Vapor Pressures of Gallium Trifluoride, Trichloride, and Triiodide and Their Standard Sublimation Enthalpies

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The vapor pressures of gallium trihalides GaF_3, $GaCl_3$, and GaI_3 were measured by a torsion effusion apparatus, and their temperature dependences fit the following equations: $\log(p/\mathrm{Pa}) = (14.30 \pm 0.30) - (12600 \pm 200)/(T/\mathrm{K})$ (from 808 to 958 K), $\log(p/\mathrm{Pa}) = 13.80 - 3800/(T/\mathrm{K})$ (from 289 to 308 K), and $\log(p/\mathrm{Pa}) = (14.00 \pm 0.50) - (5130 \pm 150)/(T/\mathrm{K})$ (from 345 to 401 K) for GaF_3, $GaCl_3$, and GaI_3, respectively. Both GaF_3 and GaI_3 vaporize practically congruently in monomeric form while $GaCl_3$ is in dimer form. Treating the vapor pressures by second- and third-law methods, the selected standard enthalpies $\Delta H°(298\ \mathrm{K}) = (252 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$, $(89 \pm 2)\ \mathrm{kJ \cdot mol^{-1}}$, and $(100.5 \pm 2.0)\ \mathrm{kJ \cdot mol^{-1}}$ associated with the sublimation of GaF_3, $GaCl_3$, and GaI_3, respectively, were obtained.

Introduction

Recently the sublimation of $GaBr_3$ was studied in this laboratory.[1] The aim of the present work was to complete the study on the sublimation of other gallium trihalides, GaF_3, $GaCl_3$, and GaI_3.

GaF_3 vaporizes practically only in the monomeric form. The dimer is present in the vapor at about 1 % in the temperature range from (805 to 940) K.[2] The vapor pressures of this compound were measured mass-spectrometrically by Zhegul'Skaya et al.[2] and by Feather et al.,[3] but their results disagree by about a factor three. $GaCl_3$ vaporizes prevalently in the dimer form, with the monomer present in a very small amount (<1 %) near room temperature. The saturated vapor pressures above solid and liquid samples were measured by several authors employing static methods.[4−9] Thermal parameters of the dissociation equilibrium of the dimer in monomer were evaluated by static methods[4,5,7−10] and by mass-spectrometric work.[11] GaI_3 sublimes prevalently in the monomeric form, and the dimer is present in detectable amounts only at high temperatures from (427 to 556) K.[12] The vapor pressures above the liquid compound were measured by Fischer and Jübermann[4] using a static method and by Riebling and Erickson[12] by transpiration. The vapor pressures of the solid were obtained by Fainer and Rumyants'ev[13] by the transpiration method and by Smith and Barrow[14] using a torsion-effusion apparatus. In the present investigation, further measurements of vapor pressures of these gallium trihalides were made by using a torsion assembly, and the sublimation enthalpies were derived from a second- and third-law treatment of the data.

Experimental and Results Section

Very pure compounds of GaF_3, $GaCl_3$, and GaI_3 (all 99.999 % pure as stated by the supplier Aldrich) were used in this investigation. As all compounds are very hygroscopic, the cells were loaded in an efficient drybox and rapidly evacuated. The assembly used is practically the same as that described in an our previous work.[15] For each of the compounds the pressure measurements in each run were made randomly in both ascending and descending temperature steps even though the data is reported in the tables as ascending. Three conventional

Table 1. Torsion Vapor Pressures of GaF_3

Cell C							
run 3		run 5		run 6		run 8	
T/K	$\log(p/\mathrm{Pa})$	T/K	$\log(p/\mathrm{Pa})$	T/K	$\log(p/\mathrm{Pa})$	T/K	$\log(p/\mathrm{Pa})$
808	−1.33	813	−1.33	810	−1.40	816	−1.33
818	−1.20	822	−1.20	820	−1.26	827	−1.10
827	−1.02	830	−1.02	827	−1.10	835	−0.96
836	−0.85	839	−0.90	837	−0.96	843	−0.85
845	−0.72	847	−0.76	843	−0.85	853	−0.66
852	−0.57	856	−0.60	846	−0.78	862	−0.50
861	−0.42	867	−0.42	855	−0.63	871	−0.36
869	−0.28	876	−0.27	864	−0.48	880	−0.21
878	−0.12	885	−0.10	872	−0.34	890	−0.06
884	−0.01	894	0.08	882	−0.19	895	0.04
893	0.15	903	0.22	890	−0.07	904	0.21
901	0.27	911	0.33	900	0.13	913	0.34
909	0.39	923	0.51	909	0.25	921	0.46
918	0.49			916	0.39		
Cell B							
run 2		run 3		run 5		run 7	
T/K	$\log(p/\mathrm{Pa})$	T/K	$\log(p/\mathrm{Pa})$	T/K	$\log(p/\mathrm{Pa})$	T/K	$\log(p/\mathrm{Pa})$
842	−0.65	844	−0.59	845	−0.55	847	−0.59
853	−0.43	854	−0.39	855	−0.33	857	−0.43
863	−0.23	863	−0.26	859	−0.22	866	−0.26
872	−0.09	871	−0.09	870	−0.05	874	−0.13
884	0.10	880	0.04	881	0.13	885	0.07
894	0.27	890	0.20	893	0.32	894	0.21
902	0.38	898	0.33	903	0.46	901	0.31
913	0.54	907	0.45	910	0.59	910	0.45
924	0.70	916	0.58	920	0.73	919	0.59
935	0.86	925	0.72	928	0.85	929	0.74
945	1.01	934	0.87	938	0.98	939	0.87
956	1.15	942	0.98	947	1.11	946	0.97
		948	1.07	958	1.23	958	1.12
		955	1.16				

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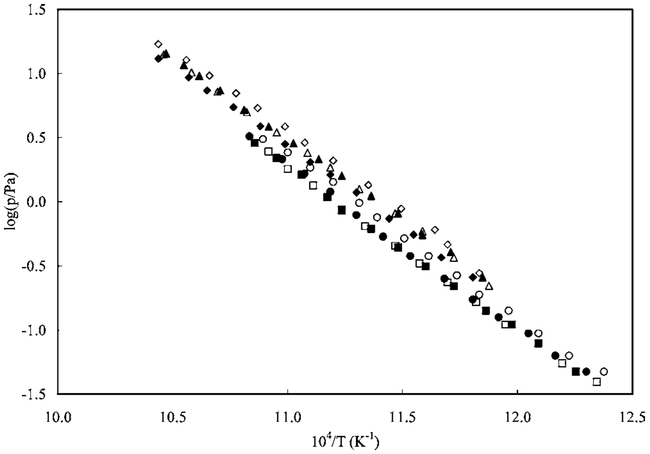

Figure 1. Torsion vapor pressures of GaF_3. Δ, cell B run 2; ▲, cell B run 3; ◇, cell B run 5; ◆, cell B run 7; ○, cell C run 3; ●, cell C run 5; □, cell C run 6; ■, cell C run 8.

graphite torsion cells with both effusion holes having a nominal diameter of 0.5 mm (cell A), 1.0 mm (cell B), and 1.6 mm (cell C) were used. The instrumental constants of these cells necessary to convert the measured torsion angles into pressure values were determined and checked in runs carried out before and during the study of the compounds by vaporizing very pure standards, the vapor pressures of which are well-known, in two different temperature ranges. In particular lead[16] from (850 to 1100) K and benzoic acid[17] from (300 to 400) K were used as standards. The torsion constants so obtained were found reproducible within about (5 to 8) % of their average values. Cell A was also employed to measure vapor pressures by the Knudsen method using the well-known equation[18] $p = K \cdot \mathrm{d}g/\mathrm{d}t \cdot (T/M)^{1/2}$. The constant K necessary to convert the rate of mass loss of the sample ($\mathrm{d}g/\mathrm{d}t$) at the experimental temperature T to pressure values was evaluated using benzoic acid in separate experiments, where M is the molecular weight of the vapor. The rate of mass loss of the sample was measured by a vacuum thermobalance (Chan 1000) to which the torsion assembly was suspended.

GaF_3. The vapor pressures of GaF_3 were measured by both the cells B and C. The results obtained are reported in Table 1 and Figure 1. The slopes and intercepts of the log p versus $1/T$ equations reported in Table 2 were obtained from linear least-squares treatment of the data obtained in each run. The results suggest a very small dependence on the cells used, probably due to a systematic error in the instrument constants. Giving equal weights to these equations, the following one is representative of the total vapor pressure of solid GaF_3 in the temperature range (808 to 958) K:

$$\log(p/\mathrm{Pa}) = (14.30 \pm 0.30) - (12600 \pm 200)/(T/\mathrm{K}) \qquad (1)$$

Table 2. Temperature Dependence of the Torsion Vapor Pressures of GaF_3, $GaCl_3$, and GaI_3

					$\log(p/\mathrm{Pa}) = A - B/(T/\mathrm{K})$	
compound	cell	run	ΔT/K	points	A^a	B^a
GaF_3	C	3	808−901	14	14.36 ± 0.16	12718 ± 140
	C	5	813−923	13	14.31 ± 0.18	12749 ± 153
	C	6	810−916	14	14.08 ± 0.14	12571 ± 121
	C	8	816−921	13	14.24 ± 0.12	12702 ± 107
	B	2	842−956	12	14.28 ± 0.13	12547 ± 113
	B	3	844−955	14	14.33 ± 0.08	12577 ± 70
	B	5	845−958	13	14.44 ± 0.18	12621 ± 159
	B	7	847−958	13	14.28 ± 0.09	12592 ± 83
$GaCl_3$	A	1	293−308	9	14.13 ± 0.33	3893 ± 98
	A	3	291−308	8	13.35 ± 0.26	3665 ± 79
	A	4	292−308	8	13.28 ± 0.46	3639 ± 137
	A	6	289−306	9	14.38 ± 0.40	3971 ± 118
GaI_3	A	1	345−382	11	13.73 ± 0.16	5012 ± 56
	A	2	346−394	16	13.57 ± 0.36	4946 ± 131
	A	4	346−401	18	14.37 ± 0.14	5265 ± 52
	A	5	349−401	18	14.46 ± 0.19	5298 ± 71
	A	7	346−398	14	13.84 ± 0.20	5063 ± 74

[a] The quoted errors are standard deviations.

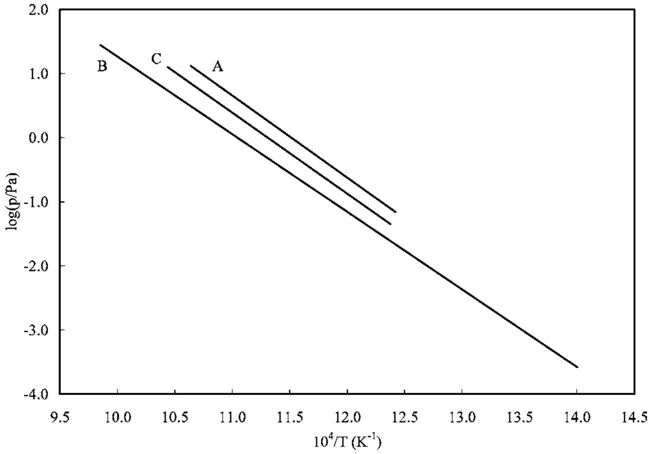

Figure 2. Comparison of the vapor pressures of GaF_3. A, Zhegul'Skaya et al.;[2] B, Feather et al.;[3] C, this work.

where the associated uncertainty and in particular that associated with the intercept, considering the small discrepancy obtained from the results obtained using two different torsion cells as illustrated in Figure 1, were estimated. For comparison, this equation with those proposed by Zhegul'Skaya et al.[2] and by Feather et al.[3] are illustrated in Figure 2 and Table 3. Considering the constitution of the vapor as only in the monomeric form, the second-law standard sublimation enthalpy of GaF_3 was calculated from the slope of eq 1 and the heat content functions ($H°(883\ \mathrm{K}) - H°(298\ \mathrm{K})$) for solid and gaseous gallium trifluoride given by the IVTANTHERMO database,[16] $\Delta H°(298\ \mathrm{K}) = (255 \pm 5)\ \mathrm{kJ \cdot mol^{-1}}$. The associated uncertainty was estimated considering also the uncertainty of about 1 $\mathrm{kJ \cdot mol^{-1}}$ for the heat content functions. Third-law values of this enthalpy were also calculated at 50 K intervals across the temperature range (800 to 950) K by using the free energy functions (fef), $[G°(T) - H°(298\ \mathrm{K})]/T$ using the IVTANTHERMO database.[16] The enthalpy values obtained are reported in Table 4 and are insensitive to temperature. Their average value, $(250 \pm 1)\ \mathrm{kJ \cdot mol^{-1}}$, agrees with that obtained by the second-law procedure so that, giving the same weight to second- and third-law results, we propose as the standard enthalpy associated with the sublimation of GaF_3 the value 252 $\mathrm{kJ \cdot mol^{-1}}$ with an uncertainty that should not exceed ± 4 $\mathrm{kJ \cdot mol^{-1}}$. Surprisingly this value is smaller than those by us obtained for other Group III A metal trifluorides, AlF_3[1] $(301 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$ and InF_3[19] $(330 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$.

$GaCl_3$. The vapor pressure of this compound is sufficiently volatile to be measurable with our torsion assembly already at room temperature. For their measurements the graphite cell (A) with a smaller effusion hole diameter (nominal 0.5 mm) was used. Since $GaCl_3$ is very hygroscopic, to exclude contact of the sample with air during the transfer from the drybox to the torsion assembly, the effusion holes of the cell were closed with small pins of naphthalene. Putting the assembly under vacuum, the pins quickly sublimed, and shortly, practically at room temperature, the experiment started measuring the first torsion angle of the cell. At each temperature the real torsion angle

Table 3. Comparison of the Temperature Dependence of the Vapor Pressures of GaF_3, $GaCl_3$, and GaI_3

						$\log(p/\mathrm{Pa}) = A - B/(T/\mathrm{K}) - C\cdot\log(T/\mathrm{K})$		
compound	ref	method	equilibrium	ΔT /K	points	A	B	C
GaF_3	Zhegul'Skaya et al.[2]	mass-spectr.	sol-vap	805−940		14.721 ± 0.102	12784 ± 524	
	Feather et al.[3]	mass-spectr.	sol-vap	714−1015	∼50	13.37 ± 0.06	12100 ± 50	
	this work	torsion-effusion	sol-vap	808−958	106	14.30 ± 0.30	12600 ± 200	
$GaCl_3$	Fischer and Jübermann[4]	static	sol-vap	641−350	4	$\log(p/\mathrm{Pa})$ = 2.78, 2.92, 2.98, and 3.09 at 341 K, 343 K, 347 K, and 350 K, respectively		
			liq-vap	351−472	19	31.2	2846	7.5
	Komshilova et al.[5]		static (manom.)	sol-vap		28.77 ± 0.33	4470 ± 110	5
				liq-vap		28.37 ± 0.02	3483 ± 2	6
	Dumas and Potier[6]	static (gauge-Bourbon)	sol-vap	323−351	10	14.00 ± 0.07[a]	3805 ± 24[a]	
			liq-vap			10.31	2509	
	Laubengayer and Schirmer[7]	static (manometer)	sol-vap	323−348	6	13.98 ± 0.19[a]	3800 ± 64[a]	
			liq-vap	353−474	13	10.32 ± 0.02[a]	2511 ± 8[a]	
	Oppermann et al.[8]	static (memb. zero-manom.)	sol-vap	328−348		13.30 ± 0.57	3548 ± 158	
			liq-vap	353−453		10.10 ± 0.10	2416 ± 51	
	Chusova et al.[9]	static (gauge-manom.)	sol-vap	313−350		12.78	4080	
			liq-vap	351−422		10.75	2676	
	this work	torsion-effusion	sol-vap	289−310	34	13.80	3800	
GaI_3	Fischer and Jübermann[4]	static	sol-vap		2	$\log(p/\mathrm{Pa})$ = 2.77 and 3.04 at 453 K and 468 K, respectively		
			liq-vap	486−615	13	42.95	6083	10.07
	Riebling and Erickson[12]	transpiration	liq-vap			11.16	3782	
	Fainer and Rumyantsev[13]	transpiration	sol-vap	423−473	7	13.71	5020	
	Smith and Barrow[14]	torsion-effusion	sol-vap	324−382	50	13.33	4950	
	this work	torsion-effusion	sol-vap	345−401	77	14.00 ± 0.50	5130 ± 150	

[a] Calculated by us from the experimental data reported in the original work. The associated errors are standard deviations.

Table 4. Third-Law Standard Sublimation Enthalpies of GaF_3

T	p	$-R\cdot\ln p$	$-\Delta$fef	$\Delta_{sub}H°$ (298 K)
K	Pa	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$kJ\cdot mol^{-1}$
800	0.0314	124.6	188.2	250.2
850	0.266	106.8	187.3	249.9
900	1.78	91.0	186.3	249.6
950	9.78	76.9	185.4	249.2
			average	249.7

Table 5. Torsion Vapor Pressures and Third-Law Sublimation Enthalpies of $GaCl_3$

Run 1				Run 3			
T		$-\Delta$fef	$\Delta H°$ (298 K)	T		$-\Delta$fef	$\Delta H°$ (298 K)
K	log (p/Pa)	$J\cdot mol^{-1}\cdot K^{-1}$	$kJ\cdot mol^{-1}$	K	log (p/Pa)	$J\cdot mol^{-1}\cdot K^{-1}$	$kJ\cdot mol^{-1}$
293.0	0.83	224.6	89.2	290.5	0.76	224.6	88.9
297.0	1.06	224.6	89.2	293.0	0.84	224.6	89.2
299.5	1.13	224.6	89.5	296.0	0.95	224.6	89.5
302.0	1.23	224.6	89.7	298.0	1.07	224.6	89.4
303.5	1.32	224.6	89.6	300.5	1.15	224.6	89.7
305.0	1.37	224.6	89.7	304.5	1.31	224.6	90.0
306.0	1.40	224.6	89.8	307.0	1.42	224.6	90.0
307.0	1.46	224.6	89.8	308.0	1.47	224.6	90.0
308.0	1.49	224.6	89.9			average	89.6
		average	89.6				
Run 4				Run 6			
292.0	0.79	224.6	89.1	289.0	0.63	224.6	89.1
294.0	0.90	224.6	89.2	292.0	0.79	224.6	89.1
297.0	1.03	224.6	89.3	293.5	0.87	224.6	89.2
299.0	1.12	224.6	89.4	295.5	0.96	224.6	89.2
301.0	1.22	224.6	89.4	297.0	1.02	224.6	89.4
303.0	1.28	224.6	89.7	298.5	1.07	224.6	89.5
305.0	1.32	224.6	90.0	300.5	1.14	224.6	89.7
308.0	1.45	224.6	90.2	303.0	1.26	224.6	89.8
		average	89.5	306.0	1.44	224.6	89.6
						average	89.4

value was obtained as difference between that measured and that measured at the end of the run (zero angle) when all of the sample was sublimed. Unfortunately in each run a limited number of points was obtained because the pressures are at the limit of the torsion effusion method and because, operating at low temperatures, for each point a long time was necessary to thermostate the cell, with consequent sublimation of a large amount of the sample. The experimental data are reported in Tables 2 and 5 and in Figure 3. The temperature dependence of the saturated vapor pressure above solid $GaCl_3$ in the small temperature range (289 to 308) K was approximated by the equation:

$$\log(p/\mathrm{Pa}) = 13.80 - 3800/(T/K) \qquad (2)$$

This equation is compared with those found in literature in Table 3 and Figure 4. In each run at some temperatures simultaneously to the torsion pressures, some vapor pressure values were also determined by Knudsen effusion,[19] considering that the dimeric form in the gas phase is decidedly predominant.[4,9,11] The data obtained are reported in Table 6 and Figure 3. Even if slightly higher, the pressure values obtained by effusion are supportive to those obtained by the torsion method. In Table 5 at each experimental temperature the corresponding third-law standard enthalpy value associated with the sublimation of Ga_2Cl_6(g) is also reported. The free energy functions used for these calculations were taken from the IVTANTHERMO database.[16] All of the values obtained are in excellent agreement, without any temperature trend, and their average value is equal to 89.5 $kJ\cdot mol^{-1}$ with an uncertainty of ± 2 $kJ\cdot mol^{-1}$. The value is higher than the second-law value obtained from the slope of eq 2, $\Delta H°(298\ K) = 73\ kJ\cdot mol^{-1}$. The evaluation of the uncertainty associated to this value is not easy, but in any case, considering the very small experimental temperature range, it is decidedly large, so we propose as standard sublimation enthalpy of $GaCl_3$ that obtained from third-law procedure, 89 ± 2 $kJ\cdot mol^{-1}$. This value is higher than those found in literature obtained by second-law treatment of the vapor pressures: Komshilova et al.,[5] (72.8 ± 2.1) $kJ\cdot mol^{-1}$, Dumas and Potier[6] and Laubengayer and Schirmer,[7] both equal to 73.5 $kJ\cdot mol^{-1}$ (as recalculated by us using the heat content functions in ref 16), Opperman et al.,[8] (68.5 ± 3.0) $kJ\cdot mol^{-1}$, and Chusova et al.[9] (80.3 and 67.2) $kJ\cdot mol^{-1}$ from second- and third-law treatments of their vapor pressures, respectively. In particular it is interesting to note that the third-law sublimation enthalpy value calculated by Chusova et al.[9] (67.2 $kJ\cdot mol^{-1}$) using heat capacities and entropies of

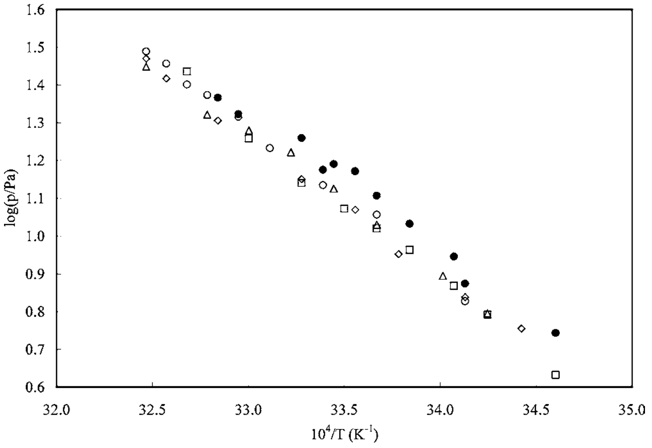

Figure 3. Torsion vapor pressures of $GaCl_3$. ○, run 1; ◇, run 3; Δ, run 4; □, run 6; ●, Knudsen vapor pressures.

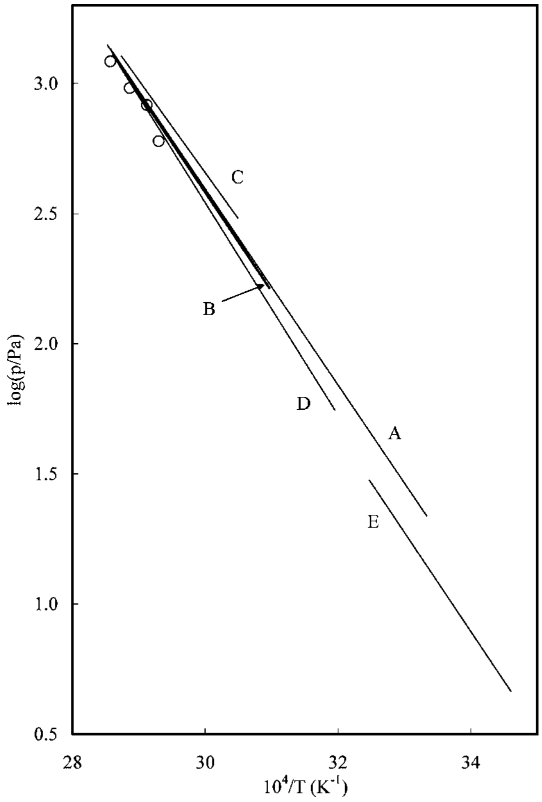

Figure 4. Vapor pressures of $GaCl_3$ above solid compound. ○, four points of Fischer and Jübermann;[4] A, Komshilova et al.;[5] B, two coincident lines of Dumas and Potier[6] and of Laubengayer and Schirmer;[7] C, Oppermann et al.;[8] D, Chusova et al.;[9] E, this work.

Table 6. Knudsen Vapor Pressures of $GaCl_3$

	$T \pm 0.5$	$\Delta t \pm 5$	$\Delta g \pm 0.2$	pressure/Pa	
run	K	s	mg	Knudsen	torsion
1	293.0	2020	22.5	7.48	6.76
	299.5	960	21.1	14.95	13.49
	303.5	979	30.1	20.99	20.89
3	298.0	1074	23.5	14.83	11.75
	304.5	700	23.8	23.23	20.42
4	297.0	1588	30.0	12.77	10.72
	299.0	1170	26.7	15.49	13.18
6	289.0	2591	21.5	5.53	4.27
	293.5	1611	21.2	8.82	7.41
	295.5	1259	20.1	10.76	9.12
	300.5	1220	32.6	18.17	13.80

Table 7. Torsion Vapor Pressures of GaI_3

run 1		run 2		run 4		run 5		run 7	
T/K	log (p/Pa)	T/K	log (p/Pa)	T/K	log (p/Pa)	T/K	log (p/Pa)	T/K	log (p/Pa)
344.5	−0.84	346.0	−0.77	346.0	−0.84	348.5	−0.84	346.0	−0.84
347.0	−0.71	349.0	−0.71	348.0	−0.71	352.0	−0.61	349.0	−0.71
349.5	−0.61	349.5	−0.53	350.0	−0.71	354.0	−0.47	352.5	−0.53
352.5	−0.47	351.5	−0.47	355.0	−0.47	355.0	−0.41	355.5	−0.36
356.0	−0.36	354.0	−0.36	357.0	−0.36	357.5	−0.31	359.0	−0.23
364.0	−0.03	357.5	−0.17	359.5	−0.27	361.5	−0.17	363.0	−0.08
367.0	0.06	362.0	−0.06	364.0	−0.11	365.5	−0.01	366.0	0.03
370.0	0.15	367.5	0.09	368.5	0.05	368.5	0.09	369.0	0.13
373.0	0.28	372.0	0.16	372.5	0.22	372.0	0.22	374.0	0.30
378.0	0.47	374.5	0.31	374.5	0.30	373.0	0.24	378.5	0.43
382.0	0.63	377.5	0.43	377.0	0.38	375.5	0.36	382.5	0.54
		381.5	0.57	380.0	0.47	379.0	0.47	390.5	0.86
		384.0	0.69	383.0	0.59	383.5	0.62	394.0	0.99
		387.5	0.82	387.5	0.78	387.5	0.80	398.0	1.13
		390.5	0.94	389.5	0.86	391.5	0.94		
		393.5	1.04	393.5	1.00	393.5	1.00		
				397.0	1.14	397.0	1.14		
				400.5	1.25	401.0	1.23		

$Ga_2Cl_6(g)$[20] and of $GaCl_3(s)$[21] found in literature is different than those recalculated by us using the IVTANTHERMO's fef,[16] (101.0 and 89.6) kJ·mol^{-1} at the extreme experimental temperatures of the work[9] and (310 and 350) K, respectively. Besides, these values show a decidedly evident temperature trend considering the small range. As for GaF_3, the sublimation enthalpy of $GaCl_3$ is lower than those of other Group III A metal trichlorides, $AlCl_3$[1] (118 ± 6) kJ·mol^{-1} and $InCl_3$[22] (158 ± 4) kJ·mol^{-1}.

***GaI_3*.** The vapor pressure of this compound was measured only with cell A. The experimental data obtained are reported in Table 7 and Figure 5. The log p versus 1/T equation was calculated from the linear squares treatment of the data of each run, and the slopes and intercepts so obtained are in Table 2. From these equations the following one representative of the vapor pressure above solid GaI_3 in the temperature range (345 to 401) K was derived:

$$\log(p/\mathrm{Pa}) = (14.00 \pm 0.50) - (5130 \pm 150)/(T/\mathrm{K}) \tag{3}$$

where the associated uncertainty was overestimated. From the slope of this equation the second-law enthalpy of the congruent sublimation of gallium triiodide in GaI_3(g) was calculated, considering that in the temperature range covered the dimer contribution is decidedly negligible.[4,23] The value obtained, $\Delta H°(273\ \mathrm{K}) = (98 \pm 3)$ kJ·mol^{-1}, was reported at $T = 298$ K by using the enthalpic increments for the solid and monomeric

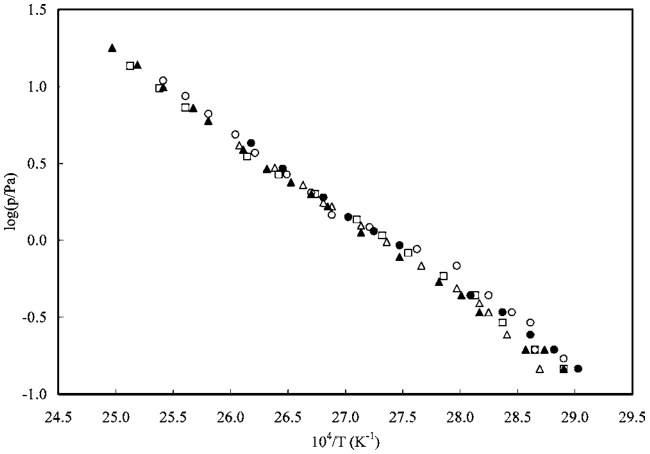

Figure 5. Torsion vapor pressures of GaI_3. ●, run 1; ○, run 2; ▲, run 4; Δ, run 5; □, run 7.

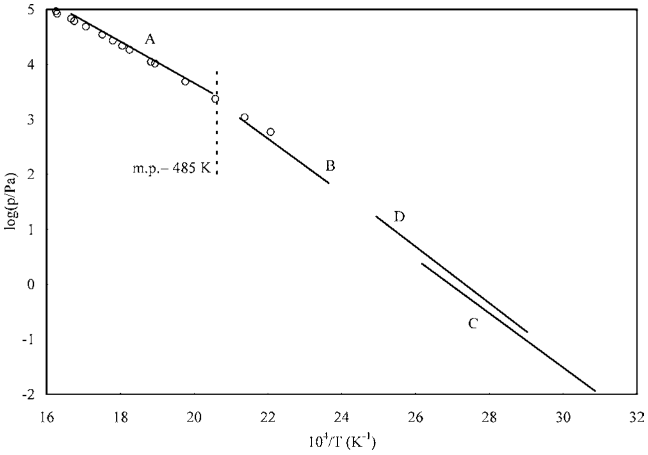

Figure 6. Comparison of vapor pressures of GaI_3. ○, Fischer and Jübermann;[4] A, Riebling and Erickson;[12] B, Fainer and Rumyantsev;[13] C, Smith and Barrow;[14] D, this work.

gaseous phase by the IVTANTHERMO database,[16] $\Delta H°(298\ K) = (100 \pm 3)\ kJ\cdot mol^{-1}$. This enthalpy was also calculated by third-law treatment of the vapor pressures at the extreme temperatures of the range covered, 350 K and 400 K. The free energy functions necessary for this calculation were those selected in ref 16. The two enthalpy values so obtained are both equal to 100.6 $kJ\cdot mol^{-1}$ without any temperature trend, in excellent agreement with the second-law result. On this basis we propose the value of 100.5 $kJ\cdot mol^{-1}$ as the standard sublimation enthalpy of GaI_3, with an uncertainty of about 2.0 $kJ\cdot mol^{-1}$. As evidenced in Figure 6, our results are decidedly in close agreement with Fainer and Rumyantsev's,[13] ((96.2 ± 1.2) $kJ\cdot mol^{-1}$ at 445 K), with Smith and Barrow's,[14] (94.77 $kJ\cdot mol^{-1}$ at T = 345 K), and with those measured calorimetrically by Timoshkin et al.[24] ((101.0 ± 0.8) $kJ\cdot mol^{-1}$ at T = 373 K and (100.2 ± 1.5) $kJ\cdot mol^{-1}$ at T = 395 K).

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