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Mass Spectrometric Study of the Vapor Phase over Neodymium Chloride and Gadolinium Chloride

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A Knudsen cell–mass spectrometric technique was used to determine the fragmentation patterns and appearance potentials for neodymium and gadolinium chlorides and for 1:1 mixtures of gadolinium chloride with lithium and sodium chlorides. Direct evidence for vapor phase complexes in these systems was obtained, but no complex species were observed above 1:1 mixtures of gadolinium chloride and magnesium chloride. From the measured appearance potentials, the ionization potentials of the species $LnCl_2$, LnCl, and Ln (Ln = Nd, Gd) were estimated. The heats of vaporization of $NdCl_3$ and $GdCl_3$ were determined.

Increased industrial application of rare earth halides has made the study of their vaporization characteristics, both as pure substances and as components in binary mixtures, of increased importance. In such studies the mass spectrometer is most useful to determine the nature of the vaporizing species as well as to provide at least approximate values of ionization and appearance potentials. With the advent of photoelectron and photoionization spectroscopy, electron impact mass spectrometry can no longer be regarded as the most accurate method of determining ionization and appearance potentials. However, in the study of high-temperature systems the experimental difficulties of applying the former methods are considerable, and in some cases prohibitive,[2] and electron impact methods still have a useful role to play. The admittedly approximate values so obtained are of assistance in the later application of the more sophisticated techniques.

Mass spectrometric studies of the rare earth halides have been restricted to the lanthanoid fluorides,[3] $LaCl_3$, $EuCl_3$, and $LuCl_3$[4a] and $EuBr_2$.[4b] We present here (i) values for the heats of vaporization of neodymium chloride ($NdCl_3$) and gadolinium chloride ($GdCl_3$), (ii) appearance potentials for the various fragment ions, and (iii) direct evidence for the complexes $LiGdCl_4$ and $NaGdCl_4$ and for the nonexistence of $MgGdCl_5$ under the same conditions.

Experimental Procedure

The quadrupole mass filter–Knudsen cell arrangement used in the present study was substantially the same as that described by Hastie and Swingler.[5] One major alteration was the use of a more versatile RF-DC generator and power supply (Electronic Associates Inc., Quad 300) to energize the quadrupole rods. Higher resolution and sensitivity were thus obtained.

The Knudsen cells used were silica-lined and made of graphite (high purity, low porosity, high density). The cells were 4 cm high and 1.2 cm in internal diameter. The molecular beam was defined by means of an 0.03-cm hole centrally punched in a thin molybdenum disk which was fitted into the Knudsen cap. Molecular effusion conditions were thus satisfied[6] for the range of pressures corresponding to the temperatures studied. These cell dimensions also favored vapor-condensed phase equilibrium, since the ratio of salt surface area to effusion orifice area was about 1000.

The molecular beam source was placed in a resistively heated furnace and the temperature was recorded by a calibrated chromel-alumel thermocouple which made contact with the base of the Knudsen cell. Temperatures could be maintained constant to within ±2 K at 970 K.

The assembly consisting of mass filter, ion source, and molecular beam source was secured into a chamber which could be evacuated to better than 5×10^{-6} Torr (1 Torr = 133.322 Nm^{-2}).

An externally operated shutter could be interposed between the cell and ion source in order to distinguish between effusing and background species. In all cases the nonshutterable fraction of the signal was insignificant. Electron energies of 50 eV were used for recording the mass spectra.

The $NdCl_3$ and $GdCl_3$ were anhydrous, of stated purity 99.9% (Koch-Light), and were not further purified. Care was taken in their transfer to the effusion cell to minimize hydrolysis. Samples were heated under dynamic vacuum to 570 K for 24–36 hr prior to making measurements.

Results and Discussion

(i) Heats of Vaporization. There is a wide range of values for the heats of vaporization (ΔH_v) of $NdCl_3$ and $GdCl_3$ in the literature (see Table I).[7–12] In order to obtain a direct comparison between different workers, the ΔH_v's were corrected to 298 K using the stated boiling point and change in the molar heat capacity of vaporization for the process liquid → vapor [$\Delta C_p(l \rightarrow v)$], where specified, and using $\Delta C_p(l \rightarrow v) = -12$ cal K^{-1} mol^{-1} otherwise. This scatter could be due either to the different techniques adopted or to impurities in the samples used. These compounds hydrolyze quite readily to form the oxyhalides[13] and the latter would be expected to be the major impurity in the previous determinations.

A Knudsen cell–mass spectrometric determination of ΔH_v then seemed desirable, since this technique is not affected by small amounts of impurity. The major disadvantage of the technique is that only a relatively small pressure range (*i.e.*, temperature range) can be studied. At pressures higher than about 1 Torr, molecular flow conditions no longer prevail.

The mass range covered was 0–350 amu and it was not

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Table I. Thermodynamics of Vaporization and Sublimation of $NdCl_3$ and $GdCl_3$

Ref	Technique	T_m, K	$\Delta C_p(s \rightarrow v)$, cal K^{-1} mol^{-1}	ΔH_s(298 K), kcal mol^{-1}	T_b, K	$\Delta C_p(l \rightarrow v)$, cal K^{-1} mol^{-1}	ΔH_v(298 K), kcal mol^{-1}
			$NdCl_3$				
7	Bp method	1023			1824		77.5
8	Effusion wt loss				1885	−14	74.0
9[a]	Effusion	1031			1963		64.4
10	Effusion	1033	−14	79.2	1947	−14	71.1
11	Bp method				1921	−18	75.4
This study	Knudsen-MS	1033	−10	75.9		−12	69.3
			$GdCl_3$				
12	Bp method			74.1	1870	−12	68.3
9	Effusion	875			1853		62.7
This study	Knudsen-MS	882	−10	71.3		−12	65.5

[a] It is assumed that quoted ΔH_v's are at T_b.

possible to observe dimeric species. Hastie, *et al.*,[4a] reported the extent of dimerization of $LaCl_3$ at 1030 K to be 0.0017 ($=P_{La_2Cl_6}/P_{LaCl_3}$). The dimer contribution in these experiments is therefore expected to be low. It might however become quite significant near the boiling point and this would add further to the uncertainty in the values obtained by the Russian workers, since their measurements were near or at the boiling point.

The relationship between pressure of a vaporizing species (p) and the molecular ion current (I) is well established and has the form $p = bIT$ (where T is the absolute temperature of the effusion cell and b is a constant incorporating the molecular ionization cross section and various apparatus constants).

Intensities of the parent molecular ions were too low to determine accurately; hence the temperature variation of $LnCl_2^+$ was recorded and assumed to be the same as that of the $LnCl_3^+$. There is no reason to believe the fragmentation pattern should vary over such a small temperature range and this is the only factor which would invalidate the above assumption.

$NdCl_3$ and $GdCl_3$ were studied in the ranges 1055-1093 and 963-1075 K, respectively. To minimize systematic errors and as a check on equilibrium inside the cell, temperatures were increased and decreased at random.

We employed a Σ plot method, similar to that used by Mann and Tickner,[14] for the treatment of our ion intensity-temperature data (see Figure 1).

The value of $\Delta C_p(l \rightarrow v) = -12$ cal K^{-1} mol^{-1}, estimated by Dudchik, *et al.*,[12] seemed to us to be the most well founded of those used (see Table I) and was adopted in our treatment. Heat capacities for the sublimation process (solid → vapor) are even more uncertain. Shimazaki and Niwa[10] used a value of −14 cal K^{-1} mol^{-1} for both the sublimation and vaporization processes. Brewer's[15] $\Delta C_p(s \rightarrow v)$ of −10 cal K^{-1} mol^{-1} (used for a similar compound–$PuCl_3$) was preferred.

The melting points, 1033 and 882 K, and heats of fusion, 8 and 7 kcal mol^{-1} for $NdCl_3$ and $GdCl_3$, respectively, were obtained from Wicks and Block.[16]

Our values for ΔH_v and the corresponding heats of sublimation (ΔH_s), included in Table I, are the averages of two runs. The estimated error limits are ±4 kcal mol^{-1}.

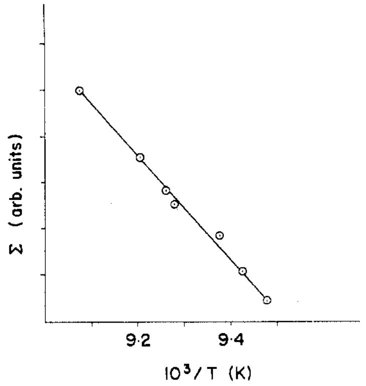

Figure 1. A typical Σ plot for $NdCl_3$.

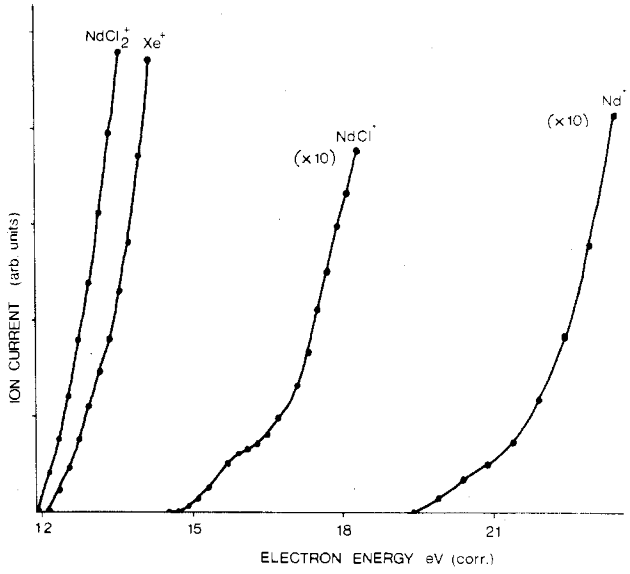

Figure 2. Ionization efficiency curves for $NdCl_3$.

(ii) Appearance Potential Measurements. Electron impact appearance potentials (AP) for the various fragment ions of $NdCl_3$ and $GdCl_3$ were determined by the vanishing-current method from experimental ionization efficiency (IE) curves. (The slopes of linear portions were made approximately parallel by suitable scale expansions; see Figures 2 and 3.) A constant Xe leak served to calibrate the electron energy scale and maintain constant ion source conditions.

There are well-known pitfalls in assigning different fragmentation processes to breaks in IE curves.[17] For example,

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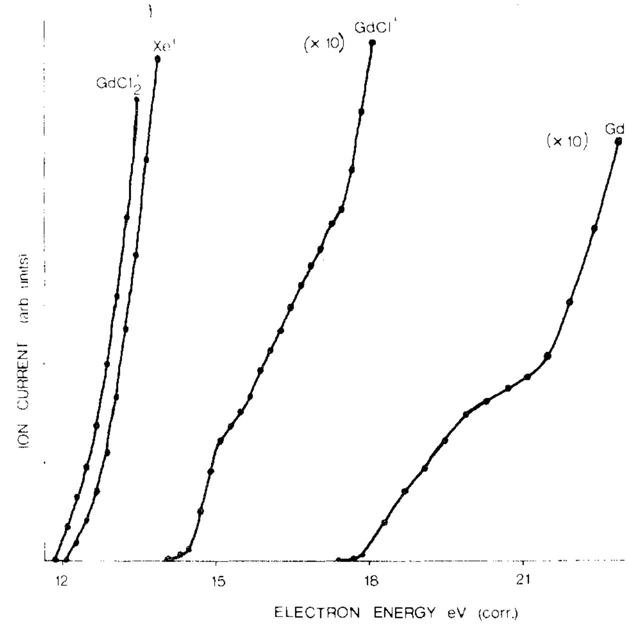

Figure 3. Ionization efficiency curves for $GdCl_3$.

Table II. AP's and Estimated IP's of $NdCl_3$ and $GdCl_3$ Fragments

Species	Rel intens[a]	AP,[b] eV	IP,[c] eV
$NdCl_3$	29.6	<11.4	<11.4
$NdCl_2$	100	11.9 ± 0.3	7.1
NdCl	18.4	17.3 ± 1.0	7.6
Nd	16	20.9 ± 1.0	6.4
$GdCl_3$	6	*d*	*d*
$GdCl_2$	100	11.9 ± 0.3	6.9
GdCl	23	17.5 ± 1.0	7.4
Gd	39	20.9 ± 1.0	5.8

[a] Ionizing electron energy 50 eV. [b] Appearance potential of the unipositive species. [c] Estimated using average E_{Ln-Cl} from Dudchik, *et al.*[21] [d] Ion intensity too low to enable determination.

Table III. Mass Spectrum of the Vapor over NaCl-$GdCl_3$ at 970 K

Ion	Rel Intens[a]	AP, eV
Gd^+	34	21.5 ± 1.0
$GdCl^+$	28	16.5 ± 1.0
$GdCl_2^+$	100	12.1 ± 0.3
$NaGdCl_3^+$	20.5	10.1 ± 0.5

[a] Ionizing electron energy 50 eV.

considering the IE curve for $GdCl^+$, it is tempting to conclude that the breaks at 14.3 (*A*), 15.3 (*B*), and 17.5 (*C*) are due to the processes $GdCl_3 + e^- \rightarrow$ (1) $GdCl^+ + Cl + Cl^- + e^-$, (2) $GdCl^+ + Cl_2 + 2e^-$, and (3) $GdCl^+ + 2Cl + 2e^-$, respectively. The differences $C - A$ (=3.2) and $C - B$ (=2.2) are approximately equal to the electron affinity of Cl (3.6 eV)[18] and bond dissociation energy of Cl_2 (2.5 eV),[19] respectively. However, the corresponding comparison in the case of $NdCl^+$ yields somewhat poorer agreement. Thus the assignment of different processes to breaks in our IE curves, although plausible, remains in some doubt.

The values given in Table II are the onset potentials of the steepest portions of our IE curves. These were assumed to be the onset potentials for the processes: $LnCl_3 + e^- \rightarrow LnCl_2^+ + Cl + 2e^-$, $LnCl_3 + e^- \rightarrow LnCl^+ + 2Cl + 2e^-$, and $LnCl_3 + e^- \rightarrow Ln^+ + 3Cl + 2e^-$. Our measured AP's are similar to those reported for the analogous species from YCl_3[20] and $LaCl_3$.[4a]

Also included in Table II are our estimates of the ionization potentials for the species Ln, LnCl, and $LnCl_2$. These estimates were made using the $\Delta H_{atom}(LnCl_3)$ of Dudchik, *et al.*,[21] with, in the case of LnCl and $LnCl_2$, the further assumption that successive bond dissociation energies were equal to the average bond dissociation energy. Thus

$$IP(Ln) = AP(Ln^+) - \Delta H_{atom}(LnCl_3)$$

$$IP(LnCl) = AP(LnCl^+) - {}^2/_3 \Delta H_{atom}(LnCl_3)$$

The IP's of Nd and Gd so obtained (6.4 and 5.8 eV) compare moderately well with the accepted values of Moore,[22] 6.31 and 6.16 eV, respectively. This agreement gives us some confidence in the combination of the data of Dudchik, *et al.*, and our data as a source of at least approximate values for the IP's of the LnCl and $LnCl_2$ species for which no values have previously been reported. However, these IP's are expected to be less accurate than those for Nd and Gd due to the simplifying assumption on bond energies.

The heats of formation of the crystalline chlorides (ΔH_f) may be calculated from

$$\Delta H_f(LnCl_3) = -\Delta H_{atom}(LnCl_3) + {}^3/_2 D^\circ(Cl_2) - \Delta H_s(LnCl_3) + L_s(Ln)$$

The $\Delta H_{atom}(LnCl_3)$ to be inserted can be taken from Dudchik or recalculated from our AP measurements and Moore's IP's. In this case we have preferred the latter course. Thus using our value for ΔH_s, $D^\circ(Cl_2) = 2.5$ eV, $L_s(Nd)^{23} = 76$ kcal mol^{-1}, and $L_s(Gd)^{23} = 84$ kcal mol^{-1}, we obtain $\Delta H_f(NdCl_3) = -250$ kcal mol^{-1} and $\Delta H_f(GdCl_3) = -240$ kcal mol^{-1}. These values are in quite good agreement with what are probably the most reliable values,[21] -245.6 and -240.1 kcal mol^{-1}, respectively.

(iii) Mixed-Halide Vaporization. The presence of complex species $LiGdCl_3$ and $NaGdCl_3$ in the vapor over 1:1 mixtures of LiCl-$GdCl_3$ and NaCl-$GdCl_3$, respectively, was inferred from the mass spectra. The relevant portion of the mass spectrum for the NaCl-$GdCl_3$ system is reproduced in Table III. It will be noted that the appearance potential of $NaGdCl_3^+$ is low, which suggests it is produced by simple ionization of the complex parent rather than from an ion-molecule reaction.

In the case of a 1:1 mixture of $GdCl_3$-$MgCl_2$ no complex species were observed within the limits of detection (0.1% of the total vapor). This is in accord with the recorded phase diagram[24] for this system.

Registry No. Nd, 7440-00-8; NdCl, 40603-46-1; $NdCl_2$, 25469-93-6; $NdCl_3$, 10024-93-8; Gd, 7440-54-2; GdCl, 40603-48-3; $GdCl_2$, 25469-95-8; $GdCl_3$, 10138-52-0; $NaGdCl_4$, 40605-01-4.

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