(9) I. Give balanced half-reactions and a balanced overall equation for the following reaction in acidic solution:

\[
\text{MnO}_4^- + H_2S \rightarrow \text{Mn}^{2+} + \text{SO}_4^{2-}
\]

\[
3 \times \frac{5e^- + 8H_3O^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4H_2O + 8H_2O}{10H_2O + 4H_2O + H_2S \rightarrow \text{SO}_4^{2-} + 10H_3O^+ + 8e^-} = \frac{14H_2O + H_2S \rightarrow \text{SO}_4^{2-} + 10H_3O^+ + 8e^-}{70H_2O + 5H_2S \rightarrow 5\text{SO}_4^{2-} + 52H_3O^+ + 40e^-}
\]

\[
3 \times \frac{14H_2O + H_2S \rightarrow \text{SO}_4^{2-} + 10H_3O^+ + 8e^-}{40e^- + 60H_3O^+ + 8\text{MnO}_4^- \rightarrow 8\text{Mn}^{2+} + 26H_2O} = \frac{14H_3O^+ + 5H_2S + 8\text{MnO}_4^- \rightarrow 5\text{SO}_4^{2-} + 8\text{Mn}^{2+} + 26H_2O}{3}
\]
(9) II. a. Boron is used in control rods in nuclear power reactors because it is a good neutron absorber. When the isotope $^{10}\text{B}$ captures a neutron, an alpha particle is emitted. What other atom is formed? Write a balanced nuclear equation.

\[
3 \overset{10}{\text{B}} + {\overset{0}{\text{n}}} \rightarrow \overset{4}{\overline{\text{a}}} + \overset{7}{\text{h}}
\]

b. There are two common decay pathways among the heavy elements. What elements would decay to form actinium by each of these two pathways? Write balanced nuclear equations. [HINT: Since you do not know the specific isotopes, you may ignore the masses.]

\[
\overset{88}{\text{Ra}} \rightarrow \overset{89}{\text{Ac}} + \overset{0}{\beta}\beta\text{ decay}
\]

\[
\overset{91}{\text{Pa}} \rightarrow \overset{89}{\text{Ac}} + \overset{4}{\beta}\alpha\text{ decay}
\]

(10) III. $^{239}\text{Pu}$ is the fissionable isotope produced in breeder reactors. It is also produced in ordinary nuclear plants and in weapons tests. It is extremely poisonous and has a half-life of 24,100 years. How many years are required for the amount of $^{239}\text{Pu}$ in a sample to be reduced to 1.0% of its original value?

\[
\ln \left( \frac{N_t}{N_0} \right) = -\lambda t
\]

\[
\ln (0.01) = - (2.87 \times 10^{-5} \text{ yr}^{-1})t
\]

\[
t = \frac{-\ln(0.01)}{2.87 \times 10^{-5} \text{ yr}^{-1}} = 160,459 \text{ or } 160,000 \text{ yr}
\]

(15) IV. Zirconium is used in the fuel rods of most nuclear power plants. The following half-cell reduction potential applies to aqueous acidic solution:

\[
\text{ZrO}_2 (s) + 4 \text{H}_2\text{O}^{+} (aq) + 4e^{-} \rightarrow \text{Zr} (s) + 6 \text{H}_2\text{O} (l) \quad E^\circ = -1.43 \text{ V}
\]

a. Can zirconium reduce water to hydrogen? Why or why not? Write a balanced overall equation for the reaction.

\[
\begin{align*}
\text{Zr} + 6\text{H}_2\text{O} & \rightarrow \text{ZrO}_2 + 4\text{H}_3\text{O}^{+} + 4e^{-} \\
E^\circ &= +1.43 \text{ V}
\end{align*}
\]

\[
\begin{align*}
2\text{Zr} + 2\text{H}_2\text{O} & \rightarrow 2\text{H}_2 + 2\text{ZrO}_2 \\
E^\circ &= 0.0 \text{ (by definition)}
\end{align*}
\]

b. Calculate $K$ for the reaction in part a at 25°C.

\[
\begin{align*}
\varepsilon &= \frac{E^\circ}{n} - \frac{0.0591}{n} \log Q \\
\varepsilon &= E^\circ - \frac{RT}{nF} \ln Q
\end{align*}
\]

\[
\varepsilon = \phi \text{ and } Q = K
\]

\[
\varepsilon^\circ = \frac{0.0591}{n} \log K
\]

\[
\frac{3}{2} \log K = 4 \times 96.9
\]

\[
K = 2.88 \times 10^4
\]
(20) V. a. Write balanced half-cell reactions and the overall reaction for the reaction in a lead-acid battery.

\[
Pb\,_{(s)} + \text{SO}_4^{2-}\,_{(aq)} \rightarrow PbSO_4\,_{(s)} + 2e^- \\
2e^- + 4H_3O^+ + PbO_2\,_{(s)} + \text{SO}_4^{2-}\,_{(aq)} \rightarrow PbSO_4\,_{(s)} + 6H_2O \\
\]

\[
Pb + PbO_2 + 4H_3O^+ + 2\text{SO}_4^{2-} \rightarrow 2\, PbSO_4 + 6H_2O \\
\]

b. What quantity of charge (in coulombs) is a fully charged 12 v lead-acid storage battery capable of furnishing if the lead available for reaction at the anode weighs 10 kg and there is excess PbO_2?

\[
(10,000\, g\, Pb) \left(\frac{6\, mol\, Pb}{207\, g}\right) = 48.3\, mol\, Pb \left(\frac{4\, \text{mol electrons}}{1\, \text{mol Pb}}\right) \left(\frac{96,485\, C}{\text{mol electrons}}\right) = 9.3 \times 10^6\, C
\]

(17) VI. In the presence of a catalyst, SO_2\, (g) reacts with excess oxygen to give SO_3\, (g):

\[
\text{SO}_2\, (g) + \frac{1}{2}\, \text{O}_2\, (g) \rightarrow \text{SO}_3\, (g)
\]

It is observed that tripling the SO_2 concentration increases the rate by a factor of 3, but tripling the SO_3 concentration decreases the rate by a factor of 1.7 (\(= \sqrt{3}\)). The rate is insensitive to the oxygen concentration, as long as an excess is present.

a. Write the rate expression for this reaction.

\[
\text{Rate} = k [\text{SO}_2]^\frac{1}{2} [\text{SO}_3]^\frac{1}{2} \\
\]

b. What are the units for the rate constant, k?

\[
\text{M}^{\frac{1}{2}}\, \text{s}^{-1}\, \text{or}\, \frac{\text{mol}^{\frac{1}{2}}\, \text{L}^{\frac{1}{2}}\, \text{s}^{-1}}{}
\]

c. If [SO_2] is multiplied by 2 and [SO_3] by 4, what change in the rate will be observed?

\[
\text{Rate} \propto [\text{SO}_2]^\frac{1}{2} [\text{SO}_3]^\frac{1}{2} \propto \frac{2}{4} = 1
\]

d. The equation for the rate constant, k, as a function of T is \(k = Ae^{(Ea/RT)}\). Identify each of the quantities on the right hand side of this equation. Indicate for each quantity whether it will likely increase, decrease, or remain the same for the reaction with a catalyst compared to the reaction without the catalyst.

- A frequency factor \(\propto E_a\) can increase
- Proporportionality constant \(E_a\) will decrease
- Energy of activation \(E_a\) will decrease
- R gas constant \(R\) no change
- Kelvin temperature \(T\) no change
(10) VII. Write the rate law that corresponds to the following reaction mechanism. Be sure to eliminate intermediates from the answers. For credit, you must show the entire derivation.

\[ 2A + B \xrightarrow{k_1} D \] (fast equilibrium)
\[ D + B \xrightarrow{k_2} E + F \] (slow)
\[ F \xrightarrow{k_3} G \] (slow)

\[ \text{Rate of reaction} = \text{rate of rate limiting (slowest) step} = k_2 [D][B] \]

To eliminate \([D]\) from the expression:

\[ \text{at equil.} \quad \frac{k_2}{k_{-1}} = k_1 [A]^2[B] \]

\[ [D] = \frac{k_1}{k_{-1}} [A]^2[B] \]

Substituting into the first equation:

\[ \text{Rate} = \frac{k_2 k_1}{k_{-1}} [A]^2[B]^2 \]

(10) VIII. a. Define nuclear fusion and nuclear fission.

2 **Nuclear fusion** is the combination of two smaller nuclei to produce a larger nucleus.

2 **Nuclear fission** is the breaking apart of a large nucleus into smaller nuclei.

b. Why are fusion processes often called thermonuclear reactions?

2 For the particles to have sufficient kinetic energy, the reactions must be run at very high temperatures.

c. A fusion power plant would have some distinct advantages over the present fission plants. Name two such advantages.

2 Reactants are not radioactive.

2 Products are not radioactive.

2 Reactants are widely available.

d. What is the major technological problem which prevents the use of fusion reactions in nuclear power plants?

2 It requires a huge amount of energy to start the reaction.

2 It is difficult to contain reactions at these temperatures.