

MASS SPECTROMETRIC STUDIES AT HIGH TEMPERATURES

XXV. VAPOR COMPOSITION OVER LaCl_3 , EuCl_3 AND LuCl_3 AND STABILITIES OF THE TRICHLORIDE DIMERS

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SUMMARY

Mass spectrometric studies of the vapors over $\text{LaCl}_3(\text{s})$, $\text{EuCl}_3(\text{s})$, $\text{EuCl}_2(\text{l})$ and the mixture $\text{EuCl}_3 + \text{LuCl}_3$ indicate the existence of dimers in small amount (1%) at pressures of less than 0.1 mm. However, the data predict dimers to be a more dominant species at temperatures approaching the boiling point. Ion current *vs.* temperature data yield heats of vaporization or sublimation that are in good agreement with previous results as well as values for the heats of dimerization. With absolute pressure data, one calculates the entropy for the reaction $2\text{LaCl}_3(\text{g}) = \text{La}_2\text{Cl}_6(\text{g})$ to be $\Delta S_{1000^\circ\text{K}}^\circ = -30.0 \pm 3.0$ e.u./mole of dimer. The proportion of dimer to monomer, as indicated by the heats of dimerization, varies considerably with the nature of the metal. No dimerization or significant disproportionation of $\text{EuCl}_2(\text{g})$ was found.

INTRODUCTION

Recent mass spectrometric studies of rare-earth fluorides¹ indicated no polymerization of the tri-fluorides in the vapor state. However, yttrium chloride, which is thermodynamically similar to the rare-earth chlorides, has been shown to form the dimer, Y_2Cl_6 , in the vapor state². If this tendency to form dimers exists also for the rare-earth chlorides, which is not unlikely, then the reported vapor pressures could be in considerable error³⁻⁷. The current basis for the assumption that rare-earth chlorides are monomeric is that electron diffraction measurements failed to detect any species other than monomers over YCl_3 , LaX_3 or NdX_3 ⁸. The method, however, is not sensitive to small concentrations of polymer species; we have, therefore, carried out a mass spectrometric investigation of the vapor for LaCl_3 , EuCl_3 , EuCl_2 and LuCl_3 . These particular salts should represent the range of properties for the rare-earth chlorides.

EXPERIMENTAL

The mass spectrometer used was a Bendix time-of-flight instrument and has

been described elsewhere⁹. The salts, obtained from the American Potash and Chemical Corporation Rare Earth Division, were better than 99.9% pure and showed the expected X-ray diffraction patterns.

Each sample was contained in a tantalum Knudsen cell which apparently did not react with the salts. The dimensions of the cell and its effusion orifice were such as to comply with the Knudsen effusion conditions for the salt pressures and temperatures used¹⁰. Temperatures were measured with a Pt/Pt-10%Rh thermocouple attached to the bottom of the Knudsen cell and were accurate to $\pm 3^\circ\text{C}$. The Knudsen weight-loss measurements of SHIMAZAKI AND NIWA⁷ for LaCl_3 were reproduced at several temperatures with this apparatus.

For the recording of ion intensities over a period of hours, it was necessary to measure these relative to an Ar^+ standard to reduce the effect of fluctuations in the sensitivity of the ion detection system. Ion current *vs.* temperature data were recorded for both increasing and decreasing Knudsen cell temperature. Each sample was baked at 400°C for several days before measurements were taken.

RESULTS AND DISCUSSION

LaCl_3

Typical mass spectral data are given in Table I, the molecular precursors being deduced on the basis of the high values of the appearance potentials of La^+ , LaCl^+ and LaCl_2^+ and the similar slopes of $\log IT(\text{LaCl}_2^+)$ and $\log IT(\text{LaCl}_3^+)$ *vs.* $1/T$ lines as shown in Fig. 1.

TABLE I

MASS SPECTRAL DATA FOR $\text{LaCl}_3(\text{s})$ AT 1030°K

<i>Ion</i>	<i>Intensity*</i> (arbitrary units)	<i>AP** (eV)</i>	ΔH_s^{***} (kcal/mole)	<i>Molecular precursor</i>
La^+	~ 0.2	23 ± 1	—	LaCl_3
LaCl^+	~ 0.2	17.5 ± 1	—	LaCl_3
LaCl_2^+	100	13.6 ± 0.5	74 ± 2	LaCl_3
LaCl_3^+	1.5	13.8 ± 1	74 ± 6	LaCl_3
La_2Cl_5^+	0.17	15 ± 1	100 ± 3	La_2Cl_6

* Non-shutterable intensity for these masses was negligible; 50 eV ionizing electron energy used.

** Appearance potentials obtained by method of first appearance using H_2O^+ to calibrate the energy scale. The values parallel those obtained from YCl_3^2 .

*** Least squares values, obtained from $\log I^+T$ *vs.* $1/T$ curves.

By using the proportionality of pressure to I^+T^{11} , one can represent the relative equilibrium constants K_1 , for the vapor equilibrium reaction:



$$\text{by } K_1 = \frac{I(\text{La}_2\text{Cl}_5^+)}{I(\text{LaCl}_2^+)^2 T}, \text{ (arbitrary units)}$$

and from the dependence of K_1 upon temperature, as shown by Fig. 1, one obtains the heat of dimerization as:

$$\Delta H_1 = -48.0 \pm 3.0 \text{ kcal mole}^{-1}$$

A similar value is obtained from a combination of the heats of sublimation, *i.e.*,

$$\Delta H_1 = 100 - 2 \times 74 = -48 \pm 4 \text{ kcal mole}^{-1}$$

With $\Delta C_p = 14 \text{ cal mole}^{-1}$ as suggested by SHIMAZAKI AND NIWA⁷, one obtains $84.5 \pm 2 \text{ kcal mole}^{-1}$ for the heat of sublimation at 298°K as compared with their value of 83.9 kcal/mole . Thus, the two sets of data are in good agreement with each other.

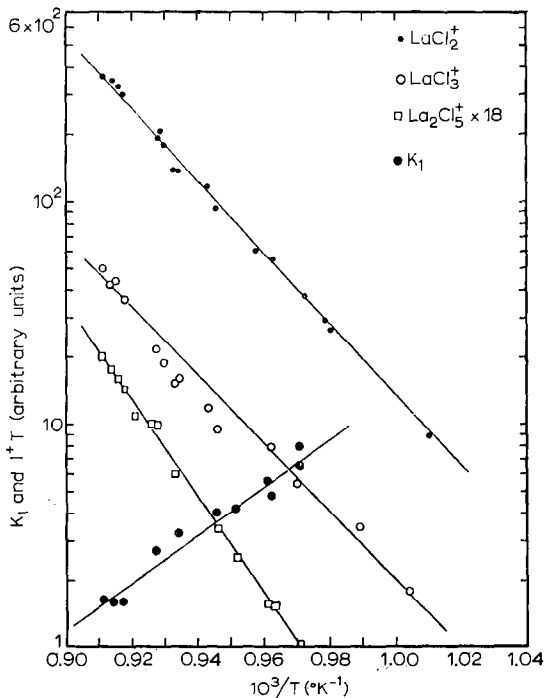


Fig. 1. Ion current analogs of pressure and equilibrium constants as a function of temperature for species over $\text{LaCl}_3(\text{s})$.

Consider the effect of the presence of La_2Cl_6 on the vapor pressure data for LaCl_3 . One can estimate the relative pressure $P(\text{La}_2\text{Cl}_6)/P(\text{LaCl}_3)$ by assuming:

$$\frac{P(\text{La}_2\text{Cl}_6)}{P(\text{LaCl}_3)} = \frac{I(\text{La}_2\text{Cl}_5^+)}{I(\text{LaCl}_2^+)}$$

The validity of this assumption has been verified for the similar case of the cesium halides¹². If one estimates the relative ionization cross-section and multiplier efficiency terms as SCHOONMAKER AND PORTER¹³ have done for the analogous FeCl_2 case then the right hand side of the above equality is reduced by 30%. One should allow for an error of a factor of two. At 1030°K this ratio is 0.0017 and therefore the dimer represents only a few tenths of one per cent of the total vapor composition at this temperature. The magnitude of the correction that one could apply to the weight-loss measurements⁷ for the presence of dimer would amount to less than the experimental error and hence the existing pressure data for LaCl_3 are correct up to at least 1100°K (*i.e.* for $P(\text{LaCl}_3) = 2.98 \times 10^{-3} \text{ mm}$). Using the weight-loss pressure data⁷

the partial pressures of LaCl_3 and La_2Cl_6 may be calculated. For example, at 1030°K , $P(\text{LaCl}_3) = 0.32 \times 10^{-3}$ mm and $P(\text{La}_2\text{Cl}_6) = 0.54 \times 10^{-6}$ mm. Combining these values with the measured heats of sublimation, one calculates the entropies of sublimation:

$$\Delta S_{\text{sub}}(\text{LaCl}_3) = 42.5 \pm 2.0 \text{ e.u.}$$

and

$$\Delta S_{\text{sub}}(\text{La}_2\text{Cl}_6) = 55.0 \pm 3.0 \text{ e.u.}$$

Similarly, the absolute equilibrium constants and hence free energies are calculated for the dimerization reaction for which an average entropy change of $\Delta S_a = -30.0 \pm 3.0$ e.u. is derived. An error in the equilibrium constants of a factor of two leads to only ± 1 kcal/mole uncertainty in the free energy values. A dimerization entropy of -30 e.u. for the analogous reaction involving AlCl_3 at 1000°K has been given¹⁴.

By using MCKINLEY'S mass spectrometric data² one calculates the enthalpy of formation for Y_2Cl_6 (g) from YCl_3 (g) as -29 ± 6 kcal/mole. The relative intensity $I(\text{Y}_2\text{Cl}_5^+)/I(\text{YCl}_2^+) = 0.03$ at 850°K , is taken as indicating the relative pressures of the molecular precursors; however, there are no reliable pressure data for this temperature range to enable an absolute calculation of free energy.

From the entropy and enthalpy values established above, the percentage of dimer, La_2Cl_6 , present at the boiling point of LaCl_3 (2085°K) is estimated to be 85%. Even at 1600°K , the temperature region at which POLYACHENOK AND NOVIKOV³ made their vapor pressure measurements, there is a significant proportion of dimer in the vapor. As POLYACHENOK AND NOVIKOV'S data were obtained by a boiling point method their pressure value at 1600°K can be taken as the total pressure of monomeric and dimeric species. Then it follows from the equilibrium data of the dimerization reaction that the degree of association is 0.12 and 6% of the total pressure is due to the dimeric species at 1600°C . Thus, the best available data for the pressures of LaCl_3 and La_2Cl_6 over the liquid state are obtained from a combination of POLYACHENOK AND NOVIKOV'S vapor-pressure equation³ (taken to represent the total pressure) with the enthalpy and entropy of formation of La_2Cl_6 from LaCl_3 presented here. For solid LaCl_3 , the data of the present work and that of SHIMAZAKI AND NIWA⁷ are in good agreement with each other.

EuCl₃

The sublimation pressures for this salt were too low to enable measurement of useful ion-intensity data over the solid. In the temperature region of the melting

TABLE II

MASS SPECTRAL DATA FOR EuCl_3 - EuCl_2 AT 1218°K

Ion	Intensity* (arbitrary units)	AP (eV) (± 0.5)	ΔH_b (kcal/mole)	Molecular precursor
Eu^{2+}	—	26.0**	—	EuCl_2
Eu^+	46	15.0	61.0 ± 2	EuCl_2
EuCl^+	100	10.3	61.0 ± 1	EuCl_2
EuCl_2^+	11.8	10.5	61.0 ± 2	EuCl_2

* 50 eV ionizing electron energy used.

** If the ionization process is: $\text{EuCl}_2 + e = \text{Eu}^{2+} + 2\text{Cl} + 3e$, then from the dissociation energy of EuCl_2 ¹⁵ the second ionization potential of Eu is calculated as 11 ± 1 eV.

point the EuCl_3^+ ion disappeared while the EuCl_2^+ intensity increased. This is explainable from the observation of POLYACHENOK AND NOVIKOV⁵ that EuCl_3 decomposes very rapidly on melting to form EuCl_2 , apparently in a pure state. Ion intensity *vs.* temperature data were recorded (Fig. 2) over the melt and typical mass spectral data are presented in Table II. As the nature of the vapors over $\text{EuCl}_2(\text{l})$ has been uncertain, owing to the possible disproportionation:



mentioned by POLYACHENOK AND NOVIKOV⁵, the ion currents and appearance potentials of all the observed ions were measured over a range of temperature. No ions corresponding to the possible dimer species, Eu_2Cl_4 or Eu_2Cl_6 were observed. As shown by Fig. 2 and Table II the ions EuCl_2^+ , EuCl^+ and Eu^+ , (no others appear), all derive from species having a heat of vaporization of $\Delta H_v = 61 \pm 1$ kcal/mole. This

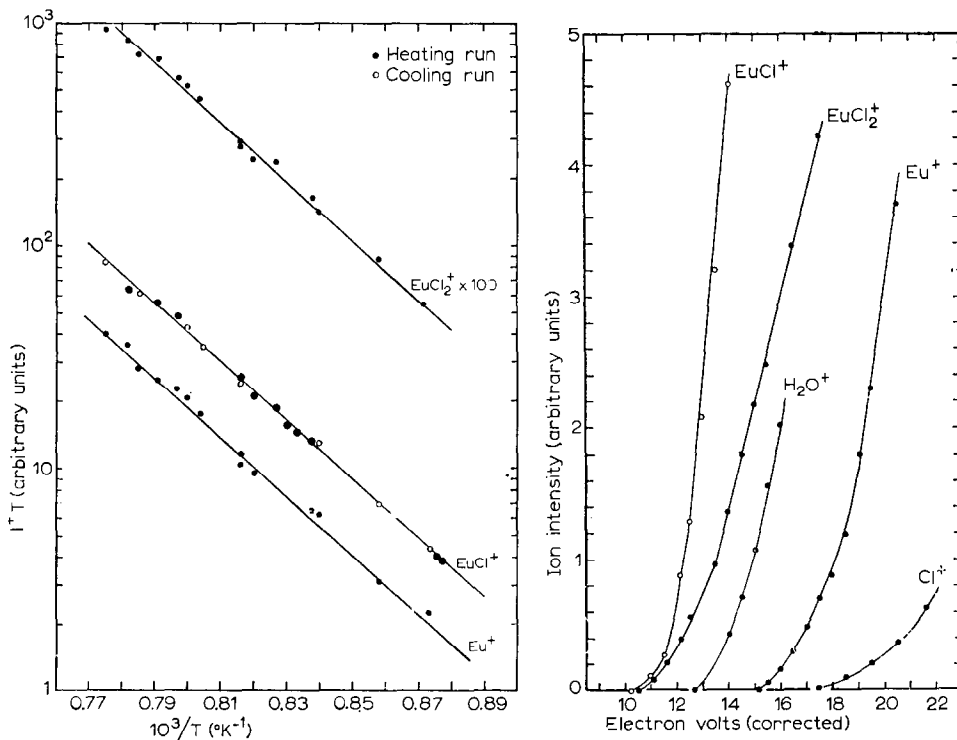


Fig. 2. Ion current *vs.* temperature data for species over $\text{EuCl}_2(\text{l})$.

Fig. 3. Ionization efficiency curves for species from EuCl_2 at 1255°K .

is in excellent agreement with the known heat of vaporization of EuCl_2 ¹⁵. The low AP values also suggest EuCl_2 as the common molecular precursor. The uncertainty of the vapor state of EuCl_2^+ is also resolved by these results, EuCl_2 being the only significant vapor species for the present temperature range of $1143^\circ\text{--}1291^\circ\text{K}$. A slight doubt remains as, at the higher temperatures the EuCl_2^+ ionization efficiency curve (Fig. 3) showed an increase in slope at an energy of about 3 eV above the appearance potential. This could be interpreted as being due to EuCl_3 being formed in small

amount at the higher temperatures according to the above reaction, although no lowering of the Eu^+ appearance potential was noted. The ion current *vs.* temperature curve for EuCl_2^+ would not necessarily alter with the presence of a small amount of EuCl_3 . If this is the case the absence of the EuCl_3^+ ion would indicate a low-ionization cross section for EuCl_3^+ relative to EuCl_2^+ .

An X-ray diffraction powder analysis of the red-brown end-product (EuCl_3 is pure white) verified the complete transformation to EuCl_2 , no lines corresponding to Eu metal or EuCl_3 being observed¹⁶.

The $\text{EuCl}_3 + \text{LuCl}_3$ system

As insufficient EuCl_3 pressure could be obtained from pure EuCl_3 no study of the possible dimer Eu_2Cl_6 was possible. The problem is to stabilize the trivalent state of Eu in chloride melts so as to prevent formation of EuCl_2 . A clue to a possible solution for this problem was provided by the observation¹⁷ that EuCl_3 forms several congruently melting compounds with KCl, namely KEu_2Cl_7 and K_3EuCl_6 , Eu remaining in the trivalent state. It is likely that Eu is present in the form of a complex ion $[\text{EuCl}_6]^{3-}$ for these molten mixtures¹⁸. We found that a mixture of EuCl_3 and LuCl_3 seemed to favor the vaporization of EuCl_3 rather than EuCl_2 , possibly for a similar reason.

TABLE III

MASS SPECTRAL DATA FOR THE $\text{EuCl}_3 + \text{LuCl}_3$ SYSTEM AT 960°K

<i>Ion</i>	<i>Intensity*</i> (arbitrary units)	<i>AP (eV)</i> (± 0.5)	<i>Molecular precursor</i>
Eu^+	—	—	EuCl_3
Lu^+	70	20.5	LuCl_3
EuCl^+	1.2	11.0, 18	EuCl_3 , $\text{EuCl}_2 (< 5\%)$
LuCl^+	35	16.0	LuCl_3
EuCl_2^+	1.5	10.7, 18	EuCl_3 , $\text{EuCl}_2 (< 5\%)$
LuCl_2^+	100	12.5 ± 0.3	LuCl_3
EuCl_3^+	3.6	13 ± 1	EuCl_3
LuCl_3^+	26	11.5	LuCl_3
Eu_2Cl_5^+	0.1	—	Eu_2Cl_6
EuLuCl_5^+	0.28	—	EuLuCl_6
Lu_2Cl_5^+	11	12.5	Lu_2Cl_6

* Measured at 50 eV ionizing electron energy.

The mass spectral results for this mixture at 960°K are presented in Table III. The ionization efficiency curves (Fig. 4) for EuCl_2^+ and EuCl^+ suggest both EuCl_2 and EuCl_3 as molecular precursors, the former molecule being present to the extent of only about 5% as compared with the latter. The appearance potential of the EuCl^+ ion is far too high for it to be interpreted as a parent ion, the rare-earth monohalides having ionization potentials around 6 ± 1 eV¹.

The ion intensity *vs.* temperature data for the species LuCl_2^+ and Lu_2Cl_5^+ are plotted in Fig. 5. The breaks in the heat of vaporization curves are interpreted as indicating the melting point for the LuCl_3 plus EuCl_3 mixture ($\approx 1000^\circ\text{K}$), the exact stoichiometry of which is unknown. The slope of the $\log I(\text{LuCl}_2^+)/T$ *vs.* $1/T$ line agrees well with the expected heat of sublimation for LuCl_3 ³.

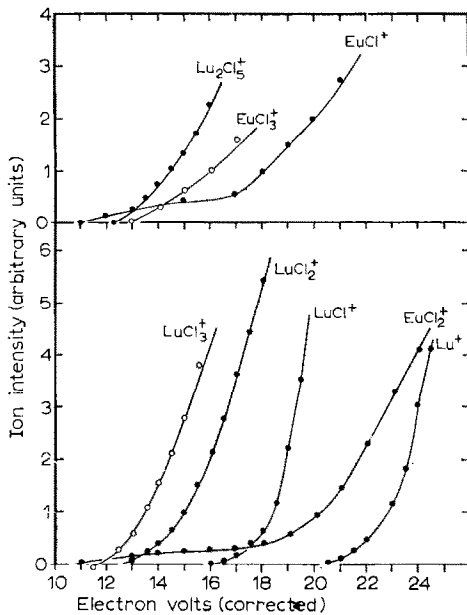


Fig. 4. Ionization efficiency curves for species containing either Eu or Lu over the $\text{EuCl}_3 + \text{LuCl}_3$ mixture at 1080°K .

The temperature dependences for the dimerization constants are represented by the curves of Figs. 5 and 6. From the slopes of these curves one obtains the following heats of dimerization:



$$K_2 = \frac{I(\text{Lu}_2\text{Cl}_5^+)}{I(\text{LuCl}_2^+)^2 T}$$

$$\Delta H_2 = -47 \pm 4 \text{ kcal mole}^{-1}$$



$$K_3 = \frac{I(\text{Eu}_2\text{Cl}_5^+)}{I(\text{EuCl}_2^+)^2 T}$$

$$\Delta H_3 = -32 \pm 6 \text{ kcal mole}^{-1}$$



$$K_4 = \frac{I(\text{EuLuCl}_5^+)}{I(\text{EuCl}_2^+)I(\text{LuCl}_2^+)T}$$

$$\Delta H_4 = -37 \pm 4 \text{ kcal mole}^{-1}$$

Absolute free energies are not obtainable for these reactions as the partial pressure data are unknown. However, the entropies are not likely to differ appreciably from the value found for the LaCl_3 reaction and therefore approximate free energy and vapor composition calculations may be made. From a comparison of the relative ion current data for the dimeric and monomeric species it is apparent that EuCl_3 and LuCl_3 form higher proportions of dimer than LaCl_3 .

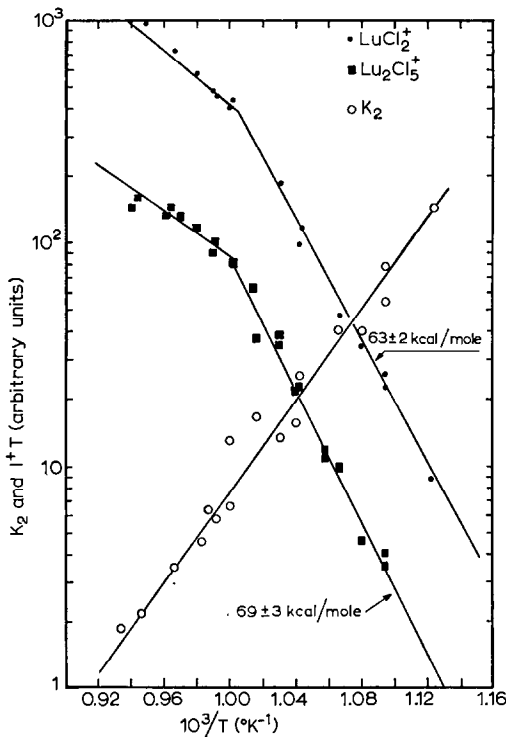


Fig. 5. Ion current analogs of pressure and equilibrium constant, as a function of temperature, for Lu-containing species over the $\text{EuCl}_3 + \text{LuCl}_3$ mixture.

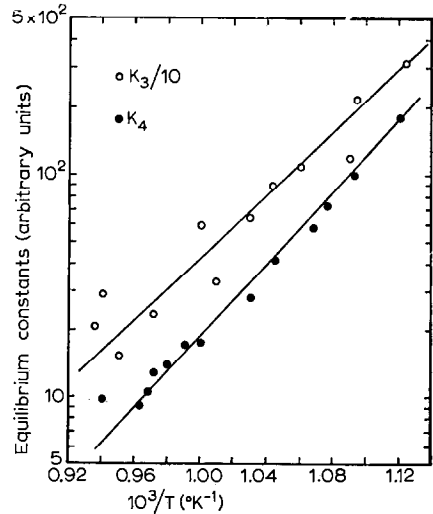


Fig. 6. Ion current analogs of equilibrium constants, as a function of temperature, involving Eu-containing species over the $\text{EuCl}_3 + \text{LuCl}_3$ mixture.

CONCLUSIONS

It has been found that the rare-earth trichlorides form dimers in the vapor state and that the proportion of dimer to monomer increases with increasing temperature. Observed values for the heats of dimerization for all the rare-earth trichlorides fall in the range -32 to -48 kcal/mole. Trends in the values of these enthalpies will probably be determined by ligand field stabilization, analogous to that observed for the heats of dissociation of the monomer¹. By using this assumption, one may predict the extent of dimerization in rare-earth trichlorides, and combine this data with the total vapor pressures reported by POLYACHENOK AND NOVIKOV³, to obtain the vapor composition. As the dimerization entropies are not likely to vary by more than several e.u. from LaCl_3 to LuCl_3 , values of $\Delta S_{a,1000^\circ\text{K}} = -30 \pm 3$ e.u. may be used in calculations for all the rare-earth trichlorides. The measured or estimated enthalpies of dimerization, $-\Delta H_{a,1000^\circ\text{K}}$ (kcal mole⁻¹), are as follows:

$\text{La}(48)$, $\text{Ce}(45)$, $\text{Pr}(43)$, $\text{Nd}(41)$, $\text{Pm}(38)$, $\text{Sm}(35)$, $\text{Eu}(32)$, $\text{Gd}(41)$, $\text{Tb}(43)$, $\text{Dy}(40)$, $\text{Ho}(37)$, $\text{Er}(34)$, $\text{Tm}(30)$, $\text{Yb}(28)$, and $\text{Lu}(47)$ with uncertainties of about ± 4 kcal mole⁻¹.

The structure of these dimers may be similar to that of Al_2Cl_6 , particularly as the entropies of formation from the monomers are similar¹⁴.

No dimers of EuCl_2 were found and it is likely that the other rare-earth dihalides behave likewise.

ACKNOWLEDGEMENT

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