

Thermal Separation of Arsenic and Antimony Oxides

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Experiments were carried out to remove arsenic from antimony trioxide by two techniques: first, by selectively volatilizing the more volatile arsenic trioxide from a mixed oxide sample; and, second, by selectively condensing the less volatile antimony tetroxide at high temperatures, leaving arsenic trioxide to condense out at a lower temperature. Thermodynamic analysis of the As-Sb-O system indicated that if arsenic and antimony oxides behave like pure solid phases, then there is no limitation to producing pure antimony oxide by these proposed techniques. The selective volatilization experiments were carried out at 379 °C to 587 °C, using both nitrogen and air as carrier gases and an industrial antimony trioxide fume containing 13.8 wt pct As. The results showed it is difficult to achieve an arsenic content below 5.0 wt pct using either air or nitrogen, and formation of solid solutions between arsenic and antimony trioxides appears to be the main barrier to the removal of arsenic. Selective condensation experiments were carried out in which a mixed oxide vapor was progressively cooled through a series of condensers over a controlled temperature profile. Injection of oxygen into the vapor improved separation, and antimony tetroxide containing as low as 0.23 wt pct As was obtained. The recovery of antimony tetroxide in the experiments seems to have been limited by kinetic factors, and the results suggest that high conversions to antimony tetroxide are likely to be achieved only in antimony-rich vapors.

I. INTRODUCTION

THE problem of separating arsenic from antimony arises as one of the purification steps in the production of commercial-grade antimony oxide (<0.5 pct As) or arsenic oxide from fume produced in metallurgical processes. A simple technique for separating arsenic oxide from antimony oxide would allow commercial production of otherwise hazardous by-products. The separation of antimony oxide from arsenic oxide has been only partially covered in any theoretical or experimental detail in the literature. In particular, there has been a lack of attention to the chemistry of the mixed oxide system. Only two industrial processes are known that separate arsenic oxide from antimony oxide. These are arsenic trioxide refining by selective condensation, which produces commercial-grade arsenic trioxide from a mixed oxide feed^[1,2] and the WR Metal Industries (WRMI) leaching process, which produces commercial-grade arsenic acid from a mixed oxide feed.^[3] In both processes, antimony oxide is recovered in an impure form. Other industrial techniques separate arsenic and antimony in their sulfide state, as metal or as chlorides in solution.

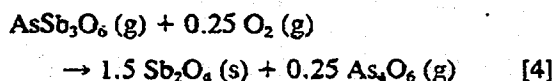
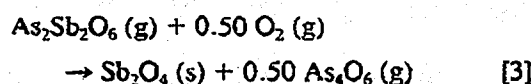
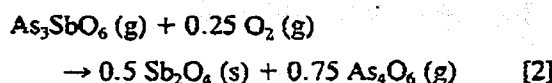
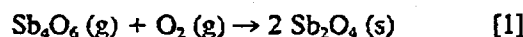
Two pyrometallurgical techniques for separating arsenic oxide from antimony oxide have been proposed.^[4]

Selective volatilization of the more volatile arsenic trioxide from a mixed oxide sample to leave high-purity antimony oxide.

Selective condensation of antimony oxide from arsenic oxide in the vapor phase, by condensing the less volatile antimony oxide at a higher temperature.

In the case of selective volatilization, no separation process producing commercial-grade product has been reported. In the case of selective condensation, the experimental work of Read^[1] showed that arsenic trioxide with less than 0.3 pct Sb can be condensed selectively from a mixed oxide vapor. The vapor forms of antimony and arsenic oxides are Sb_2O_3 and As_2O_3 . Mixed oxides also form in the gaseous state when arsenic and antimony are both present. According to Norman and Staley^[5] and Mauser,^[6] the mixed oxides of arsenic and antimony that can exist in the vapor state are As_3SbO_6 , $\text{As}_2\text{Sb}_2\text{O}_6$, and AsSb_3O_6 .

Hager and Li^[7] proposed improving the separation of antimony oxide from mixed oxide vapors by injecting oxygen to form nonvolatile antimony tetroxide, according to the following reactions:



Hager and Li carried out selective condensation experiments using an air-cooled tube at the exit of a transpiration apparatus. They observed that in an inert atmosphere, decomposition of the vapor complexes resulted in deposition of predominantly cubic As_2O_3 in the cold zone and a mixture of cubic and orthorhombic Sb_2O_3 in the hot zone of the tube. With oxygen injection at the entrance of the condenser tube, decomposition of the complexes resulted in deposition of cubic As_2O_3 in the cold zone and a mix of cubic Sb_2O_3 , orthorhombic Sb_2O_3 , and Sb_2O_4 in the hot zone. The best separation

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Manuscript submitted December 17, 1993.

Table I. Summary of Selective Condensation Experiments by Hager and Li⁽⁷⁾

Experiment	Temperature of Samples (°C)		Gas Flow (L/min)*		Condensate Analysis			
	As ₂ O ₃	Sb ₂ O ₃	O ₂	N ₂ /Ar**	Hot Zone	Pct Sb Total [†]	Cold Zone	Pct As Total [‡]
A	—	629	—	0.2	Sb ₂ O ₃ (ortho)	—	—	—
B	—	629	0.1	0.1	Sb ₂ O ₃ (ortho)	—	—	—
C	219	549	0.1	0.1	Sb ₂ O ₄ (ortho)	86	As ₂ O ₃ (cubic)	95
					Sb ₂ O ₃ (cubic)			
					Sb ₂ O ₃ (ortho)			
D	220	629	0.1	0.1	Sb ₂ O ₄ (ortho)	95	As ₂ O ₃ (cubic)	98
					Sb ₂ O ₃ (cubic)			
					Sb ₂ O ₃ (ortho)			
E	219	549	—	0.2	Sb ₂ O ₄ (ortho)	83	As ₂ O ₃ (cubic)	93
					Sb ₂ O ₃ (cubic)			
					Sb ₂ O ₃ (ortho)			
F	220	629	—	0.2	Sb ₂ O ₃ (cubic)	91	As ₂ O ₃ (cubic)	97
					Sb ₂ O ₃ (ortho)			

*The flow rates (at STP) for each experiment were not given by Hager and Li, although the description of the experimental technique indicates that flow rates are in the range given in this table.

**Mixtures of argon and nitrogen were used.

[†]Percentage of total antimony; balance condensed in cold zone.

[‡]Percentage of total arsenic; balance condensed in hot zone.

occurred with the injection of oxygen, as shown in Table I. Hager and Li speculated that with improved mixing of oxygen and better condenser design, high-purity oxide products could be produced by the complete oxidation of antimony in the vapor to antimony tetroxide. Brooks and Rankin⁽⁸⁾ have shown that antimony and arsenic trioxides form solid solutions up to moderately high concentrations of arsenic and that arsenic trioxide has limited solid solubility in antimony tetroxide. It is possible that solid-solution formation will limit the degree of separation of the oxides by selective volatilization and condensation.

II. THERMODYNAMIC ANALYSIS

Gibbs free energy minimization calculations were performed to analyze the As-Sb-O system. The possible species in the system are listed in Table II. The selection of Sb₂O₃, As₂O₃, and Sb₂O₄ as the only potential solid species is consistent with the known chemistry of the system. Thermodynamic data for the species were taken from Kaiser⁽⁹⁾ and Hager and Li⁽⁷⁾ and are summarized

Table II. Chemical Species in the As-Sb-O System

Solid species	As ₂ O ₃ (s)
	Sb ₂ O ₃ (s)
	Sb ₂ O ₄ (s)
Liquid species	As ₂ O ₃ (l)
	Sb ₂ O ₃ (l)
Gaseous species	O ₂ (g)
	Sb ₂ O ₄ (g)
	As ₂ O ₃ (g)
	As ₂ SbO ₆ (g)
	As ₂ Sb ₂ O ₆ (g)
	AsSb ₃ O ₆ (g)

in Table III. The data for arsenic trioxide ignore the transition from cubic to monoclinic; this simplification is introduced because the transition of cubic to monoclinic trioxide is not well characterized. The CHEMIX program of the CSIRO Thermochemistry System (Version 5)⁽¹⁰⁾ was used to perform the calculations.

A. Selective Volatilization

Selective volatilization was examined by considering a mixture of arsenic and antimony oxides containing 13.8 wt pct As, which is similar to the composition of the fume sample used in the experiments. The starting material was considered to be a mixture of As₂O₃ and Sb₂O₃, and it was assumed that no solid solutions were present. The amount of nitrogen used was that required just to hold all the arsenic trioxide as vapor at 379 °C (i.e., the vapor was saturated with arsenic trioxide). The results are summarized in Table IV, and they demonstrate that as the system is defined, there is no thermodynamic restriction to removing arsenic trioxide from antimony trioxide. Increasing the temperature, while not affecting the separation, increased the amount of antimony oxide in the vapor, and there was a ninefold increase between 379 °C and 587 °C.

Next, it was assumed that arsenic trioxide and antimony trioxide form a solid solution. Because antimony trioxide is the dominant (>82 pct) component of the solid solution, it was considered to have an activity coefficient of 1 and the activity coefficient of As₂O₃ was varied. The same volume of nitrogen as used for the pure solid case was used for the calculations. The results, presented in Table V, demonstrate that the formation of a solid solution greatly restricts the removal of arsenic from antimony trioxide; the only solid phases produced with an arsenic content below 0.5 wt pct As were at 535 °C and 587 °C for an activity coefficient of As₂O₃ of 10. The

Table III. Gibbs Free Energies of Formation of Oxides in the As-Sb-O System^[7,9]

$$\Delta G^\circ = a + bT + cT^2 + d/T + eT \ln T$$

(J mol)

Species	a	b	c	d	e	Temperature Range (K)
Sb ₂ O ₃ (s)	-723,257	481.43	0	0	-29,422	298 to 879
Sb ₂ O ₃ (s)	-719,448	482.06	0	0	-30,395	879 to 929
Sb ₂ O ₄ (s)	-452,025	167.48	0	0	2,3274	298 to 1173
As ₂ O ₃ (s)	-668,379	491.44	0	0	-32,178	298 to 551
As ₂ O ₃ (l)	-644,770	636.27	0.0749	100,004	-68,408	551 to 730
Sb ₂ O ₃ (l)	-674,030	433.25	0	0	-30,396	929 to 1425
As ₂ O ₆ (g)	-1,231,186	1192.9	0.1499	199,765	-136.82	>298
Sb ₂ O ₆ (g)	-1,266,139	811.87	0	0	-60,793	>298
As ₂ SbO ₆ (g)	-1,240,772	1088.3	0.1239	149,974	-117.46	730 to 850
As ₂ SbO ₆ (g)	-1,242,426	1092.7	0.1239	149,974	-117.81	880 to 920
As ₂ Sb ₂ O ₆ (g)	-1,251,321	992.12	0.0749	99,983	-98,096	730 to 850
As ₂ Sb ₂ O ₆ (g)	-1,254,586	1000.7	0.0749	99,983	-98,804	880 to 920
AsSb ₃ O ₆ (g)	-1,261,870	900.28	0.0375	49,991	-78,734	730 to 850
AsSb ₃ O ₆ (g)	-1,266,746	913.15	0.0375	49,991	-79,798	880 to 920

Table IV. Results of Gibbs Free Energy Minimization Calculations for Selective Volatilization in the As-Sb-O System at 1 Atm with Inert Gas, Assuming Pure Solid Phases (Initial Amounts 40.9 mol N₂, 75.3 mol Sb₂O₃, and 24.7 mol As₂O₃)

Temperature (°C)	Solid composition	Pct As in Vapor	Pct Sb in Vapor
379	100 pct Sb ₂ O ₃	100	1.0
425	100 pct Sb ₂ O ₃	100	1.8
479	100 pct Sb ₂ O ₃	100	3.2
535	100 pct Sb ₂ O ₃	100	5.7
587	100 pct Sb ₂ O ₃	100	9.6

Volatilization of arsenic trioxide from the solid solution was limited by the volume of nitrogen. The results of calculations performed to find the volume of nitrogen that is required to remove arsenic from the solid phase at below commercial-grade requirements for the case of an ideal solution are summarized in Table VI. The table shows that at low temperatures, a large volume of nitrogen is needed to achieve the separation, and that at higher temperatures, the removal of arsenic to the required level would be accompanied by a large loss of antimony trioxide to the vapor.

Table VI. Results of Gibbs Free Energy Minimization Calculations for Selective Volatilization in the As-Sb-O System at 1 Atm to Produce Sb₂O₃ Containing Less than 0.5 pct As in Solid Solution (Initial Amounts: 75.3 mol Sb₂O₃, and 24.7 mol As₂O₃)

Temperature (°C)	N ₂ (mol)	Pct Sb in Vapor
379	75,000	7.52
425	22,090	10.2
479	6,520	14.5
535	2,220	20.9
587	940	29.6

Because antimony can exist as the tetroxide as well as trioxide in the solid state, selective volatilization using air was examined. Initially, it was assumed that As₂O₃, Sb₂O₃, and Sb₂O₄ do not form solid solutions. The volume of air used was the same as for the inert gas cases. The results showed that the Sb₂O₃ oxidized to Sb₂O₄, which has a very low vapor pressure. There was no thermodynamic restriction to volatilizing the arsenic trioxide and, with sufficient oxygen, complete separation of arsenic and antimony oxides was achieved.

Finally, arsenic trioxide and antimony tetroxide were

Table V. Results of Gibbs Free Energy Minimization Calculations for Selective Volatilization in the As-Sb-O System with Inert Carrier Gas at 1 Atm, Assuming Solid Solution Formation (Initial Amounts: 40.9 mol N₂, 75.3 mol Sb₂O₃, and 24.7 mol As₂O₃)

Temperature (°C)	$\gamma_{As_2O_3} = 0.1$			$\gamma_{As_2O_3} = 1.0$			$\gamma_{As_2O_3} = 10.0$		
	Solid Composition* (Wt Pct Sb ₂ O ₃)	Pct As in Vapor	Pct Sb in Vapor	Solid Composition* (Wt Pct, Sb ₂ O ₃)	Pct As in Vapor	Pct Sb in Vapor	Solid Composition* (Wt Pct Sb ₂ O ₃)	Pct As in Vapor	Pct Sb in Vapor
379	81.8	0.26	0.01	84.4	16.9	0.23	96.9	85.8	0.88
425	81.9	0.83	0.04	87.4	36.0	0.73	98.2	91.9	1.64
479	82.1	2.53	0.19	92.3	57.9	1.96	98.97	5.4	3.09
535	82.7	6.49	0.69	94.2	73.5	4.29	99.37	97.3	5.57
587	83.5	13.3	2.00	97.0	82.8	7.97	99.58	98.3	9.39

*Balance As₂O₃.

considered to form a solid solution. A range of activity coefficient values for arsenic trioxide in the solid solution was considered because the actual values are not known. The higher activity coefficient range in these calculations, compared to that used in the arsenic trioxide/antimony trioxide system, reflects the greater level of chemical incompatibility of arsenic trioxide and antimony tetroxide due to their different valencies and crystal structures. The activity coefficient for antimony tetroxide was taken as unity, as it was the major component of the solution. The potential for a separate solid solution of arsenic and antimony trioxides to form was not ignored, and this potential phase was considered to behave as an ideal system. The initial mixture was equilibrated with sufficient air to just oxidize the antimony trioxide to antimony tetroxide on a stoichiometric basis. The results, summarized in Table VII, show that the formation of $\text{As}_2\text{O}_3\text{-Sb}_2\text{O}_3$ solid solution greatly restricts the removal of arsenic from antimony tetroxide. Only for a high activity coefficient ($\gamma = 100$) was arsenic removed to below commercial-grade requirements. The oxidation of antimony trioxide to the nonvolatile antimony tetroxide prevented the loss of any antimony oxide to the vapor phase. The removal of arsenic from the solid solutions in this case was limited by the volume of gas.

B. Selective Condensation

The experiments of Hager and Li were modeled thermodynamically by calculating the composition of mixed oxide vapor formed by equilibrating arsenic trioxide with inert gas and then equilibrating this gas with pure solid antimony trioxide. The vapor was then cooled in five equilibrium stages and the condensate removed at each stage. Two gas mixtures were considered, their compositions calculated for the two sets of conditions used by Hager and Li; one was comparatively rich in arsenic, and the other was comparatively rich in antimony. Initially, arsenic and antimony trioxides were considered to be pure solid phases condensing from the mixed oxide vapor in an inert carrier gas. The conditions and the results of the Gibbs free energy minimization calculations are summarized in Table VIII, which shows that there is no thermodynamic restriction to condensing pure antimony trioxide from a mixed oxide vapor in the temperature range 300 °C to 629 °C if As_2O_3 and Sb_2O_3 do not form a solid solution. Over 95 pct of the antimony was recovered as pure antimony trioxide in the hot end

of the condensation train, and arsenic trioxide contaminated with antimony trioxide formed in the cold end. Hager and Li's experiment of adding an equal volume of oxygen to the nitrogen was also modeled. The initial conditions and the results of the Gibbs free energy minimization calculations are summarized in Table IX. Complete separation was achieved with the conversion of all the antimony to antimony tetroxide in the first stage for both vapors and the formation of solid arsenic trioxide in the cold end of the condensation train.

The possibility of the formation of solid solution phases was also considered. The trioxides were assumed to form an ideal solid solution, whereas arsenic trioxide was assumed to have less affinity with antimony tetroxide and thus to have a higher activity coefficient ($\gamma = 10$). The initial conditions and the results of the calculations are summarized in Tables X and XI. The results show that with an inert carrier gas, the formation of solid solutions between arsenic and antimony trioxides results in impure compounds forming along the condensation train. The highest purity antimony trioxide condensate contained 1.16 pct As, and over 95 pct of antimony in the system was recovered in this stage (at 400 °C for the antimony rich vapor). High-purity arsenic trioxide (<0.1 Sb wt pct) was obtained below 200 °C, though approximately half of the arsenic trioxide was present in the antimony rich condensates. Greater separation was achieved when oxygen was added; all the antimony was converted to antimony tetroxide in the first stage, and only marginal dissolution of arsenic (<0.1 wt pct) occurred. This favorable result relies on the assumption that arsenic trioxide does not readily dissolve into antimony tetroxide. Pure arsenic trioxide formed at the cold end of the condensation train.

In summary, the thermodynamic analysis indicates that the formation of solid solutions between arsenic and antimony oxides is a crucial issue in the success or failure of separating arsenic and antimony oxides by selective volatilization or condensation. Assumptions concerning the activity of the species suggest that good separation by selective volatilization or condensation in inert atmospheres may be difficult to achieve and that more favorable results would be achieved in an oxidizing atmosphere. The mechanism proposed by Hager and Li for enhancing separation of arsenic and antimony oxides by injecting oxygen into a mixed oxide vapor stream has been shown to be thermodynamically sound.

Table VII. Results of Gibbs Free Energy Minimization Calculations for Selective Volatilization in the As-Sb-O System at 1 Atm with Air as Carrier Gas, Assuming Solid Solution Formation (Initial Amounts: 141.8 mol N_2 , 37.7 mol O_2 , 75.3 mol Sb_2O_3 , and 24.7 mol As_2O_3)

Temperature (°C)	$\gamma_{\text{As}_2\text{O}_3} = 1.0$			$\gamma_{\text{As}_2\text{O}_3} = 10$			$\gamma_{\text{As}_2\text{O}_3} = 100$		
	Solid Composition Sb_2O_3 Wt Pct	Pct As in Vapor	Pct Sb in Vapor	Solid Composition Sb_2O_3 Wt Pct	Pct As in Vapor	Pct Sb in Vapor	Solid Composition Sb_2O_3 Wt Pct	Pct As in Vapor	Pct Sb in Vapor
379	84.8	15.9	0	96.6	83.1	0	99.6	98.2	0
425	87.4	31.9	0	97.9	89.8	0	99.8	98.9	0
479	90.4	49.8	0	98.7	93.7	0	99.9	99.4	0
535	92.8	63.0	0	99.1	95.7	0	99.9	99.6	0
587	94.2	70.9	0	97.0	96.8	0	99.6	99.7	0

Table VIII. Summary of Gibbs Free Energy Minimization Calculations for Selective Condensation of Pure Solid Phases from As-Sb-O Vapor with Inert Carrier Gas at 1 Atm

Initial Amount	400 mol N ₂ , 1.21 mol Sb ₂ O ₃ , and 1.0382 mol As ₂ O ₃				Stage Temperature (°C)	400 mol N ₂ , 5.48 mol Sb ₂ O ₃ , and 1.0962 mol As ₂ O ₃			
	Condensate Analysis (Wt Pct)		Wt Pct of Elements Condensed			Condensate Analysis (Wt Pct)		Wt Pct of Elements Condensed	
	As	Sb	As	Sb		As	Sb	As	Sb
549	—	—	0	0	629	—	—	—	—
400	0	83.5	0	85.4	400	0	83.5	0	96.7
300	0	83.5	0	11.4	300	0	83.5	0	2.61
200	10.9	65.8	32.5	2.85	200	66.7	9.92	36.1	0.66
100	75.1	0.67	67.4	0.32	100	75.1	0.67	63.8	0.07
<100	75.5	0.31	0.04	0.01	<100	75.5	0.31	0.04	<0.01

Table IX. Summary of Gibbs Free Energy Minimization Calculations for Selective Condensation of Pure Solid Solution Phases from As-Sb-O Vapor with Oxidizing Carrier Gas at 1 Atm

Initial Amount	200 mol N ₂ , 200 mol O ₂ , 1.21 mol Sb ₂ O ₃ , and 1.038 mol As ₂ O ₃				Stage Temperature (°C)	400 mol N ₂ , 5.48 mol Sb ₂ O ₃ , and 1.0962 mol As ₂ O ₃			
	Condensate Analysis (Wt Pct)		Wt Pct of Elements Condensed			Condensate Analysis (Wt Pct)		Wt Pct of Elements Condensed	
	As	Sb	As	Sb		As	Sb	As	Sb
Stage Temperature (°C)	As	Sb	As	Sb	Stage Temperature (°C)	As	Sb	As	Sb
549	0	79.2	0	100.0	629	0	79.2	0	100.0
400	—	—	0	0	400	—	—	0	0
300	—	—	0	0	300	—	—	0	0
200	75.7	0	33.7	0	200	75.7	0	37.6	0
100	75.7	0	66.2	0	100	75.7	0	62.4	0
<100	75.7	0	0.01	0	<100	75.7	0	0.04	0

III. SELECTIVE VOLATILIZATION EXPERIMENTS

The thermodynamic analysis suggests that arsenic trioxide should be able to be separated from antimony trioxide by selective volatilization, though the purity of the product could not be predicted. To test this hypothesis and to find the level to which the arsenic content could be lowered, experiments were performed using an industrial fume consisting of arsenic and antimony oxides. A quantity of the fume was dried and homogenized, and samples were taken for characterization by X-ray fluorescence (XRF), fire assaying, X-ray diffraction (XRD), an electron microprobe (EMP), and a particle size analyzer. The results are summarized in Table XII.

A. Apparatus

A horizontal tube furnace was used for the experiments. The temperature was regulated by a three-term controller, which received its signal from a type-R thermocouple mounted centrally in the side of the furnace. Temperature profiles of the reaction tube for different temperature settings and gas flow rates were determined using a digital temperature indicator and a type-K thermocouple inserted through the ends of the tube. Each end of the mullite reaction tube was sealed with rubber stoppers during heating up, operation, and

cooling down. Silastic was used as a seal between the stoppers and the furnace tube. A stainless steel wire, passing through the stopper at the inlet end and attached to a stainless steel tray in the furnace tube, was used to maneuver the aluminosilicate sample boat, which rested on the tray. The wire was sealed tightly at the inlet stopper. The outlet gas from the furnace passed into a water-cooled glass condenser, through a wash bottle, and then to the port of an extraction system. The carrier gas was either nitrogen or air. The nitrogen was deoxidized by passing it through a small horizontal tube furnace containing copper turnings at 600 °C.

B. Procedure

Sample boats and the fume sample were dried, weighed, and stored in a desiccator. About 10 g of sample was used in each experiment. The boat containing fume was weighed, placed onto the stainless steel tray, and positioned at the inlet of the reaction tube. The stopper was then inserted into the tube, and mineral wool was packed around the protruding end of the locating wire to seal it. A "bleed" flow rate of carrier gas was established through the apparatus, and the furnace was heated to the experimental temperature. The experiment was begun by moving the boat into the hot zone by means of the wire and setting the required flow rate. At the conclusion of an experiment, the gas flow was reduced to a bleed and the boat was pulled to the cold inlet end of the work

Table X. Summary of Gibbs Free Energy Minimization Calculations for Selective Condensation of Solid Solution Phases from As-Sb-O Vapor with Inert Carrier Gas at 1 Atm

Initial Amount	400 mol N ₂ , 1.21 mol Sb ₂ O ₃ , and 1.038 mol As ₂ O ₃ *					400 mol N ₂ , 5.48 mol Sb ₂ O ₃ , and 1.0962 mols As ₂ O ₃ *			
Stage Temperature (°C)	Condensate Analysis (Wt Pct)		Wt Pct of Elements Condensed		Stage Temperature (°C)	Condensate Analysis (Wt Pct)		Wt Pct of Elements Condensed	
	As	Sb	As	Sb		As	Sb	As	Sb
549	—	—	0	0	629	—	—	0	0
400	1.19	82.2	2.35	85.9	400	1.16	82.2	11.1	97.0
300	6.16	76.7	1.70	11.2	300	6.03	76.9	1.54	2.41
200	67.4	9.15	39.2	2.81	200	67.0	9.63	34.1	0.60
100	75.6	0.20	56.7	0.08	100	75.6	0.20	53.3	0.02
<100	75.7	0	0.04	0	<100	75.7	0	0.03	0

*Sb₂O₃ and As₂O₃ assumed to form an ideal solid solution.

*Sb₂O₃ and As₂O₃ assumed to form an ideal solid solution.

Table XI. Summary of Gibbs Free Energy Minimization Calculations for Selective Condensation of Solid Solution Phases from As-Sb-O Vapor with Oxidizing Carrier Gas at 1 Atm

Initial Amount	200 mol N ₃ , 200 mol O ₂ , 1.21 mol Sb ₂ O ₃ , and 1.038 mol As ₂ O ₃ *					200 mol N ₂ , 200 mol O ₂ , 5.48 mol Sb ₂ O ₃ , and 1.096 mol As ₂ O ₃ *			
Stage Temperature (°C)	Condensate Analysis (Wt Pct)		Wt Pct of Elements Condensed		Stage Temperature (°C)	Condensate Analysis (Wt Pct)		Wt Pct of Elements Condensed	
	As	Sb	As	Sb		As	Sb	As	Sb
549	0.08	79.1	0.19	100	629	0.06	79.1	0.59	100
400	—	—	0	0	400	—	—	0	0
300	—	—	0	0	300	—	—	0	0
200	75.7	0	33.6	0	200	75.7	0	37.0	0
100	75.7	0	66.2	0	100	75.7	0	62.4	0
<100	75.7	0	0.04	0	<100	75.7	0	0.03	0

*As₂O₃ and Sb₂O₃ assumed to form an ideal solution; solution As₂O₃ and Sb₂O₃ assumed to form a nonideal solid solution in which $\gamma_{\text{As}_2\text{O}_3} = 10$ and $\gamma_{\text{Sb}_2\text{O}_3} = 1$.

tube and allowed to cool for at least 4 hours. The calcines were then recovered, weighed, and analyzed using XRF and XRD.

C. Results

Twenty-five experiments were carried out over six temperature/flow rate regimes. Reasonable repeatability of weight loss from the calcine and composition of the calcine was obtained; differences of 2.5, 0.6, and 6.8 pct relative weight losses from the average were obtained for three duplicate runs, and the differences in elemental analyses were within the uncertainties of the analytical techniques.

The results of nitrogen experiments are given in Figures 1 through 3. It was observed that there was increasing weight loss with increasing temperature (Figure 1). In general, weight loss was rapid in the first hour and decreased thereafter. This was most notable at 425 °C and 480 °C and less pronounced at 535 °C and 587 °C. Rapid removal of arsenic occurred for the first hour and decreased thereafter, as shown in Figure 2. This was accompanied by a plateauing of arsenic concentration (Figure 3) in the calcine at 425 °C, 480 °C, and

535 °C. At 379 °C, there was a steady decrease in arsenic concentration, whereas at 587 °C, there was a marked increase in arsenic concentration after 2 hours, which was accompanied by gross sintering of the calcine. Sintering and shrinkage of the calcines were observed at 535 °C and 587 °C. Removal of arsenic to the levels in commercial-grade antimony oxide (<0.5 wt pct) was not achieved. The lowest level (4.9 wt pct) was obtained after 6 hours at 535 °C; this represents 78 pct removal of arsenic, and it was accompanied by 32 pct loss of antimony. X-ray diffraction patterns of the calcines indicated that a single cubic phase was present. The peak positions were difficult to determine because of splitting and broadening, but it appears that arsenic and antimony trioxides combined in a solid solution with the same structure as the cubic polymorphs of arsenic and antimony trioxide.

The results of selective volatilization experiments carried out at 535 °C with air as carrier gas are given in Figures 4 through 6 and are compared with the results obtained with nitrogen. Initially, there was a rapid loss of weight from the calcine and then virtually no further changes (Figure 4). This was reflected in the losses of antimony and arsenic from the calcine (Figure 5). The

Table XII. Summary of Fume Characterization Results

Analytical Technique	Results
RF	Sb 68 ± 3.4 wt pct As 13.8 ± 0.7 wt pct Pb 0.105 ± 0.005 wt pct Au 0.0045 ± 0.0005 wt pct
RF assay	cubic phase (either As ₂ O ₃ or Sb ₂ O ₃ or possibly solid solution of both)—dominant Sb ₂ O ₃ (orthorhombic)—subdominant
ED Cu K _α radiation; scan 10 to 65 deg. 1 deg/min)	
Electron microprobe (1-μm-diameter beam)	five regions examined region 1 (5 points) As wt pct 14.9 to 16.9 (average 15.9) Sb wt pct 66.8 to 69.5 (average 68.0) region 2 (6 points) As wt pct 6.1 to 8.1 (average 7.4) Sb wt pct 76.9 to 78.0 (average 77.4) region 3 (7 points) As wt pct 8.7 to 13.1 (average 11.0) Sb wt pct 71.1 to 76.1 (average 73.3) region 4 (8 points) As wt pct 2.9 to 4.9 (average 4.3) Sb wt pct 77.6 to 80.8 (average 80.0) region 5 (3 points) As wt pct 1.44 to 2.50 (average 1.96) Sb wt pct 83.7 to 84.5 (average 84.0)
Particle size analysis	11.0 to 7.8 μm 1.4 vol pct 7.8 to 5.5 μm 6.3 vol pct 5.5 to 3.9 μm 13.8 vol pct 3.9 to 2.8 μm 22.2 vol pct 2.8 to 1.9 μm 39.4 vol pct 1.9 to 0.0 μm 16.7 vol pct

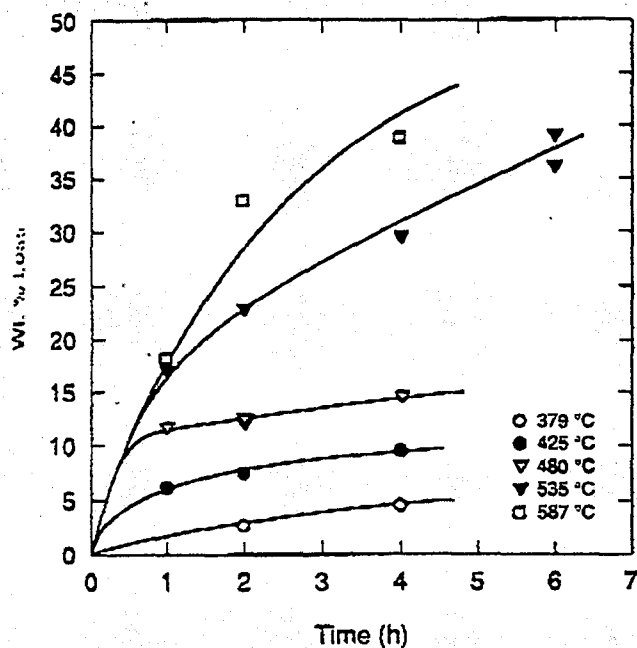


Fig. 1—Weight loss of fume samples heated in nitrogen.

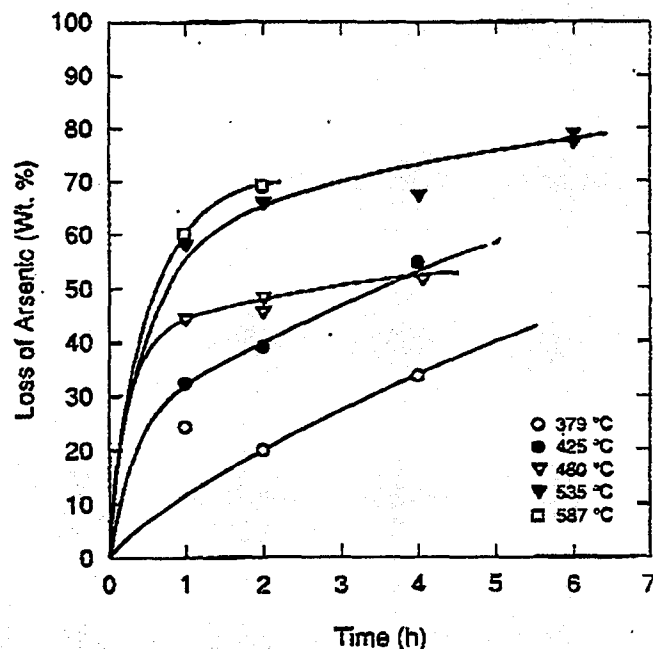


Fig. 2—Loss of arsenic from fume samples heated in nitrogen.

arsenic concentration of the calcine plateaued at around 6 wt pct (Figure 6). An increase in temperature from 535 °C to 587 °C did not result in further removal of arsenic; indeed, the higher temperature failed to achieve the level of arsenic removal of the lower temperature

(50 pct after 2 hours compared to 64 pct for the lower temperature). Partial sintering of the calcines occurred, the degree of sintering increasing with temperature and time held at temperature. Removal of arsenic to the desired commercial level (<0.5 wt pct) was not achieved;

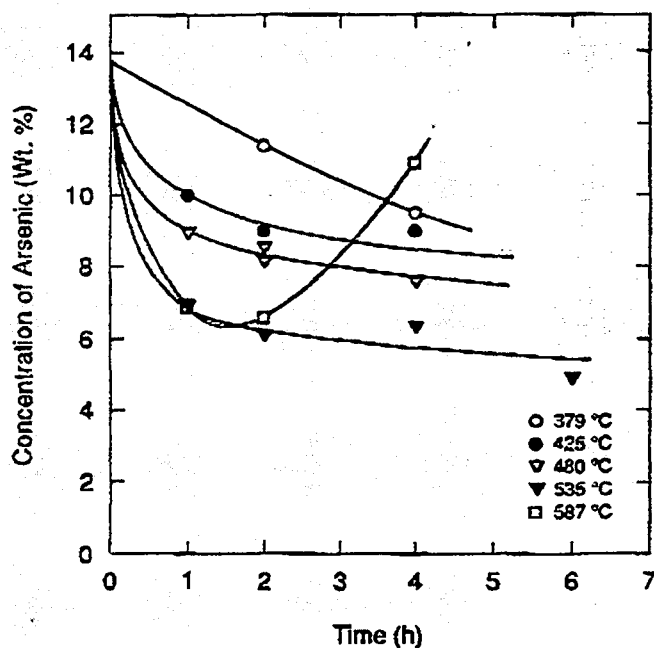


Fig. 3—Variation of arsenic concentration in fume samples heated in nitrogen.

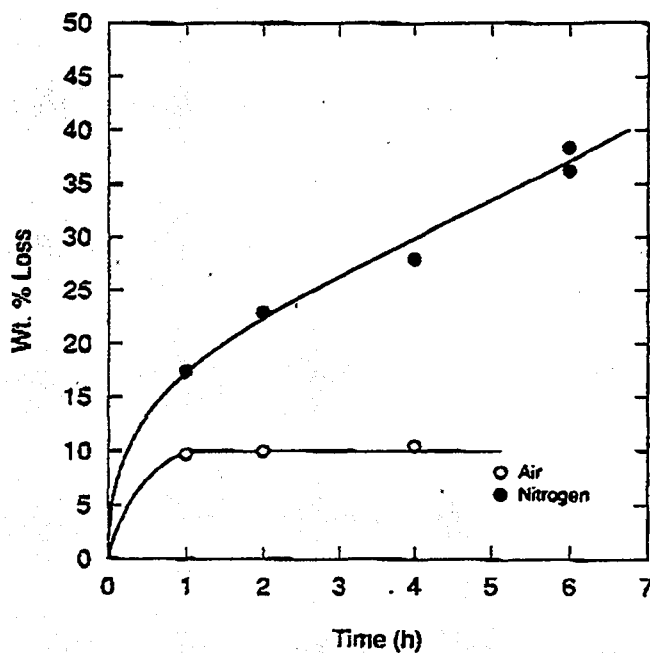


Fig. 4—Weight loss of fume samples heated at 535 °C in nitrogen and air.

the lowest level (6 wt pct) was obtained after 2 hours at 535 °C. This represents 64 pct removal of arsenic from the calcine, and it was accompanied by 3 pct loss of antimony. The loss of antimony was more pronounced at 587 °C, 18 pct after 2 hours. Comparison of the weight loss characteristics in nitrogen and air for As and Sb at 535 °C (Figure 5) shows that the arsenic loss curves are similar for the two cases, but the experiments in air are distinguished by low antimony losses from the calcine. X-ray diffraction patterns of the calcines indicated that

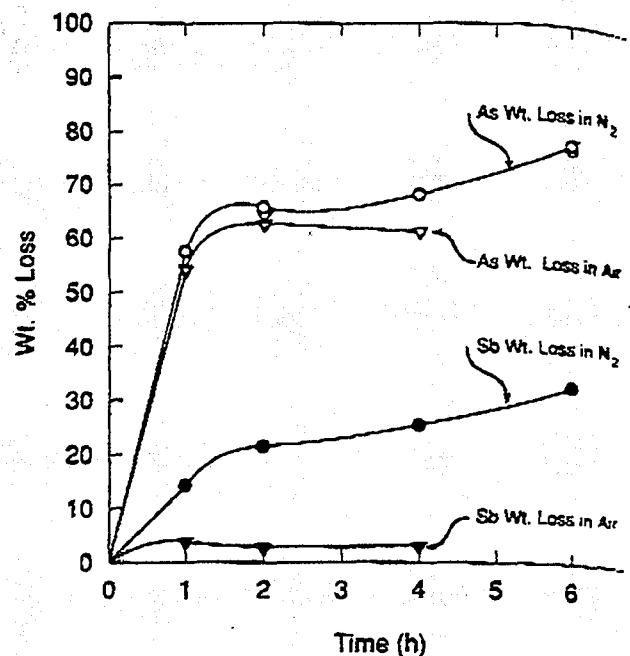


Fig. 5—Weight loss of arsenic and antimony from fume samples heated at 535 °C in nitrogen and air.

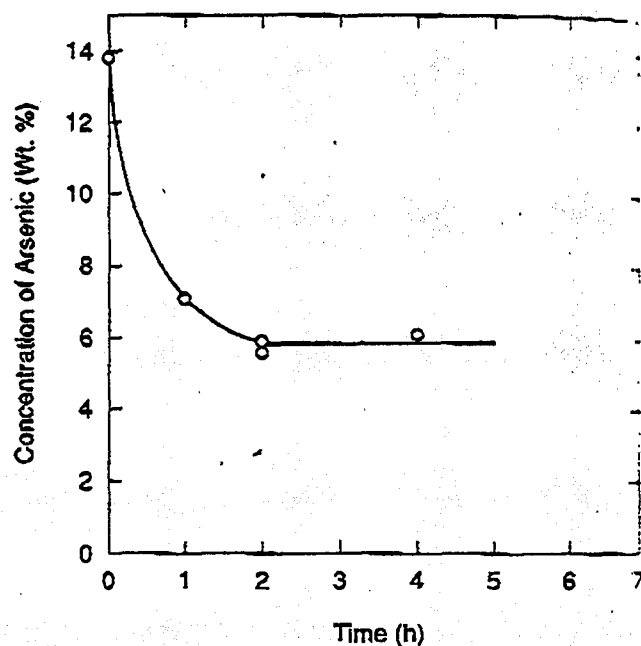


Fig. 6—Concentration of arsenic in fume samples heated at 535 °C in air.

antimony tetroxide was dominant in all cases and that a subdominant cubic phase was also present, which may have been cubic arsenic trioxide or antimony trioxide, and/or a solid solution phase, or both.

D. Discussion

The failure to obtain low levels of arsenic in antimony oxide in periods of a few hours when using nitrogen as

rier gas has several possible explanations. The rate of removal of arsenic could be limited by

the mass transfer of the vapor species from the solid-interface to the bulk gas flow,
solid solution formation, or
the diffusion of arsenic trioxide vapor through the calcine.

The experiments were carried out at comparatively high flow rates, and increasing the flow rate from 2.26 to 28 L/min did not assist in lowering the arsenic concentration. It appears that the mass transfer of reaction products to the bulk gas phase was not the rate-controlling step. The second explanation is favored because X-ray diffraction patterns of the calcines suggest that solid solutions, either single or multiple, readily formed in the calcines, and the resulting lower vapor pressure of arsenic trioxide would provide less driving force for volatilization. It is reasonable to expect that the formation of a solid solution phase would occur faster at higher temperatures, and it would follow that the lower overall rate of vapor generation would appear earlier at higher temperatures. This is supported by the trends in Figure 2, which shows that the rate of arsenic loss from calcine decreased dramatically at 480 °C and 535 °C after the first hour but not so at 379 °C and 425 °C. The third explanation is consistent with the observation of sintering of the calcine at higher temperatures. The increase in concentration of the arsenic in the calcine at 57 °C after 2 hours probably results from a decrease in the rate of arsenic volatilization relative to antimony trioxide volatilization because of sintering and the consequent decrease in the diffusion rate of arsenic vapors through the sample.

The kinetics and mass transfer aspects of the reactions in the experiments carried out in air are difficult to distinguish, because there are a large number of possible reactions and the nature of the phases in the calcine is unclear, in particular whether trioxide or tetroxide solid solutions formed. The observations that increasing the temperature from 535 °C to 587 °C decreased the rate of removal of arsenic, and that this was accompanied by an increased degree of sintering of the calcine, support the notion that the volatilizing reactions were limited by the diffusion of reaction products through the calcine. Alteration of the chemistry of the system by the formation of arsenic oxide-antimony tetroxide solid solution, however, provides another explanation. The decreased losses of antimony at higher temperatures may result from the slow diffusion of oxygen to reaction sites in virtue of sintering and the resulting greater volatilization of antimony trioxide.

IV. SELECTIVE CONDENSATION EXPERIMENTS

Apparatus

The furnace used in these experiments consisted of an outer tube, on which the resistance wire was wound, and an inner reaction tube. The element was wound in eight zones, each with a three-term temperature controller and a type-K thermocouple located at the midpoint on the

outside of the winding tube. Thermal conductivity, convection, and radiation limited the gradient between zones to a maximum of approximately 150 °C. Temperature profiles of the furnace were determined for different controller settings and flow rates using a digital temperature indicator and a long type-K thermocouple inserted into the reaction tube. Two aluminosilicate sample boats were placed on two in-line stainless steel trays and positioned, using a wire that protruded from the inlet end of the reaction tube. Copper wire was wound around the stainless steel arms connecting the trays to serve as a deoxidizing surface for any oxygen leakage into the system. Each end of the reaction tube was sealed with rubber stoppers. The wire used to maneuver the boat assembly was sealed at the inlet end by mineral wool packing. Three stainless steel condenser units were used in series. These consisted of a split body held together with stainless steel screws; the joints between the units were sealed using compressed mineral wool as a gasket. The general layout of the boats and condenser units within the reaction tube is shown in Figure 7. The carrier gas was either nitrogen or argon, and the gas was deoxidized by passing it through a small horizontal tube furnace containing copper turnings at 600 °C. In some experiments, nitrogen or oxygen was injected through a stainless steel tube into the entrance of the first condenser unit. The tube was 4 mm in diameter, with an off-center tip located at the entry of the first condensation unit. The outlet gases passed into a water-cooled glass condenser through a wash bottle and were then released to an extraction system.

B. Procedure

Sample boats containing analytical-grade arsenic trioxide and antimony trioxide were dried, weighed, and stored in a desiccator. A sample boat of each was placed onto the stainless steel tray and positioned at the inlet of the furnace, with the boat containing arsenic trioxide being located closest to the inlet end. A bleed flow rate of nitrogen or argon was maintained as the furnace was heated to the experimental temperature. An experiment was begun by positioning the boat assembly into the hot zone and introducing the required flow rate of gas. At the conclusion of an experiment, the gas rate was reduced to a bleed and the boat assembly withdrawn to the inlet end of the furnace and allowed to cool for 8 hours. The condenser units were then removed and opened, and the condensate recovered, weighed, and analyzed using XRF and XRD. The uncertainty in the XRF analyses was ± 5.0 pct relative. The temperature variation was ± 1.2 pct and the error in mass loss determination was ± 0.0003 g (which represents a total maximum error of no more than 0.05 pct relative).

C. Results

Seventeen experiments were carried out, and the conditions are summarized in Table XIII. In experiment A, antimony trioxide was vaporized and the vapors were allowed to condense in an inert atmosphere. Orthorhombic Sb_2O_3 formed as off-white needles in condenser unit 2 in the temperature range 580 °C to 526 °C. Below 526 °C, the condensate was a coarse, white crystalline

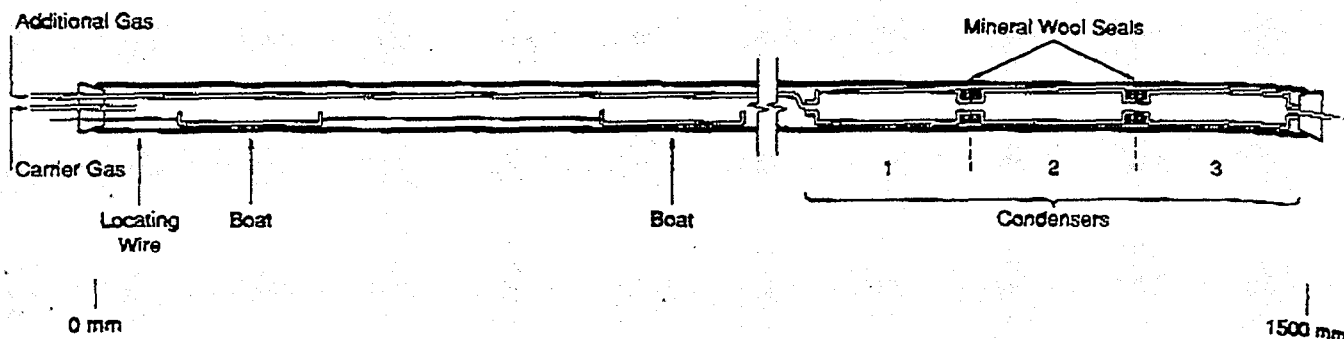


Fig. 7—Diagram of furnace assembly used for the selective condensation experiments.

material that adhered strongly to the walls of the condenser. The XRD revealed that cubic Sb_2O_3 was dominant and orthorhombic Sb_2O_3 subdominant. A white smear of condensate was observed in condenser unit 3. In experiments B and H, antimony trioxide was vaporized and oxygen was injected into the vapor stream at the beginning of the condensation train. The oxygen reacted with the antimony trioxide vapor, and antimony tetroxide dropped out immediately after the point of injection; the majority formed as large, pale yellow flakes, about 5 mm in diameter, in the bottom of the condenser. The XRD analysis of the product revealed traces of $\beta\text{-Sb}_2\text{O}_4$, along with the dominant orthorhombic Sb_2O_3 .

In experiments under conditions E, F, and G, mixed vapors with inert carrier gas were allowed to condense along the reaction tube. The general condensation characteristics were the same in all the experiments. Initially, white condensate formed on the walls of the second condenser unit; this became progressively finer along the condenser train, dropping out as "snow" in the third unit. In the relatively arsenic-rich vapor generated in experiment E, the initial wall condensate appeared at 440 °C, whereas for the antimony-rich vapors generated in experiment F, the initial wall condensate appeared at 517 °C. The condensate that formed in the higher temperature range had a lower arsenic content compared with the condensate in the lower temperature range (12.3 wt pct for condensate B compared to 34.8 wt pct). Injection of argon into the condensation train (experiment G) had virtually no effect on condensation behavior; the initial condensate appeared at 500 °C and had an arsenic content of 15.6 wt pct.

Experiments C, D, and I involved reaction of a mixed vapor with oxygen and the subsequent condensation of the vapors along the condensation train. The results are summarized in Table XIV. Due to experimental difficulties, recovery of condensates was in the range of only 55 to 70 pct of the mass volatilized. The general condensation characteristics were the same in all the experiments: yellow Sb_2O_3 formed in the first condenser near the point of injection, coarse white condensate formed on the walls of the second condenser unit, and a progressively finer condensate formed in the third unit as snow. The Sb_2O_3 contained small amounts of arsenic, the lowest content being 0.23 wt pct As in experiment I. The recovery of antimony tetroxide, as a percentage of the total condensate recovered, varied greatly in the experiments. In experiment C1 only 0.5 wt pct of the

condensate was antimony tetroxide, compared to 43.5 wt pct in experiment D3. The amount of antimony present as Sb_2O_3 in the total antimony recovered as condensate also varied widely, from 2 to 75 pct. A slow XRD scan using $\alpha\text{-SiO}_2$ as an internal standard revealed that condensates from experiments D, F, G, and I possibly contained a single cubic solid-solution phase, but splits in the peaks of the samples made it difficult to be certain that there were not multiple solid-solution phases.

D. Discussion

Some important points to emerge from these experiments are as follows.

1. Without oxygen injection, the separation of antimony oxide from arsenic oxide was poor.
2. Oxygen reacted readily with antimony trioxide vapor to form antimony tetroxide.
3. Injection of oxygen into mixed antimony and arsenic oxide vapor resulted in a high degree of separation.
4. Significant amounts of the antimony oxide in the mixed vapor did not form antimony tetroxide, as predicted by the thermodynamic calculations, and it was recovered below 550 °C in its cubic trioxide form, possibly in solid solution with cubic arsenic trioxide.

Thermodynamic calculations predict that all the antimony in the vapor should form antimony tetroxide in oxidizing conditions, regardless of whether solid solutions form. It follows that these experiments were not at equilibrium and that kinetics of the gas-phase reactions limited the formation of antimony tetroxide. It appears that the kinetics of Reaction [1] is favorable, because antimony trioxide vapor was readily oxidized. Reactions [2] through [4] differ from Reaction [1] in that they involve the formation of two reaction products, a solid and gas, rather than a single solid product. It is possible that these reactions involve more complex interactions of the reacting molecules than Reaction [1] and that steric effects may be significant.

Hager and Li⁽⁷⁾ achieved greater separation of arsenic and antimony trioxide than was obtained in this study. This better separation may in part be because of the formation of orthorhombic antimony trioxide, as it is likely that arsenic trioxide does not dissolve as readily into this structure. In Hager and Li's experiments, the better separation of the oxides was accompanied by high recovery

Table XIII. Conditions Used for the Selective Condensation Experiments

Experiment*	Temperature of Samples (°C)		Gas Flow(s) (L/min at STP)			Condenser Range °C
	As ₂ O ₃	Sb ₂ O ₃	O ₂	N ₂	Ar	
A(1)	—	617 to 630	—	0.2	—	<646
B(1)	—	617 to 630	0.1	0.2	—	<646
C(1)	246 to 264	542 to 556	0.1	0.2	—	<565
D(4)	248 to 265	617 to 630	0.1	0.2	—	<646
E(1)	246 to 264	542 to 556	—	0.2	—	<565
F(5)	248 to 265	617 to 630	—	0.2	—	<646
G(1)	248 to 265	617 to 630	—	0.2	0.1	<646
H(1)	—	616 to 627	0.1	—	0.2	<637
I(2)	210 to 236	616 to 627	0.1	—	0.2	<637

*Numbers in parentheses indicate the number of experiments carried out at these conditions.

Table XIV. Results of Selected Selective Condensation Experiments

Experiment	Pct Overall Recovery*	Pct Recovery of Volatilized Sb**	Pct Sb ₂ O ₃ in Condensate	Pct Sb as Sb ₂ O ₃ in Sb Recovered	Wt Pct As in Sb ₂ O ₃ Recovered
C1	56	30	0.5	2.0	1.94
D1	64	47	30.2	64	0.62
D2	54	31	20.0	60	0.61
D3	70	61	43.5	75	0.38
I1	66	72	22.1	26	0.23

*Total mass of condensate recovered as a percentage of total mass loss of the sample boats.

**Calculated from mass and composition of condensate and mass loss of antimony boat.

antimony in the hot zone of the condenser; in some experiments, over 90 pct of the antimony in the system was recovered as a high-purity mix of antimony tetroxide and antimony trioxide. This compares with between 74.6 and 74.6 pct recover of antimony as moderate- to high-purity antimony tetroxide in the present investigation (Table XIV). Table XV shows the theoretical composition of vapors generated under the experimental conditions of this study and those of Hager and Li calculated using Gibbs free energy minimization. The experiments with the best separation of arsenic and antimony were experiment 1 from this study and experiment 4 from Hager

and Li. These have the highest theoretical antimony contents in the vapor, with Sb₂O₃ being the dominant species in both cases. The experiment from this study with the poorest separation was experiment C1, which had the lowest theoretical antimony content in the vapor, with the vapor species As₂Sb₂O₆ being the most plentiful. These observations indicate that separation of antimony oxide from mixed oxide vapor by the formation of solid antimony tetroxide with low arsenic content is favored by a high concentration of antimony in the mixed oxide vapor, the explanation being the unfavorable kinetics of oxidation of the mixed As-Sb vapor species.

Table XV. Theoretical Vapor Compositions for Selective Condensation Experiments Calculated by Gibbs Free Energy Minimization

Species	Volume percent					Hager and Li Experiment 3*	Hager and Li Experiment 4**
	Experiment C1	Experiment D1	Experiment D2	Experiment D3	Experiment I1		
Sb ₂ O ₃	8.15	22.2	17.4	27.8	40.0	28.0	66.2
As ₂ Sb ₂ O ₆	32.4	41.1	20.4	12.1	6.40	10.9	1.11
As ₂ Sb ₂ O ₆	38.8	28.1	35.1	29.0	21.4	28.3	7.86
AsSb ₂ O ₆	20.7	8.58	27.1	31.1	32.1	32.8	24.8
Initial	574	574	574	574	574	200	200
amounts							
(mol)	Sb ₂ O ₃ 2.22	5.48	4.66	5.94	3.66	1.21	5.48
Reaction	As ₂ O ₃ 5.17	6.29	6.74	5.48	2.11	1.04	1.1062
temperature (°C)	549	624	624	624	622	549	629

*Based on nitrogen saturated with As₂O₃ at 219 °C and then equilibrated with Sb₂O₃ at 549 °C.

**Based on nitrogen saturated with As₂O₃ at 220 °C and then equilibrated with Sb₂O₃ at 629 °C.

Table XVI. Theoretical Vapor Compositions for Selective Condensation Experiments Calculated by Gibbs Free Energy Minimization

Species	Volume percent						Hager and Li Experiment ^a	Hager and Li Experiment 4 ^{**}
	Experiment C1	Experiment D1	Experiment D2	Experiment D3	Experiment I1			
Sb ₂ O ₃	8.15	22.2	17.4	27.8	40.0	28.0	66.2	
As ₂ SbO ₅	32.4	41.1	20.4	12.1	6.40	10.9	1.11	
As ₂ Sb ₂ O ₅	38.8	28.1	35.1	29.0	21.4	28.3	7.86	
AsSb ₂ O ₅	20.7	8.58	27.1	31.1	32.1	32.8	24.8	
Initial amounts (mol)	N ₂ 574	574	574	574	574	200	200	
	Sb ₂ O ₃ 5.48	5.48	4.66	5.94	5.94	1.21	5.48	
	As ₂ O ₃ 6.29	6.29	6.74	5.48	5.48	1.04	1.10	
							62	
Reaction temperature (°C)	624	624	624	624	624	549	629	

^aBased on nitrogen saturated with As₂O₃ at 219 °C and then equilibrated with Sb₂O₃ at 549 °C.

^{**}Based on nitrogen saturated with As₂O₃ at 220 °C and then equilibrated with Sb₂O₃ at 629 °C.

V. CONCLUSIONS

The thermodynamic analysis of the As-Sb-O system indicated that if arsenic and antimony oxides are present as pure solid phases, there is no theoretical limitation to their separation either by selectively volatilizing the more volatile arsenic trioxide or by separating the oxides from the vapor state by selective condensation of the individual oxides in the appropriate temperature ranges. Formation of solid solutions between antimony trioxide and arsenic trioxide limits the removal of arsenic trioxide from antimony trioxide by selective volatilization. The selective volatilization experiments using nitrogen as a carrier gas failed to produce commercial-grade antimony trioxide. The lowest arsenic level achieved using an industrial fume containing 13.8 wt pct. As was 4.9 wt pct. As, and this was obtained after 6 hours at 535 °C. This represents 78 pct removal of arsenic, and it was accompanied by 32 pct loss of antimony. Formation of solid solutions between the two trioxides precludes separation of the oxides by selectively condensing the oxides from a mixed oxide vapor. In the selective condensation experiments without oxygen addition, arsenic and antimony trioxide were recovered as a white condensate which contained significant quantities of each element, over a wide range of temperatures (<517 °C). Thermodynamic calculations allowing for solid-solution formation predict this behavior. The process suggested by Hager and Li for separating the oxides in the vapor phase by injecting oxygen into a mixed oxide vapor is sound thermodynamically, and in the experiments carried out, antimony tetroxide with between 0.23 and 1.94 wt pct. As was recovered in the region immediately after the point of injection in the temperature range 420 °C to 646 °C. Recovery of low-arsenic-containing antimony tetroxide by the mechanism proposed by Hager and Li appears to be influenced by kinetic factors. In particular, formation of antimony tetroxide by the reaction of oxygen with an-

timony trioxide vapor species occurs readily, whereas the formation of the tetroxide by the reaction of oxygen with the mixed oxide vapor species appears not to occur as readily. This means that higher conversions to antimony tetroxide are more likely to be obtained using antimony oxide-rich vapors than arsenic-rich vapors.

ACKNOWLEDGMENT

The authors are grateful to the Australian Mineral Industries Research Association Limited for partial financial support for this work. Support for this work was also provided by the Australian Government Cooperative Research Centres Program through the G.K. Williams Cooperative Research Centre, a joint venture between the CSIRO Division of Mineral and Process Engineering and the Department of Chemical Engineering. The University of Melbourne.

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HEAT OF FORMATION OF INORGANIC OXIDES

The ΔH_f values are given in gram calories per mole. The a , b , and c values listed here make it possible for one to calculate the ΔF and ΔS values by use of the following equations:

$$\Delta F_f = \Delta H_f + 2.303aT \log T + b \times 10^{-3}T^2 + c \times 10^5T^3 - IT$$

$$\Delta S_f = -a - 2.303a \log T - 2b \times 10^{-3}T + c \times 10^5T^2 - I/T$$

Ref: Bulletin 542, U. S. Bureau of Mines, 1954.

Coefficients in Free-Energy Equations

Reaction and temperature range of validity	ΔH_f	2.303a	b	c	I
$2 \text{Ac}(c) + 3/2 \text{O}_2(g) = \text{Ac}_2\text{O}_3(c)$ (298.16°-1,000° K.)	-446,090	-16.12			+109.89
$2 \text{Al}(c) + 1/2 \text{O}_2(g) = \text{Al}_2\text{O}_3(g)$ (298.16°-931.7° K.)	-31,660	+14.97			-72.74
$2 \text{Al}(l) + 1/2 \text{O}_2(g) = \text{Al}_2\text{O}_3(g)$ (931.7°-2,000° K.)	-38,670	+10.36			-51.53
$\text{Al}(c) + 1/2 \text{O}_2(g) = \text{AlO}(g)$ (298.16°-931.7° K.)	+10,740	+5.76			-37.61
$\text{Al}(l) + 1/2 \text{O}_2(g) = \text{AlO}(g)$ (931.7°-2,000° K.)	+8,170	+5.76			-34.85
$2 \text{Al}(c) + 3/2 \text{O}_2(g) = \text{Al}_2\text{O}_3(\text{corundum})$ (298.16°-931.7° K.)	-404,080	-15.68	+2.18	+3.935	+123.64
$2 \text{Al}(l) + 3/2 \text{O}_2(g) = \text{Al}_2\text{O}_3(\text{corundum})$ (931.7°-2,000° K.)	-407,950	-6.19	-78	+3.935	+102.37
$2 \text{Am}(c) + 3/2 \text{O}_2(g) = \text{Am}_2\text{O}_3(c)$ (298.16°-1,000° K.)	-422,090	-16.12			+107.89
$\text{Am}(c) + \text{O}_2(g) = \text{AmO}_2(c)$ (298.16°-1,000° K.)	-240,600	-4.61			+55.91
$2 \text{Sb}(c) + 3/2 \text{O}_2(g) = \text{Sb}_2\text{O}_3(\text{cubic})$ (298.16°-842° K.)	-169,450	+6.12	-6.01	-30	+52.21
$2 \text{Sb}(c) + 3/2 \text{O}_2(g) = \text{Sb}_2\text{O}_3(\text{orthorhombic})$ (298.16°-903° K.)	-168,060	+6.12	-6.01	-30	+50.56
$2 \text{Sb}(l) + 3/2 \text{O}_2(g) = \text{Sb}_2\text{O}_3(\text{orthorhombic})$ (903°-928° K.)	-175,370	+15.29	-7.75	-30	+33.12
$2 \text{Sb}(l) + 3/2 \text{O}_2(g) = \text{Sb}_2\text{O}_3(l)$ (928°-1,698° K.)	-173,940	-32.84	+75	-30	+166.52
$2 \text{Sb}(l) + 3/2 \text{O}_2(g) = 1/2 \text{Sb}_2\text{O}_3(g)$ (1,698°-1,713° K.)	-132,760	+10.91	+75	-30	+96
$2 \text{Sb}(g) + 3/2 \text{O}_2(g) = 1/2 \text{Sb}_2\text{O}_3(g)$ (1,713°-2,000° K.)	-234,760	-74	+75	-30	+98.17
$2 \text{Sb}(c) + 2 \text{O}_2(g) = \text{Sb}_2\text{O}_5(c)$ (298.16°-903° K.)	-208,310	+6.31	-5.36	-40	+73.02
$2 \text{Sb}(l) + 2 \text{O}_2(g) = \text{Sb}_2\text{O}_5(c)$ (903°-1,500° K.)	-215,610	+15.47	-7.10	-40	+55.61
$2 \text{Sb}(c) + 13/2 \text{O}_2(g) = \text{Sb}_2\text{O}_{11}(c)$ (298.16°-903° K.)	-649,160	+38.46	-25.13	-1.30	+192.54
$2 \text{Sb}(c) + 13/2 \text{O}_2(g) = \text{Sb}_2\text{O}_{11}(c)$ (903°-1,500° K.)	-691,370	+14.13	-30.35	-1.30	+315.93
$2 \text{Sb}(c) + 5/2 \text{O}_2(g) = \text{Sb}_2\text{O}_5(c)$ (298.16°-903° K.)	-226,060	+37.12	-22.66	-50	+18.61
$2 \text{Sb}(l) + 5/2 \text{O}_2(g) = \text{Sb}_2\text{O}_5(c)$ (903°-1,500° K.)	-240,130	+29.01	-24.40	-50	+59.74
$2 \text{As}(c) + 3/2 \text{O}_2(g) = \text{As}_2\text{O}_3(\text{orthorhombic})$ (298.16°-542° K.)	-154,870	+29.54	-21.33	-30	-8.83
$2 \text{As}(c) + 3/2 \text{O}_2(g) = \text{As}_2\text{O}_3(\text{monoclinic})$ (298.16°-586° K.)	-150,760	+29.54	-21.33	-30	-16.95
$2 \text{As}(c) + 3/2 \text{O}_2(g) = \text{As}_2\text{O}_3(l)$ (542°-730.3° K.)	-156,260	-43.29	+2.97	-30	+180.95
$2 \text{As}(c) + 3/2 \text{O}_2(g) = 1/2 \text{As}_4\text{O}_{10}(g)$ (730.3°-883° K.)	-135,930	+46	+2.97	-30	+26.88
$1/2 \text{As}_4(g) + 3/2 \text{O}_2(g) = 1/2 \text{As}_4\text{O}_{10}(g)$ (883°-2,000° K.)	-154,450	-2.90	+75	-30	+59.71
$2 \text{As}(c) + 2 \text{O}_2(g) = \text{As}_2\text{O}_5(c)$ (298.16°-883° K.)	-173,690	+21.52	-13.42	-40	+34.38
$1/2 \text{As}_4(g) + 2 \text{O}_2(g) = \text{As}_2\text{O}_5(c)$ (883°-1,500° K.)	-192,210	+18.15	-15.64	-40	+67.22
$2 \text{As}(c) + 5/2 \text{O}_2(g) = \text{As}_2\text{O}_5(c)$ (298.16°-883° K.)	-217,080	+12.32	-4.65	-50	+80.50
$1/2 \text{As}_4(g) + 5/2 \text{O}_2(g) = \text{As}_2\text{O}_5(c)$ (883°-2,000° K.)	-235,600	+8.96	-6.87	-50	+113.33
$\text{Ba}(a) + 1/2 \text{O}_2(g) = \text{BaO}(c)$ (298.16°-648° K.)	-134,590	-7.60	+87	+42	+45.76
$\text{Ba}(b) + 1/2 \text{O}_2(g) = \text{BaO}(c)$ (648°-977° K.)	-134,140	-3.34	-56	+42	+34.01
$\text{Ba}(l) + 1/2 \text{O}_2(g) = \text{BaO}(c)$ (977°-1,911° K.)	-135,900	-2.19	-56	+42	+32.37
$\text{Ba}(g) + 1/2 \text{O}_2(g) = \text{BaO}(c)$ (1,911°-2,000° K.)	-176,400	-8.01	-0.56	+0.42	+72.66
$\text{Ba}(a) + \text{O}_2(g) = \text{BaO}_2(c)$ (298.16°-648° K.)	-154,830	-11.05	+87	+42	+74.48
$\text{Ba}(b) + \text{O}_2(g) = \text{BaO}_2(c)$ (648°-977° K.)	-154,380	-6.79	-56	+42	+62.73
$\text{Ba}(l) + \text{O}_2(g) = \text{BaO}_2(c)$ (977°-1,500° K.)	-156,140	-5.64	-56	+42	+61.09
$\text{Be}(c) + 1/2 \text{O}_2(g) = \text{BeO}(c)$ (298.16°-1,556° K.)	-144,220	-1.91	-46	+1.24	+30.64
$\text{Be}(l) + 1/2 \text{O}_2(g) = \text{BeO}(c)$ (1,556°-2,000° K.)	-144,300	+6.06	-1.75	+1.485	+7.25
$\text{Bi}(c) + 1/2 \text{O}_2(g) = \text{BiO}(c)$ (298.16°-544° K.)	-50,450	-4.61			+35.51
$\text{Bi}(l) + 1/2 \text{O}_2(g) = \text{BiO}(c)$ (544°-1,600° K.)	-52,920	-4.61			+40.05
$2 \text{Bi}(c) + 3/2 \text{O}_2(g) = \text{Bi}_2\text{O}_3(c)$ (298.16°-544° K.)	-139,000	-11.56	+2.15	-30	+96.52
$2 \text{Bi}(l) + 3/2 \text{O}_2(g) = \text{Bi}_2\text{O}_3(c)$ (544°-1,090° K.)	-142,270	+2.30	-3.25	-30	+67.65
$2 \text{Bi}(l) + 3/2 \text{O}_2(g) = \text{Bi}_2\text{O}_3(l)$ (1,090°-1,600° K.)	-147,350	-32.84	+75	-30	+174.59
$2 \text{B}(c) + 3/2 \text{O}_2(g) = \text{B}_2\text{O}_3(c)$ (298.16°-723° K.)	-304,690	+11.72	-7.53	+355	+34.25
$2 \text{B}(c) + 3/2 \text{O}_2(g) = \text{B}_2\text{O}_3(g)$ (298.16°-723° K.)	-298,670	+26.57	-15.90	-30	+10.40
$2 \text{B}(c) + 3/2 \text{O}_2(g) = \text{B}_2\text{O}_3(l)$ (723°-2,000° K.)	-308,100	-38.41	+5.15	-30	+173.24
$\text{Cd}(c) + 1/2 \text{O}_2(g) = \text{CdO}(c)$ (298.16°-594° K.)	-62,330	-2.05	+71	-10	+29.17
$\text{Cd}(l) + 1/2 \text{O}_2(g) = \text{CdO}(c)$ (594°-1,038° K.)	-63,240	+2.07	-76	-10	+20.14
$\text{Cd}(g) + 1/2 \text{O}_2(g) = \text{CdO}(c)$ (1,038°-2,000° K.)	-89,320	-2.83	-76	-10	+60.05
$\text{Ca}(a) + 1/2 \text{O}_2(g) = \text{CaO}(c)$ (298.16°-873° K.)	-151,850	-6.56	+1.46	+68	+43.93
$\text{Ca}(b) + 1/2 \text{O}_2(g) = \text{CaO}(c)$ (873°-1,124° K.)	-151,730	-4.14	+41	+68	+37.03
$\text{Ca}(l) + 1/2 \text{O}_2(g) = \text{CaO}(c)$ (1,124°-1,760° K.)	-153,480	-1.36	-29	+68	+31.49
$\text{Ca}(g) + 1/2 \text{O}_2(g) = \text{CaO}(c)$ (1,760°-2,000° K.)	-194,670	-7.18	-29	+68	+73.84
$\text{Ca}(a) + \text{O}_2(g) = \text{CaO}_2(c)$ (298.16°-500° K.)	-158,230	-12.32	+1.46	+68	+78.28
$\text{C}(\text{graphite}) + 1/2 \text{O}_2(g) = \text{CO}(g)$ (298.16°-2,000° K.)	-25,400	+2.05	+27	-1.095	-28.79