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6

Boron

6.1 Introduction

Boron is a unique and exciting element. Over the years it has proved a constant challenge and stimulus not only to preparative chemists and theoreticians, but also to industrial chemists and technologists. It is the only non-metal in Group 13 of the periodic table and shows many similarities to its neighbour, carbon, and its diagonal relative, silicon. Thus, like C and Si, it shows a marked propensity to form covalent, molecular compounds, but it differs sharply from them in having one less valence electron than the number of valence orbitals, a situation sometimes referred to as “electron deficiency”. This has a dominant effect on its chemistry.

Borax was known in the ancient world where it was used to prepare glazes and hard (borosilicate) glasses. Sporadic investigations during the eighteenth century led ultimately to the isolation of very impure boron by H. Davy and by J. L. Gay Lussac and L. J. Thénard in 1808, but it was not until 1892 that H. Moissan obtained samples of 95–98% purity by reducing B_2O_3 with Mg. High-purity boron (>99%) is a product of this century, and the various crystalline forms have

been obtained only during the last few decades mainly because of the highly refractory nature of the element and its rapid reaction at high temperatures with nitrogen, oxygen and most metals. The name *boron* was proposed by Davy to indicate the source of the element and its similarity to carbon, i.e. *bor(ax + carb)on*.

Boron is comparatively un abundant in the universe (p. 14); it occurs to the extent of about 9 ppm in crustal rocks and is therefore rather less abundant than lithium (18 ppm) or lead (13 ppm) but is similar to praseodymium (9.1 ppm) and thorium (8.1 ppm). It occurs almost invariably as borate minerals or as borosilicates. Commercially valuable deposits are rare, but where they do occur, as in California or Turkey, they can be vast (see Panel). Isolated deposits are also worked in the former Soviet Union, Tibet and Argentina.

The structural complexity of borate minerals (p. 205) is surpassed only by that of silicate minerals (p. 347). Even more complex are the structures of the metal borides and the various allotropic modifications of boron itself. These factors, together with the unique structural and bonding problems of the boron hydrides, dictate that boron should be treated in a separate chapter.

Borate Minerals

The world's major deposits of borate minerals occur in areas of former volcanic activity and appear to be associated with the waters from former hot springs. The primary mineral that first crystallized was normally ulexite, $\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$, but this was frequently mixed with lesser amounts of borax, $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ (p. 206). Exposure and subsequent weathering (e.g. in the Mojave Desert, California) resulted in leaching by surface waters, leaving a residue of the less-soluble mineral colemanite, $\text{Ca}[\text{B}_3\text{O}_4(\text{OH})_3] \cdot \text{H}_2\text{O}$ (p. 206). The leached (secondary) borax sometimes reaccumulated and sometimes underwent other changes to form other secondary minerals such as the commercially important kernite, $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 2\text{H}_2\text{O}$, at Boron, California: This is the world's largest single source of borates and comprises a deposit 6.5 km long, 1.5 km wide and 25–50 m thick containing material that averages 75% of hydrated sodium tetraborates (borax and kernite). World reserves (expressed as B_2O_3 content) exceed 315 million tonnes (Turkey 45%, USA 21%, Kazakhstan 17%, China 8.6%, Argentina 7.3%). Annual world production of borates was 2.67 million tonnes in 1990. Production in Turkey has expanded dramatically in the last two decades and now exceeds that of the USA, the 1990 production figures being 1.20 and 1.09 Mt respectively. Smaller producers (10^3 t) are: "Russia" 175, Chile 132, China 27, Argentina 26 and Peru 18. The 1991 bulk price per tonne of borax in USA was \$264 for technical grade and \$2222 for refined granules.

The main chemical products produced from these minerals are (a) boron oxides, boric acid and borates, (b) esters of boric acid, (c) refractory boron compounds (borides, etc.), (d) boron halides, (e) boranes and carbaboranes and (f) organoboranes. The main industrial and domestic uses of boron compounds in Europe (USA in parentheses) are:

Heat resistant glasses (e.g. Pyrex), glass wool, fibre glass	26% (60%)
Detergents, soaps, cleaners and cosmetics	37% (7%)
Porcelain enamels	16% (3%)
Synthetic herbicides and fertilizers	2% (4%)
Miscellaneous (nuclear shielding, metallurgy, corrosion control, leather tanning, flame-proofing, catalysts)	19% (26%)

The uses in the glass and ceramics industries reflect the diagonal relation between boron and silicon and the similarity of vitreous borate and silicate networks (pp. 203, 206 and 347). In the UK and continental Europe (but not in the USA or Japan) sodium perborate (p. 206) is a major constituent of washing powders since it hydrolyses to H_2O_2 and acts as a bleaching agent in very hot water ($\sim 90^\circ\text{C}$); in the USA domestic washing machines rarely operate above 70° , at which temperature perborates are ineffective as bleaches.

Details of other uses of boron compounds are noted at appropriate places in the text.

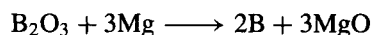
The general group trends, and a comparison with the chemistry of the metallic elements of Group 13 (Al, Ga, In and Tl), will be deferred until the next chapter.

6.2 Boron⁽¹⁾

6.2.1 Isolation and purification of the element

There are four main methods of isolating boron from its compounds:

(i) Reduction by metals at high temperature, e.g. the strongly exothermic reaction



(Moissan boron, 95–98% pure)

Other electropositive elements have been used (e.g. Li, Na, K, Be, Ca, Al, Fe), but the product is generally amorphous and contaminated with refractory impurities such as metal borides. Massive crystalline boron (96%) has been prepared by reacting BCl_3 with zinc in a flow system at 900°C .

(ii) Electrolytic reduction of fused borates or tetrafluoroborates, e.g. KBF_4 in molten KCl/KF at 800° . The process is comparatively cheap but yields only powdered boron of 95% purity.

(iii) Reduction of volatile boron compounds by H_2 , e.g. the reaction of $\text{BBr}_3 + \text{H}_2$ on a heated

¹ N. N. GREENWOOD, *Boron*, Pergamon Press, Oxford, 1975, 327 pp.; also as Chap. 11 in *Comprehensive Inorganic Chemistry*, Vol. 1, Pergamon Press, Oxford, 1973.

tantalum metal filament. This method, which was introduced in 1922 and can now be operated on the kilogram scale, is undoubtedly the most effective general preparation for high purity boron (>99.9%). Crystallinity improves with increasing temperature, amorphous products being obtained below 1000°C, α - and β -rhombohedral modifications between 1000–1200° and tetragonal crystals above this. BCl_3 can be substituted for BBr_3 but BI_3 is unsatisfactory because it is expensive and too difficult to purify sufficiently. Free energy calculations indicate that BF_3 would require impracticably high temperatures (>2000°).

(iv) Thermal decomposition of boron hydrides and halides. Boranes decompose to amorphous boron when heated at temperatures up to 900° and crystalline products can be obtained by thermal decomposition of BI_3 . Indeed, the first recognized sample of α -rhombohedral B was prepared (in 1960) by decomposition of BI_3 on Ta at 800–1000°, and this is still an excellent exclusive preparation of this allotrope.

6.2.2 Structure of crystalline boron⁽¹⁻³⁾

Boron is unique among the elements in the structural complexity of its allotropic modifications; this reflects the variety of ways in which boron seeks to solve the problem of having fewer electrons than atomic orbitals available for bonding. Elements in this situation usually adopt metallic bonding, but the small size and high ionization energies of B (p. 222) result in covalent rather than metallic bonding. The structural unit which dominates the various allotropes of B is the B_{12} icosahedron (Fig. 6.1), and this also occurs in several metal boride structures and in certain boron hydride derivatives. Because of the fivefold rotation symmetry at the individual B atoms, the B_{12} icosahedra pack rather inefficiently and there

² V. I. MATKOVICH (ed.), *Boron and Refractory Borides*, Springer-Verlag, Berlin, 1977, 656 pp.

³ GMELIN, *Handbook of Inorganic Chemistry, Boron, Supplement Vol. 2: Elemental Boron. Boron Carbides*, 1981, 242 pp.

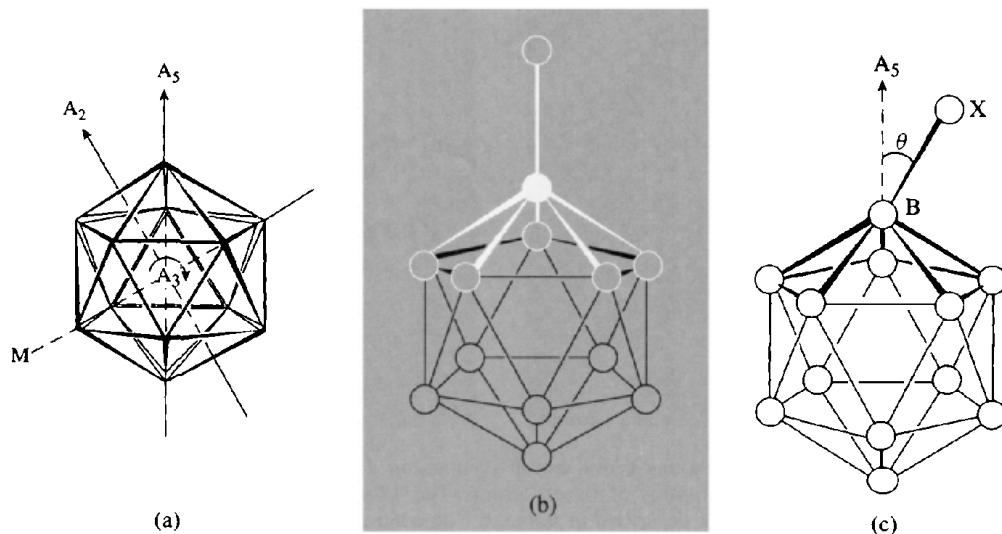


Figure 6.1 The icosahedron and some of its symmetry elements. (a) An icosahedron has 12 vertices and 20 triangular faces defined by 30 edges. (b) The preferred pentagonal pyramidal coordination polyhedron for 6-coordinate boron in icosahedral structures; as it is not possible to generate an infinite three-dimensional lattice on the basis of fivefold symmetry, various distortions, translations and voids occur in the actual crystal structures. (c) The distortion angle θ , which varies from 0° to 25°, for various boron atoms in crystalline boron and metal borides.

are regularly spaced voids which are large enough to accommodate additional boron (or metal) atoms. Even in the densest form of boron, the α -rhombohedral modification, the percentage of space occupied by atoms is only 37% (compared with 74% for closest packing of spheres).

The α -rhombohedral form of boron is the simplest allotropic modification and consists of nearly regular B_{12} icosahedra in slightly deformed cubic close packing. The rhombohedral unit cell (Fig. 6.2) has a_0 505.7 pm, α 58.06° (60° for regular ccp) and contains 12 B atoms. *It is important to remember that in Fig. 6.2, as in most other structural diagrams in this chapter, the lines merely define the geometry of the clusters of boron atoms; they do not usually represent 2-centre 2-electron bonds between pairs of atoms.* In terms of the MO theory to be discussed on p. 157, the 36 valence electrons of each B_{12} unit are distributed as follows: 26 electrons just fill the 13 available bonding MOs within the icosahedron and 6 electrons share with 6 other electrons from 6 neighbouring icosahedra in adjacent planes to

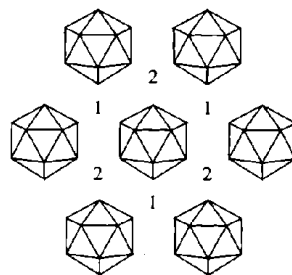


Figure 6.2 Basal plane of α -rhombohedral boron showing close-packed arrangement of B_{12} icosahedra. The B-B distances within each icosahedron vary regularly between 173–179 pm. Dotted lines show the 3-centre bonds between the 6 equatorial boron atoms in each icosahedron to 6 other icosahedra in the same sheet at 202.5 pm. The sheets are stacked so that each icosahedron is bonded by six 2-centre B-B bonds at 171 pm (directed rhombohedrally, 3 above and 3 below the icosahedron). B_{12} units in the layer above are centred over 1 and those in the layer below are centred under 2.

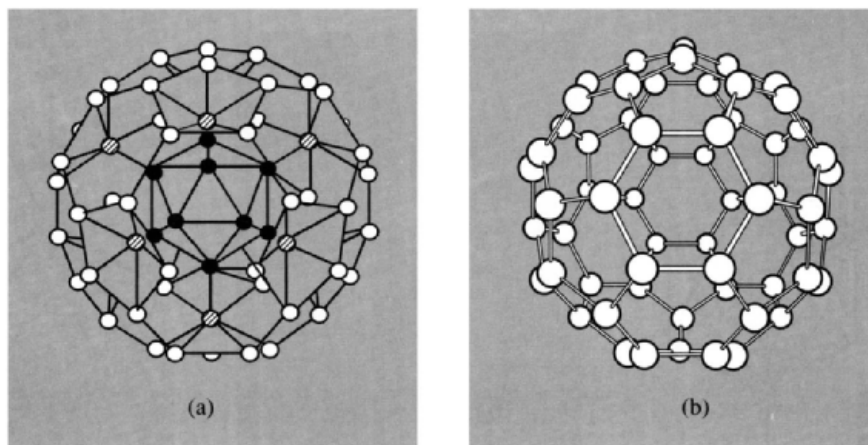


Figure 6.3 (a) The B_{84} unit in β -rhombohedral boron comprising a central B_{12} icosahedron and 12 outwardly directed pentagonal pyramids of boron atoms. The 12 outer icosahedra are completed by linking with the B_{10} subunits as described in the text. The central icosahedron (●) is almost exactly regular with B-B 176.7 pm. The shortest B-B distances (162–172 pm) are between the central icosahedron and the apices of the 12 surrounding pentagonal pyramids (⊙). The B-B distances within the 12 B_6 pentagonal pyramids (half-icosahedra) are somewhat longer (185 pm) and the longest B-B distances (188–192 pm) occur within the hexagonal rings surrounding the 3-fold symmetry axes of the B_{84} polyhedron. Note that if the 24 “internal” B atoms (● and ⊙) are removed from the B_{84} unit then a B_{60} unit (b) remains which has precisely the fullerene structure subsequently found some 25 years later for C_{60} (p. 279).

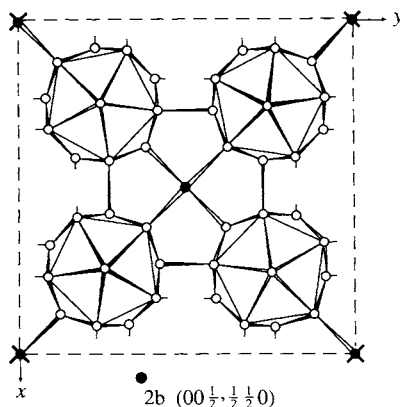


Figure 6.4 Crystal structure of α -tetragonal boron. This was originally thought to be B_{50} ($4B_{12} + 2B$) but is now known to be either $B_{50}C_2$ or $B_{50}N_2$ in which the 2C (or 2N) occupy the 2(b) positions; the remaining 2B are distributed statistically at other “vacant” sites in the lattice. Note that this reformulation solves three problems which attended the description of the α -tetragonal phase as a crystalline modification of pure B:

1. The lattice parameters showed considerable variation from one crystal to another with average values a 875 pm, c 506 pm; this is now thought to arise from variable composition depending on the precise preparative conditions used.
2. The interatomic distances involving the single 4-coordinate atoms at 2(b) were only 160 pm; this is unusually short for B–B but reasonable for B–C or B–N distances.
3. The structure requires 160 valence electrons per unit cell computed as follows: internal bonding within the 4 icosahedra ($4 \times 26 = 104$); external bonds for the 4 icosahedra ($4 \times 12 = 48$); bonds shared by the atoms in 2(b) positions ($2 \times 4 = 8$). However, 50 B atoms have only 150 valence electrons and even with the maximum possible excess of boron in the unit cell (0.75 B) this rises to only 152 electrons. The required extra 8 or 10 electrons are now supplied by 2C or 2N though the detailed description of the bonding is more intricate than this simple numerology implies.

form the 6 rhombohedrally directed normal 2-centre 2-electron bonds; this leaves 4 electrons which is just the number required for contribution to the 6 equatorial 3-centre 2-electron bonds ($6 \times \frac{2}{3} = 4$).

The thermodynamically most stable polymorph of boron is the β -rhombohedral modification which has a much more complex structure with 105 B atoms in the unit cell (a_0 1014.5 pm, α 65.28°). The basic unit can be thought of as a central B_{12} icosahedron surrounded by an icosahedron of icosahedra; this can be visualized as 12 of the B_7 units in Fig. 6.1b arranged so that the apex atoms form the central B_{12} surrounded by 12 radially disposed pentagonal dishes to give the B_{84} unit shown in Fig. 6.3a. The 12 half-icosahedra are then completed by means of 2 complicated B_{10} subunits per unit cell,

each comprising a central 9-coordinate B atom surrounded by 9 B atoms in the form of 4 fused pentagonal rings. This arrangement corresponds to 104 B ($84 + 10 + 10$) and there is, finally, a 6-coordinate B atom at the centre of symmetry between 2 adjacent B_{10} condensed units, bringing the total to 105 B atoms in the unit cell.

The first crystalline polymorph of B to be prepared (1943) was termed α -tetragonal boron and was found to have 50 B atoms in the unit cell ($4B_{12} + 2B$) (Fig. 6.4). Paradoxically, however, more recent work (1974) suggests that this phase never forms in the absence of carbon or nitrogen as impurity and that it is, in reality, $B_{50}C_2$ or $B_{50}N_2$ depending on the preparative conditions; yields are increased considerably when the BBr_3/H_2 mixture is purposely doped with a few per cent of CH_4 , $CHBr_3$ or N_2 . The

work illustrates the great difficulties attending preparative and structural studies in this area. The crystal structures of other boron polymorphs, particularly the β -tetragonal phase with 192 B atoms in the unit cell (a 1012, c 1414 pm), are even more complex and have so far defied elucidation despite extensive work by many investigators.³

6.2.3 Atomic and physical properties of boron

Boron has 2 stable naturally occurring isotopes and the variability of their concentration (particularly the difference between borates from California (low in ^{10}B) and Turkey (high in ^{10}B) prevents the atomic weight of boron being quoted more precisely than 10.811(7) (p. 17). Each isotope has a nuclear spin (Table 6.1) and this has proved particularly valuable in nmr spectroscopy, especially for ^{11}B .⁽⁴⁾ The great difference in neutron absorption cross-section of the 2 isotopes is also notable, and this has led to the development of viable separation processes on an industrial scale. The commercial availability of the separated isotopes has greatly assisted the solution of structural and mechanistic problems in boron chemistry and has led to the development of boron-10 neutron capture therapy for the treatment of certain types of brain tumour (see p. 179).

⁴ J. D. KENNEDY, Chap. 8 in J. MASON (ed.), *Multinuclear NMR*, Plenum, New York, pp. 221–58 (1987). T. L. VENABLE, W. C. HUTTON and R. N. GRIMES, *J. Am. Chem. Soc.* **106**, 29–37 (1984). D. REED, *Chem. Soc. Rev.* **22**, 109–16 (1993).

Boron is the fifth element in the periodic table and its ground-state electronic configuration is $[\text{He}]2s^22p^1$. The first 3 ionization energies are 800.6, 2427.1 and 3659.7 kJ mol⁻¹, all substantially larger than for the other elements in Group 13. (The values for this and other properties of B are compared with those for Al, Ga, In and Tl on p. 222). The electronegativity (p. 25) of B is 2.0, which is close to the values for H (2.1) Si (1.8) and Ge (1.8) but somewhat less than the value for C (2.5). The implied reversal of the polarity of B–H and C–H bonds is an important factor in discussing hydroboration (p. 166) and other reactions.

The determination of precise physical properties for elemental boron is bedevilled by the twin difficulties of complex polymorphism and contamination by irremovable impurities. Boron is an extremely hard refractory solid of high mp, low density and very low electrical conductivity. Crystalline forms are dark red in transmitted light and powdered forms are black. The most stable (β -rhombohedral) modification has mp 2092°C (exceeded only by C among the non-metals), bp \sim 4000°C, d 2.35 g cm⁻³ (α -rhombohedral form 2.45 g cm⁻³), $\Delta H_{\text{sublimation}}$ 570 kJ per mol of B, electrical conductivity at room temperature 1.5×10^{-6} ohm⁻¹ cm⁻¹.

6.2.4 Chemical properties

It has been argued⁽¹⁾ that the inorganic chemistry of boron is more diverse and complex than that of any other element in the periodic table. Indeed, it is only during the last three decades that the enormous range of structural types has begun to

Table 6.1 Nuclear properties of boron isotopes

Property	^{10}B	^{11}B
Relative mass ($^{12}\text{C} = 12$)	10.012 939	11.009 305
Natural abundance/(%)	19.055–20.316	80.945–79.684
Nuclear spin (parity)	3(+)	$\frac{3}{2}$ (–)
Magnetic moment/(nuclear magnetons) ^(a)	+1.800 63	+2.688 57
Quadrupole moment/barns ^(b)	+0.074	+0.036
Cross-section for (n, α)/barns ^(b)	3835(\pm 10)	0.005

^(a) 1 nuclear magneton = 5.0505×10^{-27} A m² in SI.

^(b) 1 barn = 10^{-28} m² in SI; the cross-section for natural boron (\sim 20% ^{10}B) is \sim 767 barns.

be elucidated and the subtle types of bonding appreciated. The chemical nature of boron is influenced primarily by its small size and high ionization energy, and these factors, coupled with the similarity in electronegativity of B, C and H, lead to an extensive and unusual type of covalent (molecular) chemistry. The electronic configuration $2s^2 2p^1$ is reflected in a predominant trivalence, and bond energies involving B are such that there is no tendency to form univalent compounds of the type which increasingly occur in the chemistry of Al, Ga, In and Tl. However, the availability of only 3 electrons to contribute to covalent bonding involving the 4 orbitals s, p_x , p_y and p_z confers a further range of properties on B leading to electron-pair acceptor behaviour (Lewis acidity) and multicentre bonding (p. 157). The high affinity for oxygen is another dominant characteristic which forms the basis of the extensive chemistry of borates and related oxo complexes (p. 203). Finally, the small size of B enables many interstitial alloy-type metal borides to be prepared, and the range of these is considerably extended by the propensity of B to form branched and unbranched chains, planar networks, and three-dimensional arrays of great intrinsic stability which act as host frameworks to house metal atoms in various stoichiometric proportions.

It is thus possible to distinguish five types of boron compound, each having its own chemical systematics which can be rationalized in terms of the type of bonding involved, and each resulting in highly individualistic structures and chemical reactions:

- (i) metal borides ranging from M_5B to MB_{66} (or even $MB_{>100}$) (see below);
- (ii) boron hydrides and their derivatives including carbaboranes and polyhedral borane-metal complexes (p. 151);
- (iii) boron trihalides and their adducts and derivatives (p. 195);
- (iv) oxo compounds including polyborates, borosilicates, peroxoborates, etc. (p. 203);
- (v) organoboron compounds and B–N compounds (B–N being isoelectronic with C–C) (p. 207).

The chemical reactivity of boron itself obviously depends markedly on the purity, crystallinity, state of subdivision and temperature. Boron reacts with F_2 at room temperature and is superficially attacked by O_2 but is otherwise inert. At higher temperatures boron reacts directly with all the non-metals except H, Ge, Te and the noble gases. It also reacts readily and directly with almost all metals at elevated temperatures, the few exceptions being the heavier members of groups 11–15 (Ag, Au; Cd, Hg; Ga, In, Tl; Sn, Pb; Sb, Bi).

The general chemical inertness of boron at lower temperatures can be gauged by the fact that it resists attack by boiling concentrated aqueous NaOH or by fused NaOH up to 500° , though it is dissolved by fused $Na_2CO_3/NaNO_3$ mixtures at $900^\circ C$. A 2:1 mixture of hot concentrated H_2SO_4/HNO_3 is also effective for dissolving elemental boron for analysis but non-oxidizing acids do not react.

6.3 Borides⁽¹⁻³⁾

6.3.1 Introduction

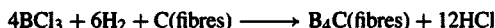
The borides comprise a group of over 200 binary compounds which show an amazing diversity of stoichiometries and structural types; e.g. M_5B , M_4B , M_3B , M_5B_2 , M_7B_3 , M_2B , M_5B_3 , M_3B_2 , $M_{11}B_8$, MB , $M_{10}B_{11}$, M_3B_4 , M_2B_3 , M_3B_5 , MB_2 , M_2B_5 , MB_3 , MB_4 , MB_6 , M_2B_{13} , MB_{10} , MB_{12} , MB_{15} , MB_{18} and MB_{66} . There are also numerous nonstoichiometric phases of variable composition and many ternary and more complex phases in which more than one metal combines with boron. The rapid advance in our understanding of these compounds during the past few decades has been based mainly on X-ray diffraction analysis and the work has been stimulated not only by the inherent academic challenge implied by the existence of these unusual compounds but also by the extensive industrial interest generated by their unique combination of desirable physical and chemical properties (see Panel).

Properties and Uses of Borides

Metal-rich borides are extremely hard, chemically inert, involatile, refractory materials with mps and electrical conductivities which often exceed those of the parent metals. Thus the highly conducting diborides of Zr, Hf, Nb and Ta all have mps > 3000°C and TiB₂ (mp 2980°C) has a conductivity 5 times greater than that of Ti metal. Borides are normally prepared as powders but can be fabricated into the desired form by standard techniques of powder metallurgy and ceramic technology. TiB₂, ZrB₂ and CrB₂ find application as turbine blades, combustion chamber liners, rocket nozzles and ablation shields. Ability to withstand attack by molten metals, slags and salts have commended borides or boride-coated metals as high-temperature reactor vessels, vaporizing boats, crucibles, pump impellers and thermocouple sheaths. Inertness to chemical attack at high temperatures, coupled with excellent electrical conductivity, suggest application as electrodes in industrial processes.

Nuclear applications turn on the very high absorption cross-section of ¹⁰B for thermal neutrons (p. 144) and the fact that this property is retained for high-energy neutrons (10⁴–10⁶ eV) more effectively than for any other nuclide. Another advantage of ¹⁰B is that the products of the (n,α) reaction are the stable, non-radioactive elements Li and He. Accordingly, metal borides and boron carbide have been used extensively as neutron shields and control rods since the beginning of the nuclear power industry. More dramatically, following the disaster at Chernobyl in the early hours of 26 April 1986, some 40 tonnes of boron carbide particles were dumped from helicopters onto the stricken reactor to prevent further runaway fission occurring. (In addition there were 800 tonnes of dolomite to provide a CO₂ gas blanket, 1800 t of clay and sand to quench the fires and filter radionuclides, plus 2400 t of lead to absorb heat by melting and to provide a liquid layer that would in time solidify and seal the top of the core of the vault.)

The principal non-nuclear industrial use of boron carbide is as an abrasive grit or powder for polishing or grinding; it is also used on brake and clutch linings. In addition, there is much current interest in its use as light-weight protective armour, and tests have indicated that boron carbide and beryllium borides offer the best choice; applications are in bullet-proof protective clothing and in protective armour for aircraft. More elegantly, boron carbide can now be produced in fibre form by reacting BCl₃/H₂ with carbon yarn at 1600–1900°C:



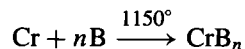
Fibre curling can be eliminated by heat treatment under tension near the mp, and the resulting fibres have a tensile strength of 3.5×10^5 psi (1 psi = 6895 N m⁻²) and an elastic modulus of 50×10^6 psi at a density of 2.35 g cm⁻³; the form was 1 ply, 720 filament yarn with a filament diameter of 11–12 μm. The fibres are inert to hot acid and alkali, resistant to Cl₂ up to 700° and air up to 800°C.

Boron itself has been used for over two decades in filament form in various composites; BCl₃/H₂ is reacted at 1300° on the surface of a continuously moving tungsten fibre 12 μm in diameter. US production capacity is about 20 tonnes pa and the price is about \$800/kg. The primary use so far has been in military aircraft and space shuttles, but boron fibre composites are also being studied as reinforcement materials for commercial aircraft. At the domestic level they are finding increasing application in golf shafts, tennis rackets and bicycle frames.

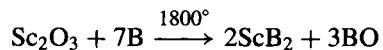
6.3.2 Preparation and stoichiometry

Eight general methods are available for the synthesis of borides, the first four being appropriate for small-scale laboratory preparations and the remaining four for commercial production on a scale ranging from kilogram amounts to tonne quantities. Because high temperatures are involved and the products are involatile, borides are not easy to prepare pure and subsequent purification is often difficult; precise stoichiometry is also sometimes hard to achieve because of differential volatility or high activation energies. The methods are:

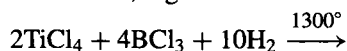
- (i) Direct combination of the elements: this is probably the most widely used technique, e.g.



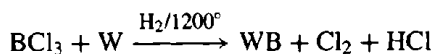
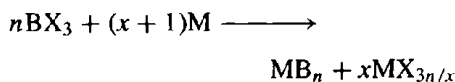
- (ii) Reduction of metal oxide with B (rather wasteful of expensive elemental B), e.g.



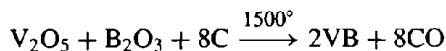
- (iii) Co-reduction of volatile mixed halides with H₂ using a metal filament, hot tube or plasma torch, e.g.



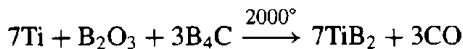
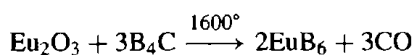
- (iv) Reduction of BCl_3 (or BX_3) with a metal (sometimes assisted by H_2), e.g.



- (v) Electrolytic deposition from fused salts: this is particularly effective for MB_6 (M = alkaline earth or rare earth metal) and for the borides of Mo, W, Fe, Co and Ni. The metal oxide and B_2O_3 or borax are dissolved in a suitable, molten salt bath and electrolysed at $700\text{--}1000^\circ$ using a graphite anode; the boride is deposited on the cathode which can be graphite or steel.
- (vi) Co-reduction of oxides with carbon at temperatures up to 2000° , e.g.

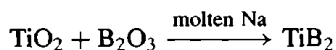


- (vii) Reduction of metal oxide (or $\text{M} + \text{B}_2\text{O}_3$) with boron carbide, e.g.



Boron carbide (p. 149) is a most useful and economic source of B and will react with most metals or their oxides. It is produced in tonnage quantities by direct reduction of B_2O_3 with C at 1600° : a C resistor is embedded in a mixture of B_2O_3 and C, and a heavy electric current passed.

- (viii) Co-reduction of mixed oxides with metals (Mg or Al) in a thermite-type reaction — this usually gives contaminated products including ternary borides, e.g. $\text{Mo}_7\text{Al}_6\text{B}_7$. Alternatively, alkali metals or Ca can be used as reductants, e.g.



The various stoichiometries are not equally common, as can be seen from Fig. 6.5; the most frequently occurring are M_2B , MB , MB_2 , MB_4 and MB_6 , and these five classes account for 75% of the compounds. At the other extreme Ru_{11}B_8 is the only known example of this stoichiometry. Metal-rich borides tend to be formed by the transition elements whereas the boron-rich borides are characteristic of the more electropositive elements in Groups 1–3, the lanthanides and the actinides. Only the diborides MB_2 are common to both classes.

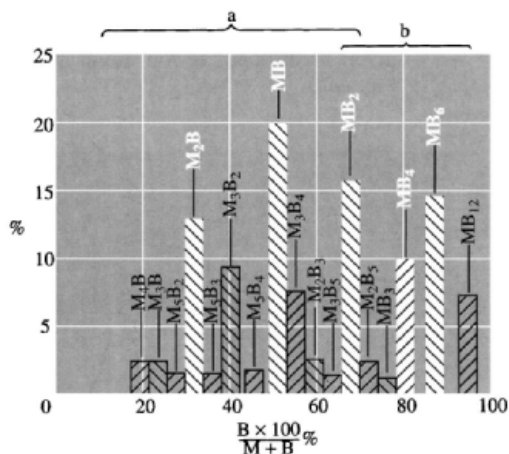


Figure 6.5 Frequency of occurrence of various stoichiometries among boride phases: (a) field of borides of d elements, and (b) field of borides of s, p and f elements.

6.3.3 Structures of borides^(1-3.5)

The structures of metal-rich borides can be systematized by the schematic arrangements shown in Fig. 6.6, which illustrates the increasing tendency of B atoms to catenate as their concentration in the boride phase increases; the B atoms are often at the centres of trigonal prisms of metal atoms (Fig. 6.7) and the various stoichiometries are accommodated as follows:

⁵ T. LUNDSTROM, *Pure Appl. Chem.* 57, 1383–90 (1985).

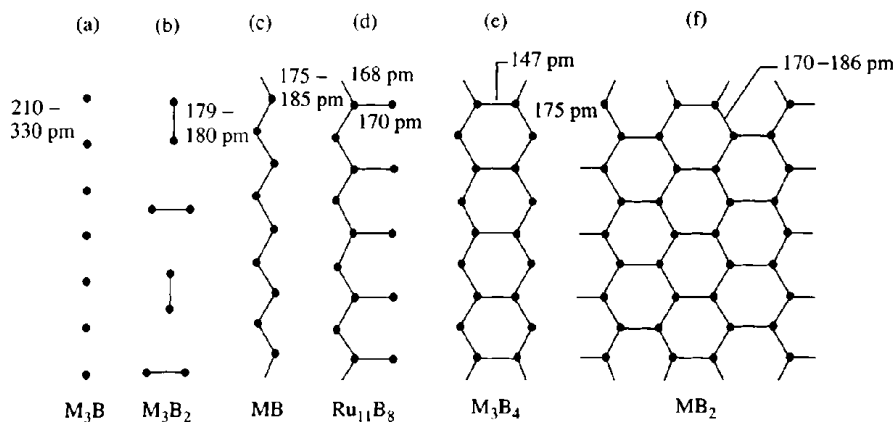


Figure 6.6 Idealized patterns of boron catenation in metal-rich borides. Examples of the structures (a)–(f) are given in the text. Boron atoms are often surrounded by trigonal prisms of M atoms as shown in Fig. 6.7.

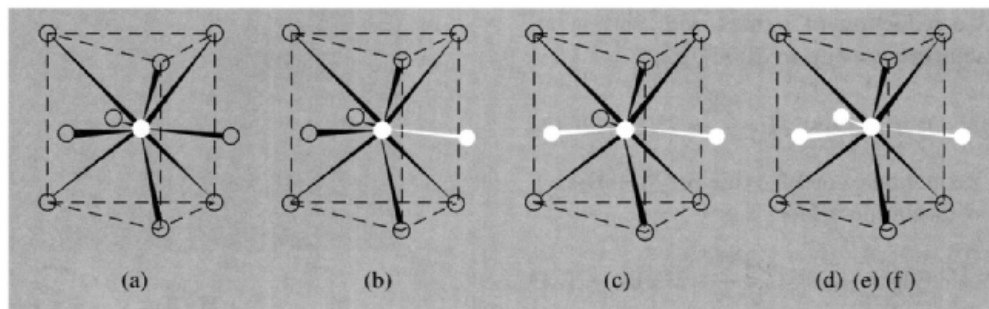


Figure 6.7 Idealized boron environment in metal-rich borides (see text): (a) isolated B atoms in M_3B and M_7B_3 ; (b) pairs of B atoms in Cr_5B_3 and M_3B_2 ; (c) zigzag chains of B atoms in Ni_3B_4 and MB ; (d) branched chains in $Ru_{11}B_8$; and (e), (f) double chains and plane nets in M_3B_4 , MB_2 and M_2B_5 .

- | | | | |
|---------------------------------|---|-------------------------------|--|
| (a) isolated B atoms: | Mn_4B ; M_3B (Tc, Re, Co, Ni, Pd); Pd_5B_2 ; M_7B_3 (Tc, Re, Ru, Rh); M_2B (Ta, Mo, W, Mn, Fe, Co, Ni); | (e) double chains of B atoms: | M_3B_4 (V, Nb, Ta; Cr, Mn); |
| (b) isolated pairs B_2 : | Cr_5B_3 ; M_3B_2 (V, Nb, Ta); | (f) plane (or puckered) nets: | MB_2 (Mg, Al; Sc, Y; Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re; Ru, Os; U, Pu); |
| (c) zigzag chains of B atoms: | M_3B_4 (Ti; V, Nb, Ta; Cr, Mn, Ni); MB (Ti, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Fe, Co, Ni); | | M_2B_5 (Ti; Mo, W). |
| (d) branched chains of B atoms: | $Ru_{11}B_8$; | | |

It will be noted from Fig. 6.6 that structures with isolated B atoms can have widely differing interatomic B–B distances, but all other classes involve appreciable bonding between B atoms, and the B–B distances remain almost invariant despite the extensive variation in the size of the metal atoms.

The structures of boron-rich borides (e.g. MB_4 , MB_6 , MB_{10} , MB_{12} , MB_{66}) are even more effectively dominated by inter-B bonding, and the structures comprise three-dimensional networks of B atoms and clusters in which the metal atoms occupy specific voids or otherwise vacant sites. The structures are often exceedingly complicated (for the reasons given in Section 6.2.2): for example, the cubic unit cell of YB_{66} has a_0 2344 pm and contains 1584 B and 24 Y atoms; the basic structural unit is the 13-icosahedron unit of 156 B atoms found in β -rhombohedral B (p. 142); there are 8 such units (1248 B) in the unit cell and the remaining 336 B atoms are statistically distributed in channels formed by the packing of the 13-icosahedron units.

Another compound which is even more closely related to β -rhombohedral boron is boron carbide, " B_4C "; this is now more correctly written as $B_{13}C_2$,⁽⁶⁾ but the phase can vary over wide composition ranges which approach the stoichiometry $B_{12}C_3$. The structure is best thought of in terms of B_{84} polyhedra (p. 142) but these are now interconnected simply by linear C–B–C units instead of the larger B_{10} –B– B_{10} units in β -rhombohedral B. The result is a more compact packing of the 13-icosahedron units so generated and this is reflected in the unit cell dimensions (a 517.5 pm, α 65.74°). A notable feature of the structure (Fig. 6.8) is the presence of regular hexagonal planar rings B_4C_2 (shaded). Stringent tests had to be applied to distinguish confidently between B and C atoms in this structure and to establish that it was indeed B_{12} CBC and not $B_{12}C_3$ as had previously been thought. [This view has recently been challenged as a result of a ^{13}C nmr study using magic-angle spinning, which suggests that the carbon is present only as C_3 chains and that the structure is in fact still best represented as $B_{12}C_3$ (or $B_{12}^{2-}C_3^{2+}$).]⁽⁷⁾ It is salutary to recall that boron carbide, which was first made by H. Moissan in 1899 and which has been manufactured in tonne amounts for several decades, still waits definitive

structural characterization. On one view the wide variation in stoichiometry from " $B_{6.5}C$ " to " B_4C " is due to progressive vacancies in the CBC chain ($B_{12}C_2 \equiv B_6C$) and/or progressive substitution of one C for B in the icosahedron [$(B_{11}C)CBC \equiv B_4C$]. Related phases are $B_{12}PBP$ and $B_{12}X_2$ ($X = P, As, O, S$). See also p. 288 for B_nC_{60-n} ($n = 1-6$).

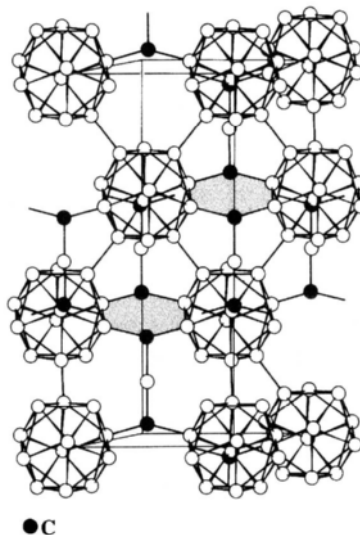


Figure 6.8 Crystal structure of $B_{13}C_2$ showing the planar hexagonal rings connecting the B_{12} icosahedra. These rings are perpendicular to the C–B–C chains.

By contrast with the many complex structures formally related to β -rhombohedral boron, the structures of the large and important groups of cubic borides MB_{12} and MB_6 are comparatively simple. MB_{12} is formed by many large electropositive metals (e.g. Sc, Y, Zr, lanthanides and actinides) and has an "NaCl-type" fcc structure in which M atoms alternate with B_{12} cubo-octahedral clusters (Fig. 6.9). (Note that the B_{12} cluster is not an icosahedron.) Similarly, the cubic hexaborides MB_6 consist of a simple CsCl-type lattice in which the halogen is replaced by B_6 octahedra (Fig. 6.10); these B_6 octahedra are linked together in all 6 orthogonal directions to give a rigid but open framework which can accommodate large,

⁶ G. WILL and K. H. KOSSOBUTZKI, *J. Less-Common Metals* **47**, 43–8 (1976).

⁷ T. M. DUNCAN, *J. Am. Chem. Soc.* **106**, 2270–5 (1984).

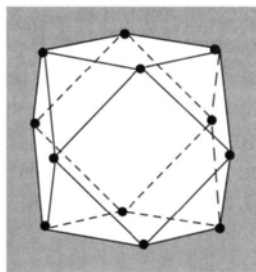


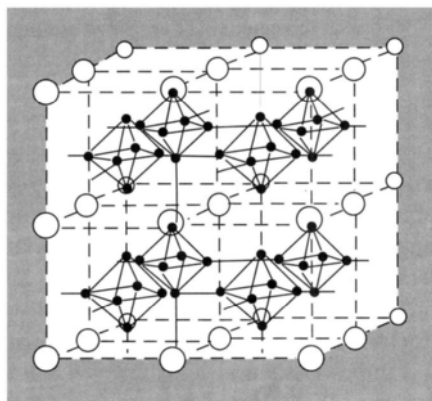
Figure 6.9 B_{12} Cubo-octahedral cluster as found in MB_{12} . This B_{12} cluster alternates with M atoms on an fcc lattice as in NaCl, the B_{12} cluster replacing Cl.

electropositive metal atoms at the corners of the interpenetrating cubic sublattice. The rigidity of the B framework is shown by the very small linear coefficient of thermal expansion of hexaborides ($6-8 \times 10^{-6} \text{ deg}^{-1}$) and by the narrow range of lattice constants of these phases which vary by only 4% (410–427 pm), whereas the diameters of the constituent metal atoms vary by 25% (355–445 pm). Bonding theory for isolated groups such as $B_6H_6^{2-}$ (p. 160) requires the transfer of 2 electrons to the borane cluster to fill all the bonding MOs; however, complete

transfer of 2e per B_6 unit is not required in a three-dimensional crystal lattice and calculations for MB_6 (Ca, Sr, Ba) indicate the transfer of only 0.9–1.0e.⁽⁸⁾ This also explains why metal-deficit phases $M_{1-x}B_6$ remain stable and why the alkali metals (Na, K) can form hexaborides. The $M^{II}B_6$ hexaborides (Ca, Sr, Ba, Eu, Yb) are semiconductors but $M^{III}B_6$ and $M^{IV}B_6$ ($M^{III} = Y, La, \text{lanthanides}$; $M^{IV} = Th$) have a high metallic conductivity at room temperature ($10^4 - 10^5 \text{ ohm}^{-1} \text{ cm}^{-1}$).

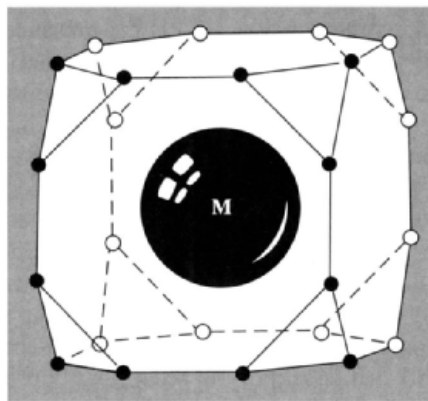
The “radius” of the 24-coordinate metal site in MB_6 is too large (215–225 pm) to be comfortably occupied by the later (smaller) lanthanide elements Ho, Er, Tm and Lu, and these form MB_4 instead, where the metal site has a radius of 185–200 pm. The structure of MB_4 (also formed by Ca, Y, Mo and W) consists of a tetragonal lattice formed by chains of B_6 octahedra linked along the c -axis and joined laterally by pairs of B_2 atoms in the xy plane so as to form a 3D skeleton with tunnels along the c -axis that are filled by metal atoms (Fig. 6.11). The pairs of boron atoms are thus surrounded by trigonal prisms of

⁸ P. G. PERKINS, pp. 31–51 in ref. 2.



○ Metal
● Boron

(a)



● Boron
○

(b)

Figure 6.10 Cubic MB_6 showing (a) boron octahedra (B–B in range 170–174 pm), and (b) 24-atom coordination polyhedron around each metal atom.