Chapter 7 Exercises

1. Use VSEPR to predict the structures of the following molecules: $[PF_4]^-$, $PhI(OH)_2$, SO_2Cl_2, $[PO_4]^{3-}$, SNF_3, IF_5, XeO_3, XeO_2F_2, I_2Cl_6.

Answers. All according to the rules of VSEPR as set out in the text and below. Diagrams of the structures are collected after the written answers. Remember that the number of lone pairs is equal to the total number of electron pairs minus the number of bonding pairs.

$[PF_4]^-$: 5 from P + 4 from F (1 from each) + 1 from the negative charge.

10 electrons, 5 pairs (4 P–F bond pairs so 1 lone pair) so based on a trigonal bipyramid with a lone pair in an equatorial position.

$PhI(OH)_2$: 7 from I (the central element) + 1 from Ph (phenyl: acts just like H in contributing 1 electron) + 2 from OH (1 from each).

10 electrons, 5 pairs (1 I–Ph bond pair and 2 I–OH bond pairs so 2 lone pairs) so based on a trigonal bipyramid with the two lone pairs in equatorial positions and the large Ph also in an equatorial position. T-shaped is how the structure would be described.

SO_2Cl_2: 6 from S + 4 from O (2 from each) + 2 from Cl (1 from each).

12 electrons, 6 pairs (2 S=O double bond pairs [hence 4 pairs altogether] and 2 S–Cl bond pairs so no lone pairs) but based on a tetrahedron not an octahedron since the molecule contains two double bonds (S=O). Both pairs in a double bond point in the same direction.

$[PO_4]^{3-}$: 5 from P + 8 from O (2 from each) + 3 from the 3– negative charge.

16 electrons, 8 pairs (4 P=O double bond pairs [hence 8 pairs altogether] so no lone pairs) but based on a tetrahedron not a square anti prism since the molecule contains four double bonds (P=O).

SNF_3: 6 from S + 3 from N + 3 from F (1 from each).

12 electrons, 6 pairs (1 S≡N triple bond pair [hence 3 pairs altogether] and 3 S–F bond pairs so no lone pairs) but based on a tetrahedron not an octahedron since the molecule contains one triple bond (S≡N). All three pairs in a triple bond point in the same direction.

IF_5: 7 from I + 5 from F (1 from each).

12 electrons, 6 pairs (5 I–F bond pairs so 1 lone pair) so based on an octahedron but five I–F bond pairs and one lone pair so the structure is described as a square-based pyramid.

XeO_3: 8 from Xe + 6 from O (2 from each).

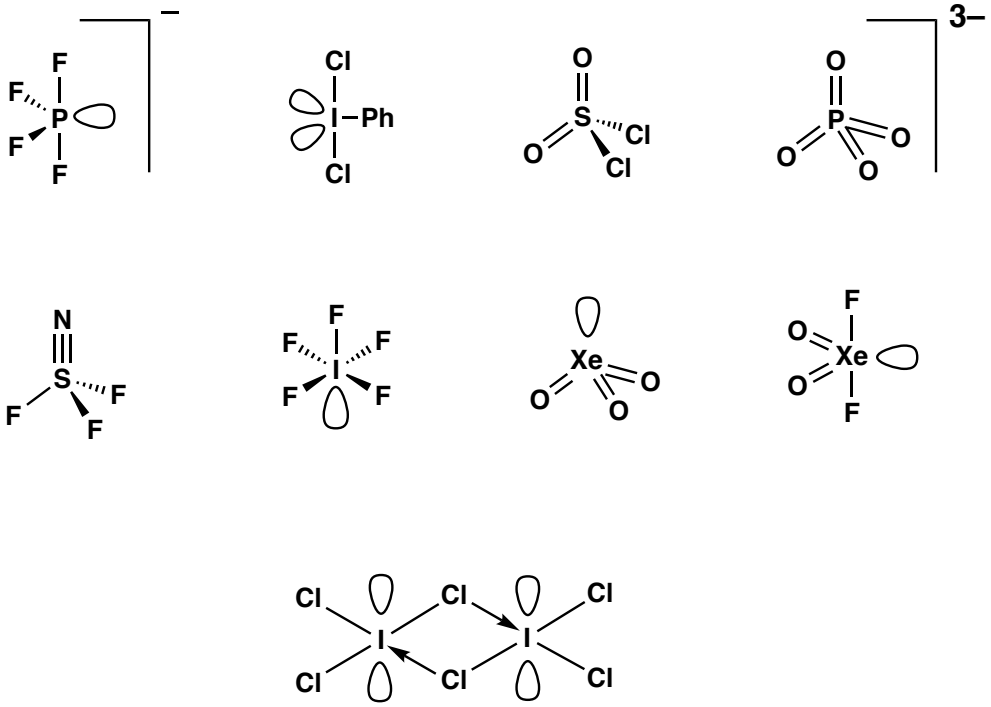
14 electrons, 7 pairs (3 Xe=O double bond pairs [hence 6 pairs altogether] so 1 lone pair) but based on a tetrahedron not a pentagonal bipyramid since the molecule contains three double bonds (Xe=O). Since there is one lone pair, the molecule is described as trigonal pyramidal.

XeO_2F_2: 8 from Xe + 4 from O (2 from each) + 2 from F (1 from each).

14 electrons, 7 pairs (2 Xe=O double bond pairs [hence 4 pairs altogether] and 2 Xe–F bond pairs so 1 lone pair) but based on a trigonal bipyramid not a pentagonal bipyramid since the molecule contains two double bonds (Xe=O). The lone pair and the two Xe=O double bonds go in the equatorial sites so the structure is described as equatorially vacant trigonal bipyramidal or disphenoidal.

I_2Cl_6: This is a dinuclear species, so the task is to determine the geometry around each central iodine. If we consider a ICl_3 monomer, then 7 from I + 3 from Cl (1 from each). 10 electrons, 5 pairs (3 I–Cl bond pairs so 2 lone pairs) with the two lone pairs equatorial. Dimerisation now occurs by lone pair donation from a bridging chlorine to each iodine centre taking the number

of pairs around each iodine centre from 5 to 6. 6 pairs point towards the vertices of an octahedron. For four bond pairs (3 original I–Cl bonds and one dative/coordinate I–Cl bond but all are treated equally) and two lone pairs, the lone pairs go *trans* and so the geometry around each iodine is described as square planar.



2. Predict possible structures for the p-block component of the following compounds: Li_2S_2, BaSn, Cs_2NaAs_7.

Answer. Li_2S_2: This compound is formally 2 Li^+ and S_2^{2-}. S being in Group 16 has 6 valence electrons which is increased to 7 for each of the S in S_2^{2-}. S_2^{2-} (which is isoelectronic with peroxide, O_2^{2-}) is therefore isoelectronic with a neutral Group 17 diatomic such as Cl_2 which is the structure adopted.

BaSn: This compound is formally Ba^{2+} and Sn^{2-}. Sn being in Group 14 has 4 valence electrons which is increased to 6 for Sn^{2-} which is therefore isoelectronic with a neutral Group 16 element. The structure adopted has a polymeric chain of Sn atoms joined by two-centre, two-electron bonds analogous to the helical structures found for elemental Se and Te (and one allotrope of S).

Cs_2NaAs_7: This compound is formally 2 Cs^+, Na^+ and As_7^{3-}. This compound does indeed contain discrete As_7^{3-} anions which are analogous to the better known P_7^{3-} anion, the structure of which is shown below. From this structure, it clear that there are 4 three-coordinate centres and 3 two-coordinate centres which is where the negative charges are localised. A negative As^- or P^- is isoelectronic with a neutral Group 16 element such as S. The corresponding neutral P_4S_3 compound is known, the structure of which is also shown below.