Vapor Pressures and Thermodynamic Properties of Lanthanide Triiodides

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The vapor pressures of the stable lanthanide triiodides from CeI_3 to TmI_3 are measured in the Knudsen cell range. The vapor pressures of these compounds are all similar, with a variation of a factor of three between CeI_3 and TmI_3, the lowest and highest vapor pressures, respectively. The standard enthalpies of sublimation of these iodides do not decrease monotonically with the atomic number of the lanthanides. Thermodynamic properties of the lanthanide triiodides are derived from the vapor-pressure data.

Extensive measurements of the vapor pressures over the liquid trichlorides and dichlorides of the lanthanides have been reported by Russian workers (*16*). Some vapor-pressure measurements over solid lanthanide halides have also been reported (*17*). However, of the iodides, only the vapor pressures over LaI_3 (*17*), PrI_3 (*8, 17*), NdI_3 (*8, 17*), and EuI_2 (*7*) have been reported. Recent mass spectrometric studies (*9*) of the normally stable lanthanide triiodides, i.e., CeI_3, PrI_3, NdI_3, GdI_3, TbI_3, DyI_3, HoI_3, and ErI_3, showed these salts to evaporate congruently as the monomer in the low vapor-pressure, Knudsen cell range. The last stable triiodide, TmI_3, also evaporates congruently (*10*).

We now have measured the vapor pressures over all of the stable lanthanide triiodides, except that for LaI_3, and the complete results are summarized herein. The earlier results (*8*) for PrI_3 and NdI_3 also are included here. Our vapor pressures for the latter two triiodides were appreciably higher than those reported by Shimazaki and Niwa (*17*) who used silica effusion cells in their measurements. Corbett (*3*) has reported that lanthanide iodides react with silica at these measurement temperatures.

Experimental

Materials preparation. The triiodides presently measured were prepared by the direct reaction of the metal with iodine vapor, as previously described (*9*). The purity of the resublimed lanthanide iodides was at least 99.99%. The lanthanide metals and their iodides were all handled in a polyethylene glove bag in a helium or argon atmosphere. The oxygen concentration in the glove bag, as measured with a solid electrolyte oxygen gage, was maintained below 5×10^{-5} torr at all times. The iodides were always stored in sealed evacuated glass vials. These vials were opened only briefly in the glove bag during each vapor-pressure run.

Measurements. The effusion measurements were made on a Cahn microbalance, Model RH, with a sensitivity of 2 μg. The Knudsen cell was hung from the balance into the fused silica furnace tube by a 3-mil tungsten wire. The distance of the cell from the balance was approximately 30 in. A dummy tantalum rod, with a Chromel-Alumel thermocouple in contact, was hung approximately ⅛ in. from the Knudsen cell for temperature control and measurement. The thermocouple was previously calibrated at the melting points of KCl(776 C) and $PbCl_2$(501 C) and by comparison with a calibrated thermometer in hot water. A split-tube electric furnace controlled by a Wheelco Controller to ±2°C was used for heating the sample. A stainless-steel tube was placed in the core of the furnace to obtain better temperature distribution and to minimize electromagnetic effects with the balance system. In the latter regard, the silica furnace tube extending above the furnace was wrapped with aluminum foil. The isothermal zone in the split-tube furnace was determined to be approximately 3.5 in., and the Knudsen cell and the thermocouple were centered in this zone. The weight loss by effusion as a function of time was recorded on a Speedomax strip chart recorder operated at a speed of 0.50 in. per minute. The recorder was usually operated at 2.00 mg full scale.

The tantalum Knudsen cell had internal dimensions of ⁵⁄₁₆-in. i.d. × ⁹⁄₁₆-in. depth with a screw cap. A 0.003-in. thick disc with an appropriate orifice drilled in its center was placed over the mouth of the bottom piece of the cell, and the threaded cap was fitted tightly so that there was no leakage of vapor around the edge of the disc. The cap had an opening of ¼ in. in the center. The orifice diameters used in these measurements were 0.010, 0.020, and 0.040 in. The Clausing factor of each orifice was determined by calibration with zinc (semiconductor grade, 99.999% pure) by using the vapor-pressure data reported by Nesmeyanov (*14*). The Clausing factors determined from the Knudsen cell measurements of zinc were 0.935, 0.999, and 0.952, respectively, for orifice diameters of 0.010, 0.020, and 0.040 in. These factors could not be accurately calculated from the orifice geometry, assuming cylindrical orifices, because the edges of the orifices acquired a knife-edge effect on drilling and polishing the thin sheets near the orifices.

Details of the measurement and Knudsen cell loading procedures have been previously described (*8*). Approximately 20 points/100° interval were obtained for each compound. The measurements with each orifice were made at increasing and at decreasing temperatures.

Results

The vapor pressures of the lanthanide triiodides were calculated from the effusion rates of the monomeric species, i.e., $LnI_3(c) \rightarrow LnI_3(g)$, where Ln is the lanthanide. Table I summarizes the data for the compounds measured here. A semilog plot of the vapor pressure against $1/T$ gave a straight line with no dependence on orifice dimensions for all of the compounds. Also, the data obtained at increasing and at decreasing temperatures were indistinguishable.

The vapor pressures, in atmospheres, were all fitted to the usual vapor-pressure equation

$$\log P = -A/T + B \qquad (1)$$

by least-squares analyses. Table II summarizes the vapor-pressure equations for all of the lanthanide triiodides measured in this laboratory, and Figure 1 shows the vapor-pressure curves for pressures between 10^{-4} and 10^{-6} atm for the seven compounds measured in this

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Table I. Vapor Pressure, in Atmosphere, over LnI_3

Orifice diam, in.	K	$p \times 10^6$	Orifice diam, in.	K	$p \times 10^6$	Orifice diam, in.	K	$p \times 10^6$
	CeI_3			CeI_3			GdI_3	
0.020	927	1.485	0.040	952	4.872	0.010	939	3.468
	941	2.438		938	2.876		956	7.405
	958	5.033		927	1.689		968	10.73
	973	8.793		917	1.131		991	2.666
	987	15.14		904	0.6754		1005	45.31
	999	24.56		894	0.4785		1025	87.63
	1015	45.59		884	0.2820		1017	61.72
	937	2.904		870	0.1678		996	30.23
	927	1.605					979	16.27
	911	0.8642					965	8.414
	963	5.797					949	5.059
	980	10.18					917	1.046
	1007	24.94				0.020	929	1.708
0.040	906	0.7591					947	4.133
	914	1.089					965	9.480
	929	2.060					985	19.13
	946	3.938					1006	38.05
	959	5.287					981	16.98
	974	10.99					966	8.973
	986	17.05					946	4.680
	1000	31.04					928	1.945
	1000	30.23					912	1.950
	1011	46.14						
	964	7.907						
	TbI_3			DyI_3			DyI_3	
0.010	919	2.459	0.040	895	1.072	0.020	996	40.20
	931	4.905		908	1.810		1012	69.65
	950	7.596		922	3.145		1030	132.9
	995	42.19		939	5.549		1045	216.6
	979	26.62		957	10.77		1060	358.6
0.020	979	24.77		970	18.22		1018	80.12
	968	16.17		989	36.58		981	22.61
	959	12.25		1006	69.59		947	7.128
	951	8.817		1023	121.4		920	3.074
	937	5.386		971	19.03		900	1.433
	936	5.142		947	8.038		885	0.9169
	923	3.408		922	2.999			

work. The vapor-pressure curves for PrI_3 and NdI_3 (*8*) fall between those for GdI_3 and ErI_3. From the equations in Table I, we calculated the temperatures at which the vapor pressures would be 1 and 10^{-2} torr, and these temperatures are tabulated in Table III.

Figure 1 and Table III show that the vapor pressure of these triiodides are quite similar in the temperature range shown, and that there is only a threefold difference between the vapor pressures of CeI_3 and of TmI_3. Comparison with the limited number of solid trichlorides and tribromides measured by Shimazaki and Niwa (*17*) shows that the vapor pressures of the triiodides are approximately 5 and 15 times higher, respectively, than those of the tribromides and trichlorides. Recently, Hariharan and Eick (*7*) reported on the vapor pressure of EuI_2. From their vapor-pressure equation, the vapor pressure of $EuI_2(l)$ at 1000K is 1.8×10^{-7} atm. The vapor pressure of $SmI_2(l)$ (*10*) at the same temperature is 4.6×10^{-7} atm. Compared to the vapor pressures of these diiodides, that of $CeI_3(c)$ at 1000K is 2.56×10^{-5} atm. The vapor-pressure curves of these diiodides are nearly parallel to those of the triiodides in the above temperature region.

Thermodynamic properties. For the process $LnI_3(c) \rightarrow LnI_3(g)$, the enthalpies of sublimation were calculated from the equations in Table II. Table IV summarizes these sublimation enthalpies at the median measurement temperature. The free energies of sublimation were calculated from the equation $\Delta G_T = -RT \ln P$, where $\ln P$ was obtained from the vapor-pressure equations in Table II. Subsequently, the entropy of sublimation was obtained from $\Delta G_T = \Delta H_T - T\Delta S_T$.

The enthalpy of sublimation was extrapolated to 298K by the second law method since there is no satisfactory free energy function for the $LnI_3(g)$ to date. For the second law extrapolations, we ave utilized the recently reported $H_T - H_{298}$ and $S_T - S_{298}$ values of Dworkin and Bredig (DB) (*4*) for $LaI_3(c)$, $NdI_3(c)$, $GdI_3(c)$, and $TbI_3(c)$. For the enthalpies and entropies for all of the $LnI_3(g)$, we have interpolated the values reported by Krasnov and Danilova (KD) (*11*) for $LaI_3(g)$. The enthalpies of formation, $\Delta H_{f298}°$, of the $LnI_3(c)$, tabulated in Table V, are those reported by Feber (*5*). These latter values are probably accurate to within ±5 kcal/mol. The entropies, $S_{298}°$, of the $LnI_3(c)$ were obtained by summing the atomic contributions tabulated by Latimer (*12*) with the magnetic contributions tabulated by Westrum (*19*). These entropies are summarized in Table V and are estimated to be accurate to within ±3 eu. The confidence limits indicated for the quantities in Table IV are standard deviations derived from the vapor-pressure data. The extrapolated entropy and free energy of sublimation are estimated to be accurate to within ±3 eu and ±2 kcal/mol, respectively.

The method of calculation to obtain the thermodynamic

Table I. Continued

Orifice diam, in.	K	$p \times 10^6$	Orifice diam, in.	K	$p \times 10^6$	Orifice diam, in.	K	$p \times 10^6$
	TbI_3			DyI_3				
	911	1.907		900	1.358			
	910	1.934		885	0.7598			
	896	1.119		870	0.3852			
	889	0.8436		861	0.2078			
	883	0.7800		843	0.1197			
			0.020	879	0.7868			
				894	1.224			
				908	1.963			
				923	3.801			
				941	7.211			
				961	14.26			
				977	22.52			
	HoI_3			ErI_3			TmI_3	
0.020	924	2.139	0.010	1016	95.09	0.010	987	51.44
	938	4.370		1007	72.61		978	41.02
	952	8.063		996	56.70		964	22.37
	971	13.62		992	53.25		963	21.76
	986	19.48		983	30.05		953	15.35
	997	35.67		971	23.00		940	9.080
	1008	55.41		965	14.74		938	8.423
	1021	82.34		957	13.78		934	6.569
	1029	107.9		941	7.903		928	5.671
	1008	53.16		940	6.496	0.020	990	56.59
	986	25.50		924	4.122		955	15.59
	969	12.16	0.020	999	53.95		942	10.05
	950	5.074		986	33.26		910	2.292
	935	2.562		980	27.94		895	1.443
0.010	951	5.802		976	24.54		893	1.169
	968	11.98		961	14.38		878	0.7131
	982	20.23		955	10.86		874	0.5198
	996	33.88		945	8.120		867	0.5051
	1014	63.46		932	4.569			
	1026	98.21		930	4.345			
	1002	40.19		919	2.763			
	976	15.71		913	1.828			
	961	10.00		905	1.556			
				898	1.004			

Table II. Vapor Pressures of Lanthanide Triiodides Expressed as Log $P = -A/T + B$, Where P Is in Atmosphere

	A	B	Temp. range, K
CeI_3	14858 ± 222	10.27 ± 0.23	870–1015
PrI_3	15281 ± 302	10.87 ± 0.32	841–1032
NdI_3	15037 ± 125	10.63 ± 0.13	857–1037
GdI_3	16009 ± 273	11.55 ± 0.28	917–1025
TbI_3	14021 ± 231	9.70 ± 0.25	889–995
DyI_3	14085 ± 133	9.79 ± 0.14	843–1060
HoI_3	15586 ± 304	11.18 ± 0.31	924–1029
ErI_3	15122 ± 244	10.90 ± 0.25	898–1016
TmI_3	14952 ± 190	10.86 ± 0.21	867–990

Table III. Temperatures at Which Vapor Pressures are 10^{-2} and 1 Torr

	T, K	
	1	10^{-2} torr
CeI_3	1129	981
PrI_3	1111	970
NdI_3	1113	970
GdI_3	1109	974
TbI_3	1114	962
DyI_3	1112	960
HoI_3	1108	970
ErI_3	1097	958
TmI_3	1088	950

properties will be described in detail for CeI_3 only, with brief pertinent descriptions for the remaining triiodides. The method of computation for all of the compounds is identical.

CeI_3. The enthalpy of sublimation was extrapolated from 943 to 298K by utilizing the $H_T - H_{298}$ value for $NdI_3(c)$, reported by DB. Since CeI_3, PrI_3, and NdI_3 have very similar properties, it was assumed in the extrapolation that $CeI_3(c)$ has two crystal phases between these temperatures, similar to $NdI_3(c)$. The enthalpy of transformation was assumed identical to the 3.33 kcal/mol for $NdI_3(c)$ (*4*). Combination of the $H_T - H_{298}$ for the solid and the $H_T - H_{298}$ for $LaI_3(g)$ (*11*) with ΔH_T = 67.99 ± 1.02 kcal/mol yields $\Delta H_{S298}°$ = 75.8 ± 1.0 kcal/mol. The 298K values will be rounded off to the first decimal place because of the assumed enthalpies for the extrapolation. The present value is in fair agreement with the earlier (*9*) mass spectrometric value of 79 ± 5 kcal/mol. Feber (*5*) had estimated a value of $\Delta H_{S298}°$ = 77 kcal/mol. From our ΔH_{S298}, the heat of formation of $CeI_3(g)$ is $\Delta H_{f298}°$ = 82 kcal/mol.

Summation of $S_{298}°$, 54.9 eu, with the $S_T - S_{298}$ for

NdI_3(c) from DB, 34.2 eu, and the entropy of sublimation at 943K, 47.0 ± 1.1 eu, yields S_{943}° = 136.1 eu for CeI_3(g). This entropy was combined with the $S_T - S_{298}$ value of LaI_3(g), 22.1 eu, to obtain S_{298}° = 114.0 eu for CeI_3(g). The free energies and entropies of formation of the solid and gaseous triiodide at 298K, shown in Table V, were then obtained by utilizing the entropy data for cerium and iodine from Stull and Sinke (*18*). The free energy and entropy of sublimation at 298K are tabulated in Table IV.

***PrI*₃**. We earlier reported (*8*) a ΔH_{S298}° = 78.9 ± 1.5 kcal/mol for PrI_3. In this extrapolation we had utilized Brewer's (*1*) ΔCp = −14 cal/mol-deg. Presently, this sublimation enthalpy is corrected to ΔH_{S298}° = 77.7 ± 1.4 kcal/mol by utilizing the enthalpies of NdI_3(c) and LaI_3(g), reported by DB and KD, respectively. The values of Shimazaki and Niwa, 75.7 kcal/mol, and that of Feber's estimate, 76 kcal/mol, are in excellent agreement with our enthalpy of sublimation.

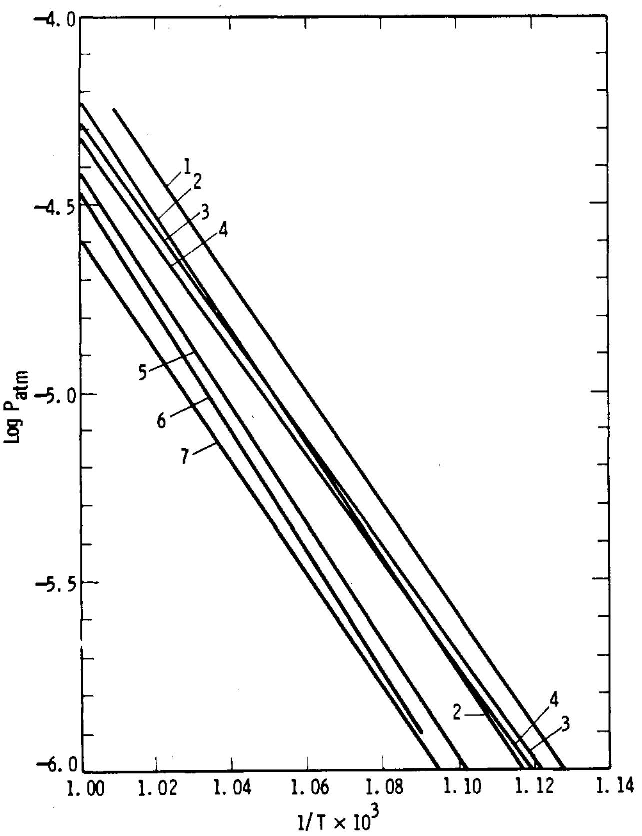

Figure 1. Vapor pressures of lanthanide triiodides: 1-TmI_3, 2-ErI_3, 3-DyI_3, 4-TbI_3, 5-HoI_3, 6-GdI_3, 7-CeI_3

The other thermodynamic properties of PrI_3 were obtained similarly to those described for CeI_3 and are tabulated in Tables IV and V. The entropy of PrI_3(g) at 937K is 139.4 eu.

***NdI*₃**. The earlier (*8*) ΔH_{S298}° = 77.9 kcal/mol, obtained by assuming ΔCp = −14 cal/deg-mol for the extrapolation, has been corrected to ΔH_{S298}° = 76.6 ± 0.6 kcal/mol by using the data of DB and KD. Shimazaki and Niwa's experimental value, 75.8 kcal/mol, is in excellent agreement with the present. Feber had estimated a value of 74.9 kcal/mol, based on the data by Shimazaki and Niwa.

The other thermodynamic properties are tabulated in Tables IV and V. The entropy of NdI_3(g) at 943K is 138.8 eu.

***GdI*₃**. Dworkin and Bredig determined the $H_T - H_{298}$ and $S_T - S_{298}$ for GdI_3(c). Combination of their data with those of KD for LaI_3(g) and our experimental heat of sublimation yields ΔH_{S298}° = 76.8 ± 1.2 kcal/mol. This value is appreciably higher than Feber's estimate of 70 kcal/mol and the mass spectrometric value of 70.5 ± 0.5 kcal/mol (*9*). The entropy of GdI_3(g) at 971K is 138.0 eu.

***TbI*₃**. The $H_T - H_{298}$ and $S_T - S_{298}$ for TbI_3(c) have been determined by DB. Combination of the enthalpy data of the solid and of LaI_3(g) with the experimental heat of sublimation yields ΔH_{S298}° = 68.0 ± 1.1 kcal/mol. Feber's estimate of 69.5 kcal/mol and the mass spectrometric value of 68.0 ± 0.5 kcal/mol are in excellent agreement with the present value. The entropy of TbI_3(g) at 942K is 129.0 eu.

***DyI*₃**. The melting points of the triiodides increase progressively from TbI_3 to TmI_3 (*2*). The former iodide undergoes a phase change at 1080K (*4*). No phase change data are available for the triiodides from DyI_3 to TmI_3. Since the vapor-pressure measurement temperatures for DyI_3 to TmI_3 are in similar ranges to that for TbI_3 (below a median temperature of 1000K), it will be assumed that the $H_T - H_{298}$ and $S_T - S_{298}$ data for TbI_3 are applicable for DyI_3 to TmI_3 without a phase change. This assumption should be valid since many properties of the second rare earth subgroup from Tb to Tm are similar.

The combination of the $H_T - H_{298}$ for TbI_3(c) and LaI_3(g) with the experimental heat of sublimation for DyI_3 at 951K gives ΔH_{S298}° = 68.4 ± 0.6 kcal/mol. The mass spectrometric value (*9*), 69.4 ± 1.6 kcal/mol, and Feber's estimate of 68.5 kcal/mol are in excellent agreement with the present value. The entropy of DyI_3(g) at 951K is 131.8 eu.

***HoI*₃**. The ΔH_{S298}° = 75.4 ± 1.4 kcal/mol for HoI_3, extrapolated similar to that for DyI_3, is in good agreement with the mass spectrometric value (*9*) of 72.5 ± 1.8

Table IV. Enthalpy of Reaction, Free Energy, and Entropy Changes for Reactions at *T* and 298K, Δ*H* and Δ*G* in kcal/mol, Δ*S* in eu

					298K		
Reaction	*T*, K	ΔH_T	ΔG_T	ΔS_T	ΔH_S°	ΔG_S°	ΔS_S°
CeI_3(c) → CeI_3(g)	943	67.99 ± 1.02	23.7 ± 1.0	47.0 ± 1.1	75.8 ± 1.0	58.0	59.1
PrI_3(c) → PrI_3(g)	937	69.93 ± 1.38	23.3 ± 1.4	49.7 ± 1.5	77.7 ± 1.4	59.0	61.7
NdI_3(c) → PrI_3(g)	943	68.81 ± 0.58	22.9 ± 0.6	48.6 ± 0.6	76.6 ± 0.6	59.0	60.8
GdI_3(c) → GdI_3(g)	971	73.22 ± 1.25	21.9 ± 1.2	52.8 ± 1.2	76.8 ± 1.2	59.0	59.0
TbI_3(c) → TbI_3(g)	942	64.16 ± 1.06	22.4 ± 1.1	44.3 ± 1.2	68.0 ± 1.1	53.0	50.0
DyI_3(c) → DyI_3(g)	951	64.45 ± 0.61	21.8 ± 0.6	44.8 ± 0.6	68.4 ± 0.6	53.0	52.0
HoI_3(c) → HoI_3(g)	976	71.29 ± 1.39	21.4 ± 1.4	51.1 ± 1.4	75.4 ± 1.4	58.0	58.1
ErI_3(c) → ErI_3(g)	957	69.17 ± 1.12	21.5 ± 1.1	49.8 ± 1.1	73.2 ± 1.1	56.0	57.0
TmI_3(c) → TmI_3(g)	929	68.39 ± 0.88	22.2 ± 0.9	49.7 ± 1.0	72.2 ± 0.9	55.0	57.0

kcal/mol. However, Feber's estimate of 68 kcal/mol is appreciably lower than our experimental result. The entropy of $HoI_3(g)$ at 976K is 139.0 eu.

ErI_3. The $\Delta H_{S298}° = 73.2 \pm 1.2$ kcal/mol was obtained by utilizing the $H_T - H_{298}$ for $TbI_3(c)$ and $LaI_3(g)$, together with the experimental enthalpy of sublimation at 957K. Our value is in fair agreement with the mass spectrometric value (*9*) of 69.4 ± 3.8 kcal/mol, but Feber's estimate of 67 kcal/mol is appreciably lower than the present experimental value. The entropy of $ErI_3(g)$ at 957K is 136.7 eu.

TmI_3. The experimental heat of sublimation was extrapolated to 298K by utilizing the $H_T - H_{298}$ data for $TbI_3(c)$ and $LaI_3(g)$ to obtain $\Delta H_{S298}° = 72.2 \pm 0.9$ kcal/mol. This value is appreciably higher than Feber's estimate at 66.5 kcal/mol. The entropy of $TmI_3(g)$ at 929K is 135.8 eu.

Discussion

The vapor pressures of the triiodides are appreciably higher than those of the corresponding bromides (*17*) chlorides (*17*), and fluorides (*20*), with the vapor pressures decreasing rapidly in the above order. This trend is expected as the covalent character of the halide increases in the order of $F^- < Cl^- < Br^- < I^-$. In fact, the lanthanide fluorides have very low volatility at temperatures in the region of 1000°C.

The second law enthalpies of sublimation at 298K, recorded in Table IV, should be accurate to within ±2 kcal/mol in view of the recent experimental enthalpies of the solid lanthanide triiodides reported by Dworkin and Bredig. The enthalpy of $LaI_3(g)$ which was used in this extrapolation should correspond very nearly to those of the other $LnI_3(g)$. However, it is still of interest to ascertain the accuracy of the $\Delta H_{S298}°$ by the third law extrapolation when spectroscopic and molecular data become available for these triiodides. Some of the thermodynamic data reported here should be taken as tentative, in view of the lack of accurate heats of formation for the $LnI_3(c)$.

It has been the general consensus that the standard enthalpies of sublimation of the lanthanide trihalides should decrease monotonically with the atomic number of the lanthanide. For the trichlorides, Polyachenok and Novikov (*15*) report such a monotonic decrease in the standard enthalpies of sublimation. In Feber's estimates of the enthalpies of sublimation of the lanthanide halides, he assumed such a decrease with atomic number of the lanthanide. However, as shown in Figure 2, the standard enthalpies of sublimation of the lanthanide triiodides do not decrease monotonically with the atomic number. In Figure 2 the dashed line through the sublimation enthalpies for PmI_3, SmI_3, and EuI_3 are taken from Feber's estimated data.

An insight to the trend in $\Delta H_S°$ perhaps may be visualized by considering the Born-Haber Cycle for these triiodides. From this cycle the sublimation enthalpy may be expressed as:

$$\Delta H_S[LnX_3] = U - \Delta H_S[Ln] + \Delta H_f[LnX_3(g)] - I_1 - I_2 - I_3 - 3/2\,D[X_2] + 3\,E[X] + 4\,RT \quad (2)$$

where $\Delta H_S[LnX_3]$ and $\Delta H_S[Ln]$ are the sublimation enthalpies of the triiodide and metal, respectively, $\Delta H_f[LnX_3(g)]$ is the enthalpy of formation of the gaseous triiodide, U is the lattice energy of the iodide, $D[X_2]$ and $E[X]$ are the dissociation energy of the iodine molecule and the electron affinity of the iodine atom, respectively, and the I_n are the nth ionization potentials of the lanthanides. The enthalpy of sublimation of the metal (*6*) may be combined with the ionization potentials (*13*), $\Sigma = \Delta H_S[Ln] + \Sigma I_n$, and Equation 2 may be rewritten:

$$\Delta H_S[LnX_3] = U - \Sigma + \Delta H_f[LnX_3(g)] + C \quad (3)$$

where C is identical for all of the lanthanide iodides. Figure 2 also shows a plot of Σ as a function of the atomic number of the lanthanides. Since the ionization potentials of Pm are not known, a dashed line is drawn between Nd and Sm. The enthalpy of formation of the $LnI_3(g)$ is derived from the enthalpy of sublimation of the triiodides, and the enthalpies of formation of the $LnI_3(c)$ decrease monotonically with the atomic number of the lanthanide.

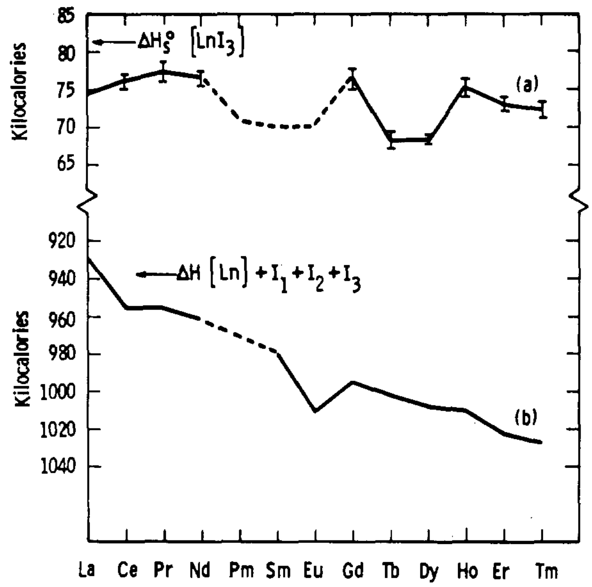

Figure 2. (a) Enthalpies of sublimation of lanthanide triiodides and (b) sum of ionization potentials and sublimation enthalpy of lanthanides as functions of atomic number

Table V. Thermodynamic Properties of Lanthanide Triiodides at 298K, $\Delta H_f°$ and $\Delta G_f°$ in kcal/mol, $\Delta S_f°$ and $S°$ in eu

	Solid				Gas			
	$-\Delta H_f°$[a]	$-\Delta G_f°$	$-\Delta S_f°$	$S°$	$-\Delta H_f°$	$-\Delta G_f°$	$\Delta S_f°$	$S°$
CeI_3	158	157	3.6	54.9	82	99	55.5	114.0
PrI_3	157	156	3.6	55.7	79	97	58.1	117.4
NdI_3	152	151	3.4	56.0	75	92	57.4	116.8
GdI_3	145	144	1.8	55.9	68	85	57.2	114.9
TbI_3	143	142	2.4	56.9	75	89	47.6	106.9
DyI_3	140.5	140	2.3	57.4	72	87	49.7	109.4
HoI_3	139	138	2.2	57.6	64	80	55.9	115.7
ErI_3	137	136	2.2	57.1	64	80	54.8	114.1
TmI_3	135.5	135	2.2	57.1	63	80	54.8	114.1

[a] Ref. *5*.

It appears, therefore, that the variations in the enthalpy of sublimation depend primarily on the lattice energy of the solid iodides.

Conclusions

The vapor pressures of all of the lanthanide triiodides are similar in the Knudsen cell range. The difference between that for CeI_3, the lowest, and that for TmI_3, the highest, is only threefold. The vapor pressures of the triiodides are appreciably higher than the more ionic bromides, chlorides, and fluorides.

Contrary to the usual consensus, the enthalpies of sublimation do not decrease monotonically with the atomic number of the lanthanides.

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Polymorphic Effects of Chloramphenicol Palmitate on Thermodynamic Stability in Crystals and Solubilities in Water and in Aqueous Urea Solution

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The differences in enthalpy and Gibbs free energy between α- and β-forms of crystalline chloramphenicol palmitate are determined in the temperature range of 36–130°C. A radiotracer method is applied for determining extremely low solubilities of the tritiated crystals in contact with water and 4 mol/l. urea solution at 20–35°C. All these results are discussed from the aspect of regular solution treatment, taking account of different sizes and shapes of these molecules in a polymorphic relationship.

For a quantitative understanding of the nature of insoluble monolayers at air–water interfaces, much information is needed on the thermodynamic data of the monolayer-composing compounds in three-dimensional crystals and in aqueous solutions (*8*). It has been shown previously (*9*) that the time-dependent character of the monolayer of chloramphenicol palmitate (CPP) is explicable by the conformational change of cis- → trans-molecules in two-dimensional crystal and that the change may correspond to the polymorphic transformation of CPP-$\alpha \rightarrow$ -β in three-dimensional crystal (*2, 17, 18*). These results are in qualitative agreement with the experimental results on crystalline structure (*1, 17, 18*), latent heat of fusion (*3, 15*), and dilatometric behavior (*2*) of CPP crystals. However, few papers have yet dealt with the thermodynamic stabilities of CPP in its crystalline states; nor has it been clarified where the transition temperature for $\alpha \rightleftarrows \beta$ transformation exists.

Additional information is definitively required on the interaction energy between CPP and water molecules, which is obtainable from the solubility data of CPP in aqueous media. Generally, however, the solubility in water is predicted to be so low as to make it possible to obtain stable monolayers on aqueous subphases. For such a sparingly soluble compound, it is always a problem to confirm the equilibrium for obtaining the solubility C_s from a gradual increase of concentration C with time t elapsed from the first contact of the solute substance with the solvent (*11, 12*). The flat portion of the $C \sim t$ relationship can hardly be determined. The ampul method (*16*) is not applicable to a sparingly soluble substance because of the perplexity in confirming the disappearance of an excess amount of the solute under a constant rate of temperature rise or at a constant temperature with varied time.

Krause and Lange (*10*) proposed a method based on the asymptotic approach of $C \sim t$ curves for under- and super-saturated solutions. For CPP, however, the polymorphic effect may cause incomplete merging of the two curves. It would be more reasonable to estimate C_s by putting $t = \infty$ in an appropriate rate equation for the dissolution process (*4–6*). Such an extrapolation method has been applied in the present study to determine the solubilities of CPP-α and -β in aqueous media by means of the radiotracer technique.

Experimental

Materials. The sample of CPP-^{3}H (Figure 1) was synthesized by condensation (*9*) of chloramphenicol and palmityl-2,3-^{3}H chloride, which was obtained by chlorination of the tritiated product of hexadecenoic acid (*14*).

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