Absolute Total Vapor Pressure of Gallium Dichloride

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The total vapor pressure of gallium dichloride was determined by the torsion method over the temperature range of (372 to 441) K, and its temperature dependence was represented by the equation $\log(p/\text{Pa}) = (14.23 \pm 0.30) - (5829 \pm 100)/(T/\text{K})$. From this equation the second-law sublimation enthalpy of a mole of gaseous mixture was derived as $\Delta_{\text{sub}}H°(406\ \text{K}) = (111 \pm 2)\ \text{kJ}\cdot\text{mol}^{-1}$.

Introduction

Apparently the only total vapor pressure values of $GaCl_2$ are old data measured above the molten compound using a glass manometer similar to a Bourdon gage.[1] Several mass-spectrometric and spectroscopic studies evidence the presence of several molecules involving gallium and chlorine in equilibrium with different condensed phase compositions. Ait-Hou et al.,[2] using a mass-spectrometric Knudsen cell, observed a complex ionic spectrum of the vapor phase including Ga_2Cl_4(g), $GaCl_3$(g), GaCl(g), Ga_2Cl_2(g), and Ga_2Cl_6(g), their relative importance depending on the change of the composition in the condensed phase due to the presence of liquid Ga above the $GaCl_2$(s) sample. The production of gallium is due to the disproportionation reaction[3−5] of GaCl(g) species present in the vapor. The dimeric form Ga_2Cl_4(g) ($GaGaCl_4$ as reported by Girichova et al.[6] who studied also the geometrical structure and the vibrational frequencies of this molecule), the gaseous species in equilibrium with $GaCl_2$(s), decomposes according to the following equilibrium reactions: $Ga_2Cl_4(g) \rightarrow GaCl(g) + GaCl_3(g)$ and $Ga_2Cl_4(g) \rightarrow 1/2Ga_2Cl_2(g) + 1/2Ga_2Cl_6(g)$. GaCl(g) in turn decomposes into Ga(l) and $GaCl_3$(g) and dimerizes in Ga_2Cl_2(g). Also, $GaCl_3$(g) dimerizes in Ga_2Cl_6. A critical assessment of the thermodynamic properties for the gaseous molecules of the Ga−Cl system was made by Chatillon and Bernard.[7]

The equilibrium constants of several gaseous reactions involving those molecules were calculated using their partial pressures evaluated from the corresponding ion intensities in the mass spectrometric investigations. These ion intensities were measured from the analysis of the breaks in the ionization efficiency curves and converted into partial pressures by the sensivity constant of the used spectrometer, the abundance of the measured isotopic ion intensity, the cross section for the electron ionization, and the gain of the electron photomultiplier, so the pressure values determined are of course influenced by these parameters. The purpose of this work is to contribute to the study of the sublimation process of $GaCl_2$ measuring the absolute values of the total vapor pressure above its solid phase.

Experimental and Results Section

A very pure sample of $GaCl_2$ was supplied by Aldrich (all 99.999 % pure as stated by the same supplier). The compound is hygroscopic and easily hydrolyzed and oxidized so that the container of the sample was opened and the cell filled with the sample in an efficient drybox in an argon atmosphere. Moreover, both of the effusion holes of the cell were closed with small pins of naphthalene. These pins sublime quickly when the cell was put under vacuum in the torsion assembly. This procedure excludes the contact of the sample with air. The vapor pressure of $GaCl_2$ was measured by the torsion assembly substantially described in previous work.[8] Two conventional graphite torsion cells, with effusion holes having a nominal diameter of (0.8 and 1.2) mm (cell A and B, respectively), were used in this study. Both values of the cell constant necessary to convert the experimental torsion angles to pressure data were obtained vaporizing very pure benzoic acid and urea, the vapor pressures of which are well-known.[9,10] The constant values obtained with these standards, checked in runs carried out during the study of the compounds, were found to be reproducible within about 5 % of their average values. This uncertainty produces a very negligible shift in the intercepts of the final log *p* versus 1/*T* equations. In each vaporization run the torsion angles and then the vapor pressures were measured randomly over both ascending and descending temperatures (although in the tables they are reported as ascending), and at the beginning and the end of each experiment the measurements were made at approximately equal temperatures. In all experiments large amounts of fresh sample (∼1 g) were used, and the torsion measurements were stopped when about (10 to 15) % of the original weight was sublimed to obtain vapor pressures above $GaCl_2$ at near unit activity, when the amount of gallium produced during the sublimation of the sample was negligible. The vapor pressures of $GaCl_2$ are reported in Table 1 and Figure 1. The experimental data of each run was treated by the linear least-squares method to represent the temperature dependence of the vapor pressures as a log *p* versus 1/*T* equation. The slope and intercept of these equations are reported in Table 1. Weighting these slopes and intercepts proportionally to the experimental points, the following

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Table 1. Torsion Total Vapor Pressures of Solid $GaCl_2$ and Their Temperature Dependence Expressed by $\log(p/\mathrm{Pa}) = A - B/(T/\mathrm{K})$[a]

cell A run 2		cell A run 3		cell A run 5		cell A run 7	
T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)
394.0	−0.61	398.0	−0.53	390.0	−0.62	386.0	−0.82
396.0	−0.53	405.0	−0.23	398.0	−0.38	391.5	−0.62
399.0	−0.47	409.0	−0.11	402.5	−0.18	394.0	−0.48
405.0	−0.17	413.0	−0.01	406.5	−0.05	398.0	−0.35
410.5	−0.06	416.0	0.15	411.5	0.12	402.0	−0.14
415.5	0.10	420.0	0.29	415.5	0.28	407.5	−0.02
421.5	0.33	424.5	0.40	418.5	0.38	410.5	0.10
426.0	0.50	428.5	0.53	422.5	0.51	415.5	0.27
430.0	0.64	432.5	0.64	427.5	0.66	420.0	0.42
434.0	0.78	436.0	0.75	432.0	0.81	424.0	0.58
438.0	0.88	441.0	0.89	436.0	0.92	428.5	0.67
441.0	0.94					432.0	0.83
						437.0	0.95
						440.0	1.04
A	B	A	B	A	B	A	B
14.25 ± 0.22	5861 ± 93	13.92 ± 0.23	5741 ± 97	14.31 ± 0.14	5832 ± 59	14.33 ± 0.16	5841 ± 66
cell A run 8		cell A run 9		cell A run 11		cell B run 12	
T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)
386.0	−0.82	383.5	−0.92	384.0	−0.92	372.0	−1.34
389.0	−0.68	388.5	−0.75	386.0	−0.75	375.0	−1.21
394.0	−0.48	393.5	−0.52	392.0	−0.52	379.0	−1.04
397.5	−0.41	399.0	−0.32	398.5	−0.32	384.0	−0.91
401.0	−0.29	403.0	−0.18	403.0	−0.18	387.0	−0.73
405.5	−0.11	410.5	0.03	406.0	−0.02	391.5	−0.56
409.0	0.01	413.5	0.18	410.0	0.08	397.5	−0.28
413.0	0.16	416.5	0.28	413.5	0.16	402.0	−0.13
417.5	0.32	418.0	0.33	416.0	0.25	404.0	−0.11
419.0	0.38	421.5	0.47	419.0	0.33	411.5	0.19
421.5	0.48	426.0	0.63	422.5	0.48	415.0	0.33
425.5	0.63	430.5	0.78	426.0	0.61	421.0	0.53
430.0	0.72	436.0	0.92	429.0	0.72	426.0	0.60
435.5	0.90	440.0	1.03	432.0	0.81	429.0	0.71
439.0	1.00					433.0	0.85
A	B	A	B	A	B	A	B
14.38 ± 0.16	5871 ± 64	14.46 ± 0.13	5904 ± 54	13.98 ± 0.24	5699 ± 99	14.30 ± 0.19	5816 ± 77
cell B run 14		cell B run 15		cell B run 16		cell B run 18	
T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)
374.0	−1.51	375.0	−1.34	378.5	−1.21	375.0	−1.47
378.0	−1.34	381.0	−1.11	382.5	−1.04	381.5	−1.17
385.0	−0.97	387.5	−0.91	386.5	−0.91	386.5	−0.99
390.5	−0.81	391.0	−0.77	391.0	−0.73	393.0	−0.73
395.0	−0.56	394.0	−0.67	395.0	−0.56	399.5	−0.52
399.5	−0.42	396.5	−0.51	399.5	−0.40	402.5	−0.41
406.0	−0.17	399.0	−0.47	403.5	−0.26	409.0	−0.15
414.5	0.11	403.0	−0.32	407.5	−0.11	414.0	0.03
417.0	0.19	408.0	−0.15	411.0	0.01	416.5	0.11
422.0	0.33	414.0	0.08	414.0	0.10	423.5	0.36
428.0	0.51	417.0	0.20	416.5	0.19	427.0	0.44
431.0	0.57	421.0	0.33	417.5	0.23	430.0	0.52
436.0	0.74	424.5	0.45	422.0	0.37		
		427.5	0.54	426.0	0.49		
				430.0	0.64		
				434.0	0.74		
A	B	A	B	A	B	A	B
14.24 ± 0.25	5869 ± 100	14.18 ± 0.18	5835 ± 73	14.13 ± 0.06	5808 ± 25	14.19 ± 0.12	5868 ± 47

[a] Runs 7 and 15 are the data obtained above the condensed vapor (see text).

final equation, representative of the total vapor pressures of solid $GaCl_2$ in the temperature range of (372 to 441) K was selected:

$$\log(p/\mathrm{Pa}) = (14.23 \pm 0.30) - (5829 \pm 100)/(T/\mathrm{K}) \tag{1}$$

where the associated uncertainties are estimated. This equation was compared in Figure 2 with those found in literature above the liquid phase.

In two preliminary isothermal experiments the compound was heated and sublimated at (413 and 430) K under vacuum in a quartz tube under nonequilibrium conditions. The vapor was opportunely condensed on a cold small plate. Using a drybox, the plate with the condensed vapor was put in the torsion cell and its vapor pressure measured. The pressures so determined in equilibrium conditions (run 7 and 15), reported in Figure 3 in comparison with the line representative of eq 1, were found to be practically equal to those measured on the original compound. This led to the conclusion that in nonequilibrium conditions $GaCl_2$ sublimes as Ga_2Cl_4(g) (or $GaGaCl_4$) that partially condensed as $GaCl_2$(s) and partially decomposed in

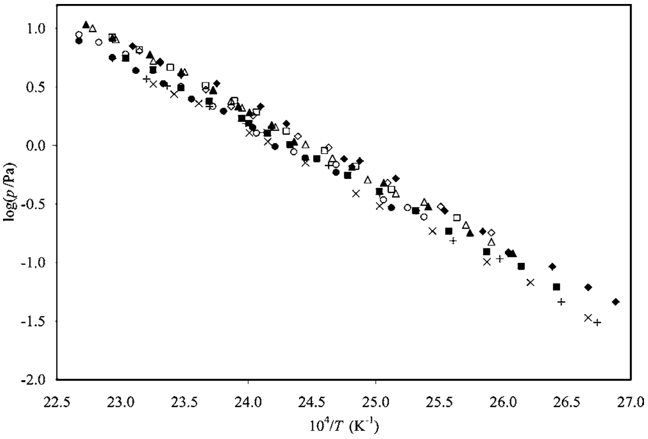

Figure 1. Torsion total vapor pressures of $GaCl_2$(s). ○, run A2; ●, run A3; □, run A5; △, run A8; ▲, run A9; ◇, run A11; ◆, run B12; +, run B14; ■, run B16; ×, run B18.

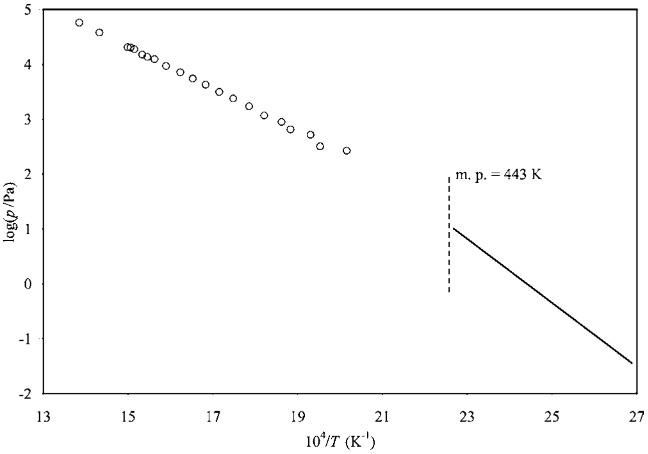

Figure 2. Comparison of the torsion total vapor pressures of $GaCl_2$(s) with those measured by Laubengayer and Schirmer[1] above the liquid compound (○).

GaCl(g) and $GaCl_3$(g). Because of its volatility $GaCl_3$(g) was completely pumped away, while GaCl(g) decomposed in turn as $GaCl_3$(g) and liquid gallium, the latter being practically not volatile over the experimental temperatures. Accidentally, at the end of the torsion experiments very small drops of pure Ga were also observed on the surface of the residue. The pure gallium was identified from scanning electron microscopy/energy-dispersive spectrometry (SEM-EDS) analysis.

From the slope of the selected eq 1, the second-law enthalpy change associated with the sublimation of a mole of gas mixture was determined to be $\Delta_{sub}H°(406\ K) = (111 \pm 2)\ kJ \cdot mol^{-1}$.

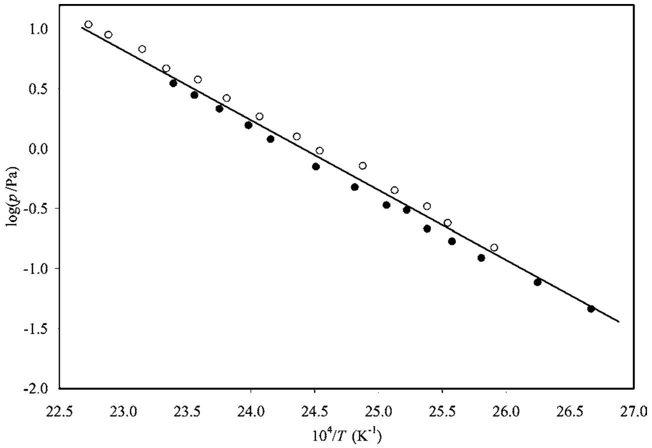

Figure 3. Torsion total vapor pressures of $GaCl_2$. ○, run A7; ●, run B15; the solid line represents eq 1.

Literature Cited

(1) Laubengayer, A. W.; Schirmer, F. B. The Chlorides of Gallium. *J. Am. Chem. Soc.* **1940**, *62*, 1578–1583.

(2) Ait-Hou, A.; Hillel, R.; Chatillon, C. Mass-Spectrometric Study of Gaseous (Gallium + Chlorine); Molar Enthalpies of Formation of Gallium Chlorides, Ga_2Cl_4 and Ga_2Cl_2. *J. Chem. Thermodyn.* **1988**, *20*, 993–1008.

(3) Kuniya, Y.; Hosaka, M. Vapor Phase Equilibriums in the Systems Indium-Indium Trichloride and Gallium - Gallium Trichloride. *J. Cryst. Growth* **1975**, *28*, 385–391.

(4) Zuegel, M. A. Vapor Phase Equilibria in the Gallium-Chlorine and Gallium Arsenide-Chlorine Systems. *J. Electrochem. Soc.* **1965**, *112*, 1153–1157.

(5) Kirwan, D. J. Reaction Equilibria in the Growth of GaAs and GaP by the Chloride Transport Process. *J. Electrochem. Soc.* **1970**, *117*, 1573–1577.

(6) Giricheva, N. I.; Girchev, G. V.; Titov, V. A.; Chusova, T. P.; Pavlova, G. Yu. Gallium Dichloride. Saturated Vapour Composition. Geometrical Structure and Vibrational Frequencies of the Gallium Chloride ($GaGaCl_4$) Molecule. *Z. Strukt. Khim.* **1992**, *33*, 50–59.

(7) Chatillon, C.; Bernard, C. Thermodynamic Calculations in CVD Growth of GaAs Compounds. 1. Critical Assessment of the thermodynamic Properties for the Gaseous Molecules of the Ga-Cl System. *J. Cryst. Growth* **1985**, *71*, 433–449.

(8) Brunetti, B.; Piacente, V.; Scardala, P. Torsion Vapor Pressures and Sublimation Enthalpies of Arsenic Triselenide and Tritelluride. *J. Chem. Eng. Data* **2007**, *52*, 24–29.

(9) Monte, M. J. S.; Santos, L. M. N. B. F.; Fulem, M.; Fonseca, J. M. S.; Sousa, C. A. D. New Static Apparatus and Vapor Pressure of Reference Materials: Naphthalene, Benzoic Acid, Benzophenone, and Ferrocene. *J. Chem. Eng. Data* **2006**, *51*, 757–766.

(10) Emel'yanenko, V. N.; Kabo, G. J.; Verevkin, S. P. Measurement and Prediction of Thermochemical Properties: Improved Increments for the Estimation of Enthalpies of Sublimation and Standard Enthalpies of Formation of Alkyl Derivatives of Urea. *J. Chem. Eng. Data* **2006**, *51*, 79–87.

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