

8 Trends in bonding

- 8.1 Explain the following features and trends of the orbital energies shown in Fig. 8.2 on page 260.
- In going across the second period from Li to Ne the energies of both the $2s$ and $2p$ AOs fall, but the $2s$ AO falls more steeply than the $2p$.
 - On going from Ne to Na there is a large decrease in the energy of the $2p$ AO.
 - The energies of the $2s$ AO in Li, the $3s$ AO in Na and the $4s$ AO in K show a gentle upward trend but in going from Li to Na, and from Na to K the nuclear charge increases by eight.
 - On going from Sc to Zn the energy of the $4s$ AO decreases rather little, but the energy of the $3d$ AO shows a greater fall in energy.
- 8.2 The atomic radii of the lanthanide elements (Ce–Lu) are remarkably similar, varying only by a few pm across all fourteen elements. Use Slater's rules (page 262) to determine the effective nuclear charge experienced by the outer electrons (the $6s$) of these elements, and hence explain why the atomic radii vary so little.
- 8.3 Explain why there is a general increase in atomic radii on moving from the first row transition metals (those in period 4) to the second row (those in period 5), but there is very little change on moving to the third row (those in period 6).
- 8.4 Rationalize the trends in the atomic radii of the Group 2 elements given in the table (the radius given for element 120 is based on a calculation, rather than experiment).

element	Be	Mg	Ca	Sr	Ba	Ra	element 120
radius / pm	112	160	197	215	222	215	200

- 8.5 When metallic gold is exposed to caesium vapour a solid compound with formula CsAu is formed; the solid is a poor conductor of electricity, but the conductivity rises sharply when the solid is molten. Discuss the likely nature of the bonding in this compound. Would you expect to be able to form a similar compound from the reaction of silver with caesium?
- 8.6 Explain the following trends in the bond strengths (in kJ mol^{-1}) of the Group 1 and Group 11 diatomics.

molecule	bond strength	molecule	bond strength
K_2	50	Cu_2	177
Rb_2	47	Ag_2	160
Cs_2	43	Au_2	225

- 8.7 (a) Construct an MO diagram for Be_2 and use it to explain why, although the bond order is zero, $s-p$ mixing results in the the molecule having a weak bond.
- (b) Explain the following observations: (i) the bond strength of Li_2 is 100 kJ mol^{-1} , a value much greater than that for Be_2 ; (ii) the enthalpy of vaporization of solid beryllium is greater than that for solid Li.
- (c) Rationalize the following bond strengths of the Group 12 homonuclear diatomics:

molecule	bond strength / kJ mol^{-1}
Zn_2	29
Cd_2	7
Hg_2	≈ 0

- (d) Suggest why metallic mercury has the lowest enthalpy of vaporization of any metal, and hence why it is a liquid at room temperature.
- 8.8 The common oxidation states of mercury are +1 and +2. While Hg^{2+} ions are found in solution, mercury(I) exists in solution as Hg_2^{2+} . The Hg–Hg bond length in mercury(I) salts is considerably less than the Hg–Hg distance in Hg(l).
- (a) By considering the $6s$ orbitals only, draw a simple MO diagram to explain the bonding in Hg_2^{2+} .
- (b) Would you expect mercury(I) salts to be paramagnetic?
- (c) Identify the species present in the ionic compound $\text{Hg}_3(\text{AlCl}_4)_2$, and describe the bonding in each. [Hint: consider the ions present in the compound.]

- 8.9 The following table gives the bond strengths (kJ mol^{-1}) for the homonuclear diatomics of the p -block.

group	13	14	15	16	17
	B_2	C_2	N_2	O_2	F_2
	297	607	945	498	159
	Al_2	Si_2	P_2	S_2	Cl_2
	133	327	490	425	243
	Ga_2	Ge_2	As_2	Se_2	Br_2
	112	264	382	333	193
	In_2	Sn_2	Sb_2	Te_2	I_2
	100	187	299	260	151
	Tl_2	Pb_2	Bi_2	Po_2	At_2
	64	87	200	187	80

Rationalize the trends in the bond strengths for both crossing the periods and descending the groups. Your answer should include a consideration of the bond orders present in each group.

Why are the bond strengths in Groups 16 and 17 generally greater than those in Groups 14 and 13 respectively? Explain any exceptions to this trend.