UDC 541.11 DOI: 10.18698/1812-3368-2021-1-109-115

THERMODYNAMIC CHARACTERISTICS OF A SERIES OF ANTIMONY COMPOUNDS: STANDARD FORMATION ENTHALPY OF ANTIMONY OXYCHLORIDE SbOCl

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Abstract

The present work opens a series of publications devoted to the description of the results of determination or clarification of the formation enthalpies of certain antimony compounds that are of significant applied interest to science and technology. The measurement results of enthalpy of interaction crystalline $SbCl_3$ and water with formation of crystalline SbOCl are given. On the basis of the obtained and literature data, the value of standard formation enthalpy of the product of this interaction — antimony oxychloride SbOCl at temperature 298.15 K is calculated. This value coincided with the reference values within the margin of error. An attempt was made to determine the dissolution enthalpy of $SbCl_3$ in a two-molar aqueous solution of hydrochloric acid: the obtained approximate value of this characteristic was -30 ± 2 kJ/mol

Keywords

Antimony compounds, antimony oxychloride, interaction enthalpy, standard formation enthalpy

Received 05.10.2020
Accepted 18.11.2020

Introduction. Antimony (Sb) is a silvery white substance with a bluish tint and metallic shine. In the crystalline state, antimony is less dense than in liquid; brittle; not oxidized by air oxygen. The latter properties determine its main application as a component of numerous alloys that gives them hardness. There are about 200 alloys containing antimony. The most widespread ones are bearing, accumulator, typography, semiconductor, etc. alloys. The first group of alloys, such as babbitts, are alloys with antimony content from 5 to 15 % (mass.); they are characterized by high strength, wear resistance, corrosion resistance [1].

The second and third groups are lead-based alloys. There is a quite big quantity of antimony produced to alloy the latter. Thus, battery plates are made

of an alloy containing 15 % (mass.) of antimony. This alloy is also used to create electrodes and cable sheaths [1, 2]. The most famous printing alloy is hart. Antimony contained in it reduces shrinkage and increases the hardness of the moveable types during printing. Printing alloys are mainly used for the production of cast stereotypes and elements of the typeset [3].

The fourth group of alloys is formed by fusion of antimony with Ge, Al, Zn, and Ga. The resulting high-quality semiconductors are widely used in the manufacture of electronic devices used primarily for the conversion and transmission of information [4].

Some antimony compounds have also found practical use. The most popular of them is its oxide Sb_2O_3. It has high heat resistance, so it is used in the manufacture of fireproof fabrics, glasses, enamels, and others. Due to its high thermodynamic stability, this oxide is an indispensable component in the preparation of paints. The latter are used to apply protective coatings on underwater parts of ships.

Antimony telluride Sb_2Te_3 is a part of thermoelectronic alloys [4], and its sulfide compound Sb_2S_3 is used for pyrotechnic devices, bullets, match heads. The second compound is also widely used for rubber vulcanization. It allows to produce particularly heat-resistant but at the same time sufficiently elastic rubber [5].

Antimony halides, its trifluoride SbF_3 and trichloride $SbCl_3$, are substances widely used in organic synthesis. If the former is used as a fluorinating agent, the latter is used as a catalyst. Both substances have found application in textile industry as a mordant in dyeing and packing of fabrics [6]. SbF_3 trifluoride is used in production of Teflon, and $SbCl_3$ is used for production of pure antimony and as a nonaqueous solvent. Antimony preparations are widely used in medicine as well [7].

The active use of antimony compounds in various fields of science and technology is restrained to some extent by the insufficiency or complete lack of information about the thermodynamic characteristics of these compounds. The majority of numerical values of these characteristics provided in handbooks are unreliable, being defined in XIX century, have no error margins. The question of thermodynamic functions of Sb^{3+} ion formation remains open.

Recently, several papers have been published, in which definitions and clarifications of the thermodynamic characteristics of such ions as Sn^{4+} [8], Cu^{2+} [9], and Ni^{2+} [10], have been considered.

The present work opens a series of publications devoted to describing the results of determining the formation enthalpy of antimony compounds, as well

as thermodynamic characteristics of the processes accompanying them, and is aimed at filling in the missing information.

Experimental. *Antimony chloride $SbCl_3$ sample preparation*. For this purpose, a gas pipe was inserted into a ceramic glass with preliminarily placed large glass fragments, the end of which almost reached its bottom. $Sb_2O_{3(cr)}$ was loaded to the bottom of the glass. HCl was fed through the gas pipe from the Würz flask, into which dry $NaCl_{(cr)}$ was placed, and the concentrated (~98 % (mass.)) solution of sulfuric acid was dripped from the drip funnel at low heating. Before feeding into ceramic glass, hydrogen chloride was preliminary dried by passing through the concentrated (~98 % (mass.)) sulfuric acid solution.

The glass with the reaction mass was heated on water bath to the temperature of 70 °C. HCl was fed into the glass until the end of the reaction, which was marked visually on the disappearance of the solid phase Sb_2O_3. The process is described by the equation

$$Sb_2O_{3(cr)} + 6HCl_{(g)} = 2SbCl_{3(sol)} + 3H_2O_{(sol)}$$

The obtained warm solution was transferred to the distillation flask for further removal of hydrogen chloride and water under the vacuum of the water jet pump. The molten $SbCl_3$ was placed into glass ampoules and then sealed. Small portions of the resulting compound were stored in glass weighing bottles in a dry chamber above the open surface of $P_2O_{5(cr)}$. The sample of preparation $SbCl_3$ synthesized in such a way had the following characteristics: $t_{melting}$= 73 °C; $t_{boiling}$ = 221 °C. All reagents (Sb_2O_3; NaCl; H_2SO_4) used in the synthesis had qualification not lower than “chemically pure” class.

Measurements of interaction enthalpy of $SbCl_{3(cr)}$ with water (hydrolysis enthalpy of $SbCl_3$). The measurements were carried out in an airtight high-sensitivity calorimeter with isothermal shell, the main characteristics of which are given in [9, 11]. Reliability of the calorimeter unit operation was checked by measuring enthalpy of potassium chloride dissolution in water at 298.15 K. The found value of the specified thermodynamic characteristic turned out to be 17.45 ± 0.08 kJ/mol at a molar concentration of 0.02 mol/kg. Within the margin of error, it coincided with the most reliable values from the literature data, where the value of 17.40 ± 0.02 kJ/mol [12, 13] is provided. Thermal value of the calorimeter was determined electrically with error not exceeding 0.08 % [14].

The interaction of $SbCl_3$ with water proceeded rather quickly — the main period of calorimetric experience with a mass of $SbCl_3$ equal to about 0.1 g, did not exceed 10 minutes. The convergence of the results at different weights is the

evidence of the completeness of the interaction. The results of interaction enthalpy measurement for $SbCl_{3(cr)}$ with water at 298.15 K are given in the Table.

Measurement of $SbCl_{3(cr)}$ dissolution enthalpy in aqueous solutions of hydrochloric acid of various concentrations. In the course of experiments, it was found out that the hydrolysis of $SbCl_3$ is observed up to the molar concentration of acid solution equal to approximately 2 mol/kg. Only in solutions of such and higher molar concentrations, the dissolution leads to the true solution, i.e., the solution without the presence of hydrolysis product — suspension or $SbOCl_{(cr)}$ precipitate.

The results of interaction enthalpy measurements for $SbCl_{3(cr)}$ interaction with water at 298.15 K

Initial experimental temperature (excluding 1000 Ω) t_0^*, Ω	Correction for heat exchange δ, Ω	Corrected experimental temperature rise $-\Delta R$, Ω	$SbCl_{3(cr)}$ mass m, mg	The amount of heat Q, J, released in the experiment through the interaction	Interaction enthalpy at the temperature of 298.15 K $\Delta_r H_{298}$, kJ/mol
64.70	1.48	7.45	134.2	22.06	−47.7
68.71	1.21	8.83	171.1	33.90	−45.2
30.53	0.60	6.74	136.0	26.19	−43.8
34.01	0.86	3.58	66.6	12.79	−46.6
39.24	0.97	12.13	221.7	45.27	−47.2
20.76	−0.32	9.78	180.3	37.07	−46.9
15.65	−0.59	5.46	104.9	20.52	−45.5

*$(t_0 - 1000)$; σ = 0.05 kJ/mol; $\sigma t_{0.05}$ = 0.1 kJ/mol (σ is standard deviation of the average result; $t_{0.05}$ is Students criterion); average mass of the $SbCl_{3(cr)}$ $m_{av} \approx 145$ mg; average value of the interaction enthalpy at 298.15 K $\Delta_r H_{298\,av} = -46.1$ kJ/mol.

At the same time, it was found that already at the hydrochloric acid molar concentration greater than 0.5 mol/kg, there is an active acid corrosion of the calorimetric vessel occurring via electrochemical mechanism. Naturally, it is accompanied by uncontrolled thermal effect. To prevent acid corrosion, the calorimeter vessel was first covered with a layer of paraffin from the inside and only then preliminary measurements were made for $SbCl_{3(cr)}$ dissolution enthalpy in a two-molar aqueous solution of choric acid with a small mass of $SbCl_{3(cr)}$ — about 50–60 mg. The obtained approximate value of the dissolution enthalpy was $\Delta H_{sol} = -30 \pm 2$ kJ/mol.

Processing and discussion of results. Measured enthalpy of interaction of $SbCl_{3(cr)}$ with water can serve as a basis for determination of the value of standard enthalpy of product formation — antimony oxychloride SbOCl, resulting from hydrolytic transformation of $SbCl_3$. Since the data in the table indicate that the interaction enthalpy does not depend on the mass of $SbCl_{3(cr)}$, the thermochemical data were attributed to the average mass, amounting to ~145 mg.

The thermochemical equation of the process under study is as follows

$$SbCl_{3(cr)} + 15\,723H_2O_{(liq)} =$$
$$= SbOCl_{(cr)} + 2HCl_{(sol,HCl\cdot 7861H_2O)} + 15\ 722H_2O_{(liq)};$$
$$\Delta_r H_{298\ av} = -46.1 \pm 0.1 \text{ kJ/mol}.$$

The calculation of the standard enthalpy of $SbOCl_{(cr)}$ formation was performed using the consequence of the Hess's law on enthalpy of substances formation:

$$\Delta_r H_{298\ av} = 2\Delta_f H_{298\,(HCl\cdot 7861H_2O)} + \Delta_f H^0_{298\,(SbOCl_{(cr)})} -$$
$$- \Delta_f H^0_{298\,(SbCl_{3(cr)})} - \Delta_f H^0_{298\,(H_2O_{(liq)})},$$

from which

$$\Delta_f H^0_{298\,(SbOCl_{(cr)})} = \Delta_r H_{298\ av} - 2\Delta_f H_{298\,(HCl\cdot 7861H_2O)} +$$
$$+ \Delta_f H^0_{298\,(SbCl_{3(cr)})} + \Delta_f H^0_{298\,(H_2O_{(liq)})}.$$

It should be noted that the error of the value $\Delta_f H^0_{298\,(SbCl_{3(cr)})}$ is not specified in the handbooks. Apparently, this is due to the fact that it was determined by the results of the work done in the late XIX century [15, 16]. The author of the above works, A. Guntz, also found the value of the enthalpy of $SbOCl_{(cr)}$ formation. According to the authors of the present work, the error of values of both thermodynamic characteristics cannot be less than 2 kJ/mol.

After substitution of numerical values, taking into account the above mentioned we have

$$\Delta_f H^0_{298\,(SbOCl_{(cr)})} = (-46.1 \pm 0.1) - 2(-166.9 \pm 0.2) - (381.2 \pm 2.0) -$$
$$- (285.83 \pm 0.04) = -379.3 \pm 2.1 \text{ kJ/mol}.$$

Conclusion. The obtained value of standard enthalpy of $SbOCl_{(cr)}$ formation coincides within the margins of error with the value given in the hand-

book and defined in 1884 by Guntz. This fact makes us respect this researcher, and numerical values of thermodynamic characteristics obtained in his works can be considered reliable and reliable.

Translated by A.V. Shokurov

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Please cite this article as:

Gurov A.A., Ozhogina A.N., Solovyev S.N. Thermodynamic characteristics of a series of antimony compounds: standard formation enthalpy of antimony oxychloride SbOCl. *Herald of the Bauman Moscow State Technical University, Series Natural Sciences*, 2021, no. 1 (94), pp. 109–115. DOI: https://doi.org/10.18698/1812-3368-2021-1-109-115