

Exercises

Review Questions

1. Define oxidation and reduction and explain the basic procedure for balancing redox reactions.
2. Explain the difference between a voltaic (or galvanic) electrochemical cell and an electrolytic one.
3. Which reaction (oxidation or reduction) occurs at the anode of a voltaic cell? What is the sign of the anode? Do electrons flow toward or away from the anode?
4. Which reaction (oxidation or reduction) occurs at the cathode of a voltaic cell? What is the sign of the cathode? Do electrons flow toward or away from the cathode?
5. Explain the purpose of a salt bridge in an electrochemical cell.
6. Which unit is used to measure the magnitude of electrical current? Which unit is used to measure the magnitude of a potential difference? Explain how electrical current and potential difference differ.
7. What is the definition of the standard cell potential (E_{cell}°)? What does a large positive standard cell potential imply about the spontaneity of the redox reaction occurring in the cell? What does a negative standard cell potential imply about the reaction?
8. Describe the basic features of a cell diagram (or line notation) for an electrochemical cell.
9. Why do some electrochemical cells employ inert electrodes such as platinum?
10. Describe the standard hydrogen electrode (SHE) and explain its use in determining standard electrode potentials.
11. How is the cell potential of an electrochemical cell (E_{cell}°) related to the potentials of the half-cells?
12. Does a large positive electrode potential indicate a strong oxidizing agent or a strong reducing agent? What about a large negative electrode potential?
13. Is a spontaneous redox reaction obtained by pairing any reduction half-reaction with one listed above it or with one listed below it in Table 19.1?
14. How can Table 19.1 be used to predict whether or not a metal will dissolve in HCl? In HNO_3 ?
15. Explain why E_{cell}° , $\Delta G_{\text{rxn}}^{\circ}$, and K are all interrelated.
16. Does a redox reaction with a small equilibrium constant ($K < 1$) have a positive or a negative E_{cell}° ? Does it have a positive or a negative $\Delta G_{\text{rxn}}^{\circ}$?
17. How does E_{cell} depend on the concentrations of the reactants and products in the redox reaction occurring in the cell? What effect does increasing the concentration of a reactant have on E_{cell} ? Increasing the concentration of a product?
18. Use the Nernst equation to show that $E_{\text{cell}} = E_{\text{cell}}^{\circ}$ under standard conditions.
19. What is a concentration electrochemical cell?
20. What are the anode and cathode reactions in a common dry-cell battery? In an alkaline battery?
21. What are the anode and cathode reactions in a lead–acid storage battery? What happens when the battery is recharged?
22. What are the three common types of portable rechargeable batteries, and how does each one work?
23. What is a fuel cell? What is the most common type of fuel cell, and what reactions occur at its anode and cathode?
24. The anode of an electrolytic cell must be connected to which terminal—positive or negative—of the power source?
25. What species is oxidized, and what species is reduced in the electrolysis of a pure molten salt?
26. If an electrolytic cell contains a mixture of species that can be oxidized, how do you determine which species will actually be oxidized? If it contains a mixture of species that can be reduced, how do you determine which one will actually be reduced?
27. Why does the electrolysis of an aqueous sodium chloride solution produce hydrogen gas at the cathode?
28. What is overvoltage in an electrochemical cell? Why is it important?
29. How is the amount of current flowing through an electrolytic cell related to the amount of product produced in

the redox reaction:

30. What is corrosion? Why is corrosion only a problem for some metals (such as iron)?
31. Explain the role of each of the following in promoting corrosion: moisture, electrolytes, and acids.
32. How can the corrosion of iron be prevented?

Problems by Topic

Note: Answers to all odd-numbered Problems can be found in [Appendix III](#). Exercises in the Problems by Topic section are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.

Balancing Redox Reactions

33. Balance each redox reaction occurring in acidic aqueous solution.

- a. $\text{K}(s) + \text{Cr}^{3+}(aq) \rightarrow \text{Cr}(s) + \text{K}^+(aq)$
- b. $\text{Al}(s) + \text{Fe}^{2+}(aq) \rightarrow \text{Al}^{3+}(aq) + \text{Fe}(s)$
- c. $\text{BrO}_3^-(aq) + \text{N}_2\text{H}_4(g) \rightarrow \text{Br}^-(aq) + \text{N}_2(g)$

34. Balance each redox reaction occurring in acidic aqueous solution.

- a. $\text{Zn}(s) + \text{Sn}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Sn}(s)$
- b. $\text{Mg}(s) + \text{Cr}^{3+}(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{Cr}(s)$
- c. $\text{MnO}_4^-(aq) + \text{Al}(s) \rightarrow \text{Mn}^{2+}(aq) + \text{Al}^{3+}(aq)$

35. Balance each redox reaction occurring in acidic aqueous solution.

- a. $\text{PbO}_2(s) + \text{I}^-(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{I}_2(s)$
- b. $\text{SO}_3^{2-}(aq) + \text{MnO}_4^-(aq) \rightarrow \text{SO}_4^{2-}(aq) + \text{Mn}^{2+}(aq)$
- c. $\text{S}_2\text{O}_3^{2-}(aq) + \text{Cl}_2(g) \rightarrow \text{SO}_4^{2-}(aq) + \text{Cl}^-(aq)$

36. Balance each redox reaction occurring in acidic aqueous solution.

- a. $\text{I}^-(aq) + \text{NO}_2^-(aq) \rightarrow \text{I}_2(s) + \text{NO}(g)$
- b. $\text{ClO}_4^-(aq) + \text{Cl}^-(aq) \rightarrow \text{ClO}_3^-(aq) + \text{Cl}_2(g)$
- c. $\text{NO}_3^-(aq) + \text{Sn}^{2+}(aq) \rightarrow \text{Sn}^{4+}(aq) + \text{NO}(g)$

37. Balance each redox reaction occurring in basic aqueous solution.

- a. $\text{H}_2\text{O}_2(aq) + \text{ClO}_2(aq) \rightarrow \text{ClO}_2^-(aq) + \text{O}_2(g)$
- b. $\text{Al}(s) + \text{MnO}_4^-(aq) \rightarrow \text{MnO}_2(s) + \text{Al}(\text{OH})_4^-(aq)$
- c. $\text{Cl}_2(g) \rightarrow \text{Cl}^-(aq) + \text{ClO}^-(aq)$

38. Balance each redox reaction occurring in basic aqueous solution.

- a. $\text{MnO}_4^-(aq) + \text{Br}^-(aq) \rightarrow \text{MnO}_2(s) + \text{BrO}_3^-(aq)$
- b. $\text{Ag}(s) + \text{CN}^-(aq) + \text{O}_2(g) \rightarrow \text{Ag}(\text{CN})_2^-(aq)$
- c. $\text{NO}_2^-(aq) + \text{Al}(s) \rightarrow \text{NH}_3(g) + \text{AlO}_2^-(aq)$

Voltaic Cells, Standard Cell Potentials, and Direction of Spontaneity

39. Sketch a voltaic cell for each redox reaction. Label the anode and cathode and indicate the half-reaction that occurs at each electrode and the species present in each solution. Also indicate the direction of electron flow.

- a. $2 \text{Ag}^+(aq) + \text{Pb}(s) \rightarrow 2 \text{Ag}(s) + \text{Pb}^{2+}(aq)$
- b. $2 \text{ClO}_2(g) + 2 \text{I}^-(aq) \rightarrow 2 \text{ClO}_2^-(aq) + \text{I}_2(s)$
- c. $\text{O}_2(g) + 4 \text{H}^+(aq) + 2 \text{Zn}(s) \rightarrow 2 \text{H}_2\text{O}(l) + 2 \text{Zn}^{2+}(aq)$

40. Sketch a voltaic cell for each redox reaction. Label the anode and cathode and indicate the half-reaction that occurs at each electrode and the species present in each solution. Also indicate the direction of electron flow.

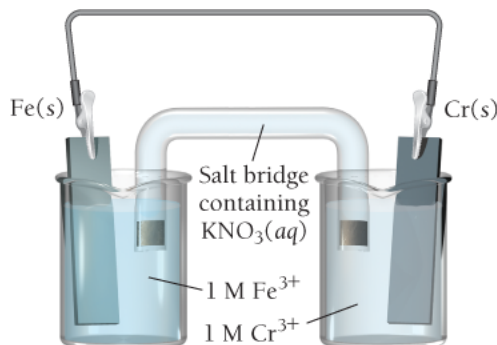
- a. $\text{Ni}^{2+}(aq) + \text{Mg}(s) \rightarrow \text{Ni}(s) + \text{Mg}^{2+}(aq)$
- b. $2 \text{H}^+(aq) + \text{Fe}(s) \rightarrow \text{H}_2(g) + \text{Fe}^{2+}(aq)$
- c. $2 \text{NO}_3^-(aq) + 8 \text{H}^+(aq) + 3 \text{Cu}(s) \rightarrow 2 \text{NO}(g) + 4 \text{H}_2\text{O}(l) + 3 \text{Cu}^{2+}(aq)$

41. Calculate the standard cell potential for each of the electrochemical cells in [Problem 39](#).

42. Calculate the standard cell potential for each of the electrochemical cells in [Problem 40](#).

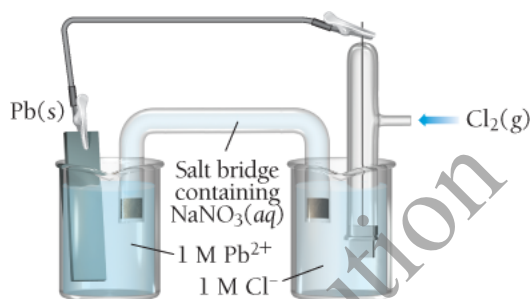
43. Consider the voltaic cell:

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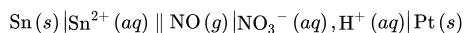
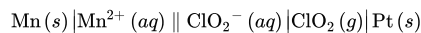


- Determine the direction of electron flow and label the anode and the cathode.
- Write a balanced equation for the overall reaction and calculate E_{cell}° .
- Label each electrode as negative or positive.
- Indicate the direction of anion and cation flow in the salt bridge.

44. Consider the voltaic cell:



- Determine the direction of electron flow and label the anode and the cathode.
- Write a balanced equation for the overall reaction and calculate E_{cell}° .
- Label each electrode as negative or positive.
- Indicate the direction of anion and cation flow in the salt bridge.

45. Use line notation to represent each electrochemical cell in **Problem 39**.46. Use line notation to represent each electrochemical cell in **Problem 40**.47. Make a sketch of the voltaic cell represented by the line notation. Write the overall balanced equation for the reaction and calculate E_{cell}° .48. Make a sketch of the voltaic cell represented by the line notation. Write the overall balanced equation for the reaction and calculate E_{cell}° .

49. Determine whether or not each redox reaction occurs spontaneously in the forward direction.

- $\text{Ni}(s) + \text{Zn}^{2+}(aq) \rightarrow \text{Ni}^{2+}(aq) + \text{Zn}(s)$
- $\text{Ni}(s) + \text{Pb}^{2+}(aq) \rightarrow \text{Ni}^{2+}(aq) + \text{Pb}(s)$
- $\text{Al}(s) + 3 \text{Ag}^+(aq) \rightarrow \text{Al}^{3+}(aq) + 3 \text{Ag}(s)$
- $\text{Pb}(s) + \text{Mn}^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{Mn}(s)$

50. Determine whether each redox reaction occurs spontaneously in the forward direction.

- $\text{Ca}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Ca}(s) + \text{Zn}^{2+}(aq)$
- $2 \text{Ag}^+(aq) + \text{Ni}(s) \rightarrow 2 \text{Ag}(s) + \text{Ni}^{2+}(aq)$
- $\text{Fe}(s) + \text{Mn}^{2+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Mn}(s)$
- $2 \text{Al}(s) + 3 \text{Pb}^{2+}(aq) \rightarrow 2 \text{Al}^{3+}(aq) + 3 \text{Pb}(s)$

51. Which metal could you use to reduce Mn^{2+} ions but not Mg^{2+} ions?52. Which metal can be oxidized with an Sn^{2+} solution but not with an Fe^{2+} solution?

53. Determine whether or not each metal dissolves in 1 M HCl. For those metals that dissolve, write a

balanced redox reaction showing what happens when the metal dissolves.

- a. Al
- b. Ag
- c. Pb

54. Determine whether or not each metal dissolves in 1 M HCl. For those metals that dissolve, write a balanced redox reaction showing what happens when the metal dissolves.

- a. Cu
- b. Fe
- c. Au

55. Determine whether or not each metal dissolves in 1 M HNO₃. For those metals that dissolve, write a balanced redox reaction showing what happens when the metal dissolves.

- a. Cu
- b. Au

56. Determine whether or not each metal dissolves in 1 M HIO₃. For those metals that dissolve, write a balanced redox equation for the reaction that occurs.

- a. Au
- b. Cr

57. Calculate E_{cell}° for each balanced redox reaction and determine if the reaction is spontaneous as written.

- a. $2 \text{Cu}(s) + \text{Mn}^{2+}(aq) \rightarrow 2 \text{Cu}^{+}(aq) + \text{Mn}(s)$
- b. $\text{MnO}_2(s) + 4 \text{H}^{+}(aq) + \text{Zn}(s) \rightarrow \text{Mn}^{2+}(aq) + 2 \text{H}_2\text{O}(l) + \text{Zn}^{2+}(aq)$
- c. $\text{Cl}_2(g) + 2 \text{F}^{-}(aq) \rightarrow \text{F}_2(g) + 2 \text{Cl}^{-}(aq)$

58. Calculate E_{cell}° for each balanced redox reaction and determine if the reaction is spontaneous as written.

- a. $\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 \text{Ag}(s) \rightarrow 4 \text{OH}^{-}(aq) + 4 \text{Ag}^{+}(aq)$
- b. $\text{Br}_2(l) + 2 \text{I}^{-}(aq) \rightarrow 2 \text{Br}^{-}(aq) + \text{I}_2(s)$
- c. $\text{PbO}_2(s) + 4 \text{H}^{+}(aq) + \text{Sn}(s) \rightarrow \text{Pb}^{2+}(aq) + 2 \text{H}_2\text{O}(l) + \text{Sn}^{2+}(aq)$

59. Which metal cation is the best oxidizing agent?

- a. Pb^{2+}
- b. Cr^{3+}
- c. Fe^{2+}
- d. Sn^{2+}

60. Which metal is the best reducing agent?

- a. Mn
- b. Al
- c. Ni
- d. Cr

Cell Potential, Free Energy, and the Equilibrium Constant

61. Use tabulated electrode potentials to calculate $\Delta G_{\text{rxn}}^{\circ}$ for each reaction at 25 °C.

- a. $\text{Pb}^{2+}(aq) + \text{Mg}(s) \rightarrow \text{Pb}(s) + \text{Mg}^{2+}(aq)$
- b. $\text{Br}_2(l) + 2 \text{Cl}^{-}(aq) \rightarrow 2 \text{Br}^{-}(aq) + \text{Cl}_2(g)$
- c. $\text{MnO}_2(s) + 4 \text{H}^{+}(aq) + \text{Cu}(s) \rightarrow \text{Mn}^{2+}(aq) + 2 \text{H}_2\text{O}(l) + \text{Cu}^{2+}(aq)$

62. Use tabulated electrode potentials to calculate $\Delta G_{\text{rxn}}^{\circ}$ for each reaction at 25 °C.

- a. $2 \text{Fe}^{3+}(aq) + 3 \text{Sn}(s) \rightarrow 2 \text{Fe}(s) + 3 \text{Sn}^{2+}(aq)$
- b. $\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 2 \text{Cu}(s) \rightarrow 4 \text{OH}^{-}(aq) + 2 \text{Cu}^{2+}(aq)$
- c. $\text{Br}_2(l) + 2 \text{I}^{-}(aq) \rightarrow 2 \text{Br}^{-}(aq) + \text{I}_2(s)$

63. Calculate the equilibrium constant for each of the reactions in **Problem 61**.

64. Calculate the equilibrium constant for each of the reactions in **Problem 62**.

65. Calculate the equilibrium constant for the reaction between $\text{Ni}^{2+}(aq)$ and $\text{Cd}(s)$ (at 25 °C).

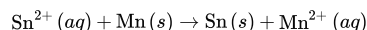
66. Calculate the equilibrium constant for the reaction between $\text{Fe}^{2+}(aq)$ and $\text{Zn}(s)$ (at 25 °C).

67. Calculate $\Delta G_{\text{rxn}}^{\circ}$ and E_{cell}° for a redox reaction with $n = 2$ that has an equilibrium constant of $K = 25$ (at 25 °C).

68. Calculate $\Delta G_{\text{rxn}}^{\circ}$ and E_{cell}° for a redox reaction with $n = 3$ that has an equilibrium constant of $K = 0.050$ (at 25 °C).

Nonstandard Conditions and the Nernst Equation

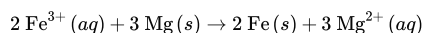
69. A voltaic cell employs the following redox reaction:



Calculate the cell potential at 25 °C under each set of conditions.

- standard conditions
- $[\text{Sn}^{2+}] = 0.0100 \text{ M}$; $[\text{Mn}^{2+}] = 2.00 \text{ M}$
- $[\text{Sn}^{2+}] = 2.00 \text{ M}$; $[\text{Mn}^{2+}] = 0.0100 \text{ M}$

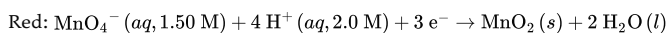
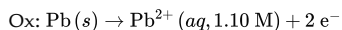
70. A voltaic cell employs the redox reaction:



Calculate the cell potential at 25 °C under each set of conditions.

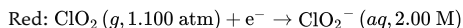
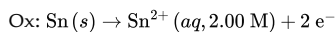
- standard conditions
- $[\text{Fe}^{3+}] = 1.0 \times 10^{-3} \text{ M}$; $[\text{Mg}^{2+}] = 2.50 \text{ M}$
- $[\text{Fe}^{3+}] = 2.00 \text{ M}$; $[\text{Mg}^{2+}] = 1.5 \times 10^{-3} \text{ M}$

71. An electrochemical cell is based on these two half-reactions:



Calculate the cell potential at 25 °C.

72. An electrochemical cell is based on these two half-reactions:



Calculate the cell potential at 25 °C.

73. A voltaic cell consists of a Zn/Zn^{2+} half-cell and a Ni/Ni^{2+} half-cell at 25 °C. The initial concentrations of Ni^{2+} and Zn^{2+} are 1.50 M and 0.100 M, respectively.

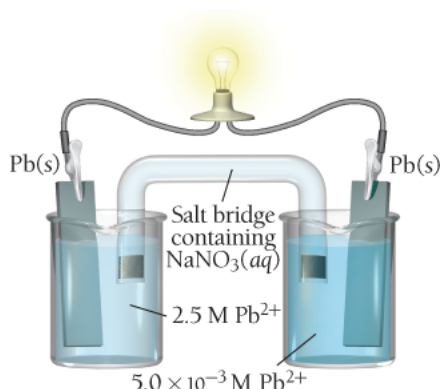
- What is the initial cell potential?
- What is the cell potential when the concentration of Ni^{2+} has fallen to 0.500 M?
- What are the concentrations of Ni^{2+} and Zn^{2+} when the cell potential falls to 0.45 V?

74. A voltaic cell consists of a Pb/Pb^{2+} half-cell and a Cu/Cu^{2+} half-cell at 25 °C. The initial concentrations of Pb^{2+} and Cu^{2+} are 0.0500 M and 1.50 M, respectively.

- What is the initial cell potential?
- What is the cell potential when the concentration of Cu^{2+} has fallen to 0.200 M?
- What are the concentrations of Pb^{2+} and Cu^{2+} when the cell potential falls to 0.35 V?

75. Make a sketch of a concentration cell employing two Zn/Zn^{2+} half-cells. The concentration of Zn^{2+} in one of the half-cells is 2.0 M, and the concentration in the other half-cell is $1.0 \times 10^{-3} \text{ M}$. Label the anode and the cathode and indicate the half-reaction occurring at each electrode. Also indicate the direction of electron flow.

76. Consider the concentration cell:



- Label the anode and cathode.
- Indicate the direction of electron flow.
- Indicate what happens to the concentration of Pb^{2+} in each half-cell.

c. indicate what happens to the concentration of I^- in each half-cell.

77. A concentration cell consists of two Sn/Sn^{2+} half-cells. The cell has a potential of 0.10 V at 25 °C.

What is the ratio of the Sn^{2+} concentrations in the two half-cells?

78. A Cu/Cu^{2+} concentration cell has a voltage of 0.22 V at 25 °C. The concentration of Cu^{2+} in one of the half-cells is $1.5 \times 10^{-3} \text{ M}$. What is the concentration of Cu^{2+} in the other half-cell? (Assume the concentration in the unknown cell to be the *lower* of the two concentrations.)

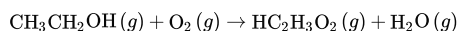
Batteries, Fuel Cells, and Corrosion

79. Determine the optimum mass ratio of Zn to MnO_2 in an alkaline battery.

80. What mass of lead sulfate is formed in a lead–acid storage battery when 1.00 g of Pb undergoes oxidation?

81. Refer to the tabulated values of ΔG_f° in Appendix IIB to calculate E_{cell}° for a fuel cell that employs the reaction between methane gas (CH_4) and oxygen to form carbon dioxide and gaseous water.

82. Refer to the tabulated values of ΔG_f° in Appendix IIB to calculate E_{cell}° for a fuel cell that employs the following reaction: (ΔG_f° for $\text{HC}_2\text{H}_3\text{O}_2(g) = -374.2 \text{ kJ/mol}$)



83. Determine whether or not each metal, if coated onto iron, would prevent the corrosion of iron.

a. Zn

b. Sn

c. Mn

84. Determine whether or not each metal, if coated onto iron, would prevent the corrosion of iron.

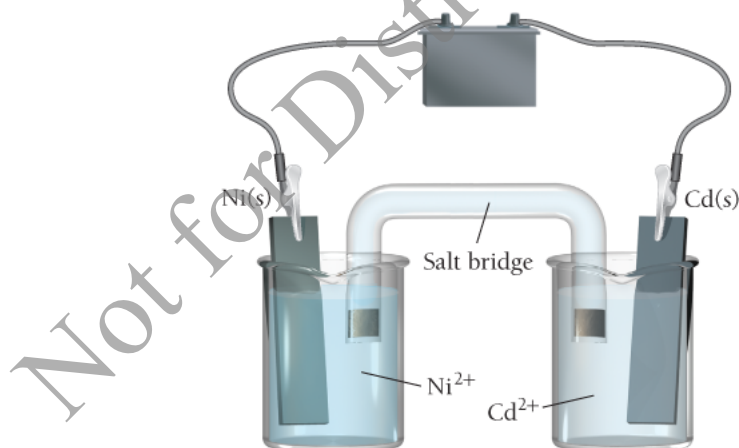
a. Mg

b. Cr

c. Cu

Electrolytic Cells and Electrolysis

85. Consider the electrolytic cell:



a. Label the anode and the cathode and indicate the half-reactions occurring at each.

b. Indicate the direction of electron flow.

c. Label the terminals on the battery as positive or negative and calculate the minimum voltage necessary to drive the reaction.

86. Draw an electrolytic cell in which Mn^{2+} is reduced to Mn and Sn is oxidized to Sn^{2+} . Label the anode and cathode, indicate the direction of electron flow, and write an equation for the half-reaction occurring at each electrode. What minimum voltage is necessary to drive the reaction?

87. Write equations for the half-reactions that occur in the electrolysis of molten potassium bromide.

88. Which products are obtained in the electrolysis of molten NaI?

89. Write equations for the half-reactions that occur in the electrolysis of a mixture of molten potassium bromide and molten lithium bromide.

90. Which products are obtained in the electrolysis of a molten mixture of KI and KBr?

91. Write equations for the half-reactions that occur at the anode and cathode for the electrolysis of each aqueous solution:

- a. $\text{NaBr}(aq)$
- b. $\text{PbI}_2(aq)$
- c. $\text{Na}_2\text{SO}_4(aq)$

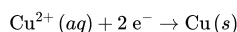
92. Write equations for the half-reactions that occur at the anode and cathode for the electrolysis of each aqueous solution:

- a. $\text{Ni}(\text{NO}_3)_2(aq)$
- b. $\text{KCl}(aq)$
- c. $\text{CuBr}_2(aq)$

93. Make a sketch of an electrolytic cell that electroplates copper onto other metal surfaces. Label the anode and the cathode and indicate the reactions that occur at each.

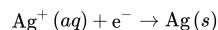
94. Make a sketch of an electrolytic cell that electroplates nickel onto other metal surfaces. Label the anode and the cathode and indicate the reactions that occur at each.

95. Copper can be electroplated at the cathode of an electrolytic cell by the half-reaction:



How much time does it take for 325 mg of copper to be plated at a current of 5.6 A?

96. Silver can be electroplated at the cathode of an electrolytic cell by the half-reaction:



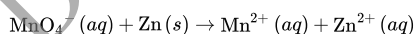
What mass of silver plates onto the cathode if a current of 6.8 A flows through the cell for 72 min?

97. A major source of sodium metal is the electrolysis of molten sodium chloride. What magnitude of current produces 1.0 kg of sodium metal in 1 hour?

98. What mass of aluminum metal can be produced per hour in the electrolysis of a molten aluminum salt by a current of 25 A?

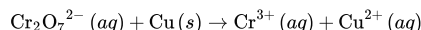
Cumulative Problems

99. Consider the unbalanced redox reaction:



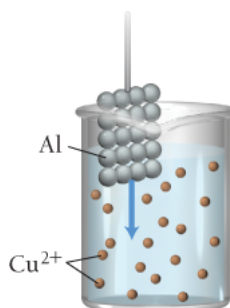
Balance the equation and determine the volume of a 0.500 M KMnO_4 solution required to completely react with 2.85 g of Zn.

100. Consider the unbalanced redox reaction:

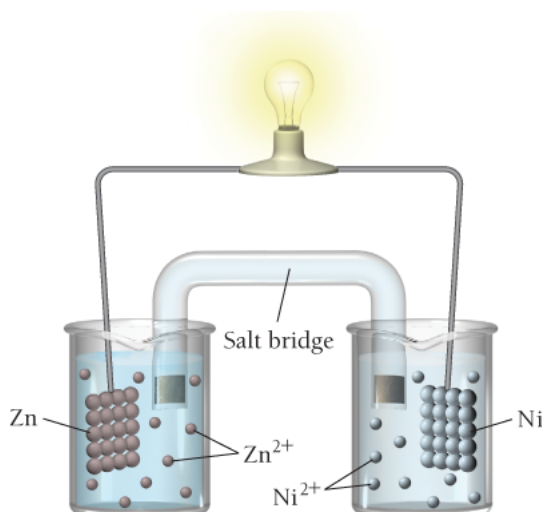
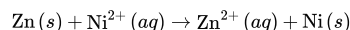


Balance the equation and determine the volume of a 0.850 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution required to completely react with 5.25 g of Cu.

101. Consider the molecular view of an Al strip and Cu^{2+} solution. Draw a similar sketch showing what happens to the atoms and ions after the Al strip is submerged in the solution for a few minutes.



102. Consider the molecular view of an electrochemical cell involving the overall reaction:



Draw a similar sketch of the cell after it has generated a substantial amount of electrical current.

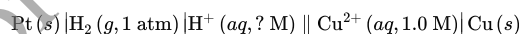
103. Determine whether HI can dissolve each metal sample. If it can, write a balanced chemical reaction showing how the metal dissolves in HI and determine the minimum volume of 3.5 M HI required to completely dissolve the sample.

- a. 2.15 g Al
- b. 4.85 g Cu
- c. 2.42 g Ag

104. Determine if HNO_3 can dissolve each metal sample. If it can, write a balanced chemical reaction showing how the metal dissolves in HNO_3 and determine the minimum volume of 6.0 M HNO_3 required to completely dissolve the sample.

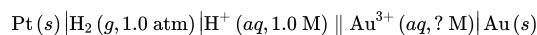
- a. 5.90 g Au
- b. 2.55 g Cu
- c. 4.83 g Sn

105. The cell potential of this electrochemical cell depends on the pH of the solution in the anode half-cell.



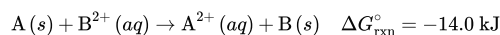
What is the pH of the solution if E_{cell} is 355 mV?

106. The cell potential of this electrochemical cell depends on the gold concentration in the cathode half-cell.



What is the concentration of Au^{3+} in the solution if E_{cell} is 1.22 V?

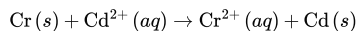
107. Consider the reaction shown here occurring at 25 °C.



Determine the value of E_{cell}° and K for the reaction and complete the table.

$[\text{B}^{2+}]$	$[\text{A}^{2+}]$	Q	E_{cell}	ΔG_{rxn}
1.00	1.00			
1.00	1.00×10^{-4}			
1.0×10^{-4}	1.0			
2.52×10^{-3}	1.0			

108. Consider the reaction shown here occurring at 25 °C.



Determine E_{cell}° , K , and $\Delta G_{\text{rxn}}^{\circ}$ for the reaction and complete the table.

$[\text{Cd}^{2+}]$	$[\text{Cr}^{2+}]$	Q	E_{cell}	ΔG_{rxn}
1.00	1.00			
1.00	1.00×10^{-5}			
1.00×10^{-5}	1.00			
4.18×10^{-4}	1.00			

109. A friend wants you to invest in a new battery she has designed that produces 24 V in a single voltaic cell. Why should you be wary of investing in such a battery?

110. What voltage can theoretically be achieved in a battery in which lithium metal is oxidized and fluorine gas is reduced? Why might such a battery be difficult to produce?

111. A battery relies on the oxidation of magnesium and the reduction of Cu^{2+} . The initial concentrations of Mg^{2+} and Cu^{2+} are 1.0×10^{-4} M and 1.5 M, respectively, in 1.0-liter half-cells.

a. What is the initial voltage of the battery?

b. What is the voltage of the battery after delivering 5.0 A for 8.0 h?

c. How long can the battery deliver 5.0 A before going dead?

112. A rechargeable battery is constructed based on a concentration cell constructed of two Ag/Ag^{+} half-cells. The volume of each half-cell is 2.0 L, and the concentrations of Ag^{+} in the half-cells are 1.25 M and 1.0×10^{-3} M.

a. How long can this battery deliver 2.5 A of current before it dies?

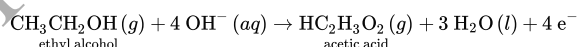
b. What mass of silver is plated onto the cathode by running at 3.5 A for 5.5 h?

c. Upon recharging, how long would it take to redissolve 1.00×10^3 g of silver at a charging current of 10.0 amps?

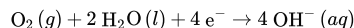
113. If a water electrolysis cell operates at a current of 7.8 A, how long will it take to generate 25.0 L of hydrogen gas at a pressure of 25.0 atm and a temperature of 25 °C?

114. One type of breathalyzer employs a fuel cell to measure the quantity of alcohol in the breath.

When a suspect blows into the breathalyzer, ethyl alcohol is oxidized to acetic acid at the anode:

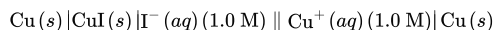


At the cathode, oxygen is reduced:

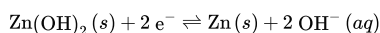


The overall reaction is the oxidation of ethyl alcohol to acetic acid and water. When a suspected drunk driver blows 188 mL of his breath through this breathalyzer, the breathalyzer produces an average of 324 mA of current for 10 s. Assuming a pressure of 1.0 atm and a temperature of 25 °C what percent (by volume) of the driver's breath is ethanol?

115. The K_{sp} of CuI is 1.1×10^{-12} . Find E_{cell} for the cell:



116. The K_{sp} of $\text{Zn}(\text{OH})_2$ is 1.8×10^{-14} . Find E_{cell} for the half-reaction:



117. Calculate $\Delta G_{\text{rxn}}^{\circ}$ and K for each reaction.

a. The disproportionation of $\text{Mn}^{2+}(aq)$ to $\text{Mn}(s)$ and $\text{MnO}_2(s)$ in acid solution at 25 °C.

b. The disproportionation of $\text{MnO}_2(s)$ to $\text{Mn}^{2+}(aq)$ and $\text{MnO}_4^-(aq)$ in acid solution at 25°C .

118. Calculate $\Delta G^\circ_{\text{rxn}}$ and K for each reaction.

a. The reaction of $\text{Cr}^{2+}(aq)$ with $\text{Cr}_2\text{O}_7^{2-}(aq)$ in acid solution to form $\text{Cr}^{3+}(aq)$

b. The reaction of $\text{Cr}^{3+}(aq)$ and $\text{Cr}(s)$ to form $\text{Cr}^{2+}(aq)$ [The electrode potential of $\text{Cr}^{2+}(aq)$ to $\text{Cr}(s)$ is -0.91 V]

119. The molar mass of a metal (M) is 50.9 g/mol ; it forms a chloride of unknown composition.

Electrolysis of a sample of the molten chloride with a current of 6.42 A for 23.6 minutes produces 1.20 g of M at the cathode. Determine the empirical formula of the chloride.

120. A metal forms the fluoride MF_3 . Electrolysis of the molten fluoride by a current of 3.86 A for 16.2 minutes deposits 1.25 g of the metal. Calculate the molar mass of the metal.

121. A sample of impure tin of mass 0.535 g is dissolved in strong acid to give a solution of Sn^{2+} . The solution is then titrated with a 0.0448 M solution of NO_3^- , which is reduced to $\text{NO}(g)$. The equivalence point is reached upon the addition of 0.0344 L of the NO_3^- solution. Find the percent by mass of tin in the original sample, assuming that it contains no other reducing agents.

122. A 0.0251-L sample of a solution of Cu^+ requires 0.0322 L of 0.129 M KMnO_4 solution to reach the equivalence point. The products of the reaction are Cu^{2+} and Mn^{2+} . What is the concentration of the Cu^{2+} solution?

123. A current of 11.3 A is applied to 1.25 L of a solution of 0.552 M HBr , converting some of the H^+ to $\text{H}_2(g)$ which bubbles out of the solution. What is the pH of the solution after 73 minutes?

124. A 215 mL sample of a 0.500 M NaCl solution with an initial pH of 7.00 is subjected to electrolysis. After 15.0 minutes, a 10.0 mL portion (or aliquot) of the solution is removed from the cell and titrated with 0.100 M HCl solution. The endpoint in the titration is reached upon addition of 22.8 mL of HCl . Assuming constant current, how much current (in A) was running through the cell?

125. An $\text{MnO}_2(s)/\text{Mn}^{2+}(aq)$ electrode in which the pH is 10.24 is prepared. Find the $[\text{Mn}^{2+}]$ necessary to lower the potential of the half-cell to 0.00 V (at 25°C).

126. To what pH should you adjust a standard hydrogen electrode to achieve an electrode potential of -0.122 V ? (Assume that the partial pressure of hydrogen gas remains at 1 atm .)

Challenge Problems

127. Suppose a hydrogen-oxygen fuel-cell generator produces electricity for a house. Use the balanced redox reactions and the standard cell potential to predict the volume of hydrogen gas (at STP) required each month to generate the electricity. Assume the home uses $1.2 \times 10^3\text{ kWh}$ of electricity per month.

128. A voltaic cell designed to measure $[\text{Cu}^{2+}]$ is constructed of a standard hydrogen electrode and a copper metal electrode in the Cu^{2+} solution of interest. If you want to construct a calibration curve for how the cell potential varies with the concentration of copper(II), what do you plot in order to obtain a straight line? What is the slope of the line?

129. The surface area of an object to be gold plated is 49.8 cm^2 , and the density of gold is 19.3 g/cm^3 . A current of 3.25 A is applied to a solution that contains gold in the $+3$ oxidation state. Calculate the time required to deposit an even layer of gold $1.00 \times 10^{-3}\text{ cm}$ thick on the object.

130. Electrodepositing all the Cu and Cd from a solution of CuSO_4 and CdSO_4 required 1.20 F of electricity ($1\text{ F} = 1\text{ mol e}^-$). The mixture of Cu and Cd that was deposited had a mass of 50.36 g . What mass of CuSO_4 was present in the original mixture?

131. Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$ in solution is oxidized to $\text{CO}_2(g)$ by MnO_4^- , which is reduced to Mn^{2+} . A 50.1-mL volume of a solution of MnO_4^- is required to titrate a 0.339 g sample of sodium oxalate. This solution of MnO_4^- is used to analyze uranium-containing samples. A 4.62-g sample of a uranium-containing material requires 32.5 mL of the solution for titration. The oxidation of the uranium can be represented by the change $\text{UO}^{2+} \rightarrow \text{UO}_2^{2+}$. Calculate the percentage of uranium in the sample.

132. Three electrolytic cells are connected in a series. The electrolytes in the cells are aqueous copper(II) sulfate, gold(III) sulfate, and silver nitrate. A current of 2.33 A is applied, and after some time 1.74 g Cu is deposited. How long was the current applied? What mass of gold and silver was deposited?

133. The cell $\text{Pt}(s)|\text{Cu}^+(1\text{ M}), \text{Cu}^{2+}(1\text{ M})||\text{Cu}^+(1\text{ M})|\text{Cu}(s)$ has $E^\circ_{\text{cell}} = 0.364\text{ V}$. The cell

$\text{Cu}(s)|\text{Cu}^{2+}(1\text{ M})||\text{Cu}^+(1\text{ M})|\text{Cu}(s)$ has $E^\circ_{\text{cell}} = 0.182\text{ V}$. Write the cell reaction for each cell and

explain the difference in E° . Calculate ΔG° for each cell reaction to help explain these differences.

explain the differences in E_{cell} . Calculate ΔG° for each cell reaction to help explain these differences.

Conceptual Problems

134. An electrochemical cell has a positive standard cell potential but a negative cell potential. Which statement is true?

- a. $K > 1$; $\mathcal{Q} > K$
- b. $K < 1$; $\mathcal{Q} > K$
- c. $K > 1$; $\mathcal{Q} < K$
- d. $K < 1$; $\mathcal{Q} < K$

135. Which oxidizing agent oxidizes Br^- but not Cl^- ?

- a. $\text{K}_2\text{Cr}_2\text{O}_7$ (in acid)
- b. KMnO_4 (in acid)
- c. HNO_3

136. A redox reaction employed in an electrochemical cell has a negative $\Delta G_{\text{rxn}}^\circ$. Which statement is true?

- a. E_{cell}° is positive; $K < 1$
- b. E_{cell}° is negative; $K > 1$
- c. E_{cell}° is negative; $K > 1$
- d. E_{cell}° is positive; $K < 1$

137. A redox reaction has an equilibrium constant of $K = 0.055$. What is true of $\Delta G_{\text{rxn}}^\circ$ and E_{cell}° for this reaction?

Questions for Group Work

Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

138. Balance the redox reactions by following the steps in the text. Rotate through the group, having each group member do the next step in the process and explaining that step to the rest of the group.

- a. $\text{I}_2(s) + \text{Fe}(s) \rightarrow \text{FeI}_2(s)$
- b. $\text{Cl}_2(g) + \text{H}_2\text{O}_2(aq) \rightarrow \text{Cl}^-(aq) + \text{O}_2(g)$ (acidic)
- c. $\text{Hg}^{2+}(aq) + \text{H}_2(g) \rightarrow \text{Hg}(l) + \text{H}_2\text{O}(l)$ (basic)
- d. $\text{CH}_3\text{OH}(l) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$ (acidic)

139. Have each group member select a half-reaction from **Table 19.1**. Each member should calculate the standard cell potential of an electrochemical cell formed between each member's half-reaction and the half-reaction of each of the other group members. For each pair of half-reactions, write the overall balanced chemical reaction that is spontaneous.

140. Calculate ΔG° and K for each reaction the group created in Question 139. For one of the reactions, explain how the sign or magnitude of each quantity (E_{cell}° , ΔG° , and K) is consistent with the fact that the reaction is spontaneous in the direction written.

141. Design a device that uses an electrochemical cell to determine the amount of Cu^{2+} in a sample of water. Describe, in detail, the construction and the theory of operation of your device. If you are able to measure voltage with one-millivolt accuracy, what will be the uncertainty in your measured concentration?

142. Using a library or the Internet, research a fuel cell that uses methanol for fuel. What is the reaction at the anode? What is the reaction at the cathode? What is the overall reaction? What is the standard cell potential? How many kWh can it generate from 1 L (0.792 kg) of methanol?

Data Interpretation and Analysis

143. In this chapter, you have seen that the voltage of an electrochemical cell is sensitive to the concentrations of the reactants and products in the cell. As a result, electrochemical cells can be used to measure the concentrations of certain species in solution. For example, the voltage of an

electrochemical cell based on the reaction $\text{H}_2(g) + \text{Cu}^{2+}(aq) \rightarrow 2\text{H}^+ + \text{Cu}(s)$ is sensitive to both the Cu^{2+} concentration and the H^+ concentration in solution. If the H^+ concentration is held constant, then the voltage only depends on the Cu^{2+} concentration, and we can use the cell to measure the Cu^{2+} concentration in an unknown solution. The tabulated data show the measured voltage in the hydrogen/copper electrochemical cell just discussed for several Cu^{2+} concentrations. Examine the data and answer the questions that follow.

$[\text{Cu}^{2+}]$	Voltage (V)
0.100	0.310
0.200	0.319
0.300	0.325
0.400	0.328
0.500	0.331
0.700	0.335
1.00	0.340

- Construct a graph of the measured voltage versus the the copper concentration. Is the graph linear?
- Determine how you might manipulate the data to produce a linear graph. (*Hint:* See the Nernst equation.)
- Reconstruct a graph of the data using the method to produce a linear graph from part b. Determine the slope and y-intercept of the best-fitting line to the points in your graph. Could you have predicted the slope and intercept from the Nernst equation?
- The voltage of two unknown solutions are measured and recorded. Use the slope and intercept from part c to determine the Cu^{2+} concentrations of the unknown solutions.

Unknown Cu^{2+} Solution	Voltage (V)
i	0.303
ii	0.338

Answers to Conceptual Connections

Cc 19.1 (a) In a voltaic cell, electrons flow from higher potential energy to lower potential energy (from the anode to the cathode).

Cc 19.2 (b) A negative electrode potential indicates that an electron at that electrode has greater potential energy than it has at a standard hydrogen electrode.

Cc 19.3 (d) The reduction of HNO_3 is listed below the reduction of Br_2 and above the reduction of I_2 in Table 19.1. Since any reduction half-reaction is spontaneous when paired with the reverse of a half-reaction below it in the table, the reduction of HNO_3 is spontaneous when paired with the oxidation of I^- but is not spontaneous when paired with the oxidation of Br^- .

Cc 19.4 (c) Ag falls above the half-reaction for the reduction of H^+ but below the half-reaction for the reduction of NO_3^- in Table 19.1.

Cc 19.5 (a) Br is more electronegative than I. If the two atoms were in competition for the electron, the electron would go to the more electronegative atom (Br). Therefore, I_2 does not spontaneously gain electrons from Br^- .

Cc 19.6 (c) Since $K > 1$, the reaction is spontaneous under standard conditions (when $\mathcal{Q} = 1$, the reaction proceeds toward the products). Therefore, E_{cell}° is positive and $\Delta G_{\text{rxn}}^\circ$ is negative.

Cc 19.7 (a) Since $K < 1$, E_{cell}° is negative (under standard conditions, the reaction is not spontaneous). Since $\mathcal{Q} < K$, E_{cell} is positive (the reaction is spontaneous under the nonstandard

conditions of the cell).

Cc 19.8 \square Cu. The electrode potential for Fe is more negative than that of Cu. Therefore, Fe oxidizes more easily than Cu.

Not for Distribution

Not for Distribution

Not for Distribution

Not for Distribution

Not for Distribution