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Thermodynamics of vaporization of gallium trichloride

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The unsaturated and saturated pressures of gallium trichloride vapor were measured by the static method with membrane-gauge manometers in wide pressure (0.2—760 Torr) and temperature (313—1071 K) intervals. Scanning calorimetry was used to determine the thermodynamic characteristics of $GaCl_3$ fusion. The thermodynamic characteristics were obtained for sublimation, fusion, vaporization, and association in the vapor of $GaCl_3$ molecules. The enthalpies of formation and the absolute entropies of $GaCl_3$ in the liquid and gaseous phases and Ga_2Cl_6 in the gaseous phase were calculated using literature data.

Key words: gallium trichloride, vapor pressure, enthalpy of sublimation, entropy of sublimation, enthalpy of vaporization, entropy of vaporization, entropy of association.

Gallium trichloride is the starting reagent for growing single crystals of semiconductors of the $A^{III}B^{V}$ type and related solid solutions. In the recent years, $GaCl_3$ found use as the catalyst in the synthesis of organic and organometallic compounds. To optimize technological processes using $GaCl_3$, one should enhance the accuracy of the thermodynamic characteristics of matter description and extend the temperature interval of the thermodynamic data presented in the literature.[1—5] The purpose of the present study is to obtain reliable information on the thermodynamics of sublimation, fusion, vaporization, and association of $GaCl_3$.

Experimental

The main difficulty in experimental studying the thermodynamic properties of $GaCl_3$ is caused by the high hygroscopicity of the compound. Therefore, we gave special attention to problems of synthesis, purification, and packing of the samples.

The studies were carried out for the samples prepared by both the authors of the present work and coworkers of the S. I. Vavilov State Optical Institute. The both batches of the substance were synthesized using a standard procedure by the "combustion" of metallic gallium in a chlorine flow.[6] The products were purified by vacuum sublimation (in this case, volatiles were frozen with liquid nitrogen) or fusion in dynamic vacuum. According to the results of chemical, X-ray diffraction, and spectral analysis, the both batches of the substances represented the individual phase of $GaCl_3$ of stoichiometric composition in which the total content of admixtures did not exceed 0.01 wt.%.

Samples for both calorimetric and tensimetric studies were packed using distillation in a closed evacuated system.

Calorimetric measurements were carried out with a Setaram DSC 111 scanning calorimeter at heating rates of 1—3 K min^{-1}. Weighed samples of the substance were 20—30 mg and during experiments were placed in evacuated glass ampules. The error of determination of the thermal effects did not exceed 2% of the determined value.

Tensimetric studies were performed by the static method using quartz membrane-gauge manometers. Errors in temperature measurements determined from calibrations by reference substances (indium, tin, lead, and antimony were used for the calibration of thermocouples; naphthalene, mercury, and argon were used for the determination of the minimum and average temperatures in the manometer) were 0.02—0.5 K, and errors in pressure measurement including the compensation error, errors related to the appearance of reversible and irreversible deformations of the movable rod of the membrane-gauge manometer, and errors of allowance for the residual pressure were 0.05—1.0 Torr.[7]

The pressures of unsaturated and saturated $GaCl_3$ vapors were studied in six series of entries differed in the amount of $GaCl_3$ and pure chlorine introduced into the membrane-type chamber and the pressure and temperature intervals. The lower boundary of measured pressures was determined by the sensitivity of the method (~0.05 Torr), and the upper boundary was determined by a possibility of appearance at elevated temperature of noticeable amounts of lower gallium chlorides, whose study is beyond the frame of the present work. To exclude a possibility of formation of lower chlorides, some measurements were carried out in the presence of excess chlorine pressure (entries *4—6*). For unsaturated vapor, 222 points were obtained in the temperature region 372—1071 K at the gallium concentration in the vapor 0.00141—0.03404 g-at. L^{-1} and free chlorine concentration 0—0.00270 g-at. L^{-1}. Ninety points were obtained for sublimation (313—349.6 K), and 90 points were obtained for vaporization (351—421.5 K).

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Since $GaCl_3$ is a very hygroscopic substance that immediately becomes blurred in air, packing in tensimetric ampules was carried out in evacuated quartz reactors, which made it possible to exclude contact of the samples under study with air. However, this procedure could introduce an error in determination of a weighed sample of the substance, which was calculated from the difference in the weight of the dumbbell-shaped ampule filled with the substance and pieces of the ampule after its contents was distilled into the membrane-gauge manometer. Therefore, the weighed sample was determined two times. After the entry, the substance from the membrane-gauge manometer was quantitatively distilled into the dumbbell-shaped ampule, which was then repeatedly sealed, incised, weighed, and broken at the site of the incision. The substance was washed out with a dilute solution of HCl, and the halves of the dumbbell were weighed. The weighed sample was determined as the arithmetical mean of the values obtained before and after the entry. When processing the experimental data on the unsaturated vapor, the initial gallium concentrations (n_{Ga}/V, g-at. L^{-1}) were among the refined parameters. The deviation of the experimental value from the refined value was 0.3—6.7%.

Before filling the membrane-gauge manometers with the substance under study, the instruments were degassed in a high vacuum (10^{-4} Torr) at ~1200 K for several hours. This procedure of filling made it possible, in most cases, to get rid of residual pressure, which appears usually when the temperature increases during the experiment due to the desorption of moisture and air from the walls of the working chamber of the membrane-gauge manometer and the partial hydrolysis of the substance under study.

The method of "temperature planes" was used in experiments performed both with the temperature increase and decrease. Coincidence of the pressures measured on the planes corresponding to the same temperature is a criterion of the fact that the measured values correspond to equilibrium. The time of equilibrium achievement in all entries was 15—30 min.

Results and Discussion

Five entries were carried out in a scanning calorimeter in the temperature interval 325—360 K. The behavior of the samples confirmed the conclusion drawn on the basis of chemical, X-ray diffraction, and spectral analyses that the substance under study is an individual phase. In the indicated temperature interval, the samples underwent the single phase transformation, *viz.*, fusion. The results of measurements are given in Table 1.

The values measured for the saturated vapor pressures above the solid and liquid phases were approximated by the equations

$$\log(p/\mathrm{Torr}) = 12.66 - 4079.7/T \; (313 \le T/K \le 349.6) \quad (1)$$

and

$$\log(p/\mathrm{Torr}) = 8.626 - 2675.7/T \; (351 \le T/\mathrm{K} \le 421.5) \quad (2)$$

respectively.

For the determination of the thermodynamic parameters of the processes under study, the experimental data were processed assuming the following chemical equilibria:

for the unsaturated vapor

$$Ga_2Cl_6\,(g) \rightleftharpoons 2\,GaCl_3\,(g),$$

for saturated vapor

$$Ga_2Cl_6\,(g) \rightleftharpoons 2\,GaCl_3\,(g),$$

$$Ga_2Cl_6\,(cond) \rightleftharpoons 2\,GaCl_3\,(g),$$

where cond means condenced phase.

Table 1. Thermodynamic characteristics of association, sublimation, vaporization, and fusion of $GaCl_3$

Equilibrium*	T/K	Type of treatment**	$\Delta_r H°(T)$ /kJ mol^{-1}	$\Delta_r S°(T)$ /J mol^{-1} K^{-1}	Reference
$Ga_2Cl_6\,(g) \rightleftharpoons 2\,GaCl_3\,(g)$	298.15	II	93.9±1.1	147.5±1.8	This work
		III	105.7±1.1	167.0±11.2	This work
		II	93.5	147.7	1
		II	100.46	158.11	2
		II	89.29	141.38	3
		II	94.10	150.41	4
$GaCl_3\,(cr) \rightleftharpoons GaCl_3\,(g)$	298.15	II	87.08±1.2	170.6±3.6	This work
		III	86.3±1.2	168.3±7	This work
		II	79.5±1.3	154.0±6.3	3
		II	72.2	—	2
$GaCl_3\,(l) \rightleftharpoons GaCl_3\,(g)$	349.6	II	72.7±0.2	129.1±0.5	This work
		III	70.5±2.0	123.7±5	This work
		II	51.5	—	1
		II	66.9	117.6	3
		II	49.4	—	2
$GaCl_3\,(cr) \rightleftharpoons GaCl_3\,(l)$	349.6	—	11.12±0.1	31.7±1	This work

* Designations g, l, and cr correspond to the gaseous, liquid, and crystalline phases, respectively.

** The number of the law of thermodynamics used in experimental data processing is indicated.

The system of equations determining the total and partial pressures in the j-th experimental point of the i-th entry from the unsaturated vapor pressure has the following form:

$$\begin{cases} p = p_{CaCl_3} + p_{Ga_2Cl_6} \\ \ln K = -2\ln p_{GaCl_3} + \ln p_{Ga_2Cl_6} \\ \Delta S^\circ(298.15)/R - \Delta H^\circ(298.15)/(RT) + \Psi(\Delta C^\circ{}_p P, T). \quad (3) \\ n_{Cl}RT/V = 3p_{GaCl_3} + 6p_{Ga_2Cl_6} \\ n_{Ga}RT/V = p_{GaCl_3} + 2p_{Ga_2Cl_6} \end{cases}$$

Here p_{GaCl_3} and $p_{Ga_2Cl_6}$ are the corresponding partial pressures, K is the equilibrium constant of association in vapor, V is the volume of the working chamber of the manometer, n_{Ga} and n_{Cl} are the amounts of g-atoms of gallium and chlorine in an entry, $\Delta H^\circ(298.15)$ and $\Delta S^\circ(298.15)$ are the standard enthalpy and entropy, and $\Delta C^\circ{}_p$ is the change in the heat capacity in the system upon the dissociation of the $GaCl_3$ dimer.

The calculations were performed by a described procedure[8] using the target function

$$\varphi = \sum_{i=1}^{N} \frac{\{p_i^{exp} - p_i^{calc}\}^2}{\Delta p_i^2 + (\partial p/\partial T)\Delta T_i^2},$$

where N is the number of experimental points; p_i^{exp} is the experimental pressure; p_i^{calc} is the pressure calculated by the accepted physicochemical model; Δp_i and ΔT_i are the ultimate units of measurement of the pressure and temperature. The use of this target function for data processing provides reliable estimates of the parameters. The errors were calculated with allowance for Student´s coefficients for the 95% confidence interval.

The experimental data were processed by the second (II) and third (III) laws of thermodynamics. In the first case, the heat capacities were considered known, and the values of enthalpies and entropies of reactions referred to 298.15 K were considered desired. When processing by the third law, the heat capacities and entropies were considered known. The temperature dependences of the heat capacities and entropies of gallium chlorides used in the calculations are presented in Table 2, and the results of calculations are given in Figs 1—3 and in Table 1.

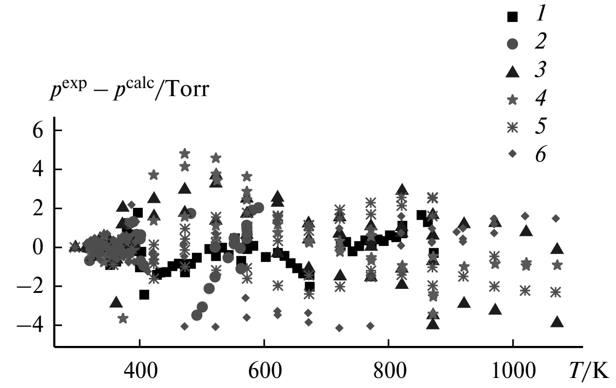

Fig. 1. Difference between the experimental and calculated pressure values of the unsaturated and saturated $GaCl_3$ vapor for entries *1—6*.

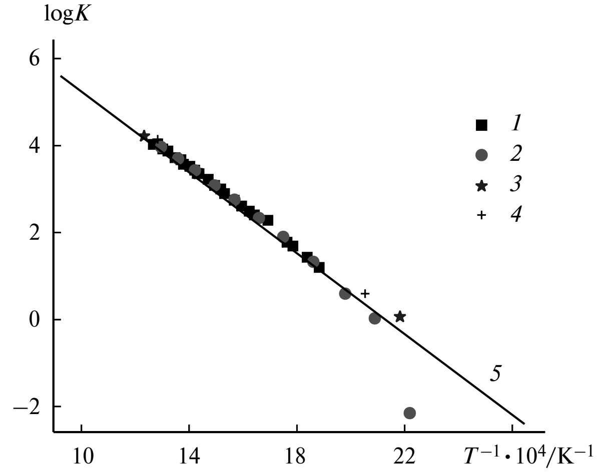

Fig. 2. Temperature plots of the equilibrium constant of the reaction $Ga_2Cl_6\ (g) \rightleftharpoons 2\ GaCl_3\ (g)$; *1*, *2*, *3*, and *4* are the experimental data from Refs 1, 2, 3, and 4, respectively; *5*, our data, calculation by Eq. (3).

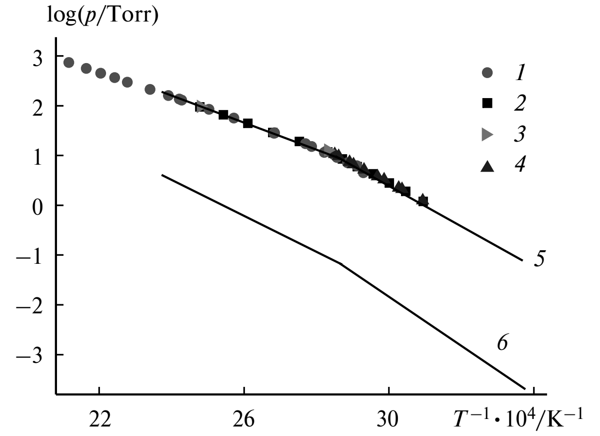

Fig. 3. Temperature plots of the saturated vapor pressure above crystalline and liquid gallium trichloride: *1*, *2*, *3*, and *4* are the experimental data from Refs 1, 2, 3, and 5, respectively; *5*, our data, calculation by Eqs (1), (2); *6*, partial pressure of $GaCl_3$ calculated from our data using Eq. (3).

The deviations of the experimental pressure values from those calculated by the corresponding Eqs (1)—(3) are shown in Fig. 1. The saturated vapor pressures of crystalline and liquid $GaCl_3$ were calculated by Eqs (1) and (2), respectively; the unsaturated vapor pressure was calculated using the system of Eqs (3). The random char-

Table 2. Standard entropies and heat capacities of $GaCl_3$ and its dimer (J mol^{-1} K^{-1})

Compound	$S°(298.15)$	$C°_p = A + BT + C/T + D/T^2$				Reference
		A	B	$-C$	D	
$GaCl_3$ (g)	329.7±5	79.777	0.00388	0	$0.136 \cdot 10^{-5}$	*
Ga_2Cl_6 (g)	493.0±10	299.34	−0.1383	39592	$0.553 \cdot 10^{-4}$	9
$GaCl_3$ (cr)	161.4±4	133.13	−0.02564	7569	—	10

* http://www.ipt.arc.nasa.gov

acter of scatter of deviations for all the processes under study from entry to entry indicates that the measurements contain no serious systematic errors.

The temperature plots of the equilibrium constant of dissociation according to our and earlier published[1–4] data are shown in Fig. 2. As can be seen from the data in Fig. 2, our data agree well with the literature data but cover a wider temperature interval, which made it possible to calculate the enthalpy and entropy of the reaction.

The temperature plots of the total and partial pressures of $GaCl_3$ above crystalline and liquid $GaCl_3$ according to our and earlier published[1–3,5] data are shown in Fig. 3. As a whole, good coincidence between the experimental data obtained by independent authors is observed for both the sublimation and vaporization processes. As can be seen from the data in Fig. 3, the major component of the gas phase is Ga_2Cl_6. At the melting point, the content of $GaCl_3$ is ~0.6% of the total pressure. At the maximum temperature of the entries (421.56 K), its amount increases to 2.1%.

The calculated thermodynamic characteristics of the processes under study are presented in Table 1. The earlier published data on the enthalpy of fusion are not given in Table 1 and have the scatter from 11.13 [11] to 21.7 [2] kJ mol^{-1}. The enthalpy of fusion determined by us (11.12±0.1 kJ mol^{-1}) virtually coincides with that obtained in Ref. 11.

As can be seen from the data in Table 1, for the dissociation reaction

$$Ga_2Cl_6\,(g) \rightleftharpoons 2\,GaCl_3\,(g)$$

the enthalpy according to different literature sources ranges within 89.3—100.5 kJ mol^{-1} and the entropy value varies within 141.4—158.1 J mol^{-1} K^{-1}. The results of our data processing by the second and third laws of thermodynamics (in the latter case, using published data for the entropies of Ga_2Cl_6 (g) and 2 $GaCl_3$ (g)) differ substantially between each other. At the same time, the enthalpies and entropies of association calculated using the second law agree well with the values obtained in Refs 1 and 4. The divergence of the results of processing of the same array by the second and third laws serves, in our opinion, for doubt about reliability of the absolute entropies of gaseous $GaCl_3$ and its dimer accepted in the literature.

Table 3. Recommended thermodynamic characteristics of $GaCl_3$ and its dimer

Compound	$-\Delta_f H°(298.15)$ /kJ mol^{-1}	$S°(298.15)$ /J mol^{-1} K^{-1}
$GaCl_3$ (cr)	524.7±4.2 [12]	161.4±0.4 [10]
$GaCl_3$ (l)	512.7±4.2	191.8±0.4
$GaCl_3$ (g)	437.6±4.2	332.0±3.6
Ga_2Cl_6 (g)	969.1±4.3	516.5±7.4

The enthalpies and entropies of dissociation obtained by us when processing the data by the second law were used in the calculations of the thermodynamic parameters of sublimation and vaporization of $GaCl_3$. The distinction from the previously published values is associated, most likely, with the use of the estimates for the heat capacity of the condensed and gas phases and with neglecting of the dissociation of the gallium trichloride dimer when experimental data processing.

The thermodynamic characteristics for the liquid and gaseous $GaCl_3$ presented as recommended data in Table 3 were calculated using the enthalpy of formation of solid $GaCl_3$ (−524.7±4.2 kJ mol^{-1})[12] and the data in Tables 1 and 2.

The study made it possible to refine the standard thermodynamic parameters of $GaCl_3$ and its dimer.

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