

## Study of High-Temperature Processes for Obtaining Antimony Sulfide and Metallic Sb

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**ABSTRACT.** The paper deals with topical questions of the processes of obtaining antimony sulfide and metallic Sb from ores. Problems of both theoretical and applied character have been considered. Complete Thermodynamic Analysis (HTA) of the heating process of Sb and  $Sb_2S_3$  in vacuum ( $P = 0.0001$  atm) and that of the systems Sb-S, Sb-S-Fe, Sb-S-Al in different media at atmospheric pressure was made. In all the cases estimations were carried out at temperatures from 400 to 1500 K at the pressure of 1 atm. The results are shown in diagrams (temperature dependence of the content composition). Experiments were conducted to obtain antimony sulfide from gold-bearing antimony ores of Zopkhito (Georgia). The kinetics of evaporation of  $Sb_2S_3$  for the ores of various fractions in a vacuum at temperatures of 500-700 °C was studied and the optimal conditions for obtaining  $Sb_2S_3$  were defined. Antimony of technical grade (95%) was obtained from antimony sulfide by iron reduction of antimony (in vacuum) followed by sublimation and condensation. By heating of technical grade antimony up to the temperatures of 400 °C, 450 °C and 500 °C in vacuum (~10-5 MPa) and holding for 3 hours (with the aim of purification of As and S), antimony of high purity (~99.2%) was obtained. © 2013 Bull. Georg. Natl. Acad. Sci.

**Key words:** antimony sulfide, antimony, thermodynamic analysis, vacuum.

This paper presents thermodynamic analysis of high-temperature processes for obtaining antimony sulfide and metallic Sb, as well as experimental data on obtaining metallic Sb.

### Materials and Method

Experiments were conducted to obtain antimony sulfide from gold-bearing antimony ores of Zopkhito (Georgia); the kinetics of evaporation of  $Sb_2S_3$  for the ores of various fractions in a vacuum at temperatures

of 500-700 °C was studied and the optimal conditions for obtaining  $Sb_2S_3$  were defined. Antimony of technical grade (95%) was obtained from antimony sulfide by iron reduction of antimony (in vacuum) followed by sublimation and condensation.

By heating of technical grade antimony up to the temperatures of 400 °C, 450 °C and 500 °C in vacuum (~10-5 MPa) and holding for 3 hours (with the aim of purification of As and S), antimony of high purity (~99.2%) was obtained.

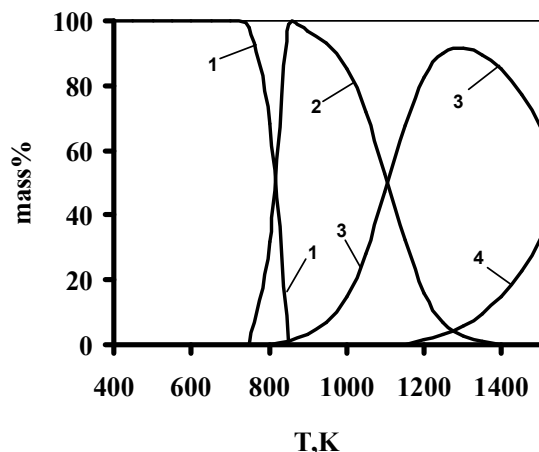


Fig. 1. The dependence of component quantity on temperature with Sb heated under vacuum ( $10^{-5}$  MPa; 0.0001 atm): 1- Sb(cond.); 2-  $Sb_4$ (gas); 3-  $Sb_2$ (gas); 4- Sb(gas).

A complete thermodynamic analysis (CTA) of the heating process of Sb and  $Sb_2S_3$  under vacuum ( $P = 0.0001$  atm) and the Sb-S, Sb-S-Fe, Sb-S-Al systems under atmospheric pressure in various media was conducted using ASTRA 4 [1] software system. In all the cases the computations were performed in the temperature range 400 - 1500 K.

The possible condensed components accounted for all systems were: Sb, S,  $Sb_2S_3$ ,  $Sb_2O_4$ ,  $Sb_2O_5$ ,  $Sb_2S_3$ , Fe, FeS,  $FeS_2$ , FeSb,  $FeSb_2$ ; gaseous: Ar, O,  $O_2$ ,  $O_3$ ,  $S_2$ ,  $S_3$ ,  $S_4$ ,  $S_5$ ,  $S_6$ ,  $S_7$ ,  $S_8$ , SO,  $SO_2$ ,  $S_2O$ , Sb,  $Sb_2$ ,  $Sb_3$ ,  $Sb_4$ , SbO,  $SbO_2$ ,  $Sb_4O_6$ , SbS, Fe.

The values of some experimentally undetermined thermodynamic functions of compounds required for conducting thermodynamic analysis (TA) were obtained using computational methods and added to the thermodynamic quantities database.

The main results for all the compositions are presented through the diagrams. Only a few of them have been shown in the paper.

The TA results of the heating process of Sb under vacuum ( $P = 0.0001$  atm) are presented in Fig. 1.

Evaporation of Sb begins at 750 K and is fully complete at 850 K (the condensed phase of Sb dissipates). Consequently, precipitation of gaseous  $Sb_4$  in the system begins at 750 K and reaches its maximum at 850 K;  $Sb_4$  (gas) decreases with the subse-

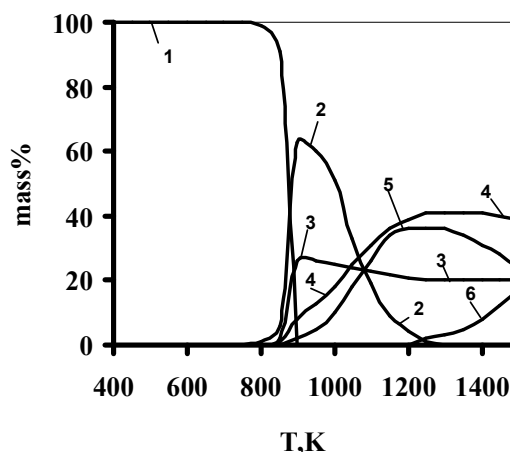


Fig. 2. The dependence of component quantity on temperature with  $Sb_2S_3$  heated under vacuum ( $10^{-5}$  MPa; 0.0001 atm): 1-  $Sb_2S_3$ (cond.); 2-  $Sb_4$ (gas); 3-  $S_2$ (gas); 4- SbS(gas); 5-  $Sb_2$ (gas); 6- Sb(gas).

quent increase in temperature and completely dissipates at 1400 K. Simultaneously, precipitation of  $Sb_2$  (gas) begins at 800 K and reaches its maximum at 1300 K; the amount of  $Sb_2$  decreases with the subsequent increase in temperature and at 1500 K it makes up ~67 mass %. Precipitation of Sb (gas) begins at 1150 K, its amount in the system makes up ~32 mass % at 1500 K.

The TA results of the heating process of  $Sb_2S_3$  under vacuum ( $P = 0.0001$  atm) are presented in Fig. 2.

It is seen that from 800 K a decrease is observed in the amount of condensed  $Sb_2S_3$ , which completely evaporates at 900 K. Approximately at 850 K  $Sb_2S_3$  begins to decompose and precipitations of  $Sb_4$  (gas),  $S_2$  (gas) and SbS (gas) begin in the system. The amounts of  $Sb_4$  (gas) and  $S_2$  (gas) reach their maximum at 900 K.  $Sb_4$  (gas) decreases with the subsequent increase in temperature and dissipates at ~1300 K;  $S_2$  (gas) also decreases and its amount remains practically unchanged above 1200 K. The amount of SbS (gas) increases to 1250 K and remains unchanged to 1500 K. Simultaneously, from 900 K the gas-phase composition of the system begins to change due to precipitation of  $Sb_2$  (gas), the amount of which increases to ~1250 K, then it decreases until it reaches 23 mass % at 1500 K. From 1200 K precipitation of Sb (gas) begins, the amount of which in-

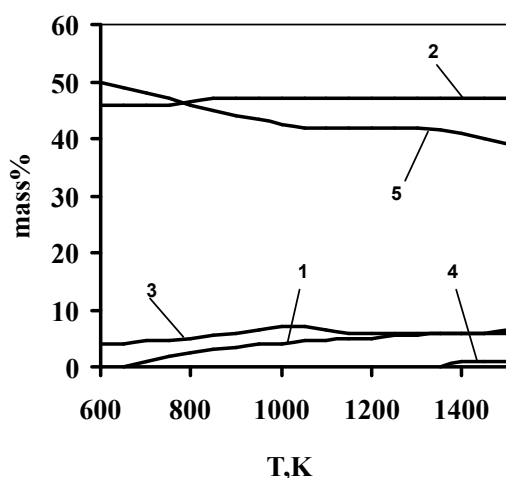


Fig. 3. The dependence of component quantity on temperature for the reaction  $\text{Sb}_2\text{S}_3 + 4\text{Fe}$ : 1 -  $\text{Sb}(\text{cond.})$ ; 2 -  $\text{FeS}_2(\text{cond.})$ ; 3 -  $\text{FeSb}(\text{cond.})$ ; 4 -  $\text{Fe}(\text{cond.})$ ; 5 -  $\text{FeSb}_2(\text{cond.})$ .

increases in the system until reaching ~17 mass % at 1500 K.

The estimations, simulating equilibrium states at heating of  $\text{Sb}_2\text{S}_3$  within the temperature range of 850-1500 K in argon atmosphere show that starting from ~1100 K, the content of  $\text{Sb}_2\text{S}_3$  decreases in the system and at ~1350 K the sulfide completely disappears. Precipitation of the condensed Sb begins at ~1100 K, its content increases rapidly from ~1200 K and reaches its maximum at ~1350 K. At higher temperatures the content of Sb decreases due to evaporation. Along with the condensed Sb,  $\text{S}_2$  (gas) begins to precipitate in the system from ~1150 K, reaching its maximum amount at 1350 K. Also,  $\text{Sb}_4$  (gas) and  $\text{SbS}$  (gas) manifest themselves in the system at ~1200 K,  $\text{Sb}_2$  (gas) manifests itself at ~1300 K, and  $\text{Sb}_3$  (gas) manifests itself at ~1350 K. Their content increases gradually as temperature increases.

The TA results of the process of  $\text{Sb}_2\text{S}_3$  heating to ~1000 K in the area of 80% Ar + 20%  $\text{O}_2$  show that the system contains a large amount of  $\text{Sb}_2\text{S}_3$ ; the condensed  $\text{Sb}_2\text{O}_3$  and gaseous  $\text{SO}_2$  are in a less amount.  $\text{Sb}_2\text{S}_3$  (in large amounts) and small amounts of  $\text{Sb}_2\text{O}_3$  and the gaseous  $\text{SO}_2$  are present in the system to 1000 K; above this temperature a decrease in the amount of  $\text{Sb}_2\text{S}_3$  is observed until its total dissipation at 1350 K, where as the concentrations of  $\text{Sb}_2\text{O}_3$

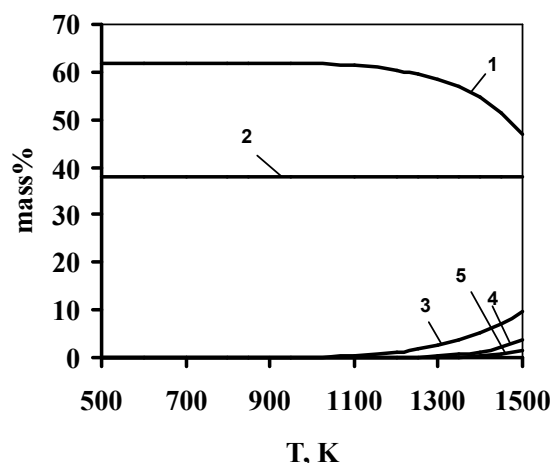


Fig. 4. The dependence of component quantity on temperature for the reaction  $\text{Sb}_2\text{S}_3 + 2\text{Al}$ : 1 -  $\text{Sb}(\text{cond.})$ ; 2 -  $\text{Al}_2\text{S}_3(\text{cond.})$ ; 3 -  $\text{Sb}_2(\text{gas})$ ; 4 -  $\text{Sb}_4(\text{gas})$ ; 5 -  $\text{Sb}_3(\text{gas})$ .

(gas) and  $\text{SO}_2$  (gas) slightly vary. Precipitation of  $\text{S}_2$  (r) begins at ~1050 K; its amount increases gradually, from ~1250 K it increases rapidly and reaches its maximum at ~1350 K; at higher temperatures a slight decrease in  $\text{S}_2$  (r) is observed. The condensed Sb appears in the system at ~1200 K. Its concentration increases significantly to ~1350 K, and with the subsequent increase in temperature it decreases rapidly due to evaporation.  $\text{Sb}_2$  (gas),  $\text{Sb}_4$  (gas) and  $\text{SbS}$  (gas) appear in the system starting from ~1200 K, and  $\text{Sb}_3$  (gas) manifests itself from ~1300 K. Their content increases as temperature increases.

The TA results for the reaction of  $\text{Sb}_2\text{S}_3 + 2\text{Sb}_2\text{O}_3 = 6\text{Sb} + 3\text{SO}_2$  show that the content of  $\text{Sb}_2\text{O}_3$  (condensed) gradually decreases (due to the evaporated  $\text{Sb}_4\text{O}_6$ ) to about 1050 K, while the content of  $\text{Sb}_2\text{S}_3$  stays unchanged. It is seen that the concentration of  $\text{Sb}_2\text{O}_3$  (cond.) in the system decreases gradually to ~1050 K (evaporation occurs as  $\text{Sb}_4\text{O}_6$ ), whereas the concentration of  $\text{Sb}_2\text{S}_3$  (cond.) does not vary. This reaction occurs above ~1050 K and  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{S}_3$  completely dissipate at ~1300 K. Precipitation of the condensed Sb in the system begins from ~1050 K, its concentration reaches its maximum at ~1300 K, and it decreases rapidly due to evaporation with the subsequent increase in temperature.  $\text{Sb}_4\text{O}_6$  manifests itself in the system at ~850 K, reaching its maximum at

1300 K; at ~1100 K the occurrence of  $\text{SO}_2$  (cond.) is observed in the system, with its concentration increasing rapidly to ~1300 K, while above this temperature it varies slightly. Simultaneously,  $\text{Sb}_4$  (gas),  $\text{Sb}_3$  (gas),  $\text{Sb}_2$  (gas) and  $\text{SbS}$  (gas) precipitate in the system in the temperature range ~1100 – 1200 K.

The interaction between antimony sulfide ( $\text{Sb}_2\text{S}_3$ ) and iron (Fe) is the primary reaction of obtaining metallic Sb. TA was conducted for the following reactions:

1.  $\text{Sb}_2\text{S}_3 + 2\text{Fe}$ ;
2.  $\text{Sb}_2\text{S}_3 + 3\text{Fe}$ ;
3.  $\text{Sb}_2\text{S}_3 + 4\text{Fe}$ ;
4.  $\text{Sb}_2\text{S}_3 + 5\text{Fe}$ ;
5.  $\text{Sb}_2\text{S}_3 + 6\text{Fe}$ .

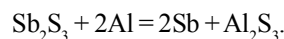
The TA results for the first reaction showed that the amount of  $\text{Sb}_2\text{S}_3$  in the system increases slightly to 800 K, then it decreases gradually to 1200 K, after that it decreases rapidly and completely dissipates at ~1450 K. From 600 K to 1000 K the amount of  $\text{FeS}_2$  decreases rapidly and dissipates, while the amount of  $\text{FeS}$ , by contrast, increases. The amount of metallic Sb also increases in the range from 600 to 1400 K, and above 1400 K it decreases slightly due to evaporation. A significant amount of metallic sulfide forms in the system as  $\text{FeSb}_2$ , its amount decreases and makes up 18 mass% at 1250 K, and as temperature increases to 1500 K it reaches 33 mass%. Precipitation of gaseous  $\text{SbS}$  (gas) and  $\text{S}_2$  (gas) begins in the system above 1200 K. As thermodynamic analysis has shown, the sulfide reduction is not fully achieved in the temperature range 600 to 1450 K, which is attributable to insufficient amounts of iron.

The TA results for reaction (2) have shown that the process proceeds in much the same way as reaction (1). In this case only a small amount of  $\text{Sb}_2\text{S}_3$  is found in the temperature range 600-1400 K, which again can be attributed to an insufficient amount of iron.

The TA results for reaction (3) are presented in Fig. 3 in this case  $\text{Sb}_2\text{S}_3$  is not found in the system any longer as confirmed in obtaining metallic sulfide experimentally.

Similar results were obtained for reactions (4) and (5).

The reduction process of antimony sulfide with aluminum proceeds according to the reaction:

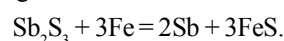


Conducting TA of this particular system was of special interest since the data on thermodynamic analysis of this reaction has not been found in the literature.

Among the possible condensed components accounted for were: Al, Sb, S,  $\text{Sb}_2\text{S}_3$ ,  $\text{AlSb}$ ,  $\text{Al}_2\text{S}_3$ ; among gaseous components were: Ar, S,  $\text{S}_2$ ,  $\text{S}_3$ ,  $\text{S}_4$ ,  $\text{S}_5$ ,  $\text{S}_6$ ,  $\text{S}_7$ ,  $\text{S}_8$ , Sb,  $\text{Sb}_2$ ,  $\text{Sb}_3$ ,  $\text{Sb}_4$ ,  $\text{SbS}$ , Al,  $\text{Al}_2$ ,  $\text{AlS}$ ,  $\text{AlS}_2$ ,  $\text{Al}_2\text{S}$ ,  $\text{Al}_2\text{S}_2$ .

The TA results for this reaction in the temperature range 500 to 1500 K are presented in Fig. 4. It is seen that antimony is fully separated below 500 K and its amount does not change to 1000 K; above this temperature the amount of Sb decreases due to evaporation. Condensed  $\text{Al}_2\text{S}_3$  is present in the system below 500 K and does not change across the whole temperature range. Gaseous  $\text{Sb}_4$  first, and subsequently  $\text{Sb}_2$  and  $\text{Sb}_3$  begin to separate above 1000 K.

As noted above, processing of antimony raw material and obtaining metallic Sb is carried out through the interaction between antimony sulfide and iron according to the reaction:



The resultant  $\text{FeS}$  represents a compound with a higher melting point. Therefore,  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{O}$  and some other sodium compounds are added to the charge material to obtain low-temperature slag.

The experiments on obtaining metallic Sb were conducted in accordance with the above reaction without the use of fluxes.

Initially, antimony sulfide ( $\text{Sb}_2\text{S}_3$ ) or so-called «crudum» was extracted from ore.

In view of its appreciable evaporation from the ore, obtaining antimony sulfide ( $\text{Sb}_2\text{S}_3$ ) is made possible by thermal evaporation and the subsequent condensation under vacuum at relatively low temperatures (500 to 700 °C).

The experiments were conducted under vacuum  $\sim 10^{-5}$  MPa on a weight loss self-recording installation constructed by us.

For obtaining antimony sulfide from the Zopkhito (Georgia) ore deposit the kinetics of the  $\text{Sb}_2\text{S}_3$  evaporation process from various fractions of the ore in the temperature range 500 - 700 °C under vacuum were studied. Regularity and optimal conditions for obtaining antimony sulfide were determined: vacuum  $\sim 10^{-5}$  MPa, fraction (-1+ 0.5) mm, temperature – 650-700 °C, duration  $\sim 40$  min, extraction – over 90 mass%.

Chemical and phase X-ray structure and metallographic analysis have shown that arsenic, which exists in ore both as arsenic sulfide and its complex compound will evolve into a condensate along with  $\text{Sb}_2\text{S}_3$ . To remove arsenic from antimony sulfide the sulfide was heated to  $\sim 450$  °C under vacuum for two hours; subsequently, the residual portion was heated to  $\sim 700$  °C, also under vacuum. As a result of these technological manipulations the amount of As in the condensate decreased significantly.

The resulting antimony sulfide and iron powder were mixed in a special mixer for 4 to 5 hours. The mixture was placed in a sealed steel container and heated in a shaft furnace to  $\sim 700$  to 800 °C for 3 hours in the argon medium under a pressure of 1 atm.

The resulting mass was ground to powder and placed in a heating unit of a kinetic installation at  $\sim 850$  °C under a vacuum  $\sim 10^{-5}$  MPa. The experiments have shown that intensive evaporation of metallic antimony and its condensation on the cool walls of

the quartz tube occurs at this temperature. According to chemical analysis the resulting condensate consists primarily of metallic antimony.

The experiments have shown that the amount of the reducing agent (Fe) greatly influences the evaporation rate and the yield of the end product. With small amounts of iron complete reduction of Sb is not achieved, resulting in a mixture of metallic antimony and unreduced sulfide. In case of large amounts of iron, complete reduction of antimony from the sulfide is achieved. However, excess iron forms compounds ( $\text{FeSb}$ ,  $\text{FeSb}_2$ ) with the reduced Sb, thus reducing the yield of the end product (i.e. metallic Sb) in the condensate.

Experimental data indicate that the best results for obtaining the end product (i.e. metallic Sb) are achieved with the mixture ratio  $\text{Sb}_2\text{S}_3/\text{Fe} = 1.5$ .

At the same time the impact of temperature on both stages of the above process was studied. As experiments have shown optimum temperature in the first stage of the process is 750 °C, while in the second stage it is 850 °C, and the best yield of the product is achieved under these conditions.

Thus the end product (metallic Sb) of technical purity ( $\sim 95$  mass%) was obtained from sulfides by a reduction of antimony with iron and its evaporation under vacuum.

Isolate arsenic and sulfur the obtained metallic antimony was heated under vacuum ( $\sim 10^{-5}$  MPa) at  $\sim 400$  °C, 450 °C and 500 °C for three hours.

As a result, high purity ( $\sim 99.2$  mass%) metallic Sb was obtained.

## ფიზიკური ქიმია

## ანტიმონის სულფიდისა და ლითონური ანტიმონის მიღების მაღალტემპერატურული პროცესის შესწავლა

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ნაშრომში განხილულია მადნიდან ანტიმონის სულფიდისა და ლითონური ანტიმონის მიღების პროცესების როგორც თეორიული, ისე გამოყენებითი ხასიათის აქტუალური საკითხები. შესრულებულია  $Sb$  და  $Sb_2S_3$  გახურების პროცესების სრული თერმოდინამიკური ანალიზი ვაკუუმში ( $P=0,0001$  ატმ) და  $Sb-S$ ,  $Sb-S-Fe$ ,  $Sb-S-Al$  სისტემების ატმოსფერულ წნევაზე. ყველა ანგარიში შესრულებულია ფართო ტემპერატურულ ინტერვალში ( $400-1500$  K). მიღებული შედეგები წარმოდგენილია დიაგრამების სახით (კომპონენტების შედგენილობის დამოკიდებულება ტემპერატურაზე). ჩატარებულია კვლევები ზოფხიტოს ოქროშემცველი ანტიმონის მადნიდან ანტიმონის სულფიდის მისაღებად, შესწავლილია  $Sb_2S_3$  აორთქლების კინეტიკა სხვადასხვა ფრაქციის მადნებისათვის ვაკუუმში  $500-700^{\circ}C$  ტემპერატურებზე და დადგენილია  $Sb_2S_3$  მიღების ოპტიმალური პირობები. ანტიმონის სულფიდიდან  $Sb$ -ის რკინით აღდგენის შედეგად და შემდგომი აორთქლებითა და კონდენსაციით, შესაძლებელი გახდა ტექნიკური სისუფთავის ლითონური ანტიმონის მიღება (95 მას.%). ვაკუუმში ( $\sim 10^{-5}$  მკა)  $400^{\circ}C$ ,  $450^{\circ}C$  და  $500^{\circ}C$  ტემპერატურებზე ტექნიკური სისუფთავის ლითონური ანტიმონის გახურებით და დაყოვნებით 3 საათის განმავლობაში (დარიშხანისა და გოგირდის მოცილების მიზნით) მიღებულ იქნა მაღალი სისუფთავის ლითონური ანტიმონი ( $\sim 99,2$  მას.%).

## REFERENCES

1. N.A. Vatolin, G.K. Moiseev, B.G. Trusov (1994), Termodinamicheskoe modelirovanie v vysokotemperaturnykh neorganicheskikh sistemakh. M., 352 p. (in Russian).
2. S.M. Mel'nikov, A.A. Rozlovskii, A.M. Shuklin (1977), Sur'ma. M., 536 p. (in Russian).

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