ANTIMONY AND ANTIMONY ALLOYS

1. Introduction

Antimony [7440-36-0], Sb, belongs to Group 15 (VA) of the Periodic Table which also includes the elements arsenic and bismuth. It is in the second long period of the table between tin and tellurium. Antimony, which may exhibit a valence of +5, +3, 0, or −3 (see ANTIMONY COMPOUNDS), is classified as a nonmetal or metalloid, although it has metallic characteristics in the trivalent state. There are two stable antimony isotopes that are both abundant and have masses of 121 (57.25%) and 123 (42.75%).

2. History and Occurrence

Antimony and the natural sulfide of antimony were known at least as early as 4000 BC. The sulfide was used as an eyebrow paint in early biblical times, and a vase found at Tello, Chaldea, was reported to be cast antimony. Copper articles covered with a thin coating of metallic antimony, found in Egypt and dating from the period 2500–2200 BC, indicate that the early Egyptians were using antimony. Pliny (50 AD) gave it the name *stibium*; Geber used the term *antimonium*; and as late as the time of Lavoisier both terms continued to be used for the sulfide. Early alchemists referred to antimony sulfide as the "wolf of metals" because it devours all metals except gold. *Triumph Wagen des Antimonii*, written by Basil Valentine in the fifteenth century, is recognized as one of the first significant accounts of antimony and its chemistry. Both Agricola (1559) and Biringuccio (~1550) mention the liquation of antimony ores. The latter enumerates the following uses for antimony: as an alloy to increase the tone of bell metal; in the production of pewter and glass and metal mirrors; as medication for ulcers; and as yellow pigment for painting earthenware, and tinting enamels and glass. A scientific treatise on the element was written by Nicolas Lemery (1645–1715).

The crustal abundance of antimony (1) is ~0.2 g/t. Antimony ore bodies are small and scattered throughout the world. The word antimony (from the Greek *anti* plus *monos*) means "a metal not found alone" and, in fact, native antimony is seldom found in nature because of its high affinity for sulfur and metallic elements such as copper, lead, and silver. Over 100 naturally occurring minerals of antimony have been identified (2–4). Occasionally native metallic antimony is found; however, the most important source of the metal is the mineral stibnite [1317-86-8] (antimony trisulfide), Sb_2S_3. In areas where stibnite has been exposed to oxidation, it is converted to oxides of antimony. The important oxide minerals are stibiconite [12340-12-4] $Sb_2O_4{\cdot}H_2O$; cervantite, Sb_2O_4, or $Sb_2O_3{\cdot}Sb_2O_5$?; valentinite [1317-98-2], orthorhombic Sb_2O_3, and senarmontite [12412-52-1], cubic Sb_2O_3; kermesite [12196-98-0], 2 $Sb_2S_3{\cdot}Sb_2O_3$, an oxysulfide ore, is also of commercial importance.

World reserves of antimony (5) are estimated to be 2.1 million metric tons. Approximately 95% of the world's primary antimony was mined in China (85%),

Table 1. **World Mine Production, Reserves, and Reserve Base**[a,b]

Country	Mine production 2000	Mine production 2001[c]	Reserves	Reserve Base
United States	W	300	80,000	90,000
Bolivia	2,800	3,000	310,000	320,000
China	100,000	95,000	900,000	1,900,000
Kyrgyzstan	200	200	120,000	150,000
Russia	5,000	3,000	350,000	370,000
South Africa	5,000	5,000	240,000	250,000
Tajikistan	2,000	2,000	50,000	60,000
other countries	3,000	6,000	25,000	75,000
World total (may be rounded)	*118,000*	*115,000*	*2,100,000*	*3,200,000*

[a] Ref. 6.

[b] Data in metric tons.

[c] Estimated.

Bolivia 12%, Russia (4%), and the Republic of South Africa (4%), China has the world's largest reserves. See Table 1 for world mine production, reserves, and reserve base for 2000–2001. Most of the antimony produced in the United States is from the complex antimony deposits found in Idaho, Nevada, Alaska, and Montana. These deposits consist of stibnite and other sulfide minerals containing base metals and silver or gold. Ores of the complex deposits are mined primarily for lead, copper, zinc, or precious metals; antimony is a by-product of the treatment of these ores.

3. Properties

Physical properties of antimony are given in Table 2. Antimony, a silvery white, brittle, crystalline solid, is a poor conductor of electricity and heat. Two unstable allotropes, a black and a yellow modification, have been observed (7). The black modification is amorphous and forms on rapid quenching of antimony vapor. The yellow modification, covalent and similar to yellow arsenic (8,9), is formed by the low (−90°C) temperature oxidation of stibine using oxygen or chlorine. Explosive antimony, sometimes referred to as a third modification, can be produced from the electrolysis of antimony chloride, iodide, or bromide under special conditions, and is believed to be in a strained amorphous state. When scratched or bent, it explodes mildly, giving the crystalline form. Sudden heating of the electrodeposit to about 125°C produces an explosion; however, gradual heating leads safely to the crystalline form. Some electrodeposits drying at room temperature have been observed to ignite and burn, though incompletely, to form the oxide. On solidification, pure antimony contracts 0.79 ± 0.14 vol% (10).

Antimony is ordinarily quite stable and not readily attacked by air or moisture. It burns emitting a bluish light when heated to redness in air. Under controlled conditions antimony reacts with oxygen to form the oxides Sb_2O_3, Sb_2O_4,

Table 2. **Physical Properties of Antimony**

Property	Value
CAS Registry Number	
Sb	[7440-36-0]
^{121}Sb	[14265-72-6]
^{123}Sb	[14119-16-5]
at wt	121.75
mp, °C	630.8
bp, °C	1753
density at 25°C, kg/m^3	6684
crystal system	hexagonal (rhombohedral)
lattice constant, nm	
a	0.4307
c	1.1273
hardness, Mohs′ scale	3.0–3.5
latent heat of fusion, J/mol[a]	19,874
latent heat of vaporization, J/mol[a]	195,250
coefficient of linear expansion at 20°C, μm/(m·°C)	8–11
electrical resistivity at 0°C, μΩ·cm	39
magnetic susceptibility at 20°C, cgs	-99.0×10^{-6}
specific heat at 25°C, J/(mol·K)^1	25.2
thermal conductivity at 0°C, W/(m·K)	25.5
capture cross-section for thermal neutrons, at 2200 m/s, 10^{-28} m^2/atom	
121.75 (at wt)	5.40 ± 0.60
121 (isotope)	6.25 ± 0.20
123 (isotope)	4.28 ± 0.16

[a] To convert J to cal, divide by 4.184

and Sb_2O_5, Antimony tetroxide [1332-81-6] may be considered a stoichiometric compound of composition $Sb_2O_3{\cdot}Sb_2O_5$, or antimony(III) antimonate(V).

Certain conditions of pH, oxidation potential, and temperature promote the corrosion or dissolution of antimony in aqueous systems (11). In nonoxidizing, ie, unaerated solutions, antimony is stable and does not dissolve over a wide pH range. As more air, or oxidizing agent, is allowed into the solution, however, antimony begins to oxidize to the tri- and pentavalent states. In the trivalent state, antimony exists in the form SbO^+, oxoantimony [22877-95-8], or Sb_2O_3, antimony(III) oxide [1309-64-4], which dissolves in solution as antimonious acid, $HSbO_2$, and antimonite [27264-01-3], SbO_2^-. The pH of the oxidized solution determines which complex is predominant. Stronger oxidants such as nitric acid, mercury oxide, sodium peroxide, or hydrogen peroxide, oxidize antimony to its pentavalent state. Under these conditions, the species SbO_2^+, antimony(V) oxide [1314-60-9], Sb_2O_5, and SbO_3^-, antimonate [15600-59-6] exist.

Nitric acid oxidizes antimony forming a gelantinous precipitate of a hydrated antimony pentoxide (9). With sulfuric acid an indefinite compound of low solubility, probably an oxysulfate, is formed. Hydrofluoric acid forms fluorides or fluocomplexes with many insoluble antimony compounds. Hydrochloric acid in the absence of air does not readily react with antimony. Antimony also forms complex ions with organic acids.

Antimony reacts vigorously with chlorine to form tri- and pentachlorides. It combines with sulfur in all proportions and forms the compounds antimony red [1345-04-6], Sb_2S_3, and golden antimony [1315-04-4], Sb_2S_5. Antimony itself does not react directly with hydrogen. However, antimony hydride [7803-52-3] (stibine), SbH_3, which is extremely poisonous, may be formed by the reaction of metal antimonides, for example, zinc antimonide [12039-40-6], Zn_3Sb_2, and acid, the reduction of antimony compounds in hydrochloric acid with zinc, aluminum, or other reducing metals, and the electrolysis of acid or alkaline solutions using an antimony cathode (see ANTIMONY COMPOUNDS).

4. Process Metallurgy

The antimony content of commercial ores ranges from 5 to 60%, and determines the method of treatment, either pyrometallurgical or hydrometallurgical. In general, the lowest grades of sulfide ores, 5–25% antimony, are volatilized as oxides; 25–40% antimony ores are smelted in a blast furnace; and 45–60% antimony ores are liquated or treated by iron precipitation. The blast furnace is generally used for mixed sulfide and oxide ores, and for oxidized ores containing up to ~40% antimony; direct reduction is used for rich oxide ores. Some antimony ores are treated by leaching and electrowinning (4) to recover the antimony. The concentrates may be leached directly or converted into a complex matte first. The most successful processes use an alkali hydroxide or sulfide as the solvent for antimony (see METALLURY, SURVEY).

4.1. Oxide Volatilization.

Removal of antimony as the volatilized trioxide is the only pyrometallurgical method suitable for low grade ores. Combustion of the sulfide components of the ore supplies some of the heat; hence, fuel requirements are minor. There are many variations of the volatilization process, the principles employed being the same but the equipment differing. In all cases, the sulfur is burned away and removed from the waste gases, whereas the volatile antimony trioxide is recovered is flues, condensing pipes, a baghouse, Cottrell precipitator, or a combination of the above. Roasting and volatilization are effected almost simultaneously by heating the ore, mixed with coke or charcoal, under controlled conditions in equipment such as a shaft furnace, rotary kiln, converter, or roaster. If the volatilization conditions are too oxidizing, the nonvolatile antimony tetroxide may form and the recovery of antimony, as antimony trioxide, is diminished. Usually, the oxide produced in this manner is impure and can be reduced to metal. However, special attention to choice of charge, volatilization conditions, and selection of product results in a high grade oxide that is suitable for use in ceramics and other applications.

A process has been developed to recover antimony and arsenic from speiss and other materials (12). The speiss is roasted along with a source of solid sulfur and coal or coke at a temperature of 482–704°C for a sufficient time to volatilize arsenic and antimony oxides. The arsenic can then be separated from the antimony through careful control of the off-gas temperature and oxygen potential (13).

4.2. Liquation. Antimony sulfide is readily but inefficiently separated from the gangue of comparatively rich sulfide ore by heating the gangue to 550–600°C in perforated pots placed in a brick furnace. The molten sulfide is collected in lower containers. A more efficient method uses a reverberatory furnace and continuous liquation; however, a reducing atmosphere must be provided to prevent oxidation and loss by volatilization. The residue, containing 12–30% antimony, is usually treated by the volatilization process to recover additional antimony. The liquated product, called crude or needle antimony, is sold as such for applications requiring antimony sulfide, or is converted to metallic antimony by iron precipitation or careful roasting to the oxide followed by reduction in a reverberatory furnace.

4.3. Oxide Reduction. The oxides of antimony are reduced with charcoal in reverberatory furnaces. An alkaline flux consisting of soda, potash, and sodium sulfate, is commonly used to minimize volatilization and dissolve residual sulfides and gangue. Part of the slag is frequently reused. Loss of antimony from the charge by volatilization is high (12–20% or more), even with use of ample slag and careful control. This necessitates the use of effective Cottrell precipitators or baghouses, and considerable recycling of oxide.

4.4. Iron Precipitation. Rich sulfide ore or liquated antimony sulfide (crude antimony) is reduced to metal by iron precipitation. This process, consisting essentially of heating molten antimony sulfide in crucibles with slightly more than the theoretical amount of fine iron scrap, depends on the ability of iron to displace antimony from molten antimony sulfide. Sodium sulfate and carbon are added to produce sodium sulfide, or salt is added to form a light fusible matte with iron sulfide and to facilitate separation of the metal. Because the metal so formed contains considerable iron and some sulfur, a second fusion with some liquated antimony sulfide and salt follows for purification.

4.5. Blast Furnace Smelting. Intermediate (25–40%) grades of oxide or sulfide or mixed ores, liquation residues, mattes, rich slags, and briquetted fines or flue dusts are processed in water-jacketed blast furnaces. In general, the blast-furnace practice used for lead is followed, employing a high smelting column, comparatively low air pressure, and separation of slag and metal in a forehearth. Slag, usually running under 1% antimony, is desired because it tends to reduce volatilization losses.

4.6. Leaching Followed by Electrolysis. At the Sunshine Mining Co. (14, 15), a silver–copper–antimony concentrate containing 15–20% antimony is batch-leached in hot concentrated sodium sulfide, Na_2S, solution. Leaching is carried out in mild-steel tanks heated with steam coils and equipped with agitators. Four metric tons of sodium sulfide solution ($\sim$300 g/L) are charged with each metric ton of tetrahedrite [12054-35-2], $Cu_{12}S_{13}Sb_4$, concentrate. The material is leached for 14 at 100°C. At completion of the leach step, the slurry is pumped to a thickener. The clear solution containing sodium thioantimonate [13776-84-6], Na_3SbS_4, is decanted and sent to the electrowinning department. The silver and copper present in the tetrahedrite are not affected by the Na_2S leach and report to the thickener underflow. This residue is washed, filtered, and shipped to a smelter.

Electrolysis, also a batch operation, is conducted in cells each consisting of nine cathodes and eight anodes. The electrodes are fabricated from mild-steel.

The busbars carry a current of 1500 A resulting in a current density of 3 A/m^2 (28 A/ft^2). The voltage drop across each cell is typically 3 V. During electrolysis, the electrolyte can become fouled with sodium compounds including the polysulfides, thiosulfates, and sulfates that hinder the deposition of antimony on the cathode. To reduce the effect of these oxidation products, two separate electrolyte solutions, an anolyte and a catholyte, are used. The two solutions are kept separate by placing the anodes in steel baskets that have canvas sides. The canvas acts as a diaphragm that permits the flow of electric current but reduces the migration of harmful oxidation products to the catholyte. Fresh anolyte is made up of NaOH and barren electrolyte. Pregnant catholyte solution ($\sim$60 g/L Sb) is added to the electrolytic cells while withdrawing an equivalent volume of barren catholyte ($\sim$10 g/L Sb). The cathode metal obtained is 95% pure antimony.

The Bunker Hill Co. (16) and ASARCO, Inc. (17) have developed processes for the leaching and electrowinning of antimony from tetrahedrite ores. As of 1998, only Sunshine Mining Co. was electrowinning antimony metal.

The filtered sodium thioantimonate solution obtained from the leaching of stibnite with sodium sulfide may also be reduced directly to metal by elemental sodium (18). Yields in excess of 95% of 95.5 pure antimony are claimed (19).

4.7. By-Product and Secondary Antimony.

Antimony is often found associated with lead ores. The smelting and refining of these ores yield antimony-bearing flue, baghouse, and Cottrell dusts, drosses, and slags. These materials may be treated to recover elemental antimony or antimonial lead from which antimony oxide or sodium antimonate may be produced.

Recycling of antimony provides a large proportion of the domestic supply of antimony. Secondary antimony is obtained from the treatment of antimony-bearing lead and tin scrap such as battery plates, type metal, bearing metal, antimonial lead, etc. The scrap are charged into blast furnaces, reverberatory furnaces, or rotary furnaces, and an impure lead bullion or lead alloy is produced. Pure lead or antimony is then added to meet the specifications of the desired lead–antimony alloy.

4.8. Refining.

The metal produced by a simple pyrometallurgical reduction is normally not pure enough for a commercial product and must be refined. Impurities present are usually lead, arsenic, sulfur, iron, and copper. The iron and copper concentrations may be lowered by treating the metal with stibnite or a mixture of sodium sulfate and charcoal to form an iron-bearing matte that is skimmed from the surface of the molten metal. The metal is then treated with an oxidizing flux consisting of caustic soda or sodium carbonate and niter (sodium nitrate) to remove the arsenic and sulfur. Lead cannot be readily removed from antimony, but material high in lead may be used in the production of antimony-bearing, lead-based alloys. The yield of refined antimony from the matting and fluxing technique is 85–90%.

Impure metal may be refined by electrolysis (20), although this procedure is not as economical as the pyrometallurgical treatment. An electrolyte containing antimony fluoride and sulfuric acid gives the best result. Most of the anode impurities are lowered by electrolysis. However, if the concentrations of copper and arsenic are high in the anode they codeposit with the antimony and are present as significant impurities in the cathode metal. The arsenic and sulfur content of the cathode metal is further lowered by melting in an oxidizing flux. The purity of electrolytic antimony under favorable conditions exceeds 99.9%.

The purity of refined antimony, normally referred to as regulus, is usually judged by the appearance of a dendritic fern or starlike pattern on the surface of the metal. This product is produced by casting the antimony in molds into which a small amount of a starring slag has been poured; the antimony freezes while surrounded by the still molten slag. The starring flux has a melting point below that of antimony. An effective flux contains a 60–40 mixture of sodium sulfide and potassium carbonate, although other formulations can be used satisfactorily (2,21). Though this practice is generally accepted, it is quite unreliable in judging purity as highly contaminated antimony can also be starred by controlling the casting conditions and the flux composition.

4.9. Alternative Methods of Production. In general, metal chlorides are more easily volatilized than metal oxides because of the relatively high vapor pressures. The advantages of chlorine-based pyrometallurgical processes over conventional oxidizing processes are the efficient removal of impurities and cost effectiveness. Antimony has been successfully removed from concentrates containing copper, silver, and gold using a chloridizing roast (22).

Microbiological leaching of copper and uranium has been commercially developed and research has indicated that microorganisms may be used to oxidize complex antimony sulfide minerals (23,24). If this technology is developed commercially, it may allow for the exploitation of many low grade antimony deposits.

5. Economic Aspects

The United States is not self-sufficient in its requirements for antimony and is heavily dependent on imports of both ore and metal. See Table 3 for United States statistics for the period 1997–2001.

5.1. Production. In 2001, mine production in the United States accounted for only a small percentage of the annual domestic supply of antimony. An important component of the domestic supply is the recovery of antimony from old scrap; such as that recovered from the recycling of scrapped batteries (25). However, the percentage has decreased because of the increased use of low maintenance batteries, which use lead alloys containing less or no antimony; and the downsizing of automotive batteries that require less antimony per battery. Other factors that influence the supply of secondary antimony are the percentage of available batteries being recycled, the demand for batteries, and the prices of lead. The remainder of the U.S. supply of antimony is imported (6).

Producers of primary metal and oxide in the United States are Amspec Chemical Corp., Anzon ore., Laurel Industries Inc., Sunshine Mining Co., and U.S. Antimony Corp. (5).

5.2. Imports and Exports. The availability of economical foreign sources of antimony, mainly from China, Mexico, South Africa, Belgium, and Bolivia has resulted in an increase in the quantity of antimony imported for consumption. The U.S. imports of antimony ore and concentrates and antimony

Table 3. **Salient Statistics for Antimony, United States**[a,b]

	Year				
	1997	1998	1999	2000	2001[c]
production					
mine (recoverable antimony)[d]	356	498	450	340	300
smelter:					
primary	26,400	24,000	23,800	20,900	18,000
secondary	7,550	7,710	8,220	7,920	7,500
imports for consumption	39,300	34,600	36,800	37,600	39,000
exports of metal, alloys, oxide, and waste and scrap[e]	3,880	4,170	3,190	1,080	1,500
shipments from Government stockpile	2,930	4,160	5,790	4,536	4,500
consumption, apparent[f]	46,600	42,700	36,500	49,376	49,800
price, metal, average, cents per pound[g]	98	72	63	66	65
stocks, year end	10,800	10,600	10,900	10,300	10,300
employment, plant, number[c]	100	80	75	70	70
net import reliance[h] as a percentage of apparent consumption	83	81	82	84	86

[a] Ref. 6.
[b] Data in metric tons.
[c] Estimated
[d] Data for 1997–2000 from the U.S. Securities and Exchange Commission 10-K report
[e] Gross weight.
[f] Domestic mine production + secondary production from old scrap + net import reliance.
[g] New York dealer price for 99.5–99.6% metal, c.i.f. U.S. ports.
[h] Defined as imports–exports + adjustments for government and industry stock changes.

oxide by country are listed in Table 4 (1999–2000). Much of the antimony imported by the United States comes from China. Export information of metal, alloys, oxide, and waste and scraps for the years 1997–2001 is listed in Table 3. The U.S. government stockpile sales continued. The Defense Logistics Agency (DLA) planned for the disposal of 5000 tons during fiscal 2002 (6).

5.3. Industrial Consumption. Reported consumption of primary antimony in 2000 was 24% above that in 1999 (15). Flame retardants accounted for much of the increase. The estimated distribution of antimony uses (2001) was flame retardants, 55%, transportation (including batteries), 18%, chemicals, 10%, glass, 7%, and others, 10%. Reported industrial consumption of primary antimony in the United States for 1999–2000 is listed in Table 5.

5.4. Prices. The price of antimony continued to decline during the first one-half of 2001. Prices started the year at \$0.68–0.73/lb (\$0.30–0.33/kg). By mid-summer, the price slipped to \$0.58–62/lb (\$0.26–0.28/kg). Prices fell because of continued world oversupply, especially from growing exports from China (6).

6. Specifications

Antimony is available as cast cakes, ingots, broken pieces, granules, shot, and single crystals. ASTM has published standards for two grades of antimony ingots

Table 4. **U.S. Imports for Consumption of Antimony, by Class and Country**[a,b]

	1999			2000		
Country	Gross weight, metric tons	Antimony content[c] metric tons	Value, $ 10^3	Gross weight, metric tons	Antimony content[c] metric tons	Value, 10^3
Antimony ore and concentrate						
Australia	1,660	1,070	710	1,750	1,150	751
Austria	95	66	307	140	98	392
Bolivia				220	144	101
China	436	398	508	1,000	1,000	1,550
France				6	3	18
Hong Kong	59	53	52	62	60	65
Mexico	1,340	1,290	1,770	937	903	1,170
Russia				499	315	193
Thailand				20	16	12
Total	*3,590*	*2,870*	*3,350*	*4,630*	*3,690*	*4,250*
Antimony oxide						
Belgium	3,290	2,730	5890	3,690	3,070	6,560
Bolivia[d]	1,770	1,470	2,110	1,150	957	1,220
Chile[d]	275	229	328			
China	9,470	7,860	11,800	13,100	10,900	17,300
France	233	193	329	66	54	230
Germany	16	14	277	47	39	802
Guatemala	249	207	428	77	64	132
Hong Kong	420	349	523	453	376	622
Japan	127	105	700	33	27	274
Kyrgyzstan				224	186	247
Mexico	3,560	2,950	4,710	5,530	4,590	7,660
Netherlands	178	148	193			
South Africa	3,220	2,680	938	3,830	3,180	999
Taiwan				29	24	53
Thailand				60	50	11
United Kingdom	224	202	699	176	146	298
Total	*23,100*	*19,100*	*28,900*	*28,500*	*23,700*	*36,500*

[a] Ref. 5, Source U.S. Census Bureau.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

[c] Antimony ore and concentrate content reported by the U.S. Census Bureau. Antimony oxide content is calculated by the U.S. Geological Survey.

[d] Antimony oxide from these countries believed to "crude" and would probably be shipped to refineries for upgrading.

(26). Grade A has a minimum antimony content of 99.8% and the following impurity maximums: arsenic 0.05%; sulfur 0.10%; lead 0.15%; and others 0.05% each. Grade B material is composed of 99.5% antimony as a minimum with maximum impurity levels of arsenic 0.1%, sulfur 0.1%, lead 0.2%; and others 0.1% each. ASTM standards are also available for pewter, babbits, and solders (27).

Table 5. **Reported Industrial Consumption of Primary Antimony in the United States, by Product**[a,b]

Product	1999[c]	2000[c]
Metal products		
antimonial lead	1,110[d]	864
bearing metal and bearings	29[d]	42
solder	136[d]	136
other[e]	1,170[d]	1,660
Total	*2,440*	*2,700*
Nonmetal products		
ammunition primers	23	26
ceramics and glass	1,120	862
pigments	1,020	620
plastics	1,580	1,960
other[f]	198	647
Total	*3,940*	*4,110*
Flame retardants		
adhesives	140	332
plastics	6,370[d]	8,920
rubber	391	382
textiles	229	221
other[g]	14	70
Total	*7,140*[d]	*9,930*
Grand total	*13,500*[d]	*16,700*

[a] Ref. 5.

[b] In metric tons of antimony context.

[c] Data are rounded to no more than three significant digits; may not add to totals shown.

[d] Revised.

[e] Includes ammunition, cable covering, casting, sheet and pipe, and type metal.

[f] Includes fireworks and rubber products.

[g] Includes paper and pigments.

7. Environmental Concerns

Antimony is a common air pollutant that occurs at an average concentration of 0.001 $\mu g/m^3$ (28). Antimony is released into the environment from buring fossil fuels and from industry (29). In the air, antimony is rapidly attached to suspended particles and thought to stay in the air for 30–40 days (29). Antimony is found at low levels in some lakes, rivers, and streams, and may accumulate in sediments. Although antimony concentrations have been found in some freshwater and marine invertebrates, it does not biomagnify in the environment (29,30). The impact of antimony and antimony compouds on the environment has not been extensively studied to date.

Antimony may enter the human body through the consumption of meats, vegetables, and seafood which all contain ~0.2–1.1 ppb antimony.

8. Recycling

The bulk of secondary antimony has been recovered as antimonial lead. Most of this material was generated and then consumed by the battery industry. Changing trends have resulted in lesser amounts produced (6).

Antimony and its compounds have been designated as priority pollutants by the EPA (31). As a result users, transporters, generators, and processors of antimony-containing material must comply with regulations of the Federal Resource Conservative and Recovery Act (RCRA).

9. Health and Safety Factors

Although metallic antimony may be handled freely without danger, it is recommended that direct skin contact with antimony and its alloys be avoided. Properly designed exhaust ventilation systems and/or approved respirators are required for operations that create dusts or fumes. As with other heavy metals, orderly housekeeping practice and good personal hygiene are necessary to prevent ingestion of (or exposure to) antimony.

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL), the NIOSH recommended exposure limit (REL), and the ACGIH threshold limit value-weighted average (TLV−TWA) for antimony and its compounds 0.5 mg/m^3. The ACGIH has listed antimony trioxide as a suspected source of human carcinogenicity with an A2 designation (32).

Antimony is not known to cause cancer, birth defects, or affect reproduction in humans. However, antimony has been shown to cause lung cancer in laboratory animals that inhaled antimony-containing dusts and prolonged exposure to antimony can cause irritation of the eyes, skin, lungs, and stomach, in the form of vomiting and diarrhea. Heart problems can also result from overexposure to antimony (33).

Stibine (SbH_3), a highly toxic gas, can form when nascent hydrogen is present with antimony metal. OSHA and the ACGIH, have recommended a permissable exposure limit for employees exposed to stibine of 0.1 ppm as a time weighted average. Adequate safeguards against overexposure to this gas are advised when handling antimony and its alloys.

10. Uses

Antimony in the unalloyed state is extremely brittle and is not easily fabricated. For this reason, the use of the pure metal is restricted to ornamental applications.

10.1. Antimony Alloys. Approximately one-half of the total antimony demand is for metal used in antimony alloys. Antimonial lead is a term used to describe lead alloys containing antimony in proportions of up to 25%. Most commercial lead−antimony alloys have antimony contents <11%. The compositions of several important antimony alloys are given in Table 6.

Table 6. **Compositional Ranges of Antimony Alloys**

	Composition, wt %			
Material	Sb	Sn	Pb	Others
type metal	2–25	2–15	balance	Cu(0–2)
battery grids				
conventional	2.5–6	0.25–1	balance	
low maintenance	1.5–2.5	0.25–1	balance	
maintenance-free	0	0.25–1	balance	Ca(0.04–0.075)
babbitt metal				
tin base	4–8.5	83–90	balance	Cu(3–8.5); As(0.1)
lead base	9–17.5	0.5–11	balance	Cu(0.5); As(0.25–1.5)
cable covering	1–6	0.25–1	balance	
sheet and pipe	4–15	0.25–1	balance	
collapsible tubes	2–3	0.25–1	balance	
solder	0–6	1–100	balance	Ag(0–6); Cu(0.1–5)
pewter	1–8	balance	0–0.05	Cu(0–3)
britannia metal	2–10	balance	0–9	Cu(0.2–5); Zn(0–5)
bullets, shrapnel	0.5–12	0.25–1.0	balance	

The largest application for antimonial lead is its use as a grid metal alloy in the lead acid storage battery (see BATTERIES, SECONDARY, LEAD–ACID). In the manufacture of grid metal, antimony imparts fluidity, increased creep resistance, and fatigure strength, as well as electrochemical stability to the lead that is particularly advantageous for battery plates required in heavy-duty cycling. A disadvantage of using antimony in grid alloy is that high antimony levels increase the self-discharge characteristics, cause high gassing, and poisoning of the negative electrode resulting from ion migration. The release of gases means that the battery must be vented, which then promotes the loss of electrolyte through evaporation.

Demand for high performance SLI batteries has led to the development of smaller, lighter batteries that require less maintenance. The level of antimony is being decreased from the conventional 3–5% to 1.75–2.75% to minimize the detrimental effects. Lead alloys that contain no antimony have also been introduced. Hybrid batteries use a low antimony–lead alloy in the positive plate and a calcium–lead alloy in the negative plate.

Tin–antimony–copper and lead–antimony–tin white bearing alloys, commonly referred to as babbitt, are used to reduce friction and wear in machinery and help prevent failure by seizure or fatigue. These alloys exhibit good rubbing characteristics even under extreme operating conditions such as high loads, fatigue, or high temperatures. Tin babbits have greater corrosion resistance than lead babbitts. However, lead babbitts are generally cheaper than tin babbitts. Addition of antimony to babbitts increases strength and hardness. The choice of babbitt depends on the application and resultant desired properties. The use of antimony in babbits has been declining because technological advances have reduced the thickness of babbitt on backing material, and there is competition from aluminum–tin alloys and nonmetallic substitutes.

Soldering is a method of joining two metallic surfaces by flowing between them a low melting point alloy. Many different alloys are used for this purpose; however, tin–lead alloys are the most widely used. Other metals are added in small amounts, depending on the desired properties. antimony is added to increase the hardness of tin–lead alloys. Rising concern over the contamination of drinking water by lead has resulted in the use of lead-free alloys for soldering copper pipes. A similar trend is occurring in the canning industry. The demand for antimony in solders used in the electronic, semiconductor, and automobile industries is still strong (see SOLDERS AND BRAZING ALLOYS).

Type metal, another tin–antimony–lead alloy, is used primarily in relief or letterpress printing. Antimony is added to increase hardness, minimize shrinkage, permit sharp definition, and reduce the melting point of the alloy. There has been a substantial decrease in the use of type metals as a result of the emergence of less expensive typesetting techniques.

Antimony hardens the lead used in the manufacture of small arms ammunition. Antimony alloyed with lead is also used in cable covering, sheet and pipe, and collapsible tubes. In these applications, antimony is utilized to increase strength and inhibit corrosion.

Precision duplication, durability, and metallic beauty have made antimonial alloys, such as pewter and britannia metal, desirable for decorative castings. Several different tin- and lead-base antimony alloys are used in the jewelry industry. These alloys are typically cast in rubber or silicone molds.

Antimony may be added to copper-base alloys such as naval brass, Admiralty Metal, and leaded Muntz metal in amounts of 0.02–0.10% to prevent dezincification. Additions of antimony to ductile iron in an amount of 50 ppm, preferably with some cerium, can make the graphite fully nodular to the center of thick castings and when added to gray cast iorn in the amount of 0.05%, antimony acts as a powerful carbide stabilizer with an improvement in both the wear resistance and thermal cycling properties (34) (see CARBIDES).

Carbon (qv) impregnated with antimony gives a dense nonporous material with a low tendency to seizure or galling that may be useful in bearings and seals under high loads and velocities at temperatures up to 500°C (35).

10.2. Semiconductor and Solar Cells. High purity (up to 99.9%) antimony has a limited but important application in the manufacture of semiconductor devices. It may be obtained by reduction of a chemically purified antimony compound with a high purity gaseous or solid reductant, or by thermal decomposition of stibine. The reduced metal may be further purified by pyrometallurgical and zone melting techniques. When alloyed with Group 13 (IIIA) elements, the Group 15 (V) semiconductors, aluminum antimonide [25152-52-7], AlSb, gallium antimonide [12064-03-8], GaSb, and indium antimonide [1312-41-0], InSb, are formed. These intermetallic semiconductor materials exhibit optoelectronic behavior, ie, they emit or absorb electromagnetic radiation, and are utilized in such applications as infrared in devices, diodes, and Hall-effect components. High efficiency solar cells have been produced that are comprised of two layers: one of gallium arsenide and the other of gallium antimonide (see SOLAR ENERGY).

Antimony is also used as a dopant in *n*-type semiconductors. It is a common additive in dopants for silicon crystals with impurities, to alter the electrical conductivity. Interesting semiconductor properties have been reported for cadmium antimonide [12050-27-0], CdSb, and zinc antimonide [12039-35-9], ZnSb. The latter has good thermoelectric properties. Antimony with a purity as low as 99.9 + % is an important alloying ingredient in the bismuth telluride [1304-82-1], Bi_2Te_3, class of alloys, which are used for thermoelectric cooling.

In the computer industry, read/write optical discs, capable of storing over 250 megabytes, utilize a thin coating consisting of a germanium, tellurium, and antimony compound (see IMAGING TECHNOLOGY).

10.3. Antimony Compounds. The greatest use of antimony compounds is in flame retardants (qv) for plastics, paints, textiles, and rubber. Antimony compounds used in flame retardants are antimony pentoxide, sodium antimonate [15593-75-6], $Na[Sb(OH)_6]$, and, most importantly, antimony trioxide. These compounds, when used alone, are poor flame retardants; however, when combined with halogen compounds, they produce mixtures that are effective.

Antimony trioxide and sodium antimonate are added to specialty glasses as decolorizing and fining agents, and are used as opacifiers in porcelain enamels. Antimony oxides are used as white pigments in paints, whereas antimony trisulfide and pentasulfide yield black, vermillion, yellow, and orange pigments. Camoulflage paints contain antimony trisulfide, which reflects infrared radiation. In the production of red rubber, antimony pentasulfide is used as a vulcanizing agent. Antimony compounds are also used in catalysts, pesticides, ammunition, and medicines (see ANTIMONY COMPOUNDS).

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