

Chapter 21

PROPERTIES OF THE *4d* AND *5d* TRANSITION METALS

Exercises

- 21.1 (a) $2 [\text{Ag}(\text{CN})_2]^{-}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow 2 \text{Ag}(\text{s}) + [\text{Zn}(\text{CN})_4]^{2-}(\text{aq})$
(b) $2 \text{Au}(\text{s}) + 3 \text{Cl}_2(\text{g}) \rightarrow 2 \text{AuCl}_3(\text{s})$
- 21.3 For the earlier part of the *4d-5d* transition metals, the maximum oxidation number is the same as the group number (that is, the sum of the *4s* and *3d* electrons). Discussing the *5d* fluorides (see Table 17.6) the oxidation number seems to ‘plateau’ at seven. For example, osmium forms OsF_7 , even though with oxygen, osmium can have an oxidation state of eight. It can be argued that it is impossible to fit more than seven fluorine atoms around a *5d* metal ion, thus limiting the oxidation state to 7+.
- 21.5 (a) automobile engine lubricant; (b) antibacterial.
- 21.7 Osmium(VIII) oxide has a melting point of 40°C , in the range typical of covalent compounds and far below that expected for ionic compounds. In addition it is very soluble in low-polarity organic solvents – for example, OsO_4 is 500 times more soluble in tetrachloromethane than in water.
- 21.9 Ruthenium, rhodium, palladium, osmium, iridium, and platinum.
- 21.11 The *3d* transition metals tend to have lower oxidation states than those of the *4d* and *5d* series. It is oxide rather than fluoride that ‘brings out’ the highest oxidation state, for example, manganese has a 7+ oxidation state in the permanganate ion, MnO_4^- . The smaller *3d* ions cannot accommodate as many ligands surrounding them as the larger *4d* and *5d* metal ions.
- 21.13 For palladium, +2 and +3 are common while +2, +4, and +6 are common for platinum. Square planar is common for the lower oxidation states and octahedral geometry for the +6 state of platinum.

- 21.15 A quadruple bond can be formed as follows:
 End-on overlap of a pair of d_{x^2} orbitals to give a σ bond;
 diagonal overlap of a pair of d_{xz} orbitals to give one π bond and the
 overlap of a pair of d_{yz} orbitals to give the other π bond; and the side-to-
 side overlap of a pair of d_{xy} orbitals to give one δ bond.
- 21.17 PdF_3 does not contain palladium in the +3 oxidation state. Instead, it has
 the formulation of: $(\text{Pd}^{2+})[\text{PdF}_6]^{2-}$.

Beyond the Basics

- 21.19 $\text{Au}^+(aq) + e^- \rightarrow \text{Au}(s)$ $E^\circ = +1.68 \text{ V}$
 $\text{Au}(s) + 2 \text{CN}^-(aq) \rightarrow \text{Au}(\text{CN})_2^-(aq)$ $E^\circ = +0.60 \text{ V}$
 $\text{Au}^+(aq) + 2 \text{CN}^-(aq) \rightarrow \text{Au}(\text{CN})_2^-(aq)$ $E^\circ = +2.28 \text{ V}$
 $\Delta G^\circ = -nFE^\circ = -RT \ln K$

$$\ln K = \frac{nFE^\circ}{RT} = \frac{1 \times (9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}) \times (+2.28 \text{ V})}{8.31 \text{ V} \cdot \text{C} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}} = 88.8$$

$$K = 3.7 \times 10^{38}$$

- 21.21 The oxidation state is +7. This is expected because rhenium, like
 manganese, exhibits oxidation states as high as +7. No; hydride being a
 strong reducing agent, it should stabilize only low oxidation states.
- 21.23 No, because in all its “normal” compounds, it has a +1 oxidation state,
 which corresponds to a d^{10} electron configuration. The ion resembles
 thallium(I) most closely in terms of compound solubility—soluble fluoride
 but all other halides insoluble.
- 21.25 +5, the expected common oxidation state of niobium.
- 21.27 It is only the terminal bromide ions that are replaced, not the bridging
 atoms. The azide ion is acting as a pseudo-halide ion.