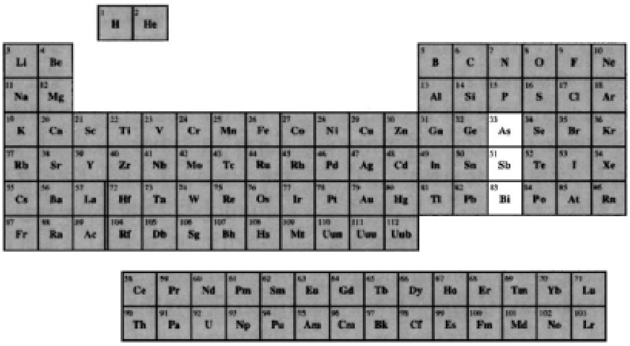

13

Arsenic, Antimony and Bismuth

13.1 Introduction

The three elements arsenic, antimony and bismuth, which complete Group 15 of the periodic table, were amongst the earliest elements to be isolated and all were known before either nitrogen (1772) or phosphorus (1669) had been obtained as the free elements. The properties of arsenic sulfide and related compounds have been known to physicians and professional poisoners since the fifth century BC though their use is no longer recommended by either group of practitioners. Isolation of the element is sometimes credited to Albertus Magnus (AD 1193–1280) who heated orpiment (As_2S_3) with soap, and its name reflects its ancient lineage. [Arsenic, Latin *arsenicum* from Greek ἀρσενικόν (*arsenicon*) which was itself derived (with addition of ὄν) from Persian *az-zarnīkh*, yellow orpiment (*zar* = gold).] Antimony compounds were also known to the ancients and the black sulfide, stibnite, was used in early biblical times as a cosmetic to darken and beautify women's eyebrows; a rare Chaldean vase of cast antimony dates from 4000 BC and antimony-coated copper articles were used in Egypt 2500–2200 BC. Pliny (~AD 50) gave it the name *stibium* and writings attributed to Jabir (~AD 800) used the form *antimonium*; indeed, both names were used for both the element and its sulfide until the end of the eighteenth century (Lavoisier). The history of the element, like that of arsenic, is much obscured by the intentionally vague and misleading descriptions of the alchemists, though the elusive Benedictine monk Basil Valentine may have prepared it in 1492 (about the time of Columbus). N. Lémery published his famous *Treatise on Antimony* in 1707. Bismuth was known as the metal at least by 1480 though its previous history in the Middle Ages is difficult to unravel because the element was sometimes confused with Pb, Sn, Sb or even Ag. The Gutenberg printing presses (1440 onwards) used type that had been cut from brass or cast from Pb, Sn or Cu, but about 1450 a secret method of casting type from Bi alloys came into use and this particular use is still an important application of the element (p. 549). The name derives from the German *Wismut* (possibly white metal or meadow mines) and this was latinized to *bisemutum* by the sixteenth-century German scientist G. Bauer (Agricola) about 1530. Despite the difficulty of assigning precise dates to discoveries made by alchemists, miners and metal workers (or indeed even discerning what those discoveries actually were), it seems clear that As, Sb and Bi became increasingly recognized in their free form during the thirteenth to fifteenth centuries; they are therefore contemporary with Zn and Co, and predate all other elements except the 7 metals and 2 non-metallic elements known from ancient times (Au, Ag, Cu, Fe, Hg, Pb, Sn; C and S).(1)

Arsenic and antimony are classed as metalloids or semi-metals and bismuth is a typical B subgroup (post-transition-element) metal like tin and lead.

13.2 The Elements

13.2.1 Abundance, distribution and extraction

None of the three elements is particularly abundant in the earth's crust though several minerals contain them as major constituents. As can be seen from Table 13.1, arsenic occurs about halfway down the elements in order of abundance, grouped with several others near 2 ppm. Antimony has only one-tenth of this abundance and Bi, down by a further factor of 20 or more, is about as unabundant as several of the commoner platinum metals and gold. In common with all the post-transition-element metals, As, Sb and Bi are chalcophiles, i.e. they occur in association with the chalcogens S, Se and Te rather than as oxides and silicates.

Arsenic minerals are widely distributed throughout the world and small amounts of the free element have also been found. Common minerals include the two sulfides realgar (As_4S_4) and orpiment (As_2S_3) and the oxidized form arsenolite (As_2O_3). The arsenides of Fe, Co and Ni and the mixed sulfides with these metals form another set of minerals, e.g. loellingite ($FeAs_2$), safforlite (CoAs), niccolite (NiAs), rammelsbergite ($NiAs_2$), arsenopyrite (FeAsS), cobaltite (CoAsS), enargite (Cu_3AsS_4), gersdorffite (NiAsS) and the quaternary sulfide glaucodot [(Co,Fe)AsS]. Elemental As is obtained on an industrial scale by smelting $FeAs_2$ or FeAsS at 650–700°C in the absence of air and condensing the sublimed element: $FeAsS \longrightarrow FeS + As(g) \longrightarrow As(s)$. Residual As trapped in the sulfide residues can be released by roasting them in air and trapping the sublimed As_2O_3 in the flue system. The oxide can then either be used directly for chemical products or reduced with charcoal at 700–800° to give more As. As_2O_3 is also obtained in large quantities as flue dust from the smelting of Cu and Pb concentrates; because of the huge scale of these operations (pp. 1174, 371) this represents the most important industrial source of As. Some production figures and major uses of As and its compounds are listed in the Panel.

Stibnite, Sb_2S_3, is the most important ore of antimony and it occurs in large quantities in China, South Africa, Mexico, Bolivia and Chile. Other sulfide ores include ullmanite (NiSbS), livingstonite ($HgSb_4S_8$), tetrahedrite (Cu_3SbS_3), wolfsbergite ($CuSbS_2$) and jamesonite ($FePb_4Sb_6S_{14}$). Indeed, complex ores containing Pb, Cu, Ag and Hg are an important industrial source of Sb. Small amounts of oxide minerals formed by weathering are also known, e.g. valentinite (Sb_2O_3), cervantite (Sb_2O_4), and stibiconite ($Sb_2O_4.H_2O$), and minor finds of native Sb have occasionally been reported. Commercial ores have 5–60% Sb, and recovery methods depend on the

Table 13.1 Abundances of elements in crustal rocks (g $tonne^{-1}$)

Element	Sn	Eu	Be	**As**	Ta	Ge	In	**Sb**	Cd	Pd	Pt	**Bi**	Os	Au
PPM	2.1	2.1	2.0	**1.8**	1.7	1.5	0.24	**0.2**	0.16	0.015	0.01	**0.008**	0.005	0.004
Order	48 =	48 =	50	**51**	52	53	61	**62**	63	67	68	**69**	70	71

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[1] M. E. WEEKS, *Discovery of the Elements*, Chap. 3, pp. 91–119, Journal of Chemical Education, Easton, Pa, 1956.

Production and Uses of Arsenic, Antimony and Bismuth(2)

Until the late 1980s the USA was the principal supplier of "white arsenic" (i.e. As_2O_3) but it now relies entirely on imports. World production has been steady for many years at about 52 000 tonnes pa and the main producers are France (10 000 tpa), Sweden (10 000 tpa), Russia (8 000 tpa) and Chile (7 000 tpa). The price of refined oxide was about $480 per tonne in 1989 and commercial grade As metal (99%+) was about $2.20/kg in 1990. High purity As (99.99%+) was $45.00/kg and zone-refined semiconductor grade even more expensive.

The main use of elemental As is in alloys with Pb and to a lesser extent Cu. Addition of small concentrations of As improves the properties of Pb/Sb for storage batteries (see below), up to 0.75% improves the hardness and castability of type metal, and 0.5–2.0% improves the sphericity of Pb ammunition. Automotive body solder is Pb (92%), Sb (5.0%), Sn (2.5%) and As (0.5%). Intermetallic compounds with Al, Ga and In give the III–V semiconductors (p. 255) of which GaAs and InAs are of particular value for light-emitting diodes (LEDs), tunnel diodes, infrared emitters, laser windows and Hall-effect devices (p. 258).

The use of As compounds as herbicides and pest controls in agriculture is now considerably restricted because of environmental considerations though arsenic acid itself, $AsO(OH)_3$, is still used in the formulation of wood preservatives. The oxide is widely used to decolorize glass.

World production capacity for antimony and its compounds (as contained Sb) was 116 000 tonnes in 1988, plus a similar amount of secondary (recycled) Sb obtained by smelting. However, actual production was somewhat below this. Typical prices (1988) were $3.50/kg for high-grade Sb_2O_3 and $2.30/kg for 99.5%+ Sb metal ($1.80/kg in 1990). Lead storage batteries use alloys containing 2.5–3% Sb and a trace of As, to minimize self-discharge, gassing and poisoning of the negative electrode. Other typical uses of Sb alloys in the USA, 1975 (tonnes of contained Sb), are shown in the Table.

Use	Sb/Pb batteries	Bearings	Ammunition	Solder	Type metal	Sheet pipe	Other metal	Non-metal products
Sb/tonnes	4143	365	216	121	68	55	144	6657
Percentage	35.2	3.5	1.8	1.0	0.6	0.5	1.2	56.5

As with arsenic, semiconductor grade Sb is prepared by chemical reduction of highly purified compounds. AlSb, GaSb and InSb have applications in infrared devices, diodes and Hall-effect devices. ZnSb has good thermoelectric properties. Applications of various *compounds* of Sb will be mentioned when the compounds themselves are discussed.

World annual production of bismuth and its compounds has hovered around 4000 tonnes of contained Bi for many years and a similar amount of secondary (refinery) Bi is also produced. Production has been dominated by China, Japan, Peru, Bolivia, Mexico, Canada, USA and Australia which, between them, account for almost of all supplies. Prices for the free element have fluctuated wildly since the 1970s, from <$4.00/kg to >$44.00/kg; at the end of 1990 it was $6.30/kg. Consumption of the metal and its compounds has also been unusual, usage in the USA dropping by a factor of 2 from 1973 to 1975, for example. The main uses are in pharmaceuticals, fusible alloys (including type metal, p. 547), and metallurgical additives.

No industrial poisoning by Bi metal has ever been reported but ingestion of compounds and inhalation of dust should be avoided.

grade. Low-grade sulfide ores (5–25% Sb) are volatilized as the oxide (any As_2O_3 being readily removed first by virtue of its greater volatility). The oxide can be reduced to the metal by heating it in a reverberatory furnace with charcoal in the presence of an alkali metal carbonate or sulfate as flux. Intermediate ores (25–40%) are smelted in a blast furnace and the oxide recovered from the flue system. Ores containing 40–60% Sb are liquated at 550–600° under reducing conditions to give Sb_2S_3 and then treated with scrap iron to remove the sulfide: $Sb_2S_3 + 3Fe \longrightarrow 2Sb + 3FeS$. Some complex sulfide ores are treated by leaching and electrowinning, e.g. the electrolysis of alkaline solutions of the thioantimonate Na_3SbS_4, and the element is also recovered from the flue dusts of Pb smelters. Impure Sb contains Pb, As, S, Fe and

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[2] *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 3, Wiley, New York, 1992; Arsenic and arsenic alloys (pp. 624–33); Arsenic compounds (633–59); Antimony and antimony alloys (367–81); Antimony compounds (382–412); Bismuth and bismuth alloys (Vol. 4, 1992 (pp. 237–45); Bismuth compounds (246–70).

Cu; the latter two can be removed by stibnite treatment or heating with charcoal/Na_2SO_4 flux; the As and S can be removed by an oxidizing flux of $NaNO_3$ and NaOH (or Na_2CO_3); Pb is hard to remove but this is unnecessary if the Sb is to be used in Pb alloys (see below). Electrolysis yields >99.9% purity and remaining impurities can be reduced to the ppm level by zone refining. The scale of production and the various uses of Sb and its compounds are summarized in the Panel.

Bismuth occurs mainly as bismite (α-Bi_2O_3), bismuthinite (Bi_2S_3) and bismutite [$(BiO)_2CO_3$]; very occasionally it occurs native, in association with Pb, Ag or Co ores. The main commercial source of the element is as a byproduct from Pb/Zn and Cu plants, from which it is obtained by special processes dependent on the nature of the main product.(2) Sulfide ores are roasted to the oxide and then reduced by iron or charcoal. Because of its low mp, very low solubility in Fe, and fairly high oxidative stability in air, Bi can be melted and cast (like Pb) in iron and steel vessels. Like Sb, the metal is too brittle to roll, draw, or extrude at room temperature, but above 225°C Bi can be worked quite well.

13.2.2 Atomic and physical properties

Arsenic and Bi (like P) each have only 1 stable isotope and this occurs with 100% abundance in all natural sources of the elements. Accordingly (p. 17) their atomic weights are known with great precision (Table 13.2). Antimony has 2 stable isotopes (like N); however, unlike N, which has 1 predominantly abundant isotope, the 2 isotopes of Sb are approximately equal in abundance (^{121}Sb 57.21%, ^{123}Sb 42.79%) and consequently (p. 17) the atomic weight is known with somewhat less accuracy. It is also noteworthy that ^{209}Bi is the heaviest stable isotope of any element; all nuclides beyond $^{209}_{83}$Bi are radioactive.

The ground-state electronic configuration of each element in the group is ns^2np^3 with an unpaired electron in each of the three p orbitals, and much of the chemistry of the group can be interpreted directly on this basis. However, smooth trends are sometimes modified (or even absent altogether), firstly, because of the lack of low-lying empty d orbitals in N, which differentiates it from its heavier congeners, and, secondly, because of the countervailing influence of the underlying filled d and f orbitals in As, Sb and Bi. Such perturbations are apparent when the various ionization energies in Table 13.2 are plotted as a function of atomic number. Table 13.2 also contains approximate data on the conventional covalent single-bond radii for threefold coordination though these values vary by about ±4 pm in various tabulations and should only be used as a rough guide. The 6-coordinate "effective ionic radii" for the +3 and +5

Table 13.2 Atomic properties of Group 15 elements

Property		N	P	As	Sb	Bi
Atomic number		7	15	33	51	83
Atomic weight (1997)		14.00674(7)	30.973762(4)	74.92160(2)	121.760(1)	208.98038(2)
Electronic configuration		$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10}4s^2 4p^3$	$[Kr]4d^{10}5s^2 5p^3$	$[Xe]4f^{14}5d^{10}$-$6s^2 6p^3$
Ionization energies/MJ mol^{-1}	(I)	1.402	1.012	0.947	0.834	0.703
	(II)	2.856	1.903	1.798	1.595	1.610
	(III)	4.577	2.910	2.736	2.443	2.466
Sum (I+II+III)/MJ mol^{-1}		8.835	5.825	5.481	4.872	4.779
Sum (IV+V)/MJ mol^{-1}		16.920	11.220	10.880	9.636	9.776
Electronegativity χ		3.0	2.1	2.0	1.9	1.9
r_{cov} (M^{III} single bond)/pm		70	110	120	140	150
r_{ionic} (6-coordinate) (M^{III})/pm		(16)	44	58	76	103
(6-coordinate) (M^{V})/pm		(13)	38	46	60	76

oxidation states are taken from R. D. Shannon's tabulation,$^{(3)}$ but should not be taken to imply the presence of M^{3+} and M^{5+} cations in many of the compounds of these elements.

Arsenic, Sb and Bi each exist in several allotropic forms$^{(4,5)}$ though the allotropy is not so extensive as in P (p. 481). There are three crystalline forms of As, of which the ordinary, grey, "metallic", rhombohedral, α-form is the most stable at room temperature. It consists of puckered sheets of covalently bonded As stacked in layers perpendicular to the hexagonal c-axis as shown in Fig. 13.1. Within each layer each As has 3 nearest neighbours at 251.7 pm and the angle As–As–As is 96.7°; each As also has a further 3 neighbours at 312 pm in an adjacent layer. The α-forms of Sb and Bi are isostructural with α-As and have the dimensions shown in Table 13.3. It can be seen that there is a progressive diminution in the difference between intra-layer and inter-layer distances though the inter-bond angles remain almost constant.

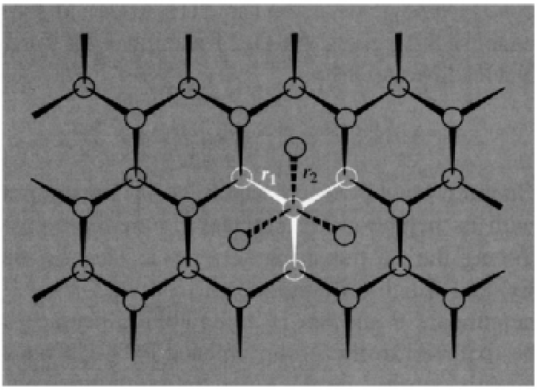

Figure 13.1 Puckered layer structure of As showing pyramidal coordination of each As to 3 neighbours at a distance r_1 (252 pm). The disposition of As atoms in the next layer (r_2 312 pm) is shown by dashed lines.

Table 13.3 Comparison of black P and α-rhombohedral As, Sb and Bi

	r_1/pm	r_2/pm	r_2/r_1	∠ M–M–M
Black P	223.1 (av)	332.4 (av)	1.490	2 at 96.3° (1 at 102.1°)
α-As	251.7	312.0	1.240	96.7°
α-Sb	290.8	335.5	1.153	96.6°
α-Bi	307.2	352.9	1.149	95.5°

In the vapour phase As is known to exist as tetrahedral As_4 molecules with (As–As 243.5 pm) and when the element is sublimed, a yellow, cubic modification is obtained which probably also contains As_4 units though the structure has not yet been determined because the crystals decompose in the X-ray beam. The mineral arsenolamprite is another polymorph, ε-As; it is possibly isostructural with "metallic" orthorhombic P.

Antimony exists in 5 forms in addition to the ordinary α-form which has been discussed above. The yellow form is unstable above −90°; a black form can be obtained by cooling gaseous Sb, and an explosive (impure?) form can be made electrolytically. The two remaining crystalline forms are made by high-pressure techniques: Form I has a primitive cubic lattice with a_0 296.6 pm: it is obtained from α-Sb at 50 kbar (5GPa, i.e. 5×10^9 N m^{-2}) by increasing the rhombohedral angle from 57.1° to 60.0° together with small shifts in atomic position so that each Sb has 6 equidistant neighbours. Further increase in pressure to 90 kbar yields Form II which is hcp with an interatomic distance of 328 pm for the 12 nearest neighbours.

Several polymorphs of Bi have been described but there is as yet no general agreement on their structures except for α-Bi (above) and ζ-Bi which forms at 90 kbar and has a bcc structure with 8 nearest neighbours at 329.1 pm.

The physical properties of the α-rhombohedral form of As, Sb and Bi are summarized in Table 13.4. Data for N_2 and P_4 are included for comparison. Crystalline As is rather volatile and the vapour pressure of the solid reaches 1 atm at 615° some 200° below its mp of 816°C (at 38.6 atm, i.e. 3.91 MPa). Antimony and Bi are

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[3] R. D. Shannon, *Acta Cryst.* **A32**, 751–67 (1976).

[4] J. Donohue, *The Structure of the Elements*, Wiley, 1974, 436 pp.

[5] H. G. von Schnering, *Angew. Chem. Int. Edn. Engl.* **20**, 33–51 (1981).

Table 13.4 Some physical properties of Group 15 elements

Property	N_2	P_4	α-As	α-Sb	α-Bi
MP/°C	−210.0	44.1	816 (38.6 atm)	630.7	271.4
BP/°C	−195.8	280.5	615 (subl)	1753	1564
Density (25°C)/g cm^{-3}	0.879 (−210°)	1.823	5.778[a]	6.684	9.808
Hardness (Mohs)	—	—	3.5	3–3.5	2.5
Electrical resistivity (20°C)/μohm cm	—	—	33.3	41.7	120
Contraction on freezing/%	—	—	10	0.8	−3.32

[a] Yellow As_4 has d_{25} 1.97 g cm^{-3}; cf. difference between the density of rhombohedral black P (3.56 g cm^{-3}) and white P_4 (1.823 g cm^{-3}) (p. 479).

much less volatile and also have appreciably lower mps than As, so that both have quite long liquid ranges at atmospheric pressure.

Arsenic forms brittle steel-grey crystals of metallic appearance. However, its lack of ductility and comparatively high electrical resistivity (33.3 μohm cm), coupled with its amphoterism and intermediate chemical nature between that of metals and non-metals, have led to its being classified as a metalloid rather than a "true" metal. Antimony is also very brittle and forms bluish-white, flaky, lustrous crystals of high electrical resistivity (41.7 μohm cm). These values of resistivity can be compared with those for "good" metals such as Ag (1.59), Cu (1.72), and Al (2.82 μohm cm), and with "poor" metals such as Sn (11.5) and Pb (22 μohm cm). Bismuth has a still higher resistivity (120 μohm cm) which even exceeds that of commercial resistors such as Nichrome alloy (100 μohm cm). Bismuth is a brittle, white, crystalline metal with a pinkish tinge. It is the most diamagnetic of all metals (mass susceptibility $17.0 \times 10^{-9}\, m^3\, kg^{-1}$ — to convert this SI value to cgs multiply by $10^3/4\pi$, i.e. $1.35 \times 10^{-6}\, cm^3\, g^{-1}$). It also has the highest Hall effect coefficient of any metal and is unusual in expanding on solidifying from the melt, a property which it holds uniquely with Ga and Ge among the elements.

13.2.3 Chemical reactivity and group trends

Arsenic is stable in dry air but the surface oxidizes in moist air to give a superficial golden bronze tarnish which deepens to a black surface coating on further exposure. When heated in air it sublimes and oxidizes to As_4O_6 with a garlic like odour (poisonous). Above 250–300° the reaction is accompanied by phosphorescence (cf. P_4, p. 473). When ignited in oxygen, As burns brilliantly to give As_4O_6 and As_4O_{10}. Metals give arsenides (p. 554), fluorine enflames to give AsF_5 (p. 561), and the other halogens yield AsX_3 (p. 559). Arsenic is not readily attacked by water, alkaline solutions or non-oxidizing acids, but dilute HNO_3 gives arsenious acid (H_3AsO_3), hot conc HNO_3 yields arsenic acid (H_3AsO_4), and hot conc H_2SO_4 gives As_4O_6. Reaction with fused NaOH liberates H_2:

$$As + 3NaOH \longrightarrow Na_3AsO_3 + \tfrac{3}{2}H_2$$

One important property which As has in common with its neighbouring elements immediately following the 3d transition series (i.e. Ge, As, Se, Br) and which differentiates it from its Group 15 neighbours P and Sb, is its notable reluctance to be oxidized to the group valence of +5. Consequently As_4O_{10} and H_3AsO_4 are oxidizing agents and arsenates are used for this purpose in titrimetric analysis (p. 577).

The ground-state electronic structure of As, as with all Group 15 elements features 3 unpaired electrons ns^2np^3; there is a substantial electron affinity for the acquisition of 1 electron but further additions must be effected against considerable coulombic repulsion, and the formation of As^{3-} is highly endothermic. Consistent with this there are no "ionic" compounds containing the arsenide ion and compounds such as Na_3As are intermetallic or alloy-like. However, despite the metalloidal character of the free element, the ionization energies and electronegativity of As are similar to those of P (Table 13.2) and the element readily forms strong covalent bonds to most non-metals. Thus AsX_3 ($X = H$, hal, R, Ar etc.) are covalent molecules like PX_3 and the tertiary arsines have been widely used as ligands to b-class transition elements (p. 909).(6) Similarly, As_4O_6 and As_4O_{10} resemble their P analogues in structure; the sulfides are also covalent heterocyclic molecules though their stoichiometry and structure differ from those of P.

Antimony is in many ways similar to As, but it is somewhat less reactive. It is stable to air and moisture at room temperature, oxidizes on being heated under controlled conditions to give Sb_2O_3, Sb_2O_4 or Sb_2O_5, reacts vigorously with Cl_2 and more sedately with Br_2 and I_2 to give SbX_3, and also combines with S on being heated. H_2 is without direct reaction and SbH_3 (p. 557) is both very poisonous and thermally very unstable. Dilute acids have no effect on Sb; concentrated oxidizing acids react readily, e.g. conc HNO_3 gives hydrated Sb_2O_5, aqua regia gives a solution of $SbCl_5$, and hot conc H_2SO_4 gives the salt $Sb_2(SO_4)_3$.

Bismuth continues the trend to electropositive behaviour and Bi_2O_3 is definitely basic, compared with the amphoteric oxides of Sb and As and the acidic oxides of P and N. There is also a growing tendency to form salts of oxoacids by reaction of either the metal or its oxide with the acid, e.g. $Bi_2(SO_4)_3$ and $Bi(NO_3)_3$. Direct reaction of Bi with O_2, S and X_2 at elevated temperatures yields Bi_2O_3, Bi_2S_3 and BiX_3 respectively, but the increasing size of the metal atom results in a steady decrease in the strength of covalent linkages in the sequence $P > As > Sb > Bi$. This is most noticeable in the instability of BiH_3 and of many organobismuth compounds (p. 599).

Most of the trends are qualitatively understandable in terms of the general atomic properties in Table 13.2 though they are not readily deducible from them in any quantitative sense. Again, the +5 oxidation state in Bi is less stable than in Sb for the reasons discussed on p. 226; not only is the sum of the 4th and 5th ionization energies for Bi greater than for Sb (9.78 vs. 9.63 MJ mol^{-1}) but the promotion energies of one of the ns^2 electrons to a vacant nd orbital is also greater for Bi (and As) than for Sb. The discussions on redox properties (p. 577) and the role of d orbitals (p. 222) are also relevant. Finally, Bi shows an interesting resemblance to La in the crystal structures of the chloride oxide, MOCl, and in the isomorphism of the sulfates and double nitrates; this undoubtedly stems from the very similar ionic radii of the 2 cations: Bi^{3+} 103, La^{3+} 103.2 pm.

All coordination numbers from 1–10 (and 12) are known for the sub-group, though 3, 4, 5 and 6 are by far the most frequently met. CN 1 is exemplified by $RC{\equiv}As$(7) ($R = 2,4,6\text{-Bu}^t{}_3C_6H_2$; cf $RC{\equiv}P$, p. 544) and by the isolated tetrahedral anions $SiAs_4{}^{8-}$ and $GeAs_4{}^{8-}$ (isoelectronic with $SiO_4{}^{4-}$ and $GeO_4{}^{4-}$) which occur in the lustrous dark metallic Zintl phases Ba_4MAs_4.(8) CN 2 (bent) is quite common in heterocyclic organic compounds (p. 592) and in cluster anions such as $As_7{}^{3-}$, $Sb_7{}^{3-}$ and $As_{11}{}^{3-}$ and their derivatives (p. 588). A rare example of linear 2-coordinate As was recently established in the bis(manganese) complex $[(\eta^5\text{-}C_5H_4Me)(CO)_2Mn{=}As{=}Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]^+$, isolated as its dark brown salt with $CF_3SO_3{}^-$: the angle at As was found to be 176.3° and the As–Mn distance was 215 pm.(9) Likewise, examples of pyramidal 3-coordinate As, Sb and Bi are endemic, but planar CN 3 is extremely rare; examples occur in

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[6] C. A. McAuliffe (ed.), *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*, Macmillan, London, 1973, 428 pp.

[7] G. Märkl and H. Sejpka, *Angew. Chem. Int. Edn. Engl.* **25**, 264 (1986).

[8] B. Eisenmann, H. Jordan and H. Schäfer, *Angew. Chem. Int. Edn. Engl.* **20**, 197–8 (1981).

[9] A. Strube, G. Huttner and L. Zsolnai, *Angew. Chem. Int. Edn. Engl.* **27**, 1529–30 (1988).

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