Volume Changes on Melting for Several Rare Earth Chlorides

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Molar volumes in the liquid state and melting points of several rare earth chlorides RCl_3 (R = La, Pr, Nd, Gd, Dy, and Y) have been measured by dilatometry and DTA, respectively. The volume changes on melting of these chlorides were evaluated on the basis of these result and available crystal structure data. The volume increase on melting of the hexagonal chlorides from $LaCl_3$ to $GdCl_3$ was found to be more than 20%. On the other hand, the volume changes of the monoclinic $DyCl_3$ and YCl_3 were less than 1%.

The volume change on melting gives information about the structure of a melt. For the alkali metal halides, the relationship between the volume change on melting and the short range arrangement of the melt near the melting point has been expressed by a semi-empirical formula by Furukawa [1]. Data on melting points of rare earth chlorides have been reported [2–9], but there are some uncertainties due to their strong hygroscopy. In this work, in order to determine exactly the volume changes on melting of $LaCl_3$, $PrCl_3$, $NdCl_3$, $GdCl_3$, $DyCl_3$, and YCl_3, their molar volumes in the liquid state and their melting points were measured while their molar volumes in the solid state were calculated on the basis of available crystal structure data [10–12].

The salts were prepared by reaction of the rare earth oxides (99.9% purity) with ammonium chloride of regante grade and purified by sublimation [13]. Impurities of the purified crystals were analysed by emission spectrography and X-ray fluorescence spectrometry. The impurity contents were almost the same as those reported previously [14–17]. The molar volumes of the melts were measured dilatometrically with the same apparatus as described in [18]. DTA was used for the measurement of melting points. The measurements were carried out, using α-Al_2O_3 as reference material, with a cooling rate of 7–11 °C/min. The DTA apparatus was calibrated with the melting points of pure Ag, Al, Zn, and Pb.

Figure 1 shows the molar volumes of the molten chlorides expressed as linear functions of the temperature obtained by a least squares fit of the data. Table 1 gives the parameters of these functions. The obtained melting points are listed in Table 2 together with those reported in the literature [2–9]. Our results are close to those measured by Spedding and Daane [3].

The crystal structure of the rare earth chlorides has been classified into two groups: the chlorides from $LaCl_3$ to $GdCl_3$ are hexagonal with the space group $P6_3/m(C^2_{6h})$ [10, 12], and $DyCl_3$ and YCl_3 are monoclinic with $C2/m(C^3_{2h})$ [11]. From these crystal data the molar volumes can be calculated by the equations

$$V_h = (\sqrt{3}/2) \times a^2 c \times N/Z \tag{1}$$

and

$$V_m = abc \times \sin B \times N/Z, \tag{2}$$

where V is the molar volume in $cm^3\,mol^{-1}$ (subscripts h and m mean hexagonal and monoclinic, respectively), a, b, and c are the lattice constants, N is Avogadro's number, B the angle between the two axes in the monoclinic crystal, and Z the number of stoichiometric units contained in the unit cell. The results are shown in Table 3. The molar volume of the hexagonal chlorides decreases slightly with increasing atomic number due to the lanthanide contraction. According to Fig. 1, the molar volume at a given temperature of these chlorides in the liquid state appears to increase with increasing atomic number. However, the molar volumes of these molten chlorides at their melting points, as obtained by an extrapolation by means of the molar volume equations, were found to give the same tendency as those of the solids (cf. Table 3).

The per cent volume changes on melting of the chlorides were calculated from the values of V_s and V_m in Table 3. The thermal expansion of these solids being not known but very small, the V_s values at room temperature have been taken. The results are listed in column 5 of Table 3. For the hexagonal chlorides, large volume increases were observed, its order seeming to follow the order of the atomic

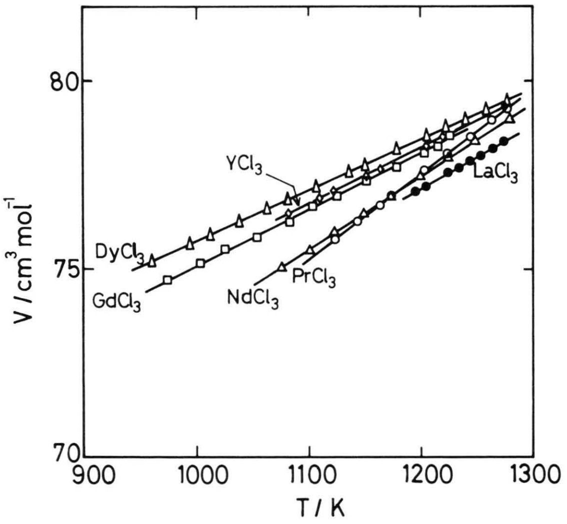

Fig. 1. Molar volumes of some molten rare earth chlorides.

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Table 1. Molar volume equations of molten pure rare earth chlorides.

$V = a + b \times T$,	$V/\mathrm{cm^3\,mol^{-1}}$, T/K	
Salt	a	$b \times 10$
$LaCl_3$	56.76	0.1699
$PrCl_3$	47.70	0.2512
$NdCl_3$	54.31	0.1909
$GdCl_3$	60.90	0.1422
$DyCl_3$	61.70	0.1399
YCl_3	61.08	0.1427

Table 2. Melting points (in K) of rare earth chlorides. This work and literature.

Salt	This work	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]
$LaCl_3$	1150	1125	1135		1143	1119	1135	1123	
$PrCl_3$	1059	1059	1059	1039	1096				
$NdCl_3$	1029	1033	1031	1013	1033	1031			
$GdCl_3$	875	882	875	863	875	866			
$DyCl_3$	928	927	920	898	920				
YCl_3	987	973	982		973				987

number. On the other hand, for the monoclinic $DyCl_3$ and YCl_3, the volume changes very little on melting. This behavior of the chlorides studied has also been reported by Cho et al. [19].

In the hexagonal solid chlorides, the rare earth metal ions are surrounded by nine chloride ions with two different distances [10, 12]. On the other hand, the metal ions in the monoclinic $DyCl_3$ and YCl_3 are surrounded by six chloride ions with three different distances [11]. The fact that the chlorides from $LaCl_3$ to $GdCl_3$ show a large volume increase on melting suggests that the nearest ionic distances and the number of ions in the first coordination shell decrease significantly on fusion, similar to the alkali halides [1]. The short range arrangement in molten $CaCl_2$ with little volume change on melting is known to be close to that of the crystal [20–22]. Also the short range arrangement in liquid $DyCl_3$ and YCl_3 is expected to be close to that in the corresponding solid.

Table 3. Molar volumes of some rare earth chlorides.

Salt	mp/K	V_s	V_m	ΔV(%)
$LaCl_3$	1150	63.90	76.30	19.1
$PrCl_3$	1059	61.40	74.30	21.0
$NdCl_3$	1029	60.47	73.65	21.8
$GdCl_3$	875	58.03	73.34	26.4
$DyCl_3$	928	74.38	74.62	0.3
YCl_3	987	74.83	75.17	0.5

V_s and V_m are the molar volumes of the solid at room temperature and the melt at the mp., respectively, in $\mathrm{cm^3\,cm^{-1}}$.

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