Chapter 11 Exercises

1. Define the oxidation and reduction processes.
2. Describe oxidizing and reducing agents. What happens to each as it functions? What property makes a good oxidizing agent? What property makes a good reducing agent?
3. Distinguish between donor and acceptor orbitals. Which orbital is on the oxidizing agent?
4. Describe the factors that are important in determining the free energy of the following redox reaction: \( \text{Pb} (s) + 2\text{Ag}^{1+} (aq) \rightarrow \text{Pb}^{2+} (aq) + 2\text{Ag} (s) \).
5. What change in potential does an electron experience when it moves from a potential of +0.5 V to one at -0.3 V? Is this a spontaneous process?
6. What is a redox couple? Give three examples.
7. The \( \text{A}^{1+}/\text{A} \) couple is 0.5 V more negative than the \( \text{B}^{2+}/\text{B} \) couple. Which of the four species is the best oxidizing agent? Which is the best reducing agent? Write the balanced chemical equation for the spontaneous process that occurs when the two couples are connected in a galvanic cell.

Use the following energy diagrams for \( \text{X}, \text{Y}, \text{V}, \text{and W} \) for Exercises 8 and 9

8. Use the energy diagram for atoms \( \text{X} \) and \( \text{Y} \) to answer the following:
   a) Draw the energy level diagram for the \( \text{X}^{2+} \) and \( \text{Y}^{2+} \) ions.
   b) Write the standard half-reactions for the reduction of \( \text{X}^{2+} \) and \( \text{Y}^{2+} \), with the more negative reduction potential on top.
   c) Of the four species, \( \text{X}, \text{Y}, \text{X}^{2+}, \text{Y}^{2+} \), which is the best oxidizing agent? Which is the best reducing agent?
   d) Write a balanced reaction, for the spontaneous reaction that occurs when \( \text{X} \) and \( \text{Y} \) are placed into solutions containing \( \text{X}^{2+} \) and \( \text{Y}^{2+} \).

9. Use the energy diagram for elements \( \text{V} \) and \( \text{W} \) to answer the following:
   a) Write the standard reduction half-reactions for \( \text{V}, \text{W}, \text{V}^{2+}, \text{and W}^{2+} \), and order them from most negative at top to most positive at the bottom.
   b) Of the species, \( \text{V}^{2+}, \text{W}^{2+}, \text{V}, \text{W}, \text{V}^{2-}, \text{W}^{2-} \), which is the best oxidizing agent? Which is the best reducing agent?
   c) Indicate whether each of the following electron transfer reactions would be extensive:
      i) \( \text{V} + \text{W}^{2+} \rightarrow \text{V}^{2+} + \text{W} \)
      ii) \( \text{V}^{2+} + \text{W} \rightarrow \text{V} + \text{W}^{2+} \)
      iii) \( \text{W}^{2+} + \text{V}^{2+} \rightarrow \text{W} + \text{V} \)
      iv) \( \text{W}^{2+} + \text{V}^{2+} \rightarrow \text{W} + \text{V} \)
      v) \( \text{V} + \text{W}^{2-} \rightarrow \text{V}^{2-} + \text{W} \)

10. Determine the oxidation state of nitrogen in each of the following molecules. See Section 4.4 for a review of oxidation states.
   a) \( \text{N}_2 \)  b) \( \text{N}_2\text{H}_4 \)  c) \( \text{NH}_3 \)  d) \( \text{N}_2\text{O} \)  e) \( \text{N}_2\text{O}_5 \)
11. Determine the oxidation state of carbon in each of the following:
   a) \( \text{CH}_4 \)  b) \( \text{CH}_2\text{O} \)  c) \( \text{CO}_2 \)  d) \( \text{CH}_3\text{F} \)  e) \( \text{CH}_3\text{OH} \)
12. Indicate whether each of the following chemical conversions requires an oxidizing agent, a reducing agent, or neither:
   a) \( \text{NO}_3^{1-} \rightarrow \text{NH}_3 \)
   b) \( \text{PO}_3^{3-} \rightarrow \text{PO}_4^{3-} \)
   c) \( \text{AgCl} \rightarrow \text{Ag}^{1+} + \text{Cl}^{1-} \)
13. Indicate whether each of the following chemical conversions requires an oxidizing agent, a reducing agent, or neither:
   a) \( \text{CO} \rightarrow \text{CO}_2 \)
   b) \( \text{BaSO}_4 \rightarrow \text{Ba} \)
   c) \( \text{Hg}_2\text{Cl}_2 \rightarrow \text{HgCl}_2 \)
14. Determine the oxidizing and reducing agents and the number of electrons transferred in each of the following reactions:
   a) \( 2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3 \)
   b) \( \text{Pb} + \text{I}_2 \rightarrow \text{PbI}_2 \)
   c) \( \text{Hg}^{2+} + \text{NO}_3^{1-} + \text{H}_2\text{O} \rightarrow \text{Hg} + 2\text{H}^{1+} + \text{NO}_3^{1-} \)
   d) \( 2\text{MnO}_4^{1-} + 3\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 3\text{SO}_4^{2-} + 2\text{OH}^{1-} \)
15. Determine the oxidizing and reducing agents and the number of electrons transferred in each of the following reactions:
   a) \( 3\text{C}_2\text{H}_4\text{OH} + 2\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^{1+} \rightarrow 3\text{CH}_3\text{COOH} + 4\text{Cr}^{3+} + 11\text{H}_2\text{O} \)
   b) \( 4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} \)
   c) \( 5\text{Pb} + 2\text{MnO}_4^{1-} + 16\text{H}^{1+} \rightarrow 5\text{Pb}^{2+} + 2\text{Mn}^{2+} + 8\text{H}_2\text{O} \)
   d) \( \text{C}_8\text{H}_16 + 12\text{O}_2 \rightarrow 8\text{CO}_2 + 8\text{H}_2\text{O} \)
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16. The following processes are all spontaneous:
   \[ A + B^{2+} \rightarrow A^{2+} + B \]  \[ B + C^{2+} \rightarrow B^{2+} + C \]
   \[ D + B^{2+} \rightarrow D^{2+} + B \]  \[ A + D^{2+} \rightarrow A^{2+} + D \]
   List the four redox couples that are involved in the above reactions in order of their standard reduction potentials in a manner similar to Table 11.1; i.e., the most negative at the top.

17. The following processes are all spontaneous:
   \[ 2Y + Z^{2+} \rightarrow 2Y^{2+} + Z \]  \[ 3Y + W^{3+} \rightarrow 3Y^{2+} + W \]
   \[ X + Z^{2+} \rightarrow X^{2+} + Z \]  \[ 2W + 3X^{2+} \rightarrow 2W^{3+} + 3X \]
   List the four redox couples that are involved in the above reactions in order of their standard reduction potentials with the most negative at the top.

18. Describe the role of the liquid junction (salt bridge) in an electrochemical cell. What type of ions (anions or cations) must flow into the cathode?

19. What is the difference between an anode and a cathode?

20. The standard reduction potentials for Hg\(^{2+}\) and Cr\(^{3+}\) are determined by measuring the voltage of the cell made by connecting a standard Cu\(^{2+}/Cu\) half-cell to the ‘Lo’ terminal of a voltmeter and a standard Hg\(^{2+}/Hg\) half-cell or standard Cr\(^{3+}/Cr\) half-cell to the ‘Hi’ terminal. The observed cell potentials were +0.54 V for Hg\(^{2+}/Hg\) and –1.10 V for Cr\(^{3+}/Cr\).
   a) What are the standard reduction potential of mercury(II) and the spontaneous cell reaction between the Hg\(^{2+}/Hg\) and the Cu\(^{2+}/Cu\) couples.
   b) What are the standard reduction potential of chromium(III) and the spontaneous cell reaction between the Cr\(^{3+}/Cr\) and the Cu\(^{2+}/Cu\) couples.
   c) A Cr\(^{3+}/Cr\) half-cell and a Hg\(^{2+}/Hg\) half-cell are connected as a galvanic cell. Which compartment is the anode, and what is the cell voltage?

21. The standard reduction potentials for U\(^{3+}\) and In\(^{3+}\) are determined by measuring the voltage of the cell made by connecting a standard Ni\(^{2+}/Ni\) half-cell to the ‘Lo’ terminal of a voltmeter and a standard U\(^{3+}/U\) half-cell or standard In\(^{3+}/In\) half-cell to the ‘Hi’ terminal.
   a) If the voltmeter reading was -1.43 V when the U\(^{3+}/U\) half-cell was attached, what is the standard reduction potential of uranium(III)? Write the spontaneous cell reaction occurring between the U\(^{3+}/U\) and the Ni\(^{2+}/Ni\) half-cells.
   b) If the voltmeter reading was -0.11 V when the In\(^{3+}/In\) half-cell was attached, what is the standard reduction potential of indium(III)? Write the spontaneous cell reaction occurring between the In\(^{3+}/In\) and the Ni\(^{2+}/Ni\) half-cells.
   c) An In\(^{3+}/In\) half-cell and a U\(^{3+}/U\) half-cell are connected as a galvanic cell. Which compartment is the anode, and what is the cell voltage?

22. Describe galvanization and passivation. Give an example of each.

23. In the following pairs of metals, one is used to protect the other by galvanization. Indicate which metal would be sacrificed.
   a) Fe and Mg
   b) Ni and Cu
   c) Fe and Pb

24. Describe the differences between electrolytic and galvanic cells.

25. Indicate whether each of the following standard cell reactions would take place in a galvanic or an electrolytic cell.
   a) \( H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g) \)
   b) \( Zn^{2+}(aq) + 2 I^-(aq) \rightarrow Zn(s) + I_2(s) \)
   c) \( Cu^{2+}(aq) + Sn(s) \rightarrow Cu(s) + Sn^{2+}(aq) \)
   d) \( 2 Fe^{3+}(aq) + Cu \rightarrow 2 Fe^{2+}(aq) + Cu^{2+}(aq) \)

26. Write net equations or ‘no appreciable reaction’ for the following:
   a) A copper strip is placed in a silver acetate solution.
   b) A lead bar is placed in aqueous bromine.
   c) \( H_2 \) is bubbled into a solution containing Ni\(^{2+}\) and Cu\(^{2+}\) ions.
   d) A mixture of metallic zinc and copper is placed in 1 M HCl.
   e) Metallic copper is placed in a solution of KI.
   f) Chlorine gas is bubbled into a solution containing Fe\(^{2+}\) ions.
   g) Lead is added to an acidified solution of KMnO₄.
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27. Write net equations or ‘no appreciable reaction’ for the following:
   a) An aluminum bar is placed in 1 M HCl.
   b) Aqueous bromine is added to a solution of Fe^{2+}.
   c) A lead bar is placed in water.
   d) KBr is dissolved in an acidified solution of Cr_{2}O_{7}^{2-}.
   e) KF is dissolved in an aqueous bromine solution.
   f) Steel wool is placed into a solution of NiSO_{4}.

28. The standard reduction half-reactions involved in the nickel-cadmium or Nicad battery are
   \[ \text{Cd(OH)}_{2}(s) + 2e^{-} \to \text{Cd}(s) + 2 \text{OH}^{-}(aq) \quad \delta^{o} = -0.86 \ \text{V} \]
   \[ \text{NiOOH}(s) + \text{H}_{2}\text{O}(l) + e^{-} \to \text{Ni(OH)}_{2}(s) + \text{OH}^{-}(aq) \quad \delta^{o} = +0.49 \ \text{V} \]
   a) Write the galvanic cell reaction and determine the cell voltage.
   b) Write the cell reaction for recharging a Nicad battery and determine the minimum voltage, to the nearest half of a volt, required to recharge a Nicad battery?

29. Lead acid batteries indicate that there should be no smoking during recharge because of the possibility of dangerous gases being released. Suggest what gas might be generated in the recharge cycle of a lead acid battery. (Hint: the gas reacts explosively with oxygen.) Write the half-reaction for its production.

30. The following redox couples are combined to make galvanic cells; in each case, indicate which couple is the anode and which is the cathode:
   a) H^{+}/H_{2} and Ag^{+}/Ag
   b) H^{+}/H_{2} and Pb^{2+}/Pb
   c) Al^{3+}/Al and Cu^{2+}/Cu
   d) Fe^{2+}/Fe and Zn^{2+}/Zn

31. The following redox couples are combined to make galvanic cells; in each case, indicate which couple is the anode and which is the cathode:
   a) Br_{2}/Br^{-} and Cl_{2}/Cl^{-}
   b) Sn^{2+}/Sn and Ag^{+}/Ag
   c) I_{2}/I^{-} and Ni^{2+}/Ni
   d) Zn^{2+}/Zn and Fe^{3+}/Fe^{2+}

32. Write the cell reaction and determine the cell potential for the galvanic cells constructed from the following redox couples (see Exercise 30):
   a) H^{+}/H_{2} and Ag^{+}/Ag
   b) H^{+}/H_{2} and Pb^{2+}/Pb
   c) Al^{3+}/Al and Cu^{2+}/Cu
   d) Fe^{2+}/Fe and Zn^{2+}/Zn

33. Write the cell reaction and determine the cell potential for the galvanic cells constructed from the following redox couples (see Exercise 31):
   a) Br_{2}/Br^{-} and Cl_{2}/Cl^{-}
   b) Sn^{2+}/Sn and Ag^{+}/Ag
   c) I_{2}/I^{-} and Ni^{2+}/Ni
   d) Zn^{2+}/Zn and Fe^{3+}/Fe^{2+}

34. Determine how many moles of electrons and how many coulombs (C = \( n \cdot F \)) must be transferred for each of the following processes:
   a) reduce 1.5 moles of silver ions to silver metal
   b) oxidize 0.22 moles of metallic nickel to nickel(II) ions
   c) produce 8.9 g of gold from Au^{3+} ions

35. Determine how many moles of electrons and how many coulombs (C = \( n \cdot F \)) must be transferred for each of the following processes:
   a) reduction of 1.3 mol Al^{3+} to Al
   b) oxidation of 3.4 mol Br^{-} to Br_{2}
   c) oxidize 2.8 g of copper to Cu^{2+}

36. A standard galvanic cell, constructed with Al/Al^{3+} and Pb/Pb^{2+} couples, is discharged until 1.6 g of Pb forms.
   a) What are the cell reaction and its standard cell potential?
   b) How many moles of electrons flow through the circuit during the discharge? (Hint: grams of Pb \to moles of Pb \to moles of electrons.)
   c) How many coulombs flow through the circuit? (Hint: use C = \( n \cdot F \))
   d) Assume that the cell potential does not change and determine the maximum work that could be done by the electrons during the discharge? (Hint: Use the answers to Parts a and d and Equation 11.3)

37. A standard galvanic cell, constructed with Ag^{+}/Ag and Zn^{2+}/Zn couples, is discharged until 3.3 g of Ag forms. For hints, see Exercise 36.
   a) What are the overall cell reaction and the standard cell potential?
   b) How many moles of electrons must flow through the circuit?
   c) How many coulombs of charge flow through the circuit?
   d) Assume that the cell potential does not change and determine the maximum work that could be done by the electrons during the discharge?