CHAPTER 21
CHEMISTRY OF THE MAIN-GROUP ELEMENTS I:
GROUPS 1, 2, 13, AND 14

PRACTICE EXAMPLES

1A (E) From Figure 21-2, the route from sodium chloride to sodium nitrate begins with electrolysis of NaCl(aq) to form NaOH(aq).

\[ 2 \text{NaCl(aq)} + 2 \text{H}_2\text{O(l)} \xrightarrow{\text{electrolysis}} 2 \text{NaOH(aq)} + \text{H}_2(g) + \text{Cl}_2(g) \] followed by addition of NO\(_2\) (g) to NaOH(aq). 2 NaOH(aq) + 3 NO\(_2\) (g) → 2 NaNO\(_3\) (aq) + NO(g) + H\(_2\)O(l)

1B (E) From Figure 21-2, we see that the route from sodium chloride to sodium thiosulfate begins with the electrolysis of NaCl(aq) to produce NaOH(aq),

\[ 2 \text{NaCl(aq)} + 2 \text{H}_2\text{O(l)} \xrightarrow{\text{electrolysis}} 2 \text{NaOH(aq)} + \text{H}_2(g) + \text{Cl}_2(g) \]

and continues through the reaction of SO\(_2\) (g) with the NaOH(aq) in an acid-base reaction [SO\(_2\) (g) is an acid anhydride] to produce

Na\(_2\)SO\(_3\) (aq): 2 NaOH(aq) + SO\(_2\) (g) → Na\(_2\)SO\(_3\) (aq) + H\(_2\)O(l) and (3) concludes with the addition of S to the boiling solution: Na\(_2\)SO\(_3\) (aq) + S(s) \xrightarrow{\text{boil}} Na\(_2\)S\(_2\)O\(_3\) (aq).

2A (M) The first reaction indicates that 0.1 mol of NaNO\(_2\) reacts with 0.3 mol of Na to yield 0.2 mol of compound X and 0.05 mol of N\(_2\). Since this reaction liberates nitrogen gas, it is very likely that compound X is an oxide of sodium. The two possibilities include Na\(_2\)O and Na\(_2\)O\(_2\). Na\(_2\)O\(_2\) will not react with oxygen, but Na\(_2\)O will. Therefore, compound X is most likely Na\(_2\)O and compound Y is Na\(_2\)O\(_2\). The balanced chemical equations for two processes are:

\[ \text{NaNO}_2(s) + 3\text{Na(s)} \rightarrow 2\text{Na}_2\text{O(s)} + \frac{1}{2}\text{N}_2(g) \]

\[ \text{Na}_2\text{O(s)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Na}_2\text{O}_2(s) \]

2B (M) Since compound X is used in plaster of Paris it must contain calcium. Calcium reacts with carbon to form calcium carbide, according to the following chemical equation:

Ca(s)+2C(s) \rightarrow CaC\(_2\) (s)

Furthermore, compound X or calcium carbide reacts with nitrogen gas to form compound Y or calcium cyanamide:

CaC\(_2\) (s)+N\(_2\) (g) \rightarrow CaCN\(_2\) (s)+C(s)

CN\(_2^2^-\) anion is isoelectronic with CO\(_2\) and it therefore contains 16 electrons. The structure of this anion is:

\[ \text{N} \cdash \text{C} \cdash \text{N} \]
3A (M) The first two reactions, are those from Example 21-3, used to produce \( \text{B}_2\text{O}_3 \).

\[
\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}(s) + \text{H}_2\text{SO}_4(l) \rightarrow 4\text{B(OH)}_3(s) + \text{Na}_2\text{SO}_4(s) + 5\text{H}_2\text{O}(l)
\]

\[
2\text{B(OH)}_3(s) \xrightarrow{\Delta} \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g)
\]

The next reaction is conversion to \( \text{BCl}_3 \) with heat, carbon, and chlorine.

\[
2\text{B}_2\text{O}_3(s) + 3\text{C}(s) + 6\text{Cl}_2(g) \xrightarrow{\Delta} 4\text{BCl}_3(g) + 3\text{CO}_2(g)
\]

\( \text{LiAlH}_4 \) is used as a reducing agent to produce diborane.

\[
4\text{BCl}_3(g) + 3\text{LiAlH}_4(s) \rightarrow 2\text{B}_2\text{H}_6(g) + 3\text{LiCl}(s) + 3\text{AlCl}_3(s)
\]

3B (M) \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow 4\text{B(OH)}_3(s) + \text{Na}_2\text{SO}_4(aq) + 5\text{H}_2\text{O}(l) \)

\[
2\text{B(OH)}_3(s) \xrightarrow{\Delta} \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(l)
\]

\[
\text{B}_2\text{O}_3(s) + 3\text{CaF}_2(s) + 3\text{H}_2\text{SO}_4(l) \xrightarrow{\Delta} 2\text{BF}_3(g) + 3\text{CaSO}_4(s) + 3\text{H}_2\text{O}(g)
\]

**INTEGRATIVE EXAMPLE**

A (M) \( \text{NaCN} \) and \( \text{Al(NO}_3)_3 \) dissociate in water according to the following equations:

\[
\text{NaCN}(aq) \rightarrow \text{Na}^+(aq) + \text{CN}^-(aq)
\]

\[
\text{Al(NO}_3)_3(aq) \rightarrow \text{Al}^{3+}(aq) + 3\text{NO}_3^-(aq)
\]

\( \text{NaCN} \) is a salt of strong base (\( \text{NaOH} \)) and weak acid (\( \text{HCN} \)) and its solution is therefore basic.

We proceed by first determining the \( [\text{OH}^-] \) concentration in a solution which is 1.0M in \( \text{NaCN} \):

\[
\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^- \\
1.0 \quad / \quad / \\
1.0-x \quad x \quad x
\]

\[
K_b = \frac{K_w}{K_a(\text{HCN})} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}
\]

\[
K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{x \times x}{1.0 - x} = \frac{x^2}{1.0 - x} = 1.6 \times 10^{-5}
\]

Assume, \( x \ll 1 \) and \( 1.0-x \approx 1.0 \)

\[
x^2 = 1.6 \times 10^{-5} \Rightarrow x = \sqrt{1.6 \times 10^{-5}} = 4.0 \times 10^{-3}
\]

\( [\text{OH}^-] = 4.0 \times 10^{-3} \)

On mixing, \( [\text{OH}^-] = 2.0 \times 10^{-3} \text{ M and } [\text{Al}^{3+}] = 0.50 \text{ M. The precipitation will occur according to the following equation:} \)

\[
\text{Al}^{3+}(aq) + 3\text{OH}^-(aq) \rightleftharpoons \text{Al(OH)}_3(s)
\]

The product \( [\text{Al}^{3+}][\text{OH}^-]^3 = 0.50 \times (2.0 \times 10^{-3})^3 = 4.0 \times 10^{-9} \) is much greater than \( K_{SP} \) for \( \text{Al(OH)}_3 \) \( (1.3 \times 10^{-33}) \) and therefore precipitation will occur.
When \( \text{BeCl}_2 \cdot 4\text{H}_2\text{O} \) is heated, it decomposes to \( \text{Be(OH)}_2\) (s), \( \text{H}_2\text{O}(g) \), and \( \text{HCl}(g) \), as discussed in Section 21-3. \( \text{BeCl}_2 \cdot 4\text{H}_2\text{O} \) comprises \([\text{Be(H}_2\text{O})_4]^{2+}\) and \( \text{Cl}^- \) ions. Because of the high polarizing power of \( \text{Be}^{2+} \), it is difficult to remove the coordinated water molecules by heating the solid and the acidity of the coordinated \( \text{H}_2\text{O} \) molecules is enhanced. When \( \text{BeCl}_2 \cdot 4\text{H}_2\text{O} \) is dissolved in water, \([\text{Be(H}_2\text{O})_4]^{2+}\) ions react with water, and \([\text{Be(H}_2\text{O})_3(\text{OH})]^+\) and \( \text{H}_3\text{O}^+ \) ions are produced. Hence, a solution of \( \text{BeCl}_2 \cdot 4\text{H}_2\text{O} \) is expected to be acidic.

When \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \) is heated, \( \text{CaCl}_2\) (s) and \( \text{H}_2\text{O}(g) \) are produced. Because the charge density and polarizing power of \( \text{Ca}^{2+} \) is much less than that of \( \text{Be}^{2+} \), it is much easier to drive off the coordinated water molecules by heating the solid. When \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \) is dissolved in water, \( \text{Ca}^{2+}(\text{aq}) \) and \( \text{Cl}^-(\text{aq}) \) are produced. However, the charge density of the \( \text{Ca}^{2+} \) ion is too low to affect the acidity of water molecules in the hydration sphere of the \( \text{Ca}^{2+} \) ion. Hence, a solution of \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \) has a neutral pH.

**EXERCISES**

**Group 1: The Alkali Metals**

1. (E) (a) \( 2\text{Cs}(s) + \text{Cl}_2(g) \rightarrow 2\text{CsCl}(s) \)
   (b) \( 2\text{Na}(s) + \text{O}_2(g) \rightarrow \text{Na}_2\text{O}_2(s) \)
   (c) \( \text{Li}_2\text{CO}_3(s) \stackrel{\Delta}{\rightarrow} \text{Li}_2\text{O}(s) + \text{CO}_2(g) \)
   (d) \( \text{Na}_2\text{SO}_4(s) + 4\text{C}(s) \rightarrow \text{Na}_2\text{S}(s) + 4\text{CO}(g) \)
   (e) \( \text{K}(s) + \text{O}_2(g) \rightarrow \text{KO}_2(s) \)

2. (a) \( 2\text{Rb}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{RbOH(aq)} + \text{H}_2(g) \)
   (b) \( 2\text{KHCO}_3(s) \stackrel{\Delta}{\rightarrow} \text{K}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O(l)} + \text{CO}_2(g) \)
   (c) \( 2\text{Li}(s) + \text{O}_2(g) \rightarrow \text{Li}_2\text{O}_2(s) \)
   (d) \( 2\text{KCl}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{K}_2\text{SO}_4(aq) + 2\text{HCl}(g) \)
   (e) \( \text{LiH}(s) + \text{H}_2\text{O}(l) \rightarrow \text{LiOH(aq)} + \text{H}_2(g) \)

3. (E) Both \( \text{LiCl} \) and \( \text{KCl} \) are soluble in water, but \( \text{Li}_3\text{PO}_4 \) is not very soluble. Hence the addition of \( \text{K}_3\text{PO}_4(\text{aq}) \) to a solution of the white solid will produce a precipitate if the white solid is \( \text{LiCl} \), but no precipitate if the white solid is \( \text{KCl} \). The best method is a flame test; lithium gives a red color to a flame, while the potassium flame test is violet.
4. **(E)** When heated, \( \text{Li}_2\text{CO}_3 \) decomposes to \( \text{CO}_2(g) \) and \( \text{Li}_2\text{O}(l) \). \( \text{K}_2\text{CO}_3(s) \) simply melts when heated. The evolution of \( \text{CO}_2(g) \) bubbles should be sufficient indication of the difference in behavior. The flame test affords a violet flame if \( \text{K}^+ \) is present, and a red flame if \( \text{Li}^+ \) is present.

5. **(M)** First we note that sodium carbonate ionizes virtually completely when dissolved in \( \text{H}_2\text{O} \) and thus is described as highly soluble in water. This is made evident by the fact that there is no \( K_{sp} \) value for \( \text{Na}_2\text{CO}_3 \). By contrast, the existence of \( K_{sp} \) values for \( \text{MgCO}_3 \) and \( \text{Li}_2\text{CO}_3 \) shows that these compounds have lower solubilities in water than \( \text{Na}_2\text{CO}_3 \). To decide whether \( \text{MgCO}_3 \) is more or less soluble than \( \text{Li}_2\text{CO}_3 \), we must calculate the molar solubility for each salt and then compare the two values. Clearly, the salt that has the larger molar solubility will be more soluble in water. The molar solubilities can be found using the respective \( K_{sp} \) expressions for the two salts.

\[
\begin{align*}
1. & \quad \text{MgCO}_3 \xrightarrow{K_{sp} = 3.5 \times 10^{-8}} \text{Mg}^{2+}(aq) + \text{CO}_3^{2-}(aq) \\
& \text{Let } s = \text{molar solubility of MgCO}_3 \text{ excess } - s \\
& s^2 = 3.5 \times 10^{-8} \\
& s = 1.9 \times 10^{-4} \text{ M}
\end{align*}
\]

\[
\begin{align*}
2. & \quad \text{Li}_2\text{CO}_3 \xrightarrow{K_{sp} = 2.5 \times 10^{-2}} 2 \text{Li}^+(aq) + \text{CO}_3^{2-}(aq) \\
& \text{Let } s = \text{molar solubility of Li}_2\text{CO}_3 \text{ excess } - s \\
& (2s)^2 \times (s) = 2.5 \times 10^{-8} \\
& 4s^3 = 2.5 \times 10^{-8} \\
& s = \sqrt[3]{\frac{2.5 \times 10^{-8}}{4}} = 0.18 \text{ M}
\end{align*}
\]

We can conclude that \( \text{Li}_2\text{CO}_3 \) is more soluble than \( \text{MgCO}_3 \). Thus, the expected order of increasing solubility in water is: \( \text{MgCO}_3 < \text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 \).

6. **(M)** We know sodium metal was produced at the cathode from the reduction of sodium ion, \( \text{Na}^+ \). Thus, hydroxide must have been involved in oxidation at the anode. The hydrogen in hydroxide ion already is in its highest oxidation state and thus cannot be oxidized. This leaves oxidation of the hydroxide ion to elemental oxygen as the remaining reaction.

\[
\begin{align*}
\text{Cathode, reduction} : & \quad \{\text{Na}^+ + e^- \rightarrow \text{Na}(l)\} \times 4 \\
\text{Anode, oxidation} : & \quad 4\text{OH}^- \rightarrow \text{O}_2(g) + 2\text{H}_2\text{O}(g) + 4e^- \\
\text{Net} : & \quad 4\text{Na}^+ + 4\text{OH}^- \rightarrow 4\text{Na}(l) + \text{O}_2(g) + 2\text{H}_2\text{O}(g)
\end{align*}
\]

7. **(M)** \( \text{H}_2(g) \) and \( \text{Cl}_2(g) \) are produced during the electrolysis of \( \text{NaCl}(aq) \).

The electrode reactions are:

\[
\begin{align*}
\text{Anode, oxidation} : & \quad 2\text{Cl}^-(aq) \rightarrow \text{Cl}_2(g) + 2e^- \\
\text{Cathode, reduction} : & \quad 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)
\end{align*}
\]

We can compute the amount of \( \text{OH}^- \) produced at the cathode.
mol OH\(^{-}\) = 2.50 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{0.810 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^{-}}{96,500 \text{ C}} \times \frac{2 \text{ mol OH}^{-}}{2 \text{ mol e}^{-}} = 1.26 \times 10^{-3} \text{ mol OH}^{-}

Then we compute the [OH\(^{-}\)] and, from that, the pH of the solution.

\[
[\text{OH}^{-}] = \frac{1.26 \times 10^{-3} \text{ mol OH}^{-}}{0.872 \text{ L soln}} = 1.45 \times 10^{-3} \text{ M}
\]

pOH = \log(1.45 \times 10^{-3}) = 2.839

pH = 14.000 - 2.839 = 11.161

(b) As long as NaCl is in excess and the volume of the solution is nearly constant, the solution pH only depends on the number of electrons transferred.

8. (M) (a) total energy = 3.0 V \times 0.50 \text{ A h} \times \frac{3600 \text{ s}}{1 \text{ hr}} \times \frac{1 \text{ C/s}}{1 \text{ A}} \times \frac{1 \text{ J}}{1 \text{ V \cdot C}} = 5.4 \times 10^{3} \text{ J}

We obtained the first conversion factor for time as follows.

\[
5.0 \mu\text{W} \times \frac{1 \times 10^{-6} \text{ W}}{1 \mu\text{W}} \times \frac{1 \text{ J/s}}{1 \text{ W}} = \frac{5.0 \times 10^{-6} \text{ J}}{1 \text{ s}}
\]

\[
time = \frac{5.4 \times 10^{3} \text{ J}}{5 \times 10^{-5} \text{ J}} = 1.1 \times 10^{9} \text{ s} \times \frac{1 \text{ hr}}{3600 \text{ s}} \times \frac{1 \text{ day}}{24 \text{ hr}} \times \frac{1 \text{ y}}{365 \text{ days}} = 34 \text{ y}
\]

(b) The capacity of the battery is determined by the mass of Li present.

\[
\text{mass Li} = 0.50 \text{ A h} \times \frac{1 \text{ C/s}}{1 \text{ A}} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ mol e}^{-}}{96485 \text{ C}} \times \frac{1 \text{ mol Li}}{1 \text{ mol e}^{-}} \times \frac{6.941 \text{ g Li}}{1 \text{ mol Li}} = 0.13 \text{ g Li}
\]

9. (M) (a) We first compute the mass of NaHCO\(_{3}\) that should be produced from 1.00 ton NaCl, assuming that all of the Na in the NaCl ends up in the NaHCO\(_{3}\). We use the unit, ton-mole, to simplify the calculations.

\[
\text{mass NaHCO}_3 = 1.00 \text{ ton NaCl} \times \frac{1 \text{ ton-mol NaCl}}{58.4 \text{ ton NaCl}} \times \frac{1 \text{ ton-mol Na}}{1 \text{ ton-mol NaCl}} \times \frac{1 \text{ mol NaHCO}_3}{1 \text{ mol Na}} \times \frac{84.0 \text{ ton NaHCO}_3}{1 \text{ ton mol NaHCO}_3} = 1.44 \text{ ton NaHCO}_3
\]

\[
\% \text{ yield} = \frac{1.03 \text{ ton NaHCO}_3 \text{ produced}}{1.44 \text{ ton NaHCO}_3 \text{ expected}} \times 100\% = 71.5\% \text{ yield}
\]

(b) NH\(_3\) is used in the principal step of the Solvay process to produce a solution in which NaHCO\(_{3}\) is formed and from which it will precipitate. The filtrate contains NH\(_4\)Cl, from which NH\(_3\) is recovered by treatment with Ca(OH)\(_2\). Thus, NH\(_3\) is simply used
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during the Solvay process to produce the proper conditions for the desired reactions. Any net consumption of \( \text{NH}_3 \) is the result of unavoidable losses during production.

10. (M) (a) \[ \text{Ca(OH)}_2(s) + \text{SO}_4^{2-}(aq) \rightleftharpoons \text{CaSO}_4(s) + 2 \text{OH}^-(aq) \]

(b) We sum two solubility reactions and combine their values of \( K_{sp} \)

\[
\begin{align*}
\text{Ca(OH)}_2(s) & \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{OH}^-(aq) & K_{sp} = 5.5 \times 10^{-6} \\
\text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) & \rightleftharpoons \text{CaSO}_4(s) & 1/K_{sp} = 1/9.1 \times 10^{-6}
\end{align*}
\]

\[
\text{Ca(OH)}_2(s) + \text{SO}_4^{2-}(aq) \rightleftharpoons \text{CaSO}_4(s) + 2 \text{OH}^-(aq) & \quad K_{eq} = \frac{5.5 \times 10^{-6}}{9.1 \times 10^{-6}} = 0.60
\]

Because \( K_{eq} \) is close to 1.00, we conclude that the reaction lies neither very far to the right (it does not go to completion) nor to the left.

(c) Reaction: \[ \text{Ca(OH)}_2(s) + \text{SO}_4^{2-}(aq) \rightleftharpoons \text{CaSO}_4(s) + 2 \text{OH}^-(aq) \]

Initial: — 1.00 M — \( \approx \) 0 M

Changes: — \( -x \) M — +2x M

Equil: — (1.00–\( x \)) M — 2x M

\[
K = \frac{[\text{OH}^-]^2}{[\text{SO}_4^{2-}]} = 0.60 = \frac{4x^2}{1.00 - x}
\]

\[
4x^2 = 0.60 - 0.60x \\
4x^2 + 0.60x - 0.60 = 0
\]

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = -\frac{-0.60 \pm \sqrt{0.36 + 9.60}}{8} = 0.32 \text{ M}
\]

\[
[\text{SO}_4^{2-}] = 1.00 - x = 0.68 \text{ M} \quad [\text{OH}^-] = 2x = 0.64 \text{ M}
\]

11. (M) Use \( \Delta G^\circ_f \) values to calculate \( \Delta G^\circ \) for the reaction and then the equilibrium constant \( K \) at 298 K.

\[
\text{Na}_2\text{O}_2(s) \rightleftharpoons \text{Na}_2\text{O}(s) + \frac{1}{2}\text{O}_2(g)
\]

\[
\Delta G^\circ_f (\text{kJmol}^{-1}) = -449.63 \quad -379.09
\]

\[
\Delta G^\circ = -379.09 - (-449.63) = 70.54 \text{kJmol}^{-1}
\]

\[
\Delta G^\circ = -R T \ln K
\]

\[
-8.314 \text{JK}^{-1}\text{mol}^{-1} \times 298 \text{K} \times \ln K = 70.54 \times 1000 \text{Jmol}^{-1}
\]

\[
\ln K = \frac{70.54 \times 1000 \text{Jmol}^{-1}}{-8.314 \text{JK}^{-1}\text{mol}^{-1} \times 298 \text{K}} = -28.47 \Rightarrow K = e^{-28.47} = 4.32 \times 10^{-13}
\]
Since \( K = \frac{1}{P_{O_2}^2} \Rightarrow P_{O_2} = K^2 = 1.87 \times 10^{-25} \). The equilibrium constant and partial pressure of oxygen are both very small at 298 K. Therefore, Na\(_2\)O\(_2\) is thermodynamically stable with respect to Na\(_2\)O(s) and O\(_2\)(g) at 298 K.

12. (M) Use \( \Delta G^o \) values to calculate \( \Delta G^o \) for the reaction and then the equilibrium constant \( K \) at 298 K.

\[
\begin{align*}
2\text{KO}_2(s) & \rightarrow \text{K}_2\text{O(s)} + \frac{3}{2}\text{O}_2(g) \\
\Delta G^o & = -240.59 \quad -322.09 \\
\Delta G^o & = -322.09 - (-2 \times 240.59) = 159.1 \text{kJmol}^{-1}
\end{align*}
\]

\[\Delta G^o = -RT \ln K\]

\[\ln K = \frac{159.1 \times 1000 \text{Jmol}^{-1}}{-8.314 \text{JK}^{-1}\text{mol}^{-1} \times 298 \text{K}} = -64 \Rightarrow K = e^{-64} = 1.604 \times 10^{-28}\]

Since \( K = \frac{2}{3}P_{O_2} \Rightarrow P_{O_2} = \frac{2}{3} = 2.952 \times 10^{-19} \). The equilibrium constant and partial pressure of oxygen are both very small at 298 K. Therefore, KO\(_2\) is thermodynamically stable with respect to K\(_2\)O(s) and O\(_2\)(g) at 298 K.

**Group 2: The Alkaline Earth Metals**

13. (M) \( \text{CaO} \xrightarrow{\Delta} \text{CaCO}_3 \xrightarrow{\text{electrolysis}} \text{CO}_2 \xrightarrow{\text{HCl}} \text{Ca(OH)}_2 \xrightarrow{\text{HCl}} \text{CaCl}_2 \xrightarrow{\text{electrolysis}} \text{Ca}\]

\[
\begin{align*}
\text{CaHPO}_4 & \rightarrow \text{H}_3\text{PO}_4 \\
\text{H}_2\text{SO}_4 & \rightarrow \text{CaSO}_4
\end{align*}
\]

The reactions are as follows.

\[
\begin{align*}
\text{Ca(OH)}_2(aq) + 2 \text{HCl}(aq) & \rightarrow \text{CaCl}_2(aq) + 2\text{H}_2\text{O}(l) \\
\text{CaCl}_2(l) & \xrightarrow{\Delta, \text{electrolysis}} \text{Ca}(l) + \text{Cl}_2(g) \\
\text{CaCO}_3(s) & \xrightarrow{\Delta} \text{CaO}(s) + \text{CO}_2(g) \\
\text{Ca(OH)}_2(s) + \text{H}_2\text{SO}_4(aq) & \rightarrow \text{CaSO}_4(s) + 2\text{H}_2\text{O}(l)
\end{align*}
\]

\[
\begin{align*}
\text{Ca(OH)}_2(s) + \text{H}_3\text{PO}_4(aq) & \rightarrow \text{CaHPO}_4(aq) + 2\text{H}_2\text{O}(l)
\end{align*}
\]

Actually CaO(s) is the industrial starting material from which Ca(OH)\(_2\) is made. CaO(s) + H\(_2\)O(l) \(\rightarrow\) Ca(OH)\(_2\)(s)

14. (M) \( \text{MgO} \xrightarrow{\Delta} \text{MgCO}_3 \xrightarrow{\text{electrolysis}} \text{Mg(OH)}_2 \xrightarrow{\text{HCl}} \text{MgCl}_2 \xrightarrow{\text{electrolysis}} \text{Mg} \xrightarrow{\text{N}_2} \text{Mg}_3\text{N}_2
\]

\[
\begin{align*}
\text{MgHPO}_4 & \rightarrow \text{H}_3\text{PO}_4 \\
\text{H}_2\text{SO}_4 & \rightarrow \text{MgSO}_4
\end{align*}
\]

Once we return to Mg(OH)\(_2\) from MgSO\(_4\), the other substances can be made by the indicated pathways. The return reaction is: MgSO\(_4\)(aq) + 2 NaOH(aq) \(\rightarrow\) Mg(OH)\(_2\)(s) + Na\(_2\)SO\(_4\)(aq). Then the other reactions are
15. (M) The reactions involved are:

\[
\begin{align*}
\text{Mg}^{2+}(aq) + \text{Ca}^{2+}(aq) + 2\text{OH}^{-}(aq) & \rightarrow \text{Mg(OH)}_2(s) + \text{Ca}^{2+}(aq) \\
\text{Mg(OH)}_2(s) + 2\text{H}^{+}(aq) + 2\text{Cl}^{-}(aq) & \rightarrow \text{Mg}^{2+}(aq) + 2\text{H}_2\text{O}(l) + 2\text{Cl}^{-}(aq) \\
\text{Mg}^{2+}(aq) + 2\text{Cl}^{-}(aq) & \rightarrow \text{MgCl}_2(s) \\
\text{MgCl}_2(s) & \rightarrow \text{Mg}(l) + \text{Cl}_2(g)
\end{align*}
\]

As can be seen, the process does not violate the principle of conservation of charge.

16. (M) (a) MgO vs. BaO: MgO would have the higher melting point because, although Mg\(^{2+}\) and Ba\(^{2+}\) have the same charge, Mg\(^{2+}\) is a smaller ion. Smaller ions have a larger electrostatic attraction to anions (here, in both cases, the anion is O\(^2-\)), which is due to the smaller charge separation (Coulomb's law).

(b) MgF\(_2\) vs. MgCl\(_2\) solubility in water. F\(^-\) is smaller than Cl\(^-\), hence, electrostatic attraction between Mg\(^{2+}\) and the halide is greater in F\(^-\) than Cl\(^-\). If we assume that hydration of the ions is similar, we expect that MgF\(_2\) is less soluble than MgCl\(_2\). (Note: \(K_{sp}\) given for MgF\(_2\), which is sparingly soluble, while no \(K_{sp}\) value is given for readily soluble MgCl\(_2\).)

17. (M) (a) \(\text{BeF}_2(s) + \text{Mg}(s) \rightarrow \text{Be}(s) + \text{MgF}_2(s)\)

(b) \(\text{Ba}(s) + \text{Br}_2(l) \rightarrow \text{BaBr}_2(s)\)

(c) \(\text{UO}_2(s) + 2\text{Ca}(s) \rightarrow \text{U}(s) + 2\text{CaO}(s)\)

(d) \(\text{MgCO}_3 \cdot \text{CaCO}_3(s) \rightarrow \text{MgO}(s) + \text{CaO}(s) + 2\text{CO}_2(g)\)

(e) \(2\text{H}_3\text{PO}_4(aq) + 3\text{CaO}(s) \rightarrow \text{Ca}_3(\text{PO}_4)_2(s) + 3\text{H}_2\text{O}(l)\)

18. (M) (a) \(\text{Mg}(\text{HCO}_3)_2(s) \rightarrow \text{heat} \rightarrow \text{MgO}(s) + 2\text{CO}_2(g) + \text{H}_2\text{O}(l)\)

(b) \(\text{BaCl}_2(l) \rightarrow \text{electrolysis} \rightarrow \text{Ba}(l) + \text{Cl}_2(g)\)

(c) \(\text{Sr}(s) + 2\text{HBr}(aq) \rightarrow \text{SrBr}_2(aq) + \text{H}_2(g)\)

(d) \(\text{H}_2\text{SO}_4(aq) + \text{Ca(OH)}_2(aq) \rightarrow \text{CaSO}_4(s) + 2\text{H}_2\text{O}(l)\)

(e) \(\text{CaSO}_4 \cdot \text{2H}_2\text{O}(s) \rightarrow \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}(s) + \frac{3}{2}\text{H}_2\text{O}(g)\)

19. (D) Let us compute the value of the equilibrium constant for each reaction by combining the two solubility product constants. Large values of equilibrium constants indicate that the reaction is displaced far to the right. Values of \(K\) that are much smaller than 1 indicate that the reaction is displaced far to the left.

(a) \(\text{BaSO}_4(s) \rightarrow \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)\)

\[K_{sp} = 1.1 \times 10^{-10}\]
\[ \text{Ba}^{2+} (aq) + \text{CO}_3^{2-} (aq) \rightleftharpoons \text{BaCO}_3 (s) \quad 1/K_{sp} = 1/(5.1 \times 10^{-9}) \]

\[ \text{BaSO}_4 (s) + \text{CO}_3^{2-} (aq) \rightleftharpoons \text{BaCO}_3 (s) + \text{SO}_4^{2-} (aq) \quad K = \frac{1.1 \times 10^{-10}}{5.1 \times 10^{-9}} = 2.2 \times 10^{-2} \]

Thus, the equilibrium lies slightly to the left.

(b) \[ \text{Mg}_3 (\text{PO}_4)_2 (s) \rightleftharpoons 3 \text{Mg}^{2+} (aq) + 2 \text{PO}_4^{3-} (aq) \quad K_{sp} = 2.1 \times 10^{-25} \]

\[ 3 \{\text{Mg}^{2+} (aq) + \text{CO}_3^{2-} (aq) \rightleftharpoons \text{MgCO}_3 (s)\} \quad 1/(K_{sp})^3 = 1/(3.5 \times 10^{-8})^3 \]

\[ \text{Mg}_3 (\text{PO}_4)_2 (s) + 3 \text{CO}_3^{2-} (aq) \rightleftharpoons 3 \text{MgCO}_3 (s) + 2 \text{PO}_4^{3-} (aq) \]

\[ K = \frac{2.1 \times 10^{-25}}{(3.5 \times 10^{-8})^3} = 4.9 \times 10^{-3} \text{ Thus, the equilibrium lies to the left.} \]

(c) \[ \text{Ca} (\text{OH})_2 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + 2 \text{OH}^- (aq) \quad K_{sp} = 5.5 \times 10^{-6} \]

\[ \text{Ca}^{2+} (aq) + 2 \text{F}^- (aq) \rightleftharpoons \text{CaF}_2 (s) \quad 1/K_{sp} = 1/(5.3 \times 10^{-9}) \]

\[ \text{Ca} (\text{OH})_2 (s) + 2 \text{F}^- (aq) \rightleftharpoons \text{CaF}_2 (s) + 2 \text{OH}^- (aq) \quad K = \frac{5.5 \times 10^{-6}}{5.3 \times 10^{-9}} = 1.0 \times 10^{3} \]

Thus, the equilibrium lies to the right.

20. (M) We expect the reaction to occur to a significant extent in the forward direction if its equilibrium constant is >> 1.

(a) \[ \text{BaCO}_3 (s) \rightleftharpoons \text{Ba}^{2+} (aq) + \text{CO}_3^{2-} (aq) \quad K_{sp} = 5.1 \times 10^{-9} \]

\[ 2 \text{HC}_2\text{H}_3\text{O}_2 (aq) \rightleftharpoons 2\text{H}^+ (aq) + 2\text{C}_2\text{H}_5\text{O}_2^- (aq) \quad K_a^2 = (1.8 \times 10^{-5})^2 \]

\[ \text{H}^+ (aq) + \text{CO}_3^{2-} (aq) \rightleftharpoons \text{HCO}_3^- (aq) \quad 1/K_{a_2} = 1/(4.7 \times 10^{-11}) \]

\[ \text{H}^+ (aq) + \text{HCO}_3^- (aq) \rightleftharpoons \text{H}_2\text{CO}_3 (aq) \quad 1/K_{a_1} = 1/(4.2 \times 10^{-7}) \]

\[ \text{BaCO}_3 (s) + 2 \text{HC}_2\text{H}_3\text{O}_2 (aq) \rightleftharpoons \text{Ba} \left(\text{C}_2\text{H}_5\text{O}_2\right)_2 (aq) + \text{H}_2\text{CO}_3 (aq) \]

\[ K = \frac{5.1 \times 10^{-9} \times \left(1.8 \times 10^{-5}\right)^2}{4.7 \times 10^{-11} \times 4.2 \times 10^{-7}} = 8.4 \times 10^{-2} \]

Thus, no significant reaction occurs (the equilibrium mixture contains appreciable amounts of all four species involved in the reaction.

(b) \[ \text{Ca} (\text{OH})_2 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + 2 \text{OH}^- (aq) \quad K_{sp} = 5.5 \times 10^{-6} \]

\[ 2 \text{NH}_4^+ (aq) + 2 \text{OH}^- (aq) \rightleftharpoons 2 \text{NH}_3 (aq) + 2 \text{H}_2\text{O(l)} \quad 1/K_{b_2} = 1/(1.8 \times 10^{-5})^2 \]

\[ \text{Ca} (\text{OH})_2 (s) + 2 \text{NH}_4^+ (aq) \rightleftharpoons \text{Ca}^{2+} (aq) + 2 \text{NH}_3 (aq) + 2 \text{H}_2\text{O(l)} \]

\[ K = \frac{5.5 \times 10^{-6}}{(1.8 \times 10^{-5})^2} = 1.7 \times 10^4 \text{ Thus, this reaction would occur to a significant extent.} \]
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(c) \[ \text{BaF}_2(s) \xrightarrow{\text{sp}} \text{Ba}^{2+}(aq) + 2\text{F}^-(aq) \quad K_{sp} = 1.0 \times 10^{-6} \]

\[ 2\text{H}_3\text{O}^+(aq) + 2\text{F}^-(aq) \xrightarrow{\text{sp}} 2\text{HF}(aq) + 2\text{H}_2\text{O}(l) \quad 1/K_a^2 = 1/(6.6 \times 10^{-4})^2 \]

This reaction would occur to some extent, but certainly not to completion.

21. (M) The \( \text{SO}_4^{2-} \) ion is a large polarizable ion. A cation with a high polarizing power will polarize the \( \text{SO}_4^{2-} \) ion and kinetically assist the decomposition to \( \text{SO}_3 \). Because \( \text{Be}^{2+} \) has the largest charge density of the group 2 cations, we expect \( \text{Be}^{2+} \) to be the most polarizing and thus, \( \text{BeSO}_4 \) will be the least stable with respect to decomposition.

22. (M) The \( \text{CO}_3^{2-} \) ion is a large polarizable ion. A cation with a high polarizing power will polarize the \( \text{CO}_3^{2-} \) ion and kinetically assist the decomposition to \( \text{CO}_2 \). A cation with a low polarizing power will not polarize the anion as much; thus, the decomposition of \( \text{CO}_3^{2-} \) to \( \text{CO}_2 \) will not occur as readily in the presence of such a cation. Because \( \text{Ba}^{2+} \) has the smallest charge density of the group 2 cations, we expect \( \text{Ba}^{2+} \) to be the least polarizing; thus, \( \text{BaSO}_4 \) will be the most stable with respect to decomposition.

Group 13: The Boron Family

23. (M) (a) \( \text{B}_4\text{H}_{10} \) contains a total of \( 4 \times 3 + 10 \times 1 = 22 \) valence electrons or 11 pairs. Ten of these pairs could be allocated to form 10 B—H bonds, leaving but one pair to bond the four B atoms together, which is clearly an electron deficient situation.

(b) In our analysis in part (a), we noted that the four B atoms had but one electron pair to bond them together. To bond these four atoms into a chain requires three electron pairs. Since each electron pair in a bridging bond replaces two “normal” bonds, there must be at least two bridging bonds in the \( \text{B}_4\text{H}_{10} \) molecules. By analogy with \( \text{B}_2\text{H}_6 \), we might write the structure below left. But this structure uses only a total of 20 electrons. (The bridge bonds are shown as dots, normal bonds—electron pairs—as dashes.) In the structure at right below, we have retained some of the form of \( \text{B}_2\text{H}_6 \), and produced a compound with the formula \( \text{B}_4\text{H}_{10} \) and 11 electron pairs. (The experimentally determined structure of \( \text{B}_4\text{H}_{10} \) consists of a four-membered ring of alternating B and H atoms, held together by bridging bonds. Two of the B atoms have two H atoms bonded to each of them by normal covalent bonds. The other two B atoms have one H atom covalently bonded to each. One final B—B bond joins these last two B atoms, across the diameter of the ring.) See the diagram that follows:
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24.  (E) (a) 
\[
\begin{array}{c}
\text{F} \\
\text{B} \\
\text{F}
\end{array}
\]
(b) 
\[
\begin{array}{c}
\text{F} \\
\text{B} \\
\text{N} \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

25.  (M) (a) 
\[2\text{BBr}_3(\ell) + 3\text{H}_2(\ell) \rightarrow 2\text{B}(s) + 6\text{HBr}(g)\]
(b) i) \[\text{B}_2\text{O}_3(\ell) + 3\text{C}(s) \xrightarrow{\Delta} 3\text{CO}(g) + 2\text{B}(s)\]
ii) \[2\text{B}(s) + 3\text{F}_2(\ell) \xrightarrow{\Delta} 2\text{BF}_3(\ell)\]
(c) \[2\text{B}(s) + 3\text{N}_2\text{O}(\ell) \xrightarrow{\Delta} 3\text{N}_2(\ell) + \text{B}_2\text{O}_3(\ell)\]

26.  (M) Each boron atom has an oxidation number of +3. The hydroxyl oxygens are each –2, while the bridging oxygens are each –1. Finally, the hydroxyl H atoms are all in the +1 oxidation state. The oxidation numbers for all the constituent atoms add up to the charge on the perborate ion, namely, 2–.

27.  (M) (a) 
\[2\text{Al}(s) + 6 \text{HCl}(aq) \rightarrow 2\text{AlCl}_3(aq) + 3\text{H}_2(\ell)\]
(b) 
\[2\text{NaOH}(aq) + 2\text{Al}(s) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{Na}^+(aq) + 2\left[\text{Al(OH)}_4^-\right](aq) + 3\text{H}_2(\ell)\]
(c) Oxidation: \[\text{Al}(s) \rightarrow \text{Al}^{3+}(aq) + 3\text{e}^-\] \times 2
Reduction: \[\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{SO}_2(\ell) + 2\text{H}_2\text{O}(l)\] \times 3
Net: \[2\text{Al}(s) + 3\text{SO}_4^{2-}(aq) + 12\text{H}^+(aq) \rightarrow 2\text{Al}^{3+}(aq) + 3\text{SO}_2(aq) + 6\text{H}_2\text{O}(l)\]

28.  (M) (a) 
\[2\text{Al}(s) + 3\text{Br}_2(\ell) \rightarrow 2\text{AlBr}_3(\ell)\]
(b) 
\[2\text{Al}(s) + \text{Cr}_2\text{O}_3(s) \xrightarrow{\text{heat}} 2\text{Cr}(l) + \text{Al}_2\text{O}_3(s)\]
29. (M) One method of analyzing this reaction is to envision the HCO$_3^-$ ion as a combination of CO$_2$ and OH$^-$. Then the OH$^-$ reacts with Al$^{3+}$ and forms Al(OH)$_3$. This method of envisioning HCO$_3^-$ does have its basis in reality. After all,

$$\text{H}_2\text{CO}_3 (= \text{H}_2\text{O} + \text{CO}_2) + \text{OH}^- \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}$$

Al$^{3+}$ (aq) + 3 HCO$_3^-$ (aq) $\rightarrow$ Al(OH)$_3$(s) + 3 CO$_2$(g)

Another method is to consider the reaction as, first, the hydrolysis of hydrated aluminum ion to produce Al(OH)$_3$(s) and an acidic solution, followed by the reaction of the acid with bicarbonate ion.

$$\left[\text{Al(H}_2\text{O)}_6\right]^{3+} (\text{aq}) + 3 \text{H}_2\text{O(l)} \rightarrow \text{Al(OH)}_3(\text{H}_2\text{O)}_3(s) + 3 \text{H}_3\text{O}^+ (\text{aq})$$

$$3\text{H}_3\text{O}^+ (\text{aq}) + 3 \text{HCO}_3^- (\text{aq}) \rightarrow 6 \text{H}_2\text{O(l)} + 3 \text{CO}_2(\text{g})$$

This gives the same net reaction:

$$\left[\text{Al(H}_2\text{O)}_6\right]^{3+} (\text{aq}) + 3 \text{HCO}_3^- (\text{aq}) \rightarrow \text{Al(OH)}_3(\text{H}_2\text{O)}_3(s) + 3 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O(l)}$$

30. (E) The Al$^{3+}$ (aq) ion hydrolyzes. Al$^{3+}$ (aq) + 3 H$_2$O(l) $\rightarrow$ Al(OH)$_3$(s) + 3 H$^+$ (aq)

Subsequently, the hydrogen ion that is produced reacts with bicarbonate ion to liberate CO$_2$ (g).

$$\text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq}) \rightarrow \text{H}_2\text{O(l)} + \text{CO}_2(\text{g})$$

31. (M) Aluminum and its oxide are soluble in both acid and base.

2 Al(s) + 6 H$^+$ (aq) $\rightarrow$ 2 Al$^{3+}$ (aq) + 3 H$_2$ (g)

Al$_2$O$_3$(s) + 6 H$^+$ (aq) $\rightarrow$ 2 Al$^{3+}$ (aq) + 3 H$_2$O(l)

2 Al(s) + 2 OH$^-$ (aq) + 6 H$_2$O(l) $\rightarrow$ 2[Al(OH)$_4$]$^-$ (aq) + 3 H$_2$ (g)

Al$_2$O$_3$(s) + 2 OH$^-$ (aq) + 3 H$_2$O(l) $\rightarrow$ 2[Al(OH)$_4$]$^-$ (aq)

Al(s) is resistant to corrosion only over the pH range 4.5 to 8.5. Thus, aluminum is inert only when the medium to which it is exposed is neither highly acidic nor highly basic.

32. (M) Both Al and Mg are attacked by acid and their ions are both precipitated by hydroxide ion.

2 Al(s) + 6 H$^+$ (aq) $\rightarrow$ 2 Al$^{3+}$ (aq) + 3 H$_2$ (g)    Mg(s) + 2 H$^+$ (aq) $\rightarrow$ Mg$^{2+}$ (aq) + H$_2$ (g)

Al$^{3+}$ (aq) + 3 OH$^-$ (aq) $\rightarrow$ Al(OH)$_3$(s)    Mg$^{2+}$ (aq) + 2 OH$^-$ $\rightarrow$ Mg(OH)$_2$(s)
But, of these two solid hydroxides, only Al(OH)$_3$(s) redissolves in excess OH$^-$ (aq).

\[ \text{Al(OH)}_3(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow [\text{Al(OH)}_4]^- (\text{aq}) \]

Thus, the analytical procedure consists of dissolving the sample in HCl(aq) and then treating the resulting solution with NaOH(aq) until a precipitate forms. If this precipitate dissolves completely in excess NaOH(aq), the sample is aluminum 2S. If at least some of the precipitate does not dissolve, the sample was magnesium.

33. (M) CO$_2$(g) is, of course, the anhydride of an acid. The reaction here is an acid-base reaction.

\[ [\text{Al(OH)}_4]^- (\text{aq}) + \text{CO}_2(\text{aq}) \rightarrow \text{Al(OH)}_3(\text{s}) + \text{HCO}_3^-(\text{aq}) \]

HCl(aq), being a strong acid, can’t be used because it will dissolve the Al(OH)$_3$(s).

34. (M) (a) Oersted: 2 Al$_2$O$_3$(s) + 3 C(s) + 6 Cl$_2$(g)$\xrightarrow{\Delta}$ 4 AlCl$_3$(s) + 3 CO$_2$(g)

(b) Wöhler: AlCl$_3$(s) + 3 K(s)$\xrightarrow{\Delta}$ Al(s) + 3 KCl(s)

35. (M) 2 KOH(aq) + 2 Al(s) + 6 H$_2$(l)$\rightarrow$ 2 K[Al(OH)$_4$](aq) + 3 H$_2$(g)

2 K[Al(OH)$_4$](aq) + 4 H$_2$SO$_4$(aq) $\rightarrow$ K$_2$SO$_4$(aq) + Al$_2$(SO$_4$)$_3$(aq) + 8 H$_2$(l)

— crystallize $\rightarrow$ 2 KAl(SO$_4$)$_2$(s)

36. (E) HCO$_3^-$ and CO$_3^{2-}$ solutions are basic (they produce an excess of OH$^-\). Al$^{3+}$(aq) in the presence of OH$^-$ (aq) will precipitate as the hydroxide Al(OH)$_3$(s).

37. (E) The structure of, and bonding in, digallane is similar to the structure of and bonding in diborane, B$_2$H$_6$.

38. (M) The structure of, and bonding in, GaH$_2$Cl$_2$ is similar to the structure of and bonding in Al$_2$Cl$_6$, except that the terminal Cl’s in Al$_2$Cl$_6$ are replaced by H’s.

Group 14: The Carbon Family

39. (E) In the sense that diamonds react imperceptibly slowly at room temperature (either with oxygen to form carbon dioxide, or in its transformation to the more stable graphite), it is essentially true that “diamonds last forever.” However, at elevated temperatures, diamond will burn to form CO$_2$(g) and thus the statement is false. Also, the transformation
C(diamond) → C(graphite) might occur more rapidly under other conditions. Eventually, of course, the conversion to graphite occurs.

40. (E) The graphite in the pencil “lead” is a good dry lubricant that will make slippery the stickiness (or reluctance) in the lock and enable it to work smoothly. The key carries the graphite to the site that needs to be lubricated within the lock mechanism.

41. (M) (a) \[ 3 \text{SiO}_2(s) + 4 \text{Al}(s) \xrightarrow{\Delta} 2 \text{Al}_2\text{O}_3(s) + 3 \text{Si}(s) \]
   (b) \[ \text{K}_2\text{CO}_3(s) + \text{SiO}_2(s) \xrightarrow{\Delta} \text{CO}_2(g) + \text{K}_2\text{SiO}_3(s) \]
   (c) \[ \text{Al}_4\text{C}_3(s) + 12 \text{H}_2\text{O}(l) \rightarrow 3 \text{CH}_4(g) + 4\text{Al(OH)}_3(s) \]

42. (M) (a) \[ 2 \text{KCN}(aq) + \text{AgNO}_3(aq) \rightarrow \text{KAg(CN)}_2(aq) + \text{KNO}_3(aq) \]
   or \[ \text{KCN}(aq) + \text{AgNO}_3(aq) \rightarrow \text{Ag(CN)}(s) + \text{KNO}_3(aq) \]
   (b) \[ \text{Si}_3\text{H}_8(l) + 5 \text{O}_2(g) \rightarrow 3 \text{SiO}_2(s) + 4 \text{H}_2\text{O}(l) \]
   (c) \[ \text{N}_2(g) + \text{CaC}_2(s) \xrightarrow{\Delta} \text{CaNCN}(s) + \text{C}(s) \]

43. (M) A silane is a silicon-hydrogen compound, with the general formula \( \text{Si}_n\text{H}_{2n} \). A silanol is a compound in which one or more of the hydrogens of silane is replaced by an \( -\text{OH} \) group. Then, the general formula becomes \( \text{Si}_n\text{H}_{2n+1}(\text{OH}) \). In both of these classes of compounds, the number of silicon atoms, \( n \), ranges from 1 to 6. Silicones are produced when silanols condense into chains, with the elimination of a water molecule between every two silanol molecules.

\[
\text{HO—Si}_n\text{H}_{2n—OH} + \text{HO—Si}_n\text{H}_{2n—OH} + \text{HO—Si}_n\text{H}_{2n—OH} + \text{H}_2\text{O}
\]

44. (M) Both the alkali metal carbonates and the alkali metal silicates are soluble in water. Hence, they also are soluble in acids. However, the carbonates will produce gaseous carbon dioxide—\( \text{CO}_2 \)—on reaction with acid,

\[
\left( \text{CO}_3^{2—}(aq) + 2 \text{H}^+(aq) \rightarrow \text{H}_2\text{CO}_3 \right) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

while the silicates will produce silica—\( \text{SiO}_2 \)—in an analogous reaction

\[
\left( \text{SiO}_4^{4—}(aq) + 4\text{H}^+(aq) \rightarrow \text{H}_4\text{SiO}_4 \right) \rightarrow 2 \text{H}_2\text{O}(l) + \text{SiO}_2(s)
\]

The silica is produced in many forms depending on reaction conditions: a colloidal dispersion, a gelatinous precipitate, or a semisolid gel. Silicates of cations other than those of alkali metals are insoluble in water, as are the analogous carbonates. However, the carbonates will dissolve in acids (witness the reaction of acid rain on limestone carvings and marble statues, both forms of \( \text{CaCO}_3 \)), while the silicates will not. (Silicate rocks are not significantly affected by acid rain.)

45. (M) (1) \[ 2 \text{CH}_4(g) + \text{S}_8(g) \rightarrow 2 \text{CS}_2(g) + 4 \text{H}_2\text{S}(g) \]
   (2) \[ \text{CS}_2(g) + 3 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l) + \text{S}_2\text{Cl}_2(l) \]
   (3) \[ 4 \text{CS}_2(g) + 8 \text{S}_2\text{Cl}_2(g) \rightarrow 4 \text{CCl}_4(l) + 3 \text{S}_8(s) \]
46. **(M) (a)** \((CH_3)_3SiCl(l) + H_2O(l) \rightarrow (CH_3)_3SiOH(aq) + HCl(aq)\)
\[2 \ (CH_3)_3SiOH(aq) \rightarrow (CH_3)_3SiO-Si(CH_3)_3(s) + H_2O(l)\]

**(b)** A silicone polymer does not form from \((CH_3)_3Si-Cl\). Only a dimer is produced.

**(c)** The product that results from the treatment of \(CH_3SiCl_3\) is two long Si—O—Si chains, with \(CH_3\) groups on the outside, linked by Si—O—Si bridges. Part of one of these chains and the beginnings of the bridges are shown below.

\[
\begin{array}{cccccccc}
    & & & & & \text{O} & & \text{O} & \text{O} \\
\text{O} & \text{O} & \text{Si} & \text{O} & \text{Si} & \text{O} & \text{Si} & \text{O} & \text{Si} & \text{O} \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \\
\end{array}
\]

47. **(D)** Muscovite or white mica has the formula \(KAl_2(OH)2(AlSi3O10)\). Since they are not segregated into \(O_2\) units in the formula, all of the oxygen atoms in the mineral must be in the –2 oxidation state. Potassium is obviously in the +1 oxidation state, as are the hydrogen atoms in the hydroxyl groups. Up to this point, we have -24 from the twelve oxygen atoms and +3 from the potassium and hydrogen atoms for a net number of -21 for the oxidation state. We still have three aluminum atoms and three silicon atoms to account for. In oxygen-rich salts such as mica, we would expect that the silicon and the aluminum atoms would be in their highest possible oxidation states, namely +4 and +3, respectively. Since the salt is neutral, the oxidation numbers for the silicon and aluminum atoms must add up to +21. This is precisely the total that is obtained if the silicon and aluminum atoms are in their highest possible oxidation states: \((3 \times (+3) + 3 \times (+4) = +21)\). Consequently, the empirical formula for white muscovite is consistent with the expected oxidation state for each element present.

48. **(D)** Crysotile asbestos has the formula \([Mg_3Si_2O_5(OH)_4]\). Since they are not segregated to \(O_2\) units in the formula, all of the oxygen atoms in the mineral must be in the –2 oxidation state. The three magnesium atoms are obviously in the +2 oxidation state, while hydrogen atoms in the hydroxyl groups have an oxidation state of +1. Up to this point, then, the sum of the oxidation numbers equals –8 (–18 from O-atoms, +6 from Mg-atoms, and +4 from H-atoms). Since the mineral is neutral, the two silicon atoms must have oxidation states that sum to +8 (–8 + 8 = neutral mineral), therefore, each silicon would need to be in the +4 oxidation state. In oxygen-rich salts such as asbestos, we would expect that the silicon atoms would be in their highest possible oxidation state, namely +4. Thus, the oxidation states for the element, in this mineral are precisely consistent with expectations.

49. **(M) (a)** \(\text{PbO(s)} + 2 \text{HNO}_3(aq) \rightarrow \text{Pb(NO}_3)_2(s) + \text{H}_2\text{O(l)}\)

**(b)** \(\text{SnCO}_3(s) \xrightarrow{\Delta} \text{SnO(s)} + \text{CO}_2(g)\)

**(c)** \(\text{PbO(s)} + \text{C(s)} \xrightarrow{\Delta} \text{Pb(l)} + \text{CO(g)}\)
(d) \(2 \text{Fe}^{3+} \text{(aq)} + \text{Sn}^{2+} \text{(aq)} \rightarrow 2 \text{Fe}^{2+} \text{(aq)} + \text{Sn}^{4+} \text{(aq)}\)

(e) \(2 \text{PbS(s)} + 3 \text{O}_2 \text{(g)} \rightarrow 2 \text{PbO(s)} + 2 \text{SO}_2 \text{(g)}\)
\(2 \text{SO}_2 \text{(g)} + \text{O}_2 \text{(g)} \rightarrow 2 \text{SO}_3 \text{(g)}\)
\(\text{SO}_3 \text{(g)} + \text{PbO(s)} \rightarrow \text{PbSO}_4 \text{(s)}\)

Or perhaps simply: \(\text{PbS(s)} + 2 \text{O}_2 \text{(g)} \rightarrow \text{PbSO}_4 \text{(s)}\)

Yet a third possibility:
\(\text{PbO(s)} + \text{SO}_2 \text{(s)} \rightarrow \text{PbSO}_3 \text{(s)}, \text{followed by} \ 2 \text{PbSO}_3 \text{(s)} + \text{O}_2 \text{(s)} \rightarrow 2\text{PbSO}_4 \text{(s)}\)

50. (M) (a) Treat tin(II) oxide with hydrochloric acid.
\(\text{SnO(s)} + 2 \text{HCl(aq)} \rightarrow \text{SnCl}_2 \text{(aq)} + \text{H}_2\text{O(l)}\)

(b) Attack tin with chlorine. \(\text{Sn(s)} + 2 \text{Cl}_2 \text{(g)} \rightarrow \text{SnCl}_4 \text{(s)}\)

(c) First we dissolve \(\text{PbO}_2 \text{(s)}\) in \(\text{HNO}_3 \text{(aq)}\) and then treat the resulting solution with \(\text{K}_2\text{CrO}_4 \text{(aq)}\) to precipitate \(\text{PbCrO}_4\text{(s)}\)
\(2 \text{PbO}_2 \text{(s)} + 4 \text{HNO}_3 \text{(aq)} \rightarrow 2 \text{Pb(NO}_3)_2 \text{(aq)} + \text{O}_2 \text{(g)} + 2 \text{H}_2\text{O(l)}\)
\(\text{Pb(NO}_3)_2 \text{(aq)} + \text{K}_2\text{CrO}_4 \text{(aq)} \rightarrow \text{PbCrO}_4 \text{(s)} + 2 \text{KNO}_3 \text{(aq)}\)

51. (M) We start by using the Nernst equation to determine whether the cell voltage still is positive when the reaction has gone to completion.

(a) Oxidation: \(\text{Fe}^{2+} \text{(aq)} \rightarrow \text{Fe}^{3+} \text{(aq)} + \text{e}^-\) \(\times 2\) \(-E^\circ = -0.771 \text{V}\)
Reduction: \(\text{PbO}_2 \text{(s)} + 4 \text{H}^+ \text{(aq)} + 2 \text{e}^- \rightarrow \text{Pb}^{2+} \text{(aq)} + 2 \text{H}_2\text{O(l)}\) \(E^\circ = +1.455 \text{V}\)

Net: \(2 \text{Fe}^{2+} \text{(aq)} + \text{PbO}_2 \text{(s)} + 4 \text{H}^+ \text{(aq)} \rightarrow 2 \text{Fe}^{3+} \text{(aq)} + \text{Pb}^{2+} \text{(aq)} + 2 \text{H}_2\text{O(l)}\)

\(E^\circ_{\text{cell}} = -0.771 \text{V} + 1.455 \text{V} = +0.684 \text{V}\)

In this case, when the reaction has gone to completion,
\([\text{Fe}^{3+}] = 0.001 \text{M}, [\text{Fe}^{2+}] = 0.999 \text{M}, \text{and} [\text{Pb}^{2+}] = 0.500 \text{M}\).

\(E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{2} \log \frac{[\text{Fe}^{3+}]^2 [\text{Pb}^{2+}]}{[\text{Fe}^{2+}]^2} = 0.684 \text{V} - \frac{0.0592}{2} \log \frac{[0.999]^2 [0.500]}{[0.001]^2} = 0.515 \text{V}\).

Thus, this reaction will go to completion.

(b) Oxidation: \(2 \text{SO}_4^{2-} \text{(aq)} \rightarrow \text{S}_2\text{O}_8^{2-} \text{(aq)} + 2 \text{e}^-\) \(-E^\circ = -2.01 \text{V}\)
Reduction: \(\text{PbO}_2 \text{(s)} + 4 \text{H}^+ \text{(aq)} + 2 \text{e}^- \rightarrow \text{Pb}^{2+} \text{(aq)} + 2 \text{H}_2\text{O(l)}\) \(E^\circ = +1.455 \text{V}\)

\(2 \text{SO}_4^{2-} \text{(aq)} + \text{PbO}_2 \text{(s)} + 4 \text{H}^+ \text{(aq)} \rightarrow \text{S}_2\text{O}_8^{2-} \text{(aq)} + \text{Pb}^{2+} \text{(aq)} + 2 \text{H}_2\text{O(l)}\)
\[ E^{\circ}_{\text{cell}} = -2.01 + 1.455 = -0.56 \text{ V} \] This reaction is not even spontaneous initially.

(c) Oxidation: \( \{\text{Mn}^{2+} (1 \times 10^{-7} \text{ M}) + 4\text{H}_2\text{O}(l) \rightarrow \text{MnO}_4^{-} (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5 \text{e}^-\} \times 2; -E^0 = -1.51 \text{ V} \)

Reduction: \( \{\text{PbO}_2 (s) + 4 \text{H}^+ (\text{aq}) + 2 \text{e}^- \rightarrow \text{Pb}^{2+} (\text{aq}) + 2 \text{H}_2\text{O}(l)\} \times 5 \quad E^0 = +1.455 \text{ V} \)

Net: \( 2\text{Mn}^{2+} (1 \times 10^{-7} \text{ M}) + 5\text{PbO}_2 (s) + 4\text{H}^+ \rightarrow 2\text{MnO}_4^{-} (\text{aq}) + 5\text{Pb}^{2+} (\text{aq}) + 2\text{H}_2\text{O}(l) \)

\[ E^{\circ}_{\text{cell}} = -1.51 + 1.455 = -0.06 \text{ V} \] The standard cell potential indicates that this reaction is not spontaneous when all concentrations are 1 M. Since the concentration of a reactant \( \text{Mn}^{2+} \) is lower than 1.00 M, this reaction is even less spontaneous than the standard cell potential indicates.

52. (M) A positive value of \( E^{\circ}_{\text{cell}} \) indicates that a reaction should occur.

(a) Oxidation: \( \text{Sn}^{2+} (\text{aq}) \rightarrow \text{Sn}^{4+} (\text{aq}) + 2 \text{e}^- \quad -E^0 = -0.154 \text{ V} \)

Reduction: \( \text{I}_2 (s) + 2 \text{e}^- \rightarrow 2 \text{I}^- (\text{aq}) \quad E^0 = +0.535 \text{ V} \)

Net: \( \text{Sn}^{2+} (\text{aq}) + \text{I}_2 (s) \rightarrow \text{Sn}^{4+} (\text{aq}) + 2 \text{I}^- (\text{aq}) \quad E^{\circ}_{\text{cell}} = +0.381 \text{ V} \)

Yes, \( \text{Sn}^{2+} (\text{aq}) \) will reduce \( \text{I}_2 \) to \( \text{I}^- \).

(b) Oxidation: \( \text{Sn}^{2+} (\text{aq}) \rightarrow \text{Sn}^{4+} (\text{aq}) + 2 \text{e}^- \quad -E^0 = -0.154 \text{ V} \)

Reduction: \( \text{Fe}^{2+} (\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe} (s) \quad E^0 = -0.440 \text{ V} \)

Net: \( \text{Sn}^{2+} (\text{aq}) + \text{Fe}^{2+} (\text{aq}) \rightarrow \text{Sn}^{4+} (\text{aq}) + \text{Fe} (s) \quad E^{\circ}_{\text{cell}} = -0.594 \text{ V} \)

No, \( \text{Sn}^{2+} (\text{aq}) \) will not reduce \( \text{Fe}^{2+} (\text{aq}) \) to \( \text{Fe} (s) \).

(c) Oxidation: \( \text{Sn}^{2+} (\text{aq}) \rightarrow \text{Sn}^{4+} (\text{aq}) + 2 \text{e}^- \quad -E^0 = -0.154 \text{ V} \)

Reduction: \( \text{Cu}^{2+} (\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu} (s) \quad E^0 = +0.337 \text{ V} \)

Net: \( \text{Sn}^{2+} (\text{aq}) + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Sn}^{4+} (\text{aq}) + \text{Cu} (s) \quad E^{\circ}_{\text{cell}} = +0.183 \text{ V} \)

Yes, \( \text{Sn}^{2+} (\text{aq}) \) will reduce \( \text{Cu}^{2+} (\text{aq}) \) to \( \text{Cu} (s) \).

(d) Oxidation: \( \text{Sn}^{2+} (\text{aq}) \rightarrow \text{Sn}^{4+} (\text{aq}) + 2 \text{e}^- \quad -E^0 = -0.154 \text{ V} \)

Reduction: \( \{\text{Fe}^{3+} (\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+} (\text{aq})\} \times 2 \quad E^0 = +0.771 \text{ V} \)

Net: \( \text{Sn}^{2+} (\text{aq}) + 2 \text{Fe}^{3+} (\text{aq}) \rightarrow \text{Sn}^{4+} (\text{aq}) + 2 \text{Fe}^{2+} (\text{aq}) \quad E^{\circ}_{\text{cell}} = +0.617 \text{ V} \)

Yes, \( \text{Sn}^{2+} (\text{aq}) \) will reduce \( \text{Fe}^{3+} (\text{aq}) \) to \( \text{Fe}^{2+} (\text{aq}) \).

53. (M) As we move down a group, the lower oxidation state is generally favored. Thus, we expect \( \text{PbCl}_2 \), with lead in the +2 oxidation state, to be the product.
54. **(M)** As we move down a group, the lower oxidation state is generally favored. The higher oxidation state is favored for elements higher in the group. Thus, we expect GeF₄, with lead in the +4 oxidation state, to be the product.

### INTEGRATIVE AND ADVANCED EXERCISES

55. **(M)** What most likely happened is that a deliquescent solid has absorbed water vapor from the air over time and formed a saturated solution. This saturated solution can be used in any circumstance where the solid would be used to prepared an aqueous solution. Of course, the concentration will have to be determined by some means other than weighing, such as a gravimetric analysis or using a standard to react with the substance in a titration. Alternatively, the saturated solution can be heated in a drying oven to drive off the water and the solid may be recovered. Often, unfortunately, a solid with an unknown percent of water results from this treatment.

56. **(D)**

   **(a)** A solution of CO₂(aq) has [CO₃²⁻] = Kₐ₂[H₂CO₃] = 5.6×10⁻¹¹ M. Since the Kₚ = 2.8×10⁻⁹ for CaCO₃, the [Ca²⁺] needed to form a precipitate from this solution can be computed.

   \[
   [\text{Ca}^{2+}] = \frac{K_p}{[\text{Ca}^{2+}]} = \frac{2.8 \times 10^{-9}}{5.6 \times 10^{-11}} = 50. \text{ M}
   \]

   This is too high to reach by dissolving CaCl₂ in solution. The reason a solid forms is that the OH⁻ produced by the Ca(OH)₂ neutralized some of the HCO₃⁻ from the ionization of CO₂(aq), thereby increasing the [CO₃²⁻] above a value of 5.6×10⁻¹¹ M.

   **(b)** The equation for redissolving can be obtained by combining several equations.

   \[
   \text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \quad K_p = 2.8 \times 10^{-9}
   \]

   \[
   \text{CO}_3^{2-}(aq) + \text{H}_3\text{O}^+(aq) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \quad 1/K_{a2} = 1/(5.6 \times 10^{-11})
   \]

   \[
   \text{CO}_2(aq) + 2 \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a1} = 4.2 \times 10^{-7}
   \]

   \[
   \text{CaCO}_3(s) + \text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{HCO}_3^-(aq) \quad K = \frac{K_p \times K_{a1}}{K_{a2}}
   \]

   \[
   K = \frac{(2.8 \times 10^{-9}) \times (4.2 \times 10^{-7})}{(5.6 \times 10^{-11})} = 2.1 \times 10^{-5} = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_2]}
   \]

   If CaCO₃(s) is precipitated from 0.005 M Ca²⁺(aq) and then redissolved, [Ca²⁺] = 0.005 M and [HCO₃⁻] = 2×0.005 M = 0.010 M. We use these values in the above expression to compute the [CO₂].

   \[
   [\text{CO}_2] = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{(2.1 \times 10^{-5})} = 0.002 \text{ M}
   \]

   We repeat the calculation for saturated Ca(OH)₂, in which [OH⁻] = 2 × [OH⁻], after first determining [Ca²⁺] in this solution.
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\[ K_{sp} = [\text{Ca}^{2+}] [\text{OH}^-]^2 = 4 \times [\text{Ca}^{2+}] = 5.5 \times 10^{-6} \]

\[ [\text{Ca}^{2+}] = \frac{5.5 \times 10^{-6}}{4} = 0.011 \text{ M} \]

\[ [\text{CO}_2^-] = [\text{Ca}^{2+}] [\text{HCO}_3^-]^2 = (0.011)(0.022)^2 = 0.25 \text{ M} \]

Thus, to redissolve the CaCO\(_3\) requires that the [CO\(_2^-\)] = 0.25 M, assuming the solution is initially saturated with Ca(OH)\(_2\)(aq).

(c) follow the solution for (b) above.

57. (M) There are two principal reasons why the electrolysis of NaCl(l) is used to produce sodium commercially rather than the electrolysis of NaOH(l). First, NaCl is readily available whereas NaOH is produced from the electrolysis of NaCl(aq). Thus the raw material NaCl is much cheaper than is NaOH. Second, but less important, when sodium is produced from the electrolysis of NaCl(l), a by-product is Cl\(_2\)(g), whereas O\(_2\)(g) is a by-product of the production of NaOH(l). Since O\(_2\)(g) can be produced more cheaply by the fractional distillation of liquid air, Cl\(_2\)(g) can be sold for a higher price than O\(_2\)(g). Thus, the two reasons for producing sodium from NaCl(l) rather than NaOH(l) are a much cheaper raw material and a more profitable by-product.

58. (M) The triiodide ion is linear (AX\(_2\)E\(_3\)). The Li\(^+\) ion has a high charge density and significant polarizing power. The Li\(^+\) ion will polarize the I\(_3^-\) to a significant extent and presumably assists the decomposition of I\(_3^-\) to I\(_2\) and I\(^-\).

59. (M) Use \(\Delta G^o\) values to calculate \(\Delta G^o\) for the reaction and then \(K\). Because \(K = P_{O_2}^{1/2}\), the value of \(K\) can then be used to calculate \(P_{O_2}\).

\[ \text{Li}_2\text{O}_2(s) \rightarrow \text{Li}_2\text{O}(s) + \frac{1}{2} \text{O}_2(g) \]

\[ \Delta G^o[kJ/mol] \quad -419.02 \quad -466.40 \]

\[ \Delta G^o = -466.40 - (-419.02) = -47.38 \text{kJmol}^{-1} \]

\[ \Delta G^o = -RT \ln K \]

\[ -8.314 \text{JK}^{-1}\text{mol}^{-1} \times 1000K \times \ln K = -47.38 \times 1000 \text{Jmol}^{-1} \]

\[ \ln K = \frac{-47.38 \times 1000 \text{Jmol}^{-1}}{-8.314 \text{JK}^{-1}\text{mol}^{-1} \times 1000K} = 5.70 \Rightarrow K = e^{5.70} = 298 \]

\[ K = P_{O_2}^{1/2} \Rightarrow P_{O_2} = K^2 = 298^2 = 8.8 \times 10^4 \]

60. (M) Use \(\Delta S_{\text{hydr}}^o = \frac{1}{2} \left( \Delta H_{\text{hydr}}^o - \Delta G_{\text{hydr}}^o \right)\) to calculate \(\Delta S_{\text{hydr}}^o\) values:
\( \Delta S^o_{\text{hydr.}}(Li^+) = \frac{1}{298} (522 - (-481)) = -0.14 \text{J/mol} \)

\( \Delta S^o_{\text{hydr.}}(Na^+) = \frac{1}{298} (-407 - (-375)) = -0.11 \text{J/mol} \)

\( \Delta S^o_{\text{hydr.}}(K^+) = \frac{1}{298} (-324 - (-304)) = -0.07 \text{J/mol} \)

\( \Delta S^o_{\text{hydr.}}(Rb^+) = \frac{1}{298} (-299 - (-281)) = -0.06 \text{J/mol} \)

\( \Delta S^o_{\text{hydr.}}(Cs^+) = \frac{1}{298} (-274 - (-258)) = -0.05 \text{J/mol} \)

All the \( \Delta S^o_{\text{hydr.}} \) values are negative because, in the process, a gas is being converted into a liquid solution. However, \( \Delta S^o_{\text{hydr.}} \) is most negative for Li\(^+\). The \( \Delta S^o_{\text{hydr.}} \) values increase as we move down the group from Li\(^+\) to Cs\(^+\). As the charge density and polarizing power of the metal cation decreases, so too does the degree of order (or organization) in the hydration sphere. Thus, the entropy change should be most negative for Li\(^+\) and least negative for Cs\(^+\).

61. (M) (a) Use the Kapustinskii equation in the form 
\[ U = \frac{120,200 z_+ z_- \nu}{r_+ + r_-} \left(1 - \frac{34.5}{r_+ + r_-}\right) \]
with \( r_+ \) and \( r_- \) in picometers, to calculate \( U \) in kJ mol\(^{-1}\). For LiO\(_2\), \( z_+ = +1 \), \( z_- = -1 \), and \( \nu = 2 \).

(b) When we apply the Born–Fajans–Haber cycle to the reaction Li(s) + O\(_2\)(g) → LiO\(_2\)(s), we get \( \Delta H_f^o = \Delta H_{\text{f,LiO}_2}^o + \text{IE}(1)_{\text{Li}} - 43 + U \). Values of \( \Delta H_{\text{f,LiO}_2}^o \) and \( \text{IE}(1)_{\text{Li}} \) are given in Appendix D and in Table 21.2, respectively.

(c) For the reaction 2 LiO\(_2\)(s) → Li\(_2\)O(s) + \( \frac{3}{2} \) O\(_2\)(g), \( \Delta H^o = \Delta H_{\text{f,Li}_2\text{O}(s)}^o - 2 \Delta H_{\text{f,LiO}_2(s)}^o \).

(d) The decomposition reaction is exothermic (\( \Delta H^o < 0 \)) and, with the assumption that entropy effects are not important, the decomposition of LiO\(_2\)(s) to Li\(_2\)O(s) and O\(_2\)(g) is thermodynamically favorable.

62. (M) (a) The mass of MgO(s) that would be produced can be determined with information from the balanced chemical equation for the oxidation of Mg(s).

\[
2 \text{Mg}(s) + \text{O}_2(g) \rightarrow 2 \text{MgO}(s)
\]

\[
\text{mass MgO} = 0.200 \text{g Mg} \times \frac{1 \text{mol Mg}}{24.305 \text{g Mg}} \times \frac{2 \text{mol MgO}}{2 \text{mol Mg}} \times \frac{40.30 \text{g MgO}}{1 \text{mol MgO}} = 0.332 \text{g MgO}
\]

(b) If the mass of product formed from the starting Mg differs from the 0.332 g MgO predicted, then the product could be a mixture of magnesium nitride and magnesium oxide. This scenario is not implausible since molecular nitrogen is readily available in the atmosphere.

\[
3 \text{Mg}(s) + \text{N}_2(g) \rightarrow \text{Mg}_3\text{N}_2(s)
\]

\[
\text{mass Mg}_3\text{N}_2 = 0.200 \text{g Mg} \times \frac{1 \text{mol Mg}}{24.305 \text{g Mg}} \times \frac{1 \text{mol Mg}_3\text{N}_2}{3 \text{mol Mg}} \times \frac{100.93 \text{g Mg}_3\text{N}_2}{1 \text{mol Mg}_3\text{N}_2} = 0.277 \text{g Mg}_3\text{N}_2
\]
We can use a technique similar to determining the percent abundance of an isotope. Let \( f \) = the mass fraction of MgO in the product. The \((1.000 - f)\) is the mass fraction of Mg\(_3\)N\(_2\) in the product. Product mass = mass MgO \( \times f \) + [mass Mg\(_3\)N\(_2\) \( \times (1.000 - f)\)]

\[
0.315 \text{ g product} = 0.332 \times f + [0.277 \times (1.000 - f)] = 0.277 + f(0.332 - 0.277)
\]

\[
f = \frac{0.315 - 0.277}{0.332 - 0.277} = 0.69
\]

The product is 69% by mass MgO.

63. (M) Reaction (21.4) is KCl(l) + Na(l) \( \xrightarrow{850^\circ\text{C}} \) NaCl(l) + K(g) It is practical when the reactant element is a liquid and the product element is a gas at the same temperature.

(a) Since Li has a higher boiling point (1347°C) than K (773.9°C), a reaction similar to (21.4) is not a feasible way of producing Li metal from LiCl.

(b) On one hand, Cs has a lower boiling point (678.5°C) than K (773.9°C), and thus a reaction similar to (21.4) is a feasible method of producing Cs metal from CsCl. However, the ionization energy of Na is considerably larger than that of Cs, making it difficult to transfer an electron from Na to Cs\(^+\).

64. (M) (a) \( 2 \text{Al}(s) + \text{Fe}_2\text{O}_3(s) \rightarrow 2 \text{Fe}(s) + \text{Al}_2\text{O}_3(s) \quad \Delta H = -852 \text{ kJ} \)

(b) \( 4 \text{Al}(s) + 3 \text{MnO}_2(s) \rightarrow 2 \text{Al}_2\text{O}_3(s) + 3 \text{Mn}(s) \quad \Delta H = -1792 \text{ kJ} \)

(c) \( 2 \text{Al}(s) + 3 \text{MgO}(s) \rightarrow \text{Al}_2\text{O}_3(s) + 3 \text{Mg}(s) \quad \Delta H = +129 \text{ kJ} \)

65. (M) \( \text{Li}^+(aq) + e^- \rightarrow \text{Li}(s) \quad \Delta G^\circ = -293.3 \text{ kJ} = -nFE^\circ = -1 \text{ mol e}^- (96,485 \text{ C/mol e}^-)E^\circ \)

\( E^\circ = -3.040 \text{ V} \) (this value is the same as the one that appears in Table 21.2.)

66. (M) The partial pressure of H\(_2\) is 748 mmHg – 21 mmHg = 727 mmHg

\[
\text{amount H}_2 = \frac{PV}{RT} = \left(\frac{727 \text{ mm Hg} \times (1 \text{ atm/760 mmHg}) \times 0.104 \text{ L}}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 296 \text{ K}}\right) = 4.10 \times 10^{-3} \text{ mol H}_2
\]

The electrode reactions are the following.

Anode : 2 Cl\(^-\) (aq) \( \rightarrow \) Cl\(_2\) (g) + 2 e\(^-\)  
Cathode : 2 H\(_2\)O(l) + 2 e\(^-\) \( \rightarrow \) 2 OH\(^-\) (aq) + H\(_2\) (g)

Thus 2 mol OH\(^-\) (aq) are produced per mole of H\(_2\)(g); 8.20 \times 10^{-3} \text{ mol OH}^- (aq) are produced.

\[
[\text{OH}^-] = \frac{8.20 \times 10^{-3} \text{ mol OH}^-}{0.250 \text{ L soln}} = 3.28 \times 10^{-2} \text{ M} = 0.0328 \text{ M}
\]

Then we compute the ion product and compare its value to the value of \( K_{sp} \) for Mg(OH)\(_2\).

\[
Q_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.220)(0.0328)^2 = 2.37 \times 10^{-4} > 1.8 \times 10^{-11} = K_{sp} \text{ for Mg(OH)}_2
\]

Thus, Mg(OH)\(_2\) should precipitate.
67. (D) (a) We determine the amount of Ca\(^{2+}\) associated with each anion in 10\(^6\) g of the water.

\[
\text{amount Ca}^{2+} (\text{SO}_4^{2-}) = 56.9 \text{ g SO}_4^{2-} \times \frac{1 \text{ mol SO}_4^{2-}}{96.06 \text{ g SO}_4^{2-}} \times \frac{1 \text{ mol Ca}^{2+}}{1 \text{ mol SO}_4^{2-}} = 0.592 \text{ mol}
\]

\[
\text{amount Ca}^{2+} (\text{HCO}_3^{-}) = 176 \text{ g HCO}_3^{-} \times \frac{1 \text{ mol HCO}_3^{-}}{61.02 \text{ g HCO}_3^{-}} \times \frac{1 \text{ mol Ca}^{2+}}{2 \text{ mol HCO}_3^{-}} = 1.44 \text{ mol}
\]

Then we determine the total mass of Ca\(^{2+}\), numerically equal to the ppm Ca\(^{2+}\).

\[
\text{mass Ca}^{2+} = (0.592 + 1.44) \text{ mol Ca}^{2+} \times \frac{40.08 \text{ g Ca}^{2+}}{1 \text{ mol Ca}^{2+}} = 81.4 \text{ g Ca}^{2+} \rightarrow 81.4 \text{ ppm Ca}^{2+}
\]

(b) The reactions for the removal of HCO\(_3\)^–(aq) begin with the formation of hydroxide ion resulting from dissolving CaO(s). Hydroxide ion reacts with bicarbonate ion to form carbonate ion, which then combines with calcium ion to form the CaCO\(_3\)(s) precipitate.

\[
\text{CaO(s) + H}_2\text{O(l) }\rightarrow\text{Ca}^{2+} (\text{aq}) + 2 \text{OH}^- (\text{aq})
\]

\[
\text{OH}^- (\text{aq}) + \text{HCO}_3^- (\text{aq}) \rightarrow \text{H}_2\text{O(l)} + \text{CO}_3^{2-} (\text{aq})
\]

\[
\text{Ca}^{2+} (\text{aq}) + \text{CO}_3^{2-} (\text{aq}) \rightarrow \text{CaCO}_3 (\text{s})
\]

For each 1.000 \times 10^6 g of water, we need to remove 176 g HCO\(_3\)^–(aq) with the added CaO(s).

\[
\text{mass CaO} = 602 \times 10^3 \text{ g water} \times \frac{176 \text{ g HCO}_3^{-}}{1.000 \times 10^6 \text{ g water}} \times \frac{1 \text{ mol HCO}_3^{-}}{1 \text{ mol OH}^-} \times \frac{1 \text{ mol OH}^-}{61.02 \text{ g HCO}_3^{-}} \times \frac{1 \text{ mol CaO}}{2 \text{ mol OH}^-} \times \frac{56.08 \text{ g CaO}}{1 \text{ mol CaO}} = 48.7 \text{ g CaO}
\]

(c) Here we determine the total amount of Ca\(^{2+}\) in 602 kg of water, and that added as CaO.

\[
\text{Ca}^{2+} = \left(\frac{602 \text{ kg}}{1 \times 10^6 \text{ kg}}\right) (0.592 + 1.44) \text{ mol Ca}^{2+} + \left(\frac{48.7 \text{ g CaO}}{56.08 \text{ g CaO}}\times\frac{1 \text{ mol CaO}}{1 \text{ mol Ca}^{2+}}\right) = 2.09 \text{ mol Ca}^{2+}
\]

The amount of Ca\(^{2+}\) that has precipitated equals the amount of HCO\(_3\)^– in solution, since each mole of HCO\(_3\)^– is transformed into 1 mole of CO\(_3^{2-}\), which reacts with and then precipitates one mole of Ca\(^{2+}\). Thus the amount of Ca\(^{2+}\) that has precipitated is (0.602)(1.44) = 0.867 mol Ca\(^{2+}\) as CaCO\(_3\)(s). Then we can determine the concentration of Ca\(^{2+}\) remaining in solution.

\[
[\text{Ca}^{2+}] = \frac{2.09 \text{ mol Ca}^{2+} \text{ total} - 0.867 \text{ mol Ca}^{2+} \text{ as CaCO}_3}{1 \times 10^6 \text{ g water}} = 2.03 \times 10^{-3} \text{ M}
\]

To consider the Ca\(^{2+}\) “removed”, its concentration should be decreased to 0.1\% (0.001) of its initial value, or 2.03 \times 10^{-6} M. We use the \(K_{sp}\) expression for CaCO\(_3\) to determine the needed [CO\(_3^{2-}\)]

\[
K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 2.8 \times 10^{-9} = 1.46 \times 10^{-6} \text{ M}
\]

\[
[\text{CO}_3^{2-}] = \frac{2.8 \times 10^{-9}}{2.03 \times 10^{-6}} = 0.0014 \text{ M}
\]
This carbonate ion concentration can readily be achieved by adding solid Na₂CO₃.

(d) The amount of CO₃²⁻ needed is that which ends up in the precipitate plus that needed to attain the 0.0014 M concentration in the 602 kg = 602 L of water.

\[
n_{\text{CO}_3^{2-}} = 602 \text{ L} \times \left( \frac{0.00203 \text{ mol Ca}^{2+}}{1 \text{ L water}} \times \frac{1 \text{ mol CO}_3^{2-}}{1 \text{ mol Ca}^{2+}} + \frac{0.0014 \text{ mol CO}_3^{2-}}{1 \text{ L water}} \right) = 2.1 \text{ mol CO}_3^{2-}
\]

This CO₃²⁻ comes from the added Na₂CO₃(s).

\[
\text{mass Na}_2\text{CO}_3 = 2.0 \text{ mol CO}_3^{2-} \times \frac{1 \text{ mol Na}_2\text{CO}_3}{1 \text{ mol CO}_3^{2-}} \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} = 2.2 \times 10^2 \text{ g Na}_2\text{CO}_3
\]

68. (M) (a) In the cell reaction, three moles of electrons are required to reduce each mole of Al³⁺.

\[
\text{mass Al} = 8.00 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1.00 \times 10^5 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^-}{96,485 \text{ C}} \times \frac{1 \text{ mol Al}}{3 \text{ mol e}^-} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 2.68 \times 10^5 \text{ g Al}
\]

The 38% efficiency is not considered in this calculation. All of the electrons produced must pass through the electrolytic cell; they simply require a higher than optimum voltage to do so, leading to resistance heating (which consumes some of the electrical energy).

(b) total energy \[
= 4.5 \text{ V} \times 8.00 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1.00 \times 10^5 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ J}}{1 \text{ V} \cdot \text{C}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.3 \times 10^7 \text{ kJ}
\]

\[
\text{mass coal} = 1.3 \times 10^7 \text{ kJ electricity} \times \frac{1 \text{ kJ heat}}{0.35 \text{ kJ electricity}} \times \frac{1 \text{ g C}}{32.8 \text{ kJ}} \times \frac{1 \text{ g coal}}{0.85 \text{ g C}} \times \frac{1 \text{ metric ton}}{10^6 \text{ g}} = 1.3 \text{ metric tons of coal}
\]

69. (M) We begin by rewriting Equation 21.25 for the electrolysis of Al₂O₃(s) with n = 12 e⁻.

\[
3 \text{ C(s)} + 2 \text{ Al}_2\text{O}_3(s) \rightarrow 4 \text{ Al(s)} + 3 \text{ CO}_2(g)
\]

\[
\Delta G^\circ = 4(0 \text{ kJ/mol}) + 3(-394 \text{ kJ}) - [3(0 \text{ kJ/mol}) + 2(-1520 \text{ kJ/mol})] = +1858 \text{ kJ}
\]

\[
\Delta G^\circ = 1.858 \times 10^6 \text{ J} = -nF \text{E}^\circ = -12 \text{ mole e}^-(96,485 \text{ C/mol e}^-)E^\circ
\]

\[
E^\circ = -1.605 \text{ V} \quad \text{Note: this is just an estimate because } \Delta G^\circ \text{ values are at 298 K, whereas the reaction occurs at a temperature that is much higher than 298 K.}
\]

If the oxidation of C(s) to CO₂(g) did not occur, then the cell reaction would just be the reverse of the formation reaction of Al₂O₃ with n = 6 e⁻.

\[
E^\circ = \Delta E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{1.520 \times 10^6 \text{ J}}{6 \text{ mole e}^- \times 96485 \text{ C/mole e}^-} = -2.626 \text{ V}
\]

70. (M) It would not be unreasonable to predict that Raoult’s law holds under these circumstances. This is predicated on the assumption, of course, that Pb(NO₃)₂ is completely ionized in aqueous solution.
Thus, there are 97 mol H\textsubscript{2}O in every 100 mol solution. The remaining 3 moles are 1 mol Pb\textsuperscript{2+} and 2 mol NO\textsubscript{3}\textsuperscript{−}. Thus there is 1 mol Pb(NO\textsubscript{3})\textsubscript{2} for every 97 mol H\textsubscript{2}O. Compute the mass of Pb(NO\textsubscript{3})\textsubscript{2} in 100 g H\textsubscript{2}O.

\[
\text{mass}_{\text{Pb(NO}_3\text{)}_2} = 100.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol Pb(NO}_3\text{)}_2}{97 \text{ mol H}_2\text{O}} \times \frac{331.2 \text{ g Pb(NO}_3\text{)}_2}{1 \text{ mol Pb(NO}_3\text{)}_2} = 19 \text{ g Pb(NO}_3\text{)}_2
\]

If we did not assume complete ionization of Pb(NO\textsubscript{3})\textsubscript{2}, we would obtain 3 moles of unionized Pb(NO\textsubscript{3})\textsubscript{2} in solution for every 97 moles of H\textsubscript{2}O. Then there would be 57 g Pb(NO\textsubscript{3})\textsubscript{2} dissolved in 100 g H\textsubscript{2}O. A handbook gives the solubility as 56 g Pb(NO\textsubscript{3})\textsubscript{2}/100 g H\textsubscript{2}O, indicating only partial dissociation or, more probably, extensive re-association into ion pairs, triplets, quadruplets, etc.

71. (M) Considerable energy is required to produce the Pb\textsuperscript{4+} cation—four ionization steps, one for the removal of each electron. It therefore needs quite a large lattice energy to compensate for its energy of production. Both Br\textsuperscript{−} and I\textsuperscript{−} are large anions, and therefore the Pb\textsuperscript{4+}—Br\textsuperscript{−} and Pb\textsuperscript{4+}—I\textsuperscript{−} interionic distances are long. But lattice energy depends on the charge of the cation (which is quite large) multiplied by the charge of the anion (which is reasonably small) divided by the square of the interionic distance (long, as we have said). Thus, we predict a small lattice energy that is insufficient to stabilize the Pb\textsuperscript{4+} cation. We would predict, however, that PbF\textsubscript{4} and PbCl\textsubscript{4} (both with small anions) and PbO\textsubscript{2} and PbS\textsubscript{2} (both with small, highly charged anions) would be stable compounds. In addition, notice that \(E^\circ \{\text{Pb}^{4+}|\text{Pb}^{2+}\} = 1.5 \text{ V (from Table 21-6)}\) is sufficient to oxidize Br\textsuperscript{−} to Br\textsubscript{2} and I\textsuperscript{−} to I\textsubscript{2}, since \(E^\circ \{\text{Br}_2|\text{Br}^{-}\} = +1.065 \text{ V and } E^\circ \{\text{I}_2|\text{I}^{-}\} = +0.535 \text{ V. Thus, even if PbI}_4 \text{ or PbBr}_4 \text{ could be prepared they would be thermodynamically unstable.}

72. (M) \(\text{Na}_2\text{B}_4\text{O}_7\cdot10 \text{ H}_2\text{O(s)} + 6 \text{ CaF}_2(s) + 8 \text{ H}_2\text{SO}_4(aq) \rightarrow 4 \text{ BF}_3(aq) + 6 \text{ CaSO}_4(aq) + 17 \text{ H}_2\text{O(l)} + 2 \text{ NaHSO}_4(aq)\)

73. (D) (a) 1.00 M NH\textsubscript{4}Cl is a somewhat acidic solution due to hydrolysis of NH\textsubscript{4}\textsuperscript{+}(aq); MgCO\textsubscript{3} should be most soluble in this solution. The remaining two solutions are buffer solutions, and the 0.100 M NH\textsubscript{3}—1.00 M NH\textsubscript{4}Cl buffer is more acidic of the two. In this solution, MgCO\textsubscript{3} has intermediate solubility. MgCO\textsubscript{3} is least soluble in the most alkaline solution, namely, 1.00 M NH\textsubscript{3}—1.00 M NH\textsubscript{4}Cl.

\[
\begin{align*}
\text{MgCO}_3(s) & \rightleftharpoons \text{Mg}^{2+}(aq) + \text{CO}_3^{2-}(aq) & K_{sp} = 3.5 \times 10^{-8} \\
\text{NH}_4^+(aq) + \text{OH}^−(aq) & \rightleftharpoons \text{NH}_3(aq) + \text{H}_2\text{O(l)} & 1/K_1 = 1/1.8 \times 10^{-5} \\
\text{CO}_3^{2−}(aq) + \text{H}_3\text{O}^+(aq) & \rightleftharpoons \text{HCO}_3^−(aq) + \text{H}_2\text{O(l)} & 1/K_2 = 1/4.7 \times 10^{-11} \\
2 \text{H}_2\text{O(l)} & \rightleftharpoons \text{H}_5\text{O}^+(aq) + \text{OH}^−(aq) & K_w = 1.0 \times 10^{-14} \\
\text{MgCO}_3(s) + \text{NH}_4^+(aq) & \rightleftharpoons \text{Mg}^{2+} + \text{HCO}_3^−(aq) + \text{NH}_3(aq)
\end{align*}
\]
Chapter 21: Chemistry of the Main-Group Elements I: Groups 1, 2, 13, and 14

\[
K = \frac{K_{sp} \times K_w}{K_b \times K_2} = \frac{3.5 \times 10^{-8} \times 1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 4.7 \times 10^{-11}} = 4.1 \times 10^{-7}
\]

In 1.00 M NH₄Cl

Reaction: \( \text{MgCO}_3(s) \) + \( \text{NH}_4^+(aq) \) ⇌ \( \text{Mg}^{2+}(aq) + \text{HCO}_3^-(aq) + \text{NH}_3(aq) \)

Initial: \(-\) \(1.00 \text{ M}\) \(0 \text{ M}\) \(0 \text{ M}\) \(0 \text{ M}\)

Changes: \(-\) \(-x \text{ M}\) \(+x \text{ M}\) \(+x \text{ M}\) \(+x \text{ M}\)

Equil: \(-\) \((1.00 - x) \text{ M}\) \(x \text{ M}\) \(x \text{ M}\) \(x \text{ M}\)

\[
K = \frac{[\text{Mg}^{2+}] [\text{HCO}_3^-] [\text{NH}_3]}{[\text{NH}_4^+]} = \frac{x \cdot x \cdot x}{1.00 - x} \approx \frac{x^3}{1.00}
\]

\[x = \sqrt[3]{4.1 \times 10^{-7}} = 7.4 \times 10^{-3} \text{ M} = \text{molar solubility of MgCO}_3 \text{ in 1.00 M NH}_4\text{Cl}
\]

\((x << 1.00 \text{ M}, \text{ thus the approximation was valid})\)

(b) In 1.00 M NH₃–1.00 M NH₄Cl

Reaction: \( \text{MgCO}_3(s) \) + \( \text{NH}_4^+(aq) \) ⇌ \( \text{Mg}^{2+}(aq) + \text{HCO}_3^-(aq) + \text{NH}_3(aq) \)

Initial: \(-\) \(1.00 \text{ M}\) \(0 \text{ M}\) \(0 \text{ M}\) \(1.00 \text{ M}\)

Changes: \(-\) \(-x \text{ M}\) \(+x \text{ M}\) \(+x \text{ M}\) \(+x \text{ M}\)

Equil: \(-\) \((1.00 - x) \text{ M}\) \(x \text{ M}\) \(+x\text{M}\) \((1.00 + x) \text{ M}\)

\[
K = \frac{[\text{Mg}^{2+}] [\text{HCO}_3^-] [\text{NH}_3]}{[\text{NH}_4^+]} = \frac{x \cdot x \cdot (1.00 + x)}{1.00 - x} \approx \frac{x^2 \cdot 1.00}{1.00}
\]

\[x = \sqrt{4.1 \times 10^{-7}} = 6.4 \times 10^{-4} \text{ M} = \text{molar solubility of MgCO}_3 \text{ in 1.00 M NH}_3-1.00 \text{ M NH}_4\text{Cl}
\]

\((x << 1.00 \text{ M}, \text{ thus the approximation was valid})\)

(c) In 0.100 M NH₃–1.00 M NH₄Cl

Reaction: \( \text{MgCO}_3(s) \) + \( \text{NH}_4^+(aq) \) ⇌ \( \text{Mg}^{2+}(aq) + \text{HCO}_3^-(aq) + \text{NH}_3(aq) \)

Initial: \(-\) \(1.00 \text{ M}\) \(0 \text{ M}\) \(0 \text{ M}\) \(0.100 \text{ M}\)

Changes: \(-\) \(-x \text{ M}\) \(+x \text{ M}\) \(+x \text{ M}\) \(+x \text{ M}\)

Equil: \(-\) \((1.00 - x) \text{ M}\) \(x \text{ M}\) \(+x\text{M}\) \((0.100 + x) \text{ M}\)

\[
K = \frac{[\text{Mg}^{2+}] [\text{HCO}_3^-] [\text{NH}_3]}{[\text{NH}_4^+]} = \frac{x \cdot x \cdot (0.100 + x)}{1.00 - x} \approx \frac{x^2 \cdot 0.100}{1.00}
\]

\[x = \sqrt[7]{\frac{4.1 \times 10^{-7}}{0.100}} = 2.0 \times 10^{-3} \text{ M} = \text{solubility of MgCO}_3 \text{ in 0.100 M NH}_3-1.00 \text{ M NH}_4\text{Cl}
\]

\((x \text{ is 2 \% of 0.100 M, so the approximation was valid})\)
74. (M) If the value of the equilibrium constant for the reaction is quite large, then the conversion will be almost complete. We write the net ionic equation and then add the two solubility reactions to obtain the net ionic equation for the conversion. The equilibrium constants are multiplied together to give the equilibrium constant for the conversion.

Net ionic equation: \[ \text{Ca(OH)}_2(s) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{CaCO}_3(s) + 2 \text{OH}^-(aq) \]

\[ \text{Ca(OH)}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{OH}^-(aq) \]

\[ K_{sp} = 5.5 \times 10^{-6} \]

\[ \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{CaCO}_3(s) \]

\[ 1/K_{sp} = 1/2.8 \times 10^{-9} \]

\[ \text{Ca(OH)}_2(s) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{CaCO}_3(s) + 2 \text{OH}^-(aq) \]

\[ K_{\text{overall}} = \frac{5.5 \times 10^{-6}}{2.8 \times 10^{-9}} = 2.0 \times 10^{3} \]

Because \( K_{\text{overall}} > 1000 \), the conversion is substantially complete.

75. (M) The density of each metal depends on two factors: its atomic size and the masses of the individual atoms. Density is thus, proportional to the atomic mass divided by the cube of the atomic radius. We calculate this ratio for each of the elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Mass</th>
<th>Atomic Radius</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>6.941 g/mol</td>
<td>1.52 Å</td>
<td>4.58</td>
</tr>
<tr>
<td>Na</td>
<td>22.99 g/mol</td>
<td>1.86 Å</td>
<td>12.1</td>
</tr>
<tr>
<td>K</td>
<td>39.10 g/mol</td>
<td>2.27 Å</td>
<td>16.3</td>
</tr>
</tbody>
</table>

We see that the calculated ratios follow the same pattern as the densities: Na > K > Li, thus explaining why Na has a higher density than both Li and K.

76. (M) We would expect MgO(s) to have a larger value of lattice energy than MgS(s) because of the smaller interionic distance in MgO(s).

**Lattice energy of MgO:**

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Enthalpy of formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(s) + O₂(g) → MgO(s)</td>
<td>( \Delta H^\circ = -6.02 \times 10^2 \text{ kJ} )</td>
<td></td>
</tr>
<tr>
<td>Mg(s) sublimation</td>
<td>Mg(s) → Mg(g)</td>
<td>( \Delta H_{\text{sub}} = +146 \text{ kJ} )</td>
</tr>
<tr>
<td>Mg(g) ionization</td>
<td>Mg(g) → Mg⁺(g) + e⁻</td>
<td>( \Delta I_1 = +737.7 \text{ kJ} )</td>
</tr>
<tr>
<td>Mg(g) ionization</td>
<td>Mg⁺(g) → Mg²⁺(g) + e⁻</td>
<td>( \Delta I_2 = +1451 \text{ kJ} )</td>
</tr>
<tr>
<td>( \frac{1}{2} ) O₂(g) dissociation</td>
<td>½ O₂(g) → O(g)</td>
<td>( \text{DE} = \frac{1}{2} \times 497.4 = 248.7 \text{ kJ} )</td>
</tr>
<tr>
<td>O(g) electron affinity</td>
<td>O(g) + e⁻ → O⁻(g)</td>
<td>( \text{EA}_1 = -141 \text{ kJ} )</td>
</tr>
<tr>
<td>O(g) electron affinity</td>
<td>O⁻(g) + e⁻ → O²⁻(g)</td>
<td>( \text{EA}_2 = +744 \text{ kJ} )</td>
</tr>
<tr>
<td>Lattice energy</td>
<td>Mg²⁺(g) + O²⁻(g) → MgO(s)</td>
<td>L.E = -3789 kJ (see below)</td>
</tr>
</tbody>
</table>
L.E = -602 kJ – 146 kJ – 737.7 kJ – 1451 kJ – 248.7 kJ + 141 kJ – 744 kJ = -3789 kJ

**Lattice energy of MgS:**

Enthalpy of formation: Mg(s) + S(g) → MgS(s) \( \Delta H_f^0 = -3.46 \times 10^3 \) kJ

Sublimation of Mg(s): Mg(s) → Mg(g) \( \Delta H_{sub} = +146 \) kJ

Ionization of Mg(g): Mg(g) → Mg\(^+\) (g) + e\(^-\) \( \Delta I_1 = +737.7 \) kJ

Ionization of Mg(g): Mg\(^+\) (g) → Mg\(^2+\) (g) + e\(^-\) \( \Delta I_2 = +1451 \) kJ

\( \frac{1}{2} \) Dissociation of S\(_2\)(g): \( \frac{1}{2} \) S\(_{\text{rhombic}}\) (g) → S(g) \( \Delta E = \frac{1}{2} \times 557.6 = 278.8 \) kJ

S(g) electron affinity: S(g) + e\(^-\) → S\(^-\) (g) \( \text{EA}_1 = -200.4 \) kJ

S(g) electron affinity: S\(^-\) (g) + e\(^-\) → S\(^2-\) (g) \( \text{EA}_2 = +456 \) kJ

Lattice energy: Mg\(^{2+}\) (g) + S\(^2-\) (g) → MgS(s) \( \text{L.E} = -3215 \) kJ

L.E = -346 kJ – 146 kJ – 737.7 kJ – 1451 kJ – 248.7 kJ + 141 kJ – 744 kJ = -3215 kJ

77. (M) In one unit cell, there are \( \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4 \) fulleride ions and \( \frac{1}{4} \times 12 + 1 + 8 = 12 \) alkali metal ions. The ratio of cations to anions is 12:4 = 3:1, and so the fulleride ion is C\(_{60}\)^{3-} and the empirical formula is M\(_3\)C\(_{60}\).

**FEATURE PROBLEMS**

78. (D) Li(s) → Li(g) \( 159.4 \) kJ; (Using \( \Delta H_{rxn}^o = \Sigma \Delta H_f^o \text{products} - \Sigma \Delta H_f^o \text{reactants} \) in Appendix D)

Li(g) → Li\(^+\) (g) + e\(^-\) \( 520.2 \) kJ; (Data given in Table 21.2, Chapter 21)

Li\(^+\) (g) → Li\(^+\) (aq) \( -506 \) kJ; (Provided in the question)

Li(s) → Li\(^+\) (aq) + e\(^-\) \( 174 \) kJ

1/2 H\(_2\)(g) → H(g) \( 218.0 \) kJ (Using \( \Delta H_{rxn}^o = \Sigma \Delta H_f^o \text{products} - \Sigma \Delta H_f^o \text{reactants} \) in Appendix D)

H(g) → H\(^+\) (g) + e\(^-\) \( 1312 \) kJ (Use R\(_H(\text{N}_A)\)Bohr theory = \( 2.179 \times 10^{-18} \) J(6.022 \times 10^{23}))

H\(^+\) (g) → H\(^+\) (aq) \( -1079 \) kJ (Provided in the question)

1/2 H\(_2\)(g) → H\(^+\) (aq) + e\(^-\) \( 451 \) kJ

(a) Li(s) + H\(^+\) (aq) → Li\(^+\) (aq) + 1/2 H\(_2\)(g) \( \Delta H^o = 174 \) kJ – 451 kJ = -277 kJ \( \approx \Delta G^o \)

\[ E_{\text{ox}}^o = \frac{\Delta G^o}{-nF} = \frac{-277 \times 10^3 \text{J}}{-1 \text{ mol e}^- \times \left( 96,485 \frac{\text{C}}{\text{mol e}^-} \right)} = 2.87 \frac{\text{J}}{\text{C}} = 2.87 \text{ V} \]
In this reaction, Li(s) is being oxidized to Li⁺(aq). If we wish to compare this to the reduction potential for Li⁺(aq) being reduced to Li(s), we would have to reverse the reaction, which would result in the same answer only as a negative value. Alternatively, we can change the sign of the oxidation potential (Li → Li⁺) to -2.87 V for the reduction potential for Li⁺ → Li.

(it appears as -3.040 V in Appendix D; here, we see much better agreement.)

\[ \Delta S = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}} \]

\[ = [1 \text{ mol } (13.4 \frac{\text{J}}{\text{Kmol}}) + 0.5 \text{ mol } (130.7 \frac{\text{J}}{\text{Kmol}})] - [1 \text{ mol } (29.12 \frac{\text{J}}{\text{Kmol}}) + 1 \text{ mol } (0 \frac{\text{J}}{\text{Kmol}})] = 49.6 \frac{\text{J}}{\text{K}} \]

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -277 \text{ kJ} - 298.15 \text{ K} \left(49.6 \frac{\text{J}}{\text{K}}\right) \times \frac{1 \text{kJ}}{1000 \text{J}} = -292 \times 10^3 \text{ J} \]

\[ E_{\text{ox}}^\circ = \frac{\Delta G^\circ}{-nF} = -\frac{-292 \times 10^3 \text{ J}}{-1 \text{ mol e}^- \left(96,485 \frac{\text{C}}{\text{mol e}^-}\right)} = 3.03 \frac{\text{J}}{\text{C}} = 3.03 \text{ V} \]

As mentioned in part (a) of this question, we have calculated the oxidation potential for the half reaction Li(s) → Li⁺(aq) + e⁻. The reduction potential is the reverse half-reaction and has a potential of -3.03 V. This is in excellent agreement with -3.040 V given in Appendix D.

79. (D) (a)  
\[ \frac{0.438 \text{ mol NaCl}}{L} \times \frac{58.443 \text{ g NaCl}}{1 \text{ mol NaCl}} = 26.6 \text{ g NaCl} \]
\[ \frac{0.0512 \text{ mol MgCl}_2}{L} \times \frac{95.211 \text{ g MgCl}_2}{1 \text{ mol MgCl}_2} = 4.87 \text{ g MgCl}_2 \]

\[ 18 \text{ tbs NaHCO}_3 \times \frac{10 \text{ g NaHCO}_3}{1 \text{ tbs NaHCO}_3} = 180 \text{ g NaHCO}_3 \]
\[ 10 \text{ tbs NaCl} \times \frac{10 \text{ g NaCl}}{1 \text{ tbs NaCl}} = 100 \text{ g NaCl} \]
\[ 8 \text{ tsp MgSO}_4 \cdot 7 \text{ H}_2\text{O} \times \frac{1 \text{ tbs}}{3 \text{ tsp}} \times \frac{10 \text{ g MgSO}_4 \cdot 7 \text{ H}_2\text{O}}{1 \text{ tbs MgSO}_4 \cdot 7 \text{ H}_2\text{O}} = 27 \text{ g MgSO}_4 \cdot 7 \text{ H}_2\text{O} \]

(b) The pH of the lake will be determined by the amphiprotic bicarbonate ion, (HCO₃⁻), which hydrolyzes in water (\( K_a_1 = 4.4 \times 10^{-7} \) or \( pK_a_1 = 6.36 \) and \( K_a_2 = 4.7 \times 10^{-11} \) or \( pK_a_2 = 10.33 \)). We saw earlier (Chapter 18, Exercise 100) that the pH of a solution of alanine, a diprotic species, is independent of concentration (as long as it is...
relatively concentrated). The pH = \left(\frac{pK_{a1} + pK_{a2}}{2}\right) = \left(\frac{6.36 + 10.33}{2}\right) = 8.35

This is not as basic as the actual pH of the lake. Addition of borax (sodium salt of boric acid) would aid in increasing the pH of the solution (since borax contains an anion that is the conjugate base of a weak acid). The lake may be more basic due to the presence of other basic anions, namely carbonate ion \((\text{CO}_3^{2-})\).

\((\text{e})\) Tufa are mostly made of calcium carbonate \((\text{CaCO}_3(s))\). Since they form near underwater springs, one must assume that the springs have a high concentration of calcium ion \((\text{Ca}^{2+}(aq))\). We then couple this with the fact that the lake has a high salinity (high carbonate and bicarbonate ion content). We can thus conclude that two major reactions are most likely responsible for the formation of a tufa (see below):

\[
\begin{align*}
\text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) & \rightarrow \text{CaCO}_3(s) \\
\text{Ca}^{2+}(aq) + 2 \text{HCO}_3^-(aq) & \rightarrow \text{Ca}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\end{align*}
\]

SELF-ASSESSMENT EXERCISES

80. (E) 
(a) A dimer is a chemical or biological entity consisting of two structurally similar subunits called monomers, which are joined by bonds, which can be strong or weak.
(b) An adduct is a product of a direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components, with formation of two chemical bonds and a net reduction in bond multiplicity in at least one of the reactants.
(c) Calcination is a thermal treatment process applied to ores and other solid materials in order to bring about a thermal decomposition, phase transition, or removal of a volatile fraction.
(d) An amphoteric oxide is an oxide that can act both as an acid and as a base. An example is aluminum oxide \((\text{Al}_2\text{O}_3)\).
(e) A three-center two-electron bond is an electron deficient chemical bond where three atoms share two electrons. The combination of three atomic orbitals form three molecular orbitals: one bonding, one non-bonding, and one anti-bonding. The two electrons go into the bonding orbital, resulting in a net bonding effect and constituting a chemical bond among all three atoms.

81. (E) 
(a) A diagonal relationship exists between certain pairs of diagonally adjacent elements in the second and third periods of the periodic table. These pairs (Li and Mg, Be and Al, B and Si, etc.) exhibit similar properties. For example boron and silicon are both semiconductors.
(b) One way to prepare deionized water is by passing it through an ion exchange column. The latter is composed of insoluble chemicals which remove both positive and negative ions from water.
(c) Thermite is a pyrotechnic composition of a metal powder and a metal oxide, which produces an aluminothermic reaction known as a thermite reaction.
(d) The inert pair effect is the tendency of the outermost $s$ electrons to remain un-ionized or unshared in post-transition compounds.

82. (E) (a) A peroxide is a compound containing an oxygen-oxygen single bond. Superoxide is an anion with the chemical formula $O_2^-$.  
(b) Calcium oxide (CaO) is commonly known as burnt lime, lime or quicklime. Calcium hydroxide (Ca(OH)$_2$) on the other hand is commonly known as slaked lime, hydrated lime, or slack lime.  
(c) Soap is an anionic surfactant used in conjunction with water for washing and cleaning. Soap consists of sodium or potassium salts of fatty acids and is obtained by reacting common oils or fats with a strong alkaline solution in a process known as saponification. Detergents, on the other hand, are prepared synthetically.  
(d) A silicate is a compound containing an ion in which one or more central silicon atoms are surrounded by electronegative ligands. Silicones are compounds containing silicon-oxygen and silicon-carbon bonds that have the capability to act as bonding intermediates between glass and organic compounds, and to form polymers with useful properties such as impermeability to water, flexibility and resistance to chemical attack.  
(e) The sol-gel process is a chemical solution deposition technique widely used in the fields of materials science and ceramic engineering. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions.

83. (E) (c) MgO

84. (E) (f) PbO$_2$

85. (M) (a) BCl$_3$NH$_3$(g) (an adduct); (b) KO$_2$(s); (c) Li$_2$O(s); (d) Ba(OH)$_2$(aq) and H$_2$O$_2$(aq); H$_2$O$_2$(aq) slowly disproportionates into H$_2$O(l) and O$_2$(g).

86. (M) The thermite reaction is evidence that aluminum will readily extract oxygen from Fe$_2$O$_3$. Aluminum can be used for making products that last and for structural purposes, because aluminum develops a coating of Al$_2$O$_3$ that protects the metal beneath it.

87. (M) (b) Ca(s) and CaH$_2$(s)

88. (M) (a) Li$_2$CO$_3$(s)$\xrightarrow{\Delta}$Li$_2$O(s)+CO$_2$(g)  
(b) CaCO$_3$(s)+2HCl(aq)$\rightarrow$CaCl$_2$(aq)+H$_2$O(l)+CO$_2$(g)  
(c) 2Al(s)+2NaOH(aq)+6H$_2$O(l)$\rightarrow$2Na[Al(OH)$_4$](aq)+2H$_2$(g)  
(d) BaO(s)+H$_2$O(l)$\rightarrow$Ba(OH)$_2$(aq, limited solubility)  
(e) 2Na$_2$O$_2$(s)+2CO$_2$(g)$\rightarrow$2Na$_2$CO$_3$(s)+O$_2$(g)
89.  (M)  (a)  \( \text{MgCO}_3(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \)  
   (b)  \( 2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g) \) followed by the reaction in Exercise 82(c)  
   (c)  \( 2\text{NaCl}(s) + \text{H}_2\text{SO}_4(\text{concd.},aq) \xrightarrow{\Delta} \text{Na}_2\text{SO}_4(s) + 2\text{HCl}(g) \)  

90.  (M)  (a)  \( \text{K}_2\text{CO}_3(aq) + \text{Ba(OH)}_2(aq) \rightarrow \text{BaCO}_3(s) + 2\text{KOH}(aq) \)  
   (b)  \( \text{Mg(HCO}_3)_2(aq) \xrightarrow{\Delta} \text{MgCO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \)  
   (c)  \( \text{SnO(s)} + \text{C(s)} \xrightarrow{\Delta} \text{Sn(l)} + \text{CO(g)} \)  
   (d)  \( \text{CaF}_2(s) + \text{H}_2\text{SO}_4(\text{concd.},aq) \xrightarrow{\Delta} \text{CaSO}_4(s) + 2\text{HF}(g) \)  
   (e)  \( \text{NaHCO}_3(s) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \)  
   (f)  \( \text{PbO}_2(s) + 4\text{HBr}(aq) \rightarrow \text{PbBr}_2(s) + \text{Br}_2(l) + 2\text{H}_2\text{O}(l) \)  
   (g)  \( \text{SiF}_4(g) + 4\text{Na}(l) \rightarrow \text{Si(s)} + 4\text{NaF}(s) \)  

91.  (M)  \( \text{CaSO}_4 \times 2\text{H}_2\text{O}(s) + (\text{NH}_4)_2\text{CO}_3(aq) \rightarrow \text{CaCO}_3(s) + (\text{NH}_4)_2\text{SO}_4(aq) + 2\text{H}_2\text{O}(l) \). The reaction proceeds to the right because \( K_{\text{sp}} \) for \( \text{CaCO}_3 < K_{\text{sp}} \) for \( \text{CaSO}_4 \)  

92.  (M)  (a)  \( 2\text{B(OH)}_3(s) \rightarrow 2\text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g) \)  
   (b)  no reaction  
   (c)  \( \text{CaSO}_4 \times 2\text{H}_2\text{O}(s)[\text{gypsum}] \xrightarrow{\Delta} \text{CaSO}_4 \times \frac{1}{2} \text{H}_2\text{O}(s)[\text{plaster of Paris}] + \frac{3}{2} \text{H}_2\text{O}(g) \)  

93.  (M)  (a)  \( \text{Pb(NO}_3)_2(aq) + 2\text{NaHCO}_3(aq) \rightarrow \text{PbCO}_3(s) + 2\text{NaNO}_3(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \)  
   (b)  \( \text{Li}_2\text{O(s)} + (\text{NH}_4)_2\text{CO}_3(aq) \rightarrow \text{Li}_2\text{CO}_3(s) + 2\text{NH}_3(g) + \text{H}_2\text{O}(l) \). \( \text{Li}_2\text{O} \) is the anhydride of the strong base \( \text{LiOH} \), which reacts with acidic \( \text{NH}_4^+ \) to liberate \( \text{NH}_3 \). \( \text{Li}_2\text{CO}_3 \) is only slightly soluble, so most of it precipitates.  
   (c)  \( \text{H}_2\text{SO}_4(aq) + \text{Ba}_2\text{O}_2(aq) \rightarrow \text{H}_2\text{O}_2(aq) + \text{BaSO}_4(s) \). The forward reaction is favored by the formation of a precipitate, \( \text{BaSO}_4(s) \).  
   (d)  \( 2\text{PbO}(s) + \text{Ca(OCl)}_2(aq) \rightarrow 2\text{PbCl}_2(aq) + \text{CaO}_2(s) \). Hypochlorite ion oxidizes lead(II) oxide to lead(IV) oxide.  

94.  (M)  (a)  Stalactites are primarily \( \text{CaCO}_3 \). (b)  Gypsum is \( \text{CaSO}_4 \times 2\text{H}_2\text{O} \). (c)  Suspension of \( \text{BaSO}_4 \) in water. (d)  \( \text{Al}_2\text{O}_3(s) \) with \( \text{Fe}^{3+} \) and \( \text{Ti}^{4+} \) replacing some \( \text{Al}^{3+} \) in the crystal structure.  

95.  (M)  Dolomite, molar mass of 184.4 g/mol yields 2 mol \( \text{CO}_2(g) \) per mol of dolomite on decomposition. The \( 5.00 \times 10^3 \) kg sample yields \( 5.42 \times 10^4 \) mol \( \text{CO}_2 \) which, under the stated conditions occupies a volume of \( 1.27 \times 10^3 \) m\(^3\).