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Mass-spectrometric study of (indium + chlorine)(g)

Enthalpies of formation of InCl(g), In_2Cl_2(g), In_2Cl_4(g), $InCl_3$(g), and In_2Cl_6(g)

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The gaseous phase in equilibrium with InCl(s or l), $InCl_2$(s or l), or $InCl_3$(s) was analysed by the Knudsen-cell mass-spectrometric method. $InCl_3$(g) and In_2Cl_6(g) are the main species vaporizing from $InCl_3$(s); InCl(g), In_2Cl_2(g), In_2Cl_4(g), and $InCl_3$(g) from InCl(s or l); and In_2Cl_4(g), $InCl_3$(g), InCl(g), In_2Cl_6(g), and In_2Cl_2(g) from $InCl_2$(s). The gas-phase analysis was performed by studying the ionization-efficiency curves and ionic-intensity ratios as a function of the temperature of vaporization and chemical composition in (indium + chlorine) for every $In_xCl_y^+$ ion ($x = 1, 2$ and $y = 0$ to 5). Enthalpies of formation were deduced from vaporization and gas-phase equilibria: $\Delta_f H_m^\circ(InCl_3, g, 298.15\,K) = -(375.7 \pm 5.0)\ kJ \cdot mol^{-1}$, $\Delta_f H_m^\circ(In_2Cl_6, g, 298.15\,K) = -(883.7 \pm 10.0)\ kJ \cdot mol^{-1}$, $\Delta_f H_m^\circ(InCl, g, 298.15\,K) = -(68.2 \pm 4.6)\ kJ \cdot mol^{-1}$, $\Delta_f H_m^\circ(In_2Cl_4, g, 298.15\,K) = -(573.2 \pm 12.6)\ kJ \cdot mol^{-1}$. A lower bound was calculated for $InCl_2$(g): $\Delta_f H_m^\circ(InCl_2, g, 298.15\,K) \geqslant -201\ kJ \cdot mol^{-1}$.

1. Introduction

A knowledge of the thermodynamic properties of gaseous indium chlorides is the first step in determining the reactions occurring in chemical vapour deposition (CVD) of InP- or InAs-based (III + V) compounds by the chloride method.(1) The limiting kinetic step can be determined by calculation of the supersaturation of each gaseous species and of relative matter flow per chlorine atom. The combination of these two variables was successful in the modelling of the chemical vapour deposition of GaAs.(2) In such a modelling study, all gaseous species must be taken into account since even a minor species might explain the evolution of the deposition rate. As our object is the explanation of CVD mechanisms of InP,(3) and InGaAsP quaternary multilayers, we need good values for the vapour phases involved. We present in this paper a mass-spectrometric study of the vapour phase in (indium + chlorine).

A set of compiled results has been published,(4) but some molecules are fully estimated *e.g.* $InCl_2$(g), while others *e.g.* In_2Cl_2(g) and In_2Cl_4(g), the existence of

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which has been assumed to interpret Bourdon-gauge experiments,(5,6) are omitted. Calculations with different sets of results can lead to erroneous interpretations of CVD processes. As for (gallium + chlorine),(7) our aim is to obtain thermodynamic values by a method which has not yet been quantitatively used for studying this system. The Knudsen-cell mass-spectrometric method(8–10) is the most suitable tool to study this complex gaseous phase since all the partial pressures can be determined over a large domain, usually from 1×10^{-6} to 10 Pa.

2. Experimental

The main features of the preparation of the indium chlorides are the same as already described for the gallium chlorides.(7) Basic materials were indium "7N" (Ventron) and $InCl_3$(s) (Merck). The quartz ampoules, loaded with appropriate mixtures of these two materials, were maintained at 600 K for about 10 h. In the case of the InCl(s) preparation, some ampoules exploded probably due to outgassing of water, since the water solubility of this chloride is less than for $InCl_3$(s). We avoided these explosions by preliminary pumping for 2 or 3 h at 373 K before sealing the ampoules.

The effusion cells were built from quartz or machined from nickel as already described, and loaded with the samples already prepared according to our previous study of gallium chlorides.(7) The mass spectrometer was a simple magnetic-focusing apparatus ($\pi/2$, 0.305 m radius) with an open Nier-type ion source (NUCLIDE 90 HT), without any magnetic focalization of the electron beam. The ionization chamber had been modified in view of *in situ* liquid-nitrogen cooling as already described.(11) The resolution was set at $\Delta m/m = 1000$ for 10 per cent of valley.

The sampling of the molecular beam was performed by two diaphragms. The source-entrance diaphragm, cooled with liquid nitrogen, and the field diaphragm were designed to sample directly the inner gaseous phase of the effusion cell as already explained.(11) Such a device prevented any parasitic re-evaporation of the outer parts of the effusing beam from entering the ionization chamber as well as any re-evaporation in this chamber of the highly volatile species of the sampled beam. As the indium chlorides had a tendency to clog the field diaphragm at high flow rates, we decided to establish a steady-state re-evaporation process of the non-useful parts of the effused beam, by heating the copper field diaphragm with a soldered thermo-coaxial resistor the temperature of which was monitored by a thermocouple and regulated at about 10 K above the cell temperature.

3. Analysis of the gaseous phase

The different ions that have been observed from the gaseous phase in equilibrium with indium chlorides are presented in table 1. At the beginning of every run with a fresh sample, we observed also Cl^+, H_2O^+, HO^+, H^+, and HCl^+, the intensities of which decreased quickly when the temperature of the cells was increased. Thus, every quantitative run was preceded by a qualitative one to purify the samples from

TABLE 1. Relative ion intensities observed on vaporization of indium chlorides. The electron beam is accelerated at 60 V

Condensed phase	T/K	$In_2Cl_5^+$	$In_2Cl_4^+$	$In_2Cl_3^+$	$In_2Cl_2^+$	In_2Cl^+	In_2^+	$InCl_3^+$	$InCl_2^+$	$InCl^+$	In^+
InCl(l)	515		0.005	0.02	3	4	0.7	0.001	0.02	100	128
$InCl_2$(l)	538	6	33	100	14	35	52	2	68	95	642
$InCl_3$(s)	544.5	16	1	0.6	0.5	2	2	3	100	19	45

water pollution. The same sample was then used for the subsequent quantitative runs for which the mass loss of the cell was measured. During the vaporization of InCl(s or l) we never detected any positive ions that might have come from the trimeric In_3Cl_3(g), although Sultanov(12) has observed $In_3Cl_3^-$. Similarly, we were not successful in the search for ions coming from the trimeric In_3Cl_6(g) and In_3Cl_9(g).

The identification of the molecular origin of the ions was performed by analysis of the evolution of all ionic-intensity ratios between any ions as well as by analysis of the evolution of the ionization-efficiency curves as a function of the temperature of the Knudsen cell and of the different condensed-phase compositions. During the vaporization of $InCl_3$(s) and InCl(s), sets of constant ionic-intensity ratios were observed that led clearly to the parent molecules as mentioned in table 2. All our observations for these chlorides agree with preceding mass-spectrometric work.(15) The different ionic-intensity ratios observed when vaporizing $InCl_2$(s or l) are presented in figure 1. The comparison with ionic-intensity ratios measured over the preceding chlorides showed clearly that the In_2Cl_4(g) is the major gaseous species in equilibrium with $InCl_2$(s or l). Molecular origins of the ions are mentioned in table 2. We observed that, contrary to the InCl(s) and $InCl_3$(s) vaporizations, the In^+ ion comes from the In_2Cl_4(g) dissociative ionization. The evolution of the normalized

TABLE 2. Observed ions and their molecular origin as a function of the vaporized indium chloride

Condensed phase	Measured ions	Molecular origin	Condensed phase	Measured ions	Molecular origin	Condensed phase	Measured ions	Molecular origin
$InCl_3$(s)	$In_2Cl_5^+$	In_2Cl_6	InCl(s)	$In_2Cl_4^+$	In_2Cl_4	$InCl_2$(s)	$In_2Cl_5^+$	In_2Cl_6
	$In_2Cl_4^+$	In_2Cl_6		$In_2Cl_3^+$	In_2Cl_4		$In_2Cl_4^+$	In_2Cl_4
	$In_2Cl_3^+$	In_2Cl_6		$InCl^+$	InCl		$In_2Cl_3^+$	In_2Cl_4
	$In_2Cl_2^+$	In_2Cl_6		In^+	InCl		In^+	In_2Cl_4
	In_2Cl^+	In_2Cl_6		$InCl_3^+$	$InCl_3$		$In_2Cl_2^+$	In_2Cl_2, In_2Cl_4
	In_2^+	In_2Cl_6		$InCl_2^+$	$InCl_3$		In_2Cl^+	In_2Cl_2, In_2Cl_4
	$InCl_3^+$	$InCl_3$		$In_2Cl_2^+$	In_2Cl_2		In_2^+	In_2Cl_2, In_2Cl_4
	$InCl_2^+$	$InCl_3$		In_2Cl^+	In_2Cl_2		$InCl^+$	InCl
	$InCl^+$	$InCl_3$		In_2Cl^+	In_2Cl_2		$InCl_3^+$	$InCl_3$
	In^+	$InCl_3$		In_2^+	In_2Cl_2		$InCl_2^+$	$InCl_3$, In_2Cl_4

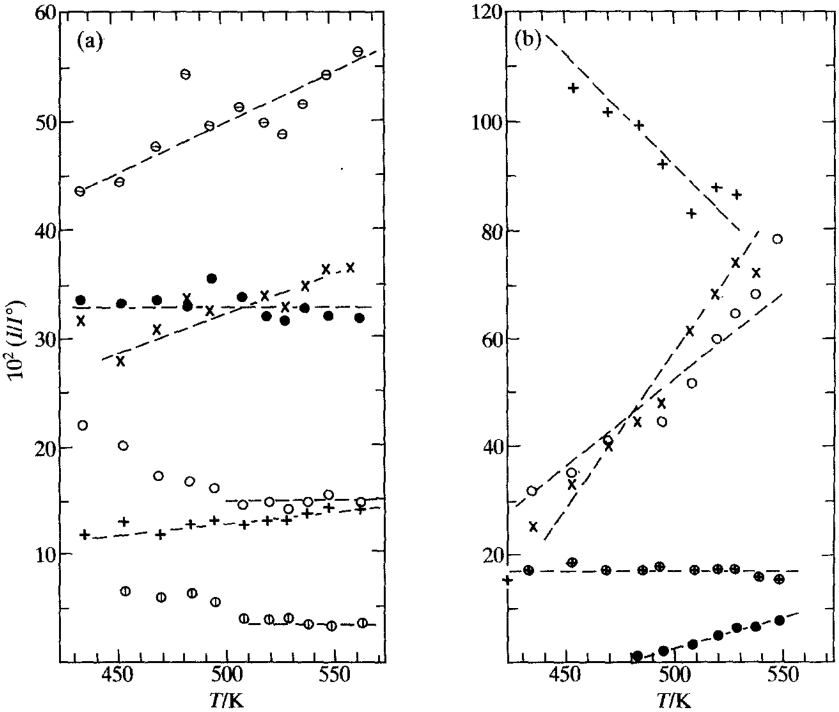

FIGURE 1. Ion-intensity ratios measured at 60 V from the vapour phase in equilibrium with $InCl_2$(s or l) as a function of temperature.
(a): ⊖, $I(In_2^+)/I(In_2Cl_3^+)$; ●, $I(In_2Cl_4^+)/I(In_2Cl_3^+)$; ×, $I(In_2Cl^+)/I(In_2Cl_3^+)$; ○, $I(InCl^+)/I(In^+)$; +, $I(In_2Cl_2^+)/I(In_2Cl_3^+)$; ⦶, $I(InCl_3^+)/I(InCl_2^+)$.
(b): +, $I(InCl^+)/I(In_2Cl_3^+)$; ×, $I(InCl_2^+)/I(InCl^+)$; ○, $I(InCl_2^+)/I(In_2Cl_3^+)$; ⊕, $I(In_2Cl_2^+)/I(In^+)$; ●, $I(In_2Cl_5^+)/I(In_2Cl_3^+)$.

ionization-efficiency curves was analysed as a function of either the temperature or the chemical conditions for vaporization *i.e.* with different condensed chlorides. In figure 2, for instance, $In_2Cl_4^+$ is a parent ion in the vapour of InCl(s) and $InCl_2$(s) but mainly a fragment ion from In_2Cl_6(g) in the vapour of $InCl_3$(s), with a slight parent contribution (about 10 per cent) from In_2Cl_4(g). From this figure, we observe that theoretically In_2Cl_4(g) is measurable when $InCl_3$(s) is vaporized and without fragment contribution at an ionizing potential lower than 19 V. The behaviour of $In_2Cl_3^+$ was similar, meaning that this ion is a fragment. In figure 3, the evolution of the different $InCl^+$ ionization-efficiency curves clearly shows a parent ion from the vapour in equilibrium with InCl(s or l), a fragment ion from the vapour of $InCl_3$(s), and mixed behaviour from the vapour phase of $InCl_2$(s).

The general conclusions of the ionization-efficiency-curve analysis of all the detected ions confirmed the preceding analysis with evolutions of ionic-intensity ratios. The different observed appearance and ionization threshold potentials are summarized in table 3. They have been checked with thermodynamic cycles as already shown in previous work on (gallium + chlorine).(7)

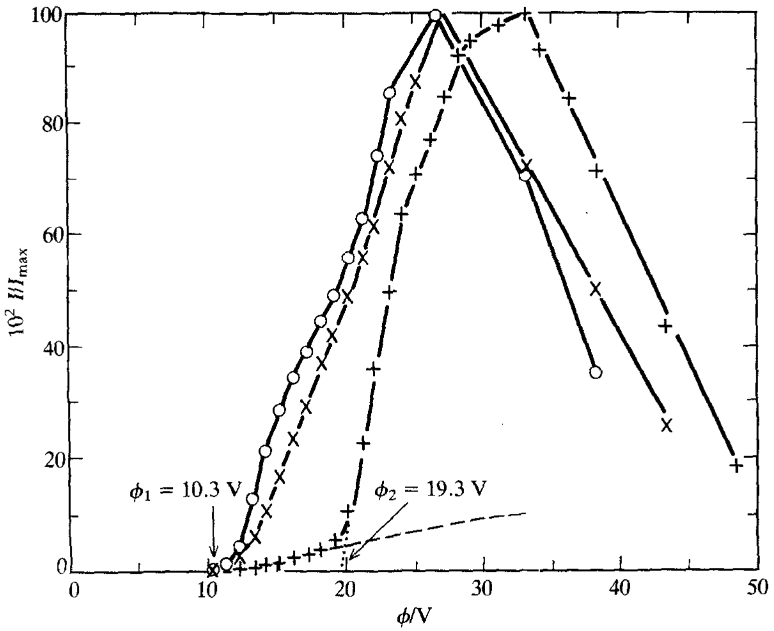

FIGURE 2. Normalized ionization-efficiency curves for $In_2Cl_4^+$ as measured from vapours in equilibrium with different condensed phases: ○, InCl(s); ×, $InCl_2$(s); and +, $InCl_3$(s). ϕ_1 is the ionization potential of In_2Cl_4(g), while ϕ_2 is the fragmentation threshold observed for the appearance of $In_2Cl_4^+$ from In_2Cl_6(g).

TABLE 3. Observed first ionization potential ϕ_a and dissociative ionization potential ϕ_b of indium chloride ions

Observed ions	ϕ_a[a]/V	ϕ_b[b]/V	Molecular origin
$In_2Cl_5^+$		13.3	In_2Cl_6
$In_2Cl_4^+$	10.3±0.3	19.3	In_2Cl_6
$In_2Cl_3^+$		11.3	In_2Cl_4
		19.3	In_2Cl_6
$In_2Cl_2^+$	7.3±0.5	19.3	In_2Cl_4
In_2Cl^+		11.9	In_2Cl_2
		21.3	In_2Cl_4
In_2^+		16.7	In_2Cl_2
		26	In_2Cl_4
$InCl_3^+$	13.3±0.3		
$InCl_2^+$		13.3	$InCl_3$
$InCl^+$	8.3±0.2	21.3	$InCl_3$
In^+		6.3	InCl
		18.1	In_2Cl_4
		22.9	$InCl_3$

[a] This ionization potential corresponds to the process: $In_iCl_j + e^- = In_iCl_j^+ + 2e^-$. The calibration of the source was performed against the appearance potential of indium.(36)

[b] The accuracy of these measurements is at worst ±0.5 V but is generally difficult to evaluate.

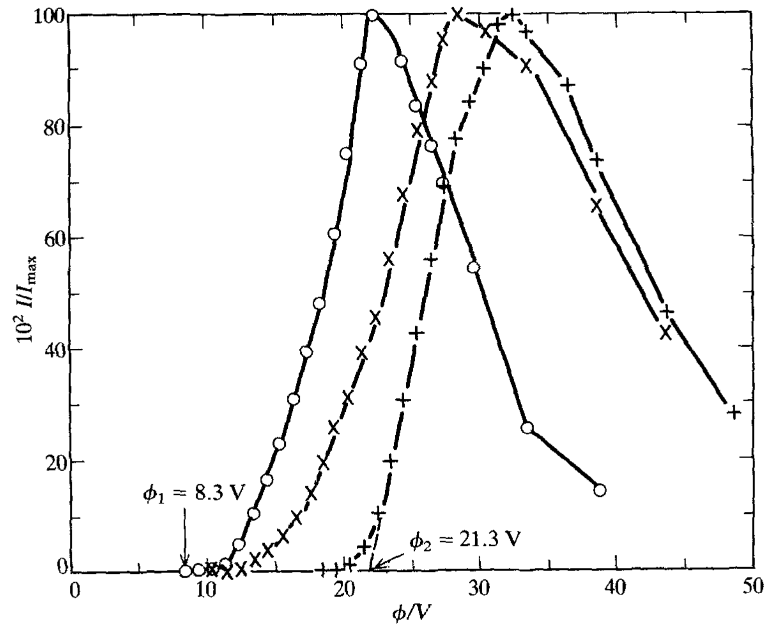

FIGURE 3. Normalized ionization-efficiency curves for $InCl^+$ as measured from vapours in equilibrium with different condensed phases: ○, InCl(s); ×, $InCl_2$(s); and +, $InCl_3$(s). ϕ_1 is the ionization potential of InCl(g) while ϕ_2 is the fragmentation threshold observed for the appearance of the fragment $InCl^+$ from $InCl_3$(g).

4. Thermodynamics of the gaseous indium chlorides

The whole set of independent reactions that are measured is in equilibrium with $InCl_3$(s):

$$InCl_3(s) = InCl_3(g), \tag{1}$$

$$In_2Cl_6(g) = 2InCl_3(g), \tag{2}$$

in equilibrium with InCl(s or l):

$$InCl(s) = InCl(g), \tag{3}$$

$$In_2Cl_2(g) = 2InCl(g), \tag{4}$$

$$In_2Cl_4(g) = InCl_3(g) + InCl(g), \tag{5}$$

and in equilibrium with $InCl_2$(s or l):

$$2InCl_2(s) = In_2Cl_4(g), \tag{6}$$

$$In_2Cl_4(g) = InCl_3(g) + InCl(g), \tag{7}$$

$$In_2Cl_6(g) = 2InCl_3(g). \tag{8}$$

All possible non-independent reactions were also checked to test the internal consistency of our measurements.

From the fundamental relation of mass spectrometry:(8–10)

$$p_iS_i = I_iT, \tag{9}$$

with

$$S_i = A\sigma_i\gamma_if_i, \tag{10}$$

where p_i is the partial pressure of the ith gaseous species in the Knudsen cell, S_i its mass-spectrometric sensitivity, I_i its measured ion intensity (for one isotope), T the temperature of the cell, A a geometrical constant, σ_i the ionization cross-section, γ_i the detector yield, and f_i the isotopic abundance. Second- and third-law calculations were used to deduce the enthalpies of reactions from the relations:

$$\mathrm{d}\ln K/\mathrm{d}(1/T) = -\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}(T)/R = \mathrm{d}\{\textstyle\sum_i\nu_i\ln(I_iT)\}/\mathrm{d}(1/T) - \mathrm{d}(\textstyle\sum_i\nu_i\ln S_i)/\mathrm{d}(1/T), \tag{11}$$

where ν_i is the stoichiometric number, and

$$\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}(T') = -RT\ln\{K^{\circ}(T)\} + T\Delta_{\mathrm{r}}\Phi^{\circ}_{\mathrm{m}}(T) + \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}(T') - \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}(0), \tag{12}$$

with $T' = 298.15\ \mathrm{K}$. As long as the sensitivity S_i of the mass spectrometer is kept constant during any run, the second-law equation (11), does not need the determination of S_i. For the third law, we need to calibrate or to estimate the S_i and to know $\Phi^{\circ}_{\mathrm{m}}$ and $\Delta_0^{T'}H^{\circ}_{\mathrm{m}}$ for each compound or gaseous species. The mass loss of the sample (or the cell) is used for calibration of the mass spectrometer, the aim being the determination of sensitivities S_i or sensitivity ratios S_i/S_j from the Hertz–Knudsen relation:(8–10)

$$\mathrm{d}n/\mathrm{d}t = \sum_{i=1}^{n} p_isC(2\pi M_iRT)^{-1/2}. \tag{13}$$

This equation relates the effused amount of substance per unit time $\mathrm{d}n/\mathrm{d}t$ to the partial pressure p_i, the molar mass M_i of the effused species, the temperature T, the effusion orifice area s, and its Clausing coefficient C.(16) R is the gas constant. From relations (9) and (13), the mass loss of the cell during one experiment is

$$\Delta m = sC(2\pi R)^{-1/2}\left\{M_1^{1/2}S_1^{-1}\int_0^t (I_1T^{1/2})\mathrm{d}t + \sum_{i=2}^{n}(S_1/S_i)(M_i/M_1)^{1/2}\int_0^t (I_iT^{1/2})\mathrm{d}t\right\}. \tag{14}$$

When $\mathrm{InCl_3(s)}$ was vaporized, the determination of the mass-spectrometric sensitivities for $\mathrm{InCl_3(g)}$ and $\mathrm{In_2Cl_6(g)}$ was performed using equation (14) and the well known equilibrium constant(17–19) for the dimerization reaction (2) in the saturated vapour phase. The sensitivity ratio had the mean value $S(\mathrm{In_2Cl_5})/S(\mathrm{InCl_2}) = (0.20 \pm 0.04)$ at 55 V for the ionizing electron-beam potential and for the main isotopes.

For the vaporization study of InCl(s or l), the sensitivities of the two main species $\mathrm{InCl(g)}$ and $\mathrm{In_2Cl_2(g)}$ were determined from equation (14) in conjunction with either the already known equilibrium constant(18) for dimerization reaction (4) or the estimate of the total ionization cross section according to previous measurements on dimeric alkali halides(20) and the compilation on dimers.(21) The

TABLE 4. Influence of the reciprocal choice of ionization cross-section ratios and dimerization enthalpies on the mass loss of the samples when vaporizing InCl(s or l). $\Delta m(\mathrm{InCl})$ and $\Delta m(\mathrm{In_2Cl_2})$ are the contributions of InCl(g) and $\mathrm{In_2Cl_2}$(g) to Δm

Assumptions for calculations	Run	$\frac{\Delta m}{\mathrm{mg}}$	$\frac{\Delta m(\mathrm{InCl})}{10^{-2}\Delta m}$	$\frac{\Delta m(\mathrm{In_2Cl_2})}{10^{-2}\Delta m}$	$\frac{\sigma(\mathrm{In_2Cl_2})}{\sigma(\mathrm{InCl})}$	$\frac{\Delta_r H^\circ_m(\mathrm{In_2Cl_2},\ g,\ 298.15\ \mathrm{K})}{\mathrm{kJ \cdot mol^{-1}}}$ third law	
						(reaction 7)	
$\Delta_r H^\circ_m$ (7)	06	106.6	86.1	13.9	0.45 [a]	94.5	−231.4 [b]
	07	163.7	86.1	13.9	0.31 [a]	95.4	−231.8 [b]
	08	112.0	86.8	13.2	0.54 [a]	95.4	−231.8 [b]
$\frac{\sigma(\mathrm{In_2Cl_2})}{\sigma(\mathrm{InCl})}$ [e]	06	106.6	95.8	4.2	1.4 [c]	90.0	−226.4 [d]
	07	163.7	96.6	3.4	1.4 [c]	91.2	−227.6 [d]
	08	112.0	94.5	5.5	1.4 [c]	89.1	−225.5 [d]

[a] These mean values are deduced from $\Delta_f H^\circ_m(\mathrm{In_2Cl_2},\ g,\ 298.15\ \mathrm{K})$ from reference 18.

[b] Resulting mean values of our experiments with calculated cross sections from reference 18. These values are evidently close to reference 18.

[c] Estimated value of total ionization cross section according to reference 21.

[d] Our third-law values with given cross sections according to reference 21.

[e] These total ionization cross sections take into account all the (parent + fragment) ions.(37)

two calibration methods are presented in table 4. Differences between deduced enthalpies of reaction are small, and will be discussed later.

When $\mathrm{InCl_2}$(s or l) were vaporized, four molecules appeared important enough to be taken into account in equation (14): $\mathrm{In_2Cl_4}$(g), InCl(g), $\mathrm{InCl_3}$(g), and $\mathrm{In_2Cl_6}$(g). Thus, such experiments have been run intermixed with InCl(s) and $\mathrm{InCl_3}$(s) vaporization runs where the InCl(g), $\mathrm{InCl_3}$(g), and $\mathrm{In_2Cl_6}$(g) sensitivities have been determined. Then, their contributions to mass loss in the $\mathrm{InCl_2}$(s) vaporization run were calculated and the $\mathrm{In_2Cl_4}$(g) sensitivity was determined. Relative contributions of each gaseous species to the total mass loss are presented in table 5. We observed that species other than $\mathrm{In_2Cl_4}$(g) never contributed to more than 25 per cent of the total mass loss and neglect of these contributions would have had an effect of $1\ \mathrm{kJ \cdot mol^{-1}}$ on the enthalpy-of-vaporization reaction of $\mathrm{In_2Cl_4}$(g).

Values of Φ°_m and $\Delta_0^{T'} H^\circ_m$ were calculated from known molecular quantities for InCl(g),(22) $\mathrm{InCl_3}$(g),(13,23–25) and deduced from the dimensional model(26) for

TABLE 5. Relative mass loss from the different gaseous species during vaporization of $\mathrm{InCl_2}$(s), where m is the total mass loss

Run [a]	$\frac{\Delta m}{\mathrm{mg}}$	$\frac{\Delta m(\mathrm{In_2Cl_4})}{10^{-2}\Delta m}$	$\frac{\Delta m(\mathrm{InCl_3})}{10^{-2}\Delta m}$	$\frac{\Delta m(\mathrm{InCl})}{10^{-2}\Delta m}$	$\frac{\Delta m(\mathrm{In_2Cl_6})}{10^{-2}\Delta m}$	$\frac{\Delta m(\mathrm{H_2O + HCl})}{10^{-2}\Delta m}$
$\mathrm{InCl_2}$–05–S	1048.7	82.5	4	11.5	2	2
$\mathrm{InCl_2}$–06–S	384.9	76.3	4.7	16.9	2	0

[a] From experiment 05 to 06, the overall composition of the sample was moving from the diphasic $\{\mathrm{InCl_2(s) + InCl_3(s)}\}$ to the diphasic $\{\mathrm{InCl_2(s) + In_4Cl_7(s)}\}$ domains. We observed that only $p(\mathrm{InCl},\ g)$ was significantly different compared with $p(\mathrm{In_2Cl_4},\ g)$.

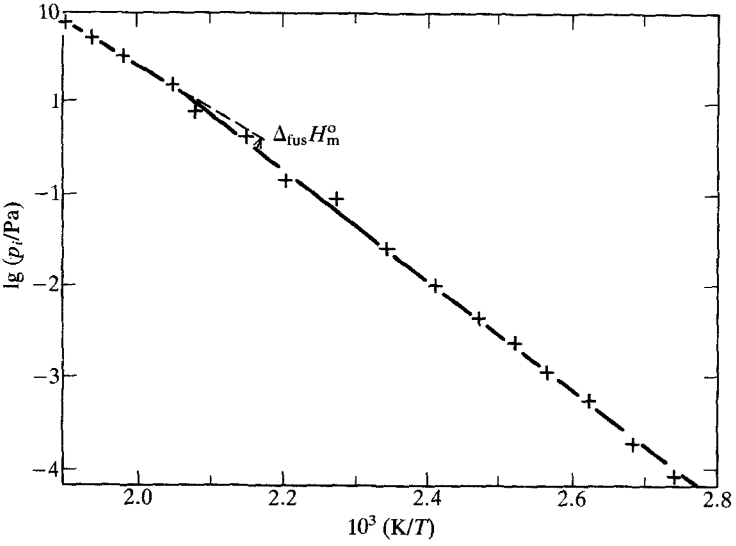

FIGURE 4. Second-law determination of the melting enthalpy $\Delta_{\text{fus}}H_{\text{m}}^{\circ}$ from measurements on InCl(s or l) = InCl(g).

In_2Cl_6(g) and In_2Cl_4(g) according to the relations:

$$\Phi_{\text{m}}^{\circ}(\text{In}_2\text{Cl}_6, \text{g}, T) = \Phi_{\text{m}}^{\circ}(\text{Ga}_2\text{Cl}_6, \text{g}, T) + 9.513R,$$

$$H_{\text{m}}^{\circ}(\text{In}_2\text{Cl}_6, \text{g}, T) - H_{\text{m}}^{\circ}(\text{In}_2\text{Cl}_6, \text{g}, 298.15\ \text{K}) \approx H_{\text{m}}^{\circ}(\text{Ga}_2\text{Cl}_6, \text{g}, T) - H_{\text{m}}^{\circ}(\text{Ga}_2\text{Cl}_6, \text{g}, 298.15\ \text{K}),$$

$$\Phi_{\text{m}}^{\circ}(\text{In}_2\text{Cl}_4, \text{g}, T) = \Phi_{\text{m}}^{\circ}(\text{C}_2\text{Cl}_4, \text{g}, T) + 14.47R,$$

$$H_{\text{m}}^{\circ}(\text{In}_2\text{Cl}_4, \text{g}, T) - H_{\text{m}}^{\circ}(\text{In}_2\text{Cl}_4, \text{g}, 298.15\ \text{K}) \approx H_{\text{m}}^{\circ}(\text{C}_2\text{Cl}_4, \text{g}, T) - H_{\text{m}}^{\circ}(\text{C}_2\text{Cl}_4, \text{g}, 298.15\ \text{K})$$

Our results for $\Phi_{\text{m}}^{\circ}(\text{In}_2\text{Cl}_6, \text{g})$ differ by less than $5.0\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ from estimates based on Ga_2Cl_6(g).(4) The thermodynamic functions of In_2Cl_2(g) and $InCl_2$(g) were calculated from estimates,(4, 28, 29) and their values were successfully checked against the dimensional model.(27)

Standard enthalpies of formation of InCl(s), $InCl_2$(s), and $InCl_3$(s) come from calorimetric determinations,(30) and their entropies and heat capacities are respectively estimated according to the Latimer and Unäl relations.(31) Estimates of melting enthalpies(31) for InCl(s) and $InCl_2$(s) appeared less accurate than our second-law results as shown in figures 4 and 5. Moreover, third-law results were very sensitive to the choice of these melting enthalpies as illustrated in figure 6. Finally, useful Φ_{m}°(s or l) of indium chlorides were calculated from our experimental second-law mean values for unknown melting enthalpies assuming constant heat capacities for liquids equal to 90 per cent of those of the solids at the melting temperatures. Basic values for the calculations are summarized in table 6.

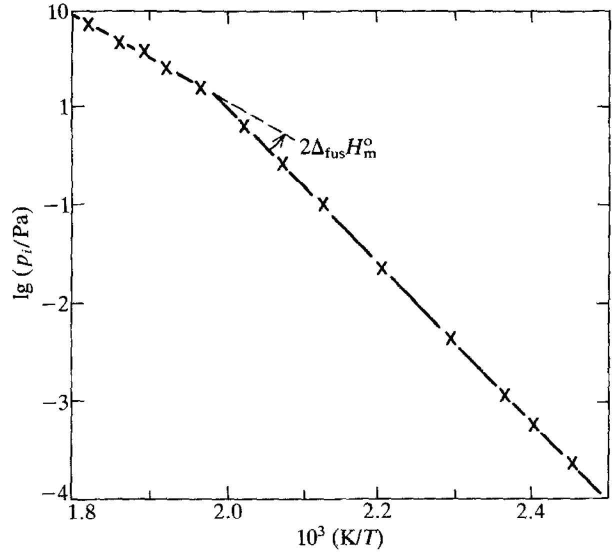

FIGURE 5. Second-law determination of the melting enthalpy $\Delta_{fus}H^\circ_m$ from measurements on $2InCl_2(s\text{ or }l) = In_2Cl_4(g)$.

Second- and third-law results are presented in table 7 together with deduced third-law enthalpies of formation for the different indium chlorides. The uncertainties are estimated from $\delta T/T = 0.005$, $\delta I_i/I_i = 0.10$, $\delta S_i/S_i \approx 0.55$ for estimated ionization cross sections as used for $S(In_2Cl_2^+)/S(InCl^+)$, or ≈ 0.30 for mass loss since the effusion process may be by-passed with surface diffusion along the orifice walls,(32) and 0.02 for estimated Φ°_ms. Thus the total uncertainty for enthalpies of formation is calculated to be less than ±5 per cent, in agreement with a preliminary test with cadmium in our cell: $\Delta_{vap}H^\circ_m(298.15\text{ K}) = (110.5 \pm 2.2)$ kJ · mol^{-1} (second law); $\Delta_{vap}H^\circ_m(298.15\text{ K}) = (112.2 \pm 0.7)$ kJ · mol^{-1} (third law); $\Delta_{vap}H^\circ_m(298.15\text{ K}) = (111.8 \pm 0.6)$ kJ · mol^{-1} (compiled).(33) The maximum deviation is ±3 per cent, taking the standard deviations into account.

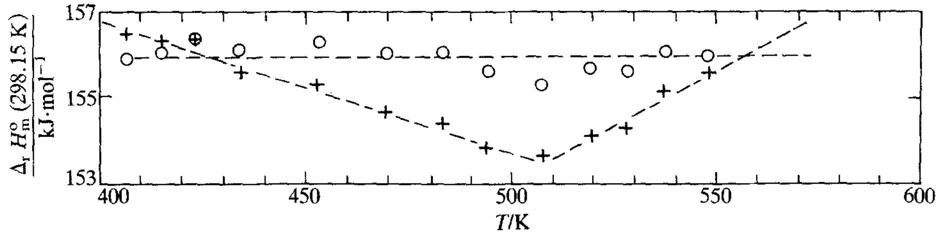

FIGURE 6. Influence of the choice of the melting enthalpy $\Delta_{fus}H^\circ_m$ on the deduced third-law standard enthalpies for the reaction: $2InCl_2(s) = In_2Cl_4(g)$: +, with $\Delta_{fus}H^\circ_m = 20.92$ J · mol^{-1} estimated from reference 31; ○, with $\Delta_{fus}H^\circ_m = 34.94$ J · mol^{-1}, the mean value of our second-law results from reaction (6).

TABLE 6. Summary of selected or estimated values used for the calculations of $\Phi_{\mathrm{m}}^{\circ}$ of solid and liquid indium chlorides; a and b are parameters of the equation $C_{p,\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = a + b(T/\mathrm{K})$[a]

Compound	$\Delta_f H_{\mathrm{m}}^{\circ}(298.15\ \mathrm{K})^{(32)}$ / $\mathrm{kJ \cdot mol^{-1}}$	$S_{\mathrm{m}}^{\circ}(298.15\ \mathrm{K})$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	a	b	T_{trs} / K	$\Delta_{\mathrm{trs}} H_{\mathrm{m}}$ / $\mathrm{J \cdot mol^{-1}}$	T_{fus} / K	$\Delta_{\mathrm{fus}} H_{\mathrm{m}}$ / $\mathrm{J \cdot mol^{-1}}$
InCl(s)	-186.2 ± 4.2	94.98	$35.14(\mathrm{s}_1)$	0.042	387 ± 10^{c}	519^{b}	484 ± 3^{b}	21255 ± 1050^{b}
			$58.58(\mathrm{s}_2)$					
			62.76(l)				487^{c}	21800 ± 7500^{c}
$\mathrm{InCl_2(s)}$	-362.8 ± 4.2	122.17	58.58(s)	0.335			503 ± 3^{c}	34940 ± 6000^{c}
			96.23(l)					
$\mathrm{InCl_3(s)}$	-537.2 ± 4.2	141.0	78.66(s)	0.0556			(856)	(27196)
			55.65(l)					

[a] Estimated at 298.15 K according to the Unäl rule(31) and at T_{fus} as $C_{p,\mathrm{m}} = 7.25n\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ where n is the number of atoms in the molecule.

[b] From reference 38; selected values for the calculations.

[c] Our values as deduced from a second-law analysis. Note that the existence of $\mathrm{InCl_2(s)}$ is not well established as discussed by several authors.(39)

5. Discussion

Our vaporization study of $\mathrm{InCl_3(s)}$ confirms the earlier Bourdon-gauge determinations(17–19) of the $\mathrm{InCl_3(g)}$ dimerization enthalpy since $\mathrm{InCl_3(g)}$ and $\mathrm{In_2Cl_6(g)}$ are the main gaseous species. In fact, at 530 K, $p(\mathrm{In_2Cl_4, g})$ is less than 0.009 of $p(\mathrm{In_2Cl_6, g})$ which is the smallest of the two main species.

The enthalpies of formation of InCl(g) and $\mathrm{In_2Cl_2(g)}$ deduced from our study of reactions (3) and (4) confirm the already selected value for InCl(g),(34) and the preceding determination on $\mathrm{In_2Cl_2(g)}$,(18) from Bourdon-gauge measurements on unsaturated vapours with $x(\mathrm{In})/x(\mathrm{Cl}) = 1$. The vapour in equilibrium with InCl(s or l) is composed mainly of InCl(g) and $\mathrm{In_2Cl_2(g)}$, but at 500 K, $p(\mathrm{InCl_3, g}) \approx p(\mathrm{In_2Cl_4, g}) \approx 0.01 p(\mathrm{InCl, g})$. As the mean partial pressure of $\mathrm{In_2Cl_2(g)}$ may vary from 0.08 to 0.045 of $p(\mathrm{InCl, g})$ over InCl(s or l) according to the choice of ionization cross sections, neglecting the simultaneous occurrence of equilibria (5) and (4) in Bourdon-gauge experiments can explain why this last enthalpy of formation value for $\mathrm{In_2Cl_2(g)}$ is slightly less negative than our value with the usual estimates(20, 21) of total-ionization-cross-section ratios. Nevertheless, as the total-ionization-cross-section ratio of dimer to monomer deduced from the enthalpy of dimerization from reference 18 is close to that measured for trichlorides in equilibrium (2), we think our best value is the one close to the preceding dimerization enthalpy determination for $\mathrm{In_2Cl_2(g)}$,(18) (table 8).

The vapour in equilibrium with $\mathrm{InCl_2}$(s or l) is composed mainly of $\mathrm{In_2Cl_4(g)}$, then InCl(g), $\mathrm{InCl_3(g)}$, $\mathrm{In_2Cl_6(g)}$, and a very small amount of $\mathrm{In_2Cl_2(g)}$. At 500 K, $p(\mathrm{InCl, g})$, $p(\mathrm{InCl_3, g})$, and $p(\mathrm{In_2Cl_6, g})$ are about 0.30, 0.06, and 0.01 of $p(\mathrm{In_2Cl_4, g})$, respectively. The partial pressures of the two last species decrease slightly when the overall composition of the condensed phase moves from the diphasic $\{\mathrm{InCl_2(s)} + \mathrm{InCl_3(s)}\}$ to the diphasic $\{\mathrm{InCl_2(s)} + \mathrm{In_4Cl_7(s)}\}$. Among the

TABLE 7. Second and third-law results from main equilibria measured during vaporization of indium chlorides; deduced third-law standard molar enthalpies of formation

Reaction	Run no.	T/K	$\Delta_r H^\circ_m\langle T\rangle$ / kJ·mol^{-1} second-law	$\langle T\rangle$/K	$\Delta_r H^\circ_m$(298.15 K) / kJ·mol^{-1} second-law	$\Delta_r H^\circ_m$(298.15 K) / kJ·mol^{-1} third-law	$\Delta_f H^\circ_m$(298.15 K) / kJ·mol^{-1} third-law
(1)	$InCl_3$-05-S	478 to 563	161.1±1.6^a	524	166.1±1.6^a	161.1±0.3^a	−375.7±5.0^b
	$InCl_3$-06-S	453 to 572	151.7±1.2	489	155.8±1.2	162.0±0.3	($InCl_3$, g)
(2)	$InCl_3$-05-S	478 to 563	124.7±2.4	531	127.9±2.4	132.6±0.2	−883.7±10.0
	$InCl_3$-06-S	453 to 572	121.9±1.6	508	124.8±1.6	132.6±0.3	(In_2Cl_6, g)^c
(3)	InCl-06-S	377 to 509	109.1±1.4	441	112.0±1.4	117.8±0.3	−68.2±4.6
	InCl-07-S	365 to 515	111.8±1.3	421	114.3±1.3	117.6±0.3	(InCl, g)
	InCl-08-S	364 to 524	117.7±1.5	420	120.1±1.5	118.4±0.3	
(4)	InCl-06-S	396 to 509	89.9±1.2	453	91.3±1.2	95.1±0.3	−232.0±8.8
	InCl-07-S	395 to 515	88.0±2.2	462	89.4±2.2	95.3±0.4	(In_2Cl_2, g)^c
	InCl-08-S	404 to 524	98.3±3.1	464	99.8±3.1	95.4±0.5	
(5)	InCl-07-S	487 to 506	−74 ±9	502	−76.1±9.0	106.8±2.7	−552.3±15
	InCl-08-S	480 to 524	107 ±21	495	108.3±21.2	108.3±1.2	(In_2Cl_4, g)^d
(6)	$InCl_2$-06-S	412 to 532	149.1±2.0	461	157.5±2.0	154.3±0.4	−571.5±9.6
	$InCl_2$-06-S	407 to 538	159.9±1.0	447	158.6±1.0	155.8±0.2	(In_2Cl_4, g)
(7)	$InCl_2$-05-S	440 to 532	141.6±3.6	503	139.4±3.6	131.9±1.3	−880.7±11.0
	$InCl_2$-06-S	435 to 538	141.5±2.2	498	139.3±2.2	128.9±0.9	(In_2Cl_6, g)

[a] Standard deviations.

[b] Total uncertainties taking into account those associated with basic reference compounds (see text).

[c] This equilibrium has been calculated with the ionization-cross-section ratio as deduced from previous third-la enthalpy determinations according to references 17 to 19.

[d] Useful sensitivity calibrations for InCl(g) and $InCl_3$(g) come from independent vaporization studies of $InCl_3$(s) an InCl(s or l).

numerous equilibria involving In_2Cl_4(g), reaction (5) needs preliminary determinations or sensitivity calibrations, namely for InCl(g) and $InCl_3$(g), but reaction (6) depends mainly on the mass-loss calibration. Consequently, enthalpy determination from reaction (6) is more accurate and is selected accordingly (table 8). Our selected experimental value (table 8) for the standard molar enthalpy of formation of In_2Cl_4(g) is slightly less negative than that determined from Bourdon-gauge measurements.$^{(5,6)}$ This difference can be explained by the large uncertainties associated with Bourdon-gauge experiments when many species exist

TABLE 8. Proposed enthalpies of formation and comparison with literature values

	$\Delta_f H^\circ_m$(298.15 K)/(kJ·mol^{-1}) This work	Literature
$InCl_3$(g)	−375.7±5.0	−371.1±6.7,$^{(18)}$ −385.7,$^{(19)}$ −381.4$^{(17)}$
In_2Cl_6(g)	−883.7±10.0	−941.8±10.5,$^{(17)}$ −870.3±14.6,$^{(18)}$ −940.6±9.6$^{(19)}$
InCl(g)	−68.2±4.6	−73.6,$^{(41)}$ −97.5±9.6,$^{(42)}$ −98.3,$^{(17)}$ −69.9±5.4$^{(18)}$
In_2Cl_4(g)	−573.2±12.6	−589.9±12.6,$^{(5)}$ −621.5$^{(16)}$
In_2Cl_2(g)	−232.0±8.8	−243.9±9.2$^{(18)}$
$InCl_2$(g)	> −201	−96±21,$^{(43)a}$ −163.2$^{(35)a}$

[a] These values are estimates.

in the gaseous phase and by the impact of the fixed values for enthalpies of formation of $In_2Cl_2(g)$ and $In_2Cl_6(g)$ that have been chosen in the interpretation of these measurements.

In agreement with preceding work we never unambiguously observed any $InCl_2(g)$. This molecule seems the least stable in (indium + chlorine) and it is then difficult to find some of its parent and fragment ions that are overlapped by those coming from $InCl_3(g)$ or $InCl(g)$. As the maximum partial pressure of $InCl_2(g)$ occurs for vaporization of $InCl_2(s)$, we tentatively estimated its maximum value from our detection threshold. Moreover, a slight systematic trend of third-law enthalpies for reaction (7) was observed (correlated with non-consistent second-law values) that can be attributed to $InCl_2^+$ the origin of which remains partly unresolved. After correction of the $InCl_2^+$ contribution from dissociative ionization of $InCl_3(g)$, the measured intensity ratio of $InCl_2^+$ to $In_2Cl_3^+$ remained quite constant at (0.183 ± 0.023) showing that $InCl_2^+$ is probably also a fragment arising from dissociative ionization of $In_2Cl_4(g)$. The maximum contribution of $InCl_2^+$ from hypothetical $InCl_2(g)$ would be comparable to the statistical uncertainty: 2.3 per cent of $In_2Cl_3^+$. Assuming that the $InCl_2(g)$ spectrometric sensitivity relative to $In_2Cl_4(g)$ obeys the same rule as for other indium chlorides: $\sigma(InCl_2)/\sigma(In_2Cl_4) \approx 0.5$ at 550 K, the calculated $p(InCl_2, g)$ is ≈ 0.17 Pa, and $\Delta_f H_m^\circ(InCl_2, g, 298.15\ K) > -201\ kJ \cdot mol^{-1}$. This calculated bound agrees with the Charkin *et al.*(35) estimate and disagrees with the one proposed by Glushko *et al.*(4) Our selected results are reported in table 8 together with published values. Our values are in close agreement with the Polyachenok and Komshilova(43) values. Critical assessment with re-interpretation of original values will be published further.

REFERENCES

1. Barybin, A. A.; Kempel, V. A.; Nechaev, V. V. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1977,** 13, 42.
2. Gentner, J. L.; Bernard, C.; Cadoret, R. J. *Crystal Growth* **1982,** 56, 332.
3. Defoort, F.; Gosnet, A. M.; Gentner, J. L.; Bernard, C. *Proc. Fifth European Conf. Chemical Vapor Deposition.* 17 to 20 June 1985, Uppsala, Sweden. Pp. 115.
4. Glushko, V. P. *et al. Thermodynamic Properties of Elementary Substances.* Nauka: Moscow. **1981,** 3, 189.
5. Polyachenok, O. G.; Komshilova, O. N. *Russ. J. Phys. Chem.* **1971,** 45, 1073.
6. Kuniya, Y.; Hosaka, M. *J. Crystal Growth* **1975,** 28, 385.
7. Ait-Hou, A.; Hillel, R.; Chatillon, C. *J. Chem. Thermodynamics* **1988,** 20, 993.
8. Inghram, M. G.; Drowart, J. *Proc. Symp. on High Temp. Techn.* McGraw-Hill: New York. **1960,** 219.
9. Svedberg, R. C. *Modern Aspects of Mass Spectrometry.* Plenum: New York. **1968,** 169.
10. Chatillon, C.; Allibert, M.; Pattoret, A. *Characterization of High Temperature Vapors and Gases.* Nat. Bur. Standards: Washington, DC. **1979,** 1, 181.
11. Tmar, M.; Chatillon, C. *J. Chem. Thermodynamics* **1987,** 19, 1053.
12. Sultanov, A. S. *Russ. J. Inorg. Chem.* **1972,** 17, 309.
13. Beattie, I. R.; Horder, J. R. *J. Chem. Soc. A* **1969,** 2655.
14. Bues, W.; Akhras, Z.; Okon, G. *Z. Anorg. Allg. Chem.* **1976,** 425, 193.
15. Schäfer, H.; Binneweis, M. *Rev. Chim. Minerale* **1976,** 13, 24.
16. Dushman, S. *Scientific Foundations of Vacuum Technique.* Wiley: New York. **1958,** 99.
17. Kuniya, Y.; Hosada, S.; Hosaka, M. *Denki Kagaku* **1974,** 42, 20.
18. Polyachenok, O. G.; Komshilova, O. N. *Izv. Akad. Nauk Biel. SSSR Ser. Fiz.-Energ.* **1970,** 2, 90.
19. Sryvtsev, V. A. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.* **1973,** 6, 63.

20. Berkowitz, J.; Tasman, H. A.; Chupka, W. A. *J. Chem. Phys.* **1962,** 36, 2170.
21. Drowart, J. *Condensation and Evaporation of Solids.* Gordon and Breach: New York. **1964,** 255.
22. Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules.* Van Nostrand Reinhold: London. **1979,** 344–345.
23. Selivanov, G. K.; Mal'tsev, A. A. *Zh. Strukt. Khim.* **1973,** 14, 943.
24. Pong, R. G. S.; Shirk, A. E.; Shirk, J. S. *J. Mol. Spectr.* **1977,** 66, 35.
25. Beattie, I. R.; Blayden, H. E.; Hall, S. M.; Jenny, S. N.; Ogden, J. S. *J. Chem. Soc. Dalton* **1976,** 666.
26. Frurip, D. J.; Chatillon, C.; Blander, M. *J. Phys. Chem.* **1982,** 86, 647.
27. Frurip, D. J.; Blander, M. *J. Phys. Chem.* **1980,** 73, 509.
28. Krasnov, K. S.; Solomonik, V. G. *Soviet High Temp.* **1972,** 5, 877.
29. Solomonik, V. G. *Russ. J. Phys. Chem.* **1979,** 53, 313.
30. Klemm, W.; Brautigam, M. *Z. Anorg. Allg. Chem.* **1927,** 163, 225.
31. Kubaschewski, O.; Alcock, C. B. *Metallurgical Thermochemistry.* 5th Ed. Pergamon: Oxford. **1979,** 181–192.
32. Ward, J. W.; Bivins, R. L.; Fraser, M. V. *J. Vac. Sci. Technol.* **1970,** 7, 206.
33. Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K.; Wagman, D. D. *Selected Values of Thermodynamic Properties of the Elements.* Amer. Soc. for Metals: Metals Park, Ohio. **1973.**
34. Barrow, R. F. *Trans. Faraday Soc.* **1960,** 56, 952.
35. Charkin, O. P.; Dyatkina, M. E. *J. Struct. Chem.* **1972,** 8, 450.
36. Vedeneyev, V. I.; Gurvich, L. V.; Kondrat'yev, V. N.; Medvedev, V. A.; Frankevich, Y. L. *Bond Energies, Ionization Potentials and Electron Affinities.* Arnold: London. **1966.**
37. Massey, H. S. W.; Burhop, E. H. S. *Electronic and Ionic Impact Phenomena, Vol. I: Collision of Electrons with Atoms.* Clarendon: Oxford. **1969.**
38. Smirnov, V. A.; Polovov, V. I.; Bronnikov, A. D. *Russ. J. Phys. Chem.* **1975,** 49, 1093.
39. Meyer, V. G.; Blachnik, R. *Z. Anorg. Allg. Chem.* **1983,** 503, 126.
40. Bulewicz, E. M.; Phillips, L. F.; Sugden, T. M. *Trans. Faraday Soc.* **1961,** 56, 921.
41. Smith, F. J.; Barrow, R. F. *Trans. Faraday Soc.* **1958,** 54, 6.
42. Fadeev, V. N.; Fedorov, P. I. *Russ. J. Inorg. Chem.* **1964,** 9, 209.
43. Polyachenok, O. G.; Komshilova, O. N. *Tepl. Vys. Temp.* **1972,** 10, 195.