

Figure 13.12 Schematic representation of the structure of the complex anion $[\text{Sb}_4\text{Cl}_{12}\text{O}]^{2-}$ showing the two different coordination geometries about Sb and the unique quadruply bridging Cl atom.

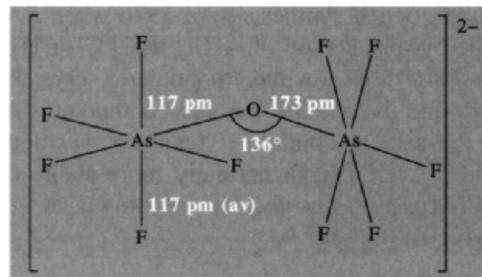


Figure 13.13 Schematic representation of the anion structure in $\text{M}_2[\text{As}_2\text{F}_{10}\text{O}]\cdot\text{H}_2\text{O}$.

contain the oxo-bridged binuclear anion $[\text{F}_5\text{As}-\text{OAsF}_5]^{2-}$ as shown in Fig. 13.13⁽⁷¹⁾ and the anhydrous salt $\text{Rb}_2[\text{Sb}_2\text{F}_{10}\text{O}]$ contains a similar anion with angle $\text{Sb}-\text{O}-\text{Sb}$ 133° , $\text{Sb}-\text{F}$ 188 pm, and $\text{Sb}-\text{O}$ 191 pm.⁽⁷²⁾ The compound of empirical formula CsSbF_4O is, in fact, trimeric with a 6-membered heterocyclic anion in the boat configuration, i.e. $\text{Cs}_3[\text{Sb}_3\text{F}_{12}\text{O}_3]$,⁽⁷³⁾ whereas the corresponding arsenic compound⁽⁷⁴⁾ has a dimeric

⁷¹ W. HAASE, *Acta Cryst.* **B30**, 1722-7 (1974).

⁷² W. HAASE, *Acta Cryst.* **B30**, 2508-10 (1974).

⁷³ W. HAASE, *Acta Cryst.* **B30**, 2465-9 (1974).

⁷⁴ W. HAASE, *Chem. Ber.* **107**, 1009-18 (1974).

anion $[\text{As}_2\text{F}_8\text{O}_2]^{2-}$ (Fig. 13.14). In both cases the Group 15 element is octahedrally coordinated by 4 F and 2 O atoms in the *cis*-configuration.

Bismuth oxide halides BiOX are readily formed as insoluble precipitates by the partial hydrolysis of the trihalides (e.g. by dilution of solutions in concentrated aqueous HX). BiOF and BiOI can also be made by heating the corresponding BiX_3 in air. BiOI , which itself decomposes above 300° , is brick-red in colour; the other 3 BiOX are white. All have complex layer-lattice structures.⁽³³⁾ When BiOCl or BiOBr are heated above 600° oxide halides of composition $\text{Bi}_{24}\text{O}_{31}\text{X}_{10}$ are formed, i.e. replacement of 5 O atoms by 10 X in $\text{Bi}_{24}\text{O}_{36}$, (Bi_2O_3).

13.3.4 Oxides and oxo compounds

The amphoteric nature of As_2O_3 and the trends in properties of several of the oxides and oxoacids

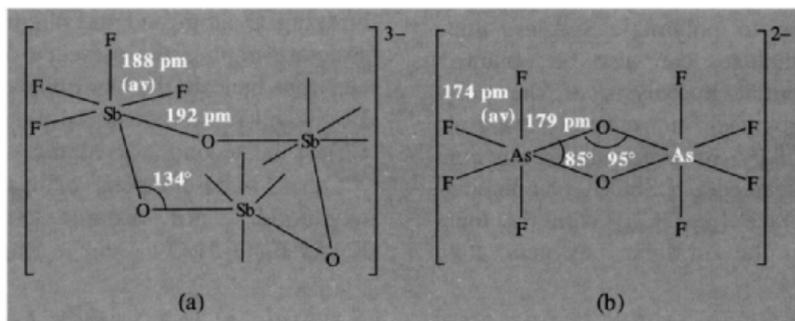


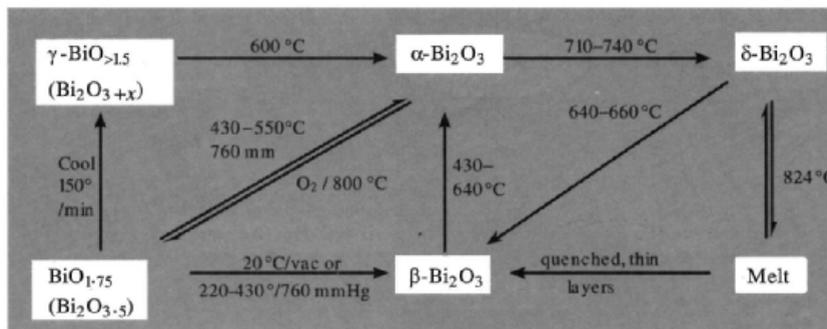
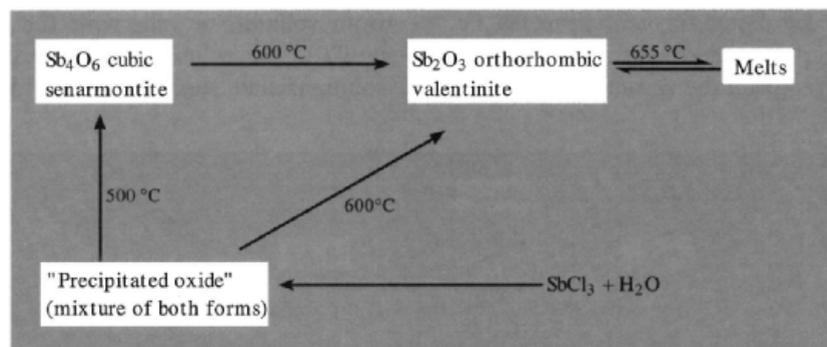
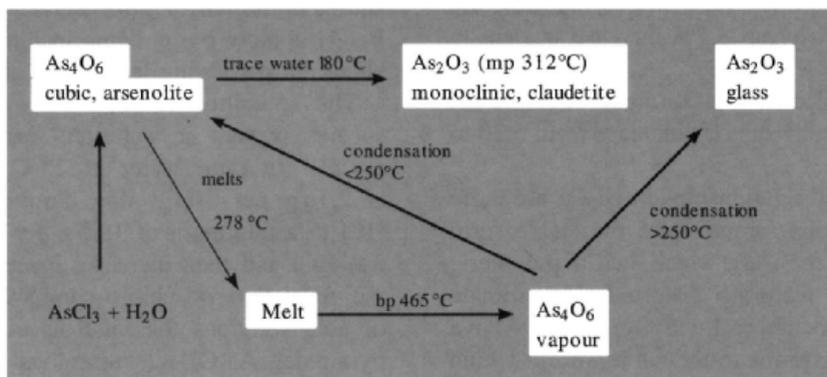
Figure 13.14 Schematic representation of the structure of (a) the trimeric anion $[\text{Sb}_3\text{F}_{12}\text{O}_3]^{3-}$, and (b) the dimeric anion $[\text{As}_2\text{F}_8\text{O}_2]^{2-}$.

of As, Sb and Bi have already been mentioned briefly on pp. 552–3. Because of the trend towards greater basicity in the sequence $\text{As} < \text{Sb} < \text{Bi}$ and the trend towards greater acidity in the sequence $\text{M}^{\text{III}} < \text{M}^{\text{V}}$, coupled with the difficulty of isolating some of the oxides from their “hydrated” forms, it is not convenient to have separate sections on oxides, hydrous oxides, hydroxides, acids, oxoacid salts, polyacid salts and mixed oxides. Accordingly, all these types of compound will be considered in the present

section; M^{III} compounds will be discussed first then intermediate $\text{M}^{\text{III}}/\text{M}^{\text{V}}$ systems and, finally, M^{V} oxo- compounds.

Oxo compounds of M^{III}

As_2O_3 (diarsenic trioxide) is the most important compound of As (Panel, p. 549). It is made (a) by burning As in air, (b) by hydrolysis of AsCl_3 or (c) industrially, by roasting sulfide



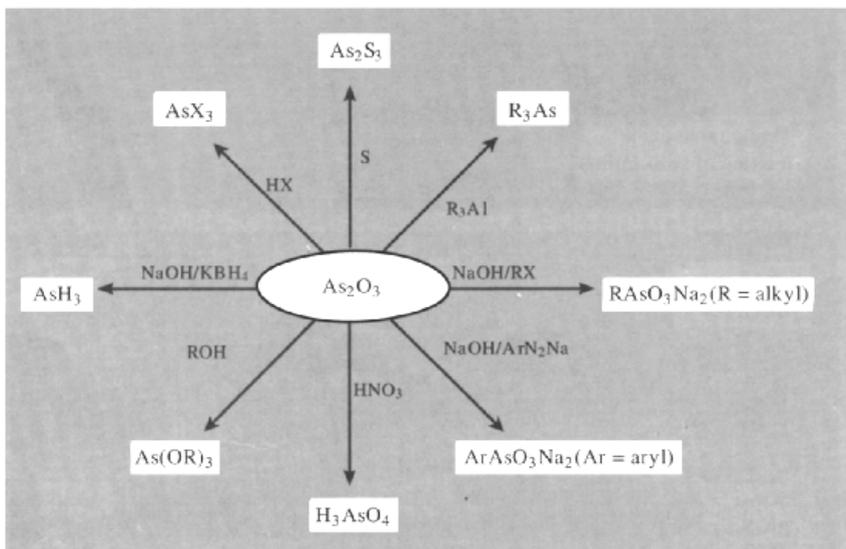
ores such as arsenopyrite, FeAsS , Sb_2O_3 and Bi_2O_3 are made similarly. All 3 oxides exist in several modifications as shown in the schemes on p. 573.⁽¹⁶⁾ In the vapour phase As_2O_3 exists as As_4O_6 molecules isostructural with P_4O_6 (p. 504), and this unit also occurs in the cubic crystalline form. Above 800° gaseous As_4O_6 partially dissociates to an equilibrium mixture containing both As_4O_6 and As_2O_3 molecules. The less-volatile monoclinic form of As_2O_3 has a sheet-like structure of pyramidal $\{\text{AsO}_3\}$ groups sharing common O atoms. This transformation from molecular As_4O_6 units to polymeric As_2O_3 is accompanied by an 8.7% increase in density from 3.89 to 4.23 g cm^{-3} . A similar change from cubic, molecular Sb_4O_6 to polymeric Sb_2O_3 results in an 11.3% density increase from 5.20 to 5.79 g cm^{-3} .

The structural relationships in Bi_2O_3 are more complex. At room temperature the stable form is monoclinic $\alpha\text{-Bi}_2\text{O}_3$ which has a polymeric layer structure featuring distorted, 5-coordinate Bi in pseudo-octahedral $\{\text{BiO}_5\}$ units. Above 717°C this transforms to the cubic δ -form which has a defect fluorite structure (CaF_2 , p. 118) with randomly distributed oxygen vacancies, i.e. $[\text{Bi}_2\text{O}_3\Box]$. The β -form and several oxygen-rich forms (in which some of the vacant sites are filled

by O^{2-} with concomitant oxidation of some Bi^{III} to Bi^{V}) are related to the $\delta\text{-Bi}_2\text{O}_3$ structure. There are also numerous double oxides $p\text{MO}_n.q\text{Bi}_2\text{O}_3$, e.g. $\text{Bi}_{12}\text{GeO}_{20}$ (i.e. $\text{GeO}_2.6\text{Bi}_2\text{O}_3$), and other mixed oxides can be made by fusing Bi_2O_3 with oxides of Ca, Sr, Ba, Cd or Pb; these latter have $(\text{BiO})_n$ layers as in the oxide halides, interleaved with M^{II} cations. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is a superconductor with $T_c = 85 \text{ K}$ (cf. p. 1182).

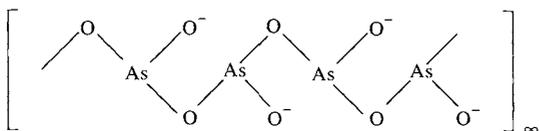
The oxides M_2O_3 are convenient starting points for the synthesis of many other compounds of As, Sb and Bi. Some reactions of As_2O_3 are shown in the scheme; Sb_2O_3 reacts similarly, but Bi_2O_3 is more basic, being insoluble in aqueous alkali but dissolving in acids to give Bi^{III} salts.

The solubility of As_2O_3 in water, and the species present in solution, depend markedly on pH. In pure water at 25°C the solubility is 2.16 g per 100 g ; this diminishes in dilute HCl to a minimum of 1.56 g per 100 g at about 3 M HCl and then increases, presumably due to the formation of chloro-complexes. In neutral or acid solutions the main species is probably pyramidal $\text{As}(\text{OH})_3$, "arsenious acid", though this compound has never been isolated either from solution or otherwise (cf. carbonic acid, p. 310). The solubility is much greater in basic solutions and spectroscopic evidence points to



the presence of such anions as $[\text{AsO}(\text{OH})_2]^-$, $[\text{AsO}_2(\text{OH})]^{2-}$ and $[\text{AsO}_3]^{3-}$, corresponding to successive deprotonation of H_3AsO_3 . The first stage dissociation constant at 25° is $K_a = [\text{AsO}(\text{OH})_2^-][\text{H}^+]/[\text{H}_3\text{AsO}_3] \simeq 6 \times 10^{-10}$, $\text{p}K_a$ 9.2; ortho-arsenious acid is therefore a very weak acid (as expected from Pauling's rules, p. 50) and is comparable in strength to boric acid (p. 203). Dissociation as a base is even weaker: $K_b = [\text{As}(\text{OH})_2^+][\text{OH}^-]/[\text{As}(\text{OH})_3] \simeq 10^{-14}$. There now seems to be less evidence for other species that were formerly considered to be present in solution, e.g. the monomeric meta-acid HAsO_2 , i.e. $[\text{AsO}(\text{OH})]$ (by loss of 1 H_2O) and the hexahydroxoacid $\text{H}_3[\text{As}(\text{OH})_6]$ or its hydrate.

Arsenites of the alkali metals are very soluble in water, those of the alkaline earth metals less so, and those of the heavy metals are virtually insoluble. Many of the salts are obtained as meta-arsenites, e.g. NaAsO_2 , which comprises polymeric chain anions formed by corner linkage of pyramidal $\{\text{AsO}_3\}$ groups and held together by Na ions:



The sparingly soluble yellow Ag_3AsO_3 is an example of an orthoarsenite. Copper(II) arsenites were formerly used as fine green pigments, e.g. Paris green, which is an acetate arsenite $[\text{Cu}_2(\text{MeCO}_2)(\text{AsO}_3)]$, and Scheele's green, which approximates to the hydrogen arsenite CuHAsO_3 or the dehydrated composition $\text{Cu}_2\text{As}_2\text{O}_5$.

Antimonious acid H_3SbO_3 and its salts are less well characterized but a few meta-antimonites and polyantimonites are known, e.g. NaSbO_2 , $\text{NaSb}_3\text{O}_5 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{Sb}_4\text{O}_7$. The oxide itself finds extensive use as a flame retardant in fabrics, paper, paints, plastics, epoxy resins, adhesives and rubbers. The scale of industrial use can be gauged from the US statistics which indicate an annual consumption of Sb_2O_3 of some 10 000 tonnes in that country.

The corresponding Bi compound $\text{Bi}(\text{OH})_3$ is definitely basic rather than acidic. It dissolves readily in acid giving solutions of Bi^{III} ions but an increase in pH causes precipitation of oxo-salts. Before precipitation, however, polymeric oxocations can be detected in solution of which the best characterized is $[\text{Bi}_6(\text{OH})_{12}]^{6+}$ in perchlorate solution. The species (Fig. 13.15) resembles $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ and has 6 Bi at the corners of an octahedron with bridging OH groups above each of the 12 edges. The shortest Bi–O distance is 233 pm and the (nonbonding) $\text{Bi} \cdots \text{Bi}$ distance is 370 pm (307 and 353 in Bi metal). This contrasts with the bicapped tetrahedral distribution of metal atoms in $[\text{Pb}_6\text{O}(\text{OH})_6]^{4+}$ (p. 395) where there is an O atom at the centre of the central tetrahedron and OH groups above the faces of the capping tetrahedra. A different arrangement of oxygen atoms around the Bi_6 octahedron has been found by X-ray and neutron diffraction studies on $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}[\text{ClO}_4]^{-} \cdot 6.7\text{H}_2\text{O}$, which can be crystallized from solutions prepared by dissolving Bi_2O_3 in 3 M HClO_4 .⁽⁷⁵⁾ The eight oxygen atoms (4 O and 4 OH) are disposed, respectively, on two tetrahedra above the eight triangular faces of the octahedron, thus giving the cluster overall

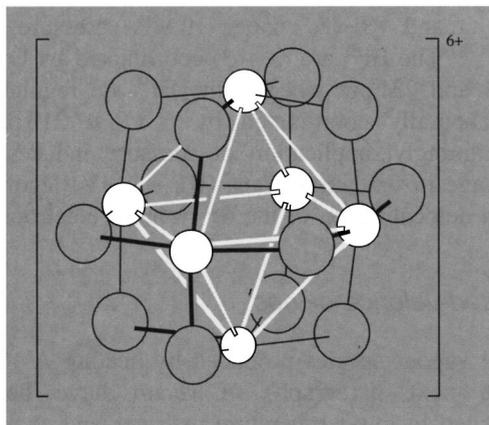


Figure 13.15 The structure of the oxocation $[\text{Bi}_6(\text{OH})_{12}]^{6+}$; the white lines indicate geometry but do not imply Bi–Bi bonds (see text).

⁷⁵ B. SUNDVALL. *Inorg. Chem.* **22**, 1906–12 (1983).

T_d symmetry and with average distances Bi–O 215 pm, Bi–O(H) 240 pm and Bi···Bi 368 pm.

The tendency of Bi^{III} oxo-groups to aggregate is also found in Li₃BiO₃, which is formed as colourless crystals by heating a mixture of Li₂O and Bi₂O₃ (in a 3.1:1 mole ratio) in Ag capsules (bombs!) at 750°C for 20 days.⁽⁷⁶⁾ The “isolated” pyramidal BiO₃³⁻ ions are arranged in apparently electrostatically unfavourable groups of eight with the 8 Bi atoms at the corners of a cube, all 24 O atoms pointing outwards and the eight lone pairs of electrons pointing inwards; Bi–O 205 pm (av), Bi···Bi 368 pm (av); cf. Bi–Bi 307.2 and 352.9 pm in Bi metal (p. 551). Likewise, colourless crystals of Ag₃BiO₃ and of Ag₅BiO₄, prepared by heating Ag₂O and Bi₂O₃ at 500–530°C under 100 MPa (1 kbar) of O₂ or hydrothermally at 350°C and 10 MPa of O₂, both feature Bi₂O₈¹⁰⁻ units. In Ag₅BiO₄ (i.e. Ag₁₀Bi₂O₈) the units are “isolated” and comprise two square-based pyramidal {BiO₅} groups *trans*-fused at a common basal edge and with Bi–O_b 231 pm (av), Bi–O_a 214 pm, Bi···Bi 379 pm. In Ag₃BiO₃ these {Bi₂O₈} groups are further linked by the remaining terminal basal O atoms to form a 3D network.⁽⁷⁷⁾ A fascinating mixed valence bismuthate Ag₂₅Bi₃O₁₈ (i.e. Bi^{III}₂Bi^V) has been prepared as black crystals by heating Ag₂O and ‘Bi₂O₅’ under 10 MPa pressure of O₂.⁽⁷⁸⁾ The Bi^{III} are (3 + 3)-coordinated by O at 221 and 231 pm whereas the Bi^V are regularly octahedrally coordinated by 6 O at 213 pm. Intriguingly, application of pressure induces a change in oxidation states (III → V) leading to a delocalization of the 6s² valence electrons.

Mixed-valence oxides

The vapour species produced by heating As₂O₅ (see next paragraph) *in vacuo* have been isolated in low-temperature matrices and shown

by vibration spectroscopy to comprise the complete series of stable molecules As₄O_{*n*} (*n* = 6–10),⁽⁷⁹⁾ analogous in structures to the phosphorus series (p. 504). The intermediate diamagnetic oxide α-Sb₂O₄ (i.e. Sb^{III}Sb^VO₄) has long been known as the massive, fine-grained, yellow, orthorhombic mineral cervantite and more recently a monoclinic β-form has been recognized. α-Sb₂O₄ can also be obtained by heating Sb₂O₃ in dry air at 460–540°C, and further heating in air or oxygen at 1130° produces β-Sb₂O₄. Both forms have similar structures with equal numbers of Sb^{III} and Sb^V. α-Sb₂O₄ is isostructural with SbNbO₄ and SbTaO₄ and consists of corrugated sheets of slightly distorted {Sb^VO₆} octahedra sharing all their vertices (as in the plane layer in K₂NiF₄); the Sb^{III} lie between the layers in positions of irregular pyramidal fourfold coordination, all four O atoms lying on the same side of the Sb^{III}. Further oxidation to anhydrous Sb₂O₅ has not been achieved (see below). For oxygen-rich Bi₂O_{3+x} see pp. 573–4 and also the preceding paragraph.

Oxo compounds of M^V

Arsenic(V) oxide, As₂O₅, is one of the oldest-known oxides, but structural analysis has been thwarted until recently because of poor thermal stability, ease of hydrolysis and the difficulty of growing a single crystal. It is now known to consist of equal numbers of {AsO₆} octahedra and {AsO₄} tetrahedra completely linked by corner sharing to give cross-linked strands which define tubular cavities (cf. the corner sharing in ReO₃ octahedra, p. 1047, and SiO₂ tetrahedra, p. 343).⁽⁸⁰⁾ The structure accounts for the reluctance of the compound to crystallize and also for the observation that only half the As atoms can be replaced by Sb (6-coordinate) and P (4-coordinate) respectively. As₂O₅ can be prepared either by heating As (or As₂O₃) with O₂ under pressure or by dehydrating crystalline

⁷⁶ R. HOPPE and R. HÜBENTHAL, *Z. anorg. allg. Chem.* **576**, 159–78 (1989).

⁷⁷ M. BORTZ and M. JANSEN, *Z. anorg. allg. Chem.* **619**, 1446–54 (1993).

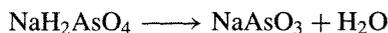
⁷⁸ M. BORTZ and M. JANSEN, *Z. anorg. allg. Chem.* **612**, 113–7 (1992).

⁷⁹ A. K. BRISDON, R. A. GOMME and J. S. OGDEN, *J. Chem. Soc., Dalton Trans.*, 2725–30 (1986).

⁸⁰ M. JANSEN, *Angew. Chem. Int. Edn. Engl.* **16**, 214 (1977).

H_3AsO_4 at about 200°C . It is deliquescent, exceedingly soluble in water (230 g per 100 g H_2O at 20°), thermally unstable (losing O_2 near the mp, *ca.* 300°C) and a strong oxidizing agent (liberating Cl_2 from HCl).

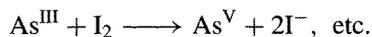
Arsenic acid, H_3AsO_4 , can be obtained in aqueous solution by oxidizing As_2O_3 with concentrated HNO_3 or by dissolving As_2O_5 in water. Crystallization below 30° yields $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ (cf. phosphoric acid hemihydrate, p. 519), whereas crystallization at 100°C or above results in loss of water and the formation of $\text{As}_2\text{O}_5 \cdot \frac{5}{3}\text{H}_2\text{O}$, i.e. ribbon-like polymeric ($\text{H}_5\text{As}_3\text{O}_{10}$) $_n$. All these materials are strongly H-bonded. Arsenic acid, like H_3PO_4 (p. 519), is tribasic with $\text{p}K_1$ 2.2, $\text{p}K_2$ 6.9, $\text{p}K_3$ 11.5 at 25° . $\text{M}^1\text{H}_2\text{AsO}_4$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$) are ferroelectric (p. 57). The corresponding sodium salt readily dehydrates to give meta-arsenate $\text{NaAs}^{\text{V}}\text{O}_3$:



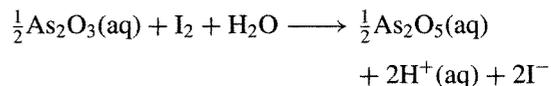
NaAsO_3 has an infinite polymeric chain anion similar to that in diopside (pp. 349, 529) but with a trimeric repeat unit; LiAsO_3 is similar but with a dimeric repeat unit whereas $\beta\text{-KAsO}_3$ appears to have a cyclic trimeric anion $\text{As}_3\text{O}_9^{3-}$ which resembles the *cyclo*-trimetaphosphates (p. 530). There is thus a certain structural similarity between arsenates and phosphates, though arsenic acid and the arsenates show less tendency to catenation (p. 526). The tetrahedral $\{\text{As}^{\text{V}}\text{O}_4\}$ group also resembles $\{\text{PO}_4\}$ in forming the central unit in several heteropolyacid anions (p. 1014).

One striking difference between arsenates and phosphates is the appreciable oxidizing tendency of the former. This is clear from the oxidation state diagram for the Group V elements shown in Fig. 13.16, which summarizes a great deal of relevant information (p. 435). Antimony is seen to resemble arsenic quite closely but $\text{Bi}^{\text{V}}\text{-Bi}^{\text{III}}$ is a much more strongly oxidizing couple and, indeed (as is clear from Fig. 13.16), it is able to oxidize water to oxygen. It is also clear that the +3 oxidation states of As, Sb and Bi do

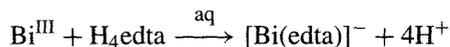
not disproportionate in solution. Nor do the elements themselves, so there are no reactions comparable to that of P_4 with alkali to give phosphine and hypophosphite (p. 513). Redox reactions have proved a useful volumetric method of analysis for both As and Sb. For example As^{III} is quantitatively oxidized in aqueous solution by I_2 , or by potassium bromate, iodate or permanganate. Such reactions can be formally represented as follows:



Thus, in an acid buffer such as borax-boric acid or $\text{Na}_2\text{HPO}_4\text{-NaH}_2\text{PO}_4$ (p. 521):



Such reactions are not available for Bi^{III} but this can readily be determined by complexometric titration using ethylenediaminetetraacetic acid or similar complexones:



Antimony(V) oxide has been obtained as a poorly characterized pale-yellow powder of ill-defined stoichiometry by hydrolysing SbCl_5 with aqueous ammonia solution and dehydrating the product at 275° . Antimonates generally feature pseudooctahedral $\{\text{SbO}_6\}$ units but polymerization by corner, edge or face sharing is rife. Some compounds which have been structurally characterized are $\text{NaSb}(\text{OH})_6$, LiSbO_3 (edge-shared), Li_3SbO_4 (NaCl superstructure with isolated lozenges of $\{\text{Sb}_4\text{O}_{16}\}^{12-}$), NaSbO_3 (ilmenite, p. 963), MgSb_2O_6 (trirutile, p. 961), AlSbO_4 (rutile, 2MO_2 with random occupancy) and $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ (defect spinel, i.e. $3\text{AB}_2\text{O}_4$, p. 248).

Bismuth(V) oxide and bismuthates are even less well established though a recent important development has been the synthesis and structural characterization of Li_3BiO_5 , prepared by heating an intimate mixture of Li_2O and $\alpha\text{-Bi}_2\text{O}_3$ at 650° for 24 h in dry O_2 . The structure is of the defect rock-salt type with an ordering of

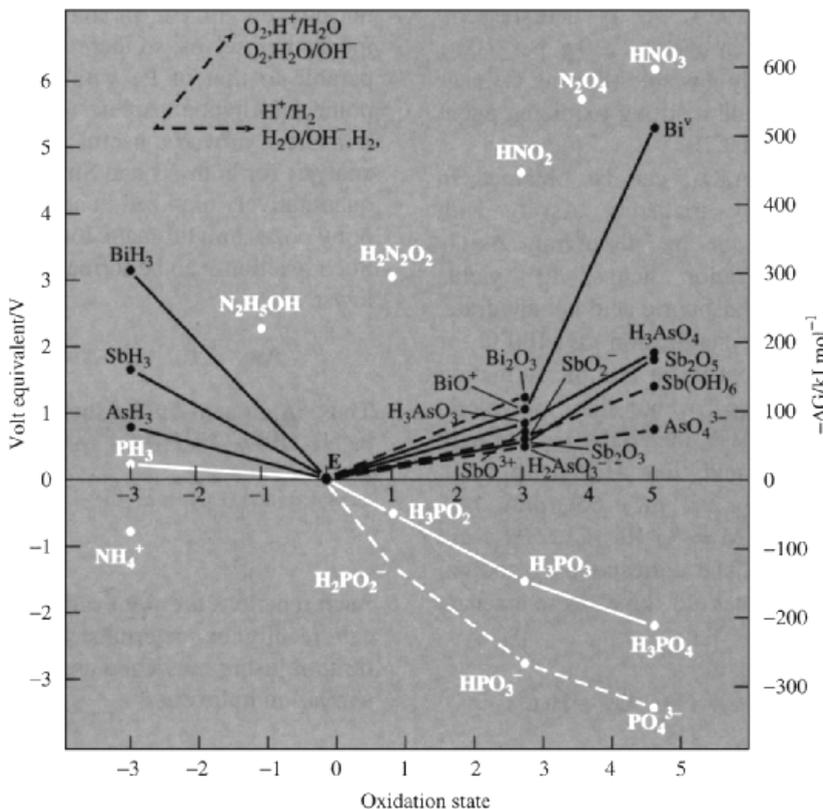


Figure 13.16 Oxidation state diagram for As, Sb and Bi in acid and alkaline solutions, together with selected data on N and P for comparison.

cations and anion vacancies similar to that found in the ordered low-temperature phase of TiO (p. 962).⁽⁸¹⁾ Note that the nominal ionic radii of Li^+ and Bi^{5+} are equal (76 pm). Strong oxidizing agents give brown or black precipitates with alkaline solutions of Bi^{III} , which may be an impure higher oxide, and $\text{NaBi}^{\text{V}}\text{O}_3$ can be made by heating Na_2O and Bi_2O_3 in O_2 . Such bismuthates of alkali and alkaline earth metals, though often poorly characterized, can be used as strong oxidizing agents in acid solution. Thus Mn in steel can be quantitatively determined by oxidizing it directly to permanganate and estimating the concentration colorimetrically.

⁸¹ C. GREAVES and S. M. A. KATIB, *J. Chem. Soc., Chem. Commun.*, 1828–9 (1987).

13.3.5 Sulfides and related compounds

Despite the venerable history of the yellow mineral orpiment, As_2S_3 , and the orange-red mineral realgar, As_4S_4 (p. 547), it is only during the past two or three decades that the structural interrelation of the numerous arsenic sulfides has emerged. As_2S_3 has a layer-structure analogous to As_2O_3 (p. 574) with each As bonded pyramidally to 3 S atoms at 224 pm and angle S–As–S 99°. It can be made by heating As_2O_3 with S or by passing H_2S into an acidified solution of the oxide. It sublimes readily, even below its mp of 320°, and the vapour has been shown by electron diffraction studies to comprise As_4S_6 molecules isostructural with P_4O_6 (p. 504). The structure can be thought