Multiple Choice Answers and Explanations

1. D. The standard free energy of formation is the free energy change of a forma-
tion reaction, one that forms one mole of a substance from its component ele-
ments in their most stable forms. Solid sodium and gaseous diatomic chlorine
are the most stable forms of those elements.

2. C. A negative ΔS denotes a change from a more random state to one of more
order. In general, solids are more ordered than liquids, which are more ordered
than gases. Liquid water is more ordered than steam. When solid NaCl dis-
solves in liquid water, it dissociates into more random aqueous ions in the liquid
phase. Carbon dioxide gas is more random than solid magnesium carbonate.

3. A. All solids melt endothermically (where $\Delta H°$ is positive) because solids must
absorb energy to overcome the strong attractive forces that hold the particles
together. All solids melt with an increase in entropy (where $\Delta S°$ is positive) be-
cause liquids are more random than solids.

4. D. The fundamental thermodynamic condition at equilibrium is when ΔG is zero.
At equilibrium, the equation $\Delta G = \Delta H - T\Delta S$ becomes $\Delta H = T\Delta S$. Because
T is the absolute temperature in Kelvin, it must be positive. A positive temperature
can only exist when the signs of ΔH and ΔS are both negative or both positive.

5. E. Entropy is the degree of randomness or disorder of a system. Gases have
higher entropies than liquids, which have higher entropies than solids. Addi-
tionally, when comparing substances having the same phase, the more complex
the substance, the higher its entropy because complex substances have more
possible rotational and vibrational modes of motion.

6. A. ΔG is positive for non-thermodynamically favored processes. When deter-
mining qualitatively the sign of ΔG, pose the question: left on its own, does it
happen? If the answer is yes, the process is thermodynamically favored and the
sign of ΔG is negative. If the answer is no, the process is not favored thermo-
dynamically and the sign of ΔG is positive. Ice will not melt spontaneously at
$-10°C$ unless it is under pressure. ΔG is negative for all the other processes
listed because left on their own, they will happen spontaneously.

7. E. $O(g)$ is not the most stable form of oxygen, so its standard free energy is nonzero. Standard heats of formation, $\Delta H°_f$, and standard free energies of formation, $\Delta G°_f$, are zero for elements in their most stable form at 25°C. The most stable forms of oxygen, potassium, and bromine are $O_2(g)$, $K(s)$, and $Br_2(l)$, respectively. The third law of thermodynamics states that the entropy, S, of a pure crystalline substance at absolute zero is zero. $Ca(s)$ at 0 K has $S = 0$.

8. A. In general, gases have more entropy than liquids and liquids have more entropy than solids. Phase changes from gas to liquid, gas to solid, and liquid to solid all are exothermic (release heat to the environment) and occur with a decrease in entropy (result in less random, more ordered products). The decomposition of liquid water to form gaseous products is endothermic and takes place with a large increase in entropy.

9. C. The given reaction is the formation reaction for $CO_2(g)$. Therefore, the values for $\Delta H°_f$ and $\Delta G°_f$ for $CO_2(g)$ are the same as the values for $\Delta H°_{rxn}$ and $\Delta G°_{rxn}$ for $CO_2(g)$. $\Delta S°_{rxn}$ can be calculated using the equation, $\Delta G°_{rxn} = \Delta H°_{rxn} - T\,\Delta S°_{rxn}$. The given Celsius temperature must be converted to Kelvin. $\Delta H°_f$ and $\Delta G°_f$ for neither $C(solid\ graphite)$ nor $O_2(g)$ are necessary because both are elements in their most stable forms, so their values are each, by definition, zero.

10. B. Use the equation, $\Delta G = \Delta H - T\Delta S$, to guide your thinking. To be thermodynamically favored requires a negative ΔG and that can only be achieved if the absolute value of the negative ΔH term is larger than the absolute value of the $T\Delta S$ term. At low temperatures, ΔG will be negative. At high temperatures, it will be positive. There is a temperature at which ΔG will be zero and the system will reach equilibrium.

Free Response Answers

1. a. $\Delta G° = -RT \ln K = -(8.314\ J/mol\ K)(25 + 273\ K) \ln (0.281)$
       $= 3145\ J/mol = 3.15\ kJ/mol$

    b. $x\ kJ/mol = (193\ J/g)(160\ g/mol)(1\ kJ/1000\ J) = 30.9\ kJ/mol$

    c. $\Delta G° = \Delta H° - T\Delta S°$
       $\Delta S° = (\Delta H° - \Delta G°)/T = (30.9 - 3.15)/298\ K$
       $= .0931\ kJ/mol\ K = 93.1\ J/mol\ K$

   d. The boiling point is the temperature at which the equilibrium vapor pressure of bromine equals the external pressure. Because the system is at equilibrium, $\Delta G = 0$.

$$\Delta G = \Delta H - T\Delta S$$
$$0 = 30.9\ kJ/mol - T(.0931\ kJ/mol\ K)$$
$$T = 30.9/.0931 = 332\ K$$

   e. $K_p = P_{Br_2}(g)$
$$K_p = (0.281\ atm)(760\ torr/atm) = 214\ torr$$

2. a. $\Delta H°_{rxn} = \Sigma\ \Delta H°_{f\,products} - \Sigma\ \Delta H°_{f\,reactants}$
$$= -(-285.85) + (-277.69) = +8.16\ kJ/mol$$

   b. $\Delta S°rxn = \Sigma S°_{products} - \Sigma S°_{reactants}$
$$= +160.7 - 69.91 - 2(130.6) - 2(5.740) = -181.9\ J/mol\ K$$

   c. $\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn}$
$$\Delta G°_{rxn} = +8.16\ kJ/mol - (298K)(-181.9\ J/mol\ K)$$
$$(1\ kJ/1000\ J) = +62.4\ kJ/mol$$
$$\Delta G° = -RT \ln K$$
$$\ln K = -(+62.4\ kJ/mol)/[(8.314\ J/mol\ K)(1\ kJ/1000\ J)$$
$$(298\ K)] = -25.2$$
$$K = e^{-25.2} = 1.14 \times 10^{-11}$$

   d. $K_p = P_{H_2}^{-2}$
$$P_{H_2} = K_p^{-1/2} = (1.14 \times 10^{-11})^{-1/2} = 2.96 \times 10^5\ atm$$

3. This question reviews the concepts learned in Topic 13 and connects them to the material in this topic.

   a. The drawing will look much like the far-right depiction in Figure 13.1, except Ca^{2+} replaces Na^+. Relatively strong ion–dipole attractions occur between the positive calcium ion and the negative ends of the water molecules.

   b. The ion–dipole force between calcium ion and water is stronger than that between sodium ion and water because calcium carries a 2+ charge, whereas sodium's charge is 1+. Coulomb's law states that the force of attraction between two particles is directly proportional to their charges.

   c. Calcium chloride dissolves exothermically as evidenced by the observation that the temperature of the solution increases. Because heat is released, the ion–dipole forces in the solution must be stronger than the ion–ion forces of the solid ionic compound.

   d. The sign of ΔG is negative because the dissolving process happens spontaneously. That is, it is thermodynamically favored.

Your Turn Answers

19.1. a. *Entropy of the system increases when helium is released from a toy balloon because the gas from the balloon mixes with the gases in the atmosphere, causing an increase in randomness or disorder.*

   b.
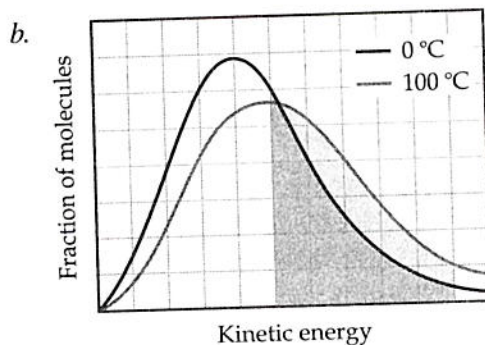
Kinetic energy

   Entropy increases with increasing temperature because the distribution of kinetic energies of the molecules increases.

19.2. *Butane, $CH_3CH_2CH_2CH_3$, has greater entropy than propane, $CH_3CH_2CH_3$, because the molecules of propane are more complex than the molecules of methane.*

   Steam has more entropy than ice because gases are more random and disordered than are solids.

19.3. *Gaseous iodine has a higher standard molar entropy than either liquid or solid iodine because gases are more random than liquids or solids. Liquid iodine has a higher value than solid iodine because liquids are more random than solids.*
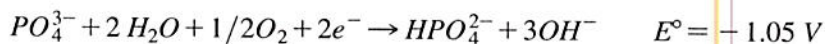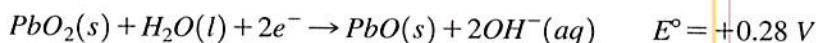
19.4. *A burning campfire is a thermodynamically favored process where ΔG is negative. For the process, ΔH is negative and ΔS is positive, so ΔG is negative at all temperatures. Thus, a burning campfire will never reach equilibrium nor become thermodynamically unfavored.*

Free Response Questions

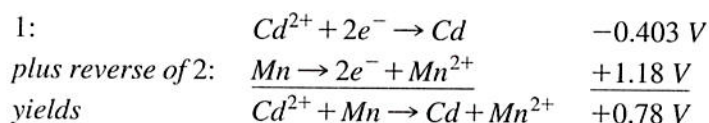1. Suppose that gold and silver half-cells are suitably connected.

   $Au^{3+} + 3e^- \rightarrow Au(s)$ $E° = +1.50$ V

   $Ag^+ + 1e^- \rightarrow Ag(s)$ $E° = +0.80$ V
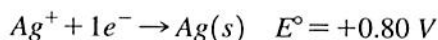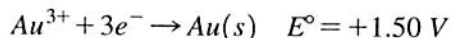
   a. i. Identify the cathode and anode half-reactions.

      ii. Write the overall cell reaction.

      iii. Calculate $E°$ for the cell.

   b. Calculate $\Delta G°$ for the cell.

   c. Calculate the equilibrium constant for the cell reaction at $25°C$.

   d. If $[Ag^+]$ is increased to 1.50 M, will the reaction be more spontaneous or less spontaneous? Will the cell voltage increase, decrease, or remain the same? Justify your answer.

   e. In a separate experiment, how many grams of gold can be plated onto a piece of jewelry if a 1.00 M solution of gold(III) nitrate is suitably electrolyzed for 45 min at 2.50 A?

   f. In yet another experiment, how many minutes are required to plate 1.00 g of silver onto an inert electrode at 1.25 A?

2. Consider the following half-reactions and their standard reduction potentials at $25°C$.

   $PbO_2(s) + H_2O(l) + 2e^- \rightarrow PbO(s) + 2OH^-(aq)$ $E° = +0.28$ V

   $IO_3^- + 2 H_2O + 4 e^- \rightarrow IO^- + 4OH^-$ $E° = +0.56$ V

   $PO_4^{3-} + 2 H_2O + 1/2 O_2 + 2e^- \rightarrow HPO_4^{2-} + 3OH^-$ $E° = -1.05$ V

   a. i. Which two half-reactions when combined will give the voltaic cell with the largest $E°$ for the cell?

      ii. Write the overall cell reaction that would take place.

      iii. Calculate $E°$ for the cell.

   b. Indicate how the E_{cell} will be affected by the following changes. Justify your answers.

      i. If the pH of both the anode and cathode compartments is decreased.

      ii. If $[OH^-]$ is fixed at 1.0 M, $O_2(g)$ is fixed at 1 atm, and all other ion concentrations are changed to 0.10 M.

      iii. If the temperature is increased while all concentrations remain at 1.0 M.
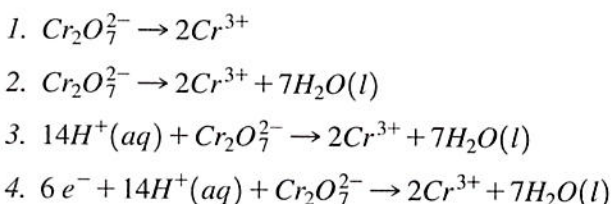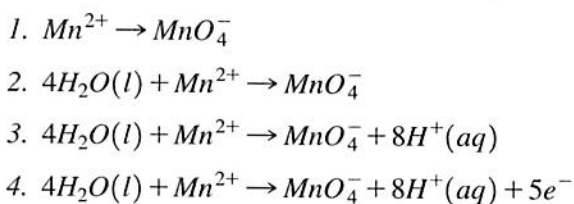
Multiple Choice Answers and Explanations

1. A. *The oxidation numbers of sulfur in CuS, $K_2S_2O_3$, SO_2, and Na_2SO_4 are -2, $+2$, $+4$, and $+6$, respectively. As a monatomic ion in CuS, sulfur has a -2 charge, so its oxidation number is equal to its charge. The oxidation number of each sulfur adds to the oxidation number of each oxygen to equal the charge in the polyatomic ion, $S_2O_3^{2-}$. $(3 \times 2-$ for each oxygen$) + (2 \times 2+$ for each sulfur$) = 2-$. (Note: In $S_2O_3^{2-}$, one sulfur carries a $4+$ oxidation number, whereas the other sulfur is zero, an average of $2+$ for each sulfur.) The oxidation number of sulfur in SO_2 is $4+$ because it adds to the oxidation numbers of each oxygen to equal the zero charge on SO_2. $4 + 2(2-) = 0$. A $6+$ oxidation number for sulfur in SO_4^{2-} adds to the four $2-$ oxidation numbers of oxygen to give a charge of $2-$. $6 + 4(2-) = 2-$.*

2. C. *For an overall reaction to be thermodynamically favored, the $E°_{cell}$ for the reaction must be positive. Half-reaction 1 adds to the reverse of half-reaction 2 to give a positive $E°_{cell}$.*

1:	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403 V
plus reverse of 2:	$Mn \rightarrow 2e^- + Mn^{2+}$	$+1.18$ V
yields	$Cd^{2+} + Mn \rightarrow Cd + Mn^{2+}$	$+0.78$ V

   The other combinations listed all yield a negative $E°_{cell}$.

3. D. *Taking apart the unbalanced equation provides two skeletal half-reactions and each is balanced according to the rules given in Table 20.2:*

   1. *Balance all elements other than H or O.*

   2. *Balance O by adding H_2O as required.*

   3. *Balance H by adding H^+ as required.*

   4. *Balance charge by adding e^- to more positive side.*

   1. $Mn^{2+} \rightarrow MnO_4^-$

   2. $4H_2O(l) + Mn^{2+} \rightarrow MnO_4^-$

   3. $4H_2O(l) + Mn^{2+} \rightarrow MnO_4^- + 8H^+(aq)$

   4. $4H_2O(l) + Mn^{2+} \rightarrow MnO_4^- + 8H^+(aq) + 5e^-$

   1. $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

   2. $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O(l)$

   3. $14H^+(aq) + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O(l)$

   4. $6e^- + 14H^+(aq) + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O(l)$

   Multiplication of the Mn and Cr half-reactions to make the electrons equal requires factors of 6 and 5, respectively. The resulting balanced equation will have a coefficient of 6 for MnO_4^-.

An alternate way to arrive at the answer is to assign oxidation numbers to all the elements and note that Mn changes by five electrons (from 2+ to 7+) and that Cr changes by three electrons (from 6+ to 3+) twice for a total of six electrons. The lowest common multiple of 5 and 6 is 30, so the Mn half-reaction must be multiplied by 6, giving the MnO_4^- a coefficient of 6.

4. C. *Cl displays a 7+ oxidation number in the perchlorate ion, ClO_4^-. Cr is 6+ in CrO_4^{2-}. C is 4+ in CO_2. Oxygen is 2+ in OF_2.*

5. C. *On the basis of their behavior in the presence of hydrochloric acid, Mg is a more active metal than Ag. Thus, Mg will react with Ag^+ ions, but Ag will not react with Mg^{2+}. Also Ag, because it does not react with HCl, does not react with H^+. E cannot be correct because both H_2 and Ag are oxidized.*

6. B. *The Ag half-reaction has the more positive voltage, so it is the reduction. The Mg half-cell is the oxidation and its voltage changes to $+2.37$ V.*
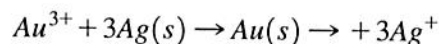
    $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox} = 0.80 + 2.37 = 3.17$ *V*

    (Note: The stoichiometry is not taken into account because voltage is independent of the number of electrons transferred.)

7. B. *Reversing the half-reaction with the most negative voltage and adding it to the other yields: $Mg + Ag^+ \rightarrow Mg^{2+} + Ag$*

8. B. *If the $[Mg^{2+}]$ decreases from its standard concentration of 1.0 M to 0.50 M, Q becomes smaller and the voltage will increase.*

Free Response Answers

1. a. i. *Cathode half-cell reaction:*

        $Au^{3+} + 3e^- \rightarrow Au(s)$ $E^\circ = +1.500$ V

        Anode half-cell reaction: $Ag(s) \rightarrow Ag^+ + 1e^-$ $E^\circ = -0.800$ V
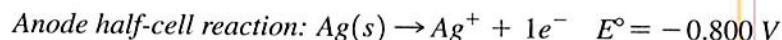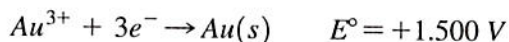
    ii. *Overall cell reaction:*

        $Au^{3+} + 3Ag(s) \rightarrow Au(s) \rightarrow +3Ag^+$

    iii. $E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = +1.50$ V $- 0.800$ V $= 0.700$ V

    b. $\Delta G^\circ = -nFE^\circ = -(3$ mol $e^-)(96{,}500$ C/mol $e^-)$

        $(0.700$ J/C$) = -203$ kJ $(1$ V $= 1$ J/C$)$

    c. $\Delta G^\circ = -RT \ln K$

        -203 kJ $= -(8.314$ J/mol K$)(1$ kJ/1000 J$)(298$ K$) \ln K$

        $\ln K = +81.9$

        $K = e^{+81.9} = 3.7 \times 10^{35}$

d. Because $[Ag^+]$ is a product of the cell reaction, an increase in $[Ag^+]$ will decrease the voltage because Q becomes smaller.

e. $x\,g\,Au = 45\,min\,(60\,s/min)(2.50\,C/s)(1\,mol\,e^-/96{,}500\,C)$
   $(1\,mol\,Au/3\,mol\,e^-)(197\,g/mol) = 4.59\,g$

f. $x\,min = 1.00\,g\,Ag\,(1\,mol/108\,g)(1\,mol\,e^-/1\,mol\,Ag)$
   $(96{,}500\,C/mole\,e^-)(1\,s/1.25\,C)(1\,min/60\,s) = 11.9\,min$

2. a. i. $IO_3^- + 2H_2O + 4\,e^- \rightarrow IO^- + 4OH^-\quad E^\circ_{red} = +0.56\,V$

   $HPO_4^{2-} + 3OH^- \rightarrow PO_4^{3-} + 2\,H_2O + 1/2\,O_2 + 2e^-\quad E^\circ_{ox} = +1.05\,V$

   ii. $2HPO_4^{2-} + 2OH^- + IO_3^- \rightarrow 2PO_4^{3-} + 2H_2O + IO^- + O_2$

   iii. $E^\circ = E^\circ_{ox} + E^\circ_{red} = +1.05\,V + 0.56\,V = +1.61\,V$

   b. i. If the pH of both the anode and cathode compartments is decreased, the net effect will be to decrease $[OH^-]$. The voltage will also decrease because Q will increase making ΔG more positive.

   ii. If $[OH^-]$ is fixed at 1.0 M and all other ion concentrations are changed to 0.10 M, the voltage will remain the same because, other than hydroxide, there are three moles of ions on both sides of the balanced equation.

   iii. If the temperature is increased while all concentrations remain at 1.0 M, the voltage will drop because the exothermic reaction will become less thermodynamically favorable. The reaction is exothermic because the voltage is positive.

Your Turn Answers

20.1. $SO_4^{2-}, 6+$; $S_2O_3^{2-}, 4+$ and 0; $S^{2-}, 2-$; $SO_3^{2-}, 4+$; $SCN^-, 2-$; $S, 0$; $SO_2, 4+$; $SO_3, 6+$. Oxidation number and charge are equivalent only in sulfide, S^{2-}, and sulfur, S.

20.2. A redox reaction is one in which one reactant transfers electrons to another reactant. As a result, the oxidation numbers of some of the atoms in the reactants change as they become products. The reactant that gains electrons is reduced. N_2 is the substance reduced because it gains electrons. The oxidation number of N changes from 0 to $3-$ as N_2 becomes NH_3. The reactant that loses electrons is oxidized. H_2 is oxidized because the oxidation number of H changes from 0 to $1+$ as it changes from H_2 to NH_3.

20.3. a. Molarity of $KMnO_4$ solution $=$ moles $KMnO_4$/liters solution
   $= (20.65\,g/158.0\,g/mol)/0.500\,L = 0.2614\,M\,KMnO_4$

   b. $5H_2O_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5O_2(g) + 2Mn^{2+}(aq)$
   $+ 8H_2O(l)$

   c. Follow the mole road from 25.00 mL of $KMnO_4$ solution to molarity of H_2O_2 solution: