27

p-Block chemistry

Answers to worked examples

WE 27.1 Bonding in the Group 15 elements

The mean bond enthalpies for the N–N and N≡N are +158 kJ mol^{-1} and +945 kJ mol^{-1} respectively. Calculate the enthalpy change for the conversion of tetrahedral N_4 into N_2 and use this value to comment on the molecular structure of nitrogen.

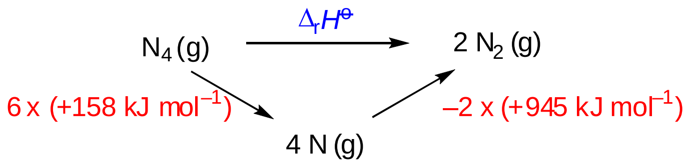
Strategy

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.

Solution

$N_4\,(g) \rightarrow 2\,N_2\,(g)$

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:



The enthalpy change is therefore (N–N) –2(N≡N)

$\Delta_r H^\circ = (6 \times +158\ \text{kJ mol}^{-1}) - (2 \times 945\ \text{kJ mol}^{-1}) = -942\ \text{kJ mol}^{-1}$

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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 27.3 Synthesis of interhalogen ions

Suggest a method of preparing IF_6^-.

Strategy

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

Solution

IF_6^- is prepared by the addition of a fluoride ion to IF_5. For example,

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

Answers to boxes

Box 27.1 Recycling aluminium

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.1201).

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, where the alumina generated is dissolved in cryolite and electrolysed. Both the digestion and electrolysis

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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

Suggest why carbon analogues of silicones, in which C atoms take the place of Si atoms, are unknown.

Strategy

Compare the strength of the bonding within a carbon analogue of the silicone with 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 CO_2.

Box 27.7 Sulfur on Io

The Hubble Space Telescope used a spectrometer to detect the presence of S_2. Would you expect the symmetric stretch of this molecule to absorb infrared radiation (see Section 11.5, p.524)?

Strategy

Consider the factors that make a vibration IR active.

Solution

No. The S=S symmetric 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 27.9 Using argon to date rocks

^{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 only be possible if there is only one source of the radioactive product.

Solution

^{40}Ca is naturally present in rocks and hence the ^{40}Ca is not the only source of the isotope. It is therefore impossible to distinguish between the ^{40}Ca created by β-emission 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.

Strategy

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 × –2	=	–12
H	4 × +1	= +	+4
			–8

So the oxidation state of P is $\frac{+8}{4} = +4$.

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

O	6 × –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 × –2	=		–8
H	4 × +1	=	+	+4
charge			–	–2
				–2

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 × –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 × –1 = –2

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

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3. Account for the difference in the B–F bond lengths observed in BF_3 (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.1203-1204 regarding the boron trihalides and secondly consider the effect of adding another ligand and a negative charge on the space between the ligands.

Solution

The BF_3 molecule is trigonal planar and is hence sp^2 hybrized. 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 BF_3 molecule is very strong as boron and fluorine are in the same group π overlap is good. This system strengthens and shortens the B–F bond. BF_4^- is sp^3 hybridized. This means that all the *p* orbitals are used in σ bonding and there is no π bonding. Secondly, there are more ligands causing more interligand repulsion (less room for each ligand) and a negative charge resulting in more electron-electron repulsion and hence weaker bonds.

5. Are the following oxides and hydroxides, acidic, basic or amphoteric:

(a) P_4O_{10}

(b) Bi_2O_3?

Strategy

Consider the action of water on the oxides to determine the acid/base character.

Solution

(a) P_4O_{10} (see Section 27.4, p.1217) dissolves in water to give phosphoric acid. Therefore acidic.

(b) Bismuth is at the bottom of Group 15 and hence forms a basic solution.

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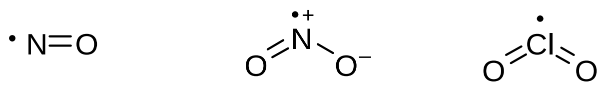
7. Which of the following are paramagnetic: NO_2; NO; N_2O_3; CO_2; CO; ClO_2; Cl_2O_7?

Strategy

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

NO_2, NO and ClO_2 are paramagnetic as they all contain an unpaired electron.



9. How would you prepare the following compounds: (a) $[IF_6]^+[SbF_6]^-$; (b) carbon suboxide; (c) XeO_3?

Strategy

Preparation reactions require knowledge of the individual reactions. See Section Section 27.6 (p.1230) on fluorine transfer reactions, Section 27.3 (p.1207) on carbon oxides and Section 27.7 (p.1238) on preparation of Group 18 compounds.

Solution

(a) $IF_7 + SbF_5 \rightarrow [IF_6]^+[SbF_6]^-$

(b) dehydration of propanedioic acid with P_4O_{10}

(c) reaction of XeF_4 with water

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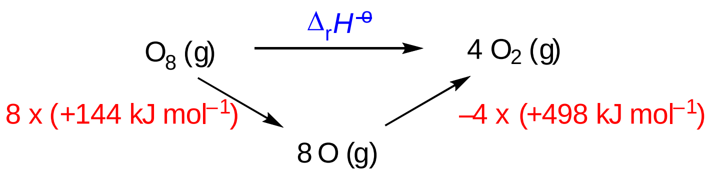
11. Use the bond enthalpy data below to explain why oxygen exists as O_2 molecules and not O_8 rings, analogues to those formed by sulfur.

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.

$O_8 \rightarrow 4\ O_2$



$\Delta_r H^{\ominus} = [(8 \times +144\ \text{kJ mol}^{-1}) + (4 \times -498\ \text{kJ mol}^{-1})] = -840\ \text{kJ mol}^{-1}$. The conversion of O_8 to 4 O_2 would be highly exothermic, so O_2 is the more stable form of oxygen. This calculation ignores the change in entropy, which is positive so also favours the formation of four O_2.

13. 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?

Cl–Cl +242 kJ mol^{-1}, O=O +498 kJ mol^{-1}, Cl–O +205 kJ mol^{-1}

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.

Solution

$Cl_2 + \frac{1}{2}\ O_2 \rightarrow Cl_2O$

This gives the following enthalpy cycle:

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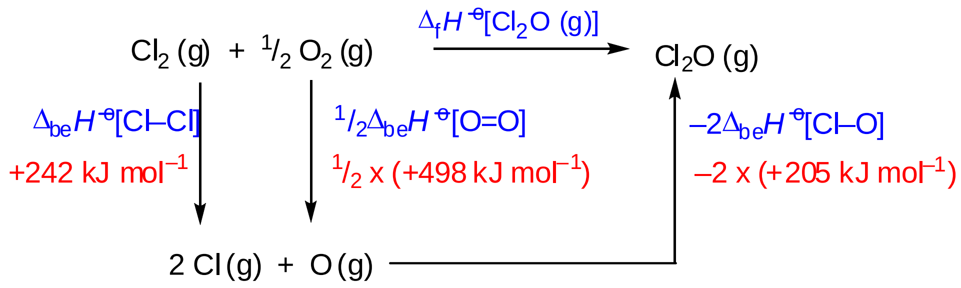

$$\Delta_f H^\ominus[Cl_2O\ (g)] = +242\ \text{kJ mol}^{-1} + (^1/_2 \times 498\ \text{kJ mol}^{-1}) - (2 \times 205\ \text{kJ mol}^{-1})$$
$$= +81\ \text{kJ mol}^{-1}$$

Since $\Delta_f H^\ominus$[Cl_2O (g)] is positive and hence endothermic, Cl_2O would not form from chlorine and dioxygen.

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