A Study on the Sublimation of Gallium Tribromide

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The temperature dependence of the total vapor pressure of $GaBr_3$ measured by the torsion-effusion method over the temperature range (300 to 357) K is represented by the following equation: $\log(p/\mathrm{Pa}) = (16.1 \pm 0.6) - (5250 \pm 200)(\mathrm{K}/T)$. This compound sublimes to the monomer and dimer species. From the temperature dependence of the dissociation, and the equilibrium constant of the dimer found in the literature, the partial pressures of both forms were evaluated from which the second- and third-law standard enthalpies of the sublimation reactions, $GaBr_3(s) = GaBr_3(g)$ and $GaBr_3(s) = 1/2Ga_2Br_6(g)$, were calculated: $\Delta_{sub}H°(298\ \mathrm{K}) = (92.5 \pm 2.0)\ \mathrm{kJ \cdot mol^{-1}}$ and $(50.5 \pm 2.0)\ \mathrm{kJ \cdot mol^{-1}}$ for the monomer and dimer forms, respectively.

Introduction

The old values were obtained by Fischer and Jübermann[1] prevalently at high temperature above the molten phase of $GaBr_3$ (only two points above the solid phase), as apparently no other vapor pressure measurements have been made. This compound vaporizes to the monomer and dimer forms, and the temperature dependence of the dimer−monomer equilibrium was studied by Fischer and Jübermann[1] and by Kulyukin and Petrov.[2] The purpose of the present study is to measure, by the torsion method, the vapor pressure of solid $GaBr_3$ over a temperature range and to calculate its standard sublimation enthalpy.

Experimental Section

Very pure $GaBr_3$ (99.8 % as stated by the supplier Aldrich) was employed. As the compound is very hygroscopic, the cell was loaded in a drybox. The vapor pressure were measured by the torsion method. The torsion-effusion technique has been described by Volmer.[3] The torsion pressure is related to the torsion angle (α) of a tungsten thin wire from which the cell is suspended. The pressure is determined from the relation $p = K \cdot \alpha$, where the constant K is related to the torsion constant and length of the wire and the geometrical factors of the effusion holes of the used cell. The torsion effusion apparatus used in this work was described in a previous work.[4] Two conventional graphite torsion cells with different nominal diameter of the effusion holes (1.2 mm and 0.8 mm for the cells A and B, respectively) were used. The values of the instrument constant of the used cells, values necessary to convert the experimental torsion angles in vapor pressure data, were determined and checked, vaporizing pure standard elements having reliable vapor pressures (cadmium[5] and benzoic acid[6]) in some runs carried out before and during the study of $GaBr_3$. The constant values so obtained were found reproducible within about (10 to 15) % of their average ones, and this produces in the final $\log p$ values a shift of about ± 0.1 of this uncertainty, in addition to the standard deviation of the experimental data, which was taken into account to evaluate the final error associated to the intercept of the selected $\log p$ versus $1/T$ equation. Because the torsion angles were measured with an uncertainty of about $\pm 3 \cdot 10^{-3}$ rad and the first points measured at low temperatures influence heavily the slopes of the $\log p$ versus $1/T$ equations, in each run the measurements were actually started when the torsion angles were greater than about 0.1 rad so that the error in their measurement was decidedly negligible. Also, the measured temperatures were fairly reliable with uncertainties that should not exceed ± 2 K. In separate experiments carried out at fixed temperatures, the molecular weight of the effusing vapor was evaluated through the Knudsen equation in the form

$$M = \frac{K \cdot T}{\alpha^2} \cdot \left(\frac{\mathrm{d}g}{\mathrm{d}t}\right)^2 \tag{1}$$

At a fixed temperature T, the mass loss rate of the sample ($\mathrm{d}g/\mathrm{d}t$) was measured simultaneously to the torsion angle α by a vacuum electrobalance (Cahn 1000) to which the torsion assembly was suspended. K is a constant including characteristics of the cell and of the torsion wire, and its value was obtained by vaporizing pure benzoic acid. The constant values so obtained for both cells were reproducible to within about 10 % of their average values. To avoid condensation of the effused vapor on the torsion apparatus with consequent error in the measurement of the seal weight loss of the sample, the assembly was opportunely heated.

Experimental Results

The total vapor pressures of $GaBr_3$ measured above the solid phase in 11 runs are reported in Table 1 and in Figures 1 and 2. In each run, the pressures were measured randomly in both ascending and decreasing temperatures, although in the table they are reported as ascending. The temperature dependence of the measured vapor pressures linearized by the least-squares treatment of the data was approximated for each run by a $\log p$ versus $1/T$ equation. Unfortunately, the results obtained with both torsion cells show shifts due probably to a small systematic error, different for every experiment, on the temperature measurements and/or to fluctuations of the instrument constant values considering that for the calculation

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Table 1. Total Vapor Pressures Over Solid $GaBr_3$

run 1 cell A		run 2 cell A		run 3 cell B		run 4 cell A	
T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)
302.5	−1.20	300.0	−1.15	311.0	−0.62	304.5	−1.07
308.0	−0.90	302.5	−1.02	313.0	−0.48	307.5	−0.90
312.0	−0.67	307.0	−0.85	315.0	−0.42	310.0	−0.77
314.5	−0.47	311.7	−0.58	317.5	−0.28	313.0	−0.59
318.5	−0.29	313.0	−0.48	321.0	−0.07	315.0	−0.47
319.5	−0.23	320.0	−0.21	324.0	0.09	316.0	−0.42
322.0	−0.12	322.0	−0.04	328.0	0.28	321.0	−0.12
327.0	0.07	323.0	0.04	331.0	0.42	322.5	−0.05
331.5	0.31	324.0	0.04	334.0	0.60	327.5	0.18
336.0	0.51	325.0	0.15	335.0	0.62	328.5	0.25
		327.5	0.21			333.0	0.41
		330.0	0.40			339.5	0.72
		332.0	0.51			343.0	0.88
		335.0	0.64			346.0	0.99

run 5 cell B		run 6 cell A		run 7 cell B		run 8 cell A	
T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)
314.0	−0.42	303.0	−1.32	315.0	−0.62	304.0	−1.14
318.0	−0.26	307.5	−1.02	317.0	−0.48	306.5	−1.01
319.5	−0.17	310.5	−0.85	319.5	−0.37	309.5	−0.84
323.0	−0.01	313.0	−0.72	322.0	−0.28	313.5	−0.66
326.0	0.15	315.5	−0.58	324.5	−0.15	317.5	−0.47
328.5	0.25	316.5	−0.54	326.5	−0.02	319.5	−0.36
331.0	0.41	321.5	−0.24	329.5	0.17	323.5	−0.14
333.5	0.52	323.0	−0.18	330.0	0.20	327.5	0.01
336.0	0.64	325.5	−0.09	332.0	0.28	333.0	0.33
338.0	0.74	328.0	0.02	334.0	0.37	337.0	0.53
341.0	0.88	330.0	0.15	336.0	0.46	340.0	0.64
347.0	1.13	333.0	0.29	338.0	0.56	343.0	0.77
351.0	1.27	336.0	0.46	340.0	0.63	346.0	0.89
		340.0	0.61	342.0	0.70	348.0	0.98
		345.0	0.82	344.0	0.79	351.0	1.07
		349.0	1.00	346.0	0.87		
				348.0	0.94		

run 9 cell B		run 10 cell A		run 11 cell B	
T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)
313.0	−0.71	305.0	−1.14	312.5	−0.77
315.0	−0.61	307.0	−1.01	314.5	−0.66
317.5	−0.47	310.0	−0.91	317.0	−0.53
322.5	−0.23	313.0	−0.71	320.0	−0.44
324.0	−0.14	316.0	−0.61	325.0	−0.14
326.0	−0.08	318.5	−0.47	326.5	−0.08
327.5	0.03	324.0	−0.17	328.5	−0.01
330.0	0.15	327.0	−0.01	335.0	0.28
333.0	0.31	329.5	0.09	336.0	0.42
335.5	0.42	332.5	0.24	338.0	0.49
338.0	0.56	333.5	0.31	341.0	0.63
343.5	0.78	336.0	0.42	345.0	0.83
344.5	0.85	340.5	0.64	346.0	0.90
346.5	0.94	344.0	0.79	349.0	1.02
349.0	1.08			350.5	1.06
352.0	1.16			354.5	1.24
				357.0	1.29

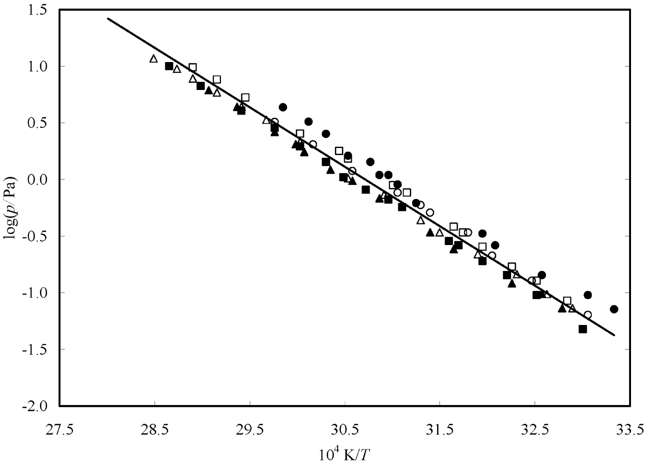

Figure 1. Torsion vapor pressures of $GaBr_3$ obtained by cell A: ○, run 1; ●, run 2; □, run 4; ■, run 6; △, run 8; ▲, run 10. The line is representative of selected eq 2.

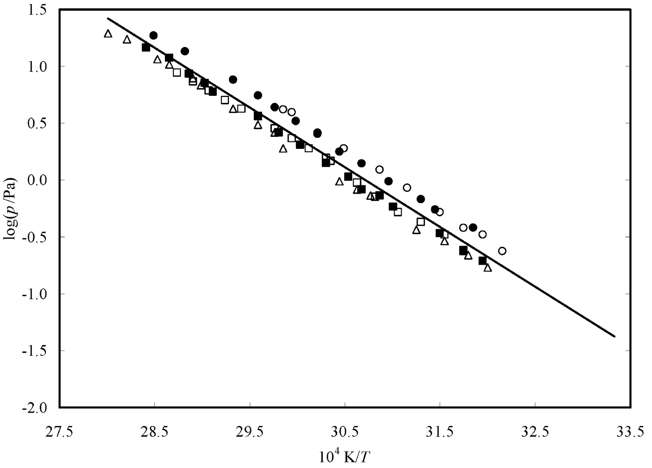

Figure 2. Torsion vapor pressures of $GaBr_3$ obtained by cell B: ○, run 3; ●, run 5; □, run 7; ■, run 9; △, run 11. The line is representative of selected eq 2.

Table 2. Temperature Dependence of Torsion Vapor of Gallium Tribromide

		ΔT		log(p/Pa) = A − B/(T/K)	
run	cell	K	no. of points	A[a]	B[a]
1	A	302.5 to 336.0	10	15.89 ± 0.33	5162 ± 105
2	A	300.0 to 335.0	14	16.04 ± 0.35	5173 ± 111
3	B	311.0 to 335.0	10	16.78 ± 0.22	5412 ± 71
4	A	304.5 to 346.0	14	16.25 ± 0.18	5267 ± 58
5	B	314.0 to 351.0	13	16.12 ± 0.17	5204 ± 57
6	A	303.0 to 349.0	16	16.13 ± 0.13	5275 ± 43
7	B	315.0 to 348.0	17	16.03 ± 0.22	5238 ± 72
8	A	304.0 to 351.0	15	15.66 ± 0.13	5111 ± 41
9	B	313.0 to 352.0	16	16.45 ± 0.12	5377 ± 41
10	A	305.0 to 344.0	14	15.95 ± 0.18	5219 ± 58
11	B	312.5 to 357.0	17	16.26 ± 0.20	5331 ± 65

[a] The quoted errors are standard deviations.

of the pressure data it was used as the average of all the instrument constants measured in the runs carried out during the study. Slopes and intercepts of the log p versus $1/T$ equations obtained in each run are reported in Table 2. Not evident dependence to the area of the effusion holes was observed. By weighting the slope and intercept of the equations proportionally to the number of the experimental points of the corresponding run, the following one was selected

$$\log(p/\text{Pa}) = (16.1 \pm 0.6) - (5250 \pm 200)(\text{K}/T) \quad \text{(from (300 to 357) K)} \qquad (2)$$

where the associated errors were estimated. We prefer to select a final equation from those obtained in each individual run and not from least-squares treatment of all the experimental data because the slope of the final equation could be conditioned from the little shifts of the experimental values. Equation 2 was drawn in Figure 3 and compared with only two points measured by Fischer and Jübermann[1] above the solid phase. Gallium tribromide vaporizes in monomer and dimer forms, and the temperature dependence of the equilibrium constant of the dissociation reaction of the dimer,

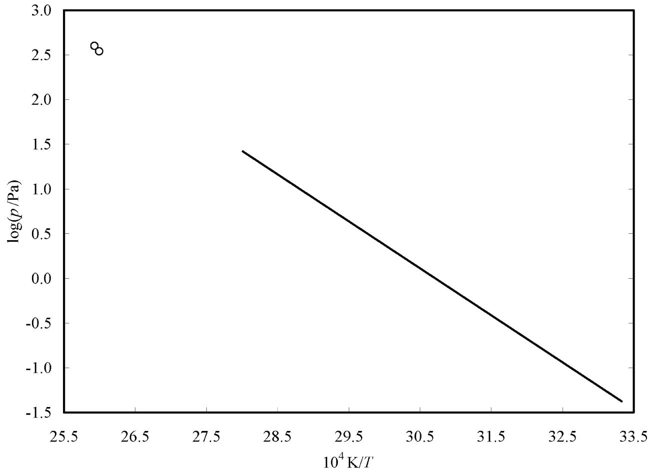

Figure 3. Comparison of the vapor pressures of $GaBr_3$: ○, ref 1.

Table 3. Molecular Weight of the Vapor Above Solid $GaBr_3$ Obtained by the Knudsen Method

$T \pm 0.5$	$\Delta t \pm 5$	$\Delta m \pm 0.2$	$\alpha \pm 0.003$	$\bar{M} \pm 20^a$	Xmon	
K	s	mg	rad	$g \cdot mol^{-1}$	(from $\bar{M}$) $\pm$ 0.06	[b]
323.5	9974	12.4	0.048	485	0.43	0.33
331.5	3650	13.2	0.140	497	0.39	0.31
338.0	1374	13.5	0.381	503	0.38	0.29
341.0	1086	14.2	0.524	475	0.46	0.28
347.0	553	12.5	0.931	457	0.52	0.27
351.0	506	15.5	1.280	479	0.45	0.26

[a] This uncertainty was estimated. [b] Obtained from eqs 2 and 3.

$K_p = p_{mon}^2/p_{dim}$, is represented as reported by Kulyukin and Petrov,[2] in the range (500 to 800) K, by the equation

$$\log(K_p/\text{Pa}) = 12.025 - 4180(\text{K}/T) \quad \text{(from (500 to 800) K)} \quad (3)$$

In separate experiments, employing always fresh samples, the molecular weight of the effusing vapor was calculated from eq 1. In Table 3 are reported at some temperatures the torsion angles and the times necessary to sublimate an amount of sample not less than of about 10 mg. The molecular weight values so determined show that the fraction of the monomeric form in the vapor does not show an evident temperature dependence, their values ranging around 0.45 ± 0.10 (see Table 3) in the temperature range (324 to 351) K. The obtained values are higher than those reported in Table 3 calculated using our total vapor pressures (eq 2) and the equilibrium monomer−dimer constants obtained by eq 3.[2]

The vaporization of $GaBr_3$ occurs according to two reactions

$$GaBr_3(s) \rightarrow GaBr_3(g) \quad (4)$$

$$GaBr_3(s) \rightarrow 1/2Ga_2Br_6(g) \quad (5)$$

The third-law sublimation enthalpies of these reactions were determined at (300 and 350) K, the approximated extreme limit of the experimental temperature ranges, using the partial pressures of $GaBr_3(g)$ and $Ga_2Br_6(g)$ from the total ones (eq 2) and the monomer fraction, or equal to that found in the present work considered constant in the whole temperature range, or calculated from the equilibrium constants of the dissociation reaction: $Ga_2Br_6(g) = 2GaBr_3(g)$ (eq 3). The necessary free energy functions (fef), $[G°(T) - H°(298\ K)]/T$, of solid and both gaseous species are those selected in IVTANTHERMO Database.[5] The obtained results are reported in Table 4. Though the difference of the two extreme temperatures is small, no evident trend of the enthalpies for both reactions were observed. In any case, a critical analysis of our procedure in the evaluation of the average molecular weight and then the monomer fraction shows that the associated error is high enough depending (i) on the uncertainty of the constant K in the eq 1, (ii) on the temperature, the small fluctuation of which (± 0.5 K) influences the amount of the vaporized sample and then the correct mass loss rate of the sample, (iii) on the torsion angle, considering that present in the quadratic form in eq 1, (iv) on a probable small condensation of the vapor on the assembly (even if heated) with an uncertainty on the evaluation of the real amount of the sublimated, and (v) on the limit of the application of the Knudsen equation considering the high vapor pressure of the sample. On this basis, we believe the results obtained using the monomeric fractions calculated from the total vapor pressures and the equilibrium constants reported in the literature are more reliable,[2] although these constants were evaluated at higher temperatures. On this basis, we selected as third-law standard enthalpies for the reactions 4 and 5 the values 92.6 $kJ \cdot mol^{-1}$ and 50.0 $kJ \cdot mol^{-1}$, respectively. The partial pressures of both gaseous species calculated at (300 and 350) K from the dissociation equilibrium constants were also used to obtain the slopes of the corresponding $\log p$ versus $1/T$ equations from which the second-law sublimation enthalpies of the reactions 4 and 5, $\Delta H°(328\ K) = 92.3\ kJ \cdot mol^{-1}$ and 52.3 $kJ \cdot mol^{-1}$, respectively, were calculated. The values were reported at 298 K by using the heat constants of solid and gaseous species taken from the IVTANTHERMO Database:[5] $\Delta H°(298\ K) = 92.9\ kJ \cdot mol^{-1}$ and 52.5 $kJ \cdot mol^{-1}$ for reactions 4 and 5, respectively, with an error associated to both values estimated not less than about 6 $kJ \cdot mol^{-1}$ considering the small temperature range and the uncertainty in the evaluation of the real amount of the gaseous species. Within these uncertainties, the second- and third-law results are decidedly in good agreement. The last, considering that the temperature

Table 4. Third-Law Sublimation Enthalpies of $GaBr_3(s)$ According the Reactions A and B

		A: $GaBr_3(s) \rightarrow GaBr_3(g)$					B: $GaBr_3(s) \rightarrow 1/2Ga_2Br_6(g)$				
T	p_{tot}[a]	p_{GaBr_3}/Pa		Δfef[b]	$\Delta_{sub}H°(298\ K)/kJ \cdot mol^{-1}$		$p_{Ga_2Br_6}$/Pa		Δfef[b]	$\Delta_{sub}H°(298\ K)/kJ \cdot mol^{-1}$	
K	Pa	[c]	[d]	$J \cdot mol^{-1} \cdot K^{-1}$	from p_{GaBr_3}[c]	from p_{GaBr_3}[d]	[c]	[d]	$J \cdot mol^{-1} \cdot K^{-1}$	from $p_{Ga_2Br_6}$[c]	from $p_{Ga_2Br_6}$[d]
300	0.0422	0.0175	0.019	−179.3	92.6	92.5	0.0247	0.024	−104.0	50.2	50.2
350	13.37	3.46	5.88	−179.0	92.6	91.0	9.91	7.49	−103.8	49.8	50.2

[a] Calculated from the selected eq 2. [b] fef = $[G°(T) - H°(298\ K)]/T$. [c] Calculated from the total vapor pressure (eq 2) and the equilibrium constant reported by Kulyukin and Petrov[2] (eq 3). See text. [d] Calculated considering the monomer amount in the vapor constant and equal to 45 % (see text).

dependence of the monomer and dimer forms have in the third-law treatment of the data for the enthalpy calculation an influence decidedly less than in the second-law one, we propose as partial sublimation enthalpies of one mole of $GaBr_3$ according to the reaction 4 and 5 the values (92.5 and 50.5) $kJ \cdot mol^{-1}$ respectively, with estimating errors for both values of 2 $kJ \cdot mol^{-1}$, values obtained giving for reaction 5 more weight to the third-law results. Combining opportunely these values, the standard enthalpy $\Delta H°(298\ K) = (84 \pm 60)\ kJ \cdot mol^{-1}$ associated with the dissociation process $Ga_2Br_6(g) = 2GaBr_3(g)$ was derived, a value comparable with that reported by Kulyukin and Petrov[2] (87 $kJ \cdot mol^{-1}$) at higher temperatures from (430 to 800) K.

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