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37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe																																																
55	Cs	56	Ba	57	La	58	Hf	59	Ta	60	W	61	Re	62	Os	63	Ir	64	Pt	65	Au	66	Hg	67	Tl	68	Pb	69	Bi	70	Po	71	At	72	Rn																																																
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7

Aluminium, Gallium, Indium and Thallium

7.1 Introduction

Aluminium derives its name from alum, the double sulfate $KAl(SO_4)_2 \cdot 12H_2O$, which was used medicinally as an astringent in ancient Greece and Rome (Latin *alumen*, bitter salt). Humphry Davy was unable to isolate the metal but proposed the name “aluminum” and then “aluminium”; this was soon modified to aluminium and this form is used throughout the world except in North America where the ACS decided in 1925 to adopt “aluminum” in its publications. The impure metal was first isolated by the Danish scientist H. C. Oersted using the reaction of dilute potassium amalgam on $AlCl_3$. This method was improved in 1827 by H. Wöhler who used metallic potassium, but the first commercially successful process was devised by H. St.-C. Deville in 1854 using sodium. In the same year both he and R. W. Bunsen independently obtained metallic aluminium by electrolysis of fused $NaAlCl_4$. So precious was the metal at this time that it was exhibited next to the crown jewels at the Paris Exposition of 1855 and the Emperor Louis Napoleon

III used Al cutlery on state occasions. The dramatic thousand-fold drop in price which occurred before the end of the century (Table 7.1) was due first to the advent of cheap electric power following the development of the dynamo by W. von Siemens in the 1870s, and secondly to the independent development in 1886 of the electrolysis of alumina dissolved in cryolite (Na_3AlF_6) by P. L. T. Héroult in France and C. M. Hall in the USA; both men were 22 years old at the time. World production rose quickly and in 1893 exceeded 1000 tonnes pa for the first time.

Gallium was predicted as eka-aluminium by D. I. Mendeleev in 1870 and was discovered by P. E. Lecoq de Boisbaudran in 1875 by means of the spectroscope; de Boisbaudran was, in fact, guided at the time by an independent theory of his own and had been searching for the missing element for some years. The first indications came with the observation of two new violet lines in the spark spectrum of a sample deposited on zinc, and within a month he had isolated 1 g of the metal starting from several hundred kilograms of crude zinc blende ore. The

Table 7.1 Price of aluminium metal (\$ per kg)

1852	1854	1855	1856	1857	1858	1886	
1200	600	250	75	60	25	17	
→ Introduction of St. C. Deville's Na/AlCl ₃ process							
1888	1890	1895	1900	1950	1965	1980	1989
11.5	5.0	1.15	0.73	0.40	0.54	1.53	1.94
→ Introduction of Héroult-Hall electrolysis				↑ minimum			

Table 7.2 Comparison of predicted and observed properties of gallium

Mendeleev's predictions (1871) for eka-aluminium, M	Observed properties (1993) of gallium (discovered 1875)
Atomic weight ~68	Atomic weight 69.723
Density/g cm ⁻³ 5.9	Density/g cm ⁻³ 5.904
MP low	MP/°C 29.767
Non-volatile	Vapour pressure 10 ⁻³ mmHg at 1000°C
Valence 3	Valence 3
M will probably be discovered by spectroscopic analysis	Ga was discovered by means of the spectroscope
M will have an oxide of formula M ₂ O ₃ , <i>d</i> 5.5 g cm ⁻³ , soluble in acids to give MX ₃	Ga has an oxide Ga ₂ O ₃ , <i>d</i> 5.88 g cm ⁻³ , soluble in acids to give salts of the type GaX ₃
M should dissolve slowly in acids and alkalis and be stable in air	Ga metal dissolves slowly in acids and alkalis and is stable in air
M(OH) ₃ should dissolve in both acids and alkalis	Ga(OH) ₃ dissolves in both acids and alkalis
M salts will tend to form basic salts; the sulfate should form alums; M ₂ S ₃ should be precipitated by H ₂ S or (NH ₄) ₂ S; anhydrous MCl ₃ should be more volatile than ZnCl ₂	Ga salts readily hydrolyse and form basic salts; alums are known; Ga ₂ S ₃ can be precipitated under special conditions by H ₂ S or (NH ₄) ₂ S; anhydrous GaCl ₃ is more volatile than ZnCl ₂

element was named in honour of France (Latin *Gallia*) and the striking similarity of its physical and chemical properties to those predicted by Mendeleev (Table 7.2) did much to establish the general acceptance of the Periodic Law (p. 20); indeed, when de Boisbaudran first stated that the density of Ga was 4.7 g cm⁻³ rather than the predicted 5.9 g cm⁻³, Mendeleev wrote to him suggesting that he redetermine the figure (the correct value is 5.904 g cm⁻³).

Indium and thallium were also discovered by means of the spectroscope as their names indicate. Indium was first identified in 1863 by F. Reich and H. T. Richter and named from the brilliant indigo blue line in its flame spectrum (Latin *indicum*). Thallium was discovered independently by W. Crookes and by

C. A. Lamy in the preceding year 1861/2 and named after the characteristic bright green line in its flame spectrum (Greek *θαλλός*, *thallos*, a budding shoot or twig).

7.2 The Elements

7.2.1 Terrestrial abundance and distribution

Aluminium is the most abundant metal in the earth's crust (8.3% by weight); it is exceeded in abundance only by O (45.5%) and Si (25.7%), and is approached only by Fe (6.2%) and Ca (4.6%). Aluminium is a major constituent of many common igneous minerals including

feldspars and micas. These, in turn, weather in temperate climates to give clay minerals such as kaolinite [$\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$], montmorillonite and vermiculite (p. 349). It also occurs in many well-known though rarer minerals such as cryolite (Na_3AlF_6), spinel (MgAl_2O_4), garnet [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$], beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$), and turquoise [$\text{Al}_2(\text{OH})_3\text{PO}_4\text{H}_2\text{O}/\text{Cu}$]. Corundum (Al_2O_3) is one of the hardest substances known and is therefore used as an abrasive; many gemstones are impure forms of Al_2O_3 , e.g. ruby (Cr), sapphire (Co), oriental emerald, etc. Commercially, the most important mineral is bauxite $\text{AlO}_x(\text{OH})_{3-2x}$ ($0 < x < 1$); this occurs in a wide belt in tropical and subtropical regions as a result of the leaching out of both silica and various metals from aluminosilicates (see Panel).

Gallium, In and Tl are very much less abundant than Al and tend to occur at low concentrations in sulfide minerals rather than as oxides, though Ga is also found associated with Al in bauxite. Ga (19 ppm) is about as abundant as N, Nb, Li and Pb; it is twice as abundant as B (9 ppm) but is more difficult to extract because of the absence of major Ga-containing ores. The highest concentrations (0.1–1%) are in the rare mineral germanite (a complex sulfide of Zn, Cu, Ge and As); concentrations in sphalerite (ZnS), bauxite or coal, are a hundredfold less. Gallium always occurs in association either with Zn or Ge, its neighbours in the periodic table, or with Al in the same group. It was formerly recovered from

flue dusts emitted during sulfide roasting or coal burning (up to 1.5% Ga) but is now obtained as a byproduct of the vast Al industry. Since bauxites contain 0.003–0.01% Ga, complete recovery would yield over 1000 tonnes pa. However, present consumption, though growing rapidly, is little more than 1% of this and production is of the order of 50 tonnes pa (1986). This can be compared with the estimate of 5 tonnes for the total of Ga metal in the 90 y following its discovery (1875–1965). Its price in 1928 was \$50 per g; in 1965 it was \$1 per g, similar to the then price of gold (\$1.1 per g), and in 1986 it was \$0.45 per g, i.e. \$450/kg for semiconductor grade metal (99.9999%).

Indium (0.24 ppm) is similar in abundance to Sb and Cd, whereas Tl (0.7 ppm) is close to Tm and somewhat less abundant than Mo, W and Tb (1.2 ppm). Both elements are chalcophiles (p. 648), indium tending to associate with the similarly sized Zn in its sulfide minerals whilst the larger Tl tends to replace Pb in galena, PbS. Thallium(I) has a similar radius to Rb^+ and so also concentrates with this element in the late magmatic potassium minerals such as feldspars and micas.

Indium is now commercially recovered from the flue dusts emitted during the roasting of Zn/Pb sulfide ores and can also be recovered during the roasting of Fe and Cu sulfide ores. Before 1925 only 1 g of the element was available in the world but production now exceeds 80 000 000 g

Bauxite

The mixed aluminium oxide hydroxide mineral bauxite was discovered by P. Berthier in 1821 near Les Baux in Provence. In temperate countries (such as Mediterranean Europe) it occurs mainly as the "monohydrate" AlOOH (boehmite and diaspore) whereas in the tropics it is generally closer to the "trihydrate" $\text{Al}(\text{OH})_3$ (gibbsite and hydrargillite). Since AlOOH is less soluble in aqueous NaOH than is $\text{Al}(\text{OH})_3$, this has a major bearing on the extraction process for Al manufacture (p. 219). Typical compositions for industrially used bauxites are Al_2O_3 40–60%, combined H_2O 12–30%, SiO_2 free and combined 1–15%, Fe_2O_3 7–30%, TiO_2 3–4%, F, P_2O_5 , V_2O_5 , etc., 0.05–0.2%.

World production in 1989 was over 101 million tonnes and this is still increasing. Reserves are immense, being of the order of 22×10^9 tonnes in all (Guinea 5.6, Australia 4.4, Brazil 2.8, Jamaica 2.0, India 1.0, USA 0.038 Gt). Australia is currently the largest producer of alumina with 36.6%, followed by Guinea 16.6%, Brazil 8.7%, Jamaica 8.2% the former Soviet Union 4.6%, India 3.9%, etc. Bauxite is easy to mine by open-cast methods since it occurs typically in broad layers 3–10 m thick with very little topsoil or other overburden. Apart from its preponderant use (>80%) in Al extraction, bauxite is used to manufacture refractories, high-alumina cements and aluminium compounds, and smaller amounts are used as drying agents and as catalysts in the petrochemicals industry.

(i.e. 80 tonnes) each year. Prices have fluctuated widely during the past 20 years, being \$270/kg for 99.97% purity in 1987.

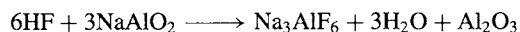
Thallium is likewise recovered from flue dusts emitted during sulfide roasting for H₂SO₄ manufacture, and from the smelting of Zn/Pb ores. Extraction procedures are complicated because of the need to recover Cd at the same time. There are no major commercial uses for Tl metal; world production in 1983 was estimated to be 5–15 tonnes p.a. and the price ranged from \$60 to \$80 per kg depending on purity and amount purchased.

7.2.2 Preparation and uses of the metals ⁽¹⁾

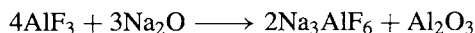
The huge difference in scale between the production of Al metal, on the one hand, and the other elements in the group is clear from the preceding section. The tremendous growth of the Al industry compared with all other non-ferrous metals is indicated in Table 7.3 and Al production is now exceeded only by that of iron and steel (p. 1072).

Production of Al metal involves two stages: (a) the extraction, purification and dehydration of bauxite, and (b) the electrolysis of Al₂O₃ dissolved in molten cryolite Na₃AlF₆. Bauxite is now almost universally treated by the Bayer process; this involves dissolution in aqueous NaOH, separation from insoluble impurities (red muds), partial precipitation of the trihydrate

and calcining at 1200°. Bauxites approximating to the “monohydrate” AlOOH require higher concentrations of NaOH (200–300 g l⁻¹) and higher temperatures and pressures (200–250°C, 35 atm) than do bauxites approximating to Al(OH)₃ (100–150 g l⁻¹ NaOH, 120–140°C). Electrolysis is carried out at 940–980°C in a carbon-lined steel cell (cathode) with carbon anodes. Originally Al₂O₃ was dissolved in molten cryolite (Héroult–Hall process) but cryolite is a rather rare mineral and production from the mines in Greenland provide only about 30 000 tonnes pa, quite insufficient for world needs. Synthetic cryolite is therefore manufactured in lead-clad vessels by the reaction of HF on sodium aluminate (from the Bayer process):



No further cryolite is actually needed once the smelting process is in operation because it is produced in the reduction cells by neutralizing the Na₂O brought into the cell as an impurity in the alumina using AlF₃:



Thus operating cells need AlF₃ rather than cryolite, much of it being produced in a fluidized bed reactor from gaseous HF and activated alumina (made by partially calcining the alumina hydrate from the Bayer process). Typical electrolyte composition ranges are Na₃AlF₆ (80–85%), CaF₂ (5–7%), AlF₃ (5–7%), Al₂O₃ (2–8% — intermittently recharged). See also p. 70 for the beneficial use of Li₂CO₃. The detailed electrolysis mechanism is still imperfectly understood but typical operating conditions require up to 10⁵ A at 4.5 V and a current density of 0.7 A cm⁻². One tonne Al metal requires 1.89 tonnes Al₂O₃, ~0.45 tonnes C anode material, 0.07 tonnes Na₃AlF₆ and about 15 000 kWh of electrical energy. It follows that cheap electric power is the overriding commercial consideration. World production (1988) exceeded 17 million tonnes pa, the leading producers being the USA (23%), China (21%), the former Soviet Union (14%), Canada (9%), Australia (7%),

Table 7.3 World production of some non-ferrous metals/million tonnes pa

Metal	1900	1950	1970	1980	1988
Al	0.0057	1.52	9.78	16.04	17.30
Cu	0.50	2.79	6.38	6.08	5.96
Zn	0.48	1.96	5.10	6.15	7.22
Pb	0.88	1.75	4.00	5.40	3.37

¹ *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 2, Aluminium and aluminium alloys, pp. 184–251; Aluminium compounds, pp. 252–345. Interscience, New York, 1992.

Brazil, Norway and Czechoslovakia (5% each). In addition to this primary production, recycling of used alloys probably adds a further 3–4 million tonnes pa to the total Al metal consumed.

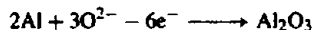
Some uses of Al and its alloys are noted in the Panel from which it will be seen that many of

the mechanical properties of pure Al are greatly improved by alloying it with Cu, Mn, Si, Mg or Zn (Table A). The example of Cu is particularly important because of the insight which it gives into the subtle solid-state diffusion processes that occur during heat treatment. At room temperature

Some Uses of Aluminium Metal and Alloys

Pure aluminium is a silvery-white metal with many desirable properties: it is light, non-toxic, of pleasing appearance, and capable of taking a high polish. It has a high thermal and electrical conductivity, excellent corrosion resistance, is non-magnetic, non-sparking and stands second only to gold for malleability and sixth for ductility. Many of its alloys have high mechanical and tensile strength. Aluminium and its alloys can be cast, rolled, extruded, forged, drawn or machined, and they are readily obtained as pipes, tubes, rods, bars, wires, plates, sheets or foils.

Aluminium resists corrosion not because of its position in the electrochemical series but because of the rapid formation of a coherent, inert, oxide layer. Contact with graphite, Fe, Ni, Cu, Ag or Pb is disastrous for corrosion resistance; the effect of contact with steel, Zn and Cd depends on pH and exposure conditions. Protection is enhanced by anodizing the metal; this involves immersing it in 15–20% H₂SO₄ and connecting it to the positive terminal so that it becomes coated with alumina:



A layer 10–20 μm thick gives excellent protection between pH 4.5–8.7 and is also adequate for external architectural use; thicker layers (50–100 μm) also impart abrasion resistance. The layer can be coloured by incorporating suitable organic or inorganic compounds in the bath and incorporation of photosensitive material enables photographic images to be developed. Decorative engraving using solutions of nitrate or NH₄HF₂ gives the metal a fine silky texture.

Table A Some aluminium alloys

1000 Series:	Commercially pure Al (<1% of other elements); good properties except for limited mechanical strength. Used in chemical equipment, reflectors, heat exchangers, buildings and decorative trim.
2000 Series:	Cu alloys (~5%); excellent strength and machinability, limited corrosion resistance. Used for components requiring high strength/weight ratio, e.g. truck trailer panels, aircraft structure parts.
3000 Series:	Mn alloys (~1.2%); moderate strength, high workability. Used for cooking utensils, heat exchangers, storage tanks, awnings, furniture, highway signs, roofing, side panels, etc.
4000 Series:	Si alloys (≤12%); low mp and low coefficient of expansion. Used for castings and as filler material for brazing and welding; readily anodized to attractive grey colours.
5000 Series:	Mg alloys (0.3–5%); good strength and weldability coupled with excellent corrosion resistance in marine atmospheres. Used for ornamental and decorative trim, street light standards, ships, boats, cryogenic vessels, gun mounts and crane parts.
6000 Series:	Mg/Si alloys; good formability and high corrosion resistance. Used in buildings, transportation equipment, bridges, railings and welded construction.
7000 Series:	Zn alloys (3–8%) plus Mg; when heat treated and aged have very high strength. Used principally for aircraft structures, mobile equipment and equipment requiring high strength/weight ratio.

Many of the uses listed in Table A are a matter of everyday observation. In addition we may note that the electrical conductivity of pure Al is 63.5% of the conductivity of an equal *volume* of pure Cu; when the lower density of Al is considered its conductivity is 2.1 times that of Cu on a wt. for wt. basis. This, coupled with its corrosion resistance and ready workability makes it an ideal metal for power lines and, indeed, more than 90% of all overhead electrical transmission lines in the USA are Al alloy.

Aluminium is now extensively used in the construction and aerospace industries throughout the world although in the USA packaging has replaced the construction industry as the largest consumer of Al and its alloys. For example, 95% of beer and soft drinks is packaged in two-piece cans comprising an Al/Mn alloy body and Al/Mg alloy ends. There is also extensive use in food packaging, aerosol cans, collapsible tubes for toiletries and pharmaceuticals and as foil (typically 0.18 mm thick).

Al dissolves only about 0.1% Cu and this has little effect on its properties. The solubility rises to a maximum of 5.65% Cu at 548°C and this remains in metastable solid solution to give a soft workable alloy when the alloy is rapidly quenched to temperatures below 65°. Subsequent ageing of the shaped material at 100–150° for a few minutes hardens the alloy due to the formation of Guinier–Preston zones: these zones, independently discovered in 1938 by A. Guinier (France) and G. D. Preston (England), are minute discs of material higher in Cu content than the matrix — they are about 4 atoms thick and up to 100 atoms across; they mesh coherently with the host lattice in two directions, the (100) planes, but not in the third. The coherency strains which thereby develop in the lattice are the basis for the hardening of the alloy. Besides its immense technological importance, this phenomenon is particularly significant in being one of the first recognized examples of a single phase which nevertheless varies regularly in composition throughout its extent.

Gallium metal is now obtained as a byproduct of the Al industry. The Bayer process for obtaining alumina from bauxite gradually enriches the alkaline solutions from an initial weight ratio Ga/Al of about 1/5000 to about 1/300; electrolysis of these extracts with an Hg electrode gives further concentration, and the solution of sodium gallate is then electrolysed with a stainless steel cathode to give Ga metal. Ultra high-purity Ga for semiconductor uses is obtained by further chemical treatment with acids and O₂ at high temperatures followed by crystallization and zone refining. Gallium has a beautiful silvery blue appearance; it wets glass, porcelain, and most other surfaces (except quartz, graphite, and teflon) and forms a brilliant mirror when painted on to glass. Its main use is in semiconductor technology (p. 258). For example, GaAs (isoelectronic with Ge) can convert electricity directly into coherent light (laser diodes) and is employed in electroluminescent light-emitting diodes (LEDs); it is also used for doping other semiconductors and in solid-state devices such as transistors.

The compound MgGa₂O₄, when activated by divalent impurities such as Mn²⁺, is used in ultraviolet-activated powders as a brilliant green phosphor. Another very important application is to improve the sensitivity of various bands used in the spectroscopic analysis of uranium. Minor uses are as high-temperature liquid seals, manometric fluids and heat-transfer media, and for low-temperature solders.

Indium, like Ga, is normally recovered by electrolysis after prior concentration in processes leading primarily to other elements (Pb/Zn). It is a soft, silvery metal with a brilliant lustre and (like Sn) it gives out a high-pitched “cry” when bent. Formerly it was much used to protect bearings against wear and corrosion but the pattern of use has been changing in recent years and now its most important applications are in low-melting alloys and in electronic devices. Thus meltable safety devices, heat regulators, and sprinklers use alloys of In with Bi, Cd, Pb and Sn (mp 50–100°C) and In-rich solders are valuable in sealing metal-nonmetal joints in high vacuum apparatus. Indium is of particular importance in the manufacture of p–n–p transistor junctions in Ge (p. 369) and to solder semiconductor leads at low temperature; the softness of the metal also minimizes stress in the Ge during subsequent cooling. So-called III–V semiconductors like InAs and InSb are used in low-temperature transistors, thermistors and optical devices (photoconductors), and InP is used for high-temperature transistors. A further minor use, which exploits the high neutron capture cross-section of In, is as a component in control rods for certain nuclear reactors.

Technical grade Tl is purified from other flue-dust elements (Ni; Zn, Cd; In; Ge, Pb; As; Se, Te) by dissolving it in warm dilute acid, then precipitating the insoluble PbSO₄ and adding HCl to precipitate TlCl. Further purification is effected by electrolysing Tl₂SO₄ in dilute H₂SO₄ with short Pt wire electrodes, followed by fusion of the deposited Tl metal at 350–400°C under an atmosphere of H₂. Both the element and its compounds are extremely toxic; skin-contact, ingestion and inhalation are all dangerous, and

the maximum allowable concentration of soluble Tl compounds in air is 0.1 mg m^{-3} . In this context the position of Tl in the periodic table will be noted — it occurs between two other poisonous heavy metals Hg and Pb. Tl_2SO_4 was formerly widely used as a rodenticide and ant killer but it is both odourless and tasteless and is now banned in many countries as being too dangerous for general use. Many suggestions have been made for the use of Tl compounds in industry but none have been substantially developed. A few specialist uses have emerged in infrared technology since TlBr and TlI are transparent to long wavelengths, and there are possibilities for photosensitive diodes and infrared detectors. The very high density of aqueous solutions of Tl formate and malonate have found application in the small-scale separation of minerals and the determination of their densities; a saturated solution containing approximately equal weights of these salts (Clerici's solution) has a density of 4.324 g cm^{-3} at 20° and progressively lower densities can be obtained by dilution.

7.2.3 Properties of the elements

The atomic properties of the Group 13 elements (including boron) are compared in Table 7.4. All have odd atomic numbers and correspondingly few stable isotopes. The varying precision of

atomic weights has been discussed (p. 17). The electronic configuration is ns^2np^1 in each case but the underlying core varies considerably: for B and Al it is the preceding noble gas core, for Ga and In it is noble gas plus d^{10} , and for Tl noble gas plus $4f^{14}5d^{10}$. This variation has a substantial influence on the trends in chemical properties of the group and is also reflected in the ionization energies of the elements. Thus, as shown in Fig. 7.1, the expected decrease from B to Al is not followed by a further decrease to Ga because of the "d-block contraction" in atomic size and the higher effective nuclear charge for this element which stems from the fact that the 10 added d electrons do not completely shield the extra 10 positive charges on the nucleus. Similarly, the decrease between Ga and In is reversed for Tl as a result of the further influence of the f block or lanthanide contraction. It is notable that these irregularities for the Group 13 elements do not occur for the Group 3 elements Sc, Y and La, which show a steady decrease in ionization energy from B and Al, all 5 elements having the same type of underlying core (noble gas). This has a decisive influence on the comparative chemistry of the two subgroups.

Boron is a covalently bonded, refractory, non-metallic insulator of great hardness and is thus not directly comparable in its physical properties with Al, Ga, In and Tl, which are all low-melting, rather soft metals having a very low electrical

Table 7.4 Atomic properties of Group 13 elements

Property	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
No. of naturally occurring isotopes	2	1	2	2	2
Atomic weight	10.811(7)	26.981538(2)	69.723(1)	114.818(3)	204.3833(2)
Electronic configuration	$[\text{He}]2s^22p^1$	$[\text{Ne}]3s^23p^1$	$[\text{Ar}]3d^{10}4s^24p^1$	$[\text{Kr}]4d^{10}5s^25p^1$	$[\text{Xe}]4f^{14}5d^{10}6p^1$
Ionization energy/ kJ mol^{-1}					
I	800.6	577.5	578.8	558.3	589.4
II	2427.1	1816.7	1979.3	1820.6	1971.0
III	3659.7	2744.8	2963	2704	2878
Metal radius/pm	(80–90)	143	135 (see text)	167	170
Ionic radius/pm (6-coord.)					
III	27 ^(a)	53.5	62.0	80.0	88.5
I	—	—	120	140	150

^(a)Nominal "ionic" radius for B^{III} .

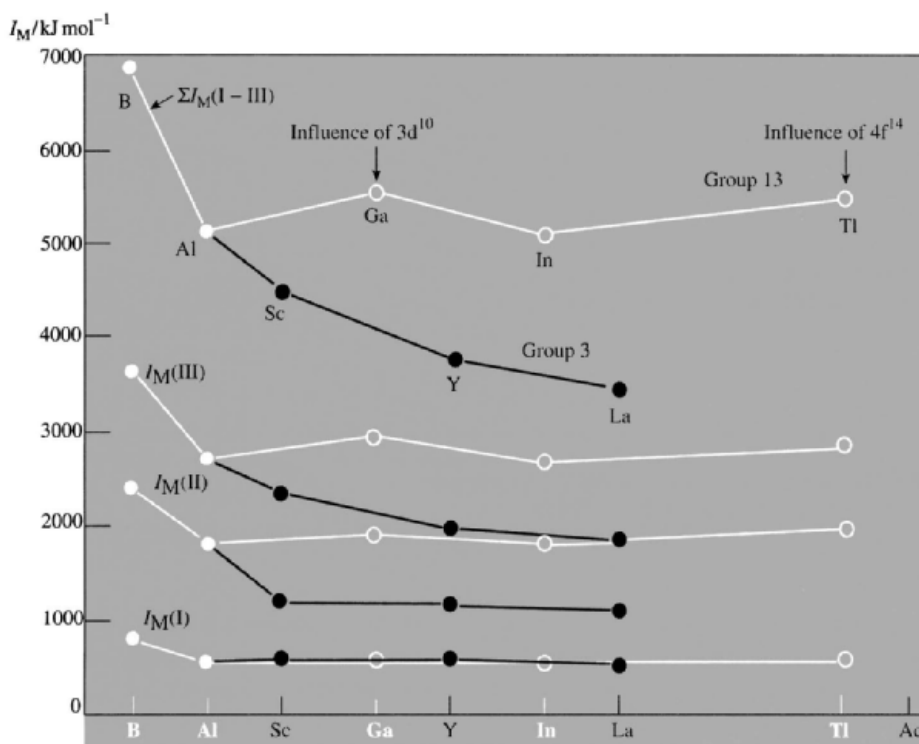


Figure 7.1 Trends in successive ionization energies $I_M(\text{I})$, $I_M(\text{II})$, and $I_M(\text{III})$, and their sum Σ for elements in Groups 3 and 13.

resistivity (Table 7.5). The heats of fusion and vaporization of the metals are also much lower than those of boron and tend to decrease with increasing atomic number. In all these properties the metals resemble the neighbouring metals Zn, Cd, Hg; Sn, Pb, etc., and it is probable that in each case the properties are related to the rather small number of electrons available for metallic bonding. Some have seen this as a manifestation of the "inert-pair effect" (see p. 226). The interatomic distances in these elements are also somewhat longer than expected from general trends.

The crystal structure of Al is fcc, typical of many metals, each Al being surrounded by 12 nearest neighbours at 286 pm. Thallium also has a typical metallic structure (hcp) with 12 nearest neighbours at 340 pm. Indium has an unusual structure which is slightly distorted from a regular close-packed arrangement: the structure is face-centred tetragonal and each In has 4 neighbours

at 324 pm and 8 at the slightly greater distance of 336 pm. Gallium has a unique orthorhombic (pseudotetragonal) structure in which each Ga has 1 very close neighbour at 244 pm and 6 further neighbours, 2 each at 270, 273 and 279 pm. The structure is very similar to that of iodine and the appearance of pseudo-molecules Ga_2 may result from partial pair-wise interaction on neighbouring atoms of the single p electron outside the $[\text{Ar}]3d^{10}4s^2$ core which immediately follows the first transition series. As such it can be compared with Hg which also has a very low mp and completes the $[\text{Xe}]4f^{14}5d^{10}6s^2$ "pseudo-noble-gas" configuration following the lanthanide elements. Note that all interatomic contacts in metallic Ga are less than those in Al, again emphasizing the presence of a "d-block contraction". Gallium is also unusual in contracting on melting, the volume of the liquid phase being 3.4% less than that of the solid; the

Table 7.5 Physical properties of Group 13 elements

Property	B	Al	Ga	In	Tl
MP/°C	2092	660.45	29.767	156.63	303.5
BP/°C	4002	2520	2205	2073	1473
Density (20°C)/g cm ⁻³	2.35	2.699	5.904	7.31	11.85
Hardness (Mohs)	11	2.75	1.5	1.2	1.2–1.3
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	50.2	10.71	5.56	3.28	4.21
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	480	294	254	232	166
ΔH_{f} (monoatomic gas)/kJ mol ⁻¹	560	329.7	286.2	243	182.2
Electrical resistivity/ $\mu\text{ohm cm}$	6.7×10^{11}	2.655	$\sim 27^{(a)}$	8.37	18
$E^\circ(\text{M}^{3+} + 3\text{e}^- = \text{M}(\text{s}))/\text{V}$	-0.890 ^(b)	-1.676	-0.529	-0.338	+1.26 ^(c)
$E^\circ(\text{M}^+ + \text{e}^- = \text{M}(\text{s}))/\text{V}$	—	0.55	-0.79(acid) -1.39(alkali)	-0.18	-0.336
Electronegativity χ	2.0	1.5	1.6	1.7	1.8

^(a)The resistivity of crystalline Ga is markedly anisotropic, the values in the three orthorhombic directions being a 17.5, b 8.20, c 55.3 $\mu\text{ohm cm}$. The resistivity of liquid Ga at 30° is 25.8 $\mu\text{ohm cm}$.

^(b) E° for reaction $\text{H}_3\text{BO}_3 + 3\text{H}^+ + 3\text{e}^- = \text{B}(\text{s}) + 3\text{H}_2\text{O}$.

^(c)This is the observed value for $E^\circ(\text{Tl}^{3+}/\text{Tl}^+)$, hence the calculated value for the corresponding $E^\circ(\text{Tl}^{3+}/\text{Tl}(\text{s}))$ is +0.73 V.

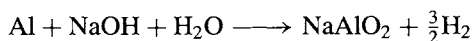
same phenomenon occurs with the next element in the periodic table Ge, and also with Sb and Bi, in addition to the well-known example of H₂O. In each case, a structural feature in the solid is broken down to permit more efficient packing of atoms in the liquid state.

The standard electrode potentials of the heavier Group 13 elements reflect the decreasing stability of the +3 oxidation state in aqueous solution and the tendency, particularly of Tl, to form compounds in the +1 oxidation state (p. 226). The trend to increasing electropositivity of the group oxidation state which was noted for Groups 1 and 2 does not occur with Group 13 but is found, as expected, in Group 3 (Fig. 7.2). Similarly, the steady decrease in electronegativity in the series B > Al > Sc > Y > La > Ac is reversed in Group 13 and there is a steady *increase* in electronegativity from Al to Tl.

7.2.4 Chemical reactivity and trends

The Group 13 metals differ sharply from the non-metallic element boron both in their greater chemical reactivity at moderate temperatures and in their well-defined cationic chemistry for aqueous solutions. The absence of a range of

volatile hydrides and other cluster compounds analogous to the boranes and carboranes is also notable. Aluminium combines with most non-metallic elements when heated to give compounds such as AlN, Al₂S₃, AlX₃, etc. It also forms intermetallic compounds with elements from all groups of the periodic table that contain metals. Because of its great affinity for oxygen it is used as a reducing agent to obtain Cr, Mn, V, etc., by means of the thermite process of J. W. Goldschmidt. Finely powdered Al metal explodes on contact with liquid O₂, but for normal samples of the metal a coherent protective oxide film prevents appreciable reaction with oxygen, water or dilute acids; amalgamation with Hg or contact with solutions of salts of certain electropositive metals destroys the film and permits further reaction. Aluminium is also readily soluble in hot concentrated hydrochloric acid and in aqueous NaOH or KOH at room temperature with liberation of H₂. This latter reaction is sometimes written as



though it is likely that the species in solution is the hydrated tetrahydroxaluminate anion $[\text{Al}(\text{OH})_4]^-$ (aq) or $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$.

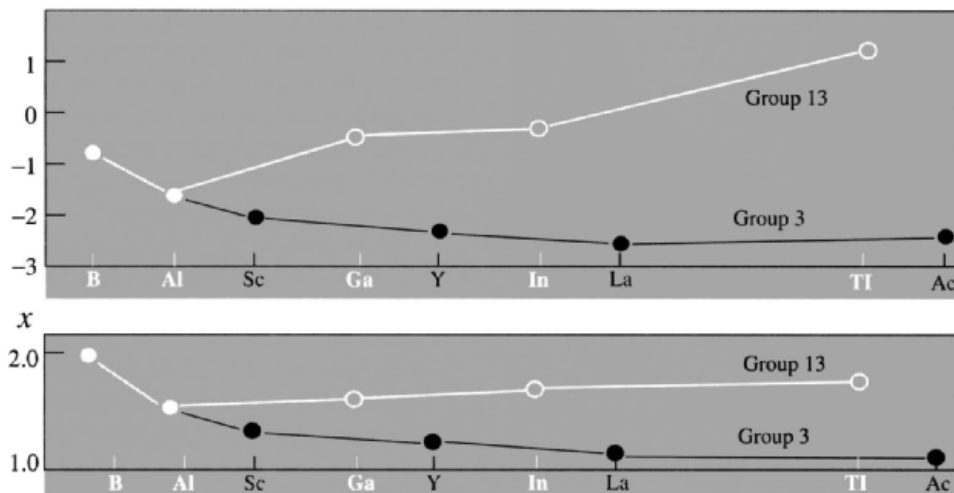
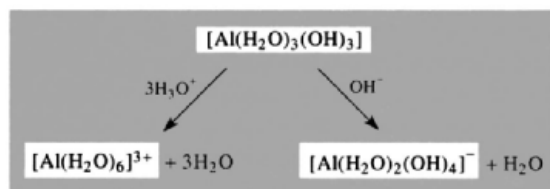
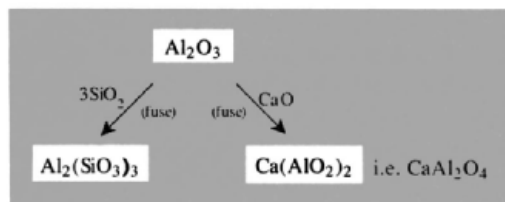
$E^\circ(M^{3+}/M)/V$ 

Figure 7.2 Trends in standard electrode potential E° and electronegativity χ for elements in Groups 3 and 13.

$Al(OH)_3$ is amphoteric, forming both salts and aluminates (Greek ἀμφοτέρως, *amphoterōs*, in both ways). Thus the freshly precipitated hydroxide is readily soluble in both acid and alkali:

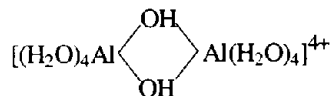


In these reactions the coordination number of Al has been assumed to be 6 throughout though direct evidence on this point is rarely available. Amphoterism is also exhibited in anhydrous reactions, e.g.:



Aluminium compounds of weak acids are extensively hydrolysed to $[Al(H_2O)_3(OH)_3]$ and the corresponding hydride, e.g. $Al_2S_3 \longrightarrow$

$3H_2S$, $AlN \longrightarrow NH_3$, and $Al_4C_3 \longrightarrow 3CH_4$. Similarly, the cyanide, acetate and carbonate are unstable in aqueous solution. Hydrolysis of the halides and other salts such as the nitrate and sulfate is incomplete but aqueous solutions are acidic due to the ability of the hydrated cation $[Al(H_2O)_6]^{3+}$ to act as proton donor giving $[Al(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_4(OH)_2]^+$, etc. If the pH is gradually increased this deprotonation of the mononuclear species is accompanied by aggregation via OH bridges to give species such as



and then to precipitation of the hydrous oxide. This is of particular use in water clarification since the precipitating hydroxide nucleates on fine suspended particles which are thereby thrown out of suspension. Still further increase in pH leads to redissolution as an aluminate (Fig. 7.3). Similar behaviour is shown by Be^{II} , Zn^{II} , Ga^{III} , Sn^{II} , Pb^{II} , etc. A detailed quantitative theory of amphoterism is difficult to construct but it is known that amphoteric behaviour occurs when (a) the cation is weakly basic, (b) its hydroxide

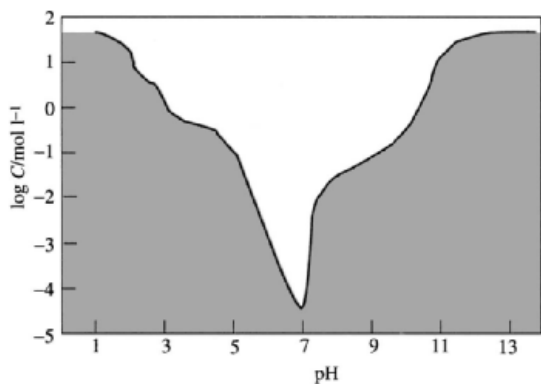
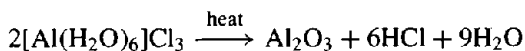


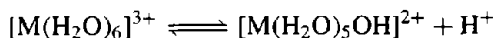
Figure 7.3 Schematic representation of the variation of concentration of an Al salt as a function of pH (see text).

is moderately insoluble, and (c) the hydrated species can also act as proton donors.⁽²⁾

Anhydrous Al salts cannot be prepared by heating the corresponding hydrate for reasons closely related to the amphoterism and hydrolysis of such compounds. For example, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is, in reality, $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ and the strength of the Al–O interaction precludes the formation of Al–Cl bonds:



The amphoteric behaviour of Ga^{III} salts parallels that of Al^{III} ; indeed, Ga_2O_3 is slightly more acidic than Al_2O_3 and solutions of gallates tend to be more stable than aluminates. Consistent with this, $\text{p}K_a$ for the equilibrium



is 4.95 for Al and 2.60 for Ga. Indium is more basic than Ga and is only weakly amphoteric. The metal does not dissolve in aqueous alkali whereas Ga does. This alternation in the sequence of basicity can be related to the electronic and size factors mentioned on p. 222. Thallium behaves as a moderately strong base but is not strictly

comparable with other members of the group because it normally exists as Tl^{I} in aqueous solution. Thus, Tl metal tarnishes readily and reacts with steam or moist air to give TlOH . The electrode potential data in Table 7.5 show that Tl^{I} is much more stable than Tl^{III} in aqueous solution and indicate that Tl^{III} compounds can act as strong oxidizing agents.

Compounds of Tl^{I} have many similarities to those of the alkali metals: TlOH is very soluble and is a strong base; Tl_2CO_3 is also soluble and resembles the corresponding Na and K compounds; Tl^{I} forms colourless, well-crystallized salts of many oxoacids, and these tend to be anhydrous like those of the similarly sized Rb and Cs; Tl^{I} salts of weak acids have a basic reaction in aqueous solution as a result of hydrolysis; Tl^{I} forms polysulfides (e.g. Tl_2S_5) and polyiodides, etc. In other respects Tl^{I} resembles the more highly polarizing ion Ag^+ , e.g. in the colour and insolubility of its chromate, sulfide, arsenate and halides (except F), though it does not form ammine complexes in aqueous solution and its azide is not explosive.

The stability of the +1 oxidation state in Group 13 increases in the sequence $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$, and numerous examples of M^{I} compounds will be found in the following sections. The occurrence of an oxidation state which is 2 less than the group valency is sometimes referred to as the “inert-pair effect” but it is important to recognize that this is a description not an explanation. The phenomenon is quite general among the heavier elements of the p block (i.e. the post-transition elements in Groups 13–16). For example, Sn and Pb commonly occur in both the +2 and +4 oxidation states; P, As, Sb and Bi in the +3 and +5; S, Se, Te and Po in the +2, +4, and +6 states. The term “inert-pair effect” is somewhat misleading since it implies that the energy required to involve the ns^2 electrons in bonding increases in the sequence $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$. Reference to Table 7.4 shows that this is not so (the sequence is, in fact, $\text{In} < \text{Al} < \text{Tl} < \text{Ga}$). The explanation lies rather in the decrease in bond energy with increase in size from Al to Tl so that the energy required

² C. S. G. PHILLIPS and R. J. P. WILLIAMS, *Inorganic Chemistry*, Vol. 1, Chap. 14; Vol. 2, pp. 524–5, Oxford University Press, Oxford, 1966.