Vaporization Thermodynamics of Lanthanide Trihalides

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Published data on the vaporization of the lanthanide trihalides have been reviewed, and enthalpies of sublimation at 298.15 K have been calculated by the second- and third-law methods using thermodynamic functions for gaseous and condensed states developed in an internally consistent manner. Preferred values of the third-law enthalpies were selected, primarily on the basis of agreement between the second- and third-law results. The selected values for the fluorides and chlorides show variations from a smooth trend across the lanthanide series greater than would be expected from experimental uncertainties, while the results for the bromides and iodides exhibit relatively smooth behavior.

There has been considerable recent interest in the vaporization behavior and thermodynamics of the lanthanide trihalides; over 20 studies have been reported in the past 15 years. Most of these investigations used the "second law" or "method of slopes" exclusively in treating the data to extract enthalpies of vaporization or sublimation. In those studies for which the "third law" method was used, the free energy functions for gaseous and condensed states were developed on a case-by-case basis which makes comparison of reported values difficult. Because of the interest in systematic trends in lanthanide compounds, as well as the need for a critical evaluation of data from different laboratories, it was decided to review the published data using uniform methods for developing needed heat capacities and entropies. The importance of using consistent sets of thermodynamic functions in comparing experimental results has recently been reemphasized by Gupta (*14*).

Thermodynamic Functions

The development of thermodynamic functions for the gaseous trihalide molecules is described elsewhere (*31*).

Absolute entropy data at 298.15 K have been reported for CeF_3(s) (*39*), $LnCl_{3(s)}$ (Ln = La, Pr, Nd, Sm, Eu, Gd) (*43*), and $EuBr_3$(s) (*7*). The remaining entropies were estimated using Westrum's lattice entropy contributions for Ln^{3+} ions (*42*). The lattice contribution for F^- in the trifluorides may be estimated by substracting the lattice contribution of Ce^{3+}, 14.7 cal mol^{-1} K^{-1}, and the electronic contribution (*31*) of Ce^{3+}, 3.6, from the measured value for CeF_3, 27.5, and dividing the result by three to give $S°_{298.15}{}^{lat}(F^-) = 3.1$ cal mol^{-1} K^{-1}. In a similar manner, the published entropies for the trichlorides (*39*) and for $EuBr_3$ (*7*) were used as a basis for estimating the lattice contribution of chloride, $S°_{298.15}{}^{lat}(Cl^-) = 6.0$ cal mol^{-1} K^{-1}, and bromide, $S°_{298.15}{}^{lat}(Br^-) = 9.1$ cal mol^{-1} K^{-1}. The lattice contribution of iodide was taken to be $S°_{298.15}{}^{lat}(I^-) = 12.0$ cal mol^{-1} K^{-1}. These values for the halides, the lattice contributions of the Ln^{3+} ions (*42*), and the electronic contributions for the Ln^{3+} ions (*31*) were used to estimate the missing entropies of the solid trihalides at 298.15 K. The electronic contributions are (cal mol^{-1} K^{-1}) the following: La, 0; Ce, 3.56; Pr, 4.37; Nd, 4.58; Pm, 4.37; Sm, 3.67; Eu, 2.21; Gd, 4.13; Tb, 5.10; Dy, 5.51; Ho, 5.63; Er, 5.51; Tm, 5.10; Yb, 4.13; Lu, 0.

High-temperature heat capacity data for the condensed fluorides have been reported by Spedding and co-workers (*37, 38*). They tabulate free-energy functions, $-(G°_T - H°_{298.15})/T$, but assume the measured entropy of CeF_3(s) at 298.15 K to be a satisfactory approximation for all the other trifluorides. Since there are differences in both lattice and electronic contributions, the values they tabulate must be corrected by adding the quantity: $S_{Ln}{}^{lat} + S_{Ln}{}^{el} - 18.26$, where the first two terms are respectively the lattice and electronic contributions at 298.15 K for the lanthanide in question, and the constant term is the sum of lattice and electronic contributions for Ce^{3+}. The necessary corrections to the free-energy functions are (cal mol^{-1} K^{-1}) the following: LaF_3, −3.1; CeF_3, 0; PrF_3, +0.7; NdF_3, +0.8; SmF_3, −0.4; EuF_3, −2.0; GdF_3, −0.2; TbF_3, +0.6; DyF_3, +0.8; HoF_3, +0.8; ErF_3, +0.5; TmF_3, 0; YbF_3, −1.1, LuF_3, −5.3. The published enthalpy increments (*37, 38*) and the free-energy functions, as corrected, were used in subsequent calculations.

The high-temperature heat content of solid and liquid $CeCl_3$ has been measured by Walden and Smith (*42*) relative to 273.15 K, and Dworkin and Bredig (*12*) have studied the enthalpy as a function of temperature for solid and liquid $LnCl_3$ (Ln = Gd, Tb, Dy, Ho), $LnBr_3$ (Ln = Ce, Nd, Gd, Ho), and LnI_3 (Ln = La, Nd, Gd, Tb). They report enthalpies and entropies of fusion and transition for the solids $TbCl_3$ and LnI_3 (Ln = La, Nd, Gd, Tb). In earlier publications (*10, 11*) they report melting points, heat capacities of solid and liquid, enthalpy and entropy of fusion, and $(H°_{T_m} - H°_{298.15})$ for the solids $LnCl_3$ (Ln = La, Pr, Nd, Ho, Er), $LnBr_3$ (Ln = La, Pr), and LnI_3 (Ln = Ce, Pr).

The heat content functions and transition and fusion data given by Dworkin and Bredig (*12*) were used with measured or estimated entropies at 298.15 K to calculate free-energy functions for solid and liquid $LnCl_3$ (Ln = Gd, Tb, Dy, Ho), $LnBr_3$ (Ln = Ce, Nd, Gd, Ho), and LnI_3 (Ln = La, Nd, Gd, Tb). The data of Walden and Smith (*42*), together with the estimated entropy at 298.15 K, were used to calculate free-energy functions for solid and liquid $CeCl_3$.

For $LnCl_3$ (Ln = La, Pr, Nd, Ho, Er), $LnBr_3$ (Ln = La, Pr), and LnI_3 (Ln = Ce, Pr), linear heat capacity expressions, $C_p = a + bT$, were derived

$$b = \frac{H - C(T_m - 298.15)}{[(T_m{}^2 - 298.15^2)/2] - T_m(T_m - 298.15)}$$

$$a = C - bT_m$$

where $H = (H°_{T_m} - H°_{298.15})$ and C is the heat capacity of the solid at the melting point, T_m, as reported by Dworkin and Bredig (*10, 11*). These heat capacity expressions, together with the respective measured or estimated entropies at 298.15 K, were used to calculate heat content and free-energy functions as a function of temperature.

The remaining compounds for which vapor pressure measurements have been reported are $LnCl_3$ (Ln = Eu, Tm, Yb, Lu), $LnBr_3$ (Ln = Tb, Dy, Er, Tm, Lu), and LnI_3 (Ln = Dy, Ho, Er, Tm). The needed thermal data, including heat capacity expressions, for these compounds were estimated. Dworkin and Bredig (*10–12*) have noted a relation between crystal structure type and thermal properties of the solid lanthanide trihalides. $EuCl_3$ has the UCl_3-type structure, as do $LaCl_3$ to $GdCl_3$, inclusive. $TmCl_3$, $YbCl_3$, and $LuCl_3$ have the $AlCl_3$-type structure, as do $DyCl_3$, $HoCl_3$, and $ErCl_3$. The tribromides from $GdBr_3$ through $LuBr_3$ all have the $FeCl_3$ structure, and the triiodides of Dy, Ho, Er, and Tm have the BiI_3 or $PuBr_3$-type structure, as do all the triiodides from SmI_3 to LuI_3 (*5*). For each structure type, a plot of ΔH_m vs. T_m is essentially linear, and, using the melting points given by Brown (*5*), enthalpies of fusion are estimated to be (kcal/mol) the following: $TmCl_3$, 8.2; $YbCl_3$, 8.6; $LuCl_3$, 9.4; $TbBr_3$, 10.0; $DyBr_3$, 11.1; $ErBr_3$, 12.1; $TmBr_3$, 12.8; $LuBr_3$, 14.4. No melting point has been published for $EuCl_3$; it is reported to decompose (*13*). A value of 1020 K has been estimated by interpolation on a plot of T_m vs. atomic number for $LnCl_3$ compounds have the UCl_3-type structure. This value leads to an estimate of 11.8 kcal/mol for the enthalpy of fusion of $EuCl_3$. Values of the enthalpy of fusion of the LnI_3 compounds are not needed since all the pressure measurements were made below their respective melting points.

Linear heat capacity expressions have been estimated for $LnCl_3$ (Ln = Eu, Tm, Yb, Lu), $LnBr_3$ (Ln = Tb, Dy, Er, Tm, Lu), and LnI_3 (Ln = Dy, Ho, Er, Tm) in the following way. Electronic contributions to the heat capacity of Ln^{3+} (Ln = Ce, Pr, Nd, Eu, Tb, Dy) ions were expressed as linear functions, $C_{p,\mathrm{el}} = a_{\mathrm{el}} + b_{\mathrm{el}}T$, using the data developed earlier (*31*). The electronic heat capacity for the other Ln^{3+} ions is negligible. The total heat capacities of those LnX_3 compounds studied in detail at elevated temperatures (*12*) were then approximated as linear functions, and the "lattice-only" heat capacities of these compounds and those studied less extensively (*10, 11*) were obtained

$$C_{p,\mathrm{lat}} = a_{\mathrm{lat}} + b_{\mathrm{lat}}T$$

where $a_{\mathrm{lat}} = (a_{\mathrm{tot}} - a_{\mathrm{el}})$ and $b_{\mathrm{lat}} = (b_{\mathrm{tot}} - b_{\mathrm{el}})$. The coefficients, a_{lat} and b_{lat}, in the lattice-only heat capacity expressions for $LnCl_3$ (Ln = Eu, Tm, Yb, Lu), $LnBr_3$ (Ln = Tb, Dy, Er, Tm, Lu), and LnI_3 (Ln = Dy, Ho, Er, Tm) were then taken as the averages of the respective coefficients for the same structure type. The total heat capacity expressions were obtained by adding the respective electronic and lattice coefficients. The resulting estimates of the coefficients are given in Table I. As needed, the heat capacities of the liquids were developed as constants in a similar manner, giving (cal mol^{-1} K^{-1}) the following: $EuCl_3$, 36.4; $LnCl_3$ (Ln = Tm, Yb, Lu), 34.0; $TbBr_3$, 35.2; $DyBr_3$, 34.6; $LnBr_3$ (Ln = Er, Tm, Lu), 33.8.

The estimated entropies at 298.15 K, heat capacity expressions, and enthalpies of fusion were used to calculate high-temperature heat contents and free-energy functions.

Treatment of Data

The vapor pressure data in the literature are usually summarized in the form $\log P = a + b/T$, from which ΔH°_T and ΔS°_T (second law) may be calculated, or these latter quantities are stated directly. In studies using a mass spectrometer, only ΔH°_T was obtained unless an absolute pressure calibration was made. The second-law values of ΔH°_T from the various experimental studies on LnX_3 compounds are given in Table II in the column headed $\Delta H^\circ_T{}^{\mathrm{II}}$. Using the $(H^\circ_T - H^\circ_{298.15})$ data for the gaseous and condensed compounds, the second-law enthalpies of sublimation at 298.15 K have been calculated and are given in the column headed $\Delta H^\circ_{298.15}{}^{\mathrm{II}}$.

In order to treat the results in terms of the third law, it was decided to calculate the pressure, using the vapor pressure equation or the second law results, at a temperature near the middle of the range covered by each reported set of measurements. These results are summarized in the column headed $-R \ln P$, and they were combined with changes in the free-energy functions, in the column headed $-\Delta(G^\circ_T - H^\circ_{298.15})/T$, to yield third-law enthalpies of sublimation which are listed in the column headed $\Delta H^\circ_{298.15}{}^{\mathrm{III}}$. This procedure was chosen since a number of the published studies (*8, 13, 24–29*) give only summary results and a conventional third-law treatment was not possible. The actual numerical difference between the results from the procedure used here and those from the conventional third-law treatment are much less than the uncertainties in either method, and, the better the second law–third law agreement, the smaller the difference. For example, the conventional third-law treatment of the mass effusion data of Suvorov et al. (*41*) for LaF_3 (poor second law–third law agreement) yields 106.6 kcal for $\Delta H^\circ_{298.15}{}^{\mathrm{III}}$ which differs by only 0.3 kcal from the result in Table II, and the conventional third-law treatment of the mass effusion data of Mar and Searcy (*23*) for LaF_3 (satisfactory second law–third law agreement) yields a result identical with that given in Table II. Third-law values are missing for mass spectrometric studies not employing an absolute pressure calibration and for torsion effusion experiments not yielding absolute pressures.

Table I. Estimates of Heat Capacity Parameters

	a, cal mol^{-1} K^{-1}	*b*, cal mol^{-1} K^{-2}
$EuCl_3(s)$	21.5	0.012
$LnCl_3(s)$ (Ln = Tm, Yb, Lu)	20.1	0.0077
$TbBr_3$	22.6	0.0044
$DyBr_3$	22.6	0.0038
$LnBr_3$ (Ln = Er, Tm, Lu)	23.4	0.0026
$DyI_3(s)$	22.9	0.0037
$HoI_3(s)$	23.1	0.0031
$LnI_3(s)$ (Ln = Er, Tm)	23.7	0.0025

Results and Discussion

It has been pointed out by Bebrick (*1*) that the most certain result of a study of ΔG of reaction as a function of T is the calculated value, ΔG_c, at the average temperature, $\bar{T}$, computed as the reciprocal of the average of $1/T$. Hence, the third-law enthalpy of sublimation calculated from $\Delta G_{c,\bar{T}}$ would be preferred to the extent that the free-energy functions used in its computation are reliable. In the present study, agreement between the second- and third-law results was adopted as a primary criterion of reliability since a wide divergence is an indication of temperature-dependent errors in experimental results or their interpretation. Other criteria include the extent of each study and the quality of experimental design. "Selected" enthalpies of sublimation are italicized in Table II, and uncertainty limits are appended.

The best mass effusion results were assumed to have experimental uncertainties of ±1.0 kcal/mol or less in ΔG_c, and hence in $\Delta H^\circ_{s,298.15}{}^{\mathrm{III}}$. The uncertainties in less-precise experiments may be 2.0 kcal/mol or greater. The estimated uncertainty from torsion effusion and from calibrated mass spectrometry experiments was each taken to be ±1.5 kcal/mol in the best cases. Results from boiling point experiments were assumed to have uncertainties of ±2.0 kcal/mol. Uncertainties in the free-energy functions of gaseous and condensed compounds were assumed to introduce additional uncertainties of ±1.5 kcal/mol for LnF_3, ±2.0 for $LnCl_3$, ±2.5 for $LnBr_3$, and ±4.0 for LnI_3. The uncertainties in $\Delta H^\circ_T{}^{\mathrm{II}}$ from uncalibrated mass spectrometry experiments are probably no less than ±4.0 kcal/mol, and uncertainties in heat content functions introduce an additional 0.5 kcal/mol uncertainty in $\Delta H^\circ_{s,298.15}{}^{\mathrm{II}}$.

There have been 16 studies of LnF_3 vaporization behavior (*2–4, 21–23, 26–29, 32, 33, 35, 36, 41, 45*) coming from six different laboratories. In those cases in which the same compound has been studied by different research groups, the third-law enthalpies of sublimation at 298.15 K agree rather well, generally within the uncertainty limits of the selected value. The second-law values show significant variation, with ranges of 15 kcal/mol and more in several cases, and thus the second law–third law agreement is often poor. No selected values of $\Delta H^\circ_{s,298.15}$ are chosen for SmF_3, EuF_3, and YbF_3 because their vaporizations are probably incongruent (*3, 32*), yielding $LnF_3(g)$, F(g) and lower fluorides in the condensed state. Under experimental conditions (*3, 32*), the vapor above $YbF_3(l)$ is predominantly $YbF_3(g)$, and treatment of the experimental data as a pseudocongruent vaporization leads to the data found in Table II for YbF_3. Searcy and co-workers (*33, 36*) have observed $La_2F_5^+$ and $Ce_2F_5^+$ in the mass spectrum of the vapor above LaF_3 and CeF_3 and report enthalpies of dimerization at 1577 K

Table II. Vaporization Thermodynamics of Lanthanide Trihalides, $LnX_3(s,l) = LnX_3(g)$

LnX_3	Ref	Method[a]	T, K	$-R \ln P$, cal mol^{-1} K^{-1}	$\Delta H°_T{}^{II}$, kcal mol^{-1}	$-\Delta(H°_T - H°_{298.15})$, kcal mol^{-1}	$-\Delta(G°_T - H°_{298.15})/T$, cal mol^{-1} K^{-1}	$\Delta H°_{298.15}{}^{II}$, kcal mol^{-1}	$\Delta H°_{298.15}{}^{III}$,[b] kcal mol^{-1}
Fluorides									
LaF_3	21	me	1320	32.42	92.3	6.4	48.22	98.7	106.4
	45	cms	1360	29.93	91.7	6.8	48.07	98.5	106.1
	41	me	1430	26.56	81.7	7.6	47.81	89.3	106.3
		te	1420		82.6	7.5		90.1	
	23	me	1500	22.32	99.4	8.5	47.54	107.9	*104.8* ± 2.5
		te	1470	23.79	104.1	8.1	47.65	112.2	105.0
	36	ms	1580		96.7	9.7		106.4	
	33	ms	1380		102.2	7.0		109.2	
CeF_3	45	ms	1390		91.2	7.3		98.5	
	41	me	1380	25.82	91.5	7.2	48.66	98.7	102.8
	33	ms	1380		100.2	7.2		107.4	
	22	te	1500	20.29	93.6	8.5	48.24	102.1	102.8
	27	me	1370	27.82	97.8	7.1	48.69	104.9	*104.8* ± 2.5
		cms	1370	27.87	98.4	7.1	48.69	105.5	104.9
PrF_3	45	ms	1410		92.9	7.3		100.2	
	41	me	1400	26.26	82.4	7.2	48.13	89.6	104.1
	35	me	1500	21.46	96.5	8.0	47.76	104.5	*103.8* ± 2.5
		te	1510	21.31	99.4	8.0	47.72	107.4	104.2
NdF_3	45	cms	1450	22.40	85.7	7.3	48.40	93.0	102.7
	41	me	1410	27.11	81.0	7.0	48.54	88.0	106.7
		te	1400		83.3	6.9		90.2	
	28	me	1400	26.93	97.8	6.9	48.57	104.7	*105.7* ± 2.5
		cms	1400	26.92	99.1	6.9	48.57	106.0	*105.7*
SmF_3	45	ms	1430		96.8	8.9		105.7[c] ?	
EuF_3	45	ms	1450		92.0	12.5		104.5[c] ?	
GdF_3	45	ms	1460		90.3	7.0		97.3	
	26	me	1460	25.72	100.6	7.0	48.92	107.6	109.0
		cms	1460	25.54	100.5	7.0	48.92	107.5	*108.7* ± 3.0
TbF_3	45	ms	1080		101.7	4.9		106.6	
	26	me	1380	28.59	99.8	7.3	48.72	107.1	*106.7* ± 2.5
		cms	1380	28.61	101.5	7.3	48.72	108.8	106.7
DyF_3	45	cms	1090	49.22	107.5	5.1	49.81	112.6	107.9
	29	me	1370	29.28	101.5	7.4	48.68	108.9	*106.8* ± 2.5
		cms	1370	29.32	102.6	7.4	48.68	110.0	106.7
	2	me	1360	29.17	106.4	7.3	48.72	113.7	105.9
		me	1520	20.96	84.3	23.5	47.50	107.8	104.1
HoF_3	45	cms	1100	47.29	106.8	4.2	50.91	111.0	108.0
	29	me	1360	30.34	103.2	5.6	50.06	108.8	109.3
		cms	1360	30.35	104.1	5.6	50.06	109.7	*109.4* ± 2.5
	2	me	1370	28.39	105.6	5.7	50.03	111.3	107.4
		me	1460	24.33	84.5	19.9	49.48	104.4	107.8
ErF_3	45	cms	1450	25.00	111.5	22.0	47.94	133.5	105.8
	29	me	1360	30.27	103.1	7.3	48.60	110.4	*107.3* ± 2.5
		cms	1360	30.16	106.8	7.3	48.60	114.1	107.1
	2	me	1370	29.25	107.0	7.4	48.56	114.4	106.6
		me	1460	24.90	88.3	22.1	47.84	110.4	106.2
TmF_3	45	cms	1340	29.17	89.6	13.8	48.83	103.4	103.2
	4	mec	1580	19.63	86.2	23.1	46.71	109.3	*104.8* ± 2.5
YbF_3	45	cms	1360	27.37	85.5	13.0	48.47	98.5	103.1
	3	mec	1570	20.93	93.0	21.0	47.58	114.0	107.6
	32	me	1690	17.54	82.5	22.2	46.49	104.7	108.2
LuF_3	45	cms	1350	28.09	96.1	11.7	49.36	107.8	*104.6* ± 4.0
Chlorides									
$LaCl_3$	34	me	1070	26.61	72.3	5.6	49.95	77.9	*81.9* ± 3.0
	30	me	1200	15.28	80.5	20.7	48.99	101.2	77.1
	8	bp	1500	8.87	57.5	26.1	44.75	83.6	80.4
	15	ms	1030		74.0	5.1		79.0	
$CeCl_3$	34	me	1040	26.50	71.1	5.3	49.54	76.4	*79.1* ± 3.0
	30	me	1180	17.15	42.4	20.1	47.45	62.5	76.2
	8	bp	1500	8.01	56.9	21.9	43.56	78.8	77.4
$PrCl_3$	34	me	1030	26.31	70.6	5.9	49.15	76.5	*77.7* ± 3.0
	30	me	1190	16.54	44.4	19.7	47.03	64.1	75.6
	9	bp	1500	7.51	55.8	23.0	43.32	78.8	76.2
$NdCl_3$	34	me	1000	27.51	69.0	5.0	50.63	74.0	*78.1* ± 3.0
	30	me	1170	16.93	40.1	19.4	48.37	59.5	76.4
	8	bp	1500	7.34	54.3	23.8	44.34	78.1	77.5
	6	ms	1070		60.1	18.0		78.1	
	13	me	1020	11.24	74.4	5.3	50.42	79.7	62.9
$EuCl_3$	30	me	1070	14.98	24.8	17.7	48.80	42.5	68.2[c] ?

Table II (continued)

LnX_3	Ref	Method[a]	T, K	$-R \ln P$, cal mol^{-1} K^{-1}	$\Delta H^\circ{}_T{}^{II}$, kcal mol^{-1}	$-\Delta(H^\circ{}_T - H^\circ{}_{298.15})$, kcal mol^{-1}	$-\Delta(G^\circ{}_T - H^\circ{}_{298.15})/T$, cal mol^{-1} K^{-1}	$\Delta H^\circ{}_{298.15}{}^{II}$, kcal mol^{-1}	$\Delta H^\circ{}_{298.15}{}^{III, b}$, kcal mol^{-1}
$GdCl_3$	30	me	1100	17.17	44.7	16.3	46.93	61.0	70.5
	8	bp	1500	6.86	54.0	21.7	42.38	75.7	*73.9* ± 4.0
	6	ms	1020		57.0	15.2		72.2	
$TbCl_3$	30	me	1190	15.87	39.0	16.1	45.74	55.1	73.3
	9	bp	1500	5.83	50.8	20.3	42.60	71.1	*72.6* ± 4.0
$DyCl_3$	30	me	1110	15.48	46.1	12.3	48.61	58.4	71.1
	9	bp	1500	5.66	51.1	17.8	45.15	68.9	*76.2* ± 4.0
$HoCl_3$	30	me	1150	15.13	60.5	13.4	48.56	73.9	73.2
	8	bp	1500	5.34	50.5	18.8	45.62	69.3	*76.4* ± 4.0
$ErCl_3$	30	me	1140	15.71	34.1	13.6	50.35	47.7	75.3
	8	bp	1500	4.92	49.9	18.6	47.00	68.5	*77.9* ± 4.0
$TmCl_3$	30	me	1120	14.47	59.6	13.4	50.09	73.0	72.3
	8	bp	1500	4.61	48.3	18.7	46.51	67.0	*76.7* ± 4.0
$YbCl_3$	30	me	1190	14.70	26.8	15.9	49.73	42.7	76.7[c] ?
$LuCl_3$	30	me	1190	13.61	42.5	5.7	50.05	58.2	75.8
	8	bp	1500	3.70	49.5	19.4	47.16	68.9	*76.3* ± 4.0
Bromides									
$LaBr_3$	34	me	1030	24.29	70.7	4.9	47.08	76.5	*73.5* ± 3.5
$CeBr_3$	34	me	970	27.46	68.6	4.2	46.88	72.8	*72.1* ± 3.5
$PrBr_3$	34	me	950	27.79	68.2	4.4	47.18	72.6	*71.2* ± 3.5
$NdBr_3$	34	me	920	29.49	67.9	3.8	47.14	71.7	*70.5* ± 3.5
$GdBr_3$	25	bp	1400	7.00	48.4	17.7	43.77	65.6	*71.1* ± 4.0
$TbBr_3$	25	bp	1400	6.20	47.0	18.6	43.85	65.6	*70.1* ± 4.0
$DyBr_3$	25	bp	1400	5.78	47.2	19.3	44.40	66.5	*70.3* ± 4.0
$HoBr_3$	24	bp	1400	5.48	47.5	20.3	44.41	67.8	*69.8* ± 4.0
$ErBr_3$	25	bp	1400	4.78	47.1	20.0	44.69	67.1	*69.3* ± 4.0
$TmBr_3$	25	bp	1400	4.38	45.2	20.5	44.86	65.7	*68.9* ± 4.0
$LuBr_3$	25	bp	1400	3.48	44.7	21.6	45.55	66.3	*68.5* ± 4.0
Iodides									
LaI_3	34	me	980	26.30	70.5	4.2	44.75	74.7	69.6
	17	me	950	25.28	72.2	3.9	44.88	76.1	*66.7* ± 5
CeI_3	20	me	940	25.33	68.0	4.6	45.94	72.6	*67.0* ± 5
	18	ms	930		69.7	4.4		74.1	
PrI_3	34	me	970	24.12	67.0	4.7	45.10	71.7	67.1
	16	me	940	24.65	69.9	4.4	45.25	74.3	*65.7* ± 5
NdI_3	34	me	980	23.78	66.3	7.5	44.60	73.8	67.0
	16	me	940	24.56	68.8	7.2	44.93	76.0	*65.3* ± 5
GdI_3	20	me	970	22.67	73.2	3.6	45.72	76.8	*66.3* ± 5
	18	ms	940		61.1	3.4		64.5	
TbI_3	20	me	940	23.87	64.2	3.7	45.70	67.9	*65.4* ± 5
	18	ms	930		58.8	3.6		62.4	
DyI_3	20	me	950	23.05	64.4	3.5	45.96	67.9	*65.6* ± 5
	18	ms	920		69.4	3.3		72.7	
HoI_3	20	me	980	21.62	71.3	3.6	45.85	74.9	*66.1* ± 5
	18	ms	880		72.5	3.0		75.5	
ErI_3	20	me	960	22.20	69.2	3.7	45.86	72.9	*65.3* ± 5
	18	ms	900		60.7	3.3		64.0	
TmI_3	20	me	930	23.87	68.4	3.5	46.04	71.9	*65.0* ± 5

[a] Experimental methods: me, mass effusion; cms, calibrated mass spectrometry; te, torsion effusion; ms, mass spectrometry (uncalibrated); mec, mass effusion-collection; bp, boiling point. [b] Selected values italicized. [c] Results uncertain because of incongruent vaporization.

of −54.2 ± 7 and −51.5 ± 7 kcal/mol dimer, respectively (*33*).

Seven papers from six laboratories (*6, 8, 9, 13, 15, 30, 34*) have been published on the vaporization of the trichlorides. Three laboratories used mass effusion (*13, 30, 34*), two used effusion mass spectrometry (*6, 15*), and the others used a boiling point technique (*8, 9*). Third-law agreement again is generally rather good within the limits of uncertainty of the selected values for the enthalpy of sublimation at 298.15 K. No selected values of $\Delta H^\circ{}_{s,298.15}$ are chosen for $EuCl_3$ and $YbCl_3$ since their vaporizations are probably incongruent. Satisfactory agreement between the second and third law results is achieved by Shimazaki and Niwa (*34*) and, for the early part of the series, by Dudchik and co-workers (*8, 9*) but the agreement for the latter authors is not as good for compounds toward the end of the series. Moiarty (*30*) collected far too few points for a meaningful second-law treatment, and his experimental design raises some serious questions. Evseeva and Zenkevich (*13*) were not able to overcome the problem of the hygroscopic behavior of their $NdCl_3$ sample.

Hastie and co-workers (*15*) have observed the $La_2Cl_5{}^+$ ion above $LaCl_3$(s) in the range 1000–1100 K, and, using the pressure data from Shimazaki and Niwa (*34*) in a second-law treatment, calculate $\Delta H = -48$ kcal/mol for formation of the dimer from the monomer at 1000 K to be −32 and −47 kcal/mol. Alternatively, one may use $\Delta H^\circ{}_{298.15}{}^{III}$ calculated from Shimazaki and Niwa's data, together with the free-energy functions used here, to calculate the pressure of the monomer at 1600 K. The total pressure may be calculated from the data given by Dudchik and co-workers (*8, 9*), and the difference is an estimate of the pressure of the dimer. If the entropy of dimerization is assumed to be the same as for the dimerization of $AlCl_3$ at 1600 K, ΔS

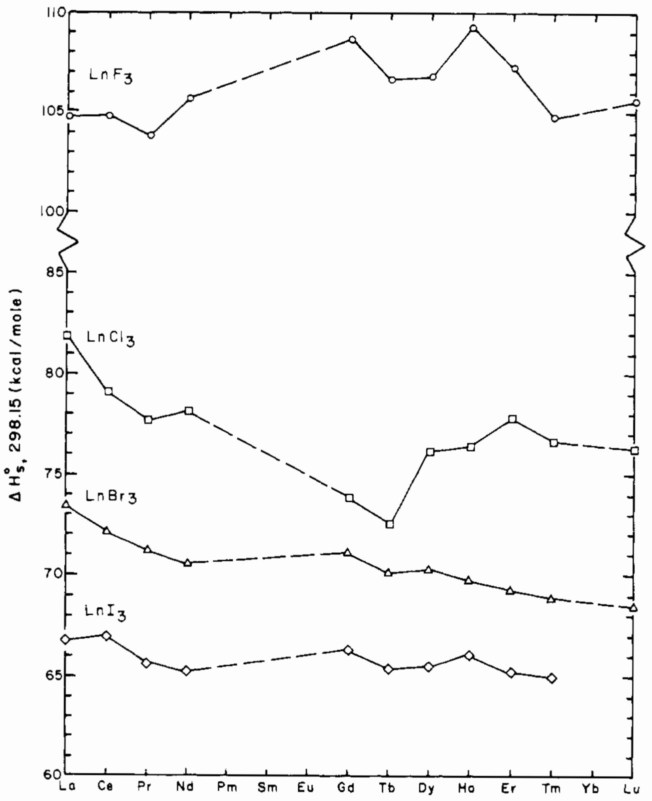

Figure 1. Selected third-law enthalpies of sublimation at 298.15 K.

= −30 cal mol^{-1} K^{-1} (*40*), the following enthalpies of dimerization are calculated at 1600 K (kcal/mol dimer): $LaCl_3$, −58.8 ± 10; $CeCl_3$, −57.9 ± 10; $PrCl_3$, −56.9 ± 10; $NdCl_3$, −52.3 ± 10.

Two laboratories have published studies of the tribromides. The mass effusion results reported by Shimazaki and Niwa (*34*) and the boiling point data of Makhmadurodov and co-workers (*24, 25*) show satisfactory second law–third law agreement.

There have been six published studies of triiodide vaporizations from two laboratories (*16–20, 34*). The third-law values are consistently lower than the second-law results, the differences being as great as 10 kcal/mol in some cases. The data of Shimazaki and Niwa (*34*) are suspect because of possible reaction of the triiodide vapors with the fused silica effusion cell (*16*). It is not certain whether the second law–third law differences in the results of Hirayama and co-workers (*16, 17, 20*) are due to experimental errors, to errors in free-energy functions for the gaseous and condensed compounds, or both. Possible sources of error in the free-energy functions which would lead to low third-law results include too great an estimated contribution of iodide to the entropy of the condensed state and/or too high estimates for the vibrational frequencies, particularly for the bending modes, in the gaseous molecules. On the other hand, the second-law results could be too high as a result of temperature-dependent errors. Hirayama and co-workers (*17*) have observed the $La_2I_5^+$ in the mass spectrum of the vapor above LaI_3 near 1000 K and calculate an enthalpy of dimerization, using the second law, of −46 kcal/mol. If the entropy of dimerization at 1000 K is assumed to be the same as for AlI_3, −29 cal/(mol K), the enthalpy of dimerization is calculated to be −39 ± 10 kcal/mol, assuming (*15*)

$$P(\text{dimer}) = 0.7[I(La_2I_5^+)/\sum_n I(LaI_n^+)]P(\text{monomer})$$

where $I(La_2F_5^+)$ and $I(LaI_n^+)$ are ion currents attributed to parent species La_2I_6 and LaI_3, respectively, and the constant is an estimate of the effects of relative ionization cross sections and multiplier yields for the two species.

The selected values of $\Delta H^\circ_{s,298.15}{}^{\text{III}}$ of the lanthanide trihalides are plotted in Figure 1 as a function of position in the lanthanide series. For the fluorides and chlorides, the departures from a smooth curve appear to be greater than can be accounted for on the basis of experimental uncertainty and must, for the moment at least, be taken as significant variations. It may be that these variations arise from different trends in ligand field stabilization energies in the solids and in the gaseous molecules across the lanthanide series. Apparent departures from smooth behavior in the bromides and iodides are well within experimental uncertainties.

This review of the vaporization thermodynamics of the lanthanide trihalides makes clear that additional research is needed. (a) Further vaporization studies are required to establish whether the enthalpy of sublimation is a monotonic function for each halide across the lanthanide series. The need for data at lower experimental temperatures for the chlorides and bromides is noteworthy. (b) The lack of molecular data for the gaseous chlorides, bromides, and iodides is critical in attempting to use a third-law treatment of experimental data. The thermodynamic functions of the gases are particularly sensitive to values of the bending frequencies. (c) There is great need for absolute entropy measurements, especially for the iodides. (d) If the variations in the enthalpies of sublimation of the fluorides and chlorides are real, then a suitable theoretical explanation must be sought.

Acknowledgment

The authors are pleased to thank Dr. John M. Haschke and Dr. R. J. Thorn for helpful discussions.

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Received for review February 4, 1977. Accepted June 24, 1977.

NEW COMPOUND SECTION

Synthesis of 5β-Chol-7-en-6-one Analogues of Ecdysone from Cholic Acid

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Starting with cholic acid, syntheses of B-ring 5β-enone steroid systems are delineated. Both methyl 3α,12α-diacetoxy-6-oxo-5β-chol-7-en-24-oate and methyl 3α,12α-dinitroxy-6-oxo-5β-chol-7-en-24-oate were inactive as insect moulting hormones. An interesting comparison between the selective synthesis and nonselective synthesis of methyl 3α,12α-diacetoxy-6-oxo-5β-chol-7-en-24-oate is made.

During the course of our pilot studies directed toward synthesis of quassin derivatives, we had a need for steroids containing the B-ring 5β-enone system characteristic of ecdysone, an insect moulting hormone. (For examples of the author's prior work with other enone systems ref 4.) Since these B-ring 5β-enone systems may provide a potentially useful starting point for elaborating other ecdysone analogues (*7*), this paper summarizes their synthesis.

Results and Discussion

The starting material, 3α,12α-dinitroxy-7α-hydroxy-5β-cholan-24-oic acid (**1**), was synthesized by a modified procedure (Scheme I) (*5, 10*). The methyl ester **2** was dehydrated with $POCl_3$ in pyridine under anhydrous conditions to yield exclusively **3**; if the methyl ester **2** is not scrupulously dried some 7β-chloro substituted product is also obtained. Allylic oxidation (*2*) of olefin **3** with excess $CrO_3 \cdot 2py$ provided enone **4**. Selective removal of the nitroxy groups by Zn dust reduction in glacial acetic acid below room temperature (*6*) followed by acetylation in pyridine yielded ene **5**. This olefin was subsequently oxidized as above to give enone **6**.

Preliminary attempts to selectively reduce the 6-oxo group in 5β-enone **6** with $NaBH_4$ in CH_3OH–THF containing ethyl acetate led to only recovered starting material. By contrast the 6-oxo group in the 5α-enone system is easily reduced under these conditions (*8*). Interestingly, if one compares the nitroxy vs. acetoxy analogues, one observes that the melting points, R_f values, and C-19 and C-18 methyl ^1H NMR chemical shifts are higher for the nitroxy analogues (compare **3** vs. **5** and **4** vs. **6**). Enones **4** and **6** were inactive as insect moulting hormones when fed admixed with food to lepidopterous larvae (cf. with acknowledgment).

In the conversion of the dinitroxy olefin **3** to diacetoxy olefin **5** in one run yielded a side product which was subsequently identified as methyl 3α,12α-diacetoxy-7β-chloro-5β-cholan-24-oate. Initially this side product was thought to be methyl 3α,12α-diacetoxy-5β-chol-8(14)-en-24-oate (**10**) because of the conspicuous absence of olefinic protons in its ^1H NMR spectrum. Thus, an attempt to synthesize olefin **10** (Scheme II) by refluxing cholic acid (50 g) with fused $ZnCl_2$ (50 g) in acetone for 0.25 h (*3*) followed by acetylation and esterification with diazomethane yielded instead a small quantity (10 g) of crude olefin **5** isolated by column chromatography through silica gel and a substantial amount of methyl 3α,7α,12α-triacetoxy-5β-cholan-24-oate (50 g). Oxidation of this crude olefin **5** (10 g) as per Scheme I, yielded 4.5 g of enone **6**. Prolonged (2.5 h) refluxing of cholic acid with fused $ZnCl_2$ in acetone followed by acetylation and esterification did result in the corresponding ester **10** of the reported apocholic acid **8** (*3*). These experiments emphasize the importance of the duration of refluxing (not reported in ref 3) in order to completely dehydrate and subsequently isomerize cholic acid to apocholic acid. In addition, if one compares the overall yields of enone **6** in the selective synthetic route (Scheme I) vs. the nonselective route (Scheme II), one obtains 25 and 9%, respectively. However, since the methyl 3α,7α,12α-triacetoxy-5β-cholan-24-oate can be hydrolyzed back to cholic acid for recycling through Scheme II, this latter synthetic route becomes economically preferred to Scheme I.

Experimental Section

General Procedure. All melting points were determined with a Fisher-Johns apparatus and are corrected. IR data reported in inverse centimeters (cm^{-1}) were obtained in $CHCl_3$ solution against a blank; ^1H NMR data, reported in ppm (δ) from Me_4Si, were obtained in $CDCl_3$ on a Varian A-60 or T-60 instrument; and mass spectra were obtained at an ionization voltage of 70 eV with a Nuclide 12-90-G single-focusing instrument having a resolution capability of 10 000.

Column chromatography was performed using silica gel (MCB Grade 62) and TLC was performed on silica gel HF_{254} (E. Merck); the latter were usually developed with 1:1 or 4:1 hexane–EtOAc. Visualization of the TLC was effected by spraying with 2% ceric sulfate in 2 N sulfuric acid followed by brief heating; **4** and **6** gave the characteristic yellow color of enones (*4*). All reactions were monitored by TLC.

***3α,12α-Dinitroxy-7α-hydroxy-5β-cholan-24-oic* (1).** A mixture of cholic acid (100 g), benzene (660 mL), pyridine (170 mL), and acetic anhydride (170 mL) was allowed to stand at room temperature for 20 h (*5*). The mixture was poured into water and the benzene layer was washed several times with dilute HCl. The