

Chapter 21

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

Exercises

- 21.2 (a) $\text{Os}(s) + 2 \text{O}_2(g) \rightarrow \text{OsO}_4(s)$
(b) $\text{ZrCl}_4(s) + 2 \text{Mg}(s) \rightarrow \text{Zr}(s) + 2 \text{MgCl}_2(s)$
- 21.4 Contrasting the fluorides of the *3d* transition metals (Table 17.5) and those of the *5d* transition metals (Table 17.6), the fluorides of the *3d* metals reach a maximum of the +6 oxidation state with chromium (and even that is only stable below -100°C) and after that the highest oxidation state declines to +4 for manganese and cobalt, +3 for iron and +2 for nickel and copper. For the *5d* fluorides, the oxidation states for the later metals are much higher, reaching a maximum of +7 with rhenium and osmium and only declining to +6 for iridium, +5 for gold, and +4 for palladium.
- 21.6 (a) Osmium(VIII) is used as a specific oxidizing agent in organic synthesis; (b) zirconium(IV) oxide is used as a gemstone and as a high-melting insulating material.
- 21.8 Copper, silver, and gold.
- 21.10 The charge transfer process can be represented as:
$$\text{Ag}^+\text{X}^- \rightarrow \text{Ag}^0\text{X}^0$$
where X represents the halide ion. As the halide ion is more readily oxidized, the absorption of light will be of lower energy—more and more in the visible part of the spectrum. As iodide is the easiest oxidized and chloride the least, this represents the order of visible color intensity.
- 21.12 Two. The copper(I) ion.
- 21.14 (a) A Keggin cluster is a large hetero-poly anion formed of clusters of molybdenum or tungsten oxo-anions. At the center of the cluster is a small oxo-anion such as phosphate or silicate (b) a heteropoly blue is formed when a phosphomolybdate cluster is partially reduced so that some

of the molybdenum(VI) ions are reduced to molybdenum(V). The resulting charge defects cause the blue color.

- 21.16 From the comparative melting points it can be inferred that the bonding in platinum(VI) fluoride is predominantly ionic while that in platinum(IV) fluoride is predominantly covalent.
- 21.18 Molybdenum may play a unique biochemical role for the following reasons: it has a stable, water-soluble, species at near-neutral pH making it transportable by biological fluids; it may possibly be transported into cells by the same mechanism as the sulfate ion (related by (n) and $(n+10)$); it has a wide range of readily-accessible oxidation states giving it redox roles; and the element is comparatively abundant in seawater, the medium in which life is believed to have originated.

Beyond the Basics

- 21.20 Fluorine tends to promote metals to their highest oxidation states, because it is a strong oxidizing agent, whereas iodide ion is a reducing agent; thus the most likely product with fluorine is WF_6 .
- 21.22 The potassium halides are all water-soluble while all of the silver halides are insoluble. Low-charge-density cations result in low lattice energies and such salts should be water soluble, as are the potassium salts. The insolubility of the silver salts suggests a high degree of covalency to the silver-halide bonding, enhancing the bonding and making hydration energetically less favorable.
- 21.24 Though thorium is an actinoid, the early actinoids behave much as pseudo-transition metals, particularly favoring oxidation states matching their analogous group number (see Chapter 9, Section 9.9). Thus thorium commonly exhibits a +4 oxidation state and would readily substitute for the other +4 ions of hafnium and zirconium.
- 21.26 In the complex shown, each iodide bridges three niobium atoms whereas those in Figure 21.8 only bridge pairs of niobium atoms. The molecular formula is $[Nb_6I_8]^{3+}$.

21.28 The Re_3Cl_9 structure involves a central triangle of rhenium atoms with bridging and terminal chlorine atoms in a polymeric structure. Addition of three more chloride ions keeps the rhenium triangle with its multiple bonding intact. The high stability of poly-metal cores of clusters is characteristic of the 4*d* and 5*d* metal ions.



