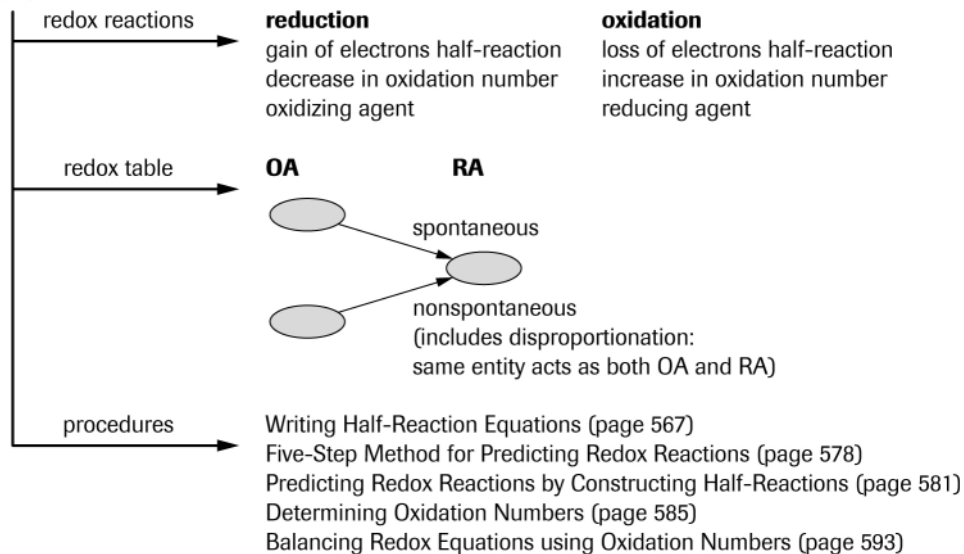


Chapter 13 SUMMARY

Make a Summary

(Page 604)

1. Redox



Five-Step Method for Predicting Redox Reactions (page 578)

Predicting Redox Reactions by Constructing Half-Reactions (page 581)

Determining Oxidation Numbers (page 585)

Balancing Redox Equations Using Oxidation Numbers (page 593)

- (1) Electrochemical reactions are characterized by a transfer of electrons. The entity with the greatest tendency to gain electrons pulls electrons from the entity with the greatest tendency to lose or give up electrons. One entity gains electrons in an electrochemical process while another entity loses electrons.
- (2) Using the experimentally determined redox table, locate the positions of the strongest oxidizing and reducing agents present in the initial mixture. If the strongest oxidizing agent appears above the strongest reducing agent in the table, then a spontaneous redox reaction should occur.
- (3) Redox stoichiometry, like other forms of stoichiometry, uses the same apparatus, procedure, and assumptions (i.e., reactions are stoichiometric). Unlike acid-base titrations, redox titrations are usually self-indicating and no extra indicator is usually required. The procedure of writing redox reactions involves a more complicated set of steps rather than a simple generalization as used previously for predicting chemical reaction equations.

Chapter 13 REVIEW

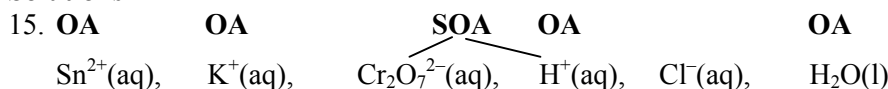
Part 1

(Pages 605–606)

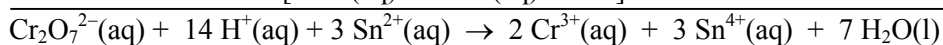
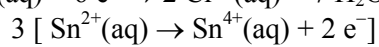
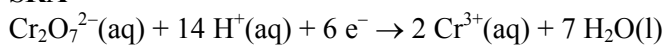
1. B
2. A
3. D
4. 1, 3, 5, 6
5. B

6. D
7. C
8. C
9. A
10. 3, 1, 1, 3
11. B
12. B
13. A
14. D
15. 65.6

Solutions



SRA



$$\begin{array}{l} 12.7 \text{ mL} \\ c \end{array} \qquad \begin{array}{l} 25.0 \text{ mL} \\ 0.100 \text{ mol/L} \end{array}$$

$$n_{\text{Sn}^{2+}} = 25.0 \text{ mL} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 2.50 \text{ mmol}$$

$$n_{\text{Cr}_2\text{O}_7^{2-}} = 2.50 \text{ mmol} \times \frac{1}{3} = 0.833 \text{ mmol}$$

$$[\text{Cr}_2\text{O}_7^{2-}(\text{aq})] = \frac{0.833 \text{ mmol}}{12.7 \text{ mL}} = 0.0656 \text{ mol/L} \text{ or } 65.6 \text{ mmol/L}$$

$$\begin{aligned} \text{or } [\text{Cr}_2\text{O}_7^{2-}(\text{aq})] &= 25.0 \text{ mL Sn}^{2+} \times \frac{0.100 \text{ mol Sn}^{2+}}{1 \text{ L Sn}^{2+}} \times \frac{1 \text{ mol Cr}_2\text{O}_7^{2-}}{3 \text{ mol Sn}^{2+}} \times \frac{1}{12.7 \text{ mL Cr}_2\text{O}_7^{2-}} \\ &= 65.6 \text{ mmol/L} \end{aligned}$$

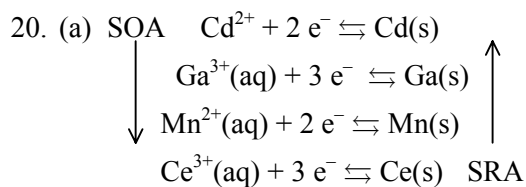
On the basis of the evidence, the amount concentration of potassium dichromate solution is 65.6 mmol/L.

Part 2

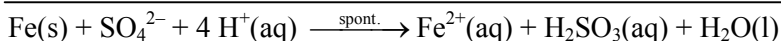
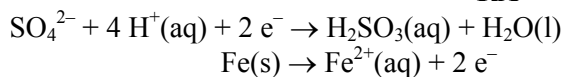
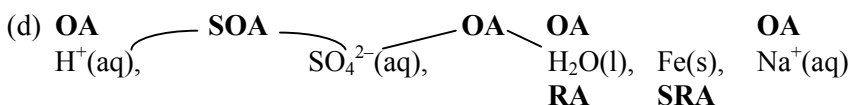
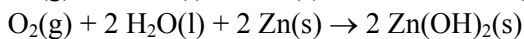
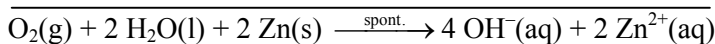
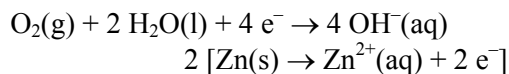
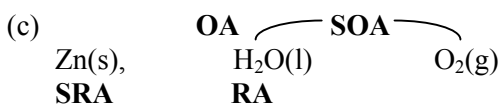
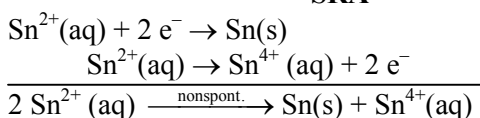
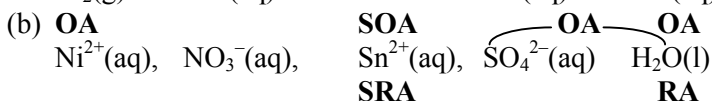
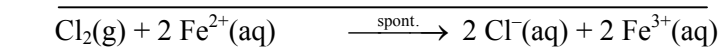
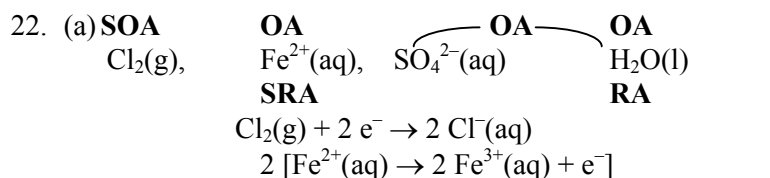
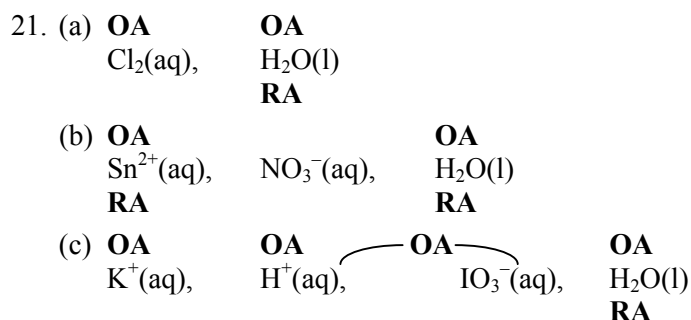
(Pages 606–609)

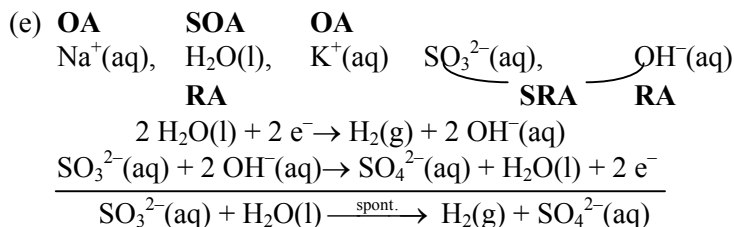
16. According to modern theory, a redox reaction involves a transfer of electrons from the reducing agent to the oxidizing agent. The reducing agent loses electrons in an oxidation half-reaction. The oxidizing agent gains those electrons in a reduction half-reaction.
17. (a) In a table of half-reactions, if the oxidizing agent is listed above the reducing agent, then the reaction is predicted to be spontaneous. If the oxidizing agent is listed below the reducing agent, then the reaction is predicted to be non-spontaneous.
 - (b) Possible evidence of a spontaneous redox reaction includes the formation of a precipitate or gas, a colour or odour change, or an energy change.
18. (a) Oxidation is defined as a loss of electrons involving an increase in oxidation number.
 - (b) Reduction is defined as a gain of electrons involving a decrease in oxidation number.
 - (c) In a redox reaction, an electron transfer takes place in which the oxidizing agent gains electrons and the reducing agent loses electrons. An atom/ion in the oxidizing agent decreases in oxidation number and an atom/ion in the reducing agent increases in oxidation number.

19. (a) $\text{HClO}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{HClO}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ (reduction)
 (b) $\text{Al}(\text{OH})_4^-(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s}) + 4 \text{OH}^-(\text{aq})$ (reduction)
 (c) $\text{Br}^-(\text{aq}) + 4 \text{H}_2\text{O}(\text{l}) \rightarrow \text{BrO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 8 \text{e}^-$ (oxidation)
 (d) $2 \text{ClO}^-(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{Cl}_2(\text{aq}) + 4 \text{OH}^-(\text{aq})$ (reduction)



(b) The strongest oxidizing agent is Cd^{2+} and the strongest reducing agent is $\text{Ce}(\text{s})$.





23. Purpose

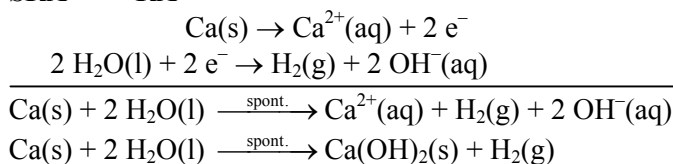
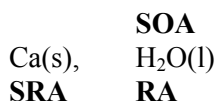
The purpose of this investigation is to test the five-step method for predicting redox reactions.

Problem

What are the products of the reaction of calcium metal with water?

Prediction

According to the five-step method and the redox table, the products of the reaction of calcium metal and water are hydrogen gas and a precipitate of calcium hydroxide.



Design

A small quantity of pure calcium metal is added to pure water. Diagnostic tests for hydrogen, the pH of the solution, and a flame test are performed. As a control, the same tests are conducted before the reaction.

Materials

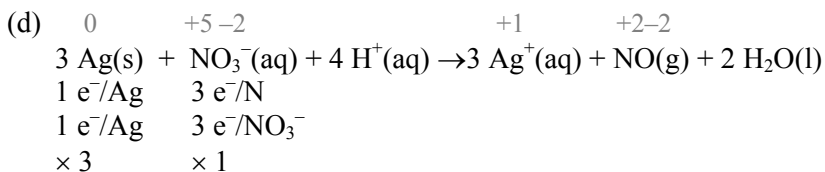
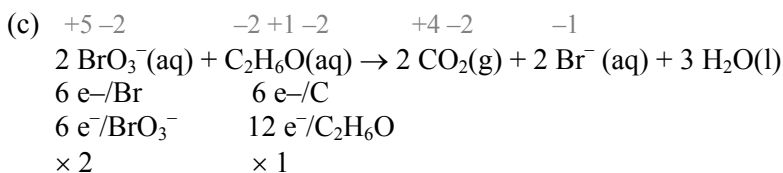
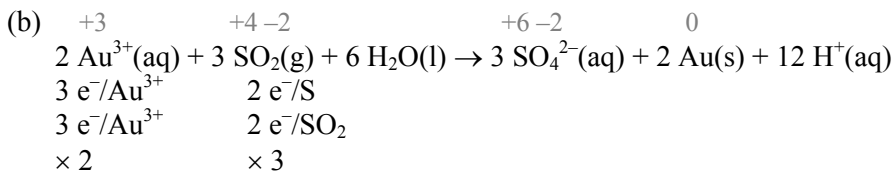
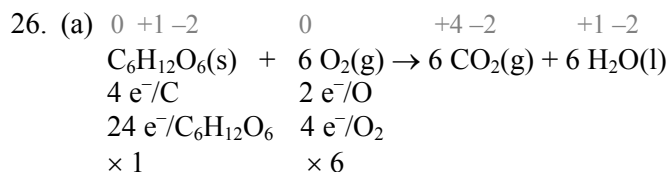
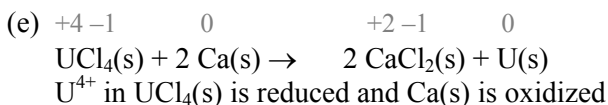
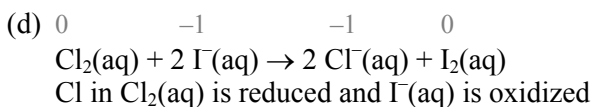
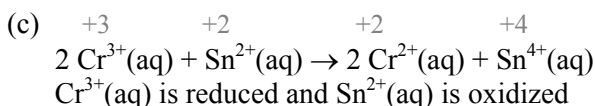
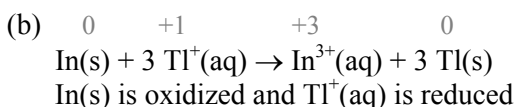
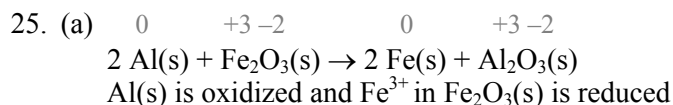
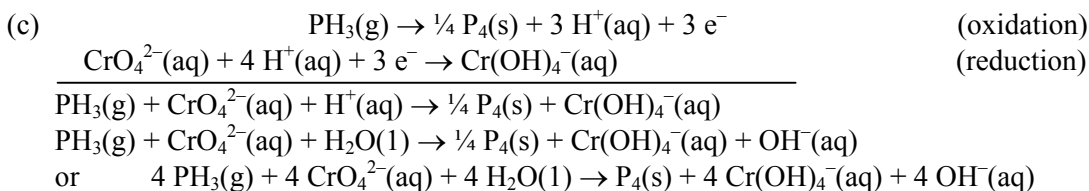
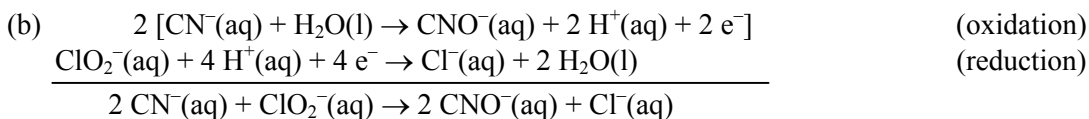
- eye protection
- small sample of Ca(s)
- 50 mL pure H₂O
- laboratory burner
- wood splint
- lab apron
- large test tube
- wire loop
- pH paper or meter
- matches

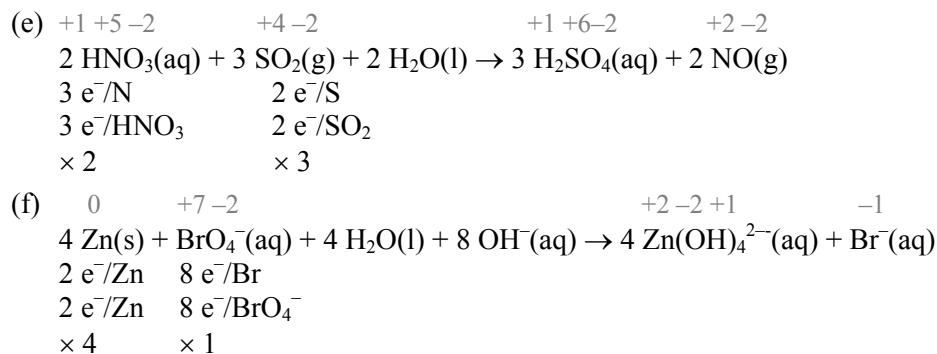
CAUTION: Calcium is a flammable solid, water reactive, and corrosive. Further, it can prove harmful and even fatal if swallowed. It is harmful if inhaled or absorbed through the skin.

Contact with the skin can also produce burns. Use protective equipment and extreme caution in performing this experiment.

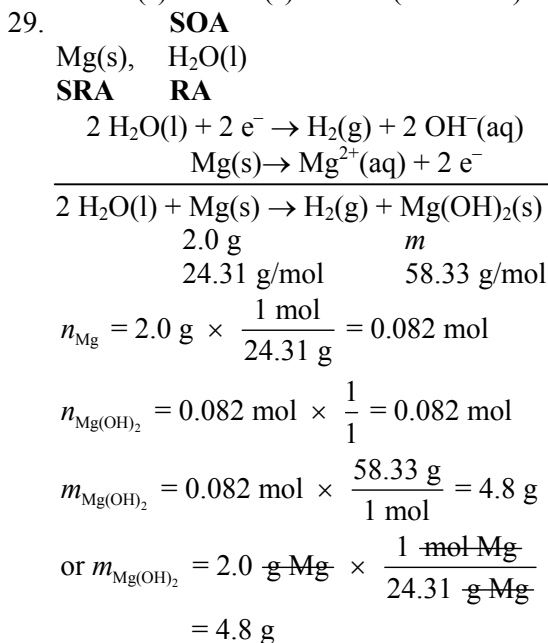
Procedure

1. Pour 50 mL of distilled water into the test tube.
 2. Test using a burning splint, pH paper, and flame test. Record your observations.
 3. Place a small piece of Ca(s) into the water and record evidence of the reaction.
 4. Place a burning splint near the mouth of the test tube.
 5. Once the Ca(s) has stopped reacting, perform diagnostic tests using pH paper and flame test on the liquid.
 6. Dispose of the mixture into the sink with lots of running water.
24. (a)
- $$\text{Pt}(\text{s}) + 6 \text{Cl}^-(\text{aq}) \rightarrow \text{PtCl}_6^{2-}(\text{aq}) + 4 \text{e}^- \quad (\text{oxidation})$$
- $$4 [\text{NO}_3^-(\text{aq}) + 2 \text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})] \quad (\text{reduction})$$
-
- $$\text{Pt}(\text{s}) + 6 \text{Cl}^-(\text{aq}) + 4 \text{NO}_3^-(\text{aq}) + 8 \text{H}^+(\text{aq}) \rightarrow \text{PtCl}_6^{2-}(\text{aq}) + 4 \text{NO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$$





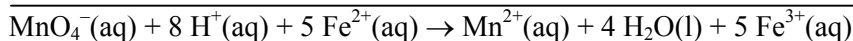
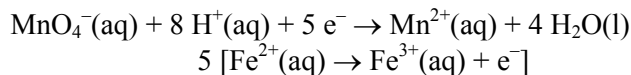
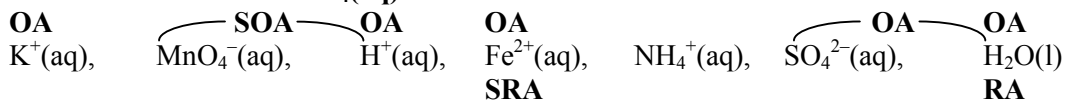
27. (a) The three methods are: the five-step method using a redox table of half-reactions; constructing half-reaction equations; and the oxidation number method.
 (b) The five-step method using a redox table also predicts the products and the spontaneity.
 (c) The oxidation number method and the method of constructing half-reaction equations both require knowledge of the primary products.
 (d) If all methods are available, I would prefer the five-step method using a redox table because this method is most efficient and least prone to error because the balanced half-reaction equations are given. *[Other opinions are possible.]*
28. (a) $\text{Zn}(\text{s}) + \text{Ag}_2\text{S}(\text{s}) \rightarrow \text{ZnS}(\text{s}) + 2 \text{Ag}(\text{s})$ (balanced by inspection)
 (b) $\text{Zn} \rightarrow \text{Zn}^{2+}$: 0 to +2
 $2 \text{Ag}^+ \rightarrow 2 \text{Ag}$: +2 to 0
 The total increase in oxidation numbers equals the total decrease.
 (c) $\text{Ag}^+(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ (reduction)
 $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{s}) + 2 \text{e}^-$ (oxidation)



According to the stoichiometric method, 4.8 g of precipitate forms from a 2.0 g strip of magnesium.

Analysis

Standardization of $\text{KMnO}_4(\text{aq})$:



$$\begin{array}{ll} 12.4 \text{ mL (trials 2-4)} & 10.00 \text{ mL} \\ c & 0.331 \text{ mol/L} \end{array}$$

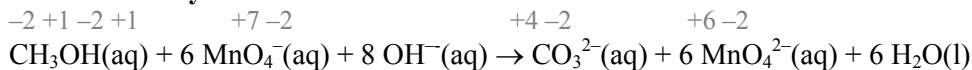
$$n_{\text{Fe}^{2+}} = 10.00 \text{ mL} \times \frac{0.331 \text{ mmol}}{1 \text{ L}} = 3.31 \text{ mmol}$$

$$n_{\text{MnO}_4^-} = 3.31 \text{ mmol} \times \frac{1}{5} = 0.662 \text{ mmol}$$

$$[\text{MnO}_4^-(\text{aq})] = \frac{0.662 \text{ mmol}}{12.4 \text{ mL}} = 0.0534 \text{ mol/L}$$

$$\begin{aligned} \text{or } [\text{MnO}_4^-(\text{aq})] &= 10.00 \cancel{\text{ mL}} \cancel{\text{ Fe}^{2+}} \times \frac{0.331 \cancel{\text{ mol}} \cancel{\text{ Fe}^{2+}}}{1 \cancel{\text{ L}} \cancel{\text{ Fe}^{2+}}} \times \frac{1 \text{ mol MnO}_4^-}{5 \cancel{\text{ mol}} \cancel{\text{ Fe}^{2+}}} \times \frac{1}{12.4 \cancel{\text{ mL}} \cancel{\text{ MnO}_4^-}} \\ &= 0.0534 \text{ mol/L} \end{aligned}$$

Chemical analysis of basic methanol:



$$\begin{array}{ll} 6 \text{ e}^-/\text{C} & 1 \text{ e}^-/\text{Mn} \\ 6 \text{ e}^-/\text{CH}_3\text{OH} & 1 \text{ e}^-/\text{MnO}_4^- \\ \times 1 & \times 6 \\ 10.00 \text{ mL} & 11.7 \text{ mL (trials 2 \& 3)} \\ c & 0.0534 \text{ mol/L} \end{array}$$

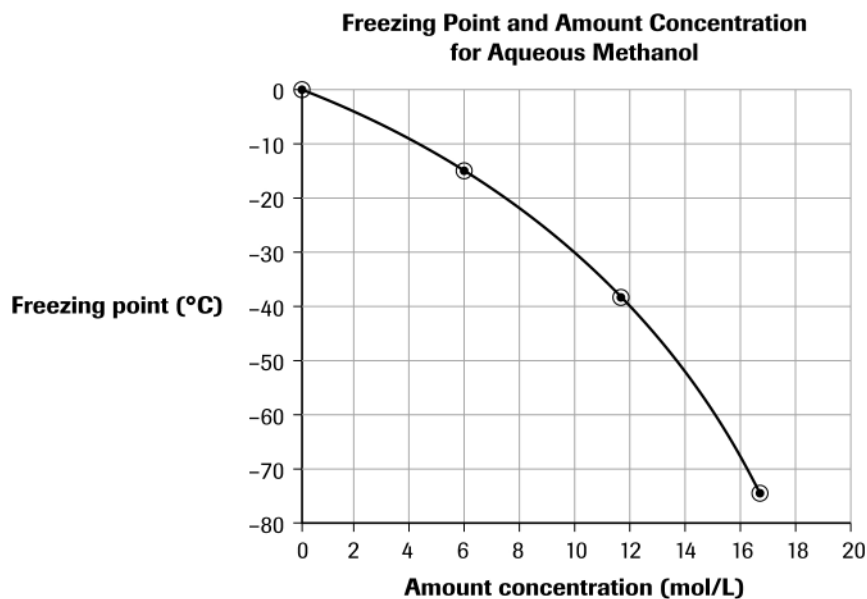
$$n_{\text{MnO}_4^-} = 11.7 \text{ mL} \times \frac{0.0534 \text{ mol}}{1 \text{ L}} = 0.625 \text{ mmol}$$

$$n_{\text{CH}_3\text{OH}} = 0.625 \text{ mmol} \times \frac{1}{6} = 0.104 \text{ mmol}$$

$$[\text{CH}_3\text{OH}(\text{aq})] = \frac{0.104 \text{ mmol}}{10.00 \text{ mL}} = 0.0104 \text{ mol/L}$$

$$\begin{aligned} \text{or } [\text{CH}_3\text{OH}(\text{aq})] &= 11.7 \cancel{\text{ mL}} \cancel{\text{ MnO}_4^-} \times \frac{0.0534 \cancel{\text{ mol}} \cancel{\text{ MnO}_4^-}}{1 \cancel{\text{ L}} \cancel{\text{ MnO}_4^-}} \times \frac{1 \text{ mol CH}_3\text{OH}}{6 \cancel{\text{ mol}} \cancel{\text{ MnO}_4^-}} \\ &\quad \times \frac{1}{10.00 \cancel{\text{ mL}} \cancel{\text{ CH}_3\text{OH}}} \\ &= 0.0104 \text{ mol/L} \end{aligned}$$

Because the windshield-washer fluid had been diluted by a factor of 1000, the amount concentration of the original windshield-washer fluid is 10.4 mol/L, according to the evidence presented and the stoichiometric method. According to the graph shown below based on the evidence in Table 5, the freezing point of a 10.4 mol/L solution of methanol is approximately -33°C .



Extension

34. Mechanical processes for producing paper involve the grinding of wood to separate the wood fibres. From a technological perspective this is an efficient process, but it produces paper that tends to be weak and discolour easily in light. Economically, this is a relatively inexpensive process. The environmental impact of mechanical processes is minimal because no harmful chemicals are used; however, there are negative environmental effects incurred from burning fossil fuels in order to generate heat used in the process. Redox chemistry includes combustion of fossil fuels and probably the discolouration of the paper.

Chemical processes for producing paper use wood chips with water, various chemicals, and heat to separate the cellulose fibres. These are then bleached to remove the lignin. From a technological perspective, this is a reliable process that can also be applied to recycled paper and produces strong, white paper products. Because of the scale of the operation, chemical processes are relatively inexpensive. All chemical processes have some negative environmental impacts. In particular, the older methods that rely on chlorine or chlorine compounds produce organochlorine waste that is often toxic. The main redox chemistry involved is associated with the bleaching of the paper using chlorine or chlorine substitutes.

In the history of implementing technological advances, many economically attractive technologies have produced harmful consequences to the environment and health of organisms. Examples of this include using elemental chlorine in the bleaching process for paper production. The cost to the environment and to companies for retrofitting and implementing safer technologies is far greater than that of spending the time and resources to develop safer technologies in the first place or placing lower value on aesthetic qualities of the paper produced.

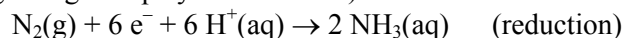
35. (a) +5 in VF_5 and V_2O_5
 +4 in VCl_4
 +3 in VBr_3
 +2 in VI_2 and VCl_2

- (b) The highest oxidation state (+5) is reached with fluorine or oxygen acting as the oxidizing agent. Therefore, these oxidizing agents are the strongest. The next-highest oxidation state is reached with chlorine, which means chlorine is the next strongest oxidizing agent. Using the same argument, bromine is the next in strength, while iodine and hydrogen ions are the least strong oxidizing agents.
- (c) According to the *CRC Handbook of Chemistry and Physics*, compounds of vanadium exhibit different colours depending upon the oxidation state of vanadium.
- +5: yellow-red in $V_2O_5(s)$
 - +4: blue in $VO_2(s)$, and red-brown in $VCl_4(l)$
 - +3: pink in $VCl_3(s)$, green-black in $VBr_3(s)$, and green in $VF_3 \cdot 6H_2O(s)$
 - +2: green in $VCl_2(s)$, and violet-rose in $VI_2(s)$
- (d) Vanadium is widespread in nature, occurring in over 65 different minerals. Vanadium and its compounds are used in the manufacture of rust-resistant, spring, and high-speed tool steels; nuclear applications; ceramics; catalysts; superconducting materials.
36. Pyrometallurgy involves using heat to treat an ore in the production of metals (e.g., smelting or roasting). A common example is the reaction of iron(III) oxide with carbon monoxide to produce iron metal. Hydrometallurgy involves the selective dissolving of metals from their ores. For example, copper oxide and carbonate ores may be treated with dilute $H_2SO_4(aq)$, thereby producing water-soluble copper sulfate. Copper can be recovered from such solutions through electrolysis. Electrometallurgy involves the preparation of active metals by electrolysis. Examples include: $Al(s)$, $Ca(s)$, $Ba(s)$, $Mg(s)$, and $K(s)$.

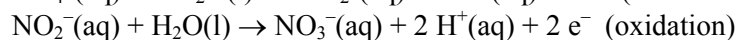
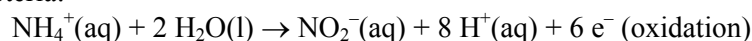
In each case, the metal in the ore is in an oxidized state (ion form) and must be reduced to its elemental state. This requires a transfer of electrons and therefore all of these processes are redox reactions.

The goal of technology, as illustrated by these processes, is to produce useful products and processes. Different technological solutions were developed to solve practical problems of obtaining pure metals, including developing the most economical and efficient method for different metal ores. Although pyrometallurgy developed largely through trial and error, the more modern methods involving electrolysis have been aided considerably by scientific advances.

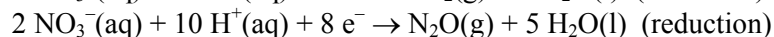
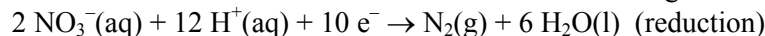
37. Nitrogen fixation is the conversion of atmospheric nitrogen gas into ammonia by bacteria (lightning also plays a small role):



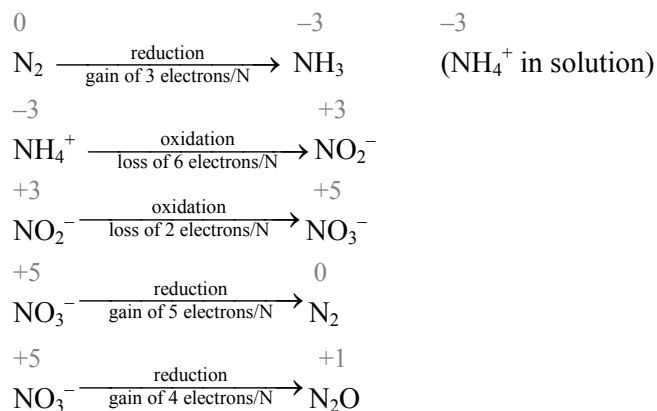
Nitrification is the oxidation of ammonium to nitrite and nitrite to nitrate by different bacteria:



Denitrification is the reduction of nitrates to elemental nitrogen or dinitrogen monoxide:



[Note that nitrogen fixation and nitrification half-reactions can also be written using either ammonia or ammonium ions. This does not change the number of electrons transferred.]



The nitrogen cycle is an essential natural process because plants (and therefore animals) are able to grow only with a suitable supply of nitrogen. A negative environmental impact is the eutrophication of lakes and water systems, indicating that the nitrogen nutrients are accumulating in the water. The denitrifying bacteria may not be keeping up because so much extra nitrogen is being added through agricultural practices that use fertilizers.