

Chapter 5 Exercises

Account for the following observations:

1. Boron trichloride, gallium trichloride and thallium trichloride are, respectively, covalent and monomeric, covalent and dimeric, and ionic.

Answer. The following explanations can be offered to account for these observations:

- (i) The increasingly greater difference in electronegativity ($\Delta\chi$) between Tl and Cl vs Ga and Cl vs B and Cl means that bonds become increasingly more polar down the group, so association is more favoured resulting in a trend from covalent (BCl_3) to polymeric (dimeric in this case) (GaCl_3) to ionic (TlCl_3).
- (ii) Larger elements can support larger coordination numbers (6 for Tl vs 4 for Ga and 3 for B in these examples).
- (iii) Some degree of π -bonding between B and Cl (first row B and small Cl) in BCl_3 will help stabilize the monomer. This is π -donation from Cl lone pairs to the vacant 2p orbital on B.

2. SnCl_2 is polymeric whereas SnCl_4 is monomeric.

Answer. The following explanations can be offered to account for these observations:

- (i) Monomeric SnCl_2 is coordinatively unsaturated (CN = 2) so can readily expand its coordination number through polymerisation (to a CN of 3 in this case).
- (ii) Monomeric SnCl_2 has a vacant orbital facilitating polymerisation through formation of dative bonds, in this case by means of bridging chlorines.
- (iii) $\Delta\chi$ is greater for the Sn(II)–Cl bonds than for the Sn(IV)–Cl bonds since Sn(II) is less electronegative (slightly) than Sn(IV). This also favours aggregation of SnCl_2 .
- (iv) Monomeric SnCl_2 has a dipole moment unlike SnCl_4 which will also favour association of the monomers.

3. CO_2 is molecular, SiO_2 is polymeric and SnO_2 is ionic and the coordination numbers around the respective Group 14 element centre increase from 2 to 4 to 6.

Answer. The following explanations can be offered to account for these observations:

- (i) The larger Si and larger still Sn can more readily support a higher coordination number, 4 (Si) and 6 (Sn) vs 2 (C).
- (ii) The Si–O bond is more polar than the C–O bond therefore more prone to polymerise due to greater $\Delta\chi$ for Si–O vs C–O; for Sn, the $\Delta\chi$ for Sn–O is sufficiently large for the compound to be considered ionic.
- (iii) Strong π -bonding for first row elements favours the formation of C=O double bonds ($\sigma + \pi$) in CO_2 whereas single Si–O bonding is much preferred for Si in preference to any Si–O multiple bonding.

4. The structure of sulfur dioxide comprises isolated SO_2 molecules whereas selenium dioxide and tellurium dioxide adopt polymeric structures with one and two bridging oxygen atoms respectively for each Group 16 atom.

Answer. The following explanations can be offered to account for these observations:

- (i) Increasing electronegativity difference between the Group 16 element and O is in the order $\Delta\chi \text{ Te-O} > \Delta\chi \text{ Se-O} > \Delta\chi \text{ S-O}$ so bonds are increasingly more polar down the group so association more favoured.
- (ii) Larger elements can support larger coordination numbers (4 for Te vs 3 for Se and 2 for S in these examples).
- (iii) Substantial π -bonding between S and O, some between Se and O and none between Te and O.

5. CCl_4 is inert to water under all but extreme conditions whereas SiCl_4 is readily hydrolysed.

Answer. The following explanations can be offered to account for these observations:

- (i) The larger Si can more readily expand its coordination number to accommodate an incoming nucleophile.
- (ii) Greater difference in electronegativity between Si and Cl (as opposed to C and Cl) means that the Si is more δ positive so more easily attacked by nucleophiles.
- (iii) The greater strength of the Si-O bonds formed (Si-O vs C-O).
- (iv) Lower energy vacant orbitals available for Si but not for C.

6. With regard to the Group 15 trihalides, account for why NF_3 is a colourless gas whereas BiI_3 is a deep orange solid.

Answer. The following explanations can be offered to account for these observations:

- (i) The two lighter elements (N and F) have many fewer electrons than the two heavier elements (Bi and I) so van der Waals forces are much stronger resulting in a marked decrease in volatility going from NF_3 to BiI_3 .
- (ii) Good overlap between N and F orbitals mean that n (lone pair) to σ^* transitions are in the UV (large HOMO-LUMO gap) whereas poorer overlap leading to a much smaller HOMO-LUMO gap in BiI_3 results in absorption in the visible and hence colour.
- (iii) Another reason would be that Bi has low-lying vacant acceptor orbitals which can lead to association through intermolecular Bi-I interactions.