

9 Bonding between the elements

- 9.1 (a) Discuss the factors which lead to the following trend in bond energies

diatomic	F ₂	Cl ₂	Br ₂	ClF
bond energy / kJ mol ⁻¹	158	242	193	297

- (b) Discuss the factors which lead to the following trend in bond lengths

bond	C-Cl	Si-Cl	Ge-Cl	Sn-Cl
bond length / Å	1.76	2.08	2.13	2.20

- 9.2 Discuss the following observations.

Solid carbon dioxide sublimates at temperatures above $-78\text{ }^{\circ}\text{C}$ to give a gas containing discrete CO₂ molecules.

Solid silicon dioxide has a giant covalent structure. It melts at around $1500\text{ }^{\circ}\text{C}$, and finally boils at temperatures over $2800\text{ }^{\circ}\text{C}$; discrete SiO₂ molecules can be detected in the gas phase.

If CO₂ is subject to extremely high pressures a solid material is produced which appears to have a giant covalent structure in which there are C-O single bonds.

- 9.3 (a) Using the data on orbital energies given below, place the following compounds on the van Arkel diagram: CaCl₂, TiB₂, S₄N₄ and AlN.

element	B	C	N	Al	S	Cl	Ca	Ti
minus valence orbital energy / eV	11.8	15.2	18.8	9.05	15.8	18.2	5.34	8.44

- (b) The following descriptions refer to the properties of the compounds listed above, but not necessarily in the same order.

W brown solid, melting point $2980\text{ }^{\circ}\text{C}$, good conductor

X orange crystals, mp $170\text{ }^{\circ}\text{C}$, soluble in organic solvents

Y white solid, mp $1418\text{ }^{\circ}\text{C}$, insulator, moderately soluble in water

Z white solid, mp $> 2400\text{ }^{\circ}\text{C}$, band gap 6 eV, insulator.

With the aid of the van Arkel diagram, and from your general knowledge, deduce which compound corresponds to which letter, giving brief reasons for your answers.

- 9.4 Pure calcium carbide, CaC₂, is a colourless solid (melting point $2300\text{ }^{\circ}\text{C}$) which does not conduct electricity in the solid state. The structure of CaC₂ is essentially an NaCl-type lattice with alternating Ca²⁺ ions and C₂²⁻ ions. The C-C bond length in these ions is 119.1 pm.

- (a) Use the van Arkel diagram to predict the sort of bonding you might expect to find in calcium carbide (the necessary orbital energies are given in the previous question). Are the properties given above consistent with the position of CaC₂ in the van Arkel diagram?
- (b) Construct an MO diagram for C₂ and use it to explain why the C-C bond length in CaC₂ is considerably shorter than that in gaseous C₂ (131.2 pm).
- (c) Lanthanum carbide, LaC₂, is thought to contain the La³⁺ ion and the C₂³⁻ ion; the C-C bond length in this ion is 130.3 pm. Use your MO diagram to explain why the C-C bond length in LaC₂ is greater than that in CaC₂.

- 9.5 At room temperature *white phosphorus* is an insulating solid. It boils at 280 °C to give a vapour which is a mixture of P₄ and P₂ molecules. If the vapour is condensed, white phosphorus reforms. The P–P bond length in P₂ is 1.90 Å, and in P₄ it is 2.21 Å.

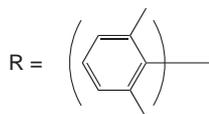
If white phosphorus is held at elevated temperatures for an extended period, various other solid allotropes are formed, none of which boil under 600 °C. One of these allotropes, *black phosphorus*, is a semiconductor.

The α allotropes of arsenic, antimony and bismuth all have similar structures to that of black phosphorus.

- Sketch the structures of P₄ and P₂, and explain their relative bond lengths.
- How would you expect the equilibrium between P₄ and P₂ to vary with temperature?
- Suggest the common structure adopted by black phosphorus and the α allotropes of the other Group 15 elements.
- Explain the differences in the physical properties of the black and white allotropes of phosphorus.
- Rationalize the trends in the bond lengths and bond angles observed in the solid form of the Group 15 elements

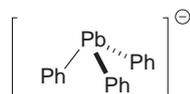
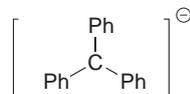
allotrope	black P	α -As	α -Sb	α -Bi
bond length / Å	2.23	2.52	2.91	3.07
bond angle / degree	98.2	96.7	96.6	95.5

- 9.6 (a) The Si–Si bond lengths in (R₂Si)₂ and the *cyclic* compound (R₂Si)₃ are 2.14 Å and 2.40 Å, respectively. Draw the structures of these two compounds and comment on the Si–Si bond orders in each.



- Suggest why naturally occurring carbon may be found in either of two allotropes, whereas silicon exists in only one allotropic form in which the Si–Si bond length is 2.35 Å.
 - The standard enthalpies of sublimation of graphite, diamond and silicon are 715 kJ mol⁻¹, 710 kJ mol⁻¹ and 456 kJ mol⁻¹, respectively. Comment on these values.
 - Explain why silicon is a semiconductor whereas diamond is an electrical insulator.
 - Explain why heating silicon with small quantities of arsenic leads to a new material with higher electrical conductivity than pure silicon.
- 9.7 At high temperatures, calcium metal reacts with silicon to give a salt with empirical formula CaSi₂, and with carbon to give a salt with empirical formula CaC₂. X-ray crystallography reveals that the structures of these two salts are very different: CaC₂ contains discrete C₂²⁻ ions, whereas in CaSi₂ the silicon atoms form sheets of (Si⁻)_n with each silicon having three Si–Si single bonds.
- Which element occurs in a form which is isoelectronic and isostructural with the C₂²⁻ anion, and which element occurs in a form which is isoelectronic and isostructural with the (Si⁻)_n sheets?
 - Why is there such a difference between the structures of the carbon and silicon anions?
 - Calcium and silicon can also react to give a compound with empirical formula CaSi, whose structure is found to contain helical chains of Si atoms. How may the structure of these chains be rationalized?

- 9.8 (a) In the anion Ph_3C^- the Ph–C bonds have a trigonal planar arrangement about the carbon, with the Ph–C–Ph bond angle being 120° . In contrast, in the anion Ph_3Pb^- the Ph–Pb bonds have a trigonal pyramidal arrangement about the Pb, with a Ph–Pb–Ph bond angle of 91° . Comment on the reasons why these two ions have such different structures.



- (b) From your answer to (a), explain why Ph_3C^- is a far stronger base than Ph_3Pb^- .
- 9.9 Discuss the likely reasons for the observation that in going from Sc to Mn the maximum oxidation state shown by successive elements increases steadily, but as we carry on from Fe to Zn there is a steady decrease in the maximum oxidation state for successive elements.