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Letter to the Editors

Further considerations on entropy estimations of actinide compounds: $AmCl_3$ and $AmCl_2$

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Abstract

The standard entropy S^0 (298.15 K) of $AmCl_2$ has been estimated by extrapolation of the available data for the lanthanide(II) chlorides to the actinide series. A further refinement of this procedure for the actinide trichlorides is also presented which, however, does not affect the value for $AmCl_3$ reported previously. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In a recent publication [1] we have estimated the standard entropies of trivalent actinide compounds using a semi-empirical method describing the total entropy as the sum of the lattice entropy S_{lat} and the excess entropy S_{exs}:

$$S^0 = S_{lat} + S_{exs}. \tag{1}$$

The lattice contribution was obtained by extrapolation of the linear relation for 4f compounds with $4f^0$, $4f^7$ and $4f^{14}$ electronic configuration to the 5f series. The excess contribution was calculated from the crystal field energies:

$$S_{exs} = R\ln(g_0) + R\ln\left(\sum_{i=1}^{n} g_i e^{-\epsilon_i/RT}\right). \tag{2}$$

where ϵ_i is the energy and g_i, the degeneracy of level i; R, the universal gas constant and T, the absolute temperature. The validity of this approach was verified for the isoelectronic lanthanide(III) compounds for which a good agreement with experimental values was observed. The results thus obtained for the americium compounds Am_2O_3, AmF_3 and $AmCl_3$ were significantly different from existing estimates.

In the present Letter this approach will be revisited for the trichlorides taking more experimental data for the lanthanide trihalides into account, and will be extended to the dichlorides, specifically to derive the entropy of $AmCl_2$ which is of specific interest to the electrorefining of actinide fuels and targets for transmutation [2,3].

2. The trichlorides revisited

The estimation of the S_{lat} for the actinide trichlorides as presented in [1] was based on the trend in the lanthanide trichlorides as derived from the experimental measurements by Sommers and Westrum [4,5]. These authors measured the low-temperature heat capacity of a number of compounds of the hexagonal $LnCl_3$ series, which extends from $LaCl_3$ to $GdCl_3$. This trend was extrapolated to the end of the lanthanide series and transposed to the actinide series. The extrapolation to the orthorhombic and monoclinic lanthanide trihalides was justified by the fact that no differences were found in S_{lat} of different crystallographic modifications of the sesquioxides (hexagonal, monoclinic and cubic) and the trifluorides (trigonal and orthorhombic).

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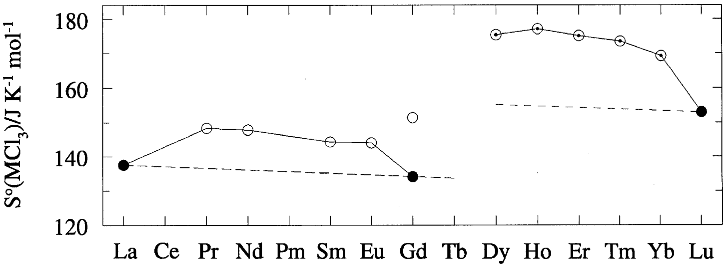

Fig. 1. The variation of S_{exp} (○, hexagonal; ⊙, monoclinic) and S_{lat} (●) in the lanthanide trichloride series at 298.15 K; the broken line shows the lattice contribution (see text).

New literature searches revealed that the low-temperature heat capacity of the monoclinic lanthanide trichlorides have been measured by Tolmach and co-workers [6–10]. The entropy values derived from these measurements are significantly higher than the extrapolation of the results for the hexagonal compounds, as shown in Fig. 1, and suggests a distinct difference between entropies of hexagonal and monoclinic crystallographic modifications. This difference is also evident in the molar volumes (Fig. 2): V_m of the lanthanide trifluorides linearly increases along the series irrespectively of the crystal structure (as is the case for the sesquioxides) whereas V_m of the lanthanide trichlorides shows a distinct difference between the hexagonal and the monoclinic compounds. It should be noted that similar observations have been made for the enthalpies of formation of the lanthanide trihalides [11,12], where the relation between quantity $\{\Delta_f H^0(LnX_n,\mathrm{cr}) - \Delta_f H^0(Ln^{3+},\mathrm{aq})\}$ and the ionic radius also shows different linear relations for the hexagonal and the monoclinic trichlorides but not for the different crystallographic modifications of the other trihalides and the sesquioxides.

The data shown in Fig. 1 are not the results reported by Tolmach and co-workers [6–10], because they did not extrapolate their measurements to 0 K in all cases. To derive S^0(298.15 K) we have assumed that the heat capacity of $LuCl_3$ represents the lattice component and S_{lat} at the lower temperature limit is derived from the results for this compound. The excess contribution at this temperature is calculated from the crystal field energies [13,14]. The 'experimental' values thus obtained for the monoclinic lanthanide trichlorides are listed in Table 1. They are in good agreement with the calculated values obtained from the sum of the lattice and excess contribution at 298.15 K, as shown in Table 2. Because there is only one 'reference' point for the lattice contribution in the monoclinic series ($LuCl_3$), the trend along the series is assumed to have the same slope as the hexagonal trichlorides which is also the case for the molar volumes.

The trichloride of americium is isostructural with the hexagonal lanthanide trichlorides [15] and therefore this modified estimation scheme does not affect the value presented in our previous paper [1], $S^0 = (146.2 \pm 6.0)$ J K^{-1} mol^{-1}. The same is true for the trichlorides of curium and berkelium.

3. The dichlorides

Tolmach and co-workers [16–20] measured the low-temperature heat capacity of the orthorhombic ($PbCl_2$-type) compounds $NdCl_2$, $SmCl_2$ and $EuCl_2$, tetragonal $DyCl_2$ and orthorhombic (SrI_2-type) compounds $TmCl_2$ and $LuCl_2$. In the Ln^{2+} series the $4f^7$ and $4f^{14}$ configurations occur at $EuCl_2$ and $YbCl_2$, respectively, whereas the $4f^0$ configuration is represented by $BaCl_2$. Fig. 3 shows that the standard entropies of these compounds form a straight line, which represents the lattice component. As was the case for the trichlorides, the results of Tolmach and co-workers were not extrapolated to 0 K in all cases and the corrected values are given in Table

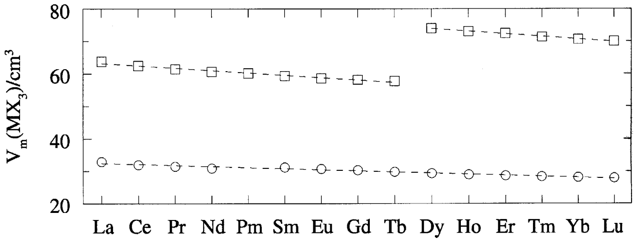

Fig. 2. The variation of the molar volume V_m in the lanthanide trichloride (□) and trifluoride (○) series at 298.15 K [15].

Table 1
The corrected standard entropy values at 298.15 K for the monoclinic lanthanide(III) and the lanthanide(II) chlorides (in J K^{-1} mol^{-1}) as derived from the work of Tolmach and co-workers [6–10,16–20]

Compounds	T_{ref}	S_{exp} (298.15 K − T_{ref})	$S_{\text{lat}}(T_{\text{ref}})$	$S_{\text{exs}}(T_{\text{ref}})$	S^0 (298.15 K)
$DyCl_3$	0	169.6	0.00	5.76	175.4
$HoCl_3$	6.61	170.1	0.25	6.74	177.1
$ErCl_3$	9.86	168.1	1.25	5.76	175.1
$TmCl_3$	15.34	166.5	3.35	3.68	173.5
$YbCl_3$	0	163.5	0.00	5.76	169.3
$NdCl_2$	8	135.5	0.28	5.76	141.5
$SmCl_2$	5	132.2	0	0	132.2
$EuCl_2$	8	121.2	0	17.29	138.5
$DyCl_2$	8.46	134.0	0.15	7.53	141.7
$TmCl_2$	6	131.6	0.08	5.76	137.4

Table 2
The revised entropies of the monoclinic lanthanide trichlorides, in J K^{-1} mol^{-1}

Compounds	Calculated			Experimental	
	S_{lat}	S_{exs}	S_{tot}	S_{exp}	Ref.
$DyCl_3$	155.15	22.83	177.98	175.4	[7]
$HoCl_3$	154.72	23.16	177.88	177.1	[8]
$ErCl_3$	154.29	22.60	176.89	175.1	[9]
$TmCl_3$	153.86	20.84	174.70	173.5	[10]
$YbCl_3$	153.43	15.80	169.23	169.3	[6]
$LuCl_3$	153.00	0.00	153.0	153.0	[7]

Table 3
The entropies of the lanthanide dichlorides, in J K^{-1} mol^{-1}

Compounds	Calculated			Experimental	
	S_{lat}	S_{exs}	S_{tot}	S_{exp}	Ref.
$BaCl_2$	123.46	0.00	123.46	123.67	[21]
$LaCl_2$	123.20	14.90	138.09		
$CeCl_2$	122.93	18.27	141.20		
$PrCl_2$	122.67	19.14	141.82		
$NdCl_2$	122.41	18.27	140.68	141.5	[20]
$PmCl_2$	122.15	17.29	139.44		
$SmCl_2$	121.89	9.32	131.21	132.2	[19]
$EuCl_2$	121.62	17.29	138.91	138.5	[16]
$GdCl_2$	121.36	21.32	142.69		
$TbCl_2$	121.10	23.05	144.15		
$DyCl_2$	120.84	23.56	144.39	141.7	[18]
$HoCl_2$	120.58	23.05	143.63		
$ErCl_2$	120.31	21.32	141.64		
$TmCl_2$	120.05	17.29	137.34	137.4	[17]
$YbCl_2$	119.79	0.00	119.79	120.0	[18]

1. These values are in good agreement with the ones calculated from the sum of the lattice and excess contribution at 298.15 K, as shown in Table 3. The excess contributions have been calculated from the ground state degeneracy of the free lanthanide(II) ions, since no crystal field energies are known for these compounds. For $PmCl_2$ and $SmCl_2$ also the effect of low-lying levels must be taken into account, as is the case for the iso-electronic $SmCl_3$ and $EuCl_3$ and we assume them to be the same as in these molecules.

To extrapolate the data of the lanthanide(II) chlorides to $AmCl_2$ we assume that the ratio $S_{\text{lat}}(AnCl_2)/S_{\text{lat}}(LnCl_2)$ is 1.09, which is the value found for the trifluorides and trichlorides. We thus obtain $S_{\text{lat}} = 130.8$ J K^{-1} mol^{-1} for $AmCl_2$, which yields $S^0(AmCl_2, \text{cr}, 298.15\ \text{K}) = (148.1 \pm 5.0)$ J K^{-1} mol^{-1} when combined with $S_{\text{exs}} = R\ln(8)$.

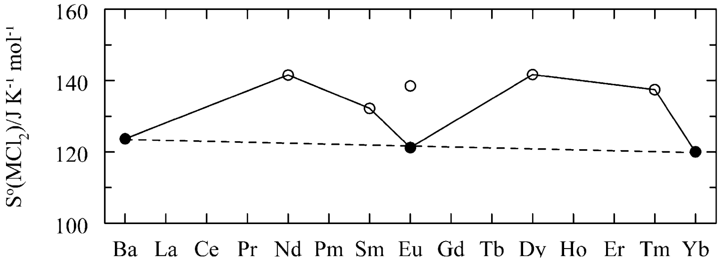

Fig. 3. The variation of the S_{exp} (○) and S_{lat} (●) in the lanthanide dichloride series at 298.15 K; the broken line shows the lattice contribution (see text).

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