analogous compound $KLa_{1.67}Cl_6$ a single crystal investigation gave a reliability value R=0.085 with a statistical occupation model.):

a=7.839±0.002 Å c=4.256±0.001 Å

$D_{exp.} = 3.60 g\cdot cm^{-3}$ $D_x = 3.56 g\cdot cm^{-3}$

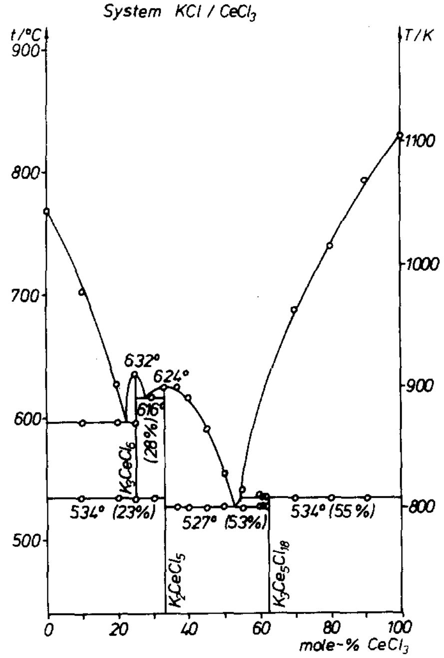

Fig.1

ΔH_R(298K) by solution calorimetry

The apparatus used was a home-built isoperibolic calorimeter [5]. From the enthalpies of solution, ΔH_L, the reaction enthalpies, ΔH_R, were calculated by $\Delta H_R = \{\Delta H_L(CeCl_3) + n\cdot\Delta H_L(KCl)\} - \Delta H_L(K_nCeCl_{n+3})$. Each ΔH_L was measured at least three times; KCl was dissolved in a solution of adequate concentration (dissolution ratio ~1:3500 moles).

$\Delta H_L(CeCl_3) = -138.9\pm0.8 kJ\cdot mol^{-1}$; $\Delta H_L(KCl) = +17.9\pm0.1 kJ\cdot mol^{-1}$

$\Delta H_L(K_{0.6}CeCl_{3.6}) = -123.2\pm0.8 kJ\cdot mol^{-1}$ $\Delta H_R = -5.0 kJ\cdot mol^{-1}$

$\Delta H_L(K_2CeCl_5) = -75.8\pm1.0 kJ\cdot mol^{-1}$ $\Delta H_R = -27.3 kJ\cdot mol^{-1}$

EMF-measurements

With the measured values of two samples a linear regression analysis was calculated. The differences between them and the standard deviations were taken for the assessment of the real range of error.

$\underline{K_{0.6}CeCl_{3.6}}$: Reaction $0.6KCl + CeCl_3 = K_{0.6}CeCl_{3.6}$ Samples: 80 and 90 mol-% $CeCl_3$
50 measured points in the range 630-790K

e.m.f./mV=84.71+0.1573·T/K $\Delta G_R/kJ\cdot mol^{-1} = -4.9 - 0.0091\cdot T/K$ ($\pm0.4 kJ\cdot mol^{-1}$)

$\Delta H_R = -4.9\pm0.1 kJ\cdot mol^{-1}$ $\Delta S_R = 9.1\pm0.2 J\cdot K^{-1}\cdot mol^{-1}$

K_2CeCl_5: Reaction $1.4KCl+K_{0.6}CeCl_{3.6}=K_2CeCl_5$ Samples: 50 and 60 mol-% $CeCl_3$
30 measured points in the range 640-800K
e.m.f./mV=178.87+0.0214·T/K ΔG_R/kJ·mol^{-1}=-24.2-0.0029·T/K
(Deviations: $\Delta G_R=\pm 0.3$kJ·mol^{-1}; $\Delta H_R=\pm 0.1$kJ·mol^{-1}; $\Delta S_R=0.2$J·K^{-1}·mol^{-1})

K_3CeCl_6: Reaction $KCl+K_2CeCl_5=K_3CeCl_6$ Two Samples with 30 mol-% $CeCl_3$
35 measured points in the range 790-870K
e.m.f./mV=-559.3+0.7041·T/K ΔG_R/kJ·mol^{-1}=+53.9-0.0679·T/K
(Deviations: $\Delta G_R=\pm 0.6$kJ·mol^{-1}; $\Delta H_R=\pm 5$kJ·mol^{-1}; $\Delta S_R=\pm 1$J·K^{-1}·mol^{-1})
$\Delta G_R=0$ at 794K.

Table 1 Energies for the formation from KCl and $LaCl_3$ at 298K

Compound	ΔG_R	ΔH_R	$-(T\cdot\Delta S)$	$\Delta H_{R,calor.}$
$K_{0.6}CeCl_{3.6}$	- 7.6	- 4.9	- 2.7	- 5.0
K_2CeCl_5	-32.7	-29.1	- 3.6	-27.3
K_3CeCl_6	+ 1.0	+24.8	-23.8	-

DISCUSSION

As table 1 shows the compounds K_2CeCl_5 and $K_{0.6}CeCl_{3.6}$ are formed with a gain in lattice enthalpy. Their stability can be discussed mainly considering lattice energies.

The compound K_3CeCl_6 is formed with a great loss of enthalpy. This is correlating with an expansion of the molar volume from 176 cm^3 ($3KCl+CeCl_3$) to 214 cm^3 (K_3CeCl_6). This enthalpy loss is compensated by a considerable gain in entropy; above 794K the Gibbs enthalpy for the formation from the adjacent compounds KCl and K_2CeCl_5 becomes negative. It can be assumed that this entropy gain is correlated to the formation of isolated octahedra in contrast to connected polyhedra in KCl and K_2CeCl_5.

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