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Vaporization of $DyI_3(s)$ and thermochemistry of the homocomplexes $(DyI_3)_2(g)$ and $(DyI_3)_3(g)$

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Abstract

The vaporization of $DyI_3(s)$ was investigated in the temperature range between 833 and 1053 K by the use of Knudsen effusion mass spectrometry. The ions DyI_2^+, DyI_3^+, $Dy_2I_4^+$, $Dy_2I_5^+$, $Dy_3I_7^+$, and $Dy_3I_8^+$ were detected in the mass spectrum of the equilibrium vapor. The gaseous species DyI_3, $(DyI_3)_2$, and $(DyI_3)_3$ were identified and their partial pressures determined. Enthalpies and entropies of sublimation resulted according to the second- and third-law methods. The following sublimation enthalpies at 298 K were determined for the gaseous species given in brackets: $274.8\pm8.2\ \mathrm{kJ\,mol^{-1}}$ [DyI_3], $356.0\pm11.3\ \mathrm{kJ\,mol^{-1}}$ [$(DyI_3)_2$], and $436.6\pm14.6\ \mathrm{kJ\,mol^{-1}}$ [$(DyI_3)_3$]. The enthalpy changes of the dissociation reactions $(DyI_3)_2 = 2\,DyI_3$ and $(DyI_3)_3 = 3\,DyI_3$ were obtained as $\Delta_d H^\circ(298) = 193.3\pm5.6$ and $390.3\pm13.0\ \mathrm{kJ\,mol^{-1}}$, respectively.

Keywords: Vaporization; Thermodynamics; DyI_3; Enthalpy of vaporization; Knudsen effusion mass spectrometry

1. Introduction

Increased industrial application of rare earth halides has made the study of their vaporization characteristics increasingly important. Earlier mass spectrometric studies of the lanthanide rare earth halides concentrated on the fluorides [1,2], chlorides ([3] and references quoted therein) and bromides ([4,5] and references quoted therein). Knowledge of metal iodides and bromides has been increased by our vaporization studies, which were summarized in a recent review article [6]. Interest in rare earth iodide vapors is stimulated by their use as additives in high-pressure metal halide lamps, which show high efficiency and good color rendering [7].

Vapor pressures and mass spectra of the lanthanide triiodides from CeI_3 to TmI_3 were first reported by Hirayama and co-workers [8–10]. Some mass spectrometric studies indicated no polymerization in the rare earth triiodide vapors [8,9]. Kaposi et al. [11] identified dimer species in the DyI_3 vapor and studied for the first time the thermodynamics of $(DyI_3)_2(g)$ by means of Knudsen effusion mass spectrometry.

The present paper reports on a mass spectrometric study of the vaporization and gas phase chemistry of DyI_3. The trimer species $(DyI_3)_3(g)$ was observed for the first time and its thermochemical properties determined. More precise thermodynamic data were obtained for the monomer and dimer gaseous species $DyI_3(g)$ and $(DyI_3)_2(g)$. Reaction enthalpies were determined using the second- and third-law methods. Molecular parameters of the gaseous species were estimated and their thermodynamic functions computed using statistical thermodynamics.

2. Experimental

The measurements were carried out with a substantially modified single-focusing CH5 mass spectrometer [12] (Finnigan MAT, Bremen, Germany), which was equipped with a Knudsen cell machined from molybdenum. The knife-edged effusion orifice had a diameter of 0.8 mm. Temperatures were measured with a chromel/alumel thermocouple calibrated at the melting point of silver. The

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Table 1
Ion intensities corrected for isotopic distribution in counts per s determined upon vaporizing DyI_3(s) in the course of run 2, and assignment of the ions to their neutral precursors

T (K)	DyI_3(g)		$(DyI_3)_2$(g)		$(DyI_3)_3$(g)	
	DyI_2^+	DyI_3^+	$Dy_2I_4^+$	$Dy_2I_5^+$	$Dy_3I_7^+$	$Dy_3I_8^+$
1053	1.93×10^5	1.35×10^5	3.89×10^3	6.73×10^4	1.65×10^2	8.16×10^2
1043	1.39×10^5	9.66×10^4	2.67×10^3	4.30×10^4	9.90×10^1	4.79×10^2
1033	1.02×10^5	7.21×10^4	1.85×10^3	2.95×10^4	6.34×10^1	2.85×10^2
1023	7.43×10^4	5.39×10^4	1.21×10^3	1.91×10^4	4.39×10^1	1.83×10^2
1013	5.45×10^4	4.12×10^4	8.41×10^2	1.32×10^4	2.87×10^1	1.15×10^2
1003	4.01×10^4	3.06×10^4	5.77×10^2	8.98×10^3	1.92×10^1	7.06×10^1
993	2.92×10^4	2.33×10^4	3.92×10^2	5.98×10^3	1.19×10^1	4.38×10^1
983	2.18×10^4	1.70×10^4	2.70×10^2	4.02×10^3		2.78×10^1
973	1.59×10^4	1.24×10^4	1.79×10^2	2.67×10^3		1.69×10^1
963	1.14×10^4	9.25×10^3	1.21×10^2	1.80×10^3		1.10×10^1
953	8.09×10^3	6.66×10^3	8.10×10^1	1.17×10^3		6.39
943	6.29×10^3	5.18×10^3	5.88×10^1	8.04×10^2		4.68
933	4.56×10^3	3.75×10^3	3.95×10^1	5.61×10^2		2.72
923	3.17×10^3	2.61×10^3	2.58×10^1	3.59×10^2		1.50
913	2.18×10^3	1.88×10^3	1.58×10^1	2.22×10^2		0.84
903	1.57×10^3	1.36×10^3	1.03×10^1	1.51×10^2		
893	1.07×10^3	9.25×10^2	6.27	8.98×10^1		
883	7.60×10^2	6.53×10^2	3.46	5.61×10^1		
873	4.96×10^2	4.37×10^2	2.66	3.37×10^1		
863	3.67×10^2	3.22×10^2		2.35×10^1		
853	2.28×10^2	2.24×10^2		1.41×10^1		
843	1.54×10^2	1.40×10^2		7.21		
833	1.02×10^2	8.70×10^1		4.26		

vapor species were ionized with an emission current of 82 mA and an electron energy of 15–17 eV.

The DyI_3(s) (nominal purity 99.9 mass%) used for the measurements was supplied by Cerac Inc., Milwaukee, USA. Three independent runs were carried out. The ion intensities obtained in the course of run 2 are given in Table 1 as an example. The temperature range and the number of measurement temperatures of each run are given in Table 2.

3. Results

3.1. Ions observed in the mass spectrum and their assignment to neutral precursors

The ions observed by the ionization of the different gaseous species in the equilibrium vapor over DyI_3(s), and the assignment to their neutral precursors are shown in

Table 2
Partial pressures of $(DyI_3)_n$(g) ($n = 1, 2, 3$) over DyI_3(s) obtained in all the runs (partial pressures at 1000 K are given for comparison)

i	Run	I[a]	ΔT (K)[b]	$\ln p(i)$ (Pa) $= -A/T + B$ A[c]	B[c]	$p(i)$ (Pa)[d] at 1000 K
DyI_3(g)	1	12	833–1053	30950 ± 92	32.417 ± 0.099	4.3
	2	23	833–1053	30160 ± 124	31.576 ± 0.131	4.1
	3	23	833–1053	30814 ± 120	32.274 ± 0.129	4.3
Selected			833–1053	30641 ± 424	32.089 ± 0.449	4.3
$(DyI_3)_2$(g)	1	12	833–1053	39789 ± 166	38.877 ± 0.177	0.40
	2	23	833–1053	38649 ± 214	37.649 ± 0.228	0.37
	3	23	833–1053	39803 ± 182	38.851 ± 0.196	0.39
Selected			833–1053	39414 ± 661	38.459 ± 0.705	0.39
$(DyI_3)_3$(g)	1	8	913–1053	48676 ± 613	42.642 ± 0.624	2.4×10^{-3}
	2	15	913–1053	47018 ± 534	40.917 ± 0.546	2.2×10^{-3}
	3	15	913–1053	47433 ± 497	41.343 ± 0.504	2.3×10^{-3}
Selected			913–1053	47709 ± 864	41.634 ± 0.896	2.3×10^{-3}

[a] Number of the measurement temperatures.
[b] Temperature range of run.
[c] Errors are standard deviations.
[d] Estimated probable overall errors of partial pressures are: ±32% for DyI_3, ±47% for $(DyI_3)_2$, and ±54% for $(DyI_3)_3$.

Table 1. The assignment of the ions was carried out on the basis of the following rules: (a) ions originating from the same neutral precursor often show similar temperature dependencies; (b) it is often observed [13] that upon ionizing metal halide vapor species M_mX_n by electron impact one halogen atom is split off thereby forming abundant $M_mX_{n-1}^+$ ions. In many cases, especially for large homocomplexes, the ion $M_mX_n^+$ formed by simple ionization is not detected. The assignment of the ions was, in addition, verified by the appearance potential measurements of different ions carried out in [11].

3.2. Partial pressures

The ion intensities belonging to the mass spectrum of the equilibrium vapor of DyI_3(s) at the temperature T are related to the partial pressure $p(i)$ of the species i by the relation [14]:

$$p(i) = \left\{ \frac{kT \sum I(i)}{\sigma(i)} \right\} \tag{1}$$

where k and $\sum I(i)$ are, respectively, the pressure calibration factor and the sum of the intensities of the ions originating from the same neutral precursor i. $\sigma(i)$ is the relative ionization cross section of the species i.

The pressure calibration factor was calculated for each run by Eq. (2) which can be derived from Eq. (1) as

$$k = \frac{p_{\text{total}}}{943} \Big/ \left(\frac{\sum I(m)}{\sigma(m)} + \sqrt{2}\frac{\sum I(d)}{\sigma(d)} + \sqrt{3}\frac{\sum I(t)}{\sigma(t)} \right) \tag{2}$$

The ion intensities $I(i)$ of the species i at the mean temperature of 943 K result from interpolation and the total equilibrium pressure of DyI_3(s) at 943 K, $p_{\text{total}} = 0.72$ Pa, was determined in [10] by using the mass-loss Knudsen effusion technique. The symbols m, d, and t denote the monomer DyI_3(g), the dimer $(DyI_3)_2$(g), and the trimer $(DyI_3)_3$(g), respectively. The relative ionization cross section of the monomer was assumed as $\sigma(m) = 1$. Those of the dimer, and trimer species were estimated as $\sigma(d) = 1.5$, and $\sigma(t) = 2.25$ by using the empirical rule $\sigma[(DyI_3)_n] = 0.75 \sum \sigma(m)$ [14] ($n = 2, 3$). The value of $k = 6.20 \times 10^{-8}$ Pa K^{-1} s resulted, for example, for the pressure calibration factor of run 2 given in Table 1.

Partial pressures were evaluated by Eq. (1) for each measurement temperature. Fig. 1 presents the partial pressures over DyI_3(s) at different temperatures determined in run 2. Equations for the partial pressures resulted by a least squares computation for each individual run and are shown in Table 2. Selected equations were obtained by the computation of mean values of the coefficients A and B determined for the individual runs. The probable overall errors for the partial pressures at 1000 K given in Table 2 are valid for the temperature range of the measurements listed additionally.

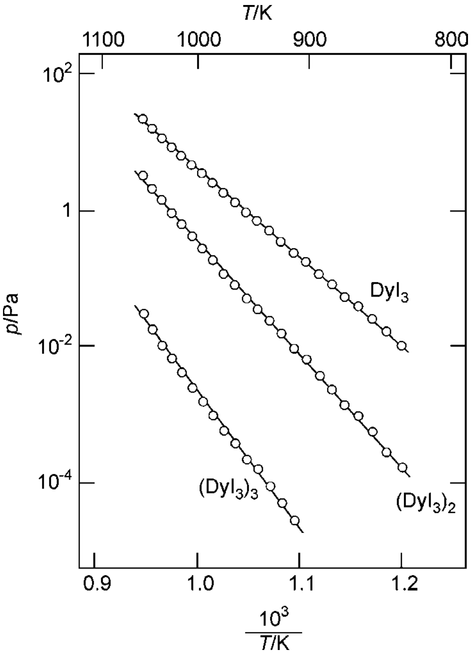

Fig. 1. Partial pressures of the gaseous species over DyI_3(s) at different temperatures obtained in run 2.

3.3. Estimations of the thermodynamic functions of the gaseous species $(DyI_3)_n$, $n = 1, 2, 3$

Despite great interest and significant experimental efforts, discrepancies still remain in the published data concerning the geometrical configuration, the structural parameters, and the vibrational frequencies of the LnX_3 molecules, Ln, lanthanide; X, halogen [3]. Both, pyramidal C_{3v} and planar D_{3h} geometries have been proposed for these molecules in recent investigations [15,16]. No experimental data are available for the structure of the dimeric and trimeric species of LnX_3. The geometry and the vibrational frequencies of DyI_3(g) used to compute the thermodynamic functions of this molecule are taken from [17]. The computation was carried out assuming a doublet electronic ground state.

The dimer and trimer species are expected to have ring structures of D_{2h} and D_{3h} symmetry, respectively, which are commonly accepted for metal halides [18]. The geometry of the molecule was estimated according to assumptions adopted elsewhere [19,20]. Generally, the bond distance of the terminal bond is taken to be equal to that of the monomer and the bond distance of the bridge bond is lengthened by an amount resulting from the comparison of the experimentally known geometries of monomers and dimers. The estimation of frequencies is based on the assumption that the stretching force constant of the terminal bond equals that of the monomer, f_r, while the force constant of the bridge bond is $f_r/2$. The bending force constants of the dimer were assumed to be the same as those of the monomer; those of the trimer were properly scaled from the dimer values.

The terminal and bridge Dy–I bond distances in $(DyI_3)_2$(g) were found to be 2.82 and 3.08 Å and the I–Dy–I bond angles as 109° (terminal) and 115° (ring), respectively. The following vibrational frequencies (cm^{-1}) of the dimer, computed using Wilson's F, G matrix method [21] are obtained: A_g (194, 126, 87, 44); A_u (30); $B_{1\mathrm{g}}$ (154, 55); $B_{2\mathrm{g}}$ (174, 45); $B_{3\mathrm{g}}$ (71); $B_{1\mathrm{u}}$ (194, 20, 19); $B_{2\mathrm{u}}$ (126, 46); $B_{3\mathrm{u}}$ (176, 103, 77). Regarding the spin multiplicity of the molecule, calculations were carried out assuming either a singlet or a triplet state.

The structure of $(\mathrm{DyI_3})_3$(g) was assumed by analogy with that of the trimer of $\mathrm{ReCl_3}$ [22]. The terminal and bridge Dy–I bond distances are estimated as 2.82 and 3.08 Å, respectively, and the terminal and bridge I–Dy–I angles as 109 and 174°, respectively. The vibrational frequencies of the molecule (cm^{-1}) are distributed as follows: A_1' (177*, 171, 166, 162*), A_2' (159*, 141), A_2'' (112, 80*, 75), A_1'' (70*), E' (65*, 62, 60*, 54, 51, 45), and E'' (35*, 30, 25*, 20*), (*) denotes doubly degenerate modes. The trimer was assumed to exist either in the quadruplet or doublet electronic state.

The thermodynamic functions of the gaseous species computed by the use of the estimated molecular parameters are reported in Table 3.

3.4. Thermodynamic properties

The equilibrium constant K_p° and the enthalpy and entropy changes of the sublimation and dissociation reactions shown in Table 4 were obtained from the partial pressures by equation

$$K_p^\circ = \left[\frac{p(i)}{p^\circ}\right]^{\nu_i} \tag{3}$$

and

$$\ln K_p^\circ = -\frac{A}{T} + B \tag{4}$$

where $p^\circ = 101{,}325\,\mathrm{Pa}$, ν_i is the stoichiometric coefficient, $A = \Delta_\mathrm{r}H^\circ(T_\mathrm{m})/R$, and $B = \Delta_\mathrm{r}S^\circ(T_\mathrm{m})/R$. T_m is the mean temperature of the study. The coefficients A and B were obtained by a least squares computation. Enthalpies and entropies of the reactions at 298 K (Table 4) were computed from those at the mean temperature T_m by using the enthalpy and entropy increments for $\mathrm{DyI_3}$(s) from [23] and for the gaseous species $(\mathrm{DyI_3})_n$, $n = 1, 2, 3$ from Table 3, which were obtained as described in the previous section.

The enthalpy change of the reactions in Table 4 determined as described above by the second-law method, were additionally obtained according to the third-law method by the following equation:

$$\Delta_\mathrm{r}H^\circ(298\,\mathrm{K}) = -T\left\{R\ln K_p^\circ + \frac{\Delta_\mathrm{r}[G^\circ(T) - H^\circ(298)]}{T}\right\} \tag{5}$$

$\Delta[G^\circ(T) - H^\circ(298)]/T$ is the change of the Gibbs energy function for the reaction considered, obtained from the data of $\mathrm{DyI_3}$(s) [23] and of the gaseous species $(\mathrm{DyI_3})_n$ (Table 3). Use of two more recent estimations of the entropy increment for $\mathrm{DyI_3}$(s) reported in [24,25] resulted in large discrepancies between obtained second- and third-law enthalpies. For this reason, the values were not considered in the present study.

The computation was carried out for each measurement temperature. Table 5 shows in detail the results of the third-law evaluation for the data of run 2. The mean values

Table 3
Thermochemical functions for $(\mathrm{DyI_3})_n$, n = 1, 2, 3, evaluated from the estimated molecular parameters (see text)

T (K)	Species					
	$\mathrm{DyI_3}$(g), multiplicity = 2[a]		$(\mathrm{DyI_3})_2$(g), multiplicity = 3[b]		$(\mathrm{DyI_3})_3$(g), multiplicity = 4[c]	
	C_p° ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$-[G^\circ(T) - H^\circ(298)]/T$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	C_p° ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$-[G^\circ(T) - H^\circ(298)]/T$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	C_p° ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$-[G^\circ(T) - H^\circ(298)]/T$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
298.15	81.158	399.80	179.30	653.49	277.72	887.7
300	81.182	399.81	179.34	653.50	277.78	887.7
400	82.024	403.00	180.88	660.55	279.89	898.7
500	82.422	409.06	181.60	673.92	280.89	919.3
600	82.640	415.87	182.00	688.93	281.43	942.6
700	82.773	422.70	182.24	704.00	281.76	965.9
800	82.859	429.32	182.40	718.57	281.98	988.4
900	82.918	435.61	182.50	732.44	282.12	1009.9
1000	82.961	441.57	182.58	745.57	282.23	1030.2
1100	82.992	447.20	182.64	757.98	282.31	1049.4
1200	83.016	452.53	182.68	769.70	282.37	1067.5
1300	83.035	457.56	182.71	780.79	282.41	1084.6
1400	83.050	462.34	182.74	791.30	282.45	1100.9
1500	83.062	466.87	182.76	801.29	282.48	1116.3

[a] $S^\circ(298\,\mathrm{K}) = 399.80\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $H^\circ(298\,\mathrm{K}) - H^\circ(0\,\mathrm{K}) = 20.456\,\mathrm{kJ\,mol^{-1}}$.

[b] $S^\circ(298\,\mathrm{K}) = 653.50\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $H^\circ(298\,\mathrm{K}) - H^\circ(0\,\mathrm{K}) = 45.26\,\mathrm{kJ\,mol^{-1}}$.

[c] $S^\circ(298\,\mathrm{K}) = 887.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $H^\circ(298\,\mathrm{K}) - H^\circ(0\,\mathrm{K}) = 70.16\,\mathrm{kJ\,mol^{-1}}$.

Table 4
Enthalpy and entropy changes of the different sublimation and dissociation reactions obtained in different runs by use of second- and third-law method

No.	Reaction	Second-law			Third-law: $\Delta_r H^\circ(298\,\mathrm{K})$[a] ($\mathrm{kJ\,mol^{-1}}$)	Selected: $\Delta_r H^\circ(298\,\mathrm{K})$ ($\mathrm{kJ\,mol^{-1}}$)[b]
		Run	$\Delta_r H^\circ(298\,\mathrm{K})$[a] ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_r S^\circ(298\,\mathrm{K})$[a] ($\mathrm{J\,mol^{-1}\,K^{-1}}$)		
1	$DyI_3(s) = DyI_3(g)$	1	276.9 ± 0.8	199.5 ± 0.8	278.2 ± 0.2	274.8 ± 8.2[c]
		2	270.3 ± 1.0	192.5 ± 1.1	278.2 ± 0.6	
		3	275.8 ± 1.0	198.3 ± 1.1	278.2 ± 0.4	
Mean			274.3 ± 8.8[c]	196.8 ± 10.1[c]	278.2 ± 23.4[c]	
2	$2DyI_3(s) = (DyI_3)_2(g)$	1	359.2 ± 1.4	259.7 ± 1.5	355.4 ± 0.9	356.0 ± 11.3[c]
		2	349.7 ± 1.8	249.5 ± 1.9	355.6 ± 0.9	
		3	359.3 ± 1.5	259.5 ± 1.6	355.7 ± 0.9	
Mean			356.1 ± 12.1[c]	256.2 ± 13.4[c]	355.6 ± 32.4[c]	
3	$3DyI_3(s) = (DyI_3)_3(g)$	1	444.7 ± 5.1	304.8 ± 5.2	435.4 ± 1.3	436.6 ± 14.6[c]
		2	430.9 ± 4.4	290.6 ± 4.5	435.6 ± 1.0	
		3	434.4 ± 4.1	294.0 ± 4.2	435.7 ± 1.0	
Mean			436.7 ± 15.4[c]	296.5 ± 16.8[c]	435.6 ± 46.8[c]	
4	$(DyI_3)_2(g) = 2\ DyI_3(g)$	1	194.6 ± 1.8	139.4 ± 2.0	201.0 ± 0.7	193.3 ± 5.6[c]
		2	191.0 ± 0.7	135.6 ± 0.7	200.8 ± 0.7	
		3	192.3 ± 1.6	137.1 ± 1.7	200.7 ± 0.8	
Mean			192.6 ± 5.9[c]	137.4 ± 7.9[c]	200.8 ± 19.3[c]	
5	$(DyI_3)_3(g) = 3\ DyI_3(g)$	1	381.7 ± 3.8	293.8 ± 3.8	399.0 ± 0.8	390.3 ± 13.0[c]
		2	398.2 ± 2.5	309.8 ± 2.5	399.9 ± 0.5	
		3	386.4 ± 3.5	298.9 ± 3.6	398.7 ± 0.7	
Mean			388.8 ± 14.1[c]	300.8 ± 16.1[c]	399.2 ± 34.3[c]	

[a] Errors are standard deviations.
[b] Weighted average of the second-law and third-law values.
[c] Errors are probable overall errors.

Table 5
Third-law evaluation of the enthalpy changes for the reactions 1–5 in Table 4, obtained in run 2

T (K)	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5
$\Delta_r H^\circ(298\,\mathrm{K})$ ($\mathrm{kJ\,mol^{-1}}$)					
1053	277.4	353.3	433.1	201.4	398.9
1043	278.0	354.4	434.3	201.6	399.6
1033	278.3	354.8	435.4	201.8	399.4
1023	278.6	355.6	435.6	201.6	400.1
1013	278.7	355.8	436.0	201.6	400.0
1003	278.8	356.6	436.4	201.7	400.1
993	278.9	356.4	436.6	201.4	400.0
983	278.9	356.5	436.5	201.3	400.1
973	279.0	356.7	436.7	201.3	400.1
963	278.9	356.7	436.2	201.2	400.5
953	279.0	356.6	436.6	201.3	400.5
943	278.4	356.5	435.0	200.4	400.2
933	278.3	355.9	435.1	200.6	399.6
923	278.4	355.9	435.4	200.8	399.6
913	278.3	356.1	435.6	200.6	399.3
903	278.0	355.5		200.6	
893	278.1	355.8		200.4	
883	277.8	355.6		200.0	
873	277.9	355.6		200.2	
863	277.2	354.4		199.9	
853	277.2	354.3		200.0	
843	277.2	355.1		199.2	
833	277.2	354.8		199.6	
Mean[a]	278.2 ± 0.6	355.6 ± 0.9	435.6 ± 1.0	200.8 ± 0.7	399.9 ± 0.5

[a] Errors are standard deviations.

of the third-law enthalpies obtained for each measurement temperature of a run are additionally incorporated in Table 4. Selected values resulted by computing the weighted average from the second- and third-law values.

4. Discussion

There is good agreement between the results of the three independent runs as well as between the results obtained according to the second- and third-law methods as shown in Table 4. This agreement shows the reproducibility and accuracy of the data of the present study. However, the agreement for reactions 1–3, involving the condensed phase was only found if the Gibbs energy function of DyI_3(s) derived from the estimated data in [23] was used. The value of the standard entropy of DyI_3(s) is reported in [23] as $S°(298\,K) = 197\,J\,mol^{-1}\,K^{-1}$. Significantly higher values of $S°(298\,K) = 227\,J\,mol^{-1}\,K^{-1}$ [24] and $S°(298\,K) = 237\,J\,mol^{-1}\,K^{-1}$ [25] are reported in the literature at a later date. Using the Gibbs energy function of DyI_3(s) in [24], the differences of the second- and third-law enthalpy values of reactions 1–3 in Table 4 resulted as 26, 60, and 137 kJ mol^{-1}, respectively. The third-law values obtained for reactions 4 and 5 by the use of the same functions agreed within 8.2 and 45 kJ mol^{-1} with the corresponding second-law enthalpies since only gaseous species are involved in these reactions. This shows that the standard entropies of DyI_3(s) in [24,25] are probably too high. The estimated thermodynamic functions of solid DyI_3 reported in [23] were, therefore, selected for the final evaluation yielding the data shown in Table 4. Spin multiplicities of three ($(DyI_3)_2$) and of four ($(DyI_3)_3$) were adopted for the dimer and trimer species given in parenthesis since a good agreement between the second- and third-law enthalpies was obtained with these values.

The sublimation enthalpy of the monomer species DyI_3(g) obtained in [11] as $\Delta_{sub}H°(298\,K) = 292 \pm 12\,kJ\,mol^{-1}$ is somewhat higher as compared to the present study. Better agreement can be found for the sublimation enthalpy of the dimer species $(DyI_3)_2$ determined in [11] as $\Delta_{sub}H°(298\,K) = 365 \pm 16\,kJ\,mol^{-1}$ and in the present study as $356.0 \pm 11.3\,kJ\,mol^{-1}$. The thermodynamic properties determined for the trimer species $(DyI_3)_3$ in this work were obtained for the first time.

Only a few reliable experimental data on the thermodynamics of the lanthanide halide dimer species can be found in the literature [3]. In contrast to this, many investigations have been carried out on the dimer vaporization in the alkali halide systems. van der Kemp et al. [26] found a strong correlation between the enthalpy of dimerization of the monomer alkali halide species and the bond distance between cation and anion in their crystal structure. The dimerization enthalpy of the AX species (A, alkali metal; X, halogen) can be estimated from the correlation in [26] with an accuracy of ±6.2 kJ mol^{-1}. Due to the similar nature of bonding in the $(AX)_2$ dimer species [3] in comparison to the $(LnX_3)_2$ species, such a correlation may also exist for the latter dimers. In Fig. 2 we present the enthalpies of dissociation obtained by us for the $(DyX_3)_2$ species, X = Cl [3] ($257.3\pm17.1\,kJ\,mol^{-1}$), X = Br [4] ($220.8\pm11.7\,kJ\,mol^{-1}$) and X = I (see Table 4) as a function of the reciprocal interatomic distance in the crystal structure of the corresponding compound. The interatomic distances were taken as the sum of the Dy^{3+} and X^- ionic radii given in [27] for the respective coordination number. The dotted line in the same picture shows the empirical correlation determined in [26] for the alkali metal halide dimer species. The correlation for the $(DyX_3)_2$ species is obvious. This correlation is shifted to higher enthalpy values in comparison to those for the $(AX)_2$ species.

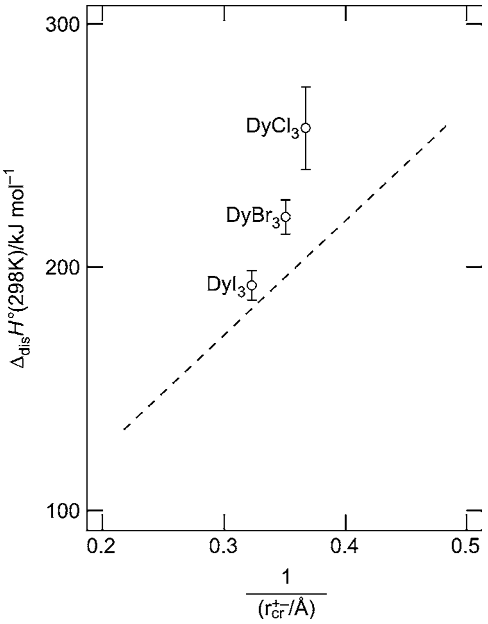

Fig. 2. Correlation between the enthalpy of dimerization for the dysprosium halides and the reciprocal interatomic distance in the solid phase (dotted line denotes the empirical correlation for alkali halides obtained in [26]).

The probable overall errors of the enthalpies and entropies of reaction and of the partial pressures of the vapor species in Tables 2 and 4 due to statistical errors and estimated uncertainties were calculated as described by Hilpert et al. [28]. The following probable uncertainties were assumed for the computation of the overall errors: ±3 K for the absolute error of the temperature measurement, ±3 K at the lowest and *3 K at the highest measurement temperature for the differential error, ±20% for $\{H°(T_m) - H°(298)\}$ and $\{S°(T_m) + S°(298)\}$, as well as ±40% for the quotient of the ionization cross section used in the computation of the K_p° values in Table 4. An uncertainty of ±30% was assumed for the total pressure of DyI_3 in [10] used for the computation of the pressure calibration constant. Moreover, uncertainties ($J\,mol^{-1}\,K^{-1}$) of ±20, ±10, ±13, and ±30 were estimated for the Gibbs energy function of DyI_3(s), DyI_3(g), $(DyI_3)_2$(g), and $(DyI_3)_3$(g), respectively.

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