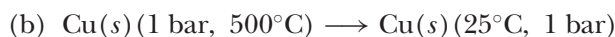


CHAPTER 23. Chemical Thermodynamics



Because ice is more ordered structurally than liquid water, ice has less positional disorder than liquid water. Thus, when compared at the same temperature and pressure, the entropy of solid water is less than the entropy of liquid water, and so $\Delta S_{\text{sys}} < 0$.



A decrease in temperature at fixed pressure decreases the energy and therefore decreases the thermal disorder of the $\text{Cu}(s)$. The decrease in thermal disorder means that the entropy decreases, and thus, $\Delta S_{\text{sys}} < 0$.



The reaction described by this equation involves the conversion of seven moles of reactants (three moles of which are gas) into two moles of solid, which corresponds to a large decrease in positional disorder; consequently $\Delta S_{\text{sys}} < 0$.

23-2. Sublimation means the direct conversion of a solid to a gas without passing through the liquid phase.



For the two-stage process

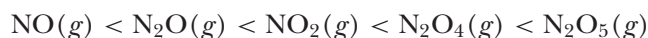


we have $\Delta S_{\text{sys}} = \Delta S_{\text{fus}} + \Delta S_{\text{vap}}$. But the initial and final states are the same as in (a) and the entropy is a state function; therefore,

$$\Delta S_{\text{sub}} = \Delta S_{\text{fus}} + \Delta S_{\text{vap}}$$

Further, because $\Delta S_{\text{fus}} > 0$ and $\Delta S_{\text{vap}} > 0$, $\Delta S_{\text{fus}} + \Delta S_{\text{vap}} > \Delta S_{\text{vap}}$. Thus, $\Delta S_{\text{sub}} > \Delta S_{\text{vap}}$.

23-3. The order is mainly based upon the number of atoms because the masses of the oxygen and nitrogen atoms are about the same; thus we have



Note that $\text{N}_2\text{O}(g)$ and $\text{NO}_2(g)$ both have three atoms per molecule, but $\text{N}_2\text{O}(g)$ has a lower molecular mass than $\text{NO}_2(g)$, and thus we predict that it has the lower entropy of the pair.

- 23-4. Because $\Delta H_{\text{rxn}}^{\circ} > 0$ and $\Delta S_{\text{rxn}}^{\circ} < 0$, the reaction is not spontaneous under any conditions. Plants use energy from the sun (photosynthesis) to drive the reaction and produce glucose. A nonspontaneous reaction will only form products upon the input from an external source of the energy needed to drive the reaction.
- 23-5. The concentrations of $\text{Ag}^+(aq)$ and $\text{Cl}^-(aq)$ before the addition of 5.0 mL of 0.10 M $\text{AgNO}_3(aq)$ are calculated from the K_{sp} expression

$$K_{\text{sp}} = 1.8 \times 10^{-10} \text{ M}^2 = [\text{Ag}^+] [\text{Cl}^-]$$

But $[\text{Ag}^+] = [\text{Cl}^-]$ and thus

$$[\text{Ag}^+] = [\text{Cl}^-] = \sqrt{1.8 \times 10^{-10} \text{ M}^2} = 1.3 \times 10^{-5} \text{ M}$$

The values of $[\text{Ag}^+]_0$ and $[\text{Cl}^-]_0$ immediately after the addition of 5.0 mL of 0.10 M $\text{AgNO}_3(aq)$ are

$$[\text{Ag}^+]_0 = \frac{(5.0 \text{ mL})(0.10 \text{ M}) + (100.0 \text{ mL})(1.3 \times 10^{-5} \text{ M})}{105.0 \text{ mL}} = 4.8 \times 10^{-3} \text{ M}$$

$$[\text{Cl}^-]_0 = \frac{(100.0 \text{ mL})(1.3 \times 10^{-5} \text{ M})}{105.0 \text{ mL}} = 1.2 \times 10^{-5} \text{ M}$$

Thus the value of Q_c is

$$Q_c = [\text{Ag}^+]_0 [\text{Cl}^-]_0 = (4.8 \times 10^{-3} \text{ M})(1.2 \times 10^{-5} \text{ M}) = 5.8 \times 10^{-8} \text{ M}^2$$

The value of ΔG_{rxn} is calculated using Equation 23.16.

$$\Delta G_{\text{rxn}} = RT \ln \frac{Q_c}{K_c} = (8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K}) \ln \left(\frac{5.8 \times 10^{-8} \text{ M}^2}{1.8 \times 10^{-10} \text{ M}^2} \right) = +14 \text{ kJ} \cdot \text{mol}^{-1}$$

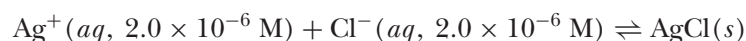
The positive value of ΔG_{rxn} is consistent with the common-ion effect that states that addition of a common ion to a solution decreases the solubility of an ionic solid.

- 23-6. $K = K_p / Q_p^{\circ} = 1.90 \text{ bar} / 1.00 \text{ bar} = 1.90$ (unitless)
- 23-7. The value of $\Delta G_{\text{rxn}}^{\circ}$ can be calculated from the value of K by using Equation 23.19.

$$\begin{aligned} \Delta G_{\text{rxn}}^{\circ} &= -RT \ln K = -(8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K}) \ln(1.54 \times 10^{88}) \\ &= -5.03 \times 10^5 \text{ J} \cdot \text{mol}^{-1} = -503 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The reaction as written is spontaneous at 25°C under standard conditions.

- 23-8. For the reaction described by the equation



we have

$$Q = \frac{Q_c}{Q_c^{\circ}} = \frac{1}{([\text{Ag}^+]_0/\text{M})([\text{Cl}^-]_0/\text{M})} = \frac{1}{(2.0 \times 10^{-6})^2} = 2.5 \times 10^{11}$$

and because $K_c = 1/K_{sp}$,

$$K = \frac{K_c}{K_c^\circ} = \frac{1}{1.80 \times 10^{-10}} = 5.6 \times 10^9$$

Thus, using Equation 23.22, we obtain for ΔG_{rxn}

$$\Delta G_{\text{rxn}} = RT \ln \frac{Q}{K} = (8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298 \text{ K}) \ln \left(\frac{2.5 \times 10^{11}}{5.6 \times 10^9} \right) = +9.41 \text{ kJ}\cdot\text{mol}^{-1}$$

The positive value of ΔG_{rxn} tells us that no $\text{AgCl}(s)$ can form under the given conditions of $[\text{Ag}^+]_0$ and $[\text{Cl}^-]_0$.

23-9. We have that

$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \Delta G_{\text{f}}^\circ[\text{CO}(g)] + \Delta G_{\text{f}}^\circ[\text{Cl}_2(g)] - \Delta G_{\text{f}}^\circ[\text{COCl}_2(g)] \\ &= (1)(-137.2 \text{ kJ}\cdot\text{mol}^{-1}) + (1)(0 \text{ kJ}\cdot\text{mol}^{-1}) - (1)(-205.9 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= 68.7 \text{ kJ}\cdot\text{mol}^{-1} = 6.87 \times 10^4 \text{ J}\cdot\text{mol}^{-1} \end{aligned}$$

Using Equation 23.19,

$$\ln K = -\frac{\Delta G_{\text{rxn}}^\circ}{RT} = -\frac{6.87 \times 10^4 \text{ J}\cdot\text{mol}^{-1}}{(8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298 \text{ K})} = -27.7$$

$$K = e^{-27.7} = 9.1 \times 10^{-13}$$

23-10. Start with (from Example 23-10)

$$\begin{aligned} \Delta G_{\text{rxn}} &= -29.4 \text{ kJ}\cdot\text{mol}^{-1} + (8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298 \text{ K}) \ln \frac{1}{P_{\text{CO}} P_{\text{H}_2}^2} \\ &= -2.94 \times 10^4 \text{ J}\cdot\text{mol}^{-1} + 2.48 \times 10^3 \text{ J}\cdot\text{mol}^{-1} \ln \frac{1}{P^3} \end{aligned}$$

where $P = P_{\text{CO}} = P_{\text{H}_2}$. We want $\Delta G_{\text{rxn}} < 0$, so we want

$$2.48 \times 10^3 \text{ J}\cdot\text{mol}^{-1} \ln \frac{1}{P^3} < 2.94 \times 10^4 \text{ J}\cdot\text{mol}^{-1}$$

or

$$\ln \frac{1}{P^3} < \frac{2.94 \times 10^4 \text{ J}\cdot\text{mol}^{-1}}{2.48 \times 10^3 \text{ J}\cdot\text{mol}^{-1}} = 11.85$$

Therefore,

$$\frac{1}{P^3} < e^{11.85} = 1.4 \times 10^5$$

$$\text{or } P > \left(\frac{1}{1.4 \times 10^5} \right)^{1/3} = 0.019 \text{ bar.}$$

23-11. Given that $\Delta H_{\text{rxn}}^\circ = +55.8 \text{ kJ}\cdot\text{mol}^{-1}$ for the reaction described by the equation



and that $K = 1.0 \times 10^{-14}$ at 25°C, we use Equation 23.28 to compute K at 37°C (human body temperature)

$$\ln \frac{K}{1.0 \times 10^{-14}} = \left(\frac{55.8 \times 10^3 \text{ J}\cdot\text{mol}^{-1}}{8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}} \right) \left[\frac{310 \text{ K} - 298 \text{ K}}{(310 \text{ K})(298 \text{ K})} \right] = 0.87$$

and

$$K = (1.0 \times 10^{-14}) e^{0.87} = 2.4 \times 10^{-14} \quad \text{at } 37^\circ\text{C}$$

Therefore,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = K^{1/2} = 1.55 \times 10^{-7} \text{ M}$$

and

$$\text{pH} = -\log([\text{H}_3\text{O}^+]/\text{M}) = 6.81$$

Because the reaction described by the equation is endothermic, we predict from Le Châtelier's principle that an increase in temperature will shift the reaction to the right, increasing the concentration of $\text{H}_3\text{O}^+(aq)$ and decreasing the pH. Thus, our results are consistent with Le Châtelier's principle.

CHAPTER 24. Oxidation-Reduction Reactions

- 24-1. (a) Applying Rule 7, we assign each oxygen atom an oxidation state of +2. From Rule 2 with x the oxidation state of each chromium atom, we have

$$2x + (7)(-2) = -2 \quad \text{or} \quad x = +6$$

Thus, the oxidation states of Cr = +6 and O = -2.

- (b) Applying Rule 4, we assign each fluorine atom an oxidation state of -1. From Rule 2 with x the oxidation state of the hydrogen atom, we have

$$x + (2)(-1) = -1 \quad \text{or} \quad x = +1$$

Thus, the oxidation states are H = +1 and F = -1.

- (c) Applying Rule 6, we assign each hydrogen atom an oxidation state of +1. From Rule 2 with x the oxidation state of the nitrogen atom, we have

$$x + (4)(+1) = +1 \quad \text{or} \quad x = -3$$

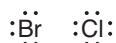
Thus, the oxidation states are H = +1 and N = -3.

- (d) Applying Rule 2 with x the oxidation state of each iodine atom, we have

$$3x = -1 \quad \text{or} \quad x = -1/3$$

Thus, the oxidation state is I = -1/3.

- 24-2. (a) The chlorine atom is more electronegative than the bromine atom, so, according to Rule 8b, we assign both electrons of the covalent bond to the chlorine atom



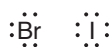
A neutral bromine atom has seven valence electrons and has been assigned six in the formula, so

$$\text{oxidation state of Br in BrCl} = 7 - 6 = +1$$

A neutral chlorine atom has seven valence electrons and has been assigned eight in the formula, so

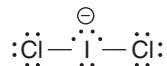
$$\text{oxidation state of Cl in BrCl} = 7 - 8 = -1$$

(b) In this case, the bromine atom is more electronegative than the iodine atom, so we have



Thus, we have an oxidation state of +1 for I and -1 for Br.

(c) The Lewis formula for ICl_2^- is



The chlorine atom is more electronegative than the iodine atom, so write



A neutral iodine atom has seven valence electrons and has been assigned six in the formula, so

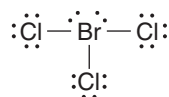
$$\text{oxidation state of I in } \text{ICl}_2^- = 7 - 6 = +1$$

A neutral chlorine atom has seven valence electrons and each has been assigned eight in the formula, so

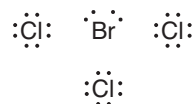
$$\text{oxidation state of Cl in } \text{ICl}_2^- = 7 - 8 = -1$$

Notice that the sum of the oxidation states of the atoms equals the overall charge, as it must for an ion.

(d) The Lewis formula of BrCl_3 is

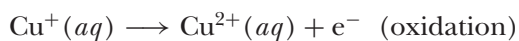


The chlorine atom is more electronegative than the bromine atom, so write



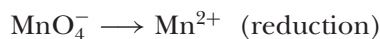
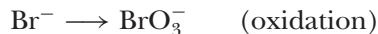
Thus, the oxidation state of Br is +3 and that of Cl is -1.

- 24-3. The oxidation state of each Mn atom in a Mn_2O_7 molecule is (Rule 7 and Rule 2) given by $2x + (7)(-2) = 0$, or $x = +7$. Therefore, there is a total of $2 \times 7 + 7 \times 6 = 56$ valence electrons in Mn_2O_7 . The Lewis formula is given in the text.
- 24-4. The oxidation state of iodine changes from -1 in an I^- ion to $-1/3$ in an I_3^- ion. Thus, I^- is the reducing agent and thus the species oxidized. The oxidation state of oxygen changes from 0 in an O_2 molecule to -2 in a OH^- ion. Thus, $\text{O}_2(aq)$ is the oxidizing agent and the species reduced.
- 24-5. The oxidation state of copper changes from +1 in a Cu^+ ion to *both* +2 in a Cu^{2+} ion and to 0 in $\text{Cu}(s)$. Thus, the half-reaction equations are

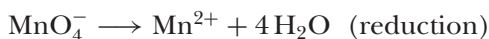


In the overall reaction, the Cu^+ ion is both oxidized (to Cu^{2+}) and reduced (to Cu). Such self oxidation-reduction reactions are called disproportionation reactions.

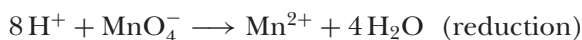
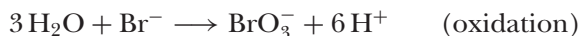
- 24-6. The $\text{H}^+(aq)$ over the reaction arrow indicates that we have an acidic solution. The unbalanced half-reaction equations are



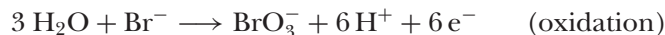
The two half-reactions are balanced with respect to the elements other than H and O. To balance each half reaction with respect to the oxygen atoms, we add three H_2O molecules to the left side of the oxidation half reaction and four H_2O molecules to the right side of the reduction half reaction.



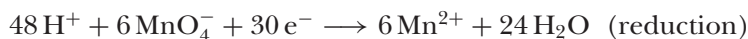
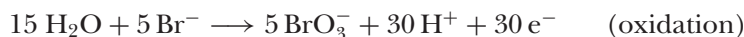
To balance each half reaction with respect to the hydrogen atoms, we add six H^+ ions to the right side of the oxidation half reaction and eight H^+ ions to the left side of the reduction half reaction.



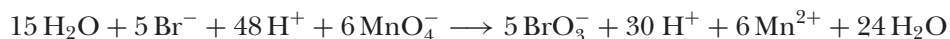
Next we balance the half-reactions with respect to charge by adding six electrons to the right side of the oxidation half reaction and five electrons to the left side of the reduction half reaction.



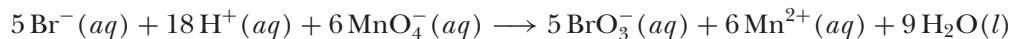
Multiplying the oxidation half-reaction equation by 5 and the reduction half-reaction equation by 6 yields



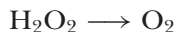
Adding the above two equations yields



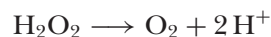
Cancelling like terms and indicating phases yield the final balanced equation.



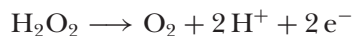
- 24-7. The oxidation state of oxygen in H_2O_2 is -1 . When H_2O_2 acts as a reducing agent, the oxidation state of oxygen increases. The oxidation state of oxygen in O_2 is zero, which is greater than -1 . Thus, we have



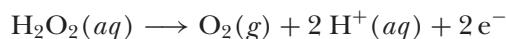
This equation is balanced with respect to all elements except hydrogen. Because we have an acidic aqueous solution, we balance the hydrogen atoms by adding 2H^+ to the right side of the equation



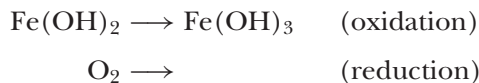
Finally, we add 2e^- to the right to balance the charge.



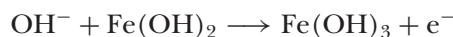
The balanced final half-reaction equation is



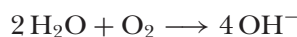
- 24-8. The oxidation state of the iron atom changes from +2 in $\text{Fe}(\text{OH})_2(s)$ to +3 in $\text{Fe}(\text{OH})_3(s)$ and thus iron is oxidized. Because iron is oxidized, the other reactant, $\text{O}_2(g)$, must be reduced. Thus we have



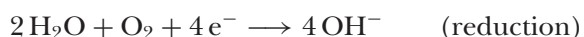
Because the oxidation half-reaction equation involves a metal hydroxide, we skip steps 3 and 4 and balance it directly by adding an OH^- to the left and an electron on the right



Because the solution is alkaline, the reduction half reaction is balanced according to steps 3 and 4 by adding $2 \text{H}_2\text{O}$ to the left side and 4OH^- to the right side



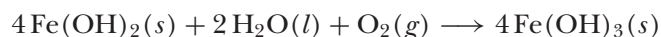
The charge is balanced by adding 4e^- to the left side



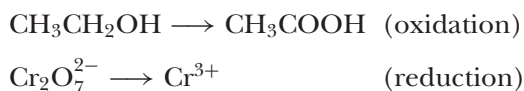
We can balance the electrons by multiplying the oxidation half-reaction equation by 4 and then adding the result to the reduction half-reaction equation to obtain



Cancellation of like terms and designation of phases yield



- 24-9. (a) The oxidation and reduction half-reaction equations are

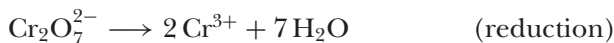
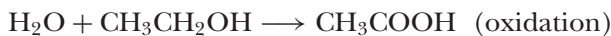


The balancing proceeds as follows:

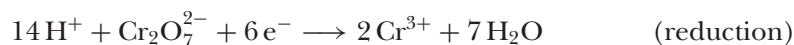
(i) elements other than O and H



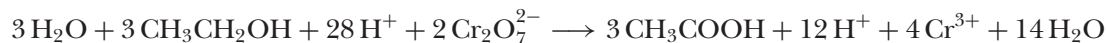
(ii) oxygen



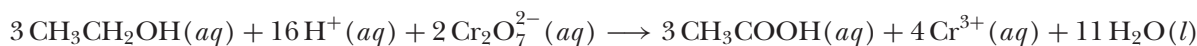
(iii) hydrogen and charge



(iv) multiplying the oxidation half-reaction equation by 3 and the reduction half-reaction equation by 2 (to balance the electrons) and adding the resulting equations yield



(v) cancellation of like terms and designating phases yields the final balanced equation



(b) The number of millimoles of $\text{Cr}_2\text{O}_7^{2-}(aq)$ consumed is given by

$$\text{millimoles of } \text{Cr}_2\text{O}_7^{2-} \text{ consumed} = (10.0 \text{ mL})(0.0100 \text{ M}) \left(\frac{10\%}{100\%} \right) = 0.0100 \text{ mmol}$$

The number of millimoles of $\text{CH}_3\text{CH}_2\text{OH}(aq)$ oxidized is

$$\text{millimoles of } \text{CH}_3\text{CH}_2\text{OH} = (0.0100 \text{ mmol } \text{Cr}_2\text{O}_7^{2-}) \left(\frac{3 \text{ mol } \text{CH}_3\text{CH}_2\text{OH}}{2 \text{ mol } \text{Cr}_2\text{O}_7^{2-}} \right) = 0.0150 \text{ mmol}$$

The number of milligrams of ethanol is

$$\text{mass of } \text{CH}_3\text{CH}_2\text{OH} = (0.0150 \times 10^{-3} \text{ mol})(46.07 \text{ g}\cdot\text{mol}^{-1}) = 6.9 \times 10^{-4} \text{ g} = 0.69 \text{ mg}$$

CHAPTER 25. Electrochemistry

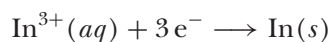
25-1. A current of 0.50 amperes corresponds to a current flow of 0.50 coulombs per second. The number of electrons that flow through a cross section in one minute is

$$\text{flow of electrons} = (0.50 \text{ C}\cdot\text{s}^{-1}) \left(\frac{1 \text{ electron}}{1.602 \times 10^{-19} \text{ C}} \right) \left(\frac{60 \text{ s}}{1 \text{ min}} \right) = 1.9 \times 10^{20} \text{ electrons}\cdot\text{min}^{-1}$$

25-2. Electrons are produced at the cadmium electrode

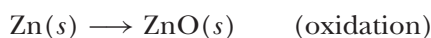


Electrons are consumed at the indium electrode.

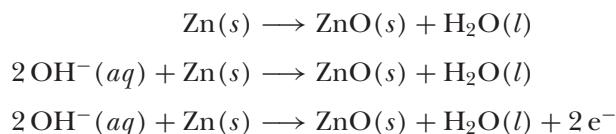


For the description of the electrochemical cell, see the text.

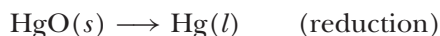
25-3. Oxidation takes place in a basic solution at the left electrode



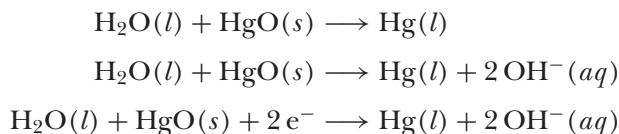
To balance this equation, we use the following steps:



Reduction takes place in a basic solution at the right electrode.



To balance this equation, we use the following steps:

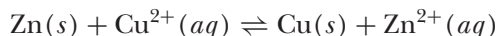


The overall equation for the reaction is the sum of the oxidation half-reaction equation and the reduction half-reaction equation.



25-4. See the text.

25-5. The cell will continue to discharge until $Q = K$, that is until chemical equilibrium is attained. When $Q = K$, $\ln(Q/K) = 1$, and the cell voltage $E = 0$, from Equation 25.7. The value of K for the equation that describes the cell reaction



is $K = 2 \times 10^{37}$ (Example 25-5). Because K is so large, the equilibrium lies far to the right and thus we express the equilibrium concentration of $\text{Cu}^{2+}(aq)$ and $\text{Zn}^{2+}(aq)$ as

$$\begin{aligned} [\text{Cu}^{2+}]_{\text{eq}} &= x \quad [\text{equilibrium concentration of unreacted } \text{Cu}^{2+}(aq)] \\ [\text{Zn}^{2+}]_{\text{eq}} &= 0.100 \text{ M} \quad (\text{original } [\text{Zn}^{2+}]) \\ &\quad + 0.100 \text{ M} \quad [\text{from complete conversion of } \text{Cu}^{2+}(aq) \text{ to } \text{Zn}^{2+}(aq)] \\ &\quad - x \quad [\text{concentration of unreacted } \text{Cu}^{2+}(aq)] \\ &= 0.200 \text{ M} - x \end{aligned}$$

Thus

$$\begin{aligned} K = 2 \times 10^{37} &= \frac{[\text{Zn}^{2+}]_{\text{eq}}}{[\text{Cu}^{2+}]_{\text{eq}}} = \frac{0.200 \text{ M} - x}{x} \approx \frac{0.200 \text{ M}}{x} \\ x &= [\text{Cu}^{2+}]_{\text{eq}} = 1 \times 10^{-38} \text{ M} \\ [\text{Zn}^{2+}]_{\text{eq}} &= 0.200 \text{ M} \end{aligned}$$

25-6. From Equation 25.13 and Example 25-6, we have

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \left(\frac{0.02570 \text{ V}}{\nu_e} \right) \ln Q \\ &= 1.10 \text{ V} - \left(\frac{0.02570 \text{ V}}{2} \right) \ln \frac{[\text{Zn}^{2+}]/\text{M}}{[\text{Cu}^{2+}]/\text{M}} \\ &= 1.10 \text{ V} - (0.01285) \ln \frac{1.00}{0.010} = 1.04 \text{ V} \end{aligned}$$

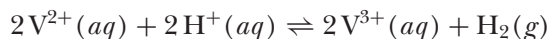
25-7. Reduction takes place at the cathode, so $E_{\text{red}}^{\circ} = 0.800 \text{ V}$. We use Equation 25.15

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ} = 0.800 \text{ V} + E_{\text{ox}}^{\circ} = 0.938 \text{ V}$$

From which we find that $E_{\text{ox}}^{\circ} = 0.138 \text{ V}$. Therefore, using Equation 25.16,

$$E_{\text{red}}^{\circ} = -E_{\text{ox}}^{\circ} = -0.138 \text{ V}$$

25-8. To liberate $\text{H}_2(g)$ from water, $\text{V}^{2+}(aq)$ must act as a reducing agent. Therefore, the equation for the reaction is



The value of E_{cell}° for this cell equation is calculated using the data from Table 25.3:

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}[\text{H}^+ | \text{H}_2] + E_{\text{ox}}^{\circ}[\text{V}^{2+} | \text{V}^{3+}] \\ &= 0 + (+0.255 \text{ V}) = +0.255 \text{ V} > 0 \end{aligned}$$

Because E_{cell}° is positive, $\text{V}^{2+}(\text{aq})$ is capable of liberating $\text{H}_2(\text{g})$ from an acidic aqueous solution when $Q = 1$ at 25.0°C .

25-9. We use Equation 25.12.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{RT}{\nu_e F} \right) \ln Q$$

where

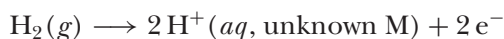
$$Q = \frac{[\text{K}^+]_{\text{inside}}/\text{M}}{[\text{K}^+]_{\text{outside}}/\text{M}} = 20$$

and $E_{\text{cell}}^{\circ} = 0 \text{ V}$ because the cell acts as a concentration cell. Thus

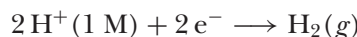
$$\begin{aligned} E_{\text{cell}} &= 0 \text{ V} - \left(\frac{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(310 \text{ K})}{(1)(96485 \text{ C} \cdot \text{mol}^{-1})} \right) \ln 20 = -(0.026714 \text{ J} \cdot \text{C}^{-1}) \ln 20 \\ &= -0.08 \text{ V} = -80 \text{ mV} \end{aligned}$$

The magnitude of E_{cell} is 80 mV to one significant figure.

25-10. The two half reactions can be written as



and



The overall equation is



The Nernst equation (Equation 25.12) reads

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{\nu_e F} \ln Q$$

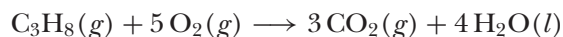
Using $E_{\text{cell}}^{\circ} = 0 \text{ V}$ for a concentration cell and Equation H3.9 from Appendix H, we have

$$\begin{aligned} E_{\text{cell}} &= 0 \text{ V} - \frac{2.303 RT}{2F} \log Q \\ &= -\frac{2.303 RT}{2F} \log \left(\frac{[\text{H}^+(\text{aq}, \text{unknown M})]/\text{M}}{[\text{H}^+(1 \text{ M})]/\text{M}} \right)^2 \\ &= -\frac{2.303 RT}{F} \log([\text{H}^+]/\text{M}) \\ &= \frac{2.303 RT}{F} \text{pH} \end{aligned}$$

or

$$\text{pH} = \left(\frac{F}{2.303 RT} \right) E_{\text{cell}}$$

25-11. The equation for the overall combustion reaction is



Each carbon atom in a C_3H_8 molecule has an oxidation state of $-8/3$ and the carbon atom in a CO_2 molecule has an oxidation state of $+4$. Thus, there is a transfer of 20 electrons

$[(3)(-8/3) \rightarrow (3)(4)]$. Using the data in Appendix D, ΔG_{rxn} for the stated equation is given by

$$\begin{aligned} \Delta G_{\text{rxn}}^{\circ} &= 3\Delta G_{\text{f}}^{\circ}[\text{CO}_2(g)] + 4\Delta G_{\text{f}}^{\circ}[\text{H}_2\text{O}(l)] \\ &\quad - \Delta G_{\text{f}}^{\circ}[\text{C}_3\text{H}_8(g)] - 5\Delta G_{\text{f}}^{\circ}[\text{O}_2(g)] \\ &= (3)(-394.4 \text{ kJ}\cdot\text{mol}^{-1}) + (4)(-237.1 \text{ kJ}\cdot\text{mol}^{-1}) - (-23.4 \text{ kJ}\cdot\text{mol}^{-1}) - 0 \text{ kJ}\cdot\text{mol}^{-1} \\ &= -2108.2 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Now we use the equation $\Delta G_{\text{rxn}}^{\circ} = -\nu_e F E_{\text{cell}}^{\circ}$ to write

$$E_{\text{cell}}^{\circ} = \frac{-\Delta G_{\text{rxn}}^{\circ}}{\nu_e F} = \frac{2108.2 \times 10^3 \text{ J}\cdot\text{mol}^{-1}}{(20)(96\,485 \text{ C}\cdot\text{mol}^{-1})} = 1.093 \text{ V}$$

25-12. The equation for the reaction at the anode says that four moles of electrons are required to produce one mole of $\text{O}_2(g)$. Therefore,

$$\text{moles O}_2(g) \text{ produced} = \left(\frac{2160 \text{ C}}{96\,485 \text{ C}\cdot\text{mol}^{-1}} \right) \left(\frac{1 \text{ mol O}_2}{4 \text{ mol e}^-} \right) = 5.60 \times 10^{-3} \text{ mol}$$

The volume of $\text{O}_2(g)$ produced at 1.0 bar and 0°C is given by

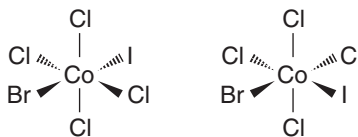
$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(5.60 \times 10^{-3} \text{ mol})(0.083145 \text{ L}\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(273 \text{ K})}{1.0 \text{ bar}} \\ &= 0.13 \text{ L} \end{aligned}$$

CHAPTER 26. The Chemistry of the Transition Metals

- 26-1. For a M(III) ion to be a d^6 ion, the corresponding M(II) ion must be a d^7 ion. The M(II) d^7 ions are Co(II), Rh(II), and Ir(II), and so the M(III) d^6 ions are Co(III), Rh(III), and Ir(III).
- 26-2. (a) The $[\text{Fe}(\text{CN})_6]^{3-}$ complex anion contains six CN^- ligands and thus, if we let x equal the oxidation state of the iron ion, we have $x + 6(-1) = -3$ and $x = +3$.
(b) The $[\text{PtCl}_6]^{2-}$ complex anion contains six Cl^- ligands; thus, the oxidation state, x , of the platinum ion is given by $x + (6)(-1) = -2$ and $x = +4$.
(c) The $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$ complex cation contains three neutral NH_3 ligands; and three Cl^- ligands; thus, the oxidation state, x , of the platinum ion is given by $x + 3(0) + 3(-1) = +1$ and $x = +4$.
- 26-3. The compound $[\text{Ag}(\text{NH}_3)_2]_3[\text{Fe}(\text{CN})_6]$ contains both a complex cation and a complex anion. The oxidation state of a silver atom in compounds is always +1, and because NH_3 is a neutral ligand, the overall oxidation state of the cation must be +1, or $[\text{Ag}(\text{NH}_3)_2]^+$. Therefore, the charge on the anion is -3 and the complex anion is $[\text{Fe}(\text{CN})_6]^{3-}$. The oxidation state, x , of the iron ion in the anion is given by $x + (6)(-1) = -3$, or $x = +3$. Thus, the salt is named diamminesilver(I) hexacyanoferrate(III), where we use the name ferrate for the iron in the anion according to Rule 5 and the entry in Table 26.10.
- 26-4. The complex hexaaquanickel(II) contains a nickel ion in the +2 oxidation state as indicated by the Roman numeral (II) and six (hexa means six) neutral H_2O ligands; thus, the formula of the complex cation is $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.
The complex anion diaquatetrabromochromate(III) contains a chromium ion in the +3 oxidation state, two neutral water ligands, and four bromide ions (Br^-). The net charge on the complex anion is $3 + 2(0) + 4(-1) = -1$. Thus, the formula of the complex anion is $[\text{Cr}(\text{H}_2\text{O})_2\text{Br}_4]^-$. It requires two -1 anions to balance the $+2$ cation; therefore, the formula of the compound is $[\text{Ni}(\text{H}_2\text{O})_6][\text{Cr}(\text{H}_2\text{O})_2\text{Br}_4]_2$.
- 26-5. (a) The compound $\text{K}_2[\text{Fe}(\text{EDTA})]$ contains the complex anion $[\text{Fe}(\text{EDTA})]^{2-}$. The charge on the EDTA ligand is -4 and thus, the oxidation state of the iron ion, x , is given by $x + (1)(-4) = -2$ or $x = +2$. The name of the compound is potassium ethylenediaminetetraacetatoferrate(II).
(b) The compound $\text{Na}[\text{Co}(\text{C}_2\text{O}_4)_2(\text{en})]$ contains the complex anion $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{en})]^-$. The charge on an oxalate ion is -2 and an ethylenediamine molecule is neutral. Thus, the oxidation state, x , of the cobalt ion is given by $x + 2(-2) + 1(0) = -1$, or $x = +3$. The name of

the compound is sodium ethylenediaminebis(oxalato)cobaltate(III), where we use the prefix bis because oxalate is a polydentate ligand (Rule 7).

- 26-6. The complex anion has six ligands and is octahedral. The two possible geometric isomers are one with the Br^- and I^- *trans* to each other and one with the Br^- and I^- *cis* to each other:



Any other placement of the six ligands gives a structure that can be rotated such that it will superimpose on one of these two structures and thus is not a separate isomer.

- 26-7. No. The mirror image of each one is superimposable on itself.
- 26-8. The ground-state d -electron configuration for V(III), a d^2 ion, is $t_{2g}^2 e_g^0$.
- 26-9. The d -electron configurations that can give rise to high-spin and low-spin complexes are d^4 , d^5 , d^6 , and d^7 ; Cr(III) is a d^3 ion; Mn(II) is a d^5 ion, and Cu(III) is a d^8 ion. Thus, of the three cases, only Mn(II) can form high-spin and low-spin complexes.
- 26-10. (a) The complex anion $[\text{Fe}(\text{CN})_6]^{3-}$ contains iron in the Fe(III) oxidation state; Fe(III) is a d^5 ion and CN^- produces a large Δ_0 value. Thus, we predict a low-spin d -electron configuration of $t_{2g}^5 e_g^0$. The complex anion has one unpaired electron per formula unit and so is paramagnetic.
- (b) The complex anion $[\text{Co}(\text{NO}_2)_6]^{3-}$ contains cobalt in the Co(III) oxidation state; Co(III) is a d^6 ion and NO_2^- produces a large Δ_0 value. Thus, we predict a low-spin d -electron configuration of $t_{2g}^6 e_g^0$. The complex anion has no unpaired electrons and so is diamagnetic.