# Tensimetric investigation of the CrCl<sub>3</sub>-Cl<sub>2</sub> system in the temperature range of 600-1200 K

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The sublimation pressure of chromium trichloride was measured by the static method with a quartz membrane-gauge manometer in the temperature range of 875–1230 K. An approximating equation for the sublimation pressure *vs.* temperature was found. The enthalpy (259.4±4 kJ mol<sup>-1</sup>) and the entropy (224.2±3.5 J mol<sup>-1</sup> K<sup>-1</sup>) of sublimation at 298 K were calculated. For the process 2 CrCl<sub>3</sub>(g) + Cl<sub>2</sub>(g) = 2 CrCl<sub>4</sub>(g), the following values were obtained:  $\Delta_r H^\circ_{298} = -207.1\pm11.6$  kJ mol<sup>-1</sup> and  $\Delta_r S^\circ_{298} = -173.6\pm10$  5 J mol<sup>-1</sup> K<sup>-1</sup>.

Key words: chromium chlorides, vapor pressure, enthalpy, entropy, sublimation, dissociation.

Anhydrous chromium trichloride is widely used as starting material in inorganic and organoelement syntheses and to produce chromium coatings. The purity of chromium is of prime importance for these purposes. Since crystalline chromium trichloride is purified by sublimation in a chlorine flow, the temperature dependence of  $CrCl_3(s)$  vaporization is needed for determining the optimal conditions of this process.

Numerous publications have been devoted to the processes that take place on heating  $CrCl_3$  *in vacuo* or under an inert gas.<sup>1–13</sup> Nevertheless, the scatter of published data on the saturated vapor pressure above solid chro-



**Fig. 1.** Saturated vapor pressure (p) above solid chromium trichloride *vs.* temperature (T) according to various authors: our data (Eq. (1)) (1), Ref. 1 (2), Ref. 3 (3), Refs 5, 6 (4), Ref. 7 (5).

mium trichloride is very large (Fig. 1), and the compositions of the equilibrium gas and condensed phases are not entirely clear as yet. The sublimation of chromium chloride at 900-1500 K is assumed to give rise to several equilibria (Scheme 1).

## Scheme 1

$$CrCl_{3}(s) \longrightarrow CrCl_{3}(g)$$

$$2 CrCl_{3}(s) \longrightarrow CrCl_{2}(s) + CrCl_{4}(g)$$

$$CrCl_{2}(s) \longrightarrow CrCl_{2}(g)$$

$$CrCl_{4}(g) \longrightarrow CrCl_{2}(g) + Cl_{2}(g)$$

The process taking place on heating of chromium trichloride in a chlorine stream

$$2 \operatorname{CrCl}_3(g) + \operatorname{Cl}_2(g) \Longrightarrow 2 \operatorname{CrCl}_4(g),$$

is the subject of two inconsistent publications.<sup>7,11</sup>

This study is devoted to determination of the saturated vapor pressure above crystalline chromium chloride in the absence and in the presence of chlorine gas aimed at eliminating the contradictions found in the literature.

#### **Experimental Procedure**

The temperature dependences of the vapor pressure above pure  $CrCl_3$  and in the presence of  $Cl_2$  were measured by the static method using a Novikov–Suvorov quartz membrane-

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gauge manometer.<sup>14</sup> The main characteristics of the setup described previously<sup>15</sup> are as follows: the limiting error of temperature measurements estimated by calibration against mercury, naphthalene, and argon did not exceed ±1 K at 900 K and increased to  $\pm 2$  K at 1200 K; the accuracy of temperature maintenance was  $\pm 0.1$  K; the maximum error in the pressure measurement caused by the diaphragm sensitivity and by the errors in the corrections for the irreversible zero drift of the pressure gauge varied from one experiment to another, being 0.2-5 Torr. The P-T data were obtained by the temperature-step method in the 573–1230 K range both with heating and with cooling. The time of equilibration was varied from 50 h at low temperatures to 10 h at high temperatures. The pressures measured from low to high temperatures and backwards were identical at the same termperature. This guaranteed the attainment of equilibrium.

Four samples of chromium trichloride prepared and purified by different methods were used. According to preliminary tensimetric experiments, all samples exhibit enhanced gas evolution on heating and require additional purification, which was carried out in the following way. The sample (0.5-1 g)was packed into 0.5-1 mL quartz tubes using an argon-filled dry box (with  $P_2O_5$  as the drying agent). The tubes were evacuated, sealed, and placed in a special 10-15-mL quartz reactor. The reactor with the tube was heated to 773-823 K with continuous evacuation (rough exhaust, liquid nitrogencooled zeolite column) to remove the adsorbed gases and water vapor from the reactor walls. Then the tube with the substance was broken inside the reactor and the sample was heated for ~20 h with a continuously operating pump. During this period, volatile fractions were deposited on the inner side of the quartz tube connecting the working volume of the device to the pump. Then the reactor was cooled and the working volume of the reactor with the sample was sealed off in vacuo and heated to the maximum temperature of the tensimetric experiment (1073-1230 K). After cooling, the working chamber was opened, evacuated, and connected to a quartz membrane-gauge manometer. Then the valve separating the working chamber from the diaphragm was broken by a magnetic striker, and the measurements were started. All of the authors of experimental studies noted the appearance of a residual pressure during the experiments. We observed this effect as ~8 Torr at 448 K. After completion of the experiments, the substance in the working chamber represented well-formed druses of bright crimson crystals of CrCl<sub>2</sub>.

According to atomic emission analysis, after the complete static study including sample preparation and pressure measurement, the samples contained Ni (0.15-0.19% (w/w)), Fe (0.02-0.09% (w/w)), and one sample was found to contain Si (0.54% (w/w)); the contents of Ag, Be, Mn, In, Cd, Ga, Cu, Co, Bi, Pb, Tl, Mo, Au, Ge, Sn, Ti, Al, Mg, Zn, Pt, Ba, As, and Te were below the detection limit.

Chlorine was prepared by thermal decomposition (833 K) of platinum dichloride whose chemical analysis is given by (% w/w): Pt, 73.42; Cl, 26.47; calculated (% w/w): Pt, 73.34; Cl, 26.66. Gaseous Cl<sub>2</sub> was condensed on cooling in a special quartz tube with a detachable tip. The used Cl<sub>2</sub> was free from HCl, O<sub>2</sub>, and H<sub>2</sub>O.<sup>16</sup> The weight of the PtCl<sub>2</sub> sample was selected in such a way that the chlorine pressure in the diaphragm zero-pressure manometer was ~100 Torr at ~20 °C.



Fig. 2. Saturated vapor pressure (p) above solid chromium trichloride *vs.* temperature (T) found in this work.

## **Results and Discussion**

Altogether six independent experiments on determination of the saturated vapor pressure of  $CrCl_3$  in the temperature range of 573–1230 K were carried out. The ratio of the sample weight to the manometer working chamber was 0.9-10.5 g L<sup>-1</sup>. The total number of experimental points involved in the processing was 73. After subtracting the residual pressure, the saturated vapor pressure did not depend on the ratio of the sample weight to the volume of the diaphragm chamber to within the error of measurements (Fig. 2). This fact indicates that the system under study is monovariant and allows combined statistical processing of the data from all experiments.

The calculations were carried out by a known procedure<sup>17</sup> using the objective function

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

where *N* is the number of the experimental points;  $p_i^{exp}$  is the experimental pressure;  $p_i^{calc}$  is the pressure calculated by the accepted physicochemical model;  $\Delta p_i$  and  $\Delta T_i$  are the maximum errors of pressure and temperature measurements, respectively.

The use of this objective function in the data processing provides reliable estimates for the desired parameters. The search for the minimum of the function  $\varphi$  was based on a program implementing the modified Newton—Gauss algorithm with a step selected along a direction. The errors of the desired values were calculated taking into account the Student's coefficients for a 95% confidence interval.

Compound	$S^{\circ}_{298}/J \text{ mol}^{-1} \text{ K}^{-1}$	а	b	С	d	е
$CrCl_3(s)^{19}$ $CrCl_3(g)^{20}$ $CrCl_4(g)^{20}$	$122.9 \pm 1.8 \\ 347.0 \pm 3 \\ 371.9 \pm 2.5$	86.075 78.442 119.96	$0.03162 \\ 1.1208 \cdot 10^{-3} \\ -1.327 \cdot 10^{-2}$	$-941.92 \\ 5.8861 \cdot 10^3 \\ 3.1199 \cdot 10^2$	$-1.4458 \cdot 10^{6}$ $-1.3479 \cdot 10^{6}$	$1.4748 \cdot 10^{-7}$ $4.2224 \cdot 10^{-6}$

**Table 1.** Entropy  $(S^{\circ}_{298})$  and temperature dependences of the heat capacity of chromium chloride as  $C_p^{\circ}(T) = a + bT + c/T + d/T^2 + eT^2$ 

Since a residual pressure has been discovered in almost each of the experiments, the temperature dependence of the total pressure was described by the formula

$$p_{\text{calc}} = \exp(-\Delta_{\text{vap}} H^{\circ}/RT + \Delta_{\text{vap}} S^{\circ}/R) + cRT,$$

where  $\Delta_{\text{vap}}H^\circ$  and  $\Delta_{\text{vap}}S^\circ$  are the enthalpy and the entropy of vaporization, respectively, at the temperature *T* and *c* is the ballast gas density.

The processing of the experimental data furnished an empirical equation for the variation of the equilibrium pressure above solid chromium trichloride *vs.* temperature

$$\ln(p/\text{Torr}) = (30.499 - 28978/T) \pm 2\delta, \tag{1}$$

$$\delta^2 = 0.022 - 50.2/T + 28500/T^2 (875 \text{ K} \le T \le 1230 \text{ K}),$$

the values of vaporization enthalpy and entropy, and the temperatures where these values are minimum:<sup>18</sup>  $\Delta_{vap}H^{\circ}_{1135.5} = 240.9 \pm 4.0 \text{ kJ mol}^{-1}, \ \Delta_{vap}S^{\circ}_{1141.0} = 198.4 \pm 3.6 \text{ J mol}^{-1} \text{ K}^{-1}.$ 

The vaporization entropy coincides, to within the determination error, with the value  $\Delta_{subl}S^{\circ}_{1141.0} = 197.6 \text{ J mol}^{-1} \text{ K}^{-1}$ , which we calculated from the third law of thermodynamics using published data (Table 1) and assuming that chromium trichloride is the only chromium-containing component of the gas phase over the whole temperature range.

$$CrCl_3(s) \Longrightarrow CrCl_3(g)$$
 (2)

This fact indicates that sublimation of  $CrCl_3$  is the major vaporization process in the temperature range studied; hence, the synthesis of high-purity chromium trichloride does not require additional purification in a chlorine flow. The thermodynamic parameters for reaction (2) under standard temperatures are presented below.

Processing method	$\Delta_{\rm subl} H^{\circ}_{298}$ /kJ mol <sup>-1</sup>	$\Delta_{\text{subl}} S^{\circ}_{298}$ /I mol <sup>-1</sup> K <sup>-1</sup>
Second law of	259.4±4	224.2±3.5
thermodynamics		
Third law of	259.2±4	224.1±3.6
thermodynamics		

It can be seen from Fig. 1 that our results concerning the vapor pressure above solid chromium trichloride coincide, to within a confidence interval, with published data.<sup>1,5</sup> The essential divergence from the data of another publication<sup>3</sup> can apparently be explained by the presence of volatile components in the samples. When processing the results, the researchers<sup>3</sup> did not subtract the residual pressure, *i.e.*, the pressure that appeared due to impurities. The underestimated data obtained in one more study<sup>7</sup> are probably due to errors in the temperature measurements (~15–20 °C understatement). In addition, the measurements<sup>7</sup> were carried out under permanent heating, and, perhaps, the equilibrium did not have enough time to be established.

A series of measurements (11 points, 850 K  $\leq T \leq 1150$  K) were carried out to study the sublimation of chromium trichloride in a Cl<sub>2</sub> atmosphere. The tensimetric data were processed assuming that three molecular species, CrCl<sub>4</sub>, CrCl<sub>3</sub>, and Cl<sub>2</sub>, exist in the gas phase.

The set of independent chemical reactions was written as follows:

$$\operatorname{CrCl}_3(s) \Longrightarrow \operatorname{CrCl}_3(g),$$
 (2)

$$2 \operatorname{CrCl}_3(g) + \operatorname{Cl}_2(g) \Longrightarrow 2 \operatorname{CrCl}_4.$$
(3)

Figure 3 shows the calculated partial pressures for the temperature range under interest. The thermodynamic characteristics under standard conditions and the temperature dependence of the equilibrium constant ( $K_{eq}$ ) for reaction (3) are shown in Table 2. The good agreement between the results obtained by two processing procedures demonstrates the adequacy of the physicochemical



**Fig. 3.** Temperature dependences of the experimental total pressure (1) and the calculated partial pressures (2-4) in the CrCl<sub>3</sub>(s) + Cl<sub>2</sub> system:  $p_{Cl_2}(2)$ ,  $p_{CrCl_3}(3)$ , and  $p_{CrCl_4}(4)$ .

 Table 2. Thermodynamic characteristics of reaction (3)

Treatment procedure	$-\Delta_{ m r} {H^{\circ}}_{298}$ /kJ	$-\Delta_r S^{\circ}_{298}$ /J K <sup>-1</sup>	Ref.
Second law of thermodynamics	207.1±11.6	173.6±10	*
Third law of thermodynamics	206.8±11.6	173.2±3.5	*
Second law of thermodynamics	221.7±6,** 205.1±12**	170.9±4**	7 11

*Note.* Temperature dependence of the equilibrium constant for reaction (3) is described by the equation  $\log K_{eq} = -8.2848 + 10346.1/T$ .

\* Data of this work.

\*\* Our calculation for standard conditions using the data of Table 1.

model we chose and the absence of significant systematic errors in both our results and published data.<sup>20</sup> The Table also gives the enthalpies and the entropies of reaction (3) available from the literature.

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