

Chapter 4 Exercises

1. What is the oxidation state and valence for the first written element in the following compounds: B_2F_4 , $[XeF_5]^-$, SO_2Cl_2 , $[NO_2]^+$?

Answer.

B:	Oxidation state (II); valence 3.
Xe:	Oxidation state (IV); valence 4.
S:	Oxidation state (VI); valence 6.
N:	Oxidation state (V); valence 5.

Account for the following observations:

1. Disulfur, S_2 , is not an allotrope of elemental sulfur under ambient conditions.

Answer. By ambient conditions, we mean room temperature and pressure. In terms of bond energies, for S, two S–S single (σ) bonds are together stronger than 1 S=S double bond ($\sigma + \pi$) so allotropes such as S_8 (S_n generally) and S_x which all contain S–S single bonds (i.e. σ bonds but not π bonds) are preferred over a species like S_2 which would have a double bond ($\sigma + \pi$) analogous to O_2 .

2. The perbromate ion, $[BrO_4]^-$, is a stronger oxidising agent than either perchlorate, $[ClO_4]^-$, or periodate, $[IO_4]^-$.

Answer. Perbromate contains Br(VII). This is the group maximum oxidation state for Br and the group maximum oxidation state is progressively harder to achieve across the 4p row due to the effects of the preceding 3d row which result in increasing Z^* due to poor shielding by 3d electrons. There are no d electrons for Cl and although there are for I (4d), the consequence is less in terms of its effect on oxidation state since I is larger.

3. ClF_5 is a strong oxidising agent.

Answer. ClF_5 contains Cl in the oxidation state Cl(V). This is quite a high oxidation state for such an electronegative element so we would expect a Cl(V) centre to be very easily reduced to a lower oxidation state hence making Cl(V), specifically ClF_5 in this case, a strong oxidising agent.

4. Thallium tri-iodide, TlI_3 , exists as the thallium(I) salt $Tl^+[I_3]^-$ rather than as a salt containing Tl(III) and three iodide anions.

Answer. This is an example of the inert pair effect in which Tl prefers the lower oxidation state, Tl(I), rather than the higher oxidation state Tl(III). The explanation for the preference for thallium to be Tl(I) rather than Tl(III) is a combination of the high s-p promotion energy of Tl not being compensated by the formation of two extra but weak Tl–I bonds.

5. PCl_5 and SbCl_5 show no tendency to lose Cl_2 and form PCl_3 and SbCl_3 at room temperature whereas AsCl_5 decomposes to AsCl_3 and Cl_2 above -50°C .

Answer. This observation reflects the reluctance of the 4p elements to achieve the group maximum oxidation state, (V) in this case. P(V) is stable as a pentachloride whereas As(V) is not and rapidly undergoes a spontaneous reduction to AsCl_3 . This reflects the consequence of As being a post 3d element, the resulting higher Z^* for which makes achieving high oxidation states more difficult. In principle, the same argument should apply for Sb (post 4d) but the fact that it is progressively lower down the group (electrons more easily lost) means that Sb(V) is stable as a pentachloride. This is very much the same general answer as for Question 2. above, i.e. the reluctance of the 4p elements to exhibit the Group maximum oxidation state.

6. SnO_2 is easily prepared by oxidation of elemental tin whereas the formation of PbO_2 requires much stronger oxidising agents.

Answer. This is another example of the so-called inert pair effect for the 6p elements (see the answer to Q 4. above) which in the case of lead results in the Group maximum oxidation state (ie, IV) being harder to achieve in terms of the substantial promotion energy not being recovered through formation of weak bonds (in this case Pb–O). Pb(II)O is therefore preferred over Pb(IV)O_2 . The issue is much less marked for Sn and oxidation of Sn to Sn(IV) in SnO_2 is much more readily achieved.