p-Block chemistry

Answers to worked examples

WE 27.1 Bonding in the Group 15 elements (on p. 1224 in *Chemistry*³)

The mean bond enthalpies for the N–N and N≡N bonds are +158 kJ mol⁻¹ and +945 kJ mol⁻¹ respectively. Calculate the enthalpy change for the conversion of tetrahedral N₄ into N₂ and use this value to comment on the molecular structure of nitrogen.

Strategy

Firstly, write the equation for the conversion and determine the number and type of bonds in each case and draw an enthalpy cycle to take account of the changes. Then use the bond enthalpy data to calculate the enthalpy change for the conversion. If the change is exothermic, this implies that the products are favoured.

<u>Solution</u>

 $N_{4}\left(g\right) \, \rightarrow \, 2N_{2}\left(g\right)$

Tetrahedral N_4 consists of six single bonds where the bonds are on the six edges of the tetrahedron. There is one triple bond in each N_2 molecule. This arrangement gives the following enthalpy cycle:

$$N_4(g)$$
 $\xrightarrow{\Delta_{\Gamma}H^{\Phi}}$ 2 $N_2(g)$
6 x (+158 kJ mol⁻¹) $\xrightarrow{-2 x (+945 kJ mol^{-1})}$
4 N (g)

The enthalpy change is therefore

 $\Delta_{\rm r} H^{\rm o} = (6 \times +158 \text{ kJ mol}^{-1}) - (2 \times 945 \text{ kJ mol}^{-1}) = -942 \text{ kJ mol}^{-1}$

The conversion of N_4 to N_2 is highly exothermic, so under standard conditions N_2 is the more stable form of nitrogen.

WE 27.2 Calculating enthalpy changes of formation of *p*-block halide compounds (on p. 1245 in *Chemistry*³)

Calculate the enthalpy change of formation of PF₃. The enthalpy change of formation of atomic phosphorus $\Delta_f H^{\theta}(P(g))$, is +315 kJ mol⁻¹.

Strategy

Write an equation for the formation of PF_3 from its elements and construct an enthalpy cycle to calculate the enthalpy change.

 $\frac{\text{Solution}}{\frac{1}{4}P_4 + \frac{3}{2}F_2} \rightarrow PF_3$

This gives the following enthalpy cycle:

Using the cycle gives:

 $\Delta_{\rm f} H^{\rm e}[{\rm PF}_3~({\rm g})] = (+315~{\rm kJ~mol}^{-1}) + (3 \times +79~{\rm kJ~mol}^{-1}) + (-3 \times 490~{\rm kJ~mol}^{-1})$ $= -918~{\rm kJ~mol}^{-1}$

WE 27.3 Synthesis of interhalogen ions (on p. 1248 in *Chemistry*³)

Suggest a method of preparing IF_6^- .

Interhalogen anions are formed by reaction of a neutral interhalogen compound with a halide ion.

Solution

 IF_6^- is prepared by the addition of a fluoride ion to IF₅. For example,

 $IF_5 \ + \ Cs^+F^- \ \rightarrow \ Cs^+[IF_6]^-$

Answers to boxes

Box 27.1 Recycling aluminium (on p. 1211 in *Chemistry*³)

Suggest why it takes so much more energy to extract aluminium from bauxite than to recycle it.

Strategy

Consider the steps involved in extracting aluminium from its ore and the energy requirements for each step and compare to the simple shredding, lacquer stripping and melting process described in Box 27.1 (p.1211).

Solution

Extraction of aluminium from bauxite requires two major steps: the Bayer process to digest the ore in hot NaOH, followed by the Hall–Heroult process, in which the alumina generated is dissolved in cryolite and electrolysed. Both the digestion and electrolysis steps are energy intensive, both in terms of the chemicals used and the electrolysis also requires high electrical energy input.

Box 27.3 Silicones—shiny hair and cosmetic surgery (on p. 1220 in *Chemistry*³) Suggest why carbon analogues of silicones, in which C atoms take the place of Si atoms, are unknown.

Compare the strength of the bonding within a carbon analogue of the silicone with that in the likely decomposition products.

Solution

The C–O bond is weaker than the Si–O bond. Carbon analogues of silicones would be thermodynamically unfavourable with respect to CO₂.

Box 27.4 Fluxional molecules (on p. 1230 in *Chemistry*³)

What would you expect to see in the ³¹P NMR spectrum of PF₅?

Strategy

Consider the effect of the Berry pseudorotation (fluxionality) on the NMR signal bearing in mind that the number of signals depends on the number of different environments.

Solution.

There is only one phosphorus environment, so only one signal would be seen. This would appear as a sextet as the phosphorus nucleus is coupled to five ¹⁹F nuclei which are all equivalent on the NMR timescale.

Box 27.7 Sulfur on Io (on p. 1235 in *Chemistry*³)

The Hubble Space Telescope used a spectrometer to detect the presence of S_2 . Would you expect this molecule to absorb infrared radiation (see Section 10.5, p.480)?

Strategy

Consider the factors that make a vibration IR active.

Solution

The S=S stretch does not involve a change in dipole, so it is not IR active. (The Hubble telescope used an ultraviolet spectrometer to detect S_2 .)

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Box 27.8 Chlorofluorocarbons and the ozone hole (on p. 1241 in *Chemistry*³)

Suggest why compounds containing Cl or Br atoms cause ozone depletion in the stratosphere, but compounds containing F or H atoms do not.

Strategy

As described in Box 27.8 (p.1241), molecules affected by sunlight can form radicals which deplete ozone by chemical reaction. The photochemical process is a result of the radiation being more energetic than the bond between the atoms meaning the bonds are broken and radicals are formed.

Solution

The C–F and C–H bonds are too strong to be broken by ultraviolet radiation from the Sun.

Box 27.9 Using argon to date rocks (on p. 1249 in *Chemistry*³)

 40 Ca is also a product of the decay of 40 K. Suggest a reason why the ratio of 40 K to 40 Ca cannot be used to date rocks.

Strategy

Consider the common elements in the Earth's crust. Isotopic dating procedures will be possible if there is only one source of the nucleus arising from the radioactive decay.

Solution

⁴⁰Ca is naturally present in rocks and hence the ⁴⁰Ca produced by β-emission is not the only source of the isotope. It is therefore impossible to distinguish between the ⁴⁰Ca created by radioactive decay and that already present.

Answers to end of chapter questions

1. Determine the oxidation state of the atom shown in red in the following molecules and ions: (a) $H_4P_2O_6$; (b) XeO_6^{4-} ; (c) $[Sn(OH)_4]^{2-}$; (d) Se_4^{2+} ; (e) S_3O_9 ; (f) S_2Cl_2 .

<u>Strategy</u>

Use the overall charge on the species and the fact that the oxygen, chlorine and hydrogen will be in their normal oxidation states of -2, -1 and +1, respectively, to find the oxidation state of the *p*-block element.

Solution

(a) The oxidation state of H is +1, and that of O is -2. Overall the molecule is neutral.

O $6 \times -2 = -12$ <u>H</u> $4 \times +1 = +$ +4-8 So the oxidation state of P is $\frac{+8}{4} = +4$.

(b) The oxidation state of O is -2. Overall the ion carries a -4 charge.

 $O \qquad 6 \times -2 = -12$ charge - -4 -8

So the oxidation state of Xe is +8.

(c) The oxidation state of H is +1, and that of O is -2. Overall the ion carries a -2 charge.

O $4 \times -2 = -8$ H $4 \times +1 = + +4$ charge -2-2

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So the oxidation state of Sn is +2.

(d) The charge on the ion is +2 and there are four selenium atoms. The average oxidation state of Se is $\frac{+2}{4} = +0.5$.

(e) The oxidation state of O is -2.

O $9 \times -2 = -18$

Overall the molecule is neutral, so the oxidation state of S is $\frac{+18}{3} = +6$.

- (f) The oxidation state of Cl is -1.
- Cl $2 \times -1 = -2$

The molecule is neutral, so the oxidation state of S is $\frac{+2}{2} = +1$.

2. Place the following elements in order of increasing first ionization energy:

- (a) antimony, arsenic, bismuth, nitrogen, phosphorus;
- (b) carbon, fluorine, nitrogen, oxygen.

Strategy

Use the arguments relating to bond enthalpies given in Section 27.1 (p.1203) to order the elements in terms of the difficulty of removing the first electron. Consider factors such as the screening of inner electrons and their effect on the nuclear charge (see effective nuclear charge and Slater's rules on p.151).

Solution

(a) As the screening of underlying electrons increases, the electrons in the valence orbital become easier to remove as they are not as tightly held. This means the enthalpy decreases down a group and as (a) is a mixture of Group 15 elements, the elements just need to be rearranged in the same sequence as the group (bottom first), *i.e.* Bi < Sb < As < P < N.

(b) Ionization enthalpies generally increase from left to right across a period as the screening of the electrons does not fully compensate for the increase in nuclear charge. However, the absolute electronic configuration does also affect the trend. The values for oxygen and nitrogen are therefore reversed as oxygen forms a half-filled shell where the spin is maximised when the electron is lost (from Hund's rule) whereas nitrogen is in this state before the electron is lost (see Section 3.7, p.154), *i.e.* C < O < N < F

3. Are the following oxides acidic, basic or amphoteric:

- (a) P_4O_{10}
- (b) Bi_2O_3
- (c) GeO₂?

<u>Strategy</u>

Consider the action of water on the oxides to determine the acid/base character. If they are insoluble, consider how they react with acid and/or base.

Solution

- (a) P_4O_{10} (see Section 27.4, p.1227) dissolves in water to give phosphoric acid. It is therefore acidic.
- (b) Bismuth is at the bottom of Group 15 and hence Bi_2O_3 forms a basic solution.
- (c) Germanium oxide dissolves in both acid and alkali, so is amphoteric.
- **4.** Account for the difference in the B–F bond lengths observed in BF₃ (130 pm) and BF_4^- (145 pm).

Strategy

The difference in bond length suggests that the bonds in BF_3 are stronger than those in BF_4^- . There are two parts to this answer, firstly use the information given on p.1213-4 regarding the boron trihalides and secondly consider the effect of adding another atom and a negative charge on the space between the atoms.

Solution

The BF₃ molecule is trigonal planar and is hence sp^2 hybridized. This leaves one remaining empty *p* orbital on the boron to interact with the full *p* orbitals on the fluorine. The $p\pi$ – $p\pi$ bonding in a trigonal planar BF₃ molecule is very strong as boron and fluorine are in the same period so π overlap is good. This system strengthens and shortens the B–F bond. BF₄⁻ is sp^3 hybridized. This means that all the *p* orbitals are used in σ bonding and there is no $p\pi$ – $p\pi$ bonding. Secondly, there are more atoms bonded to boron in BF₄⁻ causing more repulsion (less room for each atom) and a negative charge resulting in more electron-electron repulsion and hence weaker bonds.

5. The diagonal relationship between beryllium and aluminium is relatively strong. What evidence is there for this relationship?

Strategy

The basis of diagonal relationships is described in Section 26.11 (p.1196). List chemical properties that are similar for the two elements.

Solution

Examples include

- Be^{2+} and Al^{3+} both form acidic aqueous solutions due to hydrolysis.
- Beryllium and aluminium are both amphoteric, reacting with both acids and alkalis.
- The compounds of both beryllium and aluminium have considerable covalent character due to the polarizing power of the small highly charged cations.
- The chlorides are covalent, with the chlorides bridging between metal centres in either polymeric BeCl₂ or dimeric Al₂Cl₆.
- 6. Aluminium fluoride sublimes at over 1000 °C and is insoluble in benzene, whereas aluminium chloride melts at 192 °C and dissolves in benzene to give dimers. Account for these differences, and give reasons for any differences in the bonding in these compounds.

Consider the difference in size and electronegativity between chlorine and fluorine.

Solution

Fluorine is more electronegative than chlorine, so the difference in electronegativity between aluminium and fluorine is greater than that between aluminium and chlorine. As a consequence, the bonds in AlF_3 have a greater ionic character. The high sublimation temperature and insolubility in benzene observed for AlF_3 are characteristic of ionic bonding, whereas the low melting point and benzene solubility for Al_2Cl_6 are characteristic of covalent bonding.

7.

What is meant by the 'inert pair effect'? Why is the inert pair effect more important for lead than for silicon?

Strategy

The inert pair effect is described in Section 27.1 (p.1207). Consider the relative positions of silicon and lead in the Periodic Table.

Solution

The inert pair effect is the increase in importance of an oxidation state two less than the usual oxidation state for a group. The name 'inert pair' comes from the fact that the lower oxidation state has the electronic configuration ns^2 , and these two valence electrons are not used in bonding. The inert pair effect occurs because bond enthalpies decrease going down the group, itself a consequence of the larger orbitals. For Group 14, Pb–X bond enthalpies are lower than Si–X bond enthalpies, regardless of the identity of X. Using the valence bond model of bonding, energy is required to promote the *s* electrons into hybrid orbitals so they can form bonds. For the lighter elements, like silicon, this energy is compensated for by the energy released on forming two new bonds. The lower bond enthalpies for heavier elements, like lead, means that this is not the case, so formation of the higher oxidation state compound is less favoured.

8. Draw the resonance structures for N_2O_5 and NO_2^- .

Strategy

Draw out the structures of the nitrogen oxides using a mixture of single and double bonded oxygen to satisfy the octet requirement. Then consider the different possible arrangements of the double and single bonds.

Solution



9. NF_2 exists in equilibrium with N_2F_4 , whereas NH_2 dimerizes readily to form hydrazine, N_2H_4 . Account for the difference in stability of NF_2 and NH_2 with respect to dimerization.

Strategy

Bond formation is exothermic, so you might expect dimerization to be thermodynamically favourable. However, either stabilisation of the monomer and/or destabilisation of the dimer will push the equilibrium towards the monomer. Consider how replacing hydrogen with fluorine might affect both the stability of the monomer and the dimer.

Solution

Replacing the hydrogen atoms on NH_2 with more electronegative fluorine atoms will help pull electron density from the nitrogen atom, which in turn stabilizes the monomer towards dimerization. In addition, the greater electron-electron repulsion in N_2F_4 would destabilize this molecule with respect to dissociation. These two factors together explain the relative stability of NF_2 with respect to dimerization.

10. Use the data below to calculate the enthalpy changes of formation for $PCl_3(g)$ and $PI_3(g)$. Comment on the stabilities of these compounds.

$$\begin{split} \Delta_{\rm f} H^{\rm e}[{\rm P~(g)}] &= +315 \text{ kJ mol}^{-1} \\ \Delta_{\rm f} H^{\rm e}[{\rm Cl~(g)}] &= +121 \text{ kJ mol}^{-1} \\ \Delta_{\rm f} H^{\rm e}[{\rm I~(g)}] &= +107 \text{ kJ mol}^{-1} \\ {\rm P-Cl~bond~enthalpy} &= +326 \text{ kJ mol}^{-1} \\ {\rm P-I~bond~enthalpy} &= +184 \text{ kJ mol}^{-1} \end{split}$$

<u>Strategy</u>

Write an equation for the formation of PX_3 from the elements. Draw an enthalpy cycle for the formation of PX_3 from their elements in their standard states. The stability of PX_3 can be determined by calculating the enthalpy change using the cycle.

 $\frac{\text{Solution}}{\frac{1}{4}P_4 + \frac{3}{2}X_2 \rightarrow PX_3$

This gives the following enthalpy cycles:

 $\begin{array}{c|c} & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & &$

$$\Delta_{f} H^{e}[PCl_{3} (g)] = +315 \text{ kJ mol}^{-1} + (3 \times +121 \text{ kJ mol}^{-1}) + (3 \times -326 \text{ kJ mol}^{-1})$$

= -300 kJ mol⁻¹
$$\Delta_{f} H^{e}[PI_{3} (g)] = +315 \text{ kJ mol}^{-1} + (3 \times +107 \text{ kJ mol}^{-1}) + (3 \times -184 \text{ kJ mol}^{-1})$$

= +84 kJ mol⁻¹

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11. Use the bond enthalpy data below to explain why oxygen exists as O_2 molecules and not O_8 rings, analogues to those formed by sulfur.

 $O-O + 144 \text{ kJ mol}^{-1}$, $O=O + 498 \text{ kJ mol}^{-1}$

Strategy

Firstly, write out an equation for the decomposition of the single bonded O_8 ring to four double-bonded O_2 molecules. Use the equation to construct an oxygen enthalpy cycle and then use the data to calculate the enthalpy change. If the reaction is exothermic, the decomposition reaction is favoured.

Solution

An enthalpy cycle can be drawn as shown below.

$$O_8 (g) \xrightarrow{\Delta_r H^{-9}} 4 O_2 (g)$$

8 x (+144 kJ mol⁻¹)
8 O (g)

 $\Delta_r H^{\circ} = [(8 \times +144 \text{ kJ mol}^{-1}) + (4 \times -498 \text{ kJ mol}^{-1})] = -840 \text{ kJ mol}^{-1}$. The conversion of O₈ to 4O₂ would be highly exothermic, so O₂ is the more stable form of oxygen. This calculation ignores the change in entropy, which is positive so also favours the formation of four O₂ molecules.

12. In an iodine-thiosulfate titration, thiosulfate is oxidized to tetrathionate $(S_4O_6^{2-})$. What are the average oxidation states of sulfur in thiosulfate and tetrathionate?

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Write down the formulae for the anions. Assume that oxygen has an oxidation state of -2, and use this to work out the average oxidation states for the sulfur atoms in the two ions.

Solution

For $S_2O_3^{2-}$, the oxidation state of O is -2. Overall the ion carries a -2 charge.

O $3 \times -2 = -6$ <u>charge</u> -2 -4So the oxidation state of S is $\frac{+4}{2} = +2$.

For $S_4O_6^{2-}$, the oxidation state of O is -2. Overall the ion carries a -2 charge.

$$O \qquad 6 \times -2 = -12$$

charge
$$-2$$

$$-10$$

So the average oxidation state of S is $\frac{+10}{4} = +2.5$.

13. The bond angle in F_2O is 103.1°, which is less than the bond angle in water. Account for this difference.

Strategy

Differences in bond angle could arise from steric effects (*i.e.* size) or electronic effects. In this case, the smaller bond angle of F_2O when compared with that of H_2O cannot have a steric origin, as fluorine is bigger than hydrogen. Consider what electronic effect could cause this difference in bond angle.

Solution

Fluorine is more electronegative than hydrogen. As a consequence, the electrons in the bond are pulled further form the central oxygen atom, and hence repel the lone pairs less.

14. Calculate the enthalpy change of formation of $Cl_2O(g)$ given the bond enthalpies below. Would you expect to be able to prepare Cl_2O from the elements?

Strategy

Write an equation for the formation of Cl_2O from oxygen and chlorine. Draw an enthalpy cycle for the formation of Cl_2O from the elements in their standard states. Calculate the enthalpy change for formation using the enthalpy cycle.

 $\frac{\text{Solution}}{\text{Cl}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Cl}_2\text{O}}$

This gives the following enthalpy cycle:

$$\begin{array}{c} Cl_{2}(g) + \frac{1}{2}O_{2}(g) & \xrightarrow{\Delta_{f}H^{\bullet}[Cl_{2}O(g)]} \\ Cl_{2}O(g) & \xrightarrow{\Delta_{be}H^{\bullet}[Cl-Cl]} & 1/2\Delta_{be}H^{\bullet}[O=O] \\ +242 \text{ kJ mol}^{-1} & 1/2 & (+498 \text{ kJ mol}^{-1}) \\ 2 & Cl(g) + O(g) \end{array} \xrightarrow{Cl_{2}O(g)} Cl_{2}O(g) \\ \end{array}$$

 $\Delta_{\rm f} H^{\rm e}[{\rm Cl}_2{\rm O}~({\rm g})] = +242 \text{ kJ mol}^{-1} + (^1/_2 \times 498 \text{ kJ mol}^{-1}) - (2 \times 205 \text{ kJ mol}^{-1})$ = +81 kJ mol⁻¹

Since $\Delta_f H^{o}[Cl_2O(g)]$ is positive and hence endothermic, Cl_2O would not be expected to form from chlorine and dioxygen.

15. Iodine monofluoride (IF) disproportionates into IF₅ and I₂. Write a balanced equation for this reaction. Use the data below to calculate ΔH° for the disproportionation reaction.

$$\Delta_{\rm f} H^{\Theta}({\rm IF}({\rm g})) = -95 \text{ kJ mol}^{-1}, \quad \Delta_{\rm f} H^{\Theta}({\rm IF}_5({\rm g})) = -840 \text{ kJ mol}^{-1}$$

Balance the equation, making sure the oxidation state changes balance as well as the numbers of atoms. Use an enthalpy cycle to calculate ΔH^{θ} for the reaction.

Solution

The oxidation state of iodine is +1 in IF, +5 in IF₅ and 0 in I₂. The balanced equation is

$$5IF \rightarrow IF_5 + 2I_2$$

An enthalpy cycle for this is shown below.



 $\Delta_{\rm r} H^{\rm e} = -(5 \times -95) \text{ kJ mol}^{-1} + (-840 \text{ kJ mol}^{-1})$ $= -365 \text{ kJ mol}^{-1}$

16. Predict the products of each of the following reactions, and write a balanced equation in each case:

- (a) $XeF_2 + AsF_5$
- (b) $BI_3 + NH_3$
- (c) $P_4O_{10} + H_2O$
- (d) $SF_4 + BF_3$

Strategy

In each case examine what type of reaction is taking place and the ability of the species to undertake the reaction.

Solution

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- (a) Both species in this reaction contain fluoride, so it is likely that this is a fluoride transfer reaction. AsF₅ is a good fluoride ion acceptor, so the reaction will involve fluoride transfer from the Group 18 compound to this species.
 XeF₂ + AsF₅ → [XeF]⁺[AsF₆]⁻
- (b) This is an adduct formation reaction between BI₃, which is a Lewis acid and NH₃, which is a Lewis base:
 BI₃ + NH₃ → I₃B←NH₃
- (c) P_4O_{10} is an acidic oxide, so reacts with water to form an acidic solution. The phosphorus in P_4O_{10} is in the +5 oxidation state, so the acid product (also P(V)) is phosphoric acid: $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
- (d) Both species in this reaction contain fluoride, so it is likely that, like (a), this is a fluoride transfer reaction. SF₄ can act as a Lewis acid or a Lewis base, but BF₃ can only act as a Lewis acid, which in this context means a fluoride acceptor:
 SF₄ + BF₃ → [SF₃]⁺[BF₄]⁻
- 17. Which of the following oxides are paramagnetic: NO₂; NO; N₂O₃; CO₂; CO; ClO₂; Cl_2O_7 ?

A species must have unpaired electrons to be paramagnetic. Determine the number of unpaired electrons in each case by considering the valence electrons and bonding around each *p*-block atom.

Solution

NO₂, NO and ClO₂ are paramagnetic as they all contain an unpaired electron.



 N_2O_3 , CO_2 , CO and Cl_2O_7 are all diamagnetic, as all of their electrons are paired.

18. Use VSEPR theory to predict the shapes of the following molecules and ions: (a) IF₅; (b) XeF₄; (c) IO_3^- ; (d) POCl₃; (e) BrF₃; (f) XeO₂F₂.

<u>Strategy</u>

Use VSEPR theory to determine which of the geometries shown in Figure 5.7 (p.223) is adopted by each of these species. Draw a Lewis structure for the molecule or ion using a combination of single and double bonds. Count up the electrons around the central atom (remember to include the charge on the central species). Determine the number of electron pairs and whether they are σ or π electrons (remembering that only the former have an effect on the shape). Finally, in identical shapes, consider how the lone pairs affect the shape.

Solution

- (a) There are 7 electrons from the I atom and 5 electrons from 5F. This gives 12 electrons around I, which is equal to 6 electron pairs. The structure is based on an octahedron with one lone pair. The shape of the molecule is square pyramidal.
- (b) There are 8 electrons from the Xe atom and 4 electrons from 4F. This gives 12 electrons around Xe, which is equal to 6 electron pairs. The structure is based on an octahedron with two lone pairs. The lone pairs must be placed opposite to each other to minimise lone pair lone pair repulsion. The shape of the molecule is square planar.
- (c) There are 7 electrons from I atom , 6 electrons from 3O and 1 electron from the charge. This gives 14 electrons around I, which is equal to 7 electron pairs, of which 3 are π -pairs and do not contribute to the shape. This leaves 4 σ -pairs. The structure is based on a tetrahedron with one lone pair. The shape of the anion is **trigonal pyramidal**.
- (d) There are 5 electrons from the P atom, 2 electrons from O and 3 electrons from 3Cl. This gives 10 electrons around P, which is equal to 5 electron pairs, of which 1 is a π-pair and does not contribute to the shape. This leaves 4 σ-pairs. The shape of the molecule is **tetrahedral** as there are no lone pairs. The O–P–

Cl angles are wider than the Cl–P–Cl angles as the double bond takes up more space than the single bonds.

- (e) There are 7 electrons from Br and 3 electrons from 3F. This gives 10 electrons around Br, which is equal to 5 electron pairs. The structure is based on a trigonal bipyramid with two lone pairs. The molecule is **T-shaped**.
- (f) There are 8 electrons from Xe, 4 electrons from 2O and 2 electrons from 2F. This gives 14 electrons around Xe, which is equal to 7 electron pairs, of which 2 are π -pairs and do not contribute to the shape. This leaves 5 σ -pairs. The structure is based on a trigonal bipyramid with one lone pair. The lone pair is most spatially demanding and must go in the trigonal plane giving the molecule a **disphenoidal** shape. The double bonded oxygen atoms occupy the equatorial positions as this minimizes electron-electron repulsion.
- **19.** How would you prepare the following compounds: (a) $[IF_6]^+[SbF_6]^-$; (b) carbon suboxide; (c) XeO₃?

<u>Strategy</u>

Preparation reactions require knowledge of the individual reactions. See Section Section 27.6 (p.1246) on fluorine transfer reactions, Section 27.3 (p.1217) on carbon oxides and Section 27.7 (p.1248) on preparation of Group 18 compounds.

Solution

- (a) IF₇ + SbF₅ \rightarrow [IF₆]⁺[SbF₆]⁻
- (b) dehydration of propanedioic acid with P_4O_{10}
- (c) reaction of XeF_4 with water
- **20.** H_3BO_3 is a monobasic acid whereas H_3PO_3 is a dibasic acid. Account for this difference.

Draw out the structures of the two species and use these structures to determine the difference in acidity

Solution

 H_3BO_3 [B(OH)₃] acts as an acid through a Lewis acid–Lewis base interaction with H_2O , and the resulting adduct B(OH)₃(OH₂) loses a proton to form B(OH)₄⁻ (see p.1213). H_3PO_3 [HP(O)(OH)₂] is a dibasic acid as only the hydrogen atoms bonded to oxygen atoms are ionizable (see p.1227).