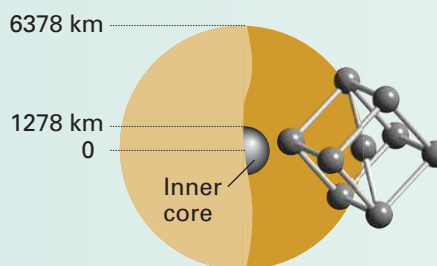


BOX 3.1 Metals under pressure

The Earth has an innermost core about 1200 km in diameter that consists of solid iron and is responsible for generating the planet's powerful magnetic field. The pressure at the centre of the Earth has been calculated to be around 370 GPa (about 3.7 million atm) at a temperature of 5000–6500°C. The polymorph of iron that exists under these conditions has been much debated with information from theoretical calculations and measurements using seismology. The current thinking is that the iron core consists of the body-centred cubic polymorph. It has been proposed that this exists either as a giant crystal or a large number of oriented crystals such that the long diagonal of the bcc unit cell aligns along the Earth's axis of rotation (Fig. B3.1, left).

The study of the structures and polymorphism of an element and compounds under high pressure conditions goes beyond the study of the Earth's core. Hydrogen, when subjected to pressures similar to those at the Earth's core, is predicted to become a metallic solid, similar to the alkali

**Fig. B3.1**

metals, and the cores of planets such as Jupiter have been predicted to contain hydrogen in this form. When pressures of over 55 GPa are applied to iodine the I_2 molecules dissociate and adopt the simple face-centred cubic structure; the element becomes metallic and is a superconductor below 1.2 K.

3.7 Atomic radii of metals

Key point: The Goldschmidt correction converts atomic radii of metals to the value they would have in a close-packed structure with 12-fold coordination.

An informal definition of the atomic radius of a metallic element was given in Section 1.9 as half the distance between the centres of adjacent atoms in the solid. However, it is found that this distance generally increases with the coordination number of the lattice. The same atom in structures with different coordination numbers may therefore appear to have different radii, and an atom of an element with coordination number 12 appears bigger than one with coordination number 8. In an extensive study of internuclear separations in a wide variety of polymorphic elements and alloys, V. Goldschmidt found that the average relative radii are related as shown in Table 3.3.

It is desirable to put all elements on the same footing when comparing trends in their characteristics; that is when comparing the intrinsic properties of their atoms rather than the properties that stem from their environment. Therefore, it is common to adjust the empirical internuclear separation to the value that would be expected if the element were in fact close-packed (with coordination number 12).

■ **A brief illustration.** The empirical atomic radius of Na is 185 pm, but that is for the bcc structure in which the coordination number is 8. To adjust to 12-coordination we multiply this radius by $1/0.97 = 1.03$ and obtain 191 pm as the radius that a Na atom would have if it were in a close-packed structure. ■

Goldschmidt radii of the elements were in fact the ones listed in Table 1.4 as ‘metallic radii’ and used in the discussion of the periodicity of atomic radius (Section 1.9). The essential features of that discussion to bear in mind now, with ‘atomic radius’ interpreted as Goldschmidt-corrected metallic radius in the case of metallic elements, are that metallic radii generally increase down a group and decrease from left to right across a period. As remarked in Section 1.9, trends in atomic radii reveal the presence of the lanthanide contraction in Period 6, with atomic radii of the elements that follow the lanthanoids found to be smaller than simple extrapolation from earlier periods would suggest. As also remarked there, this contraction can be traced to the poor shielding effect of f electrons. A similar contraction occurs across each row of the d block.

EXAMPLE 3.6 Calculating a metallic radius

The cubic unit cell parameter, a , of polonium (α -Po) is 335 pm. Use the Goldschmidt correction to calculate a metallic radius for this element.

Answer We need to infer the radius of the atoms from the dimensions of the unit cell and the coordination number, and then apply a correction to coordination number 12. Because the Po atoms of radius r are in contact along the unit cell edges, the length of the primitive cubic unit cell is $2r$. Thus, the metallic radius of 6-coordinate Po is $a/2$ with $a = 335$ pm. The conversion factor from 6-fold to 12-fold coordination from Table 3.3 ($1/0.960$) gives the metallic radius of Po as $\frac{1}{2} \times 335 \text{ pm} \times 1/0.960 = 174 \text{ pm}$.

Selftest 3.6 Predict the lattice parameter for Po when it adopts a bcc structure.

Table 3.3 The variation of radius with coordination number

Coordination number	Relative radius
12	1
8	0.97
6	0.96
4	0.88

Appendix 6

Van der Waals, metallic, covalent and ionic radii

Data are given for the *s*-, *p*- and first row *d*-block elements. The ionic radius varies with the charge and coordination number of the ion; a coordination number of 6 refers to octahedral coordination, and of 4 refers to tetrahedral unless otherwise specified. Data for the heavier *d*-block metals and the lanthanoids and actinoids are listed in Tables 22.1 and 27.1.

	Element	Van der Waals radius, r_v / pm	Metallic radius for 12-coordinate metal, r_{metal} / pm	Covalent radius, r_{cov} / pm	Ionic radius			
					Ionic radius, r_{ion} / pm	Charge on ion	Coordination number of the ion	
Hydrogen	H	120 [†]		37 [‡]				
Group 1	Li		157		76	1+	6	
	Na		191		102	1+	6	
	K		235		138	1+	6	
	Rb		250		149	1+	6	
	Cs		272		170	1+	6	
Group 2	Be		112		27	2+	4	
	Mg		160		72	2+	6	
	Ca		197		100	2+	6	
	Sr		215		126	2+	8	
	Ba		224		142	2+	8	
Group 13	B	208		88				
	Al		143	130	54	3+	6	
	Ga		153	122	62	3+	6	
	In		167	150	80	3+	6	
	Tl		171	155	89	3+	6	
					159	1+	8	
Group 14	C	185		77				
	Si	210		118				
	Ge			122	53	4+	6	
	Sn		158	140	74	4+	6	
	Pb		175	154	119	2+	6	
					65	4+	4	
				78	4+	6		
Group 15	N	154		75	171	3-	6	
	P	190		110				
	As	200		122				
	Sb	220		143				
	Bi		240	182	152	103	3+	6
						76	5+	6
Group 16	O	140		73	140	2-	6	
	S	185		103	184	2-	6	
	Se	200		117	198	2-	6	
	Te	220		135	211	2-	6	

[†] The value of 120 pm may be an overestimate; an analysis of intermolecular contacts in organic structures suggests a value of 110 pm. See: R.S. Rowland and R. Taylor (1996) *J. Phys. Chem.*, vol. 100, p. 7384.

[‡] Sometimes it is more appropriate to use a value of 30 pm in organic compounds.

Element	Van der Waals radius, r_v / pm	Metallic radius for 12-coordinate metal, r_{metal} / pm	Covalent radius, r_{cov} / pm	Ionic radius			
				Ionic radius, r_{ion} / pm	Charge on ion	Coordination number of the ion	
Group 17	F	135	71	133	1–	6	
	Cl	180	99	181	1–	6	
	Br	195	114	196	1–	6	
	I	215	133	220	1–	6	
Group 18	He	99					
	Ne	160					
	Ar	191					
	Kr	197					
	Xe	214					
First row <i>d</i>-block elements	Sc		164	75	3+	6	
	Ti		147	86 67 61	2+ 3+ 4+	6 6 6	
V		135		79 64 58 53 54 46	2+ 3+ 4+ 4+ 5+ 5+	6 6 6 5 6 5	
	Cr		129	73 80 62	2+ 2+ 3+	6 (low-spin) 6 (high-spin) 6	
		Mn		137	67 83 58 65 39 53	2+ 2+ 3+ 3+ 4+ 4+	6 (low-spin) 6 (high-spin) 6 (low-spin) 6 (high-spin) 4 6
			Fe		126	61 78 55 65	2+ 2+ 3+ 3+
	Co				125	65 75 55 61	2+ 2+ 3+ 3+
		Ni			125	55 44 69 56 60	2+ 2+ 2+ 3+ 3+
Cu				128	46 60 57 73	1+ 1+ 2+ 2+	2 4 4 (square planar) 6
	Zn			137	60 74	2+ 2+	4 6