

Chapter 20

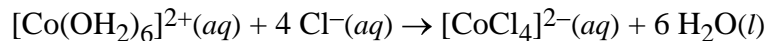
PROPERTIES OF THE 3*d* TRANSITION METALS

Exercises

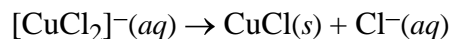
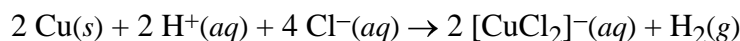
- 20.2 (a) $2 \text{VO}^{2+}(\text{aq}) + \text{Zn}(\text{s}) + 4 \text{H}^{+}(\text{aq}) \rightarrow 2 \text{V}^{3+}(\text{aq}) + \text{Zn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$
 $2 \text{V}^{3+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow 2 \text{V}^{2+}(\text{aq}) + \text{Zn}^{2+}(\text{aq})$
- (b) $2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l}) \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^{+}(\text{aq}) + 6 \text{e}^{-}$
 $\text{FeO}_4^{2-}(\text{aq}) + 8 \text{H}^{+}(\text{aq}) + 3 \text{e}^{-} \rightarrow \text{Fe}^{3+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$
 $2 \text{Cr}^{3+}(\text{aq}) + 2 \text{FeO}_4^{2-}(\text{aq}) + 2 \text{H}^{+}(\text{aq})$
 $\quad \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 2 \text{Fe}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- (c) $\text{Cu}(\text{OH})_2(\text{s}) \rightarrow \text{CuO}(\text{s}) + \text{H}_2\text{O}(\text{l})$
- (d) $2 \text{Cu}^{2+}(\text{aq}) + 4 \text{I}^{-}(\text{aq}) \rightarrow 2 \text{CuI}(\text{s}) + \text{I}_2(\text{aq})$
- (e) $2 \text{Au}(\text{s}) + 3 \text{Cl}_2(\text{g}) \rightarrow 2 \text{AuCl}_3(\text{s})$
- 20.4 (a) White pigment; (b) green pigment; (c) starting material for making other silver compounds (and as a laboratory reagent).
- 20.6 Chlorine is being reduced (from 0 to -1), and carbon is being oxidized (from 0 to $+2$).
- 20.8 Although aluminum is plentiful in the Earth's crust, it is usually found in such minerals as clays, from which extraction is very difficult. It is only from the rare bauxite ore that aluminum is commercially obtainable. Even then, high-cost electrolytic methods must be used for the extraction process. Iron can be obtained from the plentiful deposits of iron oxides by a low-cost coke reduction process.
- 20.10 The chemical equation is
$$\text{Ni}(\text{s}) + 4 \text{CO}(\text{g}) \rightarrow \text{Ni}(\text{CO})_4(\text{g})$$
Formation of this compound requires a net decrease of three moles of gas, resulting in a decrease in entropy. Hence the forward reaction must be enthalpy driven (that is, exothermic). The decomposition reaction is favored at higher temperatures. This is logical when the relationship $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ is considered. For the reverse reaction, both ΔH° and ΔS° are positive, thus as the temperature increases, $(-T\Delta S^{\circ})$ will become

increasing negative, to the point where the term exceeds ΔH° and the reverse reaction becomes spontaneous (negative ΔG°).

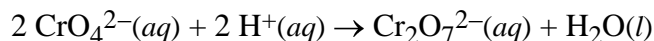
20.12 (a) Cobalt:



(b) Copper:



(c) Chromium:



20.14 A halide ion is an obvious choice because a large negative weak field ligand will favor a tetrahedral arrangement. Iodide would be the specific choice because it is the largest of the halides. Also, vanadium(II) is in a very low oxidation state for the metal. To stabilize it, a reducing anion is preferable—and iodide is strongly reducing.

20.16 The aqueous iron(III) ion hydrolyses in aqueous solution:



thus the yellow color of the hydroxy-species predominates unless acid is added to “drive” the equilibrium to the left to give the pale purple color of the hexaaquairon(III) ion.

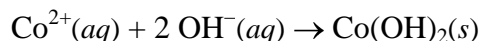
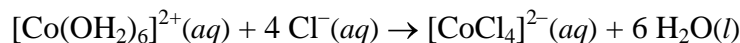
20.18 Oxygen. Iron(III) is a hard acid, while oxygen is a hard base (and sulfur is a soft base).

20.20 Chromium(VI) oxide should be acidic. It is the metal in the higher oxidation state (that is, with the more oxygens) that will exhibit the more acidic properties.

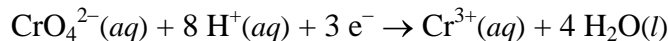
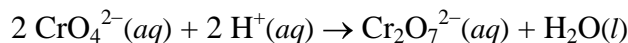
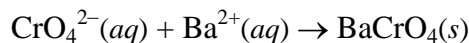
20.22 Fluoride ion; $[\text{CoF}_6]^{3-}$.

20.24 Three.

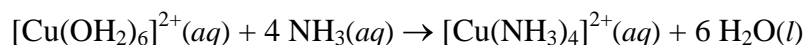
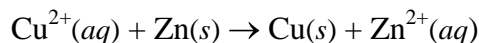
20.26 (a) Cobalt(II):



(b) Chromate:



(c) Copper(II):



20.28 (a) Copper; (b) iron; (c) iron and molybdenum; (d) cobalt.

Beyond the Basics



$$\Delta\text{H}^{\circ} = [(-602.9) - 4(-110.5)] \text{kJ}\cdot\text{mol}^{-1} = -160.9 \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta\text{S}^{\circ} = [(+410.6) - 4(+197.7) - (+29.9)] \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -410.1 \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$\begin{aligned} \Delta\text{G}^{\circ} &= \Delta\text{H}^{\circ} - \text{T}\Delta\text{S}^{\circ} = (-160.9 \text{kJ}\cdot\text{mol}^{-1}) - (298 \text{K})(-0.4101 \text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \\ &= -38.7 \text{kJ}\cdot\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \ln K &= -\Delta\text{G}^{\circ}/\text{RT} = -(-38.7 \times 10^3 \text{J}\cdot\text{mol}^{-1})/(8.31 \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{K}) \\ &= 15.6 \end{aligned}$$

$$K = 6.1 \times 10^6$$

When $K = 1$, $\Delta\text{G}^{\circ} = 0$.

$$\text{T} = \Delta\text{H}^{\circ}/\Delta\text{S}^{\circ} = (-160.9 \text{kJ}\cdot\text{mol}^{-1})/(-0.4101 \text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = 392 \text{K} = 119^{\circ}\text{C}$$

At room temperature the formation of the tetracarbonylnickel(0) is favored, but when warmed the nickel carbonyl complex decomposes again. This is the route used for nickel purification.

20.32 First we must calculate the two lattice energies:

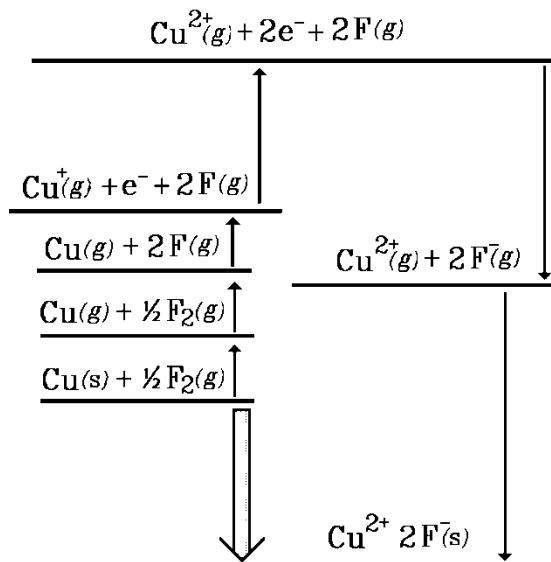
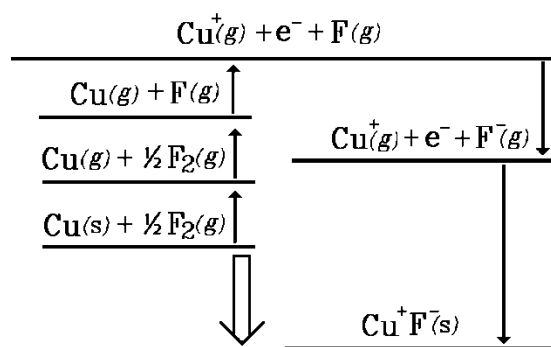
$$U_{\text{CuF}} = -\frac{(6.02 \times 10^{23} \text{ mol}^{-1}) \times 1.638 \times 1 \times 1 \times (1.602 \times 10^{-19} \text{ C})^2}{4 \times 3.142 \times (8.854 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1})(2.08 \times 10^{-10} \text{ m})} \left(1 - \frac{1}{8}\right)$$

$$= -956 \text{ kJ} \cdot \text{mol}^{-1}$$

$$U_{\text{CuF}_2} = -\frac{(6.02 \times 10^{23} \text{ mol}^{-1}) \times 2.408 \times 2 \times 1 \times (1.602 \times 10^{-19} \text{ C})^2}{4 \times 3.142 \times (8.854 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1})(2.04 \times 10^{-10} \text{ m})} \left(1 - \frac{1}{8}\right)$$

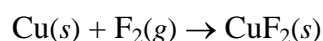
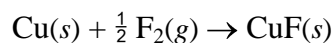
$$= -2868 \text{ kJ} \cdot \text{mol}^{-1}$$

Then we set up Born-Haber cycles:

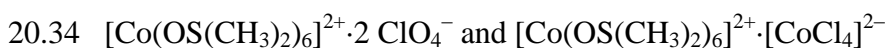


$$\begin{aligned}\Delta H_f^\circ(\text{CuF}(s)) &= [(+337) + \frac{1}{2}(155) + (752) + (-328) + (-956)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -118 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

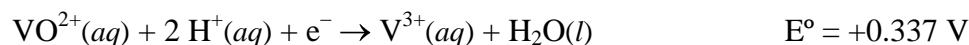
$$\begin{aligned}\Delta H_f^\circ(\text{CuF}_2(s)) &= \\ &[(+337) + (155) + (752) + (+1964) + 2(-328) + (-2868)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -316 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$



In each case, the entropy change will be negative, so the enthalpy decrease needs to be sufficient to overcome the entropy factor.



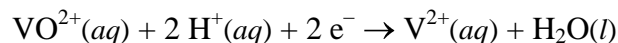
20.36 From the Appendix,



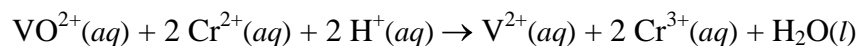
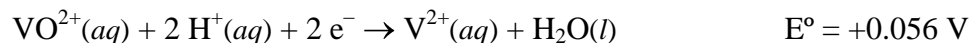
$$\Delta G^\circ = -1(F)(+0.337 \text{ V}) = -0.337 F$$



$$\Delta G^\circ = -1(F)(-0.225 \text{ V}) = +0.225 F$$



$$\Delta G^\circ = -0.112 F = -2 FE^\circ, \quad E^\circ = +0.056 \text{ V}$$



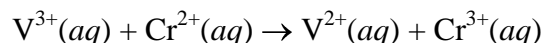
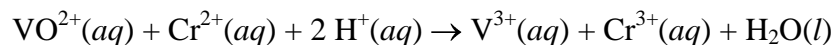
$$E^\circ = +0.480 \text{ V}$$

$$\Delta G^\circ = -nFE^\circ = -RT \ln K$$

$$\ln K = \frac{nFE^\circ}{RT} = \frac{1 \times (9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}) \times (+0.480 \text{ V})}{8.31 \text{ V} \cdot \text{C} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}} = 18.7$$

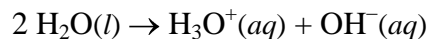
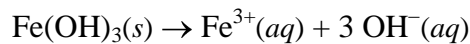
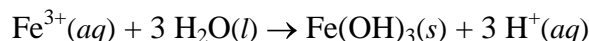
$$K = 1.3 \times 10^8$$

Probable two-step mechanism:



20.38

20.40 (a) The equations for K_w and K_{sp} can be combined to provide the required expression.



$$K = [\text{H}^+]^3/[\text{Fe}^{3+}]$$

$$K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 2.0 \times 10^{-39}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$K = \frac{K_w^3}{K_{sp}} = \frac{[\text{H}^+]^3[\text{OH}^-]^3}{[\text{Fe}^{3+}][\text{OH}^-]^3} = \frac{[\text{H}^+]^3}{[\text{Fe}^{3+}]} = 5.0 \times 10^{-4}$$

(b) Substituting:

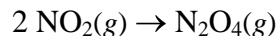
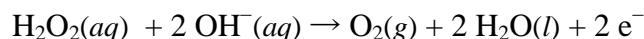
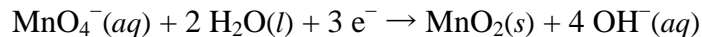
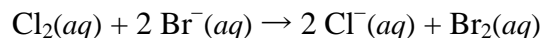
$$[\text{Fe}^{3+}] = (1.0 \times 10^{-6})^3 / (5.0 \times 10^{-4}) = 2.0 \times 10^{-15} \text{ mol}\cdot\text{L}^{-1}$$

$$\begin{aligned} \text{(c) Mol Fe}(\text{OH})_3 &= (2.0 \times 10^{-15} \text{ mol}\cdot\text{L}^{-1})(1 \times 10^6 \text{ L}) \\ &= 2 \times 10^{-9} \text{ mol} \end{aligned}$$

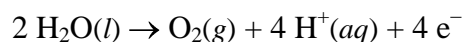
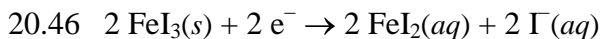
$$\text{Mass Fe}(\text{OH})_3 = (106.9 \text{ g}\cdot\text{mol}^{-1})(2 \times 10^{-9} \text{ mol}) = 2 \times 10^{-7} \text{ g}$$

Very little iron(III) hydroxide is lost!

20.42 [A] Manganese(II) nitrate; [B] manganese(IV) oxide; [C] nitrogen dioxide; [D] manganese(II) chloride; [E] dichlorine; [F] dibromine; [G] permanganate ion; [H] dioxygen; [I] dinitrogen tetraoxide.



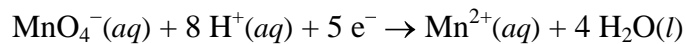
20.44 The crystal must contain some chromium(III) ions to provide the charge balance—in fact, it is easy to calculate that, of every 92 chromium ions, 76 must be chromium(II) and 16 chromium(III).



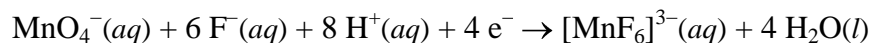
Net reaction:



20.48 Under normal acid conditions, manganese is reduced from +7 to +2 oxidation state:



Fluoride stabilizes high oxidation states, thus it would not be unreasonable to propose that reduction occurs only down to the +3 oxidation state:



This would require $(20 \text{ mL}) \times (5/4) = 25 \text{ mL}$ of titrant to oxidize the iron(II) ion.



20.52 NiCo_2O_4 contains Ni^{2+} and Co^{3+} . Cobalt is readily oxidized to the low-spin d6 configuration, making this formulation CFSE energetically favourable. Theoretical CoNi_2O_4 would require Ni^{3+} and Co^{2+} . Nickel is hard to oxidize to the 3+ state and there would not be the CFSE advantage of the other permutation (in fact the Co^{2+} would be oxidized by the Ni^{3+}).

20.54 (a) MnO : $[\text{Mn}] + [-2] = 0$, $\text{Mn} = +2$

Mn_3O_4 : $3[\text{Mn}] + 4[-2] = 0$, $\text{Mn} = +8/3$

Mn_2O_3 : $2[\text{Mn}] + 3[-2] = 0$, $\text{Mn} = +3$

MnO_2 : $[\text{Mn}] + 2[-2] = 0$, $\text{Mn} = +4$

Mn_2O_7 : $2[\text{Mn}] + 7[-2] = 0$, $\text{Mn} = +7$

(b) Mn_3O_4 is a mixed oxide containing $(\text{Mn}^{2+})(\text{Mn}^{3+})_2(\text{O}^{2-})_4$.

(c) MnO should be basic and Mn_2O_7 acidic. Low oxidation state metal oxides are basic, and high-oxidation-state metal oxides are acidic.

(d) MnO_2 is the analog of ClO_2 (Mn_2O_7 is the analog of Cl_2O_7 , but neither of these is a common oxide).

20.56 For the first reaction:

$$\begin{aligned} \Delta H &= [2\Delta H_f^\circ(\text{CO})] - [\Delta H_f^\circ(\text{CO}_2) + \Delta H_f^\circ(\text{CH}_4)] \\ &= [2 \times (-111)] - [(-394) + (-75)] \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

$$= +247 \text{ kJ}\cdot\text{mol}^{-1}$$

For the second reaction:

$$\begin{aligned}\Delta H &= [\Delta H_{\text{f}}^{\circ}(\text{CO})] - [\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}) + \Delta H_{\text{f}}^{\circ}(\text{CH}_4)] \\ &= [(-111)] - [(-242) + (-75)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= +206 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Both reaction steps are endothermic; thus they are driven by the entropy factor (increasing moles of gas).