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Thermodynamics of (gallium + chlorine)(g)

I. Vapour-pressure measurements and thermodynamic stability of GaCl(g), $GaCl_2$(g), $GaCl_3$(g), Ga_2Cl_2(g), Ga_2Cl_4(g), and Ga_2Cl_6(g)

C. BERNARD, C. CHATILLON,

Laboratoire de Thermodynamique et Physicochimie Métallurgiques,
U.A CNRS 29, E.N.S.E.E.G., Domaine Universitaire, B.P. 75,
38402 Saint-Martin d'Hères, France

A. AIT-HOU, R. HILLEL, Y. MONTEIL, and J. BOUIX

Laboratoire de Physicochimie Minérale I, U.A CNRS 116,
43, Boulevard du 11 Novembre 1918,
38402 Saint-Martin d'Hères, France

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Previously compiled thermodynamic quantities for gaseous species in (gallium + chlorine) are revised. Entropies and heat capacities of Ga_2Cl_6, Ga_2Cl_2, and Ga_2Cl_4 are re-calculated by the harmonic-oscillator rigid-rotator method taking account of recent spectroscopic quantities. Enthalpies of formation of GaCl, Ga_2Cl_2, $GaCl_2$, and Ga_2Cl_4 are deduced from vapour pressures measured by Bourdon gauge over {Ga(l) + $GaCl_3$(g)} and {GaAs(s) + $GaCl_3$(g)}. For (gallium + chlorine), enthalpy determinations were performed on the assumption that the gaseous phase is represented firstly by the major species GaCl and $GaCl_3$, and secondly by GaCl, $GaCl_3$, $GaCl_2$, Ga_2Cl_2, and Ga_2Cl_4. Another calculation was made taking account of the dilution of chlorine in the condensed phases. For (gallium + arsenic + chlorine), thermodynamic calculations were performed with a simple gaseous phase: $GaCl_3$, GaCl, As_4, and As_2; and with a complex gaseous phase represented by all the (gallium + chlorine) gaseous species. The results are discussed and allow us to propose a new set of formation enthalpies: $\Delta_f H^\circ_m(298.15\ \mathrm{K})/(\mathrm{kJ\cdot mol^{-1}})$: GaCl, $-(68.7 \pm 5.1)$; Ga_2Cl_2, $-(159 \pm 28)$; $GaCl_2$, $-(130 \pm 29)$; Ga_2Cl_4, $-(599 \pm 18)$.

1. Introduction

The main gaseous species of saturated and unsaturated vapours obtained from initial mixtures containing gallium and gallium trichloride are Ga_2Cl_6 and $GaCl_3$ for $x_{Cl}/x_{Ga} = 3$ ($373\ \mathrm{K} < T < 773\ \mathrm{K}$) and $GaCl_3$ and GaCl for $x_{Cl}/x_{Ga} < 3$ ($573\ \mathrm{K} < T < 1073\ \mathrm{K}$) as already studied by Raman spectroscopy;[1] (x_{Cl} and x_{Ga}

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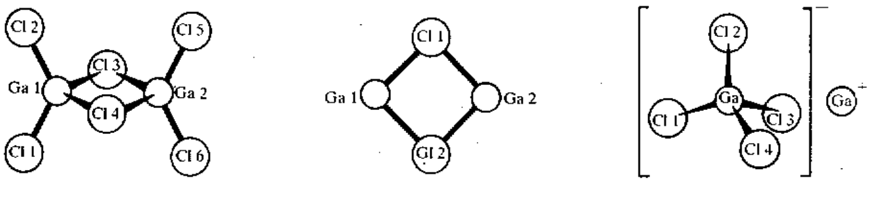
are respectively the Cl and Ga mole fractions). Partial pressures as deduced from Raman spectra are clearly different from those obtained by complex equilibrium calculations(2) from sets of compiled results for the known gaseous species in (gallium + chlorine). Qualitatively, Raman spectral observations suggest that some molecules do not exist as extensively as expected, especially Ga_2Cl_2 and Ga_2Cl_4.

As thermodynamics is of major importance for knowledge of the vapour-deposition mechanism of GaAs by the trichloride method,(3–11) our aim is to improve previous thermodynamic quantities(12, 13) for gaseous molecules in (gallium + chlorine), taking previous studies(14–17) and discrepancies(12) into account. We present in this study vapour-pressure measurements by Bourdon gauge performed with more favourable initial compositions than those used in previous works by the same method.

2. Reassessments of entropies and heat capacities

For thermodynamic interpretation of vapour-pressure measurements using the third-law method, we first discuss and select the thermodynamic functions related to the structure of the molecules. Entropies and heat capacities came from references 12 and 13 or were re-calculated by the harmonic-oscillator rigid-rotator method(18) taking account of recent spectroscopic quantities. For liquid gallium the thermodynamic functions came from reference 19.

For GaCl(g) and $GaCl_3$(g) values from the two compilations(12, 13) are in agreement since the molecular quantities came from the same set of original measurements.(20–22) For Ga_2Cl_6(g) the 2 per cent discrepancy in the entropies between references 12 and 13 came from slightly different structural and vibrational quantities.(23, 24) Recently we re-analysed(1) the assignment of vibrational frequencies and the thermodynamic functions were then calculated with the structure proposed from a recent electron-diffraction study(23) (figure 1). For $GaCl_2$(g) thermodynamic functions were estimated by Glushko,(13) structural quantities being similar to those for $GaCl_3$; the estimated vibrational frequencies



Ga_2Cl_6(g) Ga_2Cl_2(g) Ga_2Cl_4(g)

FIGURE 1. Structural quantities used in our thermodynamic calculations. For Ga_2Cl_6(g): Ga(1)–Cl(1), (0.2099±0.0002) nm; Ga(1)–Cl(3), (0.2300±0.0003) nm; Cl(1)–Ga(1)–Cl(2) angle, (2.175±0.031); Cl(3)–Ga(1)–Cl(4) angle, (1.541±0.014). For Ga_2Cl_2(g): Ga(1)–Cl(1), 0.2492 nm; Cl(1)–Ga(1)–Cl(2) angle, 1.599; Ga(1)–Cl(1)–Ga(2) angle, 1.543. For Ga_2Cl_4(g): Ga–Cl(1), 0.21 nm; $Ga–Ga^+$, 0.442 nm; Cl(1)–Ga–Cl(2) angle, 1.90. Calculated $I_A I_B I_C \times 10^{111}/(g^3 \cdot cm^6)$: for Ga_2Cl_6(g), 8.741; for Ga_2Cl_2(g), 0.28288; for the tetrahedral $GaCl_4^-$, 0.33177. Calculated $I/(g^3 \cdot cm^6)$ for the "diatomic" $(GaCl_4^-)$–(Ga^+), 1.7008×10^{-37}.

TABLE 1. Standard molar entropies and standard molar heat capacities of Ga_2Cl_6(g), Ga_2Cl_2(g), and Ga_2Cl_4(g) calculated by the harmonic-oscillator rigid-rotator method using structural quantities presented in figure 1 and vibrational quantities for Ga_2Cl_6, Ga_2Cl_2, and Ga_2Cl_4 respectively from references 1, 27, and 28, 29. $C^{\circ}_{p,\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 + d(T/\mathrm{K})^{-2}$. We adopt a 2 per cent error in the entropy as generally admitted for harmonic-oscillator rigid-rotator calculations

	$\dfrac{S^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K})}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\dfrac{C^{\circ}_{p,\mathrm{m}}(298.15\ \mathrm{K})}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	a	10^4b	10^8c	d
Ga_2Cl_6	492.6 ± 9.8	165.86	178.0438	58.91	−177.305	−1 153 487.0
Ga_2Cl_2	353.6 ± 7.1	79.74	83.0194	1.1895	−2.95386	−294 908.9
Ga_2Cl_4	446.8 ± 8.9	107.22	115.5952	8.662	−24.1756	−768 860.0

have been checked by us.(1) The entropies are in agreement with those checked(12) from analysis by the dimensional model.(25, 26) For Ga_2Cl_2 and Ga_2Cl_4(g) thermodynamic functions were estimated in reference 12 using the dimensional model.(25, 26) For Ga_2Cl_2(g), the M_2X_2 group of molecules(25) appears reliable since many molecules are known, and the values from the dimensional model are in agreement with those calculated by the harmonic-oscillator rigid-rotator method from estimates of the molecular quantities(27) (figure 1).

Estimates by dimensional analysis in the M_2X_4 set of molecules(26) show large discrepancies, probably coming firstly from lack of exact knowledge of molecular quantities for this class of molecule, and secondly from the diversity of their structures. We attempted to estimate the thermodynamic functions from recent spectroscopic studies.(28, 29) We know, at present, that the Ga_2Cl_4 molecule is an anionic one: $Ga^+[GaCl_4^-]$, the vibrational modes of which are assigned to the tetrahedral $GaCl_4^-$ ion (T_d symmetry) as already discussed in reference 1. The Ga–Cl distance in the tetrahedron is estimated as in the $GaCl_3$ molecule, and the Ga^+–Ga^{3+} distance as the sum of the preceding Ga–Cl bond: 0.21 nm, plus the covalent radius of Cl: 0.095 nm,(30) plus the ionic radius of Ga^+: 0.133 nm.(31) The molecular quantities are presented in figure 1. The thermodynamic functions were calculated as the sum of different contributions: vibrational and rotational ones for $GaCl_4^-$ and rotational and translational contributions of the "diatomic" $GaCl_4^-$–Ga^+. The electronic contribution was put equal to zero (σ state) since the $GaCl_4^-$ looks like an sp^3 hybridization and Ga^+ is a σ state. The estimated values for $Ga^+[GaCl_4^-]$ are reasonably in agreement with the dimensional model in reference 12.

The thermodynamic functions for Ga_2Cl_6, Ga_2Cl_4, and Ga_2Cl_2 are summarized in table 1.

3. Experimental

The original samples were gallium and gallium trichloride (Johnson Matthey: 99.9999 mass per cent). These samples were weighed in a glove box under pure nitrogen and mixed in ampoules. Some $GaCl_3$ samples were also prepared by reaction of an HCl gas flow over pure gallium as already described in the literature.(32) {Ga + $GaCl_3$} were placed under nitrogen flow in the Bourdon gauge which was quickly evacuated with a forepump fitted with a liquid-nitrogen trap. Simultaneously the reactor of the manometer was dipped in liquid nitrogen to avoid vaporization of $GaCl_3$, and then it was sealed. The Bourdon-gauge apparatus has been already described.(33) From previous experiments with the same apparatus(33) we estimate that the pressure measurements are accurate within ±0.1 per cent.

The chlorine content was also checked during each run in the high-temperature range where GaCl(g) is the main gaseous species. The discrepancy between the

TABLE 2. (Gallium + chlorine): vapour-pressure measurements and third-law calculations corresponding to reaction (1): $2Ga(l) + GaCl_3(g) = 3GaCl(g)$

T/K	$p/10^4$ Pa	$p(\mathrm{GaCl})/10^4$ Pa	$p(\mathrm{GaCl_3})/10^4$ Pa	$\ln K_1^\circ$	$\Delta_r H_m^\circ(298.15\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}}$	T/K	$p/10^4$ Pa	$p(\mathrm{GaCl})/10^4$ Pa	$p(\mathrm{GaCl_3})/10^4$ Pa	$\ln K_1^\circ$	$\Delta_r H_m^\circ(298.15\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}}$
Experiment 1; $x_{Cl}/x_{Ga} = 0.009$											
700	2.827	1.489	1.337	−3.730	209.75	763	4.114	3.171	0.942	−1.100	211.49
710	3.040	1.763	1.267	−3.160	211.05	778	4.458	3.627	0.831	−0.578	212.16
724	3.242	2.016	1.226	−2.720	210.25	782	4.661	3.911	0.740	−0.239	210.99
736	3.506	2.361	1.236	−2.180	211.08	802	5.066	4.448	0.618	0.325	212.26
745	3.749	2.695	1.054	−1.710	210.63	821	5.735	5.370	0.355	1.437	209.45
Experiment 2; $x_{Cl}/x_{Ga} = 0.099$											
710	3.506	1.469	2.037	−4.180	216.03	811	6.485	5.401	1.074	0.350	214.63
722	3.708	1.722	1.986	−3.670	216.32	823	6.900	5.958	0.932	0.794	214.47
739	4.134	2.270	1.864	−2.790	215.67	835	7.346	6.566	0.770	1.275	214.00
759	4.701	3.009	1.692	−1.850	215.36	844	7.660	7.001	0.659	1.620	213.79
771	5.087	3.546	1.550	−1.270	215.00	855	7.883	7.265	0.608	1.803	215.22
780	5.521	3.972	1.439	−0.860	214.59	874	8.390	7.934	0.456	2.362	215.58
789	5.705	4.357	1.348	−0.514	214.80	881	8.562	8.146	0.415	2.535	216.05
800	6.080	4.864	1.216	−0.085	214.65						
Experiment 3; $x_{Cl}/x_{Ga} = 0.116$											
688	2.330	0.851	1.479	−5.500	217.15	799	4.934	4.337	0.598	0.276	211.99
711	2.726	1.358	1.368	−4.010	215.33	810	5.208	4.701	0.507	0.685	212.00
722	2.979	1.692	1.287	−3.290	214.09	822	5.492	5.076	0.415	1.115	212.03
734	3.222	2.006	1.206	−2.730	214.04	833	5.765	5.441	0.314	1.577	211.50
747	3.496	2.371	1.125	−2.140	213.94	842	5.948	5.684	0.253	1.920	211.21
761	3.901	2.918	0.973	−1.380	213.07	854	6.211	6.039	0.172	2.486	210.14
773	4.225	3.364	0.851	−0.833	212.59	867	6.454	6.333	0.111	3.098	208.73
785	4.529	3.769	0.750	−0.370	212.70	880	6.657	6.596	0.051	3.897	205.75

Second- and third-law treatments of vapour-pressure measurements corresponding to the reaction: $2GaAs(s) + GaCl_3(g) = 3GaCl(g) + \frac{1}{2}As_4(g)$. Deduced values of the standard molar enthalpy of formation of GaCl(g)

	$\Delta_r H_m^\circ(785\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}}$	$\Delta_r S_m^\circ(785\ \mathrm{K})/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\Delta_r S_m^\circ(298.15\ \mathrm{K})/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\Delta_r H_m^\circ(298.15\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}}$		$\Delta_f H_m^\circ(\mathrm{GaCl, g, 298.15\ K})/\mathrm{kJ \cdot mol^{-1}}$	
Law:	2nd	2nd	2nd	2nd	3rd	2nd	3rd
This work	447 ± 15[a]	397 ± 15[a]	429	465 ± 15[a]	460.1 ± 3.0[a]	−66.1	−69.6
From references 12 and 35			423.5		454.1		−71.5

[a] Standard error based on 19 determinations.

GaCl(g) concentration calculated from the perfect-gas law and from the weighed initial $GaCl_3$ being about 3 per cent, we have estimated that water pollution can be neglected.(34) GaAs (99.999 mass per cent) comes from "la Radiotechnique Compelec". In the case of $\{GaAs+GaCl_3\}$, the chlorine content was checked by calculating the $GaCl_3$ concentration from unsaturated pressure values at temperatures lower than 800 K where this species predominates.

4. Enthalpy determinations with assumption of a simple gaseous phase

This first use of the vapour pressures corresponds to the assumption that the gaseous phase is represented by the major species which have been observed by Raman spectroscopy.(1) The measured pressures for three different compositions of the initial $\{Ga(s)+GaCl_3(s)\}$ are presented in table 2 and in figure 2. As already analysed by Raman spectroscopy, in the temperature range 573 to 1073 K, the main reaction is

$$2Ga(l)+GaCl_3(g) = 3GaCl(g). \qquad (1)$$

By assuming that all the chlorine is in the gas phase, that the gas mixture is perfect, and that Ga(l) occupies a negligible volume, the partial pressures are

$$p(GaCl_3) = 1.5nRT/V-0.5p \quad \text{and} \quad p(GaCl) = 1.5(p-nRT/V), \qquad (2)$$

where n is the amount of substance of $GaCl_3$ introduced into the reactor of the Bourdon-gauge, its volume V being taken as constant, and p is the measured

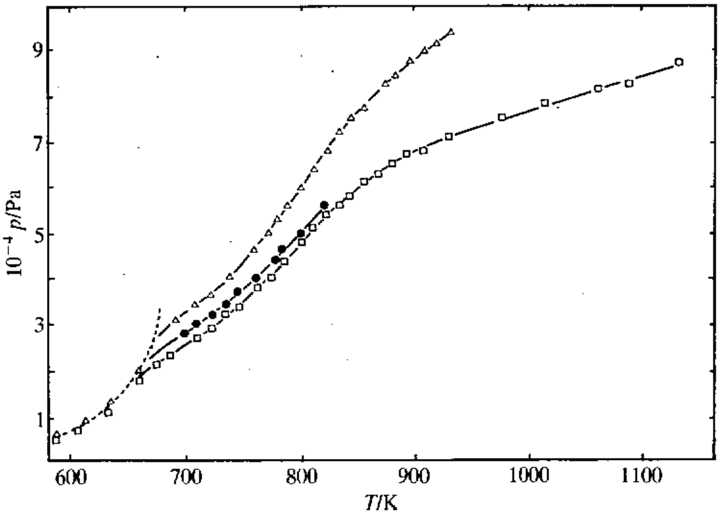


FIGURE 2. Measured total pressures with $(Ga+GaCl_3)$ mixtures: ●, $x_{Cl}/x_{Ga} = 0.009$, $V = 73.5\ \mathrm{cm^3}$, initial mass of Ga: 5.510 g, initial mass of $GaCl_3$: 40.8×10^{-3} g; Δ, $x_{Cl}/x_{Ga} = 0.099$, $V = 94.65\ \mathrm{cm^3}$, initial mass of Ga: 0.820 g, initial mass of $GaCl_3(g)$: 71.2×10^{-3} g; □, $x_{Cl}/x_{Ga} = 0.116$, $V = 93.3\ \mathrm{cm^3}$, initial mass of Ga: 0.500 g, initial mass of $GaCl_3$: 50.7×10^{-3} g. V is the volume of the Bourdon-gauge reactor. ----, Saturated vapour pressure.

TABLE 3. Second- and third-law treatments of vapour-pressure measurements for the reaction: $2Ga(l)+GaCl_3(g) = 3GaCl(g)$, and deduced values of the standard molar enthalpy of formation of GaCl(g); our calculated value depends on $\Delta_f H_m^\circ(GaCl_3, g, 298.15\ K) = -(428.4\pm8.4)\ kJ\cdot mol^{-1}$ according to reference 12

Law	$\Delta_r H_m^\circ(785\ K)$ / $kJ\cdot mol^{-1}$	$\Delta_r S_m^\circ(785\ K)$ / $J\cdot K^{-1}\cdot mol^{-1}$	$\Delta_r S_m^\circ(298.15\ K)$ / $J\cdot K^{-1}\cdot mol^{-1}$	$\Delta_r H_m^\circ(298.15\ K)$ / $kJ\cdot mol^{-1}$		$\Delta_f H_m^\circ(GaCl, g, 298.15\ K)$ / $kJ\cdot mol^{-1}$	
	2nd	2nd	2nd	2nd	3rd	2nd	3rd
This work	219.3 ± 5.4[a]	277.7 ± 7.0[a]	299.7	230.3 ± 5.4[a]	211.7 ± 0.4[a]	−63.3	−68.5
From Chatillon and Bernard's compilation(12)			275.6		202.6		-71.5 ± 2.9
From Glushko's compilation(13)			276.9		208.8		-70.5 ± 5.9

[a] Standard error based on 26 determinations.

pressure at the temperature T. The standard equilibrium constant K_1° is given by

$$K_1^\circ = \{p(GaCl)/p^\circ\}^3/\{p(GaCl_3)/p^\circ\}, \tag{3}$$

where p° is the standard pressure.† Then the (third-law) standard molar enthalpy of reaction (1) is given by

$$\Delta_r H_m^\circ(298.15\ K) = -RT\ln K_1^\circ + \Delta_r(T\Delta_0^T S_m^\circ - \Delta_{298.15\,K}^T H_m^\circ). \tag{4}$$

The one-way analysis of variance of the three experiments leads us to retain the first and the third experiments (table 2) ($F_{24}^1 = 2.41$ is smaller than the tabulated value 4.26 for 95 per cent confidence(35) only for those two experiments). The second- and third-law results considered together for those two experiments are summarized in table 3. From the third-law result, which we consider more reliable than the second-law result, and taking into account the value of the standard molar enthalpy of formation of $GaCl_3(g)$ stated in reference 12: $\Delta_f H_m^\circ(GaCl_3, g, 298.15\ K) = -(428.4\pm8.4)\ kJ\cdot mol^{-1}$, we deduce the standard molar enthalpy of formation of GaCl(g) (table 3).

The gaseous phase from initial $\{GaAs(s)+GaCl_3(s)\}$ has been analysed by Raman spectroscopy. For temperatures above 873 K, the main gaseous species are $GaCl_3$, GaCl, and As_4. So our pressure measurements (table 4) were performed by assuming that the main reactions are

$$2GaAs(s)+GaCl_3(g) = 3GaCl(g)+\tfrac{1}{2}As_4(g), \tag{5}$$

$$As_4(g) = 2As_2(g). \tag{6}$$

At equilibrium, the amounts of substance are (n_2-2x) of GaAs, (n_1-x) of $GaCl_3$, $3x$ of GaCl, y of As_4, and $(x-2y)$ of As_2, where n_1 and n_2 are the amounts of $GaCl_3$ and of GaAs introduced into the reactor of the Bourdon gauge. Values of the standard equilibrium constant of reaction (6):

$$(x-2y)^2(p/p^\circ)/\{y(n_1+3x-y)\}, \tag{7}$$

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† Throughout this paper p° is taken as 101 325 Pa.

TABLE 4. (Gallium + arsenic + chlorine): vapour-pressure measurements and third-law calculations for reaction (5): $2\mathrm{GaAs(s)}+\mathrm{GaCl_3(g)} = 3\mathrm{GaCl(g)}+\frac{1}{2}\mathrm{As_4(g)}$. The initial conditions were mass of GaAs, 183.6 mg; mass of $\mathrm{GaCl_3}$, 29.4 mg; volume of the Bourdon gauge reactor, 72.7 $\mathrm{cm^3}$

T/K	$p/10^4\ \mathrm{Pa}$	$\ln K_5^\circ$	$\Delta_r H_m^\circ(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}}$	T/K	$p/10^4\ \mathrm{Pa}$	$\ln K_5^\circ$	$\Delta_r H_m^\circ(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}}$
892	1.864	−12.946	464.00	982	2.786	−6.823	459.35
906	2.026	−10.792	454.77	988	2.959	−6.215	456.86
908	1.945	−12.018	465.29	993	2.989	−6.151	458.55
927	2.077	−10.709	464.48	1012	3.384	−5.086	458.00
928	2.108	−10.387	462.38	1015	3.283	−5.390	461.74
946	2.361	−8.600	457.06	1022	3.242	−5.515	463.09
954	2.381	−8.585	460.79	1030	3.435	−5.019	461.68
960	2.472	−8.105	459.75	1047	3.840	−4.093	457.12
964	2.594	−7.496	456.29	1048	3.911	−4.055	464.60
973	2.655	−7.302	458.82				

from reference 35 were used to solve for y for given x and then to solve for x in $p = (n_1+3x-y)RT/V$. The calculated partial pressures allow us to obtain the standard equilibrium constant of reaction (5):

$$K_5^\circ = \{p(\mathrm{GaCl})/p^\circ\}^3\{p(\mathrm{As_4})/p^\circ\}^{0.5}/\{p(\mathrm{GaCl_3})/p^\circ\}. \tag{8}$$

The second- and third-law treatments, using the enthalpies and heat capacities of GaAs(s) and $\mathrm{As_4}$(g),(36, 37) are presented in table 4.

Our measurements performed with $x_{\mathrm{Cl}}/x_{\mathrm{Ga}} \leqslant 0.116$ for $\{\mathrm{Ga}+\mathrm{GaCl_3}\}$, and for $\{\mathrm{GaAs}+\mathrm{GaCl_3}\}$, confirm the analysis done in the previous compilation,(12) that explained the trend in the determinations of $\Delta_f H_m^\circ(\mathrm{GaCl, g})$ by the presence of other complex gaseous molecules in the gas phase when initial mixtures were richer in chlorine than our present measurements. Our values for $\Delta_f H_m^\circ(\mathrm{GaCl, g})$ are in agreement with the range proposed in references 12 and 13 since the mole fractions of complex gaseous species are small as already suggested by Raman spectroscopy.(1) Nevertheless, minor species may be present in the gaseous phase, as already calculated in reference 12 but at mole fractions lower than the Raman-detection threshold.

5. Enthalpy determinations with assumption of a complex gaseous phase

Entropies of all the molecules and enthalpies of well known molecules ($\mathrm{Ga_2Cl_6}$, $\mathrm{GaCl_3}$, $\mathrm{As_2}$, and $\mathrm{As_4}$), were introduced as polynomials in the temperature, calculated from Chatillon and Bernard's compilation.(12) For (gallium + chlorine) for x_{Cl} as low as 0.1, we have shown(12) that $p(\mathrm{Ga_2Cl_6})$ may be neglected, as long as $\{\mathrm{Ga}+\mathrm{GaCl_3}\}$ are not saturated and the temperature is high enough. So in our determinations, we assumed that the gaseous phase contained only GaCl, $\mathrm{Ga_2Cl_2}$, $\mathrm{GaCl_2}$, $\mathrm{Ga_2Cl_4}$, and $\mathrm{GaCl_3}$. The independent set of equilibria which were taken into account were

$$2\mathrm{Ga(l)}+\mathrm{GaCl_3(g)} = 3\mathrm{GaCl(g)}, \tag{1}$$

$$\mathrm{Ga_2Cl_4(g) = GaCl(g) + GaCl_3(g)}, \tag{9}$$

$$\mathrm{Ga_2Cl_4(g) = 2GaCl_2(g)}, \tag{10}$$

$$\mathrm{Ga_2Cl_2(g) = 2GaCl(g)}. \tag{11}$$

The measured pressure p is

$$p = p(\mathrm{GaCl_3}) + p(\mathrm{GaCl}) + p(\mathrm{Ga_2Cl_4}) + p(\mathrm{GaCl_2}) + p(\mathrm{Ga_2Cl_2}). \tag{12}$$

The chlorine mass balance is

$$3nRT/V = 3p(\mathrm{GaCl_3}) + p(\mathrm{GaCl}) + 4p(\mathrm{Ga_2Cl_4}) + 2p(\mathrm{GaCl_2}) + 2p(\mathrm{Ga_2Cl_2}), \tag{13}$$

where n is the initial amount of substance of $\mathrm{GaCl_3}$. These two equations, with the aid of the four standard equilibrium constants K_1°, K_9°, K_{10}°, and K_{11}° lead to

$$\begin{aligned}&\{p(\mathrm{GaCl})/p^\circ\}^4 + 0.75K_9^\circ\{p(\mathrm{GaCl})/p^\circ\}^3 + \\ &\quad + 0.5\{(K_1^\circ K_9^\circ/K_{10}^\circ) + (K_1^\circ K_9^\circ K_{11}^\circ)^{1/2}\}\{p(\mathrm{GaCl})/p^\circ\}^2 + 0.25K_1^\circ K_9^\circ\{p(\mathrm{GaCl})/p^\circ\} \\ &\qquad - 0.75nRT/p^\circ V = 0. \end{aligned} \tag{13}$$

The equilibrium constants, according to third law are written

$$\ln K_i^\circ = -\Delta_\mathrm{r} H_\mathrm{m}^\circ(298.15\ \mathrm{K})/RT + \Delta_\mathrm{r}(T\Delta_0^T S_\mathrm{m}^\circ - \Delta_{298.15\,\mathrm{K}}^T H_\mathrm{m}^\circ)/RT, \tag{14}$$

i corresponding to reactions (1), (9), (10), and (11). The second term was calculated from heat capacities and entropies (section 2) and the different equilibrium constants used are presented in table 5. A least-squares fit produces directly $\Delta_\mathrm{r} H_\mathrm{m}^\circ(298.15\ \mathrm{K})$ for reactions (1), (9), (10), and (11). From the well-known $\Delta_\mathrm{f} H_\mathrm{m}^\circ(\mathrm{GaCl_3}, \mathrm{g}, 298.15\ \mathrm{K})$,[12] the standard molar enthalpies of formation of the other gallium chlorides were deduced. With such use of the vapour-pressure measurements, adding minor species may influence the stability of main gaseous species as determined in section 4.

As $\mathrm{Ga_2Cl_4}$ has been found by Raman spectroscopy of the same compositions[1] we always kept this molecule in our calculations. We discarded first $\mathrm{GaCl_2(g)}$ since

TABLE 5. Equilibrium constant expressions K_1°, K_9°, K_{10}°, and K_{11}° as functions of temperature T used in enthalpy determinations for a complex gaseous phase. The $\Delta_\mathrm{r} H_\mathrm{m}^\circ(i)$ are determined by least-squares fits

$\mathrm{2Ga(l) + GaCl_3(g) = 3GaCl(g)}$

$$\begin{aligned}\ln K_1^\circ = &-\Delta_\mathrm{r} H_1^\circ(298.15\ \mathrm{K})/RT + 13.866 \times 10^{-5}(T/\mathrm{K}) + 34286.58(\mathrm{K}/T)^2 \\ &+ 22.4697 \times 10^{-9}(T/\mathrm{K})^2 - 11.8336 \ln(T/\mathrm{K}) - 3743.1051(\mathrm{K}/T) + 218.229.\end{aligned}$$

$\mathrm{Ga_2Cl_4(g) = GaCl(g) + GaCl_3(g)}$

$$\begin{aligned}\ln K_9^\circ = &-\Delta_\mathrm{r} H_9^\circ(298.15\ \mathrm{K})/RT - 33.702 \times 10^{-4}(T/\mathrm{K}) + 624\,444.93(\mathrm{K}/T)^2 \\ &+ 35.4753 \times 10^{-8}(T/\mathrm{K})^2 + 0.3549 \ln(T/\mathrm{K}) - 4365.652(\mathrm{K}/T) + 73.3543.\end{aligned}$$

$\mathrm{Ga_2Cl_4(g) = 2GaCl_2(g)}$

$$\begin{aligned}\ln K_{10}^\circ = &-\Delta_\mathrm{r} H_{10}^\circ(298.15\ \mathrm{K})/RT + 23.8743 \times 10^{-3}(T/\mathrm{K}) + 650\,718.11(\mathrm{K}/T)^2 \\ &+ 41.756 \times 10^{-8}(T/\mathrm{K})^2 - 1.1652 \ln(T/\mathrm{K}) - 2572.181(\mathrm{K}/T) + 85.646.\end{aligned}$$

$\mathrm{Ga_2Cl_2(g) = 2GaCl(g)}$

$$\begin{aligned}\ln K_{11}^\circ = &-\Delta_\mathrm{r} H_{11}^\circ(298.15\ \mathrm{K})/RT - 8.6563 \times 10^{-5}(T/\mathrm{K}) + 77698.34(\mathrm{K}/T)^2 \\ &+ 5.2543 \times 10^{-8}(T/\mathrm{K})^2 - 3.8438 \ln(T/\mathrm{K}) - 1672.22(\mathrm{K}/T) + 91.487.\end{aligned}$$

it has never been found or measured, and second $GaCl_2(g)$ and $Ga_2Cl_2(g)$ because their enthalpies suffer from large uncertainties. All the results are summarized in table 6.

The selection of the more reliable assumptions about the number of molecules in the gaseous phase was done by considering the calculated values of $\Delta_f H^\circ_m(\mathrm{GaCl, g, 298.15\ K})$. As this enthalpy had already been accurately selected in the compilation:(12) $-(71.5 \pm 2.9)\ \mathrm{kJ \cdot mol^{-1}}$, and also was confirmed in section 4 of this study: $-(68.5\ \mathrm{kJ \cdot mol^{-1}})$, a non-realistic value was found from the second assumption in table 6, out of the uncertainty range. The first and third assumptions might be retained, but the scatter shows either that the results are very sensitive to experimental uncertainties or to the thermodynamics of the condensed phase. Another calculation was made taking account of the thermodynamic properties of the liquid (gallium + chlorine) at infinite dilution of chlorine:

$$\mathrm{Ga(l) + Cl(l) = GaCl(g)}, \tag{15}$$

$$K^\circ_{15} = \{p(\mathrm{GaCl})/p^\circ\}/\{f^\infty_{\mathrm{Cl}} x_{\mathrm{Cl}}(1 - x_{\mathrm{Cl}})\}, \tag{16}$$

where f^∞_{Cl} is the infinite-dilution activity coefficient of chlorine in gallium. The mass balance is done on Ga and on Cl in the Bourdon gauge. The calculated enthalpies of formation are quite close to the preceding values (assumption 1), the f^∞_{Cl}s being similar from one experiment to the other as presented in table 6. The x_{Cl} values are very small, around 10^{-7}. The enthalpies of formation of $Ga_2Cl_2(g)$ and $GaCl_2(g)$

TABLE 6. Enthalpy determinations from measured pressures over $\{Ga + GaCl_3\}$ with the assumption of a complex gaseous phase

(a), Taking account the equilibria 1, 9, 10, and 11 for the first assumption; 1, 9, and 10 for the second assumption; and 1 and 9 for the third assumption

Equilibria taken into account		$x_{\mathrm{Cl}}/x_{\mathrm{Ga}}$	T/K	$\Delta_f H^\circ_m(298.15\ \mathrm{K})/(\mathrm{kJ \cdot mol^{-1}})$ GaCl	Ga_2Cl_2	$GaCl_2$	Ga_2Cl_4
	1						
First	9	0.116	670 to 850	−68.9	−184.6	−128.9	−599.8
assumption	10	0.099	660 to 820	−68.0	−189.6	−128.3	−595.0
	11	0.009	710 to 820	−69.0	−146.2	−126.2	−517.7
Second	1	0.116	675 to 892	−95.6	−248.2		−573.8
assumption	9	0.099	738 to 930	−85.8	−246.2		−579.4
	10	0.009	710 to 820	−83.8	−245.7		−563.3
Third	1	0.116	722 to 854	−68.1			−538.7
assumption	9	0.099	693 to 823	−67.3			−533.5
		0.009	710 to 820	−69.0			−540.4

(b), Taking account the equilibria 1, 9, 10, and the condensed phase

$x_{\mathrm{Cl}}/x_{\mathrm{Ga}}$	T/K	$\Delta_f H^\circ_m(298.15\ \mathrm{K})/(\mathrm{kJ \cdot mol^{-1}})$ GaCl	Ga_2Cl_2	$GaCl_2$	Ga_2Cl_4	$10^2 f^\infty_{\mathrm{Cl}}$
0.116	711 to 854	−68.9	−122.8	−122.6	−599.6	1.093
0.099	693 to 823	−67.8	−150.5	−113.1	−592.8	1.150
0.009	700 to 801	−71.0	−239.0	−161.0	−610.3	0.985

are scattered probably because of their very small concentrations {their pressures do not exceed $10^{-6}p(Ga_2Cl_4)$}.

For (gallium + arsenic + chlorine), mass balance and the equilibria:

$$2GaAs(s)+GaCl_3(g) = 3GaCl(g)+\tfrac{1}{2}As_4(g), \quad (5)$$

$$As_4(g) = 2As_2(g), \quad (6)$$

$$Ga_2Cl_4(g) = GaCl(g)+GaCl_3(g), \quad (9)$$

$$Ga_2Cl_4(g) = 2GaCl_2(g), \quad (10)$$

$$Ga_2Cl_2(g) = 2GaCl(g), \quad (11)$$

$$Ga_2Cl_6(g) = 2GaCl_3(g), \quad (17)$$

were taken into account by calculation from vapour-pressure measurements presented in Section 5. As in the preceding Section, different assumptions were made. The results are presented in table 7. The second and third assumptions should lead to a Ga_2Cl_2 molecule stable enough to have been measured in Raman-spectral observations,(1, 2) occulting the Ga_2Cl_4 molecule. The two other assumptions suffer from large uncertainties related to very low calculated partial pressures for Ga_2Cl_2, $GaCl_2$, and Ga_2Cl_4 (10^{-3} to 10^{-7} Pa). The standard molar enthalpy of formation of GaCl(g) is similar to that deduced with a simple gas-phase assumption (Section 4), since all complex molecules have small concentrations.

6. Discussion

From our different assumptions we retain the assumption of a simple gaseous phase for (gallium + chlorine) and (gallium + arsenic + chlorine) (third-law treatments: tables 3 and 4); the assumption of a complex gaseous phase for (gallium + chlorine), cases 1 and 3 (table 6); and the assumption of complex gaseous and condensed phases for (gallium + chlorine) (table 6).

These three apparently most reliable modes of calculations are summarized in table 8. To display our Raman observations(1, 2) and our Bourdon-gauge experiments, we simulated these experiments by complex equilibrium calculations from thermodynamic quantities from reference 12 or table 8. In figure 3 we compare experimental Raman partial pressures,(2) with calculated ones. Discrepancies are

TABLE 7. Enthalpy determinations from measured pressures over {GaAs+$GaCl_3$} with the assumption of a complex gaseous phase

Assumption	Equilibria taken into account	$\Delta_f H^\circ_m(298.15\ K)/(kJ\cdot mol^{-1})$ GaCl	Ga_2Cl_2	$GaCl_2$	Ga_2Cl_4
1	6, 7, 9, 10, 11, 18	−69.5	−130.0	−75.1	−488.9
2	6, 7, 9, 10, 18	−66.5	−289.6		−642.8
3	6, 7, 11, 18	−67.6	−280.6		
4	6, 7, 9, 10, 18	−69.5		−94.1	−527.2

TABLE 8. Selected standard molar enthalpies of formation of gaseous GaCl, Ga_2Cl_2, $GaCl_2$, and Ga_2Cl_4. Values of the standard molar enthalpies of formation of $GaCl_3$(g): $-(428.4 \pm 8.4)$ kJ · mol^{-1} and of Ga_2Cl_6(g): $-(958 \pm 13)$ kJ · mol^{-1} come from reference 12

Treatment of the vapour-pressure measurements	$\Delta_f H^\circ_m$(298.15 K)/(kJ · mol^{-1})			
	GaCl	Ga_2Cl_2	$GaCl_2$	Ga_2Cl_4
Enthalpy determination with the assumption of a simple gaseous phase (gallium + chlorine)	−68.5			
(gallium + arsenic + chlorine)	−69.5			
Enthalpy determinations with the assumption of a complex gaseous phase	−68.9	−184.6	−128.9	−599.8
without condensed phase	−68.0	−189.6[a]	−128.3	−595.0
	−69.0	−146.2	−126.2	−517.7[a]
	−68.1			−538.7[a]
	−67.3			−533.5[a]
	−69.0			−540.4[a]
with condensed phase	−68.9	−122.8	−122.6	−599.6
	−67.8	−150.5	−113.1	−592.8
	−71.0	−239.0[a]	−161.0	−610.3
mean values	−68.7	−172.0	−129.7	−569.9
Selected values with estimated uncertainties	−68.7 ± 5.1	−159 ± 28	−130 ± 29	−599 ± 18

[a] Discarded value.

important for the compiled quantities,(12) since the agreement is quite good with table 8 for GaCl and $GaCl_3$ species. The Ga_2Cl_2 molecule, very important with compiled quantities(12) becomes a minor species in agreement with our detection threshold in Raman spectroscopy.(1) The Ga_2Cl_4 pressure follows the same trend, but remains the most important species compared with Ga_2Cl_2. This pressure value explains why we were able to observe it(1) although with difficulties. So, our values in table 8 show that the Ga_2Cl_2 and Ga_2Cl_4 molecules are less stable than proposed in reference 12.

Looking at the evolution of the Ga_2Cl_6 pressure when the enthalpy of formation of Ga_2Cl_4 increases, we observe that Ga_2Cl_6 should be detectable by Raman spectroscopy. So, we are able to calculate the limits of enthalpies of formation which are compatible with our Raman and Bourdon observations. Two steps are necessary in our complex equilibrium calculations. The first is the competition between Ga_2Cl_2 and Ga_2Cl_4 molecules. With a mean value of -569.9 kJ · mol^{-1} for the standard molar enthalpy of formation of Ga_2Cl_4, the standard molar enthalpy of formation of Ga_2Cl_2 would be greater than -186.2 kJ · mol^{-1} to have this species undetectable. The second step is the competition between Ga_2Cl_4 and Ga_2Cl_6. The standard molar enthalpy of formation of Ga_2Cl_4 has to be less than -581.6 kJ · mol^{-1} to prevent Ga_2Cl_6 from appearing in the spectrum. So, comparing our enthalpy values in table 8, we had to discard those non-compatible with these limits and we decided to select the means of retained values. Their overall uncertainties were estimated taking into account these limits of compatibility. For $GaCl_2$(g) the uncertainty includes all the values in table 8. For GaCl(g) the overall

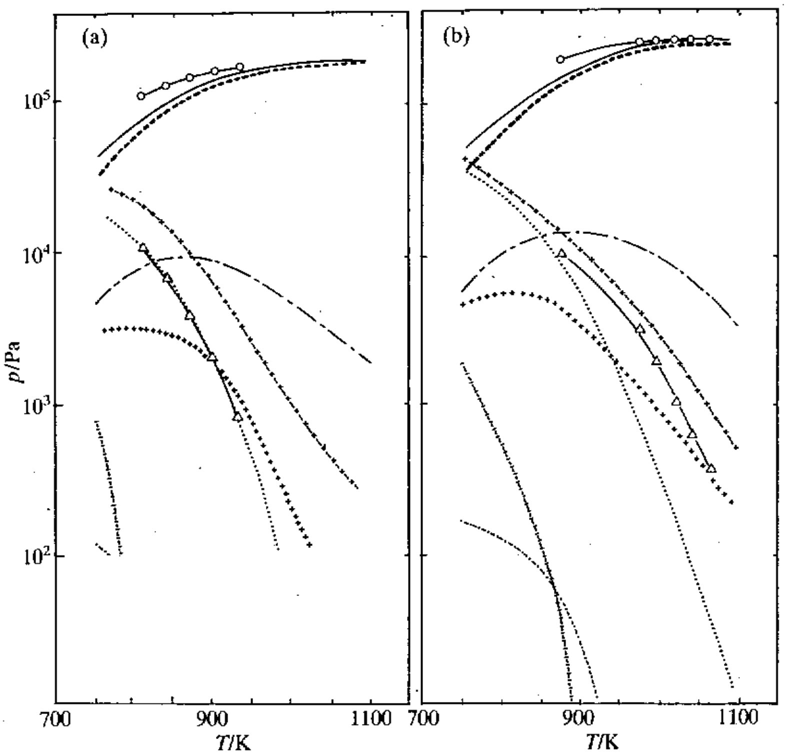

FIGURE 3. Gaseous phase composition corresponding to the initial conditions: (a), $x_{Cl}/x_{Ga} = 0.122$; initial mass of Ga: 0.177 g; initial mass of $GaCl_3$: 19.1 mg; volume of the Raman cell: 15.7 cm^3; (b), $x_{Cl}/x_{Ga} = 1$; initial mass of Ga: 25.6 mg; initial mass of $GaCl_3$: 26.4 mg; volume of the Raman cell: 14.5 cm^3. Partial pressures from calculations performed using thermodynamic quantities from reference 12: — — —, $p(GaCl)$; + + +, $p(GaCl_3)$; ····, $p(Ga_2Cl_4)$; - — -, $p(Ga_2Cl_2)$. Partial pressures from calculations performed using our selected results: ——, $p(GaCl)$; +–+–, $p(GaCl_3)$; –·–·, $p(Ga_2Cl_4)$; |—|—|, $p(Ga_2Cl_6)$. Partial pressures determined by the use of Raman spectra (reference 2): △–△–△, $p(GaCl_3)$; -○-○-, $p(GaCl)$.

uncertainty of 5.1 $kJ \cdot mol^{-1}$ is based on a standard error of ± 1.0 $kJ \cdot mol^{-1}$ and includes the uncertainty in the standard molar enthalpy of formation of $GaCl_3(g)$. (The number 5.1 is equal to $(1.0 \times 2.262 + 8.4/3)$, where 2.262 is the value of Student's *t* for 9 degrees of freedom for 95 per cent confidence and 8.4 is the inaccuracy of $\Delta_f H^{\circ}_m(GaCl_3, g)$ given in reference 12; 8.4 is divided by 3 considering that $\Delta_f H^{\circ}_m(GaCl, g)$ is deduced from the standard molar enthalpy of the reaction: $2Ga(l) + GaCl_3(g) = 3GaCl(g)$. The uncertainty on $\Delta_f H^{\circ}_m(Ga, l)$ was neglected.) The different standard molar enthalpies of formation at 298.15 K that we propose for the gaseous species GaCl, Ga_2Cl_2, $GaCl_2$, Ga_2Cl_4, $GaCl_3$, and Ga_2Cl_6 are presented in table 8.

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