Answers to self-tests and exercises

Please note that just the final numerical solutions and short-answer solutions are supplied. For full worked solutions, please refer to the Solutions Manual by Alen Hadzovic (9780198701712).

CHAPTER 1

Self-tests

S1.1 779967m⁻³, 1.28 × 10⁻⁴ m or 1280 nm.
S1.2 3d set of orbitals, 5 orbitals
S1.3 4
S1.4 3p
S1.5 The s electron already present in Li repels the incoming electron more strongly than the p electron already present in B repels the incoming p electron, because the incoming p electron goes into a new orbital.
S1.6 Ni :[Ar]3d⁸ 4s², Ni⁺⁺ :[Ar]3d⁸
S1.7 Period 4, Group 2, s block
S1.8 Generally, going down a group the atomic radius increases and the first ionization energy generally decreases.
S1.9 Group 14.
S1.10 The electron-gain process for N is unfavourable
S1.11 Na⁺

Exercises

1.1 \( E(\text{He}^+)/E(\text{Be}^{3+}) = Z^2(\text{He}^+)/Z^2(\text{Be}^{3+}) = 2^2/4^2 = 0.25 \)

1.2 (a) At nucleus
(b) Exactly at Bohr radius, \( a_0 \)
(c) \( 3+\sqrt{3}a_0 \)

1.3 \( E(\text{H}, n = 1) – E(\text{H}, n = 6) = 13.6 \text{ eV} – 0.378 \text{ eV} = 13.2 \text{ eV} \).

1.4 0.544 eV. The discrepancy is due to the shielding effect
1.5 14.0 eV, 4.16 eV

1.6 102.5 nm, 1.937 × 10⁻¹⁸ J

1.7 1.524 × 10⁻³ nm⁻¹, 656.3 nm

1.8 \( \frac{1}{\lambda} = R \left( \frac{1}{l^2} – \frac{1}{n^2} \right) = 1.0974 × 10^7 \text{ m}^{-1} \)

1.9 For a given value of \( n \), the angular momentum quantum number \( l \) can assume all integer values from 0 to \( n – 1 \).

1.10 \( n^2 \) (e.g., \( n^2 = 1 \) for \( n = 1 \), \( n^2 = 4 \) for \( n = 2 \), etc.)

1.11

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l )</th>
<th>( m_l )</th>
<th>Orbital designation</th>
<th>Number of orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>+1, 0, –1</td>
<td>2p</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>+2, –1</td>
<td>3d</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>⋯, –2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>4s</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>+3, +2</td>
<td>4f</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>⋯, –3</td>
<td></td>
</tr>
</tbody>
</table>

1.12 When \( n = 5 \), \( l = 3 \) (for the f orbitals) and \( m_l = –3, –2, –1, 0, 1, 2, 3 \), which represent the seven orbitals that complete the 5f subshell. The 5f orbitals represent the start of the actinoids, starting with Th and ending with Lr.

1.13 Comparing the plots for 1s (Figure 1.10) and 2s (Figure 1.12) orbitals, the radial distribution function for a 1s orbital has a single maximum, and that for a 2s orbital has two maxima and a minimum (at \( r = 2a_0/Z \) for hydrogenic 2s orbitals). The presence of the node at \( r = 2a_0/Z \) for \( R(2s) \) requires the presence of the two maxima and the minimum in the 2s radial distribution function. The absence of a radial node for \( R(2p) \) requires that the 2p radial distribution function has only a single maximum.
1.14

Each 4p orbital has one nodal plane; the total number of nodes is 3.

1.15

\[ \text{d}_{xy} \quad \text{Function: } xyR(r) \quad \text{Label: } xy \]

1.16

The first ionization energies of strontium, barium, and radium are 5.69, 5.21, and 5.28 eV. Radium has a higher first ionization energy because it has such a large \( Z_{\text{eff}} \) due to the insertion of the lanthanides.

1.17

The 1s electrons shield the positive charge from the 2s electrons, which are further out from the nucleus than the 1s electrons. Consequently, the 2s electrons “feel” less positive charge than the 1s electrons for beryllium.

1.18

The higher value of \( I_2 \) for Cr relative to Mn is a consequence of the special stability of half-filled subshell configurations and the higher \( Z_{\text{eff}} \) of a 3d electron vs. a 4s electron.

1.20

Both of these atoms have an electron configuration that ends with 4s\(^2\); Ca is [Ar]4s\(^2\) and Zn is [Ar]3d\(^{10}\)4s\(^2\). An atom of zinc has 30 protons in its nucleus and an atom of calcium has 20, so clearly zinc has a higher nuclear charge than calcium. However it is effective nuclear charge (\( Z_{\text{eff}} \)) that directly affects the ionization energy of an atom. Since \( I(Zn) > I(Ca) \), it would seem that \( Z_{\text{eff}}(Zn) > Z_{\text{eff}}(Ca) \).

1.21

Both the first and the second ionization processes remove electrons from the 4s orbital of these atoms, with the exception of Cr. In general, the 4s electrons are poorly shielded by the 3d electrons, so \( Z_{\text{eff}}(4s) \) increases from left to right and \( I_2 \) also increases from left to right.

1.22

\[ \begin{align*}
\text{(a)} & \quad \text{[He]2s}^22p^2 \\
\text{(b)} & \quad \text{[He]2s}^22p^6 \\
\text{(c)} & \quad \text{[Ar]4s}^2 \\
\text{(d)} & \quad \text{[Ar]3d}^{10} \\
\text{(e)} & \quad \text{[Xe]4f}^{14}5d^{10}6s^26p^3 \\
\text{(f)} & \quad \text{[Xe]4f}^{14}5d^{10}6s^2
\end{align*} \]

1.23

\[ \begin{align*}
\text{(a)} & \quad \text{[Ar]3d}^{1.4s}^2 \\
\text{(b)} & \quad \text{[Ar]3d}^5 \\
\text{(c)} & \quad \text{[Ar]3d}^6 \\
\text{(d)} & \quad \text{[Ar]3d}^6 \\
\text{(e)} & \quad \text{[Ar] or [Ar]3d}^0 \\
\text{(f)} & \quad \text{[Kr]4d}^2
\end{align*} \]

1.24

\[ \begin{align*}
\text{(a)} & \quad \text{[Xe]4f}^{14}5d^{10}6s^2 \\
\text{(b)} & \quad \text{[Kr]4d}^6 \\
\text{(c)} & \quad \text{[Xe]4f}^6 \\
\text{(d)} & \quad \text{[Xe]4f}^7 \\
\text{(e)} & \quad \text{[Ar] or [Ar]3d}^0 \\
\text{(f)} & \quad \text{[Kr]4d}^2
\end{align*} \]

1.26

\[ \begin{align*}
\text{(a)} & \quad \text{S} \\
\text{(b)} & \quad \text{Sr} \\
\text{(c)} & \quad \text{V} \\
\text{(d)} & \quad \text{Tc} \\
\text{(e)} & \quad \text{In} \\
\text{(f)} & \quad \text{Sm}
\end{align*} \]

1.27

See Figure 1.22 and the inside front cover of the book.

1.28

In general, \( I_1 \), \( A_e \), and \( \chi \) all increase from left to right across period 3. The cause of the
general increase across the period is the gradual increase in $Z_{\text{eff}}$, which itself is caused by the incomplete shielding of electrons of a given value of $n$ by electrons with the same $n$.

1.29 $2s^2$ and $2p^3$

1.30 One $2s$ and three $2p$

**CHAPTER 2**

**Self-tests**

**S2.1**

(a) Bent

(b) Tetrahedral

(c) Trigonal-bipyramidal

**S2.2**

(a) Bent

(b) Tetrahedral

(c) Trigonal-bipyramidal

**S2.3**

(a) Linear

(b) Bent

(c) Linear

**S2.4**

(a) 2, 1, 0

(b) $1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 2\pi_u^4 2\pi_g^4$

$1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 2\pi_u^4 2\pi_g^4 4\pi_u^1$

**S2.5**

$1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^4$

$\frac{1}{2}[2-2+4+2] = 3$

**S2.7**

Bond length (shortest to longest): C≡N, C≡N, and C–N; Bond strength (strongest to weakest): C≡N > C≡N > C–N.

**S2.8**

24 kJ mol$^{-1}$

**S2.9**

(a) +1/2

(b) +5

(c) 6

(d) +3

**Exercises**

2.1 (a) $\text{N} \equiv \text{O}^-\quad \text{b}$

2.2

(a) Angular

(b) Tetrahedral

(c) Tetrahedral

2.3

(a) Angular

(b) Tetrahedral

(c) Tetrahedral

2.4

(a) Trigonal-planar

(b) Trigonal-pyramidal

(c) Square-pyramidal

2.5

(a) Octahedral

(b) T-shaped

(c) Square pyramidal

2.6

(a) T-shaped

(b) Square planar

(c) Linear

2.7 $\text{ICl}_6^-$

2.8 Tetrahedral and octahedral

2.9

(a) 176 pm

(b) 217 pm

(c) 221 pm

2.10 The single bond covalent radii decrease if we move horizontally from left to right in the periodic table. The atomic radii decrease while the $Z_{\text{eff}}$ increases in the same direction.
As a consequence of these two trends, the valence electrons are held tighter and closer to the atomic nucleus. This means that, as we move from left to right, the distance between two non-metallic atoms has to decrease in order for the covalent bond to be formed. This results in a shorter internuclear separation and as a consequence smaller covalent radii in the same direction.

As we go down a group the valence electrons are found in the atomic orbitals of higher principal quantum number. There are more core electrons between the valence electrons and the nucleus that shield the valence electrons from the influence of the nucleus. As a consequence, the valence electrons are further away from the nucleus. This means that when a covalent bond is formed, two atomic nuclei are further apart as we go down the group and the covalent radii increase.

2.11 2(Si–O) – (Si=O) = 2(466 kJ) – (640 kJ) = 292 kJ
Therefore two single bonds will always be better enthalpically than one double bond.

2.12 If N$_2$ were to exist as N$_4$ molecules with the P$_4$ structure, then two N=N triple bonds would be traded for six N–N single bonds, which are weak. The net enthalpy change can be estimated to be 2(945 kJ) – 6(163 kJ) = 912 kJ.
The net enthalpy change for 2P$_2$ → P$_4$ can be estimated to be 2(481 kJ) – 6(201 kJ) = -244 kJ.

2.13 -483 kJ

2.14 The atoms that obey the octet rule are O in BeO, F in NF, and O in O$_2$.

2.15 (a) 0 kJ
(b) 205 kJ

2.16 (a) +4
(b) +3
(c) +6
(d) +5
(e) +5

2.17 AD < BD < AC < AB

2.18 (a) Covalent

(b) Ionic
(c) Ionic

2.19 (a) sp$^2$
(b) sp$^3$
(c) sp$^3$d or sp$^3$d$^1$
(d) sp$^3$d$^2$

2.20 (a) 1
(b) 1
(c) 0
(d) 2

2.21 (a) 1σ$^2$2σ$^2$

(b) 1σ$^2$1σ$^2$2π$^2$

(c) 1σ$^2$1σ$^2$2π$^2$2σ$^2$

(d) 1σ$^2$1σ$^2$2σ$^2$1π$^4$1π$^3$

2.22 The configuration of C$_2^-$ would be 1σ$^2$2σ$^2$1π$^4$2π$^2$. The bond order would be $\frac{1}{2}[2-2+4+2] = 3$. So C$_2^-$ has a triple bond. The configuration for the neutral C$_2$ would be
1σ_g^21σ_u^21π_u^4. The bond order would be \(\frac{1}{2}[2-2+4] = 2\).

2.23 See figure 2.18. The bond order would be \(\frac{1}{2}[2-2+4] = 2\).

2.24 See figure 2.22.

2.25 (a) The 5p and 5s of I, and the 4p and 4s of Br
(b) \(\frac{1}{2}[2+2-2+4-4] = 1\)

2.26 (a) \((1/2)((2+4+2)-(2+2)) = 2\)
(b) \((1/2)((2+4+2)-(2+4)) = 1\)
(c) \((1/2)((2+2+4)-2) = 3\)

2.27 (a) Bond order increases from 2 to 2.5; bond in O_2^+ becomes shorter
(b) N_2^- has a weaker and longer bond than N_2
(c) Increase the bond order from 2.5 to 3, making the bond in NO^- stronger

2.28 The line at about 15.2 eV corresponds to excitation of the electrons from 3σ molecular orbital (the HOMO of CO). The group of four peaks between 17 and about 17.8 eV correspond to the excitation of 1π electrons, and finally the last peak (highest in energy) corresponds to the excitation of 2σ electrons.

The UV photoelectron spectrum of SO should have one more line at even lower energies corresponding to the ionization from 2π degenerate set of molecular orbitals.

2.29 Four atomic orbitals can yield four independent linear combinations

2.30 Probably not stable in isolation; unstable in solution.

2.31 3/3 = 1

2.32 More S character

2.33 Your molecular orbital diagram for the N_2 molecule should look like the one shown on Figure 2.18, whereas the diagrams for O_2 and NO should be similar to those shown on Figures 2.12 and 2.22 respectively. The variation in bond lengths can be attributed to the differences in bond orders.

2.35 (a) Hypothetical example of (4c,2e) bonding; not likely to exist.
(b) It is electron precise. It could very well exist.

CHAPTER 3

Self-tests

S3.1 P- type lattice of chloride anions with caesium cation in cubic hole.
S3.2

![Image of a crystal structure]

S3.3  
(a) 52%  
(b) 68%

S3.4  
\[ r_r = (\frac{3}{2})^{1/2} - 1 \]  
\[ r = 0.225 \]

S3.5  
Each unit cell contains eight tetrahedral holes, each inside the unit cell. As outlined in Example 3.5, the ccp unit cell has four identical spheres. Thus, the spheres-to-tetrahedral holes ratio in this cell is 4 : 8 or 1 : 2.

S3.6  
409 pm

S3.7  
401 pm

S3.8  
FeCr₃

S3.9  
X₂A₃.

S3.10  
The coordination of O²⁻ is two Ti⁴⁺ and four Ca²⁺ and longer distances.

S3.11  
LaInO₃

S3.12  
NaCl structure, TiO₂ structure

S3.13  
2421 kJ mol⁻¹

S3.14  
Unlikely

S3.15  
\( \text{MgSO}_4 < \text{CaSO}_4 < \text{SrSO}_4 < \text{BaSO}_4 \)

S3.16  
NaClO₄

S3.17  
(a) Frenkel defects  
(b) Schottky defects

S3.18  
Phosphorus and aluminium.

S3.19  
The \( d_{2x2} \) and \( d_{3z} \) have lobes pointing along the cell edges to the nearest neighbor metals.

S3.20  
\( n \)-type, \( p \)-type

Exercises

3.1  
\( a \neq b \neq c \) and \( \alpha = 90°, \beta = 90°, \gamma = 90° \)

3.2  

![Image of cell structures]

3.3  
Points on the cell corners are (0,0,0), (1,0,0), (0,1,0), (0,0,1), (1,1,0), (1,0,1), (0,1,1), and (1,1,1); the fractional coordinates for the points at the centre of each face are \( (\frac{1}{2},\frac{1}{2},0) \), \( (\frac{1}{2},1,\frac{1}{2}) \), \( (0,\frac{1}{2},\frac{1}{2}) \), \( (\frac{1}{2},\frac{1}{2},1) \), \( (\frac{1}{2},1,\frac{1}{2}) \), and \( (1,\frac{1}{2},\frac{1}{2}) \).

3.4  
Perovskite-type structure

3.5  
(c) and (f)

3.6  
(a) MX  
(b) M₂A

3.7  
K₃C₆₀

3.8  

![Image of a structure diagram]

3.9  
6, W₂C₃

3.10  
429 pm

3.11  
Cu₃Au, primitive cubic, 12 carat

3.12  
Alloy

3.13  
(a) 6:6 and 8:8  
(b) Larger when RbCl has the caesium-chloride structure

3.14  
6

3.15  
(a) Coordination number of O atoms is two; coordination number of Re atoms is six

To accompany Inorganic Chemistry, Sixth Edition by Weller, Overton, Rourke, and Armstrong
(b) Perovskite-type structure

3.16 Cations in site A have coordination number 12, whereas those in site B have coordination number six.

3.17 CaF$_2$

3.18 (a) MX$_2$  
(b) MX$_2$  
(c) M$_2$X$_3$

M: (a) 6 and (b) 4  
X: (a) ½-3 and (b) 2

3.19 (a) TiO$_2$-type  
(b) CsCl-type  
(c) ZnS-type  
(d) NaCl or NiAs-type

3.20 $r$(Mg$^{2+}$) = 79.8 pm, $r$(Ca$^{2+}$) = 102.8 pm, $r$(Sr$^{2+}$) = 118.8 pm, and $r$(Ba$^{2+}$) = 138.3 pm

3.21 (a) (6,6)  
(b) (6,6)  
(c) (6,6)  
(d) (6,6)

3.22 Each of the complex ions in this exercise ([PtCl$_6^{2-}$], [Ni(H$_2$O)$_6^{2+}$], [SiF$_6^{2-}$]) is highly symmetric and their shape can be approximated with a sphere. For example, K$_2$PtCl$_6$ has an antifluorite structure with anions [PtCl$_6^{2-}$] forming a ccp array and K$^+$ cations occupying each tetrahedral hole.

3.23 Calcite has a rhombohedral unit cell, whereas NaCl has a cubic one. Both rhombohedral and cubic unit cells have all three dimensions equal ($a = b = c$) but they differ in the angles, with cubic unit cell having all angles at 90° and rhombohedral all angles equal but different from 90°.

3.24 The most important terms will involve the lattice enthalpies for the di- and the trivalent ions. Also, the bond dissociation energy and third electron gain enthalpy for nitrogen (N$_2$) will be large.

3.25 MgO: 3144 kJ mol$^{-1}$  
AlN: 7074 kJ mol$^{-1}$

3.26 (a) 1990 kJ mol$^{-1}$  
(b) The massive second ionization energy for K, 3051 kJ mol$^{-1}$

3.27 From the Born-Haber cycle for CaCl, 
$\Delta H$(CaCl) = +176 kJ mol$^{-1}$ + 589 kJ mol$^{-1}$ + 122 kJ mol$^{-1}$ − 355 kJ mol$^{-1}$ − 717 kJ mol$^{-1}$ = −185 kJ mol$^{-1}$, showing that CaCl is an exothermic salt.

Although CaCl has a favourable (negative) $\Delta H$, this compound does not exist and would convert to metallic Ca and CaCl$_2$ (2CaCl → Ca + CaCl$_2$). This reaction is very favourable because CaCl$_2$ has a higher lattice enthalpy (higher cation charge). The higher lattice enthalpy combined with gain of $I_1$ for Ca (Ca$^{2+}$ + e$^-$ → Ca(g)) are sufficient to compensate for $I_2$ (Ca$^{2+}$ → Ca$^{2+}$ + e$^-$) required to form CaCl$_2$.

3.28 Hexagonal ZnS

3.29 (b) Ca$^{2+}$ and Hg$^{2+}$

3.30 (a) 10906 kJ mol$^{-1}$  
(b) 1888 kJ mol$^{-1}$  
(c) 664 kJ mol$^{-1}$

3.31 (a) CaSeO$_4$  
(b) NaBF$_4$

3.32 CsI < RbCl < LiF < CaO < NiO < AlN

3.33 Ba$^{2+}$, Na$^+$, Ba$^{2+}$

3.34 (a) MgCO$_3$  
(b) CsI$_3$

3.35 (a) Schottky defects  
(b) Frenkel defects

3.36 In sapphire, the blue colour is due to the electron transfer between Fe$^{2+}$ and Ti$^{4+}$ substituting for Al$^{3+}$ in adjacent octahedral sites in Al$_2$O$_3$ structure. As beryl also contains Al$^{3+}$ in octahedral sites, it is plausible that the blue colour of aquamarine is due to the same two dopants.

3.37 Vanadium carbide and manganese oxide

3.38 The formation of defects is normally endothermic because as the lattice is disrupted the enthalpy of the solid rises. However, the term $-T\Delta S$ becomes more negative as defects are formed because they introduce more disorder into the lattice and the entropy rises. As temperature is raised, this minimum in $G$ shifts to higher defect concentrations. Increase in pressure would result in fewer defects in the solid. This is because at higher pressures, lower coordination numbers (tighter packing) are preferred.

3.39 UO$_{2+x}$
3.40  (a) p-type
(b) n-type
(c) n-type

3.41  TiO and VO have metallic properties

3.42  A semiconductor is a substance with an electrical conductivity that decreases with increasing temperature. It has a small, measurable band gap. A semimetal is a solid whose band structure has a zero density of states and no measurable band gap.

3.43  Ag₂S and CuBr: p-type
VO₂: n-type

3.44  Both KC₃ and C₈Br should have metallic properties.

CHAPTER 4

Self-tests

(b) Carbonate ion, base; hydrogen carbonate, or bicarbonate, conjugate acid; H₂O, acid; hydroxide ion, conjugate base.
(c) Ammonia, base; NH₄⁺, conjugate acid; hydrogen sulphide, acid; HS⁻, conjugate base.

S4.2  pH= 2.24
S4.3  pH=1.85
S4.4  [Na(H₂O)₆]⁺ < [Mn(H₂O)₆]²⁺ < [Ni(H₂O)₆]²⁺ < [Sc(H₂O)₆]³⁺

S4.5  (a) 3. The actual value, given in Table 4.3, is 2.1.
(b) 8. The actual value, given in Table 4.3, is 7.4.
(c) 13. The actual value, given in Table 4.3, is 12.7.

S4.6  H₂O₂ would not react with Ti(IV) since Ti(IV) cannot be further oxidized.

S4.7  (a) The acid FeCl₃ forms a complex, [FeCl₄]⁻, with the base Cl⁻.
(b) The acid I₂ forms a complex, I⁻, with the base I⁻.

Exercises

4.1  See the diagram below for the outline of the acid-base properties of main group oxides. The elements that form basic oxides have symbols printed in bold, those forming acidic oxides are underlined, and those forming amphoteric oxides are in italics.

4.2  (a) [Co(NH₃)₆(OH)]²⁺
(b) SO₄⁻
(c) CH₃O⁻
(d) HPO₄²⁻
(e) SiO(OH)$_3^-$
(f) S$^2^-$

4.3
(a) C$_3$H$_7$N$^+$
(b) H$_3$PO$_4^-$
(c) OH$^-$
(d) CH$_3$C(OH)$_2^+$
(e) HCo(CO)$_4$
(f) HCN

4.4
$[\text{H}_3\text{O}^+] = 1.4 \times 10^{-3}$
$p\text{H}=2.85$

4.5
$5.6 \times 10^{-10}$

4.6
$5.6 \times 10^{-6}$

4.7 Base

4.8

![Chloric acid and chlorous acid structures]

Chloric acid, the predicted $pK_a = -2$; actual value = -1.
Chlorous acid, the predicted $pK_a = 3$; actual value = 2.

4.9
(a) CO$_3^{2^-}$ is of directly measurable base strength. O$_2^-$ is too strong to be studied experimentally in water.
ClO$_4^{2^-}$ and NO$_3^-$ are too weak to be studied experimentally.
(b) HSO$_4^-$, not too strong to be studied experimentally.
NO$_3^-$ is of directly measurable base strength in liquid H$_2$SO$_4$.
ClO$_4^-$ cannot be studied in sulfuric acid.

4.10 Electron withdrawing.

4.11 The difference in $pK_a$ values can be explained by looking at the structures of the acids in question.

4.12
Na$^+$ < Sr$^{2+}$ < Ca$^{2+}$ < Mn$^{3+}$ < Fe$^{3+}$ < Al$^{3+}$

4.13
HClO$_4^-$ > HBrO$_3^-$ > H$_2$SO$_4^-$ > HNO$_2$.

4.14
(a) The Fe(III) complex, [Fe(OH)$_2$)$_6$]$^{3+}$, is the stronger acid.
(b) The aluminum-aqua ion is more acidic.
(c) Si(OH)$_4$ is more acidic.
(d) HClO$_4$ is a stronger acid.
(e) HMnO$_4$ is the stronger acid.
(f) H$_2$SO$_4$ is a stronger acid.

4.15
Cl$_2$O$_7$ < SO$_3^{2-}$ < CO$_2$ < B$_2$O$_3$ < Al$_2$O$_3$ < BaO.

4.16
NH$_3$ < CH$_3$GeH$_3$ < H$_2$SiO$_4$ < HSO$_4^-$ < H$_2$O$^+$ < HSO$_3^-$F.

4.17
The Ag$^+$ ion is the stronger acid.

4.18
Polycation formation reduces the overall positive charge of the species by +1 per M.

4.19
(a)
H$_3$PO$_4$(aq) + HPO$_4^{2-}$(aq) $\rightleftharpoons$ 2H$_2$PO$_4^-$(aq)
(b)
CO$_2$(aq) + CaCO$_3$(s) + H$_2$O(l) $\rightleftharpoons$ Ca$^{2+}$(aq) + 2HCO$_3^-$

4.20
H$_2$SO$_4$ + HF $\rightleftharpoons$ H$_2$SO$_4^+$ + F$^-$

NH$_4^+$ + HF $\rightleftharpoons$ NH$_3$ + H$_2$F$^+$

4.21
As you go down a family in the periodic chart, the acidity of the homologous hydrogen compounds increases.

4.22
Fluorine’s high electronegativity results in electron withdrawal from the central Si atom making the Si very nucleophilic. This fact, combined with the small size of F atom (little steric hindrance at Si) makes SiF$_4$ the strongest Lewis acid of the four.

The order of Lewis acidity for boron halides is due to additional electronic effects. See Section 4.7(b) Group 13 Lewis acids in the textbook.
4.23 (a) The acids in this reaction are the Lewis acids SO₃ and H⁺ and the base is the Lewis base OH⁻. This is a displacement reaction.

(b) This is a displacement reaction. The Lewis acid Hg²⁺ displaces the Lewis acid [B₁₂⁺] from the Lewis base CH₃⁻.

(c) This is also a displacement reaction. The Lewis acid SnCl₂ displaces the Lewis acid K⁺ from the Lewis base Cl⁻.

(d) It is a displacement reaction. The very strong Lewis acid SbF₅ (one of the strongest known) displaces the Lewis acid [AsF₅]⁺ from the Lewis base F⁻.

(e) A Lewis–base complex formation reaction between EtOH (the acid) and py (the base) produces the adduct EtOH–py, which is held together by a hydrogen bond.

4.24 (a) Boron tribromide; the acceptor orbital on boron is involved to a greater extent in π bonding in BF₃ and BCl₃ than in BBF₃.

(b) The smaller Lewis base NMe₃ is the stronger in this case.

4.25 (a) Less than 1.

(b) Greater than 1.

(c) Less than 1.

(d) Greater than 1.

4.26 (a) CsF + BrF₃ → Cs⁺ + BrF₅⁻; in this case F⁻ is a Lewis base whereas BrF₅ is a Lewis acid.

(b) ClF₃ + SbF₅ → ClF₅⁻ + SbF₃⁻; again F⁻ is a Lewis base, whereas SbF₅ is Lewis acid.

(c) B(OH)₃ + H₂O → [B(OH)₄(H₂O)]⁻ → [B(OH)₄]⁻ + H⁺; the Lewis acid in this reaction is B(OH)₃, whereas the Lewis base is H₂O.

(d) B₂H₆ + 2PMe₃ → 2[BH₄(PMe₃)]⁻; the base is PMe₃ and the acid is B₂H₆.

4.27 Trimethylamine is sterically large enough to fall out of line with the given enthalpies of reaction.

4.28 (a) DMSO is the stronger base; the ambiguity for DMSO is that both the oxygen atom and sulfur atom are potential basic sites.

(b) Depending on the $E_A$ and $C_A$ values for the Lewis acid, either base could be stronger.

4.29

\[
\text{SiO}_2 + 6\text{HF} \rightarrow 2\text{H}_2\text{O} + \text{H}_2\text{SiF}_6
\]

\[
\text{SiO}_2 + 4\text{HF} \rightarrow 2\text{H}_2\text{O} + \text{SiF}_4
\]

The Brønsted reaction involves the transfer of protons from HF molecules to O²⁻ ions, whereas the Lewis reaction involves complex formation between Si(IV) centre and F⁻ ions.

4.30 \[
\text{Al}_2\text{S}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{S}
\]

An equilibrium is established between two hard acids, Al(III) and H⁺, and the bases O²⁻ and S²⁻:

4.31 (a) The ideal solvent properties in this case would be *weak, hard,* and *acidic,* for example HF.

(b) Alcohols such as methanol or ethanol would be suitable.

(c) A solvent that is a hard base is suitable, for example diethyl ether.

(d) The solvent must be a softer base than Cl⁻ and have an appreciable dielectric constant, for example acetonitrile.

4.32 An alumina surface, such as the partially dehydroxylated one shown below, would also provide Lewis acidic sites that could abstract Cl⁻:

4.33 Mercury(II) is a soft Lewis acid, and so is found in nature only combined with soft Lewis bases, the most common of which is S²⁻.

Zinc(II), which exhibits borderline behaviour, is harder and forms stable compounds (i.e., complexes) with hard bases such as O²⁻, CO₃²⁻, and silicates, as well as with S²⁻.

4.34 (a) CH₃CH₂OH + HF \rightarrow CH₃CH₂OH₂⁺ + F⁻

(b) NH₃ + HF \rightarrow NH₄⁺ + F⁻
(c) \( \text{C}_6\text{H}_5\text{COOH} + \text{HF} \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^- + \text{H}_2\text{F}^+ \)

4.35 Both a Brønsted acid–base reaction and a Lewis acid–base reaction.

4.36 Very hard.

4.37 -20.0 kJ/mol

4.38 The lowest solvation energy is going to be observed for the largest cation of the group.

4.39

\[
\begin{align*}
\text{CO}_2(\text{g}) & \rightleftharpoons \text{CO}_2(\text{aq}) & (1) \\
\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) & \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) & (2) \\
\text{M}_2\text{SiO}_4(\text{s}) + 4\text{H}_2\text{CO}_3(\text{aq}) & \rightleftharpoons 2\text{M}^{2+} + \text{Si(OH)}_4(\text{aq}) + 4\text{HCO}_3^-(\text{aq}) & (3)
\end{align*}
\]

4.40 (a) \( \text{Fe}^{3+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Fe(OH)}_3(\text{s}) + 3\text{H}^+ \)

(b) 0.1547 M; pH = 1.6; neglected Fe\(^{3+}\) containing species are Fe(OH)\(^{2+}\) and Fe(OH)\(^{2+}\). 4.41 With increasing charge density the attraction between M\(^{2+}\) cation and partially negative O atom in H\(_2\)O is increasing. For the same reason, the acidity of these aqua acids is increasing showing that two trends correlate closely.

4.42 [AlCl\(_3\)(NCCH\(_3\))\(_4\)]\(^+\) and Cl\(^-\) (sol)

4.43 Equation (b) is better in explaining the observations described in the exercise.

4.44 The borderline does agree with describing S\(^{2-}\) as a softer base than O\(^{2-}\).

4.45

\[
\begin{align*}
\text{SO}_2 + \text{Cl}^- & \rightleftharpoons \text{SO}_2\text{Cl}^- & \\
\text{SO}_2\text{Cl}^- + \text{SOCl}_2 & \rightleftharpoons \text{SOCl}_2 + \text{SO}_2\text{Cl}^- & \text{SO}_2\text{Cl}^- + \text{SO}_2 + \text{Cl}^- & \\
\text{SOCl}_2 + \text{SbCl}_3 & \rightleftharpoons \text{SOCl}_2\text{SbCl}_3 & \\
\text{SOCl}_2\text{SbCl}_3 & \rightleftharpoons \text{SOCl}_2 + \text{SbCl}_3 & \\
\text{SOCl}_2 + \text{SbCl}_3 & \rightleftharpoons \text{SOCl}_2\text{SbCl}_3 & \\
\text{SOCl}_2\text{SbCl}_3 & \rightleftharpoons \text{SOCl}_2 + \text{SbCl}_3
\end{align*}
\]

4.46 The reasons for the difference in stability are steric.

4.47 (a) Less than 1
(b) Greater than 1
(c) Greater than 1

4.48 (a) Fe(ClO\(_4\))\(_3\)
(b) Mg(NO\(_3\))\(_2\)
(c) Zn(NO\(_3\))\(_2\)

4.49 Cations such as I\(^{2+}\) and Se\(^{2+}\) should behave like good Lewis acids while anions such as S\(_4\)^\(^{2-}\) and Pb\(_4\)^\(^{2-}\), are good Lewis bases.

4.50 For titration of a weak base with a strong acid we have to find a solvent other than water in which a weak base is going to behave as strong one and give us a sharp and easy to detect end point. To achieve this, we have to find solvent more acidic than water, which can be acetic acid.

**CHAPTER 5**

**Self-tests**

S5.1 \( 2\text{MnO}_4^- (\text{aq}) + 5\text{Zn}(\text{s}) + 16\text{H}^+(\text{aq}) \rightarrow 5\text{Zn}^{2+}(\text{aq}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) \)

S5.2 No.

S5.3 Fe\(^{2+}\) will be oxidized to Fe\(^{3+}\) by dichromate; a side reaction with Cl\(^-\) should be expected.

S5.4 + 1.25 V

S5.5 The aqueous solution of SO\(_4\)^\(^{2-}\) and H\(^+\) ions precipitates as acid rain.

S5.6 No.

S5.7 Ru(II) preferentially. 17 orders of magnitude decreased.

S5.8 +0.223 V.

S5.9 (a) Pu(IV) disproportionates to Pu(III) and Pu(V) in aqueous solution.
(b) Pu(V) does not disproportionate into Pu(VI) and Pu(IV).

S5.10

![Graph showing oxidation number vs. E when V graphed for Tl\(^0\) and Tl\(^{3+}\).](image)
S5.11 Mn²⁺(aq) is the most stable species present because it has the most negative ΔG. Therefore, Mn²⁺(aq) will be the final product of the redox reaction when MnO₄⁻ is used as an oxidizing agent in aqueous acid.

S5.12 Nitrate is a stronger oxidizing agent in acidic solution than in basic solution.

S5.13 Fe(OH)₃ is not stable and Fe²⁺(aq) will be the predominant species.

S5.14 2000°C or above.

Exercises

5.1 2 NO(g) + O₂(g) → 2 NO₂(g)
+2 -2 0 +4 -2

2Mn³⁺(aq) + 2H₂O → MnO₂ + Mn²⁺ + 4H⁺(aq)
+3  +1-2 +4 -2 +2 +1

LiCoO₂(s) + C(s) → LiC(s) + Co₂O₃(s)
+1 +3 -2 0 +1-1 +4 -2

Ca(s) + H₂(g) → CaH₂(s)
0 0 +2 -1

5.2 (a) S₂O₃²⁻, H₂O₂, α-PbO₂ or MnO₄⁻ to oxidize Cl₂ to Cl₂.

(b) Metallic manganese, metallic zinc, or NH₃OH⁺.

(c) The reduced form of any couple with a reduction potential less than 0.799 V, for example Cu²⁺/Cu (+0.340 V).

(d) The reduced form of any couple with a reduction potential less than 0.535 V for example S/H₂S (+0.144 V).

5.3 (a) 4Cr²⁺(aq) + O₂(g) + 4H⁺(aq) → 4Cr³⁺(aq) + 2H₂O(l)
E⁰ = 1.65 V

(b) 4Fe²⁺(aq) + O₂(g) + 4H⁺(aq) → 4Fe³⁺(aq) + 2H₂O(l)
E⁰ = 0.46 V

(c) No reaction.

(d) No reaction.

(e) 2Zn(s) + O₂(g) + 4H⁺(aq) → 2Zn²⁺(aq) + 2H₂O(l)
E⁰ = 1.99 V

A competing reaction is:
Zn(s) + 2H⁺(aq) → Zn²⁺(aq) + H₂(g) (E⁰ = 0.763 V).

5.4 (a) (i) Fe²⁺ will not oxidize water.
(ii) Fe²⁺ will not reduce water.
(iii) Fe²⁺ will reduce O₂ and in doing so will be oxidized to Fe³⁺.
(iv) Disproportionation will not occur.

(b) Ru³⁺ will not oxidize or reduce water. Ru²⁺ will reduce O₂ and in doing so will be oxidized to Ru⁴⁺. Ru²⁺ will disproportionate in aqueous acid to Ru³⁺ and metallic ruthenium.

(c) HClO₂ will oxidize water, will not reduce O₂. HClO₂ will reduce O₂ and in doing so will be oxidized to ClO⁻. HClO₂ will disproportionate in aqueous acid to ClO⁻ and HClO.

(d) Br₂ will not oxidize or reduce water. Br₂ will not reduce O₂. Br₂ will not disproportionate in aqueous acid to Br⁻ and HBrO.

5.5 The change in temperature has the opposite effect on one or both K values for the two complexes.

5.6 2MnO₄⁻(aq) + 5H₂SO₃(aq) + H⁺(aq) → 2Mn²⁺(aq) + 5HSO₄⁻(aq) + 3H₂O(l)
The potential decreases as the pH increases.

5.7 ΔOxH equals +445 kJ mol⁻¹

5.8 (a) 

\[
Q = \frac{1}{p(O_2)[H^+]^4} \quad \text{and} \quad E = E^0 - \frac{0.059V}{4} \log \left( \frac{1}{p(O_2)[H^+]^4} \right)
\]

In terms of pH:

\[
E = E^0 - \frac{0.059V}{4} \log \left( \frac{1}{p(O_2)[H^+]^4} \right) = E^0 - \frac{0.059V}{4} \left( \log \frac{1}{p(O_2)} + 4pH \right)
\]

+0.81 V

(b) 

\[
Q = 1/[H^+]^6 \quad \text{and} \quad E = E^0 - RT/V_F \log(1/[H^+]^6)
\]

In terms of pH:

\[
E = E^0 - \frac{(RT/V_F) \log([H^+]^6)}{6} = E^0 - \frac{0.059 V}{6} \times \log([H^+]^6) = E^0 - \frac{0.059 V}{6} \times 6pH = E^0 - 0.059V \times pH.
\]
ANSWERS TO SELF-TESTS AND EXERCISES

5.9  (a) \( \text{Cl}_2 \) is thermodynamically susceptible to disproportionation to \( \text{Cl}^- \) and \( \text{ClO}_3^- \) when it is dissolved in aqueous base.

The oxidation of \( \text{ClO}^- \) is slow, so a solution of \( \text{Cl}^- \) and \( \text{ClO}^- \) is formed when \( \text{Cl}_2 \) is dissolved in aqueous base.

(b) \( \text{Cl}_2 \) will not disproportionate. \( \text{Cl}_2 \) is thermodynamically capable of oxidizing water.

(c) \( \text{ClO}_3^- \) should disproportionate, the failure of it to exhibit any observable disproportionation must be due to a kinetic barrier.

5.10  (a)

\[
5\text{N}_2\text{O}(aq) + 2\text{OH}^-(aq) \rightarrow 2\text{NO}_3^-(aq) + 4\text{N}_2(g) + \text{H}_2\text{O}(l)
\]

(b)

\[
\text{Zn}(s) + \text{I}_3^-(aq) \rightarrow \text{Zn}^{2+}(aq) + 3\text{I}^-(aq)
\]

(c)

\[
3\text{I}_2(s) + 5\text{ClO}_3^-(aq) + 3\text{H}_2\text{O}(l) \rightarrow 6\text{IO}_3^-(aq) + 5\text{Cl}^- (aq) + 6\text{H}^+(aq)
\]

5.11  \(-0.21 \text{ V}\)

5.12  (a) Base

(b) Acid

(c) Base

(d) Acid or base, no difference.

5.13  \(+1.275 \text{ V}\)

5.14  \(+1.392 \text{ V}\)

\[
2\text{ClO}_4^-(aq) + 16\text{H}^+(aq) + 14e^- \rightarrow \text{Cl}_2(g) + 8\text{H}_2\text{O}(l)
\]

5.15  \(+0.387 \text{ V}\)

5.16  \(+0.98 \text{ V}\)

5.17  \(4.37 \times 10^{10}\)

5.18  \(5.7 \times 10^{38}\)

5.19  The reduction potentials become less positive.

5.20

\[A_{\text{DPA}}\]

5.21  (a) \(+0.5 \text{ to } +0.6 \text{ V}; \text{Fe(OH)}_3\)

(b) \(+0.55 \text{ V}; \text{solid Mn}_2\text{O}_3\)

(c) At pH 0, 0.387 V. At pH 14, \( \text{SO}_4^{2-} \) would again predominate. \( \text{HSO}_4^- \) is the predominant sulfur species at pH 6.

5.22  Air oxidation of iron is favored in acidic solution: lower pH values would have more positive \( E_{\text{corr}} \). Increased levels of carbon dioxide and water generate carbonic acid that lowers the pH of the medium, which makes the corrosion process more favorable.

5.23  \(-0.1 \text{ V}\)

5.24  Any boundary between a soluble species and an insoluble species will change as the concentration of the soluble species changes. The boundaries between the two soluble species, and between the two insoluble species, will not depend on the choice of \([\text{Fe}^{2+}]\).

5.25  Above about 1600ºC. This is a rather high temperature, achievable in an electric arc furnace.

5.26  (a) Reduction potentials that couple transfer of both electrons and protons decrease (become more negative) as the pH is increased (solution becomes more basic).

(b)
ANSWERS TO SELF-TESTS AND EXERCISES

5.27  (a) 0.716 V, -207.2 kJ mol\(^{-1}\), 2.1 \times 10^{16}
(b) 0.726 V, -70.0 kJ mol\(^{-1}\), 1.9 \times 10^{12}

5.28  \(\Delta H^\circ = 1386.1 \text{ kJ mol}^{-1}\)
\(\Delta S^\circ = -0.282 \text{ kJ K}^{-1} \text{ mol}^{-1}\)
\(\Delta G^\circ = 1302 \text{ kJ mol}^{-1}\)

5.29  

5.30  (i) Ru\(^{2+}\) should be less stable than Fe\(^{2+}\)
(ii) Expected reaction is oxidation of Fe(s) to Fe\(^{2+}\) by H\(^{+}\)
(iii) 3.7 \times 10^{62}

5.31  See Section 5.10.

CHAPTER 6

Self-tests

S6.1  Three \(S_4\) axes.
6.2  (a) CO₂? i
      (b) C₃H₂? i.
      (c) BF₃? neither.
      (d) SO₄²⁻? three different S₄.

6.3  (a) NH₂Cl? C₃
      (b) CO₂? D₃h
      (c) SiF₄? T₄
      (d) HCN? C∞v.
      (e) SiFClBrI? C₁.
      (f) BrF₂⁺? D₃n.

6.4  7; C₆H₃Cl₃.

6.5  (a) An infinite number of mirror planes that pass through both lobes and include the long axis of the orbital. In addition, the long axis is a Cₙ axis, where n can be any number from 1 to ∞.
      (b) Center of symmetry, three mutually perpendicular C₃ axes, three mutually perpendicular mirror planes of symmetry, two planes that are rotated by 45° about the z axis from the xz plane and the yz plane.
      (c) In addition to the symmetry elements possessed by a p orbital: (i) a center of symmetry, (ii) a mirror plane that is perpendicular to the Cₙ axis, (iii) an infinite number of C₂ axes that pass through the center of the orbital and are perpendicular to the Cₙ axis, and (iv) an S₄ axis.

6.6  (a) C₃v
      (b) 2
      (c) 3pₓ and 3pᵧ orbitals are doubly degenerate.

6.7  (a) D₃h.
      (b) 2.

6.8  12 vibrational modes; six Raman bands: 2A₁′ + 3E′ + E″

6.9  (a) 5
      (b) 1

6.10 (a) SF₆? None.
      (b) BF₃⁺? The E′ modes are active in both IR and Raman.

6.11 s = (1/2)(φ₁ + φ₂ + φ₃ + φ₄) (= A₁)
      p₁ = (1/2)(φ₁ - φ₂ + φ₃ - φ₄) (= T₂)
      p₂ = (1/2)(φ₁ + φ₂ - φ₃ + φ₄) (= T₂)
      p₃ = (1/2)(φ₁ + φ₂ - φ₃ - φ₄) (= T₂)

The MOs would be constructed from SALCs with H1s and 2s and 2p atomic orbitals on C.

6.12 (a) BF₃⁺
      (1/√3)(φ₁ + φ₂ + φ₃) (= A₁′)
      (1/√6)(2φ₁ - φ₂ - φ₃) and (1/√3)(φ₂ - φ₃) (= E′)
      (b) PF₃⁺?
      (axial F atoms are φ₁ + φ₃)
      (1/√2)(φ₁ + φ₃) (= A₁′)
      (1/√2)(φ₁ - φ₃) (= A₂″)
      (1/√3)(φ₁ + φ₂ + φ₃) (= A₄′)
      (1/√6)(2φ₁ - φ₂ - φ₃) and (1/√3)(φ₂ - φ₃) (= E′)

CHAPTER 7

Self-tests

S7.1  (a) [PtCl₂(OH₂)₂]
      (b) [Cr(NCS)₆(NH₃)₂]⁺
      (c) [Rh(κ²N₂H₂NCH₂CH₂NH₂)³⁺] abbreviated to [Rh(en)₃]³⁺
      (d) [MnBr (CO)₃].
      (e) [RhCl(PPh₃)₃].
S7.2 The hydrate isomers and linkage isomers of the NO$_2$ group. Also, [Cr(ONO)(H$_2$O)$_5$]NO$_2$·H$_2$O.

S7.3 The NMR data indicate that isomer A is the trans isomer. Isomer B is the cis isomer.

S7.4

Non-superimposable

(a) Chiral
(b) Not chiral
(c) Not chiral

S7.6 $K_{f3} = K_{f1} \times 0.42 = 1 \times 10^5 \times 0.42 = 4.2 \times 10^4$

$K_{f4} = K_{f2} \times 0.53 = 4.2 \times 10^4 \times 0.53 = 2.23 \times 10^4$

$K_{f5} = K_{f3} \times 0.56 = 2.23 \times 10^4 \times 0.56 = 1.25 \times 10^4$

$K_{f6} = K_{f5} \times 0.53 = 1.25 \times 10^4 \times 0.53 = 6.61 \times 10^3$

$K_{f7} = K_{f6} \times 0.42 = 6.61 \times 10^3 \times 0.42 = 2.77 \times 10^3$

$\beta_6 = 1 \times 10^3 \times 4.2 \times 10^3 \times 2.23 \times 10^4 \times 1.25 \times 10^3 \times 6.61 \times 10^3 \times 2.77 \times 10^3 = 2.14 \times 10^{25}$

Exercises

7.1 (a) Tetracyanidonickelate(II)

(b) Tetrachlorocobaltate (II)

(c) Hexaamminemanganese(II)

7.2 (a) [CoCl(NH$_3$)$_2$]Cl$_2$
(b) [Fe(OH)$_2$]$_3$[NO$_3$]$_3$
(c) cis-[RuCl$_2$(en)$_2$]
(d) [Cr(NH$_3$)$_3$-μ–OH–Cr(NH$_3$)$_3$]Cl$_3$

7.3 (a) cis-tetraaminedichloridochromium(III)
(b) trans-diamminetetra(kN-thiocyanato)chromate(III)
(c) bis(1,2-diaminoethane)ethylenediamineoxalatocobalt(III)

7.4 (a)

(b) For a tetrahedral complex there are no isomers for MA$_2$B$_2$; however, for a square-planar complex, there are two isomers, cis and trans.

7.5 Trigonal bipyramidal: A = axial ligands, E = equatorial ligands
Square-based pyramidal: A = axial ligand, B = basal ligands

7.6 (a)

(b) The trigonal prism is rare

7.7 A monodentate ligand can bond to a metal atom only at a single atom, a bidentate ligand can bond through two atoms, a quadridentate ligand can bond through four atoms.


7.8 Linkage isomers can arise with ambidentate ligands. An example is the thiocyanide anion NCS–.

NCS–M (thiocyanato-κS)  SCN–M (thiocyanato-κN)

7.9 (a) Bis(dimethylphosphino) ethane (dmpe): bidentate, chelating ligand that could also be a bridging ligand

(b) 2,2'-Bipyridine (bpy) is a bidentate, chelating ligand

(c) Pyrazine is a monodentate ligand. The ligand can only bond to one metal; it can, however, bridge two metals.

(d) Diethylenetriamine (dien) can be a tridentate ligand, can also act as a bidentate ligand and could be a bridging ligand.

(e) Tetraazacyclododecane ligand could be a tetradeutate, macrocyclic ligand. This ligand could be bidentate and bridging.

7.10

7.11 Ionization isomers.

7.12 [CoBrCl(OH₂)₂]

7.13 [PdBrCl(PEt₃)₂] has two isomers:

[IrHCO(PR₃)₂] has two isomers

7.14 [IrCl₃(PEt₃)₂]:

[Ru(bpy)₃]²⁺:

[CoCl₂(en)(NH₃)₂]⁺:

7.15 Including optical isomers, 15 isomers are possible.

7.16 (a) All octahedral tris(bidentate ligand) complexes are chiral.
ANSWERS TO SELF-TESTS AND EXERCISES

Self-tests

S8.1 XRD pattern for CrO$_2$ will show identical reflections to those of rutile TiO$_2$ but shifted to slightly higher diffraction angles.

S8.2 Technique would require X-ray sources of higher intensity which are obtained using synchrotron radiation.

S8.3 TiO$_2$ particles absorb the ultraviolet radiation.

S8.4 Linear molecule, 4 total vibrational modes. modes cannot be both IR and Raman active.

S8.5 (a) Two different chemical shifts in $^{19}$F NMR: one for F$_a$ and one for F$_b$. The intensity of these signals should have relative ratios 1 : 4. The F$_a$ resonance would be split into five equally spaced lines by four basal F atoms with line intensities 1 : 4 : 6 : 4 : 1 according to Pascal’s triangle. The signal due to F$_b$ atoms will be split into a doublet by one F$_a$ with line intensities 1 : 1.

(b) The hydride resonance couples to three nuclei that are 100% abundant and all of which have I = ½. The first doublet is observed due to the coupling between hydride and rhodium. Since the two atoms are directly bonded, the coupling constant is going to be large. Then, through coupling with P atom trans to the hydride, each line of the first doublet is going to be split into a doublet creating doublet of doublets. Finally, due to the coupling to the P atom cis to the hydride, every line of the doublet of doublets is going to be further split into a doublet giving the observed doublet of doublets of doublets pattern. Since the three coupling constants are different, the effect is to split the signal into a doublet of doublet of doublets, thus generating eight lines in the NMR of equal intensity.

S8.6 Three signals in $^{29}$Si-MASNMR of this compound: one for SiO$_4^{4-}$ (with intensity 1) and two for Si$_3$O$_8^{8-}$ (with intensities 1 : 2 for central and end Si atoms).

S8.7 14% of the naturally occurring tungsten is $^{183}$W, which has I = ½. Owing to this spin, the signal is split into two lines. This will be superimposed on a nonsplit signal that arises from the 86% of tungsten that does not have a spin.

S8.8 Below 0.2 mm s$^{-1}$.

CHAPTER 8
S8.9 The energy of XAS K-edge is expected to gradually increase with an increase in oxidation state of sulfur from S(-II) in $S^2$ to S(VI) in $SO_4^{2-}$.

S8.10 The lightest isotopomer of ClBr$_3$ is $^{35}$Cl$^{79}$Br$_3$ at 272 u and the heaviest is $^{37}$Cl$^{81}$Br$_3$ at 280 u. Three other molecular masses are possible, giving rise to a total of five peaks in the mass spectrum. The differences in the relative intensities of these peaks are a consequence of the differences in the percent abundance for each isotope.

S8.11 Because the atomic masses of 5d metals are significantly higher than the atomic masses of 3d metals, the hydrogen percentages will be less accurate as they correspond to smaller fractions of the overall molecular masses of the compounds.

S8.12 Because the three elements (Mg, Al, and Si) are next to each other in the periodic table; thus we can expect some peak overlapping.

S8.13 2:5.

S8.14 Should see one reversible peak in the cyclic voltamograms in this pH range.

**Exercises**

8.1 Powder X-ray diffraction.

8.2 0.5 µm × 0.5 µm × 0.5 µm; 500 µm × 500 µm × 500 µm.

8.3 Because a hydrogen atom has only one electron it lacks sufficient electron density around the nucleus for their location to be determined with a high accuracy. However both Se and O have a sufficient number of electrons for accurate determination of their locations in the crystal structure. Hydrogen bonding can also further reduce the accuracy.

8.4 180 pm; suitable for diffraction studies.

8.5 The X-ray analysis always underestimates element-hydrogen bond lengths because of very low electron density at H nucleus. This is not an issue with neutron diffraction because neutrons will be scattered by hydrogen nucleus giving a very accurate location.

The C–H bond is of low polarity and the bonding pair is more equally distributed between the two nuclei so we would expect to see less discrepancy between X-ray diffraction and neutron diffraction with measurement of C–H bonds.

8.6 Na(SiH)$_3$ is planar and thus N is at the center of the molecule and does not move in the symmetric stretch. Na(CH$_3$)$_3$ is pyramidal and the N–C symmetric stretch involves displacement of N.

8.7 $2404 \text{ cm}^{-1}$

8.8 The smaller effective mass of the oscillator for CN causes the molecule to have the higher stretching frequency because they are inversely proportional. The bond order for NO is 2.5, and N is heavier than C, hence CO has a higher stretching frequency than NO.

8.9 In the region of 1800 cm$^{-1}$; Raman.

8.10 The $^{19}$F NMR of $^{77}$SeF$_3$ would consist of two doublet of triplets with relative intensity 1 : 1. The $^{77}$Se NMR would consist of triplet of triplets.

8.11 XeF$_5$ has a pentagonal planar molecular geometry, so all five of the F atoms are magnetically equivalent and thus the molecule shows a single $^{19}$F resonance. Approximately 25% of the Xe is present as $^{129}$Xe, which has $I = 1/2$, and in this case the $^{19}$F resonance is split into a doublet. The final result is a composite: two lines each of 12.5% intensity from the $^{19}$F coupled to the $^{129}$Xe, and one line of 75% intensity for the remainder.

8.12 The structure is fluxional at room temperature and the CO ligands are exchanging bridging and terminal position sufficiently fast so that an average signal is seen and only one peak is observed.

8.13 If the $^{31}$P MASNMR of PCl$_3$ shows two resonances, one of which is similar to the one found in the $^{31}$P MASNMR of the salt, that means solid PCl$_3$ contains PCl$_3^-$ anions. The second resonance must belong to some other P-containing species in PCl$_5$, which in this case is the cation PCl$_4^+$.

8.14 1.94, 1.74, and 1.56

8.15 EPR

8.16 Room temperature; molecular tumbling is fast removing effect of g-value anisotropy; expect derivative-type spectrum, possibly exhibiting hyperfine structure that is centred at the average g value.
Frozen solution: $g$-value anisotropy can be observed, averaging from molecular tumbling does not apply.

8.17 Below +0.2 mm s$^{-1}$.

8.18 Mössbauer spectroscopy

8.19 Because there is no isotope with this mass number. Compounds that contain silver will have two mass peaks flanking this average mass.

8.20 Major peaks would be at 258, 230, 200, 186, 174

8.21 \( n = 7 \)

8.22 The complex undergoes a reversible one-electron reduction with a reduction potential of 0.21 V. Above 0.720 V the complex is oxidized to a species that undergoes a further chemical reaction, and thus is not re-reduced. This step is not reversible.

8.23 The regular crystalline periodicity is required for Bragg diffraction in order to have constructive interference of the X-rays that leads to observable peaks in the XRD pattern. Glass, however, is a network covalent solid with no long-range periodicity or order; as such it will not diffract X-rays. The observation of X-ray diffraction pattern after the glass sample was heated indicates that at least a part of the sample crystallized. The fact that the exothermic event was observed suggests either change of phase or chemical reaction that yielded a crystalline product.

8.24 For each mole of Co there are three moles of acac$^-$.

8.25 (a) Voltamogram would not be reversible, and would be unsymmetrical.
(b) One peak in voltamogram with twice the height of single peaks shown in Figure 8.53(a).

CHAPTER 9

Self-tests

S9.1 Cd and Pb will be found as sulfides.
Rb and Sr can be found in aluminosilicate minerals.
Cr and Pd can be found in both oxides and sulfides.

S9.2 $\text{V}^{3+}(aq)$ and/or $\text{VO}^{2+}$

S9.3 Owing to oxygen’s strong tendency to form strong double bonds, it is very unlikely that longer-chain polyoxoanions would exist. Sulfur is much less likely to form $\pi$ bonds and therefore more likely to generate catenated polysulfide anions.

S9.4 It is evident from the values that as we move down the group, steric crowding of the fluorines is minimized.

S9.5 We would have to know the products formed upon decomposition and thermodynamic data for the product.

S9.6 A tetrahedral geometry; OsO$_4$.

Exercises

9.1 (a) Ba, +2; (b) As, +5; (c) P, +5; (d) Cl, +7; (e) Ti, +4; (f) Cr, +6

9.2 The alkaline earth metals or Group 2 elements.

9.3 Elements in Group 15.

9.4 Chromium group of Group 6.

9.5 The second ionization energy of sodium is 4562 kJ mol$^{-1}$ and is responsible for the fact that the compound does not exist.

9.6 Beyond Group 15 we see inert pair effect influencing the favoured +3 oxidation state for elements such as Bi and Sb and we also find stable +5 oxidation states for the halogens in Group 17. The inert pair effect would manifest itself the most for Po, the heaviest member of the Group 16.

9.7 Metallic character and ionic radii decrease across a period and down a group. Ionization energy increases across a period and decreases down a group.

9.8 (a) Be  
(b) C  
(c) Mn

9.9 (a) Na  
(b) O

9.10 (a) Saline  
(b) Molecular  
(c) Molecular  
(d) Saline
ANSWERS TO SELF-TESTS AND EXERCISES

9.11 (a) Basic (b) Acidic (c) Amphoteric (d) Acidic (e) Amphoteric (f) Basic

9.12 CrF$_2$ < CrF$_3$ < CrF$_6$

9.13 (a) MgCO$_3$, magnesite (b) Al$_2$O$_3$, bauxite (c) PbS, galena (d) Magnetite Fe$_3$O$_4$

9.14 V (vanadium)

9.15 $\Delta H^o = -1397$ kJ mol$^{-1}$.

CHAPTER 10

Self-tests

S10.1 CH$_4$, the strongest Bronsted acid. GeH$_4$ would be the best hydride donor.

S10.2 (a) Ca(s) + H$_2$(g) $\rightarrow$ CaH$_2$(s).
(b) NH$_3$(g) + BF$_3$(g) $\rightarrow$ H$_3$N–BF$_3$(g).
(c) LiOH(s) + H$_2$(g) $\rightarrow$ NR.

S10.3 $\Delta G$(Pd) = 227 kJ mol$^{-1}$

S10.4 Et$_3$SnH + 2 Na $\rightarrow$ 2Na$^+$ Et$_3$Sn$^-$ + H$_2$

$\text{2Na}^+ \text{Et}_3\text{Sn}^- + \text{CH}_3\text{Br} \rightarrow \text{MeEt}_3\text{Sn} + \text{NaBr}$

Exercises

10.1 Hydrogen has one valence electron like the group 1 metals and is stable as H$^+$, especially in aqueous media. Hydrogen can fill its 1s orbital and make a hydride H$^-$. The halogens are diatomic gases just like hydrogen, but chemically it fits well in both group 1 and group 17. There are no compelling reasons for hydrogen to be placed in group 14.

10.2 (a) H = +1, S = –2.
(b) H = –1, K = +1.
(c) H = –1, Re = +7.
(d) H = +1, O = –2, S = +6.
(e) H bonded to an oxygen atom = +1. H bonded to the phosphorus atom? If they are assigned an oxidation number of +1, and O = –2, then P = +1.

10.3 (i) CH$_4$(g) + H$_2$O $\rightarrow$ CO(g) + 3H$_2$(g) (1000°C)
(ii) C(s) + H$_2$O $\rightarrow$ CO(g) + H$_2$(g) (1000°C)
(iii) CO(g) + H$_2$O $\rightarrow$ CO$_2$(g) + H$_2$(g)
(iv) Zn(s) + 2HCl(aq) $\rightarrow$ Zn$^{2+}$(aq) + 2Cl$^-$ (aq) + H$_2$(g)
(v) NaH(s) + H$_2$O $\rightarrow$ Na$^+$(aq) + OH$^-$ (aq) + H$_2$(g)

10.4 (a) Your result should look like Figure 10.2.
(b) Your result should reflect the data shown in Table 10.1.
(c) Those in Group 13 are electron-deficient, those in Group 14 are electron-precise, and those in Groups 15 through 17 are electron-rich.

10.5 It most likely would be a gas at room temperature. We can estimate a boiling point of about –50°C or below for H$_2$O without H-bonding. It would be expected that ice would be denser than water.

10.6 O–H···S because the electrostatic interaction between the more positive H in H$_2$O and a lone electron pair on S is stronger.

10.7 (a) Barium hydride. It is a saline hydride.
(b) Silane. It is an electron-precise molecular hydride.
(c) Ammonia. It is an electron-rich molecular hydride.
(d) Arsine. It is also an electron-rich molecular hydride.
(e) Palladium hydride. It is a metallic hydride.
(f) Hydrogen iodide. It is an electron-rich molecular hydride.

10.8 (a) Barium hydride
BaH$_2$(s) + 2H$_2$O(l) $\rightarrow$ 2H$_2$(g) + Ba(OH)$_2$(s)

Net reaction: 2H$^+$ + 2H$^+$ $\rightarrow$ 2H$_2$

(b) Hydrogen iodide
HI + H$_2$O $\rightarrow$ I$^-$ + H$_3$O$^+$

(c) PdH$_{0.9}$

(d) NH$_3$

NH$_3$(g) + BMe$_3$(g) $\rightarrow$ H$_2$NBMe$_3$(g)
10.9 BaH$_2$ and PdH$_{0.9}$ are solids; none is a liquid; and SiH$_4$, NH$_3$, AsH$_3$, and HI are gases. Only PdH$_{0.9}$ is likely to be a good electrical conductor.

10.10 All hydrides of the Group 1 metals have the rock-salt structure. This means that in all Group 1 hydrides H$^-$ has a coordination number 6 and is surrounded by cations in an octahedral geometry. The sizes of cations increase down the group (i.e., \( r(\text{Li}^+) < r(\text{Na}^+) < r(\text{K}^+) < r(\text{Cs}^+) \)); as a consequence both the sizes of octahedral holes and the apparent radius of H$^-$ will increase in the same direction.

No clear trend for Group 2 hydrides. Whereas CaH$_2$ and BaH$_2$ adopt the fluorite structure, MgH$_2$ has a rutile structure.

10.11 Reaction (b) will produce 100% HD and no H$_2$ or D$_2$.

10.12 (CH$_3$)$_3$SnH, the tin compound is the most likely to undergo radical reactions with alkyl halides.

10.13 B (2.04), Al (1.61), and Ga (1.81); AlH$_3^-$ is the strongest reducing agent.

GaH$_4$ + 4HCl(aq) → GaCl$_4^-$ (aq) + 4H$_2$(g)

10.14 The period 2 hydrides, except for BeH$_2$ and B$_2$H$_6$, are all exergonic. Their period 3 homologues either are much less exergonic or are endergonic.

Period 2 compounds tend to be weaker Brønsted acids and stronger Brønsted bases than their period 3 homologues.

The bond angles in period 2 hydrogen compounds reflect a greater degree of sp$^3$-hybridization than the homologous period 3 compounds.

As a consequence of hydrogen bonding, the boiling points of HF, H$_2$O, and NH$_3$ are all higher than their respective period 3 homologues.

10.15 It is expected that it would be very difficult to prepare a sample of BiH$_3$. The current method for the synthesis of bismuthine, BiH$_3$, is by the redistribution of methylbismuthine, BiH$_2$Me.

10.16 Clathrate hydrate. Clathrate hydrate consists of cages of water molecules found in ice, all hydrogen bonded together, each surrounding a single krypton atom.

10.17 The first difference is that the surface for the H$_2$O, Cl$^-$ system has a double minimum because it is an unsymmetrical H bond, whereas the surface for the bifluoride ion has a single minimum. The second difference is that the surface for the H$_2$O, Cl$^-$ system is not symmetric because the proton is bonded to two different atoms whereas the surface for bifluoride ion is symmetric.

10.18 Dihydrogen can behave both as a reducing and oxidising agent because hydrogen can have two oxidation states in its compounds: +1 and –1.

H$_2$ is an oxidizing agent in this case:

\[
2\text{Na}(s) + \text{H}_2(g) \rightarrow 2\text{NaH}(s)
\]

H$_2$ as a reducing agent:

\[
2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O} (l\ or\ g)
\]

10.19 Overall an oxidative addition.

10.20 (a) Incorrect: some p-block hydrides are not thermodynamically stable

(b) Incorrect: the isotope of mass number 3 is radioactive, not of mass number 2.

(c) Incorrect: not all hydrides of Group 2 are ionic; H$^-$ is not compact and as a consequence it does not have a well-defined radius.

(d) Incorrect: not all structures can be predicted by VSEPR theory

(e) Incorrect: while NaBH$_4$ is a common reagent, it does not have greater hydridic character (hydridicity) than a saline hydride such as NaH.

(f) Incorrect: boron hydrides are electron-deficient because they lack the electrons required to fill the bonding and non-bonding molecular orbitals.

10.21 2074 cm$^{-1}$

10.22
The [H – He] bond should be polarized with a partial negative charge on He and a partial positive charge on H.

Most common solvents (such as water, alcohols, and alike) would easily deprotonate this species. Other surfaces would also heterolytically cleave this species into H⁺ and He.

CHAPTER 11

Self-tests

S11.1 (a) The observed major peak in the Bragg pattern would shift to lower two theta values upon heating through the phase transition according to the Bragg relation

(b) \( d = 2(196 + 220)/3^{1/2} \text{ pm} = 481 \text{ pm} \); data are consistent with the prediction

S11.2 966.8 kJ mol⁻¹; 713.9 kJ mol⁻¹

LiF is insoluble, because the hydration enthalpy for Li⁺ (956 kJ mol⁻¹) is insufficient to compensate for the lattice enthalpy of LiF.

Hydration enthalpy for Cs⁺ (710 kJ mol⁻¹) is about the lattice enthalpy for CsF, and it is expected that CsF should be more soluble than LiF.

S11.3 We would expect that, on warming, NaO₃ would decompose first and CsO₃ last.

S11.4

\[
\begin{align*}
\text{M}_2\text{CO}_3(\text{s}) & \rightarrow \text{M}_2\text{O}(\text{s}) + \text{CO}_2(\text{g}) \\
2\text{M}^+(\text{g}) + \text{CO}_3^{2-}(\text{g}) & \rightarrow 2\text{M}^+(\text{g}) + \text{O}_2^-(\text{g}) + \text{CO}_2(\text{g})
\end{align*}
\]

S11.5 KNO₃ decomposes in two steps at two different temperatures.

\[
\begin{align*}
\text{KNO}_3(\text{s}) & \rightarrow \text{KNO}_2(\text{s}) + ^{1/2}\text{O}_2(\text{g}) \\
2\text{KNO}_2(\text{s}) & \rightarrow \text{K}_2\text{O}(\text{s}) + 2\text{NO}_2(\text{g}) + ^{1/2}\text{O}_2(\text{g})
\end{align*}
\]

LiNO₃ decomposes in one step.

\[
\begin{align*}
\text{LiNO}_3(\text{s}) & \rightarrow ^{1/2}\text{Li}_2\text{O}(\text{s}) + \text{NO}_2(\text{g}) + ^{1/4}\text{O}_2(\text{g})
\end{align*}
\]

S11.6 Two peaks in the NMR spectrum at low temperature. Only one resonance in the NMR at high temperature.

Exercises

11.1 (a) They have one valence electron in the ns¹ subshell, and relatively low first ionization energies.

(b) They are large, electropositive metals and have little tendency to act as Lewis acids.

11.2 The caesium-bearing silicate minerals are digested with sulfuric acid and Cs and Al are precipitated as alum. The simple sulfate, obtained after roasting with carbon, is then converted to chloride using anion exchange. The isolated CsCl is then reduced with Ca or Ba.

11.3 LiH: NaCl structure type
NaH: NaCl structure type
KH: CsCl structure type
RbH: CsCl structure type
CsH: CsCl structure type
FrH: CsCl structure type
Your plot should look like a part of Figure 11.6. Fluoride is a hard Lewis base and will form strong complexes with hard Lewis acids. The trends reverse for the chloride ion.

11.5 (a) Edta$^{4−}$ is expected to give a more stable complex with Cs$^+$ compared to acetate. (b) $K^+$ is more likely to form a complex with the cryptate ligand C2.2.2 than Li$^+$.

11.6 (i) $A = LiOH; B = Li_2O; C = none; D = LiNH_2$

(ii) $A = CsOH; B = CsO_2; C = Cs_2O; D = CsNH_2$

11.7 Solubility is lower if cation and anion have similar radii.

11.8 FrI, FrBr

11.9 The difference in lattice energy between metal carbonate and metal oxide decreases down the group, which results in increased stability.

11.10 See Figure 11.4 and Figure 11.5. Na$^+$ is six-coordinate, whereas Cs$^+$ is eight-coordinate. The compounds have different structures because Na$^+$ is smaller than Cs$^+$ resulting in a different $r_{+}/r_{−}$ for the same anion.

11.11 (a) $Li(CH_3) + LiBr$

(b) $Mg(C_2H_3)Br + LiCl$

(c) $LiC_6H_5 + C_2H_6$

CHAPTER 12

Self-tests

S12.1 BeCl$_2$ is covalent with a polymeric, molecular structure; BaCl$_2$ is ionic and likely to adopt a CaF$_2$-type ionic structure.

S12.2 Calcium oxide and calcium peroxide are 3465 kJ mol$^{-1}$ and 3040 kJ mol$^{-1}$. Trend is confirmed.

S12.3 Close to ZnS-like structure.

S12.4 (i) Anhydrous BeSO$_4$ with loss of all four water molecules.

(ii) SrO and BeO with elimination of two equivalents of H$_2$O.

S12.5 MgF$_2$ is 2945 kJ mol$^{-1}$; MgBr$_2$ is 2360 kJ mol$^{-1}$ and MgI$_2$ is 2193 kJ mol$^{-1}$.

Lattice enthalpies decrease with an increase in the ionic radius of the halide anion; can expect the increase in solubility in the same direction.

Exercises

12.1 Be$^{2+}$ has large polarizing power and a high charge density due to its small radius. Also, beryllium has the highest electronegativity among Group 2 elements. Descending Group 2 the atoms of elements increase in size, they are more electropositive

12.2 Because of the diagonal relationship between Be and Al.

12.3 Metallic bond.

12.4 $A = Ba(OH)_2$ $B = BaCO_3$ $C = BaC_2$ $D = BaCl_2$

12.5 BeF$_2$ adopts SiO$_2$-like arrangement which forms vitreous matter when melted because of the strength of the Si-O bonds.

12.6 BeH$_2$: 18.2%

MgH$_2$: 7.6%

BeH$_2$ cannot be prepared directly from the elements

12.7 Group 1 hydroxides are more soluble than group 2 hydroxides, and therefore have higher OH$^−$ concentrations.

12.8 MgSeO$_4$

12.9 Ra$^{2+}$ could be selectively precipitated by addition of a large anion.

12.10 Anhydrous Mg and Ca sulphates; because of the higher affinity of Mg and Ca sulphates for water.

12.11 ZnS-like structure; NaCl-like structure.

12.12 Covalent; ionic.

12.13 C$_3$H$_5$MgBr will be tetrahedral with two molecules of solvent coordinated to the
magnesium. The bulky organic group in 2,4,6-(CH₃)₂C₆H₄MgBr leads to a coordination number of two.

12.14  (a) LiCl + (C₂H₅)MgCl or 2LiCl + Mg(C₂H₅)₂
(b) Mg(C₂H₅)₂ + Hg
(c) C₃H₇MgCl + Hg

CHAPTER 13

Self-tests

S13.1  4 lines of equal intensity (1 : 1 : 1 : 1).

S13.2  B₂H₆ + 2R₂O → 2H₂B – OR₂

H₂B – OR₂ + H₂C=CHCH₃ → H₂BCH₂ – CH₂CH₃ + OR₂

and:

B₂H₆ + 2THF → 2H₂B – THF

H₂B – THF + NH₄Cl → H₂ + H₂B – NH₂ + HCl

S13.3  (a) BCl₃(g) + 3 EtOH(l) → B(OEt)₃(l) + 3 HCl(g)
(b) BCl₃(g) + py(l) → Cl₃B – py(s)
(c) BB₃(l) + F₂BN(CH₃)₃(s) → BF₃(g) + Br₃BN(CH₃)₃(s)

S13.4  3[CH₃NH]Cl + 3BCl → Heat → 9HCl + Cl₃BNCH₃

Cl₃BNCH₃ + 3CH₃MgBr → (CH₃)₂Br₃N₃(CH₃)₂ + 3Mg(Br, Cl)₂

S13.5  (a) Seven electron pairs per cluster structure; arachno
(b) Nido structure type.

S13.6  B₂H₆; the cluster is nido and is based on closo-B6 octahedral cage.

S13.7  [B₁₀H₁₁(AlCH₃)₉]⁺

S13.8  Closo structure (octahedral).

Exercises

13.1  B₂O₃ + 3Mg → 2B + 3MgO  ΔH < 0

13.2  (a) Covalent.
(b) In the solid state, a layered structure. At melting point, dimeric form, Al₂Cl₆, with 2c, 2e bridging bonds.
(c) Electron-deficient dimer with 3c, 2e bridging bonds.

13.3  BCl₃ > BF₃ > AlCl₃

(a) BF₃N(CH₃)₃ + BCl₃ → BCl₃N(CH₃)₃ + BF₃ (BCl₃ > BF₃)
(b) BH₂CO + BBr₃ → NR

13.4  Na[TlBr₄]; Na⁺ is the cation and [TlBr₄]⁻ is the anion.

13.5  A = B₂H₆
B = B(OH)₃
C = B₂O₃

13.6  NO₂; B₂H₆ + 3 O₂ → B₂O₃ + 3 H₂O or B₂H₆ + 3 O₂ → 2B(OH)₃

13.7  (a) 3
(b) 2

13.8  (a) BH₃ + 3(CH₃)₂C≡CH₂ → B[CH₃(CH(CH₃)₂)₃]
(b) BH₃ + 3CH₂=CH → B(=CH₂)₃

13.9  −73,172 kJ; Diborane is extremely toxic and the boron containing product of combustion is a solid, B₂O₃.

13.10  2BCl₃ + 2H₂ → 2BCl₄ + 2HCl

B₂Cl₄ + 4AgF → B₂F₄ + 4AgCl

B₂F₄ + C₃H₆ → F₃BH₃CH₂BF₂
13.11 (a) $\text{NaBH}_4 + 4\text{HCl(ether sol.)} \rightarrow \text{BCl}_3 + \text{NaCl(s)} + 4\text{H}_2(g)$

(b) $[\text{HN(C}_2\text{H}_5]_3\text{Cl} + \text{NaBH}_4 \rightarrow \text{H}_2 + \text{H}_3\text{BN(C}_2\text{H}_5]_3 + \text{NaCl}$

13.12

13.13 In general, boron hydrides with more hydrogen atoms are thermally unstable. We expect $\text{B}_6\text{H}_{10}$ to be stable relative to $\text{B}_6\text{H}_{12}$.

13.14 14 skeleton electrons in total.

13.15 (a) $2\text{B}_5\text{H}_9(l) + 12\text{O}_2(g) \rightarrow 5\text{B}_2\text{O}_3(s) + 9\text{H}_2\text{O}(l)$

(b) The boron-containing product of combustion is a solid, $\text{B}_2\text{O}_3$; if an internal combustion engine is used, the solid will eventually coat the internal surfaces, increasing friction, and will clog the exhaust valves.

13.16 (a) Nido

(b) 12 electron pairs

(c) Valence electrons for $\text{B}_{10}\text{H}_{14}$ is $(10\times3)+(14\times1) = 44$. Ten $2e^-2c^-$ $\text{B}–\text{H}$ bonds, which account for 20 of the total valence electrons; the number of cluster electrons is the remainder of 44-20=24.

13.17 (a) Arachno-type structure

(b) Nido-type structure

13.18 $\text{B}_9\text{H}_12$; cluster is arachno and is based on closo-$\text{B}_8$ structure cage.

13.19 Tetraborane(10); arachno

Pentaborane(9); nido

1,2-closo-dodecaborane(12); closo

13.20 (1) $\text{B}_{10}\text{H}_{14} + 2\text{SEt}_2 \rightarrow \text{B}_{10}\text{H}_{12}(\text{SEt}_2)_2 + \text{H}_2$

(2) $\text{B}_{10}\text{H}_{12}(\text{SEt}_2)_2 + \text{C}_2\text{H}_2 \rightarrow \text{B}_{10}\text{C}_2\text{H}_{12} + 2\text{SEt}_2 + \text{H}_2$

(3) $2\text{B}_9\text{C}_2\text{H}_{12} + 2\text{EtO}^- + 4\text{EtOH} \rightarrow 2\text{B}_9\text{C}_2\text{H}_{12}^- + 2\text{BO}(\text{Et})_3 + 2\text{H}_2$

(4) $\text{Na}[\text{B}_9\text{C}_2\text{H}_{12}] + \text{NaH} \rightarrow \text{Na}_2[\text{B}_9\text{C}_2\text{H}_{11}] + \text{H}_2$

(5) $2\text{Na}_2[\text{B}_9\text{C}_2\text{H}_{11}] + \text{FeCl}_2 \rightarrow 2\text{NaCl} + \text{Na}_2[\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})_2]$

13.21 Closa; corresponds to the icosahedral structure with one BH unit replaced with an NH unit.

13.22 (a) Both of these substances have layered structures.

(b) Graphite reacts, boron nitride is unreactive.

(c) The large HOMO–LUMO gap in BN means it is more difficult to remove an electron from it than from the HOMO of graphite.

13.23 (a) $3[\text{PhNH}_3]\text{Cl} + 3\text{BCl}_3 \rightarrow \text{Ph}_3\text{N}_3\text{B}_3\text{Cl}_3 + 9\text{HCl}$

(b) $3\text{MeNH}_3\text{Cl} + 3\text{BCl}_3 \rightarrow \text{Me}_3\text{N}_3\text{B}_3\text{Cl}_3 + 9\text{HCl}$

$\text{Me}_3\text{N}_3\text{B}_3\text{Cl}_3 + 3\text{LiH} \rightarrow \text{Me}_3\text{N}_3\text{B}_3\text{H}_3 + 3\text{LiCl}$

13.24 $\text{B}_3\text{H}_6 < \text{B}_9\text{H}_0 < \text{B}_{10}\text{H}_{14}$

13.25 All of the structures in the given series are dimeric and have $\text{B}–\text{H}–\text{B}$ bridges.

13.26 (a) $^{11}\text{B}$ NMR spectrum of $\text{BH}_3\text{CO}$ would show one quartet resonance.

(b) The $^{11}\text{B}$ NMR should show two signals in relative intensity 1:5 both of which should be doublets.

13.27 (a) Incorrect; only boron has some nonmetallic properties

(b) Incorrect; hardness decreases down the group
(c) Partially correct; Lewis acidity of BX₃ does increase from F to Br, it is not due to stronger B–Br π bonding but the opposite.
(d) Incorrect; *arachno* boron hydrides are less stable than *nido*-borohydrides and skeletal electron count is n+3.
(e) Correct.
(f) Partially incorrect; layered BN and graphite have similar structures but layered BN has a very large HOMO-LUMO gap and is an insulator.

CHAPTER 14

**Self-tests**

S14.1 (a) Results in a material with a higher conductivity.
(b) Bromine can remove electrons from the π-symmetry HOMOs of graphite. This also results in a material with a higher conductivity.

S14.2 CH₄: ΔH = –61 kJ mol⁻¹
SiH₄: ΔH = +39 kJ mol⁻¹

S14.3

\[ ^{13}\text{CO}(g) + 2\text{MnO}_2(s) \rightarrow ^{13}\text{CO}_2(g) + \text{Mn}_2\text{O}_3(s) \]

\[ 2\text{Li}(s) + \text{D}_2 \rightarrow 2\text{LiD}(s) \]

\[ ^{13}\text{CO}_2(g) + \text{LiD}(et) \rightarrow \text{Li}^+\text{D}^{13}\text{CO}_2(\text{et}) \]

S14.4 Decrease in bond order—from 3 to 2.5; C–C bond length in C₂⁻ would be longer than in C₂²⁻.

**Exercises**

14.1 (a) Incorrect; tin and lead are metallic
(b) Correct
(c) Partially correct but CS₂ is softer than CO₂
(d) Incorrect; zeolites are framework aluminosilicates and do contain metal cations.
(e) Correct

14.2 (a) Diamond with silicon – both have diamond-type structure which results in a wide energy gap between filled and empty bands—a gap that is, however, smaller for Si(diamond) than for C(diamond). As a consequence, C(diamond) is generally considered an insulator, whereas Si(diamond) is a semiconductor.
(b) Striking differences between C and the rest of the elements of the Group 14 are the properties and structures of the oxides.

14.3

\[ \begin{array}{c}
\text{F} \\
\text{Cl} \quad \text{Cl} \\
\text{Si} \quad \text{Si} \\
\text{Cl} \quad \text{Cl} \\
\text{F} \quad \text{F} \\
\text{SiCl}_2\text{F} & \text{SiCl}_2\text{F}_2 & \text{SiClF}_3
\end{array} \]

14.4 The bond enthalpy of a C–F bond is higher than the bond enthalpy of a C–H bond, making C–F bond more difficult to break. Further, the combustion produces not only CO₂ but H₂O as well that is thermodynamically a very stable compound.

14.5 (a) Cation:

\[ \begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\text{N} \\
\text{H}_3\text{C} \\
\text{H}_3\text{C}
\end{array} \]

Anion:

\[ \begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{Si} \\
\text{F}
\end{array} \]

(b) In the structure of the anion there are two different fluorine environments: axial and equatorial.

14.6

Charge is -8

14.7 Spectrum would show a single environment for \( ^{119}\text{Sn} \) (I = \( \frac{1}{2} \)) nucleus in a tetrahedral geometry, split into 13 lines.
14.8 Spectrum would show a doublet peak for $^1\text{H}$ ($I = \frac{1}{2}$) nucleus.

14.9 \(110 \text{ kJ mol}^{-1}, 86 \text{ kJ mol}^{-1}\)

14.10 A = SiCl$_4$
B = SiRCl$_3$
C = RSi(OH)$_3$
D = RSiOSiR
E = SiR$_4$
F = SiO$_2$

14.11 (a) $+4$ is the most stable oxidation state for the lighter elements, but $+2$ is the most stable oxidation state for Pb; Pb displays the inert-pair effect.
(b) \[\text{Sn}^{2+} + \text{PbO}_2 + 4 \text{H}^+ \rightarrow \text{Sn}^{4+} + \text{Pb}^{2+} + 2 \text{H}_2\text{O}\]
\[2 \text{Sn}^{2+} + \text{O}_2 + 4 \text{H}^+ \rightarrow 2 \text{Sn}^{4+} + 2 \text{H}_2\text{O}.\]

14.12 +1.31 \text{ V}; 1.08 \text{ V}

14.13 Silicon:
SiO$_2$(s) + C(s) → Si(s) + CO$_2$(g) \(\Delta H < 0\)
(reaction takes place in an electric arc furnace)

Germanium:
GeO$_2$(s) + 2 H$_2$(g) → Ge(s) + 2 H$_2$O(g) \(\Delta H < 0\)
or
GeO$_2$(s) + 2CO(g) → Ge(s) + 2CO$_2$(g)

14.14 (a) Decrease in band gap energy from carbon (diamond) to grey tin.
(b) Increase.

14.15 See Figure 14.12 and Section 14.13.

14.16 (a) Formed by heating graphite with potassium vapour or by treating graphite with a solution of potassium in liquid ammonia. It has a layered structure of alternating sp$^2$ carbon atoms and potassium ions and is an example of a saline carbide.
(b) 2 ways of preparing calcium carbide, both require temperatures \(\geq 2000^\circ\text{C}\). The first is the direct reaction of the elements, and the second is the reaction of calcium oxide with carbon. Calcium carbide contains discrete C$_2$$^-$ ions with carbon–carbon triple bonds. This carbide is ionic.
(c) A solution of C$_{60}$, in a high boiling point solvent (such as toluene), can be treated with elemental potassium to form this compound. It is also ionic, and it contains discrete K$^+$ ions and C$_{60}$$^{3-}$ ions.

14.17 \[\text{K}_2\text{CO}_3(\text{aq}) + 2\text{HCl(aq)} \rightarrow 2\text{KCl(}aq) + \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}\]
Na$_3$SiO$_4$(aq) + 4HCl(aq) → 4NaCl(aq) + SiO$_2$(s) + 2H$_2$O(l)

14.18 The [SiO$_4$$^{2-}$]$_n$ ions in jadeite are a linear polymer of SiO$_4$ tetrahedra; the two-dimensional aluminosilicate layers in kaolinite represent another way of connecting SiO$_4$ tetrahedra.

14.19 (a) 48
(b) The polyhedron at the centre has six octagonal faces and eight smaller square faces.

14.20 The phyllosilicates are characterised with two-dimensional sheets composed of vertex-sharing SiO$_4$-tetrahedra; each SiO$_4$-tetrahedron is connected to three neighbouring SiO$_4$-tetrahedra via bridging O atoms. These sheets are negatively charged and held together via electrostatic interactions with cations sandwiched between the sheets. Because of this layered structure, both pyrophyllite and muscovite have excellent cleavage parallel to the layers (just like graphite).

14.21 Glasses (many uses), activated carbon (adsorbent), carbon fibres (can be added to plastic to increase strength), carbon black (pigment).

14.22 Ca$^{2+}$ cations are too large for the octahedral holes, and it is more likely that they will be found in larger holes with coordination number 12.

CHAPTER 15

Self-tests

S15.1 (a) Yes.
(b) Triple bond between two N atoms; means that it is unreactive, a gas, and diamagnetic.

S15.2 Dimehylhydrazine ignites spontaneously and produces less CO$_2$.

S15.3 Sulphur.

S15.4 (a) Unlike NO$_2$, the colourless NO is rapidly oxidized by O$_2$ in air producing NO$_2$. N$_2$O is unreactive for purely kinetic reasons.
(b) \[\text{NH}_3 + \text{ClO}^- + \text{H}^+ \rightarrow [\text{H}_3\text{N}—\text{Cl}–\text{O}]^- + \text{H}^+ \rightarrow \text{H}_2\text{NCl} + \text{H}_2\text{O}\]
H₂NCl + NH₃ → H₂NNH₂ + HCl
Both can be thought of as redox reactions.

**S15.5** There are \((30.4 \text{ cm}^3)/(7.6 \text{ cm}^3) = 4\) strongly acidic OH groups per molecule.

### Exercises

#### 15.1

<table>
<thead>
<tr>
<th>Type of element</th>
<th>Diatomic gas?</th>
<th>Achieves maximum oxidation state?</th>
<th>Displays inert pair effect?</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>P</td>
<td>no</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>As</td>
<td>no</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Sb</td>
<td>no</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Bi</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

#### 15.2

(a) \(2 \text{Ca}_3(\text{PO}_4)_2 + 10 \text{C} + 6\text{SiO}_2 \rightarrow \text{P}_4^+ + 10\text{CO} + 6\text{CaSiO}_3\)

P₄ (pure) + 5O₂ → P₄O₁₀
P₁₀O₁₀ + 6H₂O → 4H₃PO₄ (pure)

(b) \(\text{Ca}_3(\text{PO}_4)_2\text{OH} + 5\text{H}_2\text{SO}_4 \rightarrow 3\text{H}_3\text{PO}_4 \text{ (impure)} + 5\text{CaSO}_4 + \text{H}_2\text{O}\)

(c) Fertilizer-grade phosphoric acid involves a single synthetic step for a product that requires little or no purification.

#### 15.3

(a) \(6\text{Li}(s) + \text{N}_2(g) \rightarrow 2\text{Li}_3\text{N}(s)\)

2Li₃N(s) + 3H₂O(l) → 2NH₃(g) + 3LiOH(aq)

(b) \(\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)\)

(c) The second process is considerably cheaper than the first, because lithium is very expensive.

#### 15.4

\(\text{NH}_2\text{NO}_3(s) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)\)

#### 15.5

\(\text{N}_2\) itself, with a triple bond between the two atoms, is strikingly unreactive.

#### 15.6

The only isolable nitrogen chloride is NCl₃, and it is thermodynamically unstable. Both PCl₁ and PCl₃ are stable.

#### 15.7

(a) Tetrahedron.

(b) A see-saw.

(c) A trigonal bipyramid.

#### 15.8

(a) \(\text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10}\)

(b) \(\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4\)

#### 15.9

(a) \(4\text{NH}_3(aq) + 7\text{O}_2(g) \rightarrow 6\text{H}_2\text{O}(g) + 4\text{NO}_2(g)\)

High temperature
3NO₂(aq) + H₂O(l) → 2HNO₃(aq) + NO(g)

(b) \(2\text{NO}_2(aq) + 2\text{OH}^-(aq) \rightarrow \text{NO}_2^-(aq) + \text{NO}_3^-(aq) + \text{H}_2\text{O}(l)\)

(c) Cold aqueous acidic solution
\(\text{NO}_2^- (aq) + 2\text{HSO}_3^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_3\text{OH}^+ (aq) + 2\text{SO}_4^{2-}(aq)\)

(d) At elevated temperatures:
3NaNH₂(l) + NaNO₃ → NaN₃ + 3NaOH + NH₃(g)
2NaNH₃(l) + N₂O → NaN₃ + NaOH + NH₃

#### 15.10

\(\text{P}_4(s) + 5\text{O}_2(g) \rightarrow \text{P}_4\text{O}_{10}(s)\)

\(\text{P}_4\) is a tetrahedron

#### 15.11

(i) Bi(III) is much more stable than Bi(V), and (ii) P(III) and P(V) are both about equally stable.

#### 15.12

The rates of reactions in which nitrite ion is reduced are increased as the pH is lowered.

\(\text{HNO}_2(aq) + \text{H}^+(aq) \rightarrow \text{NO}^+(aq) + \text{H}_2\text{O}(l)\)

#### 15.13

The rate law must be more than first order in NO concentration. It turns out to be second order; an equilibrium between NO and its dimer N₂O₂ precedes the rate-determining reaction with oxygen.

\(E_{\text{red}} = -0.736\text{V}\)

#### 15.14

\(\text{PO}_{1.5}(\text{Cl})_{3.5}\)
PCl₅ + H₂O → POCl₃ + 2HCl
(b) 2PCl₅(g) + 8H₂O(l) → 2H₃PO₄(aq) + 10HCl(aq)
(c) Tetrahedral.
PCl₅ + AlCl₃ → [PCl₄]⁻[AlCl₄]⁻
(d) Cyclic molecules or linear chain polymers
nPCl₅ + nNH₄Cl → [(N = P(Cl)₂)ₙ]⁻ + 4nHCl

P atom in POF₃ is more deshielded and its resonance will appear downfield in comparison to the P resonance in PF₃.

HPO₃²⁻ and H₂PO₂⁻ ions will be much better reducing agents than oxidizing agents.

12 valence skeletal electrons, nido, trigonal bipyramid.

(a) A = AsCl₃
(b) B = AsCl₅
(c) C = AsR₃
(d) D = AsH₃

The cis isomer gives two ¹⁹F signals and the trans isomer gives one signal.

15.17 E° = 0.839 V.
HPO₃²⁻ and H₂PO₂⁻ ions will be much better reducing agents than oxidizing agents.

15.18 12 valence skeletal electrons, nido, trigonal bipyramid.

(a) A = NO₂
(b) B = HNO₃; C = NO
(c) D = N₂O₃
(d) E = NO₂
(e) F = NH₄⁺

15.22 The species of N and P that disproportionate are N₂O₄, NO, N₂O, NH₃OH⁺, H₃P₂O₆, and P.

CHAPTER 16

Self-tests

S16.1 The decomposition of H₂O₂ is thermodynamically favored in presence of Br⁻.
The decomposition of H₂O₂ is also thermodynamically favored in presence of Cl⁻.

S16.2 (a) The SO₃ molecule is planar and belongs to the D₃h point group.
(b) The SO₃⁻F⁻ anion is tetrahedral, but the point group is C₃v.

S16.3 S₄N₄ is aromatic

Exercises

16.1 CO₂, SO₃, and P₂O₅ are acidic, Al₂O₃ is amphoteric, MgO and K₂O are basic.

16.2 The bond order in O₂ molecule is ½[2 – 2 + 2] = 2, and it corresponds to the bond length of 121 pm.
The bond order in O₂⁺ cation is ½[2 – 2 + 2 + 4 – 1] = 2.5, higher than in O₂ molecule. This higher bond order is reflected in a shorter bond length of 112 pm.
The bond order for O₂⁻ is ½[2 – 2 + 4 – 4] = 1. Of the three dioxygen species, O₂⁻ has the lowest bond order and the longest bond: 149 pm.

16.3 (a) +1.068 V.
(b) Cr²⁺ is not capable of decomposing H₂O₂.
(c) ΔG° = 157 kJ. For the disproportionation of H₂O₂ (part (a)), ΔG° = 103 kJ.

16.4 (a) Incorrect; this group exhibits alternation effect.
(b) Partially correct; the ground state of O₂ is a triplet state but it does not react as an electrophile in Diels-Alder reactions.
(c) Partially correct; while ozone is considered a pollutant, it is very unlikely that the ozone pollution is caused by the diffusion of this gas from the stratosphere.

16.5 O–H⁻ S

16.6 Ethylenediamine is a better solvent than sulfur dioxide.

16.7 S₂O₈²⁻ > SO₄²⁻ > SO₃²⁻

16.8 Mn (⁺VII, +VI, +V, +IV, +III) will be reduced by sulfite ions in basic solution.

16.9 (a) H₅TeO₆⁻ and HSO₄⁻
(b) Tellurium is a larger element than sulfur and can increase its coordination number.

16.10 S₂O₆²⁻ and S₅O₂²⁻.
16.11 SeO$_3^{2-}$ is marginally more stable in acid solutions.

16.12 All will be reduced as their potentials are greater than the potential of thiosulfate.

16.13 SF$_4$ trigonal pyramidal, BF$_3$ tetrahedral.

16.14 (a) SF$_2$ + (CH$_3$)$_2$NF → [(CH$_3$)$_2$NF]$^+$[SF$_4$]$^-$; (b) square pyramidal structure; (c) two F environments.

16.15 A = S$_2$Cl$_2$, B = S$_2$N$_4$, C = S$_2$N$_2$, D = K$_2$S$_2$O$_3$, E = S$_2$O$_6^{2-}$, F = SO$_2$.

16.16 (a) Expected to exhibit inorganic aromaticity. (b) Expected to be aromatic. (c) Not expected to be aromatic.

16.17 Sulfuric and selenic acids are rather similar; telluric acid is remarkably different from sulfuric and selenic acid.

**CHAPTER 17**

**Self-tests**

S17.1 Both. SO$_2$ is cheaper.

S17.2 2 resonances – a sextet and a triplet.


S17.4 Examples include I$_3^-$, IBr$_2^-$, ICl$_3^-$, and IF$_2^-$.

S17.5 (a) Br$_2$ and BrO$^{-}$: 
Br$_2$ + 2OH$^-$ → Br$^-$ + BrO$^{-}$ + H$_2$O
BrO$^{-}$ + 2OH$^-$ → Br$^-$ + BrO$_2^-$ + H$_2$O
(b) I$_2$ and IO$^-$:
I$_2$ + 2OH$^-$ → I$^-$ + IO$^-$ + H$_2$O
IO$^-$ + 2OH$^-$ → I$^-$ + IO$_3^-$ + H$_2$O

**Exercises**

17.1

17.2 For F:
CaF$_2$ + H$_2$SO$_4$ → CaSO$_4$ + 2 HF
2 HF + 2 KF → 2 K$^+$$^-$HF$_2$
2 K$^+$$^-$HF$_2^-$ + electricity → F$_2$ + H$_2$ + 2 KF

**ANSWERS TO SELF-TESTS AND EXERCISES**

<table>
<thead>
<tr>
<th></th>
<th>Physical state</th>
<th>Electronegativity</th>
<th>Hardness of halide</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>F$_2$</td>
<td>gas</td>
<td>highest (4.0)</td>
<td>hardest</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl$_2$</td>
<td>gas</td>
<td>lower</td>
<td>softer</td>
</tr>
<tr>
<td>Bromine</td>
<td>Br$_2$</td>
<td>liquid</td>
<td>lower</td>
<td>softer</td>
</tr>
<tr>
<td>Iodine</td>
<td>I$_2$</td>
<td>solid</td>
<td>lowest</td>
<td>softest</td>
</tr>
</tbody>
</table>

For Cl:
2 Cl$^-$ + 2 H$_2$O + electricity → Cl$_2$ + H$_2$ + 2 OH$^-$

For Br and I:
2 X$^-$ + Cl$_2$ → X$_2$ + 2 Cl$^-$ (X$^-$ = Br, I$^-$)

17.3 A drawing of the cell is shown in Figure 17.3.

- anode: 2 Cl$^-$ (aq) → Cl$_2$(g) + 2 e$^-$
- cathode: 2 H$_2$O(l) + 2 e$^-$ → 2 OH$^-$(aq) + H$_2$(g)
- unwanted reaction:
  2 OH$^-$(aq) + Cl$_2$(aq) → ClO$^-$(aq) + Cl$(aq)$ + H$_2$O(l)

17.4 Since the 2$\sigma_u^*$ antibonding orbital is the LUMO for a X$_2$ molecule, it is the orbital that accepts the pair of electrons from a Lewis base.

17.5 Cl$_2$ and F$_2$.

17.6 (a) Ammonia exhibits very strong hydrogen bonding.
(b) The strong electron-withdrawing effect in NF$_3$ reduces the basicity.

17.7 (a) (CN)$_2$(aq) + 2 OH$^-$(aq) → CN$^-$(aq) + NCO$^-$(aq) + H$_2$O(l)
(b) 2SCN$^-$(aq) + MnO$_2$(s) + 4 H$^+$aq) → (SCN)$_2$(aq) + Mn$^{2+}$(aq) + 2 H$_2$O(l)
(c) Trimethylsilyl cyanide contains an Si–CN single bond.
17.8 (a) \([\text{N(CH}_3\text{)}_2][\text{IF}_4]\).
(b) Three bonding pairs and two lone pairs on the iodine yield trigonal bipyramidal electron geometry and T-shaped molecular geometry.

The shape of anion \(\text{IF}_5^-\) is Square planar. The shape of cation \((\text{CH}_3\text{)}_4\text{N}\)^+ is Tetrahedral.

(c) \(\text{IF}_3\), two. \(\text{IF}_4^-\), one.

17.9 \(\text{SbCl}_3\) is trigonal bipyramidal, \(\text{FCIO}_3\) is pyramidal, and \([\text{ClF}_6]^+\) is octahedral.

17.10 \([\text{ClF}_4]^+\)\([\text{SbF}_5]^-\).

17.11 \(\text{MCl}_4\text{F}_2\), the cis isomer, 1; the trans isomer, 2. \(\text{MCl}_3\text{F}_3\), the fac isomer, 1; the mer isomer, 2.

17.12 (a) \(\text{IF}_6^+\), octahedral; \(\text{IF}_7\), pentagonal bipyramid.
(b) \(\text{IF}_7^+ + \text{SbF}_5 \rightarrow [\text{IF}_6^+][\text{SbF}_6]\)

17.13 Planar dimer (\(\text{I}_2\text{Cl}_6\)) with bridging Cl atoms. The point group of \(\text{I}_2\text{Cl}_6\) is \(D_{2h}\).

17.14 Trigonal pyramidal, \(C_s\) symmetry.

17.15 (a) Increases the acidity of \(\text{BrF}_3\).
(b) No effect on the acidity or basicity of \(\text{BrF}_3\).
(c) Increases the basicity of \(\text{BrF}_3\).

17.16 Two different I–I bond lengths: longer central I-I distances (290 pm) and shorter terminal I-I distances (268 pm). The difference in bond lengths can be explained by different bond order. This gives us one description of \(\text{I}_5^+\) structure as a hybrid of two structures.

17.17 Two resonances: a doublet and a quintet.

17.18 (a) Since \(\text{SbF}_5\) cannot be oxidized, it will not form an explosive mixture with \(\text{BrF}_3\).
(b) Methanol, being an organic compound, is readily oxidized by strong oxidants.
(c) The two will not form an explosive mixture but will react.
(d) \(\text{S}_2\text{Cl}_2\) will be oxidized to higher valent sulfur fluorides.

17.19 \(\text{Br}_3^- + \text{I}_2 \rightarrow 2 \text{IBr} + \text{Br}^-\)

17.20 Large cations stabilize large, unstable anions.

17.21 (a) Angular shape, point group is \(C_{2v}\).

(b) One iodine atom is trigonal pyramidal; the other iodine atom is tetrahedral. The point group is \(C_i\).
E = CsClF₂
B = OF₂
C = HF
D = SiF₄
G = CaF₂

17.31 (a) BrO₄⁻ is capable of oxidizing water. This makes preparation and isolation of KBrO₄ very difficult.
(b) All compounds are kinetically reasonably stable to be isolated.
(c) IO₂⁻ ion is too unstable for its salts to be isolated.
(d) BrO⁻ and IO⁻ are disproportionating too rapidly to be isolated.

17.32 (a) Correct
(b) Incorrect - the two anions do not have identical structures.
(c) Incorrect - it is the nucleophilicity of the Cl atom in ClO⁻ that is crucial for the oxidation mechanism.
(d) Correct.

CHAPTER 18

Self-tests

S18.1

2 HXeO₄⁻ (aq) + 2 OH⁻ (aq) → XeO₆⁴⁻(aq) + Xe(g) + O₂(g) + 2 H₂O(l)

Exercises

18.1 Earth’s gravitational field is not strong enough to hold light gases such as He and H₂, and they eventually diffuse away into space.
18.2 (a) Helium.
(b) Xenon.
(c) Argon.
18.3 (a) Xe and F₂ at 400°C, or photolyze Xe and F₂ in glass:
   Xe(g) + F₂(g) → XeF₂(s)
(b) High temperature, but have a large excess of F₂:
   Xe(g) + 3 F₂(g) → XeF₆(s)
(c) XeF₆(s) + 3 H₂O(l) → XeO₃(s) + 6 HF(g)

18.4

18.5 (a) XeF₆. The anion has a square-planar geometry.
(b) Linear geometry. Isostructural with XeF₂.
(c) Trigonal pyramidal geometry. Isostructural with XeO₃.
(d) Isostructural with the cation XeF⁺.

18.6 (a)

(b) Speculate that would be pentagonal bipyramid; actually capped octahedral.

18.7 He²⁺ = 0.5, Ne²⁺ = 0.5.

18.8 (a) Electron pair geometry: trigonal bipyramid. Molecular geometry: trigonal planar.
(b) Electron pair geometry: octahedral. Molecular geometry: t-shaped.
(c) Electron pair geometry: octahedral. Molecular geometry: square pyramidal.
(d) Electron pair geometry: pentagonal bipyramid. Molecular geometry: pentagonal planar.

18.9 A = XeF₂(g)
B = [XeF⁺][MeBF₃]⁻
C = XeF₆
D = XeO₃
E = XeF₄(g).

18.10 1:3:3:1 quartet

18.11 Strong central line, two other lines symmetrically distributed around the central line.

CHAPTER 19

Self-tests
S19.1 $V_2O_3$ is more stable than VO in presence of oxygen.

S19.2 Discrete molecular species such as $Re_3Cl_{12}^{3-}$ or $Re_3Cl_6(PPh_3)_3$ are formed.

**Exercises**

19.1 Mn, MnO$^4_-$; Ru/Os. Within a group, the heavier elements can achieve higher oxidation states than first-row members.

19.2 (a) The most oxidizing state for Cr and Mo is +6. Tungsten has no species with oxidizing properties.

(b) For Cr, Cr(IV) and Cr(V) are susceptible to disproportionation. Other elements do not have species that would be expected to disproportionate.

19.3 (a)

(b)

(c)

(d)

19.4 The oxides FeO$_2$ and Co$_2$O$_9$ contain iron and cobalt in oxidation states +8 and +9 respectively, which are not stable for either element.

19.5 Statement (c) is not true.

19.6 The most likely compounds of general formula MM$^+$ are rubidium and cesium aurides, RbAu and CsAu, containing Au$^+$. The difference in density can be explained by difference in atomic mass for Hf and Zr.

19.7 $Hg_2^{2+}$ will not disproportionate. Rather, $Hg$ and $Hg^{2+}$ would comproportionate to $Hg_2^{2+}$.

19.8 Pigments should be permanent and stable. They should also be non-toxic and have low vapour pressure.

**CHAPTER 20**

**Self-tests**

S20.1 A high-spin $d^7$ configuration is $t^2_2g^5e^2_g$. High spin, $0.8 \Delta$. 

S20.2 $t^2_2g^3e^2_g$ 

S20.3 If it were not for ligand field stabilization energy (LFSE), $MF_2$ lattice enthalpies would increase from Mn(II) to Zn(II).

S20.4 In the spectrum of $[Mo(CO)_6]$, the ionization energy around 8 eV was attributed to the $t^2_2g$ electrons that are largely metal-based. The differences in the 6–8 eV region can be attributed to the lack of $d$ electrons for Mg(II).

S20.5 $1^F$ and $3^F$ terms are possible.

S20.6 (a) $3^P$ (called a “triplet P” term).

(b) $3^D$ (called a “doublet D” term).

S20.7 F terms are $3^{1T_g}$, $3^{2T_g}$, and $3^{3A_g}$. Similarly, D terms are $1^{T_g}$ and $1^{E_g}$.

S20.8 17500 cm$^{-1}$ and 22400 cm$^{-1}$.

S20.9 (i) The very low intensity of the band at 16,000 cm$^{-1}$ is a clue that it is a spin-forbidden transition, probably $2^E_g \leftrightarrow 4^A_{2g}$.

(ii) Spin-allowed but Laporte-forbidden bands typically have $\varepsilon \sim 100$ M$^{-1}$ cm$^{-1}$, so it is likely that the bands at 17,700 cm$^{-1}$ and 23,800 cm$^{-1}$ are of this type.
The band at 32,400 cm\(^{-1}\) is probably a charge transfer band, since its intensity is too high to be a ligand field (\(d-d\) band).

**Exercises**

**20.1**

(a) \(d^6\), low spin, no unpaired electrons, LFSE = 2.4\(\Delta_0\).

(b) \(d^9\), high spin, four unpaired electrons, LFSE = 0.4\(\Delta_0\).

(c) \(d^4\), low spin, one unpaired electron. LFSE is 2.0\(\Delta_0\).

(d) \(d^3\), three unpaired electrons, low spin, LFSE = 1.2\(\Delta_0\).

(e) \(d^5\), low spin, no unpaired electrons, LFSE = 2.4\(\Delta_0\).

(f) \(d^6\), high spin, four unpaired electrons, LFSE = 0.6 \(\Delta_T\).

(g) \(d^{10}\), 0 unpaired electrons, LFSE = 0.

**20.2**

No.

There are two ways for a complex to develop a large value of \(\Delta_0\), by possessing ligands that are \(\pi\)-acids or by possessing ligands that are strong \(\sigma\)-bases (or both).

**20.3**

Spin-only contributions are:

<table>
<thead>
<tr>
<th>Complex</th>
<th>(N)</th>
<th>(\mu/\mu_B = [(N)(N + 2)]^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(NH}_3\text{)}_6]^3+)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>([\text{Fe(OH}_2\text{)}_6]^3+)</td>
<td>4</td>
<td>4.9</td>
</tr>
<tr>
<td>([\text{Fe(CN)}_6]^3-)</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_6]^3+)</td>
<td>3</td>
<td>3.9</td>
</tr>
<tr>
<td>([\text{W(CO)}_6]^3-)</td>
<td>4</td>
<td>4.9</td>
</tr>
<tr>
<td>([\text{Ni(CO)}_4]^0)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\([\text{CoCl}_4]^2-\) is blue, \([\text{Co(NH}_3\text{)}_6]^3+\) is yellow, \([\text{Co(OH}_2\text{)}_6]^3+\) is pink.

**20.4**

(a) The chromium complex.
(b) The \(\text{Fe}^{3+}\) complex.
(c) \([\text{Fe(CN)}_6]^3-\).
(d) The ruthenium complex.
(e) The \(\text{Co}^{2+}\) complex.

**20.5**

There are two factors that lead to the values: (i) decreasing ionic radius from left to right across the \(d\) block, and (ii) LFSE.

**20.6**

20.7 (a)

![Graph showing \(\Delta_0\) vs. number of d electrons](image)

(b)

<table>
<thead>
<tr>
<th>Ion</th>
<th>(\text{Ca}^{2+})</th>
<th>(\text{V}^{2+})</th>
<th>(\text{Cr}^{3+})</th>
<th>(\text{Mn}^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta_n) (in (\text{cm}^{-1}))</td>
<td>0</td>
<td>12600</td>
<td>13900</td>
<td>7800</td>
</tr>
<tr>
<td>(\Delta_{OE}) (in (\text{kJ mol}^{-1}))</td>
<td>0</td>
<td>105.5</td>
<td>166.1</td>
<td>93.2</td>
</tr>
<tr>
<td>LFSE (kJ mol(^{-1}))</td>
<td>0</td>
<td>(-)</td>
<td>(-99.6)</td>
<td>0</td>
</tr>
</tbody>
</table>

(c) The straight line now shows the expected trend in \(\Delta_{OE}\) as a function of cationic radius only without electronic effects.

**20.8**

Shift from square planar to tetragonal complex.

**20.9**

Elongated octahedron.

**20.10**

The electronic excited state of \([\text{Ti(OH}_2\text{)}_6]^{3+}\) has the configuration \(t_{2g}^6e_g^{\downarrow}\), and so the excited state possesses \(e_g^{\downarrow}\) degeneracy. Therefore, the “single” electronic transition is really the superposition of two transitions, one from an \(O_b\) ground-state ion to an \(O_b\) excited-state ion, and a lower energy transition from an \(O_h\) ground-state ion to a lower energy distorted excited-state ion.

**20.11**

(a) \(^3\text{S}\)
(b) $^4\text{F}$
(c) $^3\text{D}$
(d) $^3\text{P}$

20.12 (a) $^3\text{F}$.
(b) $^3\text{D}$
(c) $^6\text{S}$

20.13 (a) $^2\text{S}$.
(b) $^1\text{D}$, $^3\text{P}$, $^1\text{S}$. The ground term is $^3\text{P}$.

20.14 $B = (12920\ \text{cm}^{-1})/15 = 861.33\ \text{cm}^{-1}$ and $C = 3167.7\ \text{cm}^{-1}$.

20.15 (a) $^1\text{A}_1\text{g}$.
(b) $^2\text{T}_2\text{g}$
(c) $^6\text{A}_{1\text{g}}$

20.16 (a) $\Delta_0 = 8500\ \text{cm}^{-1}$ and $B \approx 770\ \text{cm}^{-1}$.
(b) $\Delta_0 = 10,750\ \text{cm}^{-1}$ and $B \approx 720\ \text{cm}^{-1}$.

20.17 The presence of two moderate-intensity bands in the visible/near-UV spectrum of $[\text{Co(NH}_3\text{)}_6]^{3+}$ suggests that it is low spin. The very weak band in the red corresponds to a spin-forbidden transition such as $^3\text{T}_{2\text{g}} \rightarrow ^1\text{A}_{1\text{g}}$.

20.18 No spin-allowed transitions are possible for the Fe$^{3+}$; the complex is expected to be colorless. The $d^6$ Co$^{3+}$ ion in $[\text{CoF}_6]^{3-}$ is also high spin, but in this case a single spin-allowed transition makes the complex colored and gives it a one-band spectrum.

20.19 Ammonia and cyanide ion are both $\sigma$-bases, but cyanide is also a $\pi$-acid.

20.20 First, the intense band at relatively high energy is undoubtedly a spin-allowed charge-transfer transition. The two bands with $\epsilon_{\text{max}} = 60$ and $80\ \text{M}^{-1}\ \text{cm}^{-1}$ are probably spin-allowed ligand field transitions. The very weak peak is most likely a spin-forbidden ligand field transition.

20.21 The faint green color, which is only observed when looking through a long pathlength of bottle glass, is caused by spin-forbidden ligand field transitions.

20.22 The blue-green color of the Cr$^{3+}$ ions in $[\text{Cr(H}_2\text{O}_6]^{3+}$ is caused by spin-allowed but Laporte-forbidden ligand field transitions. The relatively low molar absorption coefficient is the reason that the intensity of the color is weak. The oxidation state of chromium in dichromate dianion is Cr(VI); the intense yellow color is due to LMCT transitions.

20.23 The Cl atom lone pairs of electrons can form $\pi$ molecular orbitals with $d_{xy}$ and $d_{yz}$. These metal atomic orbitals are $\pi$-antibonding MOs, and so they will be raised in energy.

20.24 The oxidation state of manganese in permanganate anion is Mn(VII), which is $d^5$. Therefore, no ligand field transitions are possible. The difference in energy between the two transitions, $E(t_2) - E(e) = 13700\ \text{cm}^{-1}$, is just equal to $\Delta_T$.

CHAPTER 21

Self-tests

S21.1 $k_{\text{d(NO}_2^-)} = 10^{0.71} = 5.1\ \text{M}^{-1}\ \text{s}^{-1}$

S21.2

S21.3 $K = 1\ \text{M}^{-1}$, $k = 1.2 \times 10^2\ \text{s}^{-1}$.

Exercises

21.1 Dissociative.

21.2 The rate of an associative process depends on the identity of the entering ligand so it is not an inherent property of $[\text{M(OH}_2\text{)}_6]^{3+}$. 
21.14 (a) cis-[PtCl₂(PR₃)₂]  
(b) trans-[PtCl₂(PR₃)₂]  
(c) trans-[PtCl₂(NH₃)(py)]

21.15 The order of increasing rate is [Ir(NH₃)₃]³⁺ < [Rh(NH₃)₃]³⁺ < [Co(NH₃)₆]³⁺ < [Ni(OH₂)₆]²⁺ < [Mn(OH₂)₆]³⁺.

21.16 (a) Decreased rate.  
(b) Decreased rate.  
(c) This change will have little or no effect on the rate.  
(d) Decreased rate.

21.17 The inner-sphere pathway:
\[
\text{[Co(N₃)(NH₃)₃]^{2+} + [V(OH₂)₆]^{2+} \rightarrow [\text{[Co(N₃)(NH₃)₃]^{2+} + [V(OH₂)₆]^{2+}}}}
\]
\[
\text{[Co(N₃)(NH₃)₃]^{2+} + [V(OH₂)₆]^{2+} \rightarrow [\text{[Co(N₃)(NH₃)₃]^{2+} + [V(OH₂)₆]^{2+}} + H₂O]
\]
\[
\text{[Co(N₃)(NH₃)₃]^{2+} + [V(OH₂)₆]^{2+} \rightarrow [\text{[Co(N₃)(NH₃)₃]^{2+} + [V(OH₂)₆]^{2+}} + H₂O]
\]
\[
\text{[(NH₃)₅Co-N=N=N–V(OH₂)₆]^{4+} \rightarrow [(NH₃)₅Co–N=N=N–V(OH₂)₆]^{4+}}
\]
\[
\text{[(NH₃)₅Co–N=N=N–V(OH₂)₆]^{4+} \rightarrow [\text{(NH₃)₅Co–N=N=N–V(OH₂)₆]^{4+}}}
\]
\[
\text{[(NH₃)₅Co–N=N=N–V(OH₂)₆]^{4+} \rightarrow [\text{(NH₃)₅Co–N=N=N–V(OH₂)₆]^{4+}} + N₅}
\]

21.18 Appears to be an inner-sphere electron transfer reaction.

21.19 The reduction of \([\text{Co(NH₃)₆(OH)}₂]^{2+}\) proceeds via inner-sphere mechanism. The \([\text{Co(NH₃)₆(OH)}₂]^{2+}\) has no bridging ligands and the only mechanistic pathway for the electron-transfer is outer sphere. Both reactions with \([\text{Ru(NH₃)₆}^{2+}]\) as a reducing agent likely proceed via the same mechanism, the outer-sphere mechanism.

21.20 (a) \(k = 4.53 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}\)
(b) \(k = 1.41 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}\)

The reduction of the Ru complex is more thermodynamically favoured and faster.

21.21 (a) \(k_{11} \text{ (Cr}^{3+/Cr}^{2+}) = 1 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}; k_{22} \text{ (Ru}^{3+/Ru}^{2+} \text{ for the hexamine complex)} = 6.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}; f_{12} = 1; K_{12} = e^{\Delta f/RT}\)
where $\epsilon_0 = 0.07 \text{ V} - (-0.41 \text{ V}) = 0.48 \text{ V}$; $n = 1; F = 96485 \text{ C}/\text{mol}; R = 8.31 \text{ J mol}^{-1} \text{K}^{-1}$ and $T = 298 \text{ K}$. Using these values gives $K_{12} = 1.32 \times 10^8$.

Substitution of these values in the Marcus-Cross relationship gives $k_{12} = 2.95 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}$.

(b) $k_{11} (Cr^{3+}/Cr^{2+}) = 1 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}$; $k_{22} (Fe^{3+}/Fe^{2+} \text{ for the aqua complex}) = 1.1 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}$; $f_{12} = 1$; $K_{12} = e^{[\text{MP}]}$ where $\epsilon_0 = 0.77 \text{ V} - (-0.41 \text{ V}) = 1.18 \text{ V}$; $n = 1; F = 96485 \text{ C}; R = 8.31 \text{ J mol}^{-1} \text{K}^{-1}$ and $T = 298 \text{ K}$. Using these values we get $K_{12} = 2.96 \times 10^9$. Substitution of these values in the Marcus-Cross relationship gives $k_{12} = 3.19 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}$.

(c) $k_{11} (Cr^{3+}/Cr^{2+}) = 1 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}$; $k_{22} (Ru^{3+}/Ru^{2+} \text{ for the bipy complex}) = 4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}$; $f_{12} = 1$; $K_{12} = e^{[\text{MP}]}$ where $\epsilon_0 = 1.26 \text{ V} - (-0.41 \text{ V}) = 1.67 \text{ V}$; $n = 1; F = 96485 \text{ C}; R = 8.31 \text{ J mol}^{-1} \text{K}^{-1}$ and $T = 298 \text{ K}$. Using these values gives $K_{12} = 1.81 \times 10^{16}$. Substitution of these values in the Marcus-Cross relationship gives $k_{12} = 8.51 \times 10^{15} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}$.

21.22 The product will be $[W(CO)_3(NEt_3)]$, and the quantum yield will be 0.4.

21.23 ~250 nm.

CHAPTER 22

Self-tests

S22.1 No.

S22.2 Electron count, 16; oxidation number, +2.

S22.3 Dibromocarbonylmethylbis(triphenylphosphine)iridium(III).

S22.4 Fe(CO)$_3$

S22.5 (a) $\eta^5$-C$_5$H$_5$ = 6 electrons, Mo atom = 6, carbonyl = 2 electrons, total = 18.

(b) $\eta^1$-C$_5$H$_5$ = 6 electrons, Mo atom = 6, 3 COs = 6, total = 18.

S22.6

Mn$_2$(CO)$_{10}$ + 2 Na → 2Na[Mn(CO)$_3$]


[Mn(CH$_3$)(CO)$_3$] + PPh$_3$ → [Mn(CO)$_3$(CO)$_3$(PPh$_3$)]

S22.7 Bridging

S22.8 It will not.

22.2

S22.9 TA tetrahedron with 4 terminal Cp rings and four capping COs.

S22.10 PMe$_3$ would be preferred, because of its smaller size.

S22.11 Fluorenyl compounds are more reactive than indenyl.

S22.12 The decrease in both coordination number and oxidation number by 2.

S22.13 The ethyl group in [Pt(P(chl)$_3$)$_2$(Et)(Cl)] is prone to $\beta$-hydride elimination.

Exercises

22.1  (a) Pentacarbonyliron(0), 18e$^-$;

(b) Decacarbonyldimanganese(0), 18e$^-$;

(c) Hexacarbonylferrate(0), 18e$^-$; can be easily reduced to [V(CO)$_3$]

(d) Tetracarbonylferrate$^-$ (−2), 18e$^-$;

(e) Tris(pentamethylcyclopentadienyl)lanthanum(III), 18e$^-$;

(f) $\eta^1$-allyltricarbonylchloridoiron(II), 18e$^-$;

(g) Tetracarbonyltrihethylphosphineiron(0) 18e$^-$

(h) Dicarbonylmethyltriphenylphosphineberadium(1),16e$^-$; a square planar complex, undergoes oxidative addition easily.

(i) Chloridomethylbis(triphenylphosphine)palladium(II), 16e$^-$; a square planar complex, undergoes oxidative addition easily

(j) $\eta^1$-cyclopentadienyl-$\eta^1$-tetrphenylcyclobutiencobalt(I), 18e$^-$

(k) $\eta^1$-cyclopentadienylidicarbonyliron(0), 18e$^-$

(l) $\eta^6$-benzene-$\eta^6$-cycloheptatrienechromium(0), 18e$^-$

(m) Trichloridobis($\eta^5$-cyclopentadienyl)tanatalum(V), 18e$^-$

(n) $\eta^1$-cyclopentadienyl nitrosyl nickel(II),16e$^-$; a rather reactive complex
22.3  (a) $\eta^2$
(b) Can be $\eta^1$, $\eta^3$, or $\eta^3$.
(c) $\eta^4$, $\eta^1$, and $\eta^3$.
(d) $\eta^2$ and $\eta^4$.
(e) $\eta^4$, $\eta^6$, $\eta^4$, $\eta^2$.

22.4  (a) 16, very common for group 9 and group 10 elements.
(b) 18.
(c) 18.

22.5  
(1) $\text{Mo(s)} + 6 \text{CO(g)} \rightarrow \text{Mo(CO)}_6(s)$ (high temperature and pressure required)

(2) $2 \text{CoCO}_3(s) + 2 \text{H}_2(g) + 8 \text{CO(g)} \rightarrow \text{Co}_2\text{(CO)}_8(s) + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$

The reason that the second method is preferred is kinetic.

22.6  A complex that has $C_s$ symmetry will have the greatest number of bands. A fragment with $D_{2h}$ symmetry will give rise to one band, a fragment with $C_3v$ symmetry will give rise to two bands, and a fragment with $C_s$ symmetry will give rise to three bands.

22.7  (a) CO bands of the trimethylphosphine complex are 100 cm$^{-1}$ or more lower in frequency. PMe$_3$ is primarily a $\sigma$-donor ligand. PF$_3$ is primarily a $\pi$-acid ligand.

(b) CO bands of the Cp* complex are lower in frequency than the corresponding bands of the Cp complex. Cp* is a stronger donor ligand than Cp.

22.8  (a)
22.15 (a) Reflux Mo(CO)₆ with cycloheptatriene to give [Mo(η⁶-C₇H₈)(CO)₃]; treat with the trityl tetrafluoroborate to give [Mo(η⁷-C₇H₇)(CO)₃]BF₄.
(b) React [IrCl(CO)(PPh₃)₂] with MeCl, then expose to CO atmosphere to give [IrCl₂(COMe)(CO)(PPh₃)₂].

22.16

Compound A:
[Fe(η⁵-C₅H₅)(CO)₃]

Compound B:
[Fe(η⁵-C₅H₅)(CO)₂(H)]

Compound C:
[Fe(η⁵-C₅H₅)(CO)₃]₂

The compound B shows two ¹H NMR resonances due to Fe-H proton and the aromatic Cp ring. C shows a single ¹H NMR resonance because of aromatic Cp ring.

22.17 In either case compounds formed are tetraalkyl titanium(IV) complexes, TiR₄. Neither the methyl or trimethylsilyl groups have β hydrogens. Thus, unlike [TiEt₄], [TiMe₄] and [Ti(CH₂SiMe₃)₄] cannot undergo a low energy β-hydride elimination decomposition reaction.

22.18 Considering that Cp⁻ can both “slip” and rotate, at room temperature we see only one resonance as an effect of averaging the proton environments. At -40°C we observe two different signals of equal intensity. This tells us that there are two different environments, both of which contain two Cp rings.

22.19 (a) [Fe(η⁵-C₅H₅)] + CH₃COCl → [Fe(η⁵-C₅H₅)] + CH₃COH
(b) [Fe(η⁵-C₅H₅)(CO)₂] + HCl

22.20 See resource section 5. d₂ and s orbitals have an a₁′ symmetry and thus have correct symmetry to form the MOs with the a₁′ symmetry-adapted orbital on Cp rings. Therefore, three a₁′ MOs will be formed.

22.21 The reason that the Ni complex is protonated at a carbon atom is that a more stable (i.e., 18-electron) product is formed.

22.22 (a)

![Chemical Reaction](image)

22.23 One of the possible routes involves initial slip of Cp⁻ ring from η⁵ to η³ bonding mode creating a 16-electron complex that can coordinate a phosphine ligand producing new 18-electron [Mo(η⁵-C₅H₅)(CO)₃Me(PR₃)] complex. This complex loses one CO ligand giving a new 16-electron intermediate [Mo(η⁵-C₅H₅)(CO)₂Me(PR₃)] that converts to
the stable 18-electron complex [Mo(η⁵-C₅H₅)(CO)₂Me(PR₃)].

The second route starts with CO insertion (or methyl group migration) to produce a 16-electron acyl complex. This complex can coordinate one PR₃ ligand to give an 18-electron species, which if heated can lose one CO ligand and undergo reverse alkyl group migration.

22.24  (a) 86: 90  
(b) Yes for trigonal prismatic; no for octahedral arrangement.  
(c) The iron complex probably contains an octahedral Fe₆ array, whereas the cobalt complex probably contains a trigonal-prismatic Co₆ array.

22.25  (a) SiCH₃ group  
(b) Iodine atom

22.26  The cobalt complex will exhibit faster exchange. This is because metal–metal bond strengths increase down a group in the d-block.

CHAPTER 23

Self-tests

S23.1  ³H₁₈  
S23.2  Likely to result in a product containing two (Cp)₂Ln units bridged by a ligand system. In fact the product consists of two (Cp)₂Ln units bridged by a hydrido ligand.

S23.2  UO₂⁺ if sufficient oxygen is present.

S23.4  ![](image)

Exercises

23.1  (a) 2 Ln(s) + 6 H₂O⁺(aq) → 2 Ln³⁺(aq) + 3 H₂(g) + 6 H₂O(l)  
(b) The potentials for the Ln⁰/Ln³⁺ oxidations in acid solution range from a low of 1.99 V for europium to 2.38 V.  
(c) Ce⁴⁺, Eu³⁺.

23.2  The lanthanide contraction.

23.3  Unusual oxidation states were used in separation procedures.

23.4  UF₆ is a molecular solid—its solid state structure contains isolated, octahedral UF₆ molecules held together via relatively weak intermolecular forces. UF₃ and UF₄ form network solids in which each U atom is surrounded by nine and eight fluorines respectively.

23.5  Could contain Pu(III), Pu(IV), Pu(V), and even Pu(VI) species. Addition of F⁻ to the solution is likely going to precipitate PuF₃.

23.6  See Figure 23.16. Bond order is 3. All these fragments are linear because this geometry maximizes the strong σ-overlap between 2p orbitals on the oxygen atoms and 6d² and 5f³ orbitals on the An atom.

23.7  Tb³⁺: ⁷F₆  
Nd⁴⁺, ⁴I₉/₂  
Ho³⁺: ⁵I₈  
Er³⁺: ⁴I₁₅/₂  
Lu³⁺: ¹S₀

23.8  (a) Correct  
(b) Incorrect - Ln³⁺ cations exchange water molecules very rapidly  
(c) Correct

23.9  It would shake the theoretical foundation of the claim that the lanthanide 4f subshell is rather inert. A good candidate could be Pr.

23.10  Both have 2+ as a stable oxidation state.

23.11  With the lanthanoids, the 5d orbitals are empty, and the 4f orbitals are deeply buried in the inert [Xe] core and cannot participate in bonding.

23.12  ![](image)

23.13  The 5f orbitals of the actinide ions interact strongly with ligand orbitals, and the splitting of the 5f subshell, as well as the color of the complex, varies as a function of ligand.
23.14 Rock-salt structure.

CHAPTER 24

Self-tests

S24.1 (a) From SrCO$_3$ and TiO$_2$ in 1 : 1 ratio. The two are grinded together and heated.
(b) 3 : 2 stoichiometry (SrCO$_3$ : TiO$_2$); alternatively, it can be prepared from SrTiO$_3$ and SrO in 2 : 1 stoichiometry.

S24.2 Because K$^+$ is a larger ion than Na$^+$.

S24.3 The A$^{2+}$ ions (Fe$^{2+}$ in this example) occupy tetrahedral sites and the B$^{3+}$ ions (Cr$^{3+}$) occupy octahedral sites.

Exercises

24.1 (a) By heating a 1 : 1 mixture of MgCO$_3$ (or Mg(NO$_3$)$_2$) and (NH$_4$)$_2$Cr$_2$O$_7$ at high temperature.
(b) By coprecipitating La$^{3+}$ and Fe$^{3+}$ hydroxides and then, after filtration, heating the precipitate and eliminating water.
(c) By heating Ta$_2$O$_5$ under a flow of NH$_3$ at high temperature.
(d) By heating a molar mixture of LiH and MgH$_2$ (under hydrogen or an inert gas) in a direct reaction, or by heating a mixture of the elements under hydrogen.
(e) Can be prepared from solution of CuBr$_2$ and KF as a precipitate.
(f) Can be prepared starting from sodium gallate, NaGaO$_2$ and sodium silicate. The reaction would be undertaken hydrothermally in a sealed reaction vessel.

24.2 (a) LiCoO$_2$
(b) Sr$_5$WMnO$_6$

24.3 The electronic conductivity of the solid increases owing to formation of (Ni$_{1-x}$Li$_x$)O.

24.4 Fe$_3$O contains vacancies.

24.5 Using electron microscopy and X-ray diffraction.

24.6 (a) Na$^+$
(b) Ca$^{2+}$ or Na$^+$

24.7 For the 1 : 1 Na:Re ratio the structure type can be described as that of perovskite (CaTiO$_3$).

24.8 Below 122 K.

24.9 ZnCr$_2$S$_4$; NiLi$_2$F$_4$

24.10 All except Gd$_2$Ba$_2$Ti$_2$Cu$_2$O$_{11}$ (compound c), are superconductors.

24.11 White Ta$_2$O$_5$ reacts with ammonia at high temperature to produce red Ta$_3$N$_5$.

24.12 Formation of a glass is favoured for the substances that have polyhedral, corner-sharing oxygen atoms and that can retain the coordination sphere around a glass-forming element while having variable bond angles around O atom.

24.13 BeO, B$_2$O$_3$, and to some extent GeO$_2$ are glass forming. Transition metal and rare earth oxides are typically non–glass-forming oxides.

24.14 Any metal sulfide glasses would involve metalloid and non-metal sulfides.

24.15 1. Direct combination of lithium and TiS$_2$ at elevated temperatures. 2. Electrointercalation.

24.16 Both [Co(η$^5$-C$_5$H$_5$)$_2$] and [Co(η$^5$-C$_5$Me$_5$)$_2$] are 19-electron species and can be easily oxidized to 18-electron species. Ferrocene [Fe(η$^5$-C$_5$H$_5$)$_2$] is an 18- electron compound and cannot be easily oxidized.

24.17 The Mo$_6$S$_8$ units are bonded via Mo – S bridges. The S atoms in one cube donate an electron pair from a filled p orbital to the empty 4d$_{z^2}$ orbital on Mo located on a neighbouring cube.

To accompany Inorganic Chemistry, Sixth Edition by Weller, Overton, Rourke, and Armstrong
24.18 Be, Ga, Zn, and P all form stable tetrahedral units with oxygen. Mg would prefer an octahedral environment (i.e., the structure of brucite, Mg(OH)$_2$), whereas Cl would likely be an anion.

24.19 The following zeotypes are possible: (AlP)O$_4$, (BP)O$_4$, (ZnP)$_2$O$_6$.

24.20 Ambidentate ligands.

24.21 10.6%; however elevated temperatures for decomposition are required to liberate the hydrogen gas.

24.22 Li$_{x}$Mg$_{1-x/2}$Al$_{y/3}$H$_{2+z}$; heating an alloy with desired Li : Mg : Al ratio (which can be prepared by mulling) under H$_2$ atmosphere.

24.23 Because it is thermodynamically unstable.

24.24 The Cu site in Egyptian blue is square planar and thus has a centre of symmetry; in copper aluminate spinel blue, the site is tetrahedral with no centre of symmetry.

24.25 In the solution an anionic radical S$_3^-$ is present. In solution polysulfide, radical anions are very sensitive to O$_2$ from the atmosphere; upon oxidation the colour is lost.

24.26 (a) High efficiency of light absorption (b) efficient electron-hole separation process and (c) high surface area of bulk material.

24.27 BN > C(diamond) > AlP > InSb.

24.28 In Na$_2$C$_{60}$, all of the tetrahedral holes are filled with sodium cations within the close-packed array of fulleride anions. In Na$_3$C$_{60}$, all of the tetrahedral holes and all of the octahedral holes are filled with sodium cations within the fcc lattice of fulleride anions.

24.29 (a) $1.256 \times 10^3$ nm$^2$ versus $1.256 \times 10^7$ nm$^2$ (a factor of $10^5$),
(b) The 10 nm particle can be considered a nanoparticle, whereas the 1000 nm particle cannot.
(c) A true nanoparticle should have a localized surface plasmon without characteristic momentum and of high intensity.

24.30 (a) Top-down: requires one to “carve out” nanoscale features from a larger object e.g. lithography.
Bottom up: requires one to “build up” nanoscale features from smaller entities e.g. thin film deposition of quantum wells.

24.31 (a) reacting species and additives must be solvated; stable nuclei of nanometer dimensions must be formed from solution; growth of particles to the final desired size.
(b) So that nucleation fixes the total number of particles and growth leads to a controlled size and a narrow size distribution.
(c) Stabilizers prevent unwanted Ostwald ripening.

24.32 Smaller particles present in the solution dissolve and this redisolved material precipitates again but on the surface of existing particles.

24.33 (a)
(b) i) Solution based: grow the core in solution and add the additive and material for the growth of shell. ii) Vapor-deposition: deposit the material for the core and then the material for the shell.
(c) Biosensing.

24.34 Hexagonal boron nitride, Sheet silicates, Molybdenum sulphide.

CHAPTER 25

Self-tests

S25.1 Cyclohexanecarboxaldehyde.
S25.2 the rate of hydroformylation will be decreased by added phosphine.
S25.3 Bands near 1465 cm$^{-1}$
S25.4 Not an active catalyst; contains Si–OH groups, which are only moderate Brønsted acids.
S25.5 The polymerization of mono-substituted alkenes introduces sterogenic centres along the carbon chain at every other position. Without R groups attached to the Zr centre there is no preference for specific binding of new alkenes during polymerization and thus the repeat is random or atactic.

Exercises

25.1 (a) Genuine example of catalysis; the platinum can be recovered unchanged after many turnovers.
(b) Not an example of catalysis as the activation energy of the reaction is not lowered.
(c) Not an example of catalysis as both substances are consumed.

25.2 (a) The amount of product formed per unit time per unit amount of catalyst.
(b) A measure of how much of the desired product is formed relative to undesired by-products.
(c) A substance that increases the rate of a reaction but is not itself consumed.
(d) A sequence of chemical reactions, each involving the catalyst, that transform the reactants into products.
(e) In cases where a heterogeneous catalyst does not remain a finely divided pure substance with a large surface area under the reaction conditions, it must be dispersed on a support material.

25.3 (a) Since the substances are all present in the same phase, this is an example of homogeneous catalysis.
(b) Heterogeneous catalysis – the reactants and products are in the liquid phase but the catalyst is a solid.
(c) The substrate and catalyst are in the same phase so this is homogeneous catalysis.

25.4 (a) Since water is a thermodynamically stable compound, it would not be a worthwhile endeavour to try to develop a catalyst to split water into hydrogen and oxygen.
(b) As with (a) you would be trying to catalyze the decomposition of a very stable compound so it would not be worthwhile.
(c) This would be a candidate for catalyst development, however the process can be readily set up with existing technology.

25.5 The catalytic cycle for homogeneous hydrogenation of alkenes by Wilkinson’s catalyst, [RhCl(PPh₃)₃], is shown in Figure 25.5.

25.6 Hydrogenation is faster for hexene than for cis-4-methyl-2-pentene (a factor of 2910/990 ≈ 3). It is also faster for cyclohexene than for 1-methylcyclohexene (a factor of 3160/60 ≈ 53). In both cases, the alkene that is hydrogenated slowly has a greater degree of substitution and so is sterically more demanding. The reaction (C) → (D) is the rate-determining step for hydrogenation by RhCl(PPh₃)₃.

25.7 The selectivity step is the hydride migration onto the coordinated prop-1-en in [HCo(CO)₄(H₂C=CHCH₃)] complex.

25.8 The resulting polymer is going to be isotactic: it is going to have a high melting point and will be semicrystalline.

25.9 The transformation of (E) into [CoH(CO)₄] and product must be the rate-determining step in the absence of added PBu₃. In the presence of added PBu₃, the formation of either (A) or (E), or their phosphine-substituted equivalents, is the rate-determining step.

25.10 HI would hydrolyse MeCOOMe and produce MeI and MeCOOH (instead of water). The reaction of the ethanolic acid with the acetyl iodide (produced at the end of the catalytic cycle) leads to ethanoic anhydride.

25.11 (a) ROMP can result in reduced steric strain, thereby providing a thermodynamic driving force for the reaction.
(b) RCM results in the loss of ethane, and by removing this gas, the position of equilibrium can easily be driven to favour the ring product.

25.12 (a)
(c) Yes.

25.13 (a) When Al$^{3+}$ replaces Si$^{4+}$ on lattice site, the charge is balanced by H$_2$O$^+$, increasing the acidity of the solid catalyst. (b) Other 3+ ions—for example Ga$^{3+}$, Co$^{3+}$, or Fe$^{3+}$, would have similar effect as Al$^{3+}$.

25.14 Because it increases the surface area.

25.15 The steps necessary for deuterium substitution into an alkane include the dissociative chemisorption of an R–H bond, the dissociative chemisorption of D$_2$, and the dissociation of R–D. The second observation (a given ethyl group is completely deuterated before another one incorporates any deuterium) can be explained by invoking a mechanism for rapid deuterium exchange of the methyl group in the chemisorbed –CHR(CH$_3$) group (R = C(CH$_3$)$_3$C$_2$H$_5$).

25.16 Platinum not only has a strong tendency to chemisorb H$_2$, but it also has a strong tendency to chemisorb CO.

25.17 Electro catalysts are compounds that are capable of reducing the kinetic barrier for electrochemical reactions.

25.18 (a) While it is true that a catalyst introduces a new reaction pathway it does so by lowering the Gibbs energy of activation, not enthalpy of activation. (b) First, the catalyst does not make the Gibbs energy of a reaction more favourable but rather the Gibbs energy of activation. Second, even if the Gibbs energy of activation was implied, a catalyst is not only reducing the Gibbs energy, but it can also dictate the formation of a specific product. (c) The Ziegler–Natta catalyst is a heterogeneous catalyst. (d) Highly favourable Gibbs energies for the attachment of reactants and products to a catalyst are not good for catalysis at all.

CHAPTER 26

Self-tests

S26.1 Uncomplexed Fe$^{3+}$ is present at very low concentrations.

S26.2 The protein’s tertiary structure can place any particular atom or group in a suitable position for axial coordination.

S26.3 If a patient was given an intravenous fluid containing KCl instead of NaCl, the potential across the cell membrane would collapse, with severe consequences.

S26.4 Calmodulin does not bind to the pump unless Ca$^{2+}$ is coordinated to it. As the Ca$^{2+}$ concentration increases in the cell, the Ca-calmodulin complex is formed. The binding of this Ca-calmodulin complex to the pump is thus a signal informing the pump that the cytoplasmic Ca$^{2+}$ level has risen above a certain level and to start pumping Ca$^{2+}$ out.

S26.5 Starting from a Fe(II) porphyrin complex (L is a neutral axial ligand throughout the sequence) we first obtain a peroxo bridged Fe(III) porphyrin dimer. Peroxo bridge can oxidatively cleave producing two equivalents of oxido Fe(IV) porphyrin monomers. This rather reactive species can react with another equivalent of the starting Fe(II) porphyrin complex producing an oxido-bridged Fe(III) porphyrin dimer.

S26.6 Hydrogen bonding and replacement of one cysteine with a histidine should lead to an increase in the reduction potential of an Fe-S cluster.

S26.7 There is greater covalence in blue Cu centres than in simple Cu(II) compounds.

S26.8 Likely to be highly oxidizing, and probably diamagnetic with a preference for square-planar geometry.

S26.9 Species such as CH$_3$Hg$^+$ and (CH$_3$)$_3$Hg are hydrophobic and can penetrate cell membranes. Cobalamins are very active methyl-transfer reagents that can methylate anything in the cell, which is bad news for the human body.

S26.10 Spectroscopic measurements that are metal specific, such as EPR, could be used on both enzyme and isolated cofactor. Attempts could be made to grow single crystals from the solution and perform single-crystal X-ray diffraction and EXAFS to reveal molecular geometry, bond distances, and angles between Fe or Mo and the sulphur ligands.

S26.11 Cu(I) has an ability to undergo linear coordination by sulphur-containing ligands.

Exercises
For a channel or ionophore to be Na\(^+\) specific it must have smaller cavity than K-channel. Ca\(^2+\) is going to bind more tightly than either Na\(^+\) or K\(^+\) to the residues that have negative charge. It is also a cation of a s-block element and has no LFSE that could dictate a preferred geometry. Cl\(^-\) is obviously different from the other three by being an anion. Thus, to move Cl\(^-\) we would need to have a large cavity and rely on hydrogen bonds formed with –NH and –OH functional groups.

The larger size of lanthanides is compensated for by their higher charge, although they are likely to have higher coordination numbers.

Co(II) commonly adopts distorted tetrahedral and five-coordinate geometries typical of Zn(II) in enzymes. When substituted for Zn(II), the enzyme generally retains catalytic activity. Zn(II) is d\(^{10}\) and therefore colourless; however, Co(II) is d\(^7\), and its peaks in the UV-Vis spectrum are quite intense.

Acidity of coordinated water molecules is in the order Fe(III) > Zn(II) > Mg(II). Ligand-binding rates are Mg(II) > Zn(II) > Fe(III).

Either EPR or Mössbauer spectroscopy.

The two central lines correspond to Fe\(^{3+}\). The two new ones show a larger quadrupole coupling and a higher isomer shift, characteristics consistent with high-spin Fe\(^{3+}\). Since the signals from Fe\(^{2+}\) and Fe\(^{3+}\) in the reduced form are well separated, there is no delocalization.

The change in structure suggests that the coupling of proton and electron transfer can also occur at the P-cluster by controlling protonation of the exchangeable ligands.

Co(I) and Co(III); Fe(II) or Zn(II)

Would indicate the presence of photosynthesis and consequently some life-form that is capable of photosynthesis.

EPR spectroscopy; use of isotopically labelled water molecules, for example H\(_2\)\(^{17}\)O, can be combined with Raman and IR spectroscopies.

**CHAPTER 27**

**Self-tests**

S27.1 By modifying R substituents (R\(^1\)–R\(^5\)) on the ligand backbone.

**Exercises**

27.1 Both have a preference for square planar geometry that seems to be necessary for the activity of Pt(II) anticancer drugs. Au(III) is also a soft Lewis acid, meaning that it has low preference for Cl\(^-\) and O-donor ligands. The major difference is that Au(III) is easily reduced under hypoxic conditions to Au(I), which prefers linear geometry as in [AuCl\(_2\)]\(^-\).

27.2 Copper slowly oxidises in air producing copper oxides. The epidermis is slightly acidic, meaning a small amount of the oxide can dissolve to produce Cu\(^2+\), which is water soluble and can pass through the skin.

27.3 B(OH\(_3\)), H\(_2\), CO, and OH\(^-\). In neutral or mildly acidic medium it would be protonated to produce hydrogenboranocarbonate. Hydrogenboranocarbonate can eliminate OH\(^-\) to produce [H\(_3\)BCO] adduct. [H\(_3\)BCO] is unstable when not under CO atmosphere and CO can be easily displaced by water molecules. The intermediate aquo adduct [H\(_3\)B(OH\(_3\))] rapidly decomposes to give H\(_2\)BOH and H\(_2\), H\(_2\)BOH reacts rapidly with another two water molecules to produce the final products B(OH\(_3\)) and two more equivalents of H\(_2\).

27.4 Choose a trace element (not CHNOPS); list what its important chemical properties are, including aqueous chemistry, redox chemistry; identify proteins in which such an element appears; discuss how the element’s chemical properties suit it for its task.

27.5 Gallium(III) can bind to transferrin and lactoferrin, and can even be incorporated into ferritin. These enzymes use nitrogen and oxygen donors to bind iron. Since Ga(III) also has a good affinity for the same donors, it can compete with Fe(III) for the binding sites.

27.6 In the strongly acidic environment (pH ~ 3) that abounds in organic acids, Bi(III) compounds form polymeric species and clusters that can form a protective layer (or coating) on the stomach.