

Unit 5
Organic Chemistry

5

Organic Chemistry

“Syncrude Canada was just about to begin operating its oil sands plant when I was graduating. I had attended several talks about the oil sands, so my primary reason for interviewing with the company was to see their pilot plants. When they offered me a job, however, I accepted. One of the advantages of working in such a large company is that I have had the opportunity to carry out research in numerous areas. I like the variety of the work.

When I joined the work force, I was concerned whether I had the correct qualifications for the job. I have since learned that my formal training was really just the beginning of my learning. What I learned in school is how to approach a problem. On the job, I’ve expanded my knowledge and learned how to work in diverse teams to solve our problems.”



Jean Cooley,
Research Associate,
Syncrude Canada

As you progress through the unit, think about these focusing questions:

- What are the common organic compounds and what is the system for naming them?
- How does society use the reactions of organic compounds?
- How can society ensure that the technological applications of organic chemistry are assessed to ensure future quality of life and a sustainable environment?





GENERAL OUTCOMES

In this unit, you will

- explore organic compounds as a common form of matter
- describe chemical reactions of organic compounds

Knowledge

1. According to Lewis' theory, the number of bonding electrons in an atom determines the number of bonds the atom will form. Complete **Table 1** for five elements that are often involved in organic compounds.

Table 1 Atomic Structures of Some Common Nonmetals

Element	Atomic number	Number of electrons	Number of valence electrons	Lewis symbol	Number of bonding electrons
carbon					
hydrogen					
oxygen					
nitrogen					
sulfur					

2. Different formulas for molecules can be used to predict the types of intermolecular bonding that exist in a substance. Complete **Table 2** for some common compounds of carbon.

Table 2 Some Common Carbon Compounds

IUPAC name	Molecular formula	Lewis formula	Structural formula	Types of intermolecular forces
	CH ₄ (g)			
dichloromethane	CH ₂ Cl ₂ (l)			
methanol				
methyl amine	CH ₃ NH ₂ (l)			
ethane				
ethene	C ₂ H ₄ (g)			
ethyne		H : C :: C : H	H — C ≡ C — H	
	C ₂ H ₅ OH(l)			
ethyl mercaptan	C ₂ H ₅ SH(l)			

3. Use VSEPR theory to predict the shapes of each of the following molecules. Predict whether each molecule is polar or nonpolar.
 - (a) chloromethane, CH₃Cl(g), used as a refrigerant
 - (b) carbon dioxide, CO₂(g), produced by hydrocarbon combustion
 - (c) formaldehyde, HCHO(g), used as a disinfectant
 - (d) ethyne, C₂H₂(g), used as a fuel for welding
 - (e) ethene, C₂H₄(g), used to make plastics
4. The octane used in automobile fuel is considered nonrenewable because it is produced from petroleum, a fossil fuel. Ethanol is considered a renewable fuel since it can be produced from biomass, such as grain.
 - (a) Write a balanced chemical equation for the combustion of octane, C₈H₁₈(l).
 - (b) Write a balanced chemical equation for the combustion of ethanol, C₂H₅OH(l).
 - (c) Describe some diagnostic tests for the reaction products in (a) and (b).

Prerequisites

Concepts

- atomic structure
- physical and chemical properties of molecular compounds
- covalent bonding
- polar and nonpolar molecules
- intermolecular forces

Skills

- drawing diagrams and writing formulas of molecules
- building molecular models
- conducting and analyzing diagnostic tests
- describing safety and disposal

You can review prerequisite concepts and skills in the **Chemistry Review unit**, on the **Nelson Web site**, and in the **Appendices**.

A Unit Pre-Test is also available online.

www.science.nelson.com



5. Photosynthesis is the formation of carbohydrates and oxygen from carbon dioxide, water, and sunlight, catalyzed by chlorophyll in the green parts of a plant (**Figure 1**).
- Write a balanced chemical equation for photosynthesis, using $C_6H_{12}O_6(aq)$ for the carbohydrate.
 - During summer in the Northern Hemisphere, the level of carbon dioxide in the atmosphere decreases slightly. Use the chemical equation in (a) to explain this phenomenon.

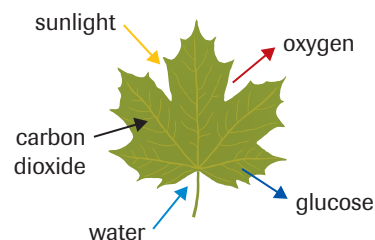


Figure 1
Photosynthesis consumes carbon dioxide and produces oxygen.

Skills

6. Boiling point is a measure of the strength of the intermolecular forces in a substance. There is evidence to suggest that London forces exist among all molecules in the liquid or solid state. Chemists explain the strength of London forces as being dependent on the number of electrons in the molecule. Polar molecules exert relatively weak dipole–dipole forces in addition to London forces. Molecules with OH, NH, or FH groups have relatively strong hydrogen bonds in addition to London forces. The purpose of this activity is to test the ability of the theoretical concepts of London forces, dipole–dipole forces, and hydrogen bonding to predict the relative boiling points of three families of compounds. Complete the Prediction, Analysis, and Evaluation (2, 3) of the investigation report.

Problem

What are the trends in boiling point for three families of carbon compounds?

Design

The boiling points of twelve organic compounds (from three chemical families) are measured experimentally. The boiling point evidence is used to test the Prediction. The polarity of the molecules and the hydrogen bonding are controlled variables within each family of compounds.

Evidence

Table 3 Boiling Points of Three Families of Carbon Compounds

Hydrocarbon	Boiling point (°C)	Organic halide	Boiling point (°C)	Alcohol	Boiling point (°C)
$CH_4(g)$	-164	$CH_3Cl(g)$	-24	$CH_3OH(l)$	65
$C_2H_6(g)$	-89	$C_2H_5Cl(g)$	12	$C_2H_5OH(l)$	78
$C_3H_8(g)$	-42	$C_3H_7Cl(l)$	47	$C_3H_7OH(l)$	97
$C_4H_{10}(g)$	-0.5	$C_4H_9Cl(l)$	78	$C_4H_9OH(l)$	117

7. Liquid hydrocarbons are readily flammable and often evaporate easily to form explosive mixtures with air.
- What WHMIS symbol is found on a container of a liquid hydrocarbon?
 - Outline the precautions that must be taken when working with liquid hydrocarbons.
 - Describe an acceptable method for handling waste flammable liquids.

Hydrocarbons from Petroleum

► In this chapter

-  Exploration: Burning Fossil Fuels
-  Investigation 9.1: Classifying Fossil Fuels
-  Case Study: Fossil Fuel Industries in Alberta
-  Web Activity: Coal in Alberta
-  Explore an Issue: Coalbed Methane
-  Investigation 9.2: Structures and Properties of Isomers
-  Web Activity: West Nile Denial
-  Lab Exercise 9.A: Chemical Properties of Aliphatics and Aromatics
-  Lab Exercise 9.B: Boiling Points of Sample Aliphatics and Aromatics
-  Investigation 9.3: Fractional Distillation (Demonstration)
-  Web Activity: Karl Chuang
-  Case Study: Octane Number
-  Investigation 9.4: Bitumen from Oil Sands
-  Investigation 9.5: Solvent Extraction
-  Case Study: The Athabasca Oil Sands
-  Investigation 9.6: Complete and Incomplete Combustion

The most widely accepted explanation of the origin of fossil fuels is that they come from decaying plant and animal material. The carbon cycle is a model connecting the organic reactions of photosynthesis, digestion, and respiration (**Figure 1**). The formation of fossil fuels can be seen as the end of the natural processes in the carbon cycle and the beginning of the technological processes described in this chapter.

Humans have invented methods to extract fossil fuels from below the surface of Earth. We mostly burn fossil fuels to produce heat and useful energy. These combustion reactions produce carbon dioxide, which feeds back into the carbon cycle.


Recently, we have developed many other technological uses of fossil fuels. We now produce vast quantities of petrochemicals (chemicals created from fossil fuels), most of which are not meant to be burned. Petrochemicals include methanol (windshield antifreeze), ethylene glycol (radiator antifreeze), chlorofluorocarbons (CFCs: refrigerator and air conditioner coolants), plastics (polyethylene and polyvinylchloride (PVC)), and pesticides. In this chapter, you will learn about the extraction and refining of fossil fuels. In the next chapter, you will learn about the use of fossil fuels to create petrochemicals. For both uses, fossil fuels are a very valuable nonrenewable resource. The impact of fossil fuel use on our lives and our planet is everywhere around us.

Historically, natural resources were seen as assets to be developed, and it was usual to imagine technological solutions to problems. In recent times, however, we have come to realize that technology is limited in its ability to cope with resource depletion and pollution. Many people, including scientists, believe we need to move toward an Aboriginal viewpoint that sees natural resources as gifts to be treasured for future generations. In order to save our planet from irreparable harm, we have a responsibility to live in harmony with nature for the mutual benefit of nature and humanity.

STARTING Points

Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.

1. What are the origins and sources of fossil fuels?
2. How are fossil fuels extracted and refined?
3. What are the main hydrocarbon families, and how do they differ?
4. What are some uses of fossil fuels and their components?

 Career Connections:
Petroleum Engineer; The Petroleum Industry

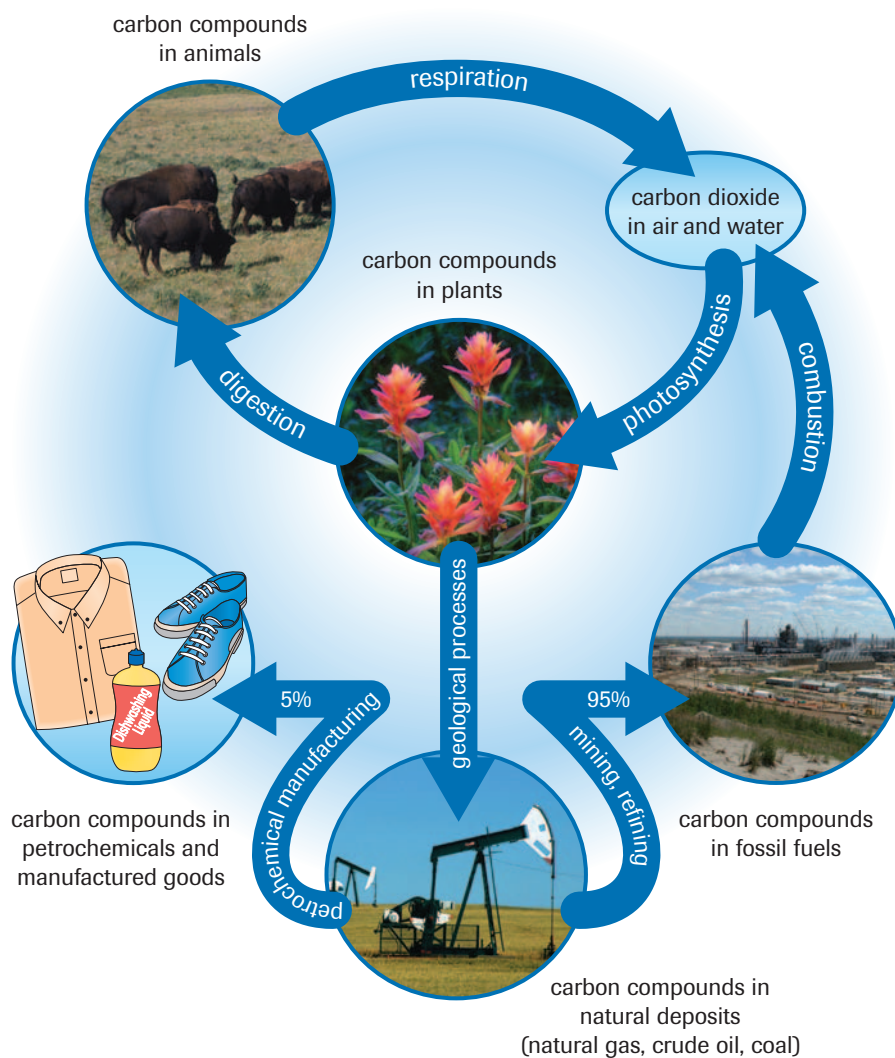


Figure 1

The carbon cycle is an illustration of the interrelationship of all living things with the environment and with technologies that refine and use fossil fuels.

► Exploration *Burning Fossil Fuels*

Scientists agree that fossil fuels are a nonrenewable, finite resource. Fossil fuels in Alberta include coal, natural gas, crude oil, oil sands, and heavy oil. Studies have indicated that about 95% of the fossil fuels used in Alberta is used for energy production, including natural gas and propane for home heating, and gasoline and diesel fuel for cars, trucks, and buses. The evidence indicates that about 5% of fossil fuels is converted into petrochemicals (such as plastics) through technologies based on chemical reactions. Two issues related to burning fossil fuels for energy production are

- whether we should be burning a very valuable resource at the current rate
- whether we should be saving more of this resource for petrochemical use in the future

Investigate the first of these issues as you work through Chapter 9, and the second issue in Chapter 10.

Issue Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Issue | <input checked="" type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Resolution | <input checked="" type="radio"/> Evidence | <input checked="" type="radio"/> Evaluation |

Resolution: The burning of fossil fuels for heat and transportation should be significantly reduced.

While progressing through Chapter 9, complete the Design, Evidence, Analysis, and Evaluation components of the first issue report.

Governments, industry, and citizens alike speak of sustainable development. The United Nations Commission on Environment and Development defines sustainable development as development that meets the needs of the present without compromising the ability of future generations to meet their own needs. Keep this concept in mind while completing this unit-long exploration.

9.1 Fossil Fuels

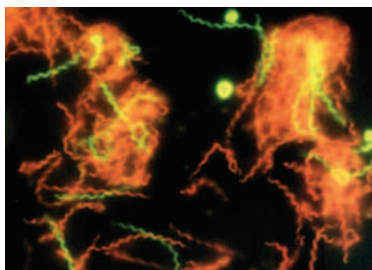


Figure 1







Extremophiles are microorganisms that thrive in harsh environments, such as boiling water, acid, rocks, the coolant of a nuclear reactor, and toxic wastes. Identification of these carbon-based organisms raises the hopes of astrobiologists that basic life forms may exist on moons and planets in the universe. On Earth, the study of organic chemistry began with living things. Beyond Earth, scientists look for evidence of living things.

Life as we know it is based on carbon chemistry (**Figure 1**). Therefore, it is not surprising that the early definition of organic chemistry was related to compounds obtained only from living things. Today, **organic chemistry** is a major branch of chemistry that deals with compounds of carbon, excluding oxides (such as CO(g)) and ionic compounds of carbon-based ions such as carbonate, cyanide, and carbide ions, for example, $\text{Na}_2\text{CO}_3(\text{s})$, $\text{NaCN}(\text{s})$, and $\text{SiC}(\text{s})$, respectively. In spite of this broader definition, the major source of carbon compounds is still living or previously living things, such as plants, animals, and all types of fossil fuels.

Coal, oil sands, heavy oil, crude oil, and natural gas are nonrenewable sources of fossil fuels. They are also the primary sources of **hydrocarbons**—compounds containing carbon atoms bonded to hydrogen atoms. Hydrocarbons are the starting points in the synthesis of thousands of products, including specific fuels, plastics, and synthetic fibres. Some hydrocarbons are obtained directly by physically refining oil and natural gas (both called petroleum), whereas others come from further (chemical) refining (**Table 1**).

Refining is the technology that includes physical and chemical processes for separating complex mixtures into simpler mixtures or near-pure components. The refining of coal and natural gas involves physical processes; for example, coal may be crushed. Components of natural gas are separated either by solvent extraction or by condensation and distillation. Oil sands refining involves a chemically enhanced physical process followed by the complex refining of the bitumen/tar. Crude oil refining is more complex than coal or gas refining, but many more products are obtained from crude oil.

Table 1 Refining of Fossil Fuels—a Preview

Fossil fuel ¹	Extraction	Physical processing ²	Chemical processing	Sample uses
Natural gas ³ 	natural pressure underground	condensation and distillation	removal of hydrogen sulfide and carbon dioxide at a gas plant	heating buildings; source of ethane, propane, and butane
Coalbed methane 	water removed from underground, if necessary	removal and disposal of saline water, if necessary	removal of non-combustibles at a gas plant	same as natural gas, including production of hydrogen and methanol
Crude oil 	water or gas injection underground	water, sand, and salt removal, and fractional distillation in a tower	hydrocracking and catalytic reforming	gasoline, jet fuel, and asphalt
Heavy oil 	steam injection underground	separation from water and solids; fractional distillation	heavy oil hydrocracking and catalytic reforming	same as crude oil
Oil sands (bitumen) 	physical mining and in situ steam or hot water injection	hot water extraction and floatation; centrifugation; fractional distillation	coking, hydrocracking, hydrotreating	synthetic crude used as crude oil
Coal 	surface and underground mines	sorting, crushing, and/or grinding	none or gasification for alternative delivery	energy for producing electricity

1. These Alberta fossil fuels are listed in order of increasing density. 2. In many cases, physical processing also includes removing water and solid contaminants from the raw material. 3. For natural gas, the chemical processing precedes the physical processing.

**INVESTIGATION 9.1 Introduction****Report Checklist****Classifying Fossil Fuels**

Alberta has many different fossil fuels. Samples of fossil fuels can be described and classified in terms of their physical properties of colour, transparency, viscosity, and density. In this investigation, the focus is on density.

Purpose

The purpose of this investigation is to use the known properties of fossil fuels to analyze the provided samples.

Problem

What are the classes of the fossil fuel samples provided?

- | | | |
|----------------------------------|--|--|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 3) |
| <input type="radio"/> Hypothesis | <input checked="" type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Design

Equal-volume samples of fossil fuels are provided in sealed containers of equal mass. The mass of each sample, including the container, is determined. The fossil fuel samples are classified based on their densities.

To perform this investigation, turn to page 401.

**Case Study****Fossil Fuel Industries in Alberta**

Alberta is very rich in fossil fuels. The most widely accepted hypothesis for the origin of these fossil fuels is that they formed from sand, silt, and plant and animal remains starting about 500 Ma ago. The majority of hydrocarbons found in Canada exist in the Western Canada Sedimentary Basin, which covers all but the northeast corner of Alberta (**Figure 2**).

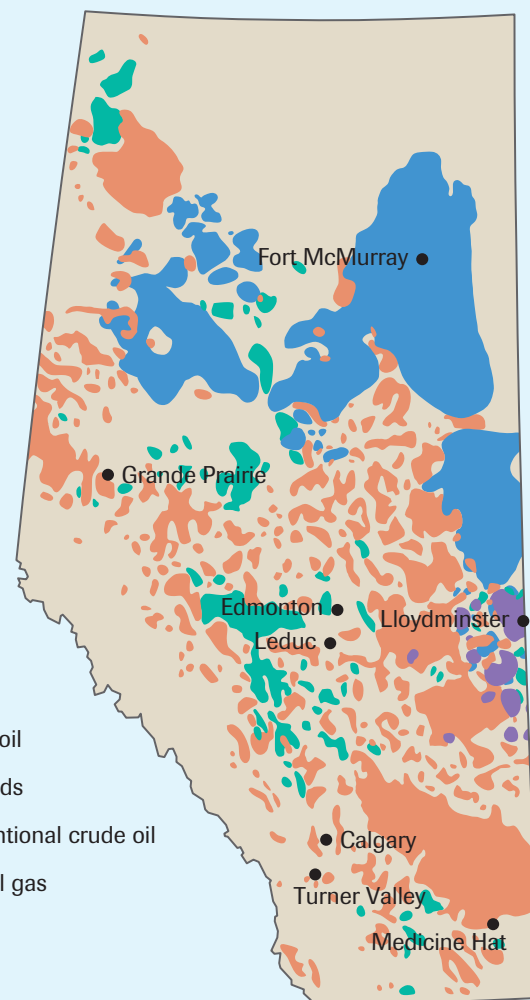
Coal, oil sands, heavy oil, crude oil, natural gas, and coalbed methane are fossil fuels found in significant quantities in Alberta. From a technological perspective, each of these fuels has historically had to go through several cycles of discovery, research, and development.

Discovery, Research, and Development

Discovery has occurred throughout history, from Aboriginal peoples discovering oil sands along the banks of the Athabasca River and farmers digging fence-post holes and finding coal, to today's sonar equipment used for conducting underground seismic surveys. Research and development (R & D) has historically been conducted separately and sequentially: research by universities and development by industry. However, this model of R & D has changed and continues to change, with more overlap of the roles of universities and industries. For example, on a small scale, government (the Alberta Research Council) scientists did research and development on the hot-water process for extracting oil from the oil sands. Industry and engineers then ran larger-scale tests and developed the sophisticated technologies required for economical world-scale plants. Researchers continue the R & D cycle in their attempts to extract oil from deep oil sands and depleted oil wells.

Petroleum Discoveries

Natural gas was first discovered by chance near Medicine Hat, Alberta, in 1883. The drillers were looking for water, and found a methane-rich flammable gas. The discovery, and the many subsequent fires, prompted author Rudyard Kipling to refer to

**Legend**

- Heavy oil
- Oil sands
- Conventional crude oil
- Natural gas

Figure 2
Fossil fuels in Alberta

Medicine Hat as Hell's Kitchen. The plentiful gas made Medicine Hat famous for natural gas street lights and pottery furnaces. Natural gas was then discovered in Cessford, Turner Valley, Suffield, Bow Island, and Viking, Alberta.

Hell's Half Acre was the nickname for Turner Valley, Alberta, where oil was discovered in 1914 and in 1936—beneath the natural gas. The next important discovery of crude oil was Leduc 1 on February 13, 1947 (**Figure 3**). This gusher near Devon, south of Edmonton, started an oil rush. Oil was struck in the Devonian Formation after Imperial Oil had drilled 133 unsuccessful wells. Perseverance, it appears, is just as important for technologists as it is for scientists (and students).

The largest oil field in Canada is the Pembina field, near Drayton Valley, Alberta. Geologists continue to search for oil and gas in the sedimentary basin to Rainbow Lake, Norman Wells, and the Beaufort Sea. Much of the exploration in Alberta today is to find coalbed methane gas and oil sands (see the Explore an Issue on page 365 and the Case Study on page 395). The search for crude oil also continues.

Infrastructure

With the discovery and production of oil and natural gas came the need for infrastructure: oil and gas pipelines, gas plants, and oil refineries. Pipelines are needed to transport the oil or gas to a refinery, to local consumers, and to national and international consumers. These pipelines criss-cross Alberta—as evidenced by cut-lines and road-crossing signs. Pipelines were, and continue to be, built to eastern Canada, the west coast, and the United States.

Oil refineries were first built in 1923 and 1939 in Calgary. As the discovery of oil moved northward, so did the refineries. As the size of the discoveries grew, so did the size of the refineries. Refineries continue to be built, especially for the refining of bitumen (from oil sands) and heavy oil. The refining of natural gas in Alberta requires over 800 gas plants to remove impurities (such as hydrogen sulfide) and to extract the valuable components from the gas (including ethane, propane, and butane).

Social and Environmental Challenges

The advantages to Albertans of the large quantities of fossil fuels found in Alberta are numerous. Major examples include using gasoline (from crude oil) to propel our cars and trucks, using natural gas to heat our homes, and using coal to produce our electricity. In general, the fossil fuel industry in Alberta has important effects on our economy and our lifestyles.

Our fortune of fossil fuels also presents challenges. Some of these challenges include the effects on communities and infrastructure. For example, in fast-growing communities close to fossil fuel extraction and refining plants, there is a higher



Figure 3
Leduc 1

probability of a shortage of housing and social services. Rapid and extensive development of resources also presents environmental challenges. For example, the extraction and refining of many fossil fuels requires water. The extraction process disturbs surface land and air, and creates water pollution to varying degrees.

There are nearly always trade-offs (a negative for a positive result) when we decide to develop a natural resource. Research and technological fixes can only solve so many problems. The demands (needs and wants) of society and of individuals may be justified in our minds, but we also need to consider the potential negative consequences of our everyday actions.

Case Study Questions

- (a) Based upon Figure 2 on the previous page, which are the most widespread fossil fuel deposits in Alberta?
(b) What fossil fuels found in Alberta are not depicted in Figure 2?
- (a) What is the classical relationship between research and development?
(b) Which group of people performed each of the R & D?
- What technological infrastructure is necessary for processing and transporting fossil fuels?
- Give an example of a trade-off between a positive and a negative consequence of fossil fuel production.

Extension

- Research and report alternative hypotheses to the currently accepted hypothesis for the formation of fossil fuels, such as the organic and the inorganic hypotheses.

www.science.nelson.com



- In what general regions of Alberta have we found
(a) oil sands, heavy oil, crude oil, and natural gas?
(b) coal and coalbed methane?
(c) significant wind, solar, biomass, and geothermal energy production?

www.science.nelson.com



- Research when and where natural gas was discovered in Canada's Northwest Territories.

www.science.nelson.com



- Continue your research on the Resolution in the Exploration on page 357: The burning of fossil fuels for heat and transportation should be significantly reduced. Gather statements, pro and con, from a variety of perspectives. Focus on the effects of the discovery and extraction of fossil fuels in Alberta.

www.science.nelson.com





Case Study—Coal in Alberta

Research indicates that the most abundant fossil fuel reserve in Alberta and Canada is coal. To help describe coal, scientists have classified it into four broad classes based upon the percentage of carbon. From highest carbon content to lowest, the classes of coal are anthracite, bituminous, sub-bituminous, and lignite. You will find out more about coal as you pursue this Case Study.

www.science.nelson.com



CBC radiONE

QUIRKS & QUARKS

Could the Athabasca Tar Sands Catch Fire?

The tar sands, or oil sands, are rich in fossil fuels. So could a huge fire spread through the vast deposits? Listen to a University of Calgary professor's answer to find out.

www.science.nelson.com



Section 9.1 Questions

- Classify the following chemicals as organic or inorganic.

(a) $\text{CaCO}_3(\text{s})$	(e) $\text{CH}_3\text{COOH}(\text{l})$
(b) $\text{C}_{25}\text{H}_{52}(\text{s})$	(f) $\text{CO}_2(\text{g})$
(c) $\text{Ca}_2\text{C}(\text{s})$	(g) $\text{KCN}(\text{s})$
(d) $\text{CCl}_4(\text{l})$	(h) $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$
- List six different types of fossil fuels found in Alberta.
- All fossil fuels require some refining after being extracted from the ground. State the two major kinds of refining and describe how, in general, they are different.
- Write molecular and structural formula equations for the combustion of the following hydrocarbon components of natural gas. Assume complete combustion.
 - lighting a butane lighter, $\text{C}_4\text{H}_{10}(\text{g})$
 - burning pentane, $\text{C}_5\text{H}_{12}(\text{l})$, in winter gasoline
- The carbon dioxide gas produced by combustion of hydrocarbons enters the atmosphere.
 - What change can the carbon dioxide induce on the climate? Explain briefly.
 - Write an equation to represent the production of an acid component of acid rain from carbon dioxide.
- Classify the following statements as pro or con to the Resolution in the Exploration on page 357. Also classify the perspective from which the statement is made.
 - Research is being done to reduce or reuse carbon dioxide emissions.
 - Alternative energy sources, such as wind and solar power, may reduce energy-use effects on the environment.
- Industries producing ethanol from grain should receive the same tax breaks as industries producing synthetic crude oil from oil sands.
- The yields of crude oil from wells and of synthetic crude from oil sands are increasing due to better and better equipment and techniques.
- Votes can be gained by accelerating the extraction of crude oil and of coalbed methane from available deposits.
- The laws governing the extraction of fossil fuels by energy companies need to be more stringently enforced.
- Developing our fossil fuel resources is the morally right thing to do—it helps people.
- Communities depend on the energy industries for supporting their families and way of life.
- What kinds of energy sources do you use in your home and from what fossil fuels do they come?
- List three renewable sources of energy naturally available in Alberta.
- What kinds of jobs are available working on oil and gas drilling rigs? Look at the options and choose an occupation on or around the rigs. Describe the job, its requirements, and the recommended salary. Where would you go to train for this job?

www.science.nelson.com









9.2 Alkanes from Natural Gas

Natural gas is removed from underground by drilling a deep hole into the ground where geologists have predicted that natural gas and/or oil is to be found. Nature makes the geologists' task of predicting the presence of oil and gas very challenging, as illustrated in **Figure 1**, but modern technologies provide increased certainty to their predictions. From a chemistry perspective, the separation of the rock and water from the oil and gas can be explained by solubility theory. For example, nonpolar substances (such as oil) do not dissolve in polar substances (such as water). Some ionic substances (such as limestone) are only slightly soluble in water, and no ionic substances dissolve in oil.

Some common types of traps for oil and gas

1. Limestone reef trap of the type found in Leduc and Redwater.
2. Reservoirs in folded and faulted strata. Turner Valley's oil was found in traps like this.
3. Stratigraphic trap of the type found in southeast Saskatchewan.
4. Displacement of rock layers along a fault. This type of structure is found in some areas of the Peace River district.

Legend

	Sandstone
	Limestone
	Shale
	Gas
	Oil
	Water

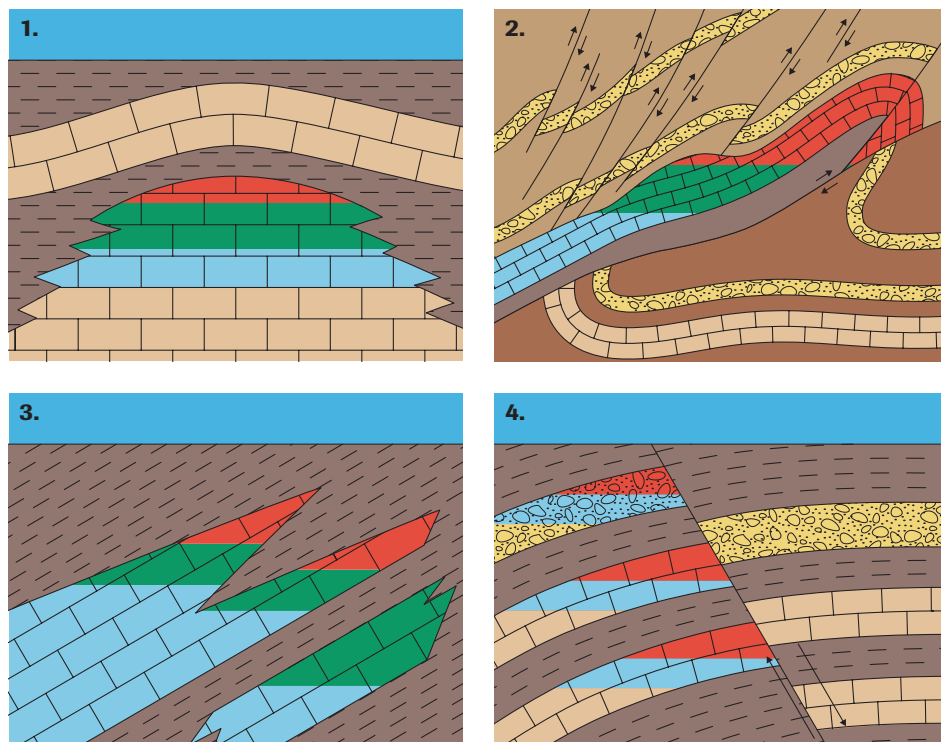


Figure 1

Trapping of natural gas and crude oil in geological formations (limestone and sandstone)

Natural gas has varying composition but it is primarily methane, $\text{CH}_4(\text{g})$ (**Table 1**). Methane is the smallest of the alkane molecules. An *alkane* is a class of hydrocarbons that contains only single bonds and only carbon and hydrogen atoms. In this section, first you will learn about the natural occurrence and the technological extraction and refining of natural gas. Then you will learn about the chemical and physical properties of alkanes. Finally, you will investigate the theoretical structure and nomenclature of this important class of hydrocarbons.

Raw natural gas often contains impurities that make it “sour.” This means that it contains the very toxic gas hydrogen sulfide, which forms acidic solutions when mixed with water. The hydrogen sulfide gas (also called rotten-egg gas) presents a major safety problem for gas-field workers. Exposure to only a small quantity of this gas is deadly. Fortunately, the human nose is extremely sensitive to hydrogen sulfide gas—an early warning system.

DID YOU KNOW?

Smelly Additives

Mercaptans are added to natural gas and to propane. Natural gas and propane are odourless, which makes them difficult to detect and a potential explosion hazard. Mercaptans, however, have a very strong odour. The addition makes gas leaks much more noticeable, and, therefore, much safer.

Natural Gas Refining

Raw natural gas is piped from the well site to one of more than 800 gas treatment plants in Alberta. At the plant, water and liquid hydrocarbons are removed from the gas before it is chemically refined in an absorber tower. During this technological process, the sour natural gas reacts with an amine such as aqueous diethanolamine, $(\text{C}_2\text{H}_4\text{OH})_2\text{NH}(\text{aq})$, under relatively high pressure and low temperature. The amine “sweetens” the gas by removing any hydrogen sulfide (H_2S) and carbon dioxide gases, which are then released from the amine in a regenerator tower. The hydrogen sulfide then partially reacts with oxygen to produce sulfur dioxide. The mixture is then sent to a sulfur recovery unit containing Claus converters (**Figure 2**). The Claus converters convert the H_2S and SO_2 mixture to elemental sulfur and water vapour. You may have seen large yellow blocks of sulfur beside gas plants in Alberta (**Figure 3**). Natural gas may range from 0% to 80% hydrogen sulfide. Sweet natural gas directly from a well contains no hydrogen sulfide but still needs to have water, liquid hydrocarbons, and carbon dioxide removed before being pumped into a natural gas pipeline.

Sweet natural gas (natural or refined) is a mixture of hydrocarbons (**Table 1**). The composition of natural gas depends on the region of the province and the specific well within the region from which it comes. Some industries may preferentially purchase gas with the composition that best suits them, such as high percentages of propane to sell to customers.

Table 1 Typical Composition of Sweet Natural Gas

Component	Chemical formula	Mole fraction (~%)	Boiling point (°C)
nitrogen	$\text{N}_2(\text{g})$	2.7	-196
carbon dioxide	$\text{CO}_2(\text{g})$	0.3	-78
methane	$\text{CH}_4(\text{g})$	83.6	-162
ethane	$\text{C}_2\text{H}_6(\text{g})$	11.6	-89
propane	$\text{C}_3\text{H}_8(\text{g})$	1.75	-42
butane	$\text{C}_4\text{H}_{10}(\text{g})$	0.15	-0.5
pentanes*	$\text{C}_5\text{H}_{12}(\text{l/g})$	0.08	vary (e.g., ~36)
hexanes*	$\text{C}_6\text{H}_{14}(\text{l/g})$	0.07	vary (e.g., ~69)

* Pentanes and hexanes are liquids under normal room conditions, but are vapour components of natural gas (just like water is a vapour component of air).

Although some of the natural gas may be burned directly or exported as a mixture of gases, most of the natural gas consumed in Alberta is further refined into separate components. At these refining (fractional distillation) plants, a simplified description is that the natural gas is cooled under high pressure to condense all the components except the methane gas. The condensed (liquid) portion is then slowly distilled to separate out the ethane, propane, butane, and pentane fractions (**Figure 4**). Some of the uses of these fractions are presented in **Table 2**.

Table 2 Uses of Natural Gas Components

Component	Some uses for the component
methane, $\text{CH}_4(\text{g})$	heating homes, fueling taxis, producing hydrogen and methanol
ethane, $\text{C}_2\text{H}_6(\text{g})$	cracked into ethene for producing many petrochemicals
propane, $\text{C}_3\text{H}_8(\text{g})$	heating homes and vacation trailers; fueling barbecues and stoves
pentane, $\text{C}_5\text{H}_{12}(\text{l/g})$	winter additive to gasoline for greater vaporization



Figure 2

An upgraded sulfur recovery unit was installed at Shell's Burnt Timber sour gas processing plant, 117 km northwest of Calgary, in the early 1990s. This facility processes natural gas from seven different gas fields that contain 0–28% hydrogen sulfide.



Figure 3

This photo shows a block of sulfur at the Caroline-Shantz sulfur-forming facility near Sundre, Alberta. Only about 60 out of 800 gas plants recover sulfur. Most gas plants process sweet (non-sulfur) natural gas.



Figure 4

Fractionation of natural gas provides a supply of propane.

DID YOU KNOW?

Helium From Natural Gas

Air ships used before and during the First World War were filled with explosive hydrogen gas. Looking for a safer alternative, Canadian John McLennan invented a method for extracting the tiny quantities of helium from natural gas. McLennan designed and built a plant in Calgary during the First World War to provide helium for safer air ships for the Allies.

DID YOU KNOW?

Pipelines and Gas Processing Plants

Crude oil, synthetic crude, diluted bitumen, natural gas, ethane, and other pipelines criss-cross Alberta and Canada. Many farm fields in Alberta have one or more pipeline(s) under the ground. There are in excess of 800 natural gas processing plants in Alberta. These plants remove water, carbon dioxide, and/or poisonous hydrogen sulfide from the gas. The hydrogen sulfide is recovered and converted to sulfur to produce, for example, sulfuric acid. Is there a pipeline or a gas processing plant near you?

www.science.nelson.com



+ EXTENSION



CBC **radiONE**

QUIRKS & QUARKS

Mining Methane

In a fuel-hungry world, geologists and researchers are searching everywhere for new resources. The Mallik 2002 drilling program explored buried deposits of methane in Canada's Arctic, and has raised hopes that these resources might be financially viable. There could be as much fuel here as in the entire world's reserves of traditional fossil fuels.

www.science.nelson.com



Practice

- Describe the two main stages in the refining of most natural gas. Identify which changes are physical and which are chemical.
- Draw structural formulas for the first four members of the alkanes. Show all atoms and bonds.
- Chemists have determined the boiling point of the components of natural gas (see Table 1 on the previous page).
 - What is the trend in boiling point as the number of carbon atoms increases for the alkane family?
 - Explain any trend that you identify that relates the size of an alkane molecule to its boiling point.
- Geologists are able to use various technologies to empirically determine the geological features of oil- and gas-containing formations (Figure 1). Use intermolecular force and solubility theories to help explain the separation of
 - water and crude oil
 - limestone (assume $\text{CaCO}_3(\text{s})$) and crude oil
 - crude oil and natural gas
- Chemical engineers indicate that hydrocarbon gases, such as methane ($\text{CH}_4(\text{g})$), evaporate from or are easily boiled off from crude oil.
 - Use what you know about solubility to explain the presence of methane in crude oil.
 - Use what you know about crude-oil-containing geological formations to create a hypothesis as to how the methane may have gotten into the crude oil.
- There is an increasing use of natural gas and a decreasing use of petroleum in Canada (Figure 5).

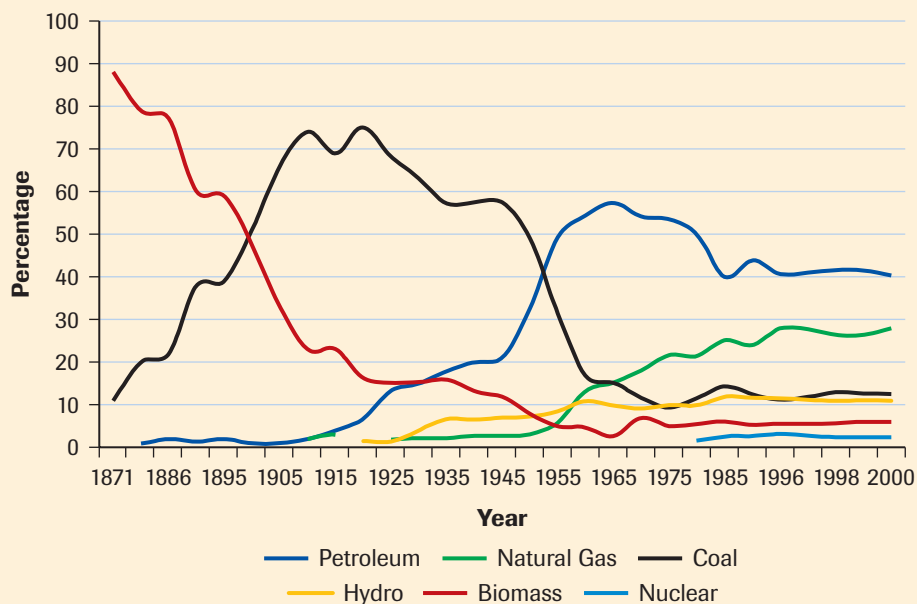


Figure 5

Energy use in Canada since 1871

- Suggest some reasons for the changes in use of natural gas and petroleum in Canada.
- Revisit your work on the Exploration: Burning Fossil Fuels at the beginning of this chapter. Add some of the statements from this section of study to your perspectives sheet relating to the resolution that the burning of fossil fuels should be decreased.


EXPLORE an issue

Coalbed Methane

Coal miners have known about coalbed methane for centuries. Sudden releases of methane underground have killed hundreds of miners by suffocation or explosions. Similar gas releases have even been the subject of hypotheses to explain strange happenings in the Bermuda Triangle (see Chapter 4, Figure 2, page 185). Productively controlling the release of methane from coal beds is a developing technology in Alberta. Coalbed methane has been described as the oil sands of natural gas. Alberta geologists have mapped a potentially huge resource for coalbed methane (**Figure 6**). The methane is held underground by the surrounding pressure of trapped water. Releasing that pressure releases the methane. The method of extraction involves drilling a well to the methane-rich coal seam and, in many cases, pumping the water out (**Figure 7**). Removing the water releases the pressure on the methane and the low-pressure methane flows to the surface. A (potentially noisy) compressor at the surface pumps the methane along a pipeline to a natural gas refining site. Recall that natural gas is mainly methane. Coalbed methane is a natural gas that comes from underground coal beds. This



Figure 6
Zones with coalbed methane potential in Alberta

Issue Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Issue | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Resolution | <input checked="" type="radio"/> Evidence | <input checked="" type="radio"/> Evaluation |

coalbed natural gas has a very high percentage of methane, hence its name. The water removed from the coalbed is typically saline (salty) and is placed in holding ponds until it can be pumped back down the well.

Unlike natural gas wells, where only a couple of wells are needed to recover the gas on an owner's land, up to eight coalbed methane wells may be needed on a section of land. The landowners are paid for leasing the land to the natural gas company. Landowners do not, typically, own the mineral rights to the methane underground. They only own the surface rights.

Issue

Accessing coalbed methane may present challenges with land, noise, and water.

Resolution

Coalbed methane extraction in Alberta should be stopped until further research has been conducted.

Design

Research, from a variety of perspectives, the pros and cons of coalbed methane extraction in Alberta.

www.science.nelson.com 

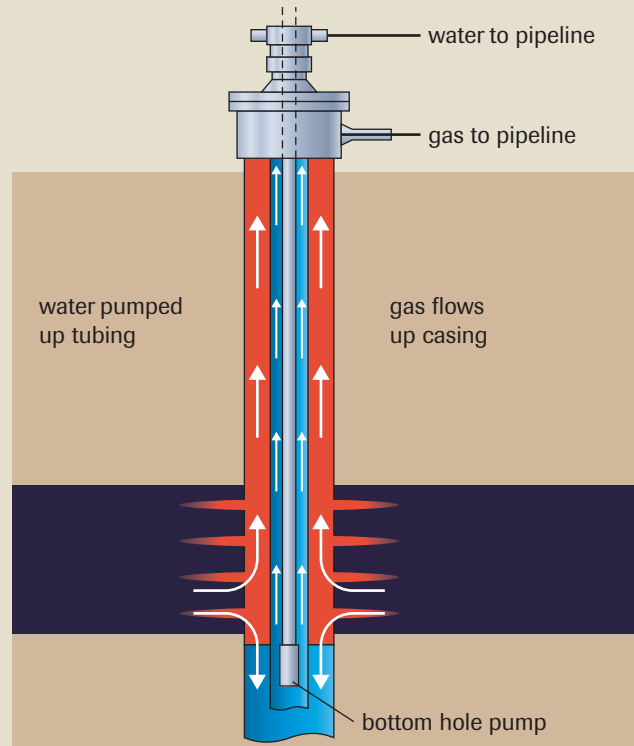


Figure 7
Coalbed methane extraction

Table 3 The Alkane Family of Organic Compounds

IUPAC Name	Formula
methane	CH ₄ (g)
ethane	C ₂ H ₆ (g)
propane	C ₃ H ₈ (g)
butane	C ₄ H ₁₀ (g)
pentane	C ₅ H ₁₂ (l)
hexane	C ₆ H ₁₄ (l)
heptane	C ₇ H ₁₆ (l)
octane	C ₈ H ₁₈ (l)
nonane	C ₉ H ₂₀ (l)
decane	C ₁₀ H ₂₂ (l)
-ane	C _n H _{2n+2}

Learning Tip

Memorize the prefixes indicating one to ten carbon atoms. See Table 3.

Naming Alkanes

Although hydrocarbons can be classified according to empirical properties, a more common classification is based upon the chemical formulas of the compounds. Hydrocarbons whose empirically determined molecular formulas indicate that the carbon-to-carbon bonds are only single bonds are called **alkanes**. The simplest member of the alkane series is methane, CH₄(g), which is the main constituent of the natural gas sold for home heating. The molecular formulas of the smallest alkanes (the first six of which are all typical constituents of natural gas) are shown in **Table 3**. Each formula in the series has one more CH₂ group than the one preceding it. Derived from empirically determined formulas and from bonding capacity, the general molecular formula for all alkanes is C_nH_{2n+2}; that is, a series of CH₂ units plus two terminal hydrogen atoms.

Alkanes are an example of what chemists call a **homologous series**—a sequence of molecules with similar structure and differing only the number of repeating units; e.g., CH₂. Chemists also classify alkanes as **saturated hydrocarbons**—compounds of carbon and hydrogen containing only carbon-carbon single bonds with the maximum number of hydrogen atoms bound to each carbon.

The first syllable in the name of an alkane is a prefix that indicates the number of carbon atoms in the molecule (**Figure 8**). The prefixes shown in **Table 3** are used in naming all organic compounds.

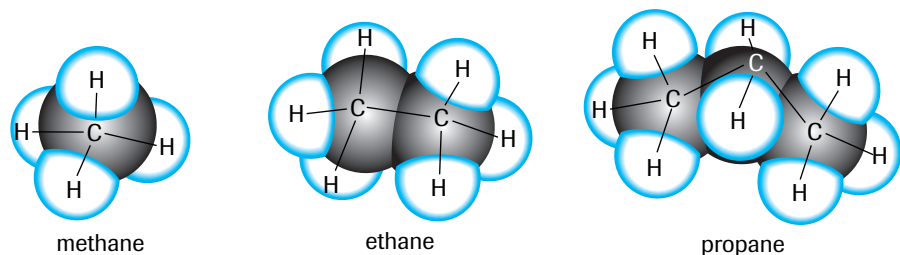
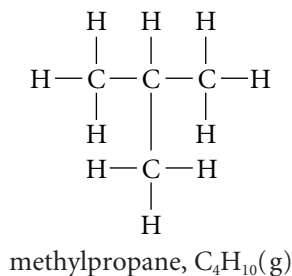
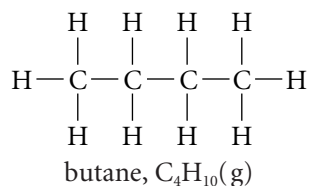


Figure 8

The prefix *meth*— indicates one carbon atom, *eth*— signifies two carbon atoms, and *prop*— signifies three carbon atoms. The ending *-ane* indicates a chain of carbon atoms with single bonds only.

Structural Isomers

Chemical formulas, such as the ones in Table 3, tell you the total number of each kind of atom in a molecule. Except for the three smallest molecules (**Figure 8**), there are several structures that can have the same molecular formula. For example, C₄H₁₀ has two different structural formulas, both satisfying the rules for chemical bonding.



So, while we can say that butane always has the formula, C₄H₁₀, we cannot say that a compound with the formula C₄H₁₀ is always butane.

Compounds with the same molecular formula, but with different structures, are called **structural isomers**. Chemists created this theoretical concept to explain why isomers (different compounds with the same molecular formula) could have different physical and

chemical properties. Compounds with the same molecular formula but different properties must be differentiated in some way. For this reason, the two structures for C_4H_{10} shown above must have different names to avoid confusion. (See the next subsection.)

As the number of carbon atoms in a hydrocarbon increases, the number of possible isomers increases dramatically. For example, $C_{10}H_{22}$ has 75 possible isomers, $C_{20}H_{42}$ has 366 319, and $C_{30}H_{62}$ has 4 111 846 763 possible isomers. No wonder there are more compounds of carbon than compounds of all other elements combined!

Names and Structures of Branched Alkanes

The name of the compound indicates whether there are branches on a carbon chain. Prefixes (as in **Table 3**) identify groups of atoms that form branches on the structures of larger molecules. A *branch* is any group of atoms that is not part of the main structure of the molecule. For example, a branch consisting of only carbon and hydrogen atoms is called an **alkyl branch**. In the names of alkyl branches, the prefixes are followed by a *-yl* suffix (**Table 4**). For example, consider the three isomers of C_5H_{12} shown in **Figure 9**. The unbranched isomer on the left is named pentane.

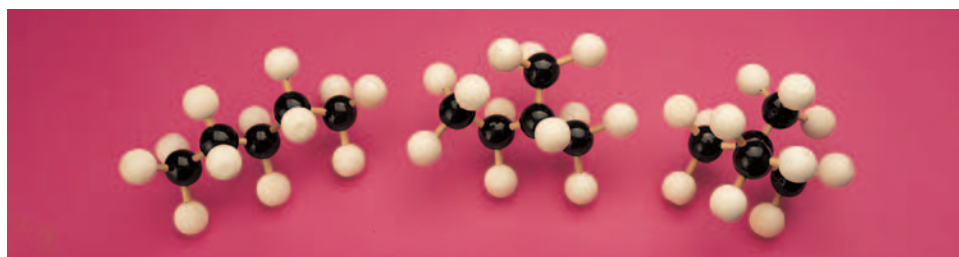
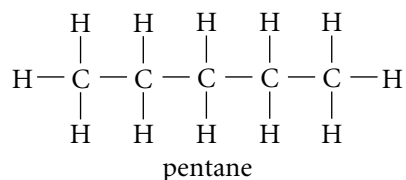


Figure 9

Each of the three isomers of C_5H_{12} has different physical and chemical properties.

The “straight” chain description of C_5H_{12} is shown below. Of course, there is a tetrahedral arrangement of bonds around each carbon atom, which produces the “saw-tooth” chain of carbon atoms modelled in Figure 9.



In the second isomer, there is a continuous chain of four carbon atoms with a methyl group on the second carbon atom. To name this structure, identify the *parent chain*—the longest continuous chain of carbon atoms. Here, the four carbons indicate that the parent chain is butane. Since a methyl group is added as a branch to the longest continuous chain of four carbon atoms, this isomer is called methylbutane. The same name applies when the methyl group replaces any of the four hydrogen atoms on the middle two carbon atoms of butane.

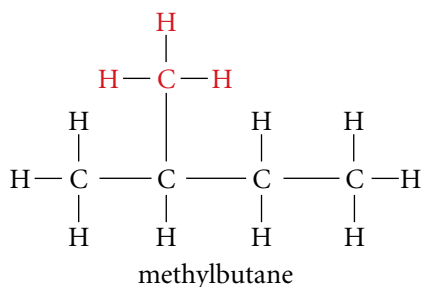


Table 4 Examples of Alkyl Branches

Branch	Name
$-\text{CH}_3$	methyl
$-\text{C}_2\text{H}_5$ ($-\text{CH}_2\text{CH}_3$)	ethyl
$-\text{C}_3\text{H}_7$ ($-\text{CH}_2\text{CH}_2\text{CH}_3$)	propyl

Learning Tip

Computer models of molecules can be displayed as

- wireframe (line structural)
- sticks (structural)
- ball and stick (structural)
- space filling

Interact with some of the alkane models at the following Web link.

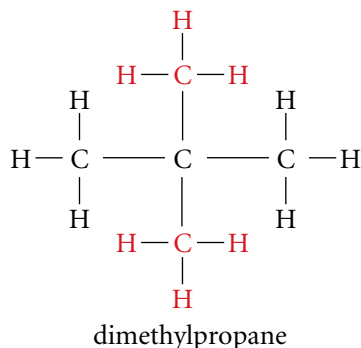
www.science.nelson.com



Learning Tip

To decide whether two different-looking structural formulas are the same molecule, rotate the structure top to bottom or left to right. If, by rotating the molecule, you can make it the same as another molecule, then it is the same molecule and has the same name (and is not a different isomer).

In the third isomer of C_5H_{12} in Figure 9, two methyl groups are attached to a three-carbon (propane) parent chain. This third pentane isomer is named dimethylpropane. There is no other isomer of dimethylpropane. Attaching one of the two methyl groups to an end carbon makes the molecule methylbutane. Attaching a methyl group to each end of propane makes the molecule pentane. See Figure 9.



Since there is only one methylbutane isomer and only one dimethylpropane isomer, we do not use numbers in the names of these molecules: 2-methylbutane and 2,2-dimethylpropane are incorrect names. In some cases, however, we need to number the carbon atoms to indicate the position(s) of branch(es) (substitution group(s)). In these cases, follow the steps below to name the branched hydrocarbon.

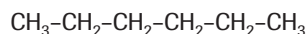
Learning Tip

Although IUPAC allows for alkyl groups (or any other atoms or groups of atoms substituted for hydrogen) to be placed in alphabetical order *or* in order of complexity (least to greatest), this textbook uses the rule of alphabetical order, for example, 3-ethyl-2,2-dimethylhexane. (Ignore the “di” and pay attention only to the “e” of ethyl and the “m” of methyl.)

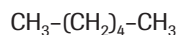
Learning Tip

Structural formulas show all bonds between atoms. This system is not efficient, especially for C–H bonds. Thus, the diagram is often simplified by not showing the bonds with H atoms, as shown in Sample Problem 9.1.

Long-chain hydrocarbons such as



can be represented as



Both of these formulas and the one in Sample Problem 9.1 are *condensed structural formulas*.

SUMMARY Naming Branched Alkanes

Step 1: Identify the longest continuous chain of carbon atoms—the parent chain—in the structural formula. Number the carbon atoms, starting from the end closest to the branch(es), so that the numbers are the lowest possible.

Step 2: Identify any branches and their location number on the parent chain.

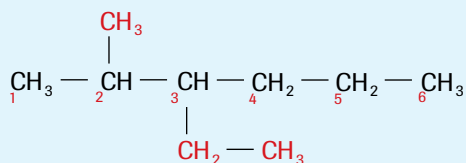
Step 3: Write the complete IUPAC name, following this format:

(number of location, if necessary) – (branch name)(parent chain).

When writing the name of the alkane, list the branches in alphabetical order, ignoring, for example, the di- and tri- prefixes.

SAMPLE problem 9.1

Write the IUPAC name corresponding to the following condensed structural formula for a component of gasoline:



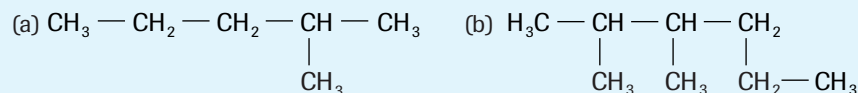
Step 1: The longest continuous chain has six carbon atoms. Therefore, the name of the parent chain is hexane.

Step 2: There is a methyl group branch at the second carbon atom, and an ethyl group branch at the third carbon atom of the parent chain.

Step 3: With the branches named in alphabetical order, the compound is *3-ethyl-2-methylhexane*.

▶ COMMUNICATION example 1

Write the names from the condensed structural formulas for the following components of gasoline. The second component (b) is an isomer of octane.



Solution

(a) 2-methylpentane

(b) 2,3-dimethylhexane

A structural formula can illustrate an IUPAC name. For example, in the Communication Example above, 2,3-dimethylhexane has a hexane parent chain consisting of six carbon atoms joined by single covalent bonds. “2,3-dimethyl” tells us that there is a methyl group attached to the second carbon and another attached to the third carbon.

Above you have learned to name a branch-chained hydrocarbon when given the structural formula. The reverse process is to draw a structural formula when given the name. Both of these processes emphasize the conventions of communication agreed upon worldwide. These conventions are necessary for chemists to communicate their research in internationally distributed scientific journals and for health providers, for example, to administer the correct medication.

SUMMARY

Drawing Branched Alkane Structural Formulas

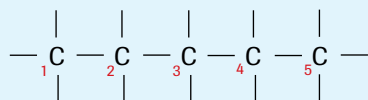
Step 1: Draw a straight chain containing the number of carbon atoms represented by the name of the parent chain, and number the carbon atoms from left to right.

Step 2: Attach all branches to their numbered locations on the parent chain.

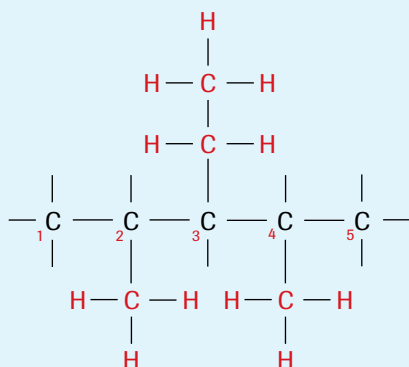
Step 3: Add enough hydrogen atoms to show that each carbon has four single bonds.

▶ SAMPLE problem 9.2

Draw a structural formula for 3-ethyl-2,4-dimethylpentane—possible component of gasoline.



Numbering this straight chain from left to right establishes the location of the branches. An ethyl branch is attached to the third carbon atom and a methyl branch is attached to each of the second and fourth carbon atoms.



Learning Tip

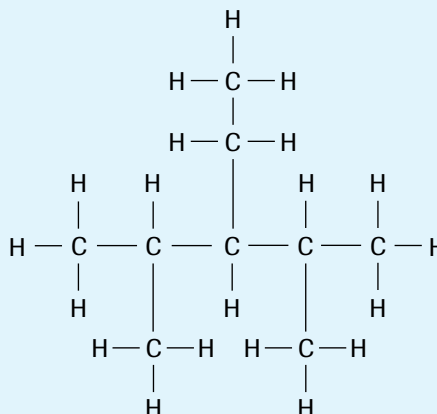
A molecular formula of an organic compound is not very useful because many isomers are often possible. To more clearly specify a particular compound, the structure needs to be indicated either by the IUPAC name or by a diagram. Chemists have invented many different kinds of diagrams to show the structure of a molecule. For our purposes, the structural formula (either full or condensed) is the most useful.

Because structure is so important to the physical and chemical properties of organic molecules, chemists make extensive use of molecular models such as space-filling models (Figure 8) and ball-and-stick models (Figure 9). Just as there are many other kinds of diagrams, there is also a variety of molecular models.

For a little more practice naming alkanes, follow the electronic link.

www.science.nelson.com 

In the following structural formula, hydrogen atoms are shown at any of the four bonds around each carbon atom that are left after the branches have been located.



COMMUNICATION example 2



There are many different hydrocarbon molecules in gasoline, including many isomers. Draw the structural formula for the first isomer and the condensed structural formula for the second isomer of octane.

(a) 2,3,4-trimethylpentane

(b) tetramethylbutane

Solution

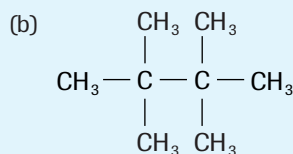
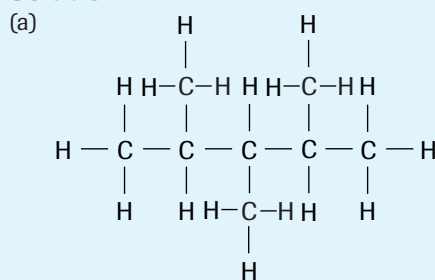


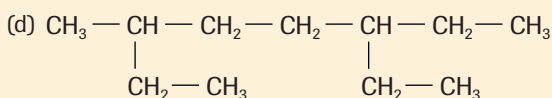
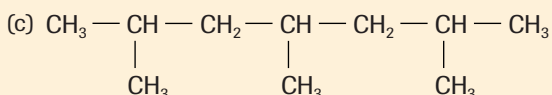
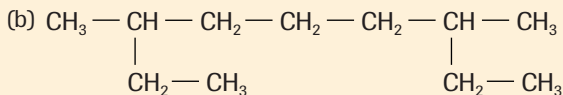
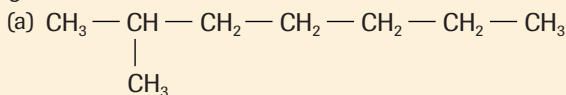
Figure 10

There are many different hydrocarbon mixtures that can be found at hardware stores.

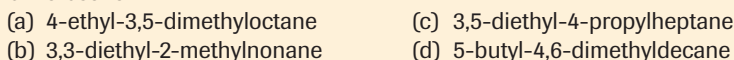
Practice

- Draw the structural formula of each alkane found in crude oil.
 - 2-methylpentane
 - 3-methylpentane
 - 2-methylhexane
 - 3-methylhexane
 - 3,4-dimethylhexane
 - 3-ethyl-2-methylhexane
 - 3,3-dimethylpentane
 - 2,5-dimethyl-4-propyloctane
- There are many different naphtha mixtures. Petroleum naphtha, commonly used as a camping fuel, is a mixture of alkanes with 5 or 6 carbon atoms per molecule (Figure 10).
 - Draw structural formulas and write the IUPAC names for all the isomers of C_6H_{14} .
 - Why are these isomers highly soluble in each other?

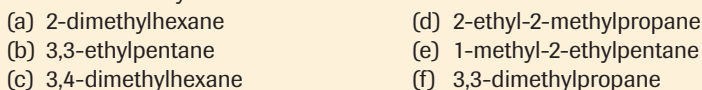
9. Automotive gasoline is a mixture that is largely composed of alkanes containing 5 to 12 carbon atoms per molecule. Write IUPAC names for the following components of gasoline:



10. Kerosene, used as a fuel for diesel and jet engines, contains alkanes with 12 to 16 carbon atoms per molecule. Draw structural formulas for the following components of kerosene:



11. IUPAC tries to standardize chemical communication throughout the world. For each of the following names, determine if it is a correct name for an organic compound. Give reasons for your answer and include a correct name.



DID YOU KNOW?

Chewing Gum

American Aboriginal peoples introduced Europeans to chewing spruce gum, which the Europeans quickly commercialized. In the 1950s, paraffin wax, a solid alkane, became the base for chewing gum. Today, more than one thousand varieties of gum are manufactured using various synthetic materials to replace natural gum ingredients.

Cycloalkanes

On the evidence of empirical formulas and chemical properties, chemists believe that organic carbon compounds sometimes take the form of cyclic hydrocarbons—hydrocarbons with a closed ring. When all the carbon–carbon bonds in a cyclic hydrocarbon are single bonds, the compound is called a **cycloalkane** (C_nH_{2n}).

Cycloalkanes are named by placing the prefix *cyclo* in front of the alkane name, as in cyclopropane and cyclobutane (**Figure 11**). If branches are present, treat the cycloalkane as the parent chain and identify the branches. Since there is no end at which to start the numbering for the location of the branches, use the lowest possible numbers.

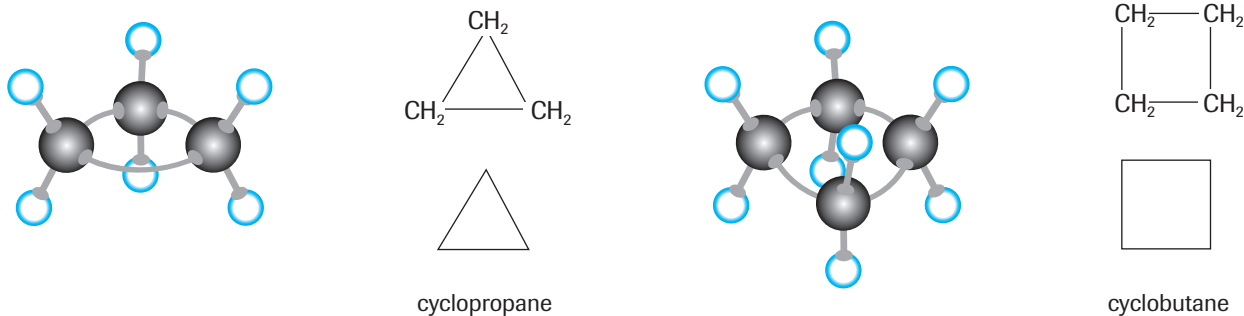


Figure 11

Cycloalkanes such as cyclopropane and cyclobutane are similar to alkanes, except that the two ends of the molecule are joined to form a ring of atoms. This figure shows computer-generated, condensed structural, and line structural models of these two cycloalkanes. These models help to provide a logically consistent theoretical explanation for empirically determined formulas and help chemists to visualize the molecules.

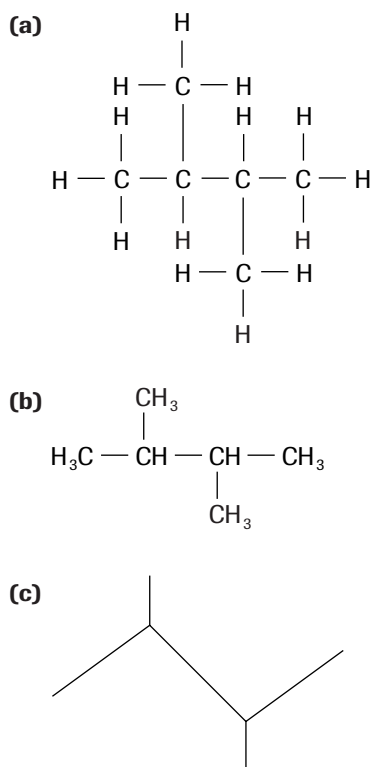


Figure 12
2,3-dimethylbutane can be represented by
(a) a structural formula,
(b) a condensed structural formula,
or
(c) a line structural formula.

Start with the location of one of the branches. Omit the “1” if only one branch is present. For example, methylcyclopropane is a cyclopropane ring with a methyl branch on one of three equivalent carbon atoms of the ring.

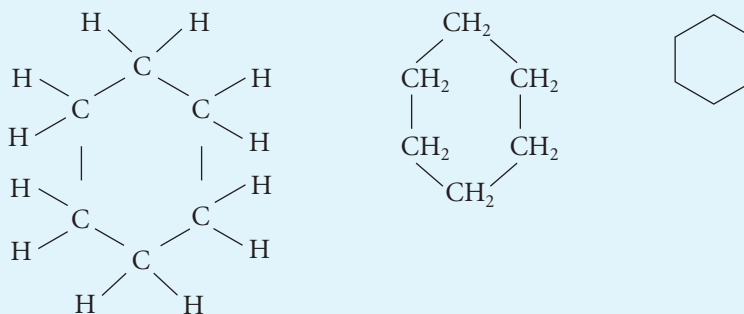
In addition to structural and condensed structural formulas, we can use *line structural formulas*. Line structural formulas of hydrocarbons show the position of the carbon atoms as the intersections and ends of bonding lines; they do not show hydrogen atoms (Figure 12(c)).

COMMUNICATION example 3



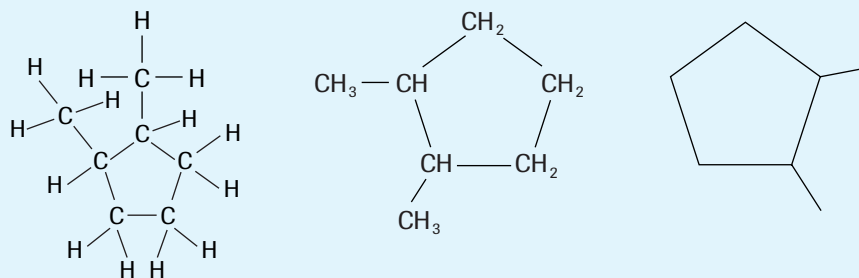
Provide structural, condensed structural, and line structural formulas for cyclohexane.

Solution



COMMUNICATION example 4

Write the IUPAC name for this hydrocarbon, communicated with a structural, a condensed structural, and a line structural formula.



Solution

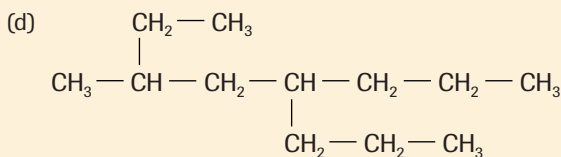
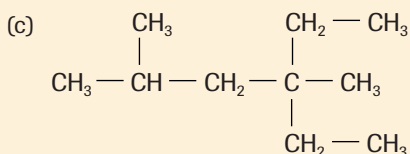
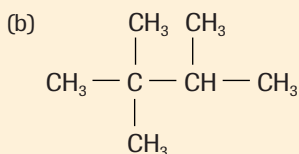
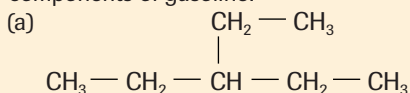
1,2-dimethylcyclopentane

Note that rotating the 1,2-dimethylcyclopentane molecule in Communication Example 4 does not change its name—all of the formulas represent 1,2-dimethylcyclopentane. We count from the carbon atom that gives the lowest possible first number.


Section 9.2 Questions

- List the alkanes that are typically present in natural gas before it is refined. How does this composition compare with the natural gas you use in your homes for heating?
- What is the difference between sweet and sour natural gas? Why is it important to know the difference?
- Describe a process used to remove alkanes, other than methane, from natural gas.
- Natural gas burns readily with oxygen from the air. The primary product is energy.
 - List two consumer, two commercial, and two industrial uses of the energy obtained from natural gas.
 - Look around the room you are in. List some items in the room that likely required energy from natural gas for their production.

5. Draw structural formulas for all reactants and products in the following organic reactions:
- methane + butane → pentane + hydrogen
 - propane + pentane → octane + hydrogen
 - decane + hydrogen → heptane + propane
 - 3-ethyl-5-methylheptane + hydrogen →
ethane + propane + methylbutane
 - cyclohexane + ethane → ethylcyclohexane + hydrogen
6. Write the IUPAC names for each of the following possible components of gasoline:



7. For each of the following chemical equations, write the IUPAC names for all reactants and products.
- $\text{CH}_3 - \text{CH}_2 - \text{CH}_3 + \text{CH}_3 - (\text{CH}_2)_3 - \text{CH}_3 \rightarrow$
 $\text{CH}_3 - (\text{CH}_2)_6 - \text{CH}_3 + \text{H} - \text{H}$
 - $\text{CH}_3 - (\text{CH}_2)_4 - \text{CH}_3 \rightarrow$

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 - Draw condensed structural and line structural formulas, and write the IUPAC names for two other isomers of the product given in (b).
8. Complete the following equations for complete combustion, using molecular formulas to write a balanced chemical equation. Include the structural formula or IUPAC name for each hydrocarbon.
- 2,2,4-trimethylpentane + oxygen →
 - $$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \end{array} + \text{O} = \text{O} \rightarrow$$
 -  + O = O →
9. Why do companies find and develop petroleum resources? Suggest an answer from at least two perspectives.

10. (a) Use the information in **Table 5** to plot a graph showing the relationship between the number of carbon atoms and the boiling points of the alkanes. Describe the relationship and propose an explanation for it.
- (b) Research a use for each of the first 10 alkanes, and suggest why each is appropriate for this use.

www.science.nelson.com 

Table 5 Boiling Points of the First 10 Straight-Chain Alkanes

Formula	Name	B.p. (°C)
CH ₄ (g)	methane	-161
C ₂ H ₆ (g)	ethane	-89
C ₃ H ₈ (g)	propane	-42
C ₄ H ₁₀ (g)	butane	-1
C ₅ H ₁₂ (l)	pentane	36
C ₆ H ₁₄ (l)	hexane	68
C ₇ H ₁₆ (l)	heptane	98
C ₈ H ₁₈ (l)	octane	125
C ₉ H ₂₀ (l)	nonane	151
C ₁₀ H ₂₂ (l)	decane	174

11. Use the information in this section and from your own research to continue gathering perspective statements concerning the statement that the burning of fossil fuels should be reduced.

Extension

12. Oil spills in or near water, like the 2005 rail-car spill near Wabamum, cause a wide variety of environmental problems. Use your knowledge of alkanes to describe and explain what happens physically and chemically when oil is spilled from a tanker car into water.
13. Alberta has extensive natural gas fields that supply gas for use by provincial consumers and industries. The Alberta government collects royalties on the production of all fossil fuels, including natural gas.
- Describe or sketch a map of the distribution of natural gas fields in Alberta.
 - Approximately how much natural gas is produced in one year and how much of it is used within Alberta?
 - How much royalty has the Alberta government collected recently for natural gas? How does this sum compare with the total royalties the Alberta government collects for non-renewable resources?

www.science.nelson.com 

14. Aboriginal peoples used waxes to waterproof footwear, bags, and other clothing. Technologically, paraffins are waxes and chemically, paraffins are alkanes with twenty or more carbons; for example, C₂₅H₅₂(s). Explain why waxes, such as paraffin, can be used as a waterproofing agent.

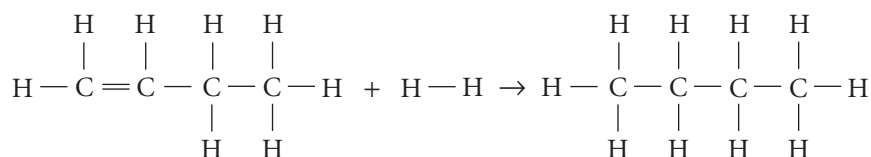
www.science.nelson.com 

9.3 Alkenes and Alkynes—Cracking Natural Gas

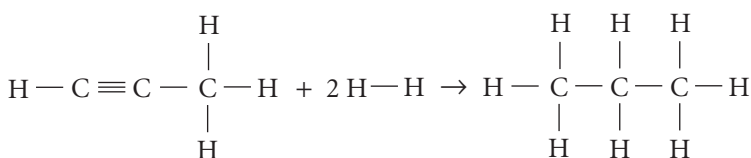
Alkenes and Alkynes

Analysis reveals that hydrocarbons containing double or triple covalent bonds make up a small percentage of petroleum (such as crude oil and natural gas). These compounds are also often formed during chemical refining and are valuable components of gasoline. Hydrocarbons containing double or triple bonds are important in the petrochemical industry because they are the starting materials for the manufacture of many derivatives, including plastics.

A double or a triple bond between two carbon atoms in a molecule affects the chemical and physical properties of the molecule. Organic compounds with carbon–carbon double bonds are said to be *unsaturated*, because they have fewer hydrogen atoms than compounds with carbon–carbon single bonds. Unsaturated hydrocarbons can react readily (usually in the presence of a catalyst) with small diatomic molecules, such as hydrogen. This type of reaction is an addition reaction. Addition of a sufficient quantity of hydrogen, called **hydrogenation**, converts unsaturated hydrocarbons to saturated ones. Saturated hydrocarbons (alkanes) have no double or triple bonds. An excess of hydrogen is needed to convert an alkyne to an alkane, otherwise some of the alkyne is only converted to an alkene.

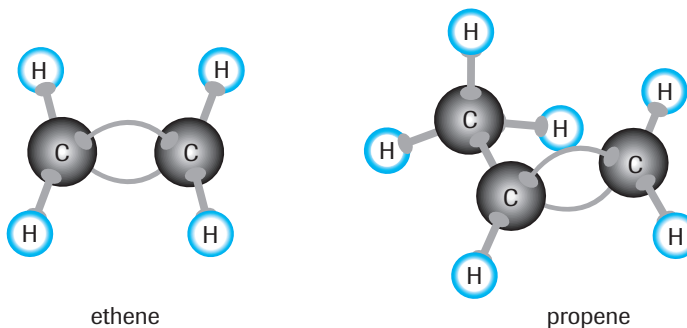


unsaturated hydrocarbon (e.g., an alkene) + hydrogen → saturated hydrocarbon



unsaturated hydrocarbon (e.g., an alkyne) + excess hydrogen → saturated hydrocarbon

Hydrocarbons with carbon–carbon double bonds are members of the **alkene** family (Figure 1). They all have the general formula of C_nH_{2n} . The names of alkenes with only one double bond have the same prefixes as the names of alkanes, together with the ending *-ene* (Table 1). (Ethene is the starting material for a huge variety of consumer, commercial, and industrial products, some of which are listed in Chapter 10, page 415.) Isomers exist for all alkenes larger than propene. Cycloalkanes are isomers of alkenes.



DID YOU KNOW?

Margarine

Margarine containing vegetable oils whose molecules have many double bonds is said to be *polyunsaturated*. The molecules of *saturated* fats, in animal products such as butter, are fully hydrogenated (have only single bonds).

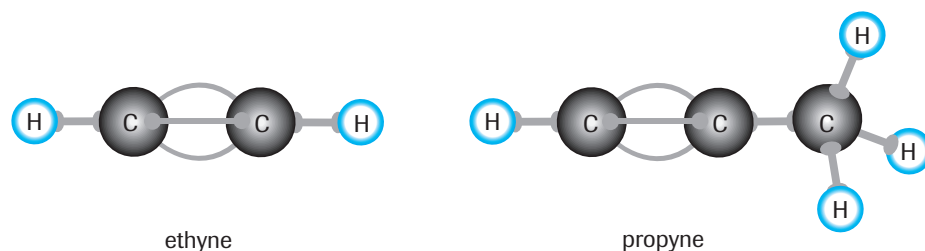
Table 1 The Alkene Family of Organic Compounds

IUPAC name (common name)	Molecular formula
ethene (ethylene)	$C_2H_4(g)$
propene (propylene)	$C_3H_6(g)$
butene (butylene)	$C_4H_8(g)$
pent-1-ene	$C_5H_{10}(l)$
hex-2-ene	$C_6H_{12}(l)$
-ene	C_nH_{2n}

Note: See Naming Alkenes and Alkynes on the next page for an explanation of the numbering system.

Figure 1

The two simplest and most commonly used alkenes are ethene (known as ethylene) and propene (propylene).

**Figure 2**

Sophisticated laboratory research indicates that the triple covalent bonds of ethyne (acetylene) and propyne are the shortest, strongest, and most reactive of all carbon-carbon bonds.

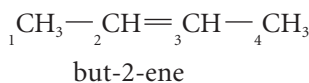
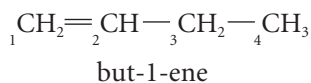
The **alkyne** family has chemical properties that can be explained only by the presence of a triple bond between carbon atoms (**Figure 2**). Like alkenes, alkynes are unsaturated and can react with small molecules such as hydrogen or bromine in an addition reaction. Alkynes are named like alkenes, except for the *-yne* ending. The simplest alkyne, ethyne (acetylene), is commonly used in an oxyacetylene torch for cutting and welding metals. **Table 2** lists the first five members of the alkyne family. Empirical studies indicate that all alkynes with one triple bond have the general formula C_nH_{2n-2} . Isomers exist for all alkynes larger than propyne. Cycloalkenes are isomers of alkynes.

Naming Alkenes and Alkynes

Since the location of a multiple bond affects the chemical and physical properties of a compound, an effective naming system should specify the location of the multiple bond. Alkenes and alkynes are named much like alkanes, with two additional points to consider.

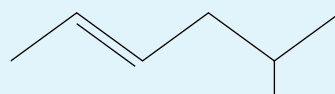
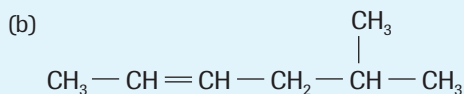
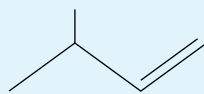
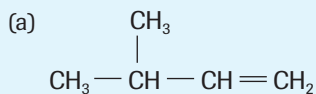
- The longest or parent chain of carbon atoms must contain the multiple bond, and the chain is numbered from the end closest to the multiple bond.
- The number that indicates the position of the multiple bond on the parent chain follows the prefix of the name of the compound's parent chain.

For example, there are two possible butene isomers, but-1-ene and but-2-ene.



COMMUNICATION example 1

Name the hydrocarbons communicated by the following condensed structural and line structural formulas.



Solution

The IUPAC name for (a) is 3-methylbut-1-ene.

The IUPAC name for (b) is 5-methylhex-2-ene.

Table 2 The Alkyne Family of Organic Compounds

IUPAC name (common name)	Molecular Formula
ethyne (acetylene)	$C_2H_2(g)$
propyne	$C_3H_4(g)$
but-2-yne	$C_4H_6(g)$
pent-1-yne	$C_5H_8(l)$
hex-3-yne	$C_6H_{10}(l)$
-yne	C_nH_{2n-2}

Note: See Naming Alkenes and Alkynes at left for an explanation of the numbering system.

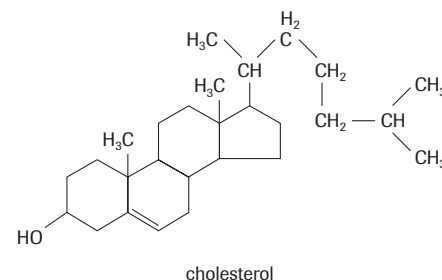
DID YOU KNOW?

Steroids

Steroids are unsaturated compounds based on a structure of four rings of carbon atoms. The best known and most abundant steroid is cholesterol, which is an essential constituent of cell walls, but which has also been associated with diseases of the cardiovascular system. Cholesterol that coats the interior surfaces of arteries contributes to health problems such as high blood pressure. Other steroids include the male and female sex hormones, and anti-inflammatory agents such as cortisone. Oral contraceptives include two synthetic steroids. Some athletes have used anabolic steroids to enhance muscle development and physical performance, but such use may cause permanent damage.

You can view a computer-generated 3-D molecular model of cholesterol by visiting the Nelson Web site.

www.science.nelson.com



Learning Tip

Note that the numbering of carbons for alkenes and alkynes always starts from the end of the molecule closest to the double and triple bond(s). This method yields the lowest possible number for the position of the multiple bond.

Learning Tip

The two general rules used throughout organic nomenclature are:

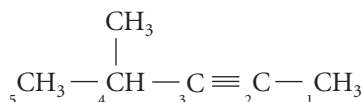
- use the longest continuous chain containing the primary characteristic group of the molecule to determine the prefix and ending of the parent name

Prefix (number of C atoms in longest chain)	+ Ending (characteristic group)
e.g., meth (1)	ane (C—C)
eth (2)	ene (C=C)
prop (3)	yne (C≡C)

For example,
2-methylhexane
2-methylhex-3-ene
2-methylhex-3-yne

- use the lowest set of numbers to indicate the first characteristic feature and then the branches or substituents in the molecule

In the following branched alkyne structure, the parent chain is pentyne.



4-methylpent-2-yne

When numbering the carbon atoms of an alkene or alkyne parent chain, chemists give more importance to the location of the multiple bond(s) than to the location of any branches (alkyl groups). The IUPAC name, 4-methylpent-2-yne, follows the same format as that used for alkanes.

Drawing Structural Formulas of Alkenes and Alkynes

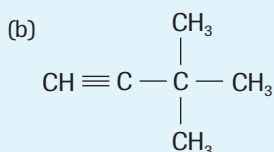
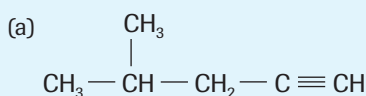
Whenever you need to draw a structural formula for any hydrocarbon, first look at the end of the name to find the parent chain. Draw the parent alkene or alkyne first, and then add the branches listed in the name. Be sure to finish the formula with sufficient hydrogen atoms to complete four bonds for each carbon atom. The following Communication Example shows some typical examples of alkenes and alkynes.

COMMUNICATION example 2

Draw condensed structural formulas for the following alkyne petrochemicals:

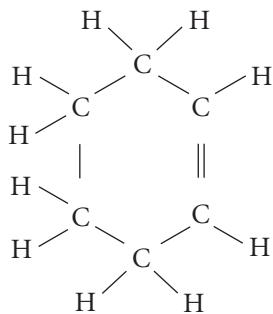
- 4-methylpent-1-yne
- dimethylbut-1-yne

Solution

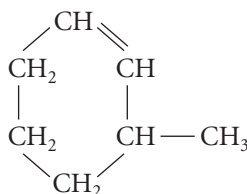


Cycloalkenes and Cycloalkynes

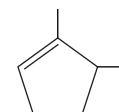
In addition to alkanes, cycloalkanes, alkenes, and alkynes, chemists discovered hydrocarbons whose properties can only be explained by creating a new class of hydrocarbons, called **cycloalkenes**. As the name of this class of hydrocarbons suggests, its molecules have a cycle of carbon atoms with at least one double bond. The structural formulas and names of cycloalkenes follow the same IUPAC rules as those for cycloalkanes. Here are some examples.



cyclohexene
(structural formula)



3-methylcyclohexene
(condensed structural formula)



2,3-dimethylcyclopentene
(line structural formula)

Note that, when naming cycloalkenes with side branches, the numbering for the carbon atoms begins with the double bond: the carbons of the double bond are carbons 1 and 2. The carbons are numbered so as to provide the lowest numbers possible, as for all other hydrocarbons. The system for naming all hydrocarbons is logically consistent—the same rules apply to all classes of hydrocarbons.

There are few known cycloalkenes and cycloalkynes. Chemists explain this low membership by considering the bond-angle stress put on the double and triple bonds when a cyclic hydrocarbon is created.

Cycloalkanes are isomers of alkenes with the same number of carbon atoms, both with the general formula C_nH_{2n} . Similarly, cycloalkenes are isomers of alkynes, both with the general formula C_nH_{2n-2} . Isomers of alkenes and alkynes exist with different locations of the double or triple bond and by changing a straight-chain hydrocarbon into a branched hydrocarbon or into a cyclic hydrocarbon. If you find that several structures have the same formula but different names, then the structures are isomers. For example, cyclohexene is an isomer of the alkyne hexyne. Both have the same molecular formula, $C_6H_{10}(l)$ (**Figure 3**).

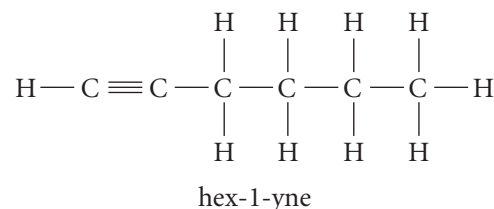
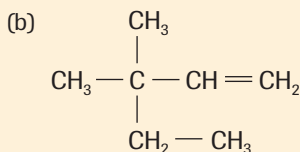
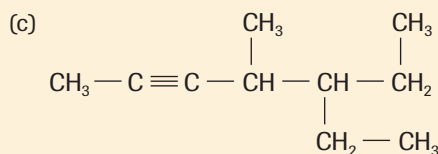
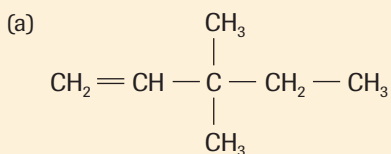


Figure 3

Hex-1-yne is an isomer of cyclohexene. Cycloalkenes are isomers of alkynes and vice versa.

Practice

- Classify each of the following hydrocarbons as an alkane, alkene, or alkyne, and/or as a cycloalkane or cycloalkene:
 - $C_2H_4(g)$
 - $C_3H_8(g)$
 - $C_4H_6(g)$
 - $C_5H_{10}(l)$
- Draw a structural formula and write a chemical formula for each of the following:
 - propane
 - propene
 - propyne
 - cyclopropane
- Draw a condensed structural formula for each of the following petrochemicals.
 - propene
 - but-2-ene
 - 2,4-dimethylpent-2-ene
 - but-1-yne
- Why are no numbers required for the location of the multiple bond in propene or propyne?
- Draw line structural formulas and write IUPAC names for each of the following structures:



- Draw line structural formulas and write the IUPAC names for the four structural isomers of $C_4H_8(g)$. (Remember cyclo compounds.)
- Alkenes and alkynes are the starting materials in the manufacture of a wide variety of organic compounds. Draw structural formulas for the following starting materials that are used to make the products named in parentheses.
 - propene (polypropylene)
 - methylpropene (synthetic rubber)

+ EXTENSION



Interactive Models

There are more and more computer-generated 3-D molecular models being created on Web sites. These models help chemists, teachers, and students to visualize the structures of molecules. (Crystallographic research from, for example, X-ray analysis, provides the data points for the atoms.) Most of the computer models allow you to select line, ball-and-stick, and space-filling models. You can also rotate the molecule by using your computer mouse. Many examples are provided at the following link. Using Internet resources such as this will help to increase your knowledge and feel for organic molecules.

www.science.nelson.com





INVESTIGATION 9.2 Introduction

Report Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Structures and Properties of Isomers

Molecular models are visual representations of molecules that help us to understand some of the properties and structures of molecules. In addition to building models, this investigation asks you to consult references to obtain data gathered by chemists over many years of laboratory work.

Purpose

The purpose of this investigation is to use models and a reference, respectively, to examine the structures and physical properties of some isomers of unsaturated hydrocarbons.

Problem

What are the structures and physical properties of the isomers of C_4H_8 and C_4H_6 ?

Design

Structures of possible isomers are determined by means of a molecular model kit. Once each structure is named, the boiling and melting points are obtained from a reference such as the *CRC Handbook of Chemistry and Physics* or *The Merck Index*.

To perform this investigation, turn to page 401.

Table 3 Boiling Points of Simple Alkanes in Natural Gas

Alkane	Boiling point (°C)
methane	-162
ethane	-89
propane	-42
methyl propane	-12
butane	-0.5
dimethylpropane	10
methylbutane	28
pentane	36

Ethane Cracking

The low boiling points in natural gas make it difficult to separate these components (Table 3). Alberta has several specialized gas plants where the various components of natural gas are separated. (See the list in the margin: Ethane Extraction Plants.) The condensation of the natural gas components is achieved with temperatures down to $-100\text{ }^\circ\text{C}$ and pressures up to 1500 to 5000 kPa (15 to 50 atm). The components are also known as LPGs (liquid petroleum gases) and are sold separately (or as a mixture) once they are removed from natural gas. The most familiar LPG to us is propane, used for combustion in barbecues, automobiles, and homes. From a chemical industry perspective, the most important LPG is ethane, used for manufacturing ethene. The uncondensed methane is returned to the natural gas pipeline for consumer, commercial, or industrial combustion or petrochemical use. Methane is the refined natural gas that may heat your home and your water.

Ethene (ethylene) is produced world wide by cracking either ethane or naphtha (a mixture of C_5-C_7 hydrocarbons). **Cracking** is an industrial process in which larger hydrocarbon molecules are broken down at high temperatures, with or without catalysts, to produce smaller hydrocarbon molecules. The large hydrocarbon molecules are known as cracking stock. Since there is a large quantity of ethane available from natural gas in Alberta, ethene is manufactured in western Canada by cracking ethane. First the ethane must be extracted from the natural gas. According to Table 1 on page 363, a typical mole fraction of ethane in natural gas is 11.6% (although this value can vary considerably).

The ethane that is separated from the natural gas is put in a pipeline and piped to an ethane cracking plant in Alberta (such as the one in Joffre) or in eastern Canada or the United States. Sometimes the LPGs are stored in large salt caverns 1 to 2 km below the surface (Figure 4).

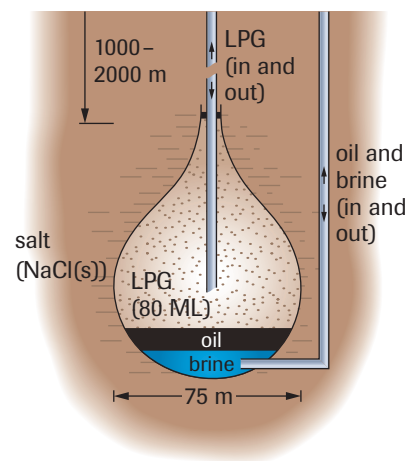


Figure 4

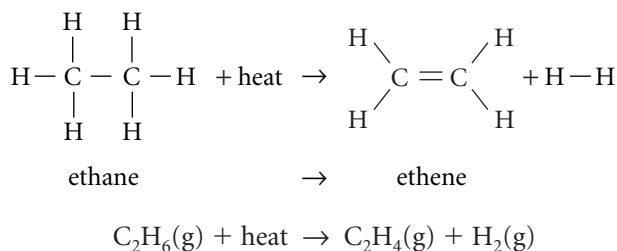
The salt caverns near Fort Saskatchewan, Alberta are enormous: about 80 ML or 80 m^3 . Situated at least 1 km below the surface, a typical salt cavern holds a volume equivalent to about 32 Olympic-size swimming pools.

Learning Tip

The use of the term “cracking” in this chapter has two meanings. The first meaning, presented here, is that of removing (cracking) hydrogen from ethane to produce ethene. Technically this is not “real” cracking, but *ethane cracking* is a widely used term in industry.

The meaning presented in Section 9.5 is that of breaking or cracking a molecule between two carbon atoms to make smaller hydrocarbon molecules. This is the more common usage of the term cracking.

Ethane cracking is also called dehydrogenation. The term cracking usually refers to breaking a large molecule down into a smaller molecule. In the case of ethane cracking, two hydrogen atoms are removed (“cracked”) from an ethane molecule to convert it into an ethene molecule. A catalyst is used to increase the rate of the reaction and the hydrogen product is used in the plant.



You will find out much more about the reactions of ethane and ethene in Chapter 10. As with most chemical processes, the process is not as simple as the equation suggests. Temperature and pressure must be optimized, and a suitable catalyst must be found through experimentation. The incoming gas must be very pure: impurities such as carbon dioxide must be removed before cracking. During cracking, many side reactions produce hydrocarbons such as methane, ethyne (acetylene), propane, and butane. For economic and environmental reasons, some of the by-products are burnt rather than released into the atmosphere. The propene made at Joffre is sold as feedstock to produce other products, and the hydrogen is used to make ammonia (used in fertilizer production).

Aliphatic Hydrocarbons

So far you have encountered many different kinds of hydrocarbons: some with straight chains, some with branches, and some that are cyclic. You have also learned about saturated and unsaturated hydrocarbons. All of these compounds are classed together as **aliphatic** hydrocarbons. In the next section, you will encounter another class of hydrocarbons: the aromatics.

SUMMARY *Alkenes and Alkynes*

- Alkenes are hydrocarbons that contain at least one carbon–carbon double bond, usually C_nH_{2n} ; e.g., propene, $\text{C}_3\text{H}_6(\text{g})$ or $\text{CH}_2=\text{CH}-\text{CH}_3$.
- Alkynes are hydrocarbons that contain at least one carbon–carbon triple bond, usually $\text{C}_n\text{H}_{2n-2}$; e.g., propyne, $\text{C}_3\text{H}_4(\text{g})$ or $\text{CH}\equiv\text{C}-\text{CH}_3$.
- Alkenes and alkynes are unsaturated compounds that are easily converted to saturated (alkane) compounds by the addition of hydrogen (called hydrogenation).
 $\text{alkene/alkyne} + \text{H}_2(\text{g}) \rightarrow \text{alkane}$
 e.g., but-2-ene + hydrogen \rightarrow butane
 $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 + \text{H}-\text{H} \rightarrow \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$
- Rules for Naming
 - Number the longest chain containing the multiple bond from the end closer to the multiple bond.
 - Identify the type and location of each branch.
 - Write the IUPAC name using the format:
 (branch location, if necessary)-(branch name)(alkene/alkyne prefix)-(multiple bond location)-(ene/yne); e.g., propene and 2-methylbut-2-yne
- Alkenes are isomers of cycloalkanes and alkynes are isomers of cycloalkenes.
- The cracking of ethane to ethene is a very important chemical reaction in Alberta.

DID YOU KNOW?

Ethane Extraction Plants

Alberta has over a dozen plants that extract (fractionate) ethane from natural gas. The ethane is gathered and distributed by pipelines.

The major extraction plants include

- Cochrane
- Empress
- Joffre

Other locations include

- Harmattan
- Judy Creek (near Swan Hills and Barrhead)
- Jumping Pound (near Sibbald Flats)
- Bonnie Glen (near Wetaskiwin)
- Waterton (near Pincher Creek)
- Elmworth and Wapiti (near Grande Prairie)
- Edmonton (23 Avenue)

Is there an ethane extraction plant near you?

Learning Tip

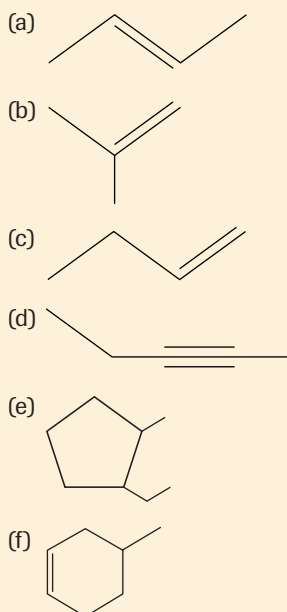
Classroom research indicates that the kind of learning required here is assisted by memorizing the rules, practising on many examples, and learning from your initial mistakes.

Initially there is a lot of memorizing, but eventually the logic of the nomenclature systems and of the structural formulas becomes easy when you persevere.

Section 9.3 Questions

- Alkanes, alkenes, and alkynes are the three main families of aliphatic hydrocarbons.
 - What is the general molecular formula for each family?
 - What is the main structural feature of each family?
 - Why does the number of hydrogen atoms in the molecular formula decrease by two as you go from alkanes to alkenes, and then to alkynes?
- Why are there more possible isomers of an alkene than an alkane with the same number of carbon atoms?
- State one major use of the first member of the alkene and alkyne families.
- Explain what is meant by the term “unsaturated” as applied to a hydrocarbon.
- Draw structural formulas and write IUPAC names for the five aliphatic structural isomers of C_5H_{10} .
- Write IUPAC names for the following hydrocarbons that are communicated as condensed structural formulas.
 - $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$
 - $CH_3 - CH = CH - CH_2 - CH_3$
 - $CH \equiv C - CH_2 - CH_2 - CH_3$
 - $CH_2 = CH - CH_2 - CH_3$
 - $$\begin{array}{c}
 CH_3 - CH - CH = CH - CH_3 \\
 | \\
 CH_3
 \end{array}$$

- Write IUPAC names for the following hydrocarbons that are communicated as line structural formulas.



- Use structural or condensed structural formulas for some simple cycloalkanes to determine the general molecular formula for cycloalkanes.

- Draw a line structural formula and write the IUPAC name for a cyclic hydrocarbon that is a structural isomer of but-1-yne.
- Draw condensed structural formulas, labelled with IUPAC names, for all the straight-chain isomers of $C_4H_6(g)$.
- Draw a line structural formula for each of the following hydrocarbons:
 - 3-ethyl-4-methylpent-2-ene
 - 5-ethyl-2,2,6-trimethylhept-3-yne
- Use the information in this section and from your own research to continue gathering pro and con perspective statements concerning the resolution that the burning of fossil fuels should be reduced.

Extension

- Ethyne (acetylene) is used in large quantities by industrial processes. Normally, gaseous substances are liquefied under high pressure and stored in steel cylinders in order to provide a reasonably large quantity for use; cylinders of propane are a typical example. Research why it is not advisable to highly compress acetylene, and how solubility is used to store $C_2H_2(g)$ in cylinders. Present your findings.

www.science.nelson.com

- Use a map of Alberta to find where the ethane extraction and ethane cracking plants are located. Which one is closest to where you live? In what ways does the presence of this plant affect you or your community?

www.science.nelson.com

- Use the Internet to find the home page of one of the companies involved with ethane production in Alberta. Access their career or human resources page and find information on the education required to work there.

www.science.nelson.com

- Computer-generated 3-D molecular models communicate the research done by chemists and help everyone visualize the shape of molecules. Find some alkenes, alkynes, and cycloalkenes at the following Web link. How has your personal view of these molecules changed when moving from viewing 2-D static models in this textbook or elsewhere to viewing 3-D (interactive) models on the Internet?

www.science.nelson.com

Aromatics 9.4

Historically, organic compounds with an aroma or odour were called *aromatic compounds*. Today, chemists define **aromatics** as benzene, $C_6H_6(l)$, and all other carbon compounds that contain benzene-like structures and properties. Aromatic hydrocarbons are found naturally in petroleum (such as crude oil and natural gas) and are most often burned. Research has identified benzene as a potential carcinogen (cancer-producing substance), however. As a result, government legislation and industry innovations have reduced the benzene content of, for example, gasoline to no more than 1%. At the same time, refinery emissions of benzene have been reduced by about 90%. Research on urban air quality has shown that these reductions have, in fact, improved the air breathed by urbanites.

The molecular structure of benzene intrigued chemists for many years because they could not explain the properties of this compound (listed below), using accepted theories of bonding and reactivity.

- The molecular formula of benzene, based on its percentage composition and molar mass, is C_6H_6 .
- The melting point of benzene is $5.5\text{ }^\circ\text{C}$, the boiling point is $80.1\text{ }^\circ\text{C}$, and tests show that the molecules are non-polar.
- There is no empirical support for the idea that there are double or triple bonds in benzene. For example, it is very unreactive with hydrogen.
- X-ray diffraction indicates that all the carbon–carbon bonds in benzene are the same length.
- Evidence from chemical reactions indicates that all carbons in benzene are identical and that each carbon is bonded to one hydrogen.

The empirical formula for benzene, $C_6H_6(l)$, was determined in 1825 by Michael Faraday (1791–1867). Visualizing a model of the benzene molecule that followed accepted bonding rules proved difficult. Finally, in 1865, August Kekulé (1829–1896) proposed a cyclic structure for benzene. The combination of the theoretical work on structural formulas by Kekulé and the empirical work of Josef Loschmidt (1821–1895) proved fruitful. Since evidence indicates that all bonds between the carbon atoms in benzene are identical in length and in strength, an acceptable model requires the even distribution of the extra six unbonded valence electrons around the entire molecule (**Figures 1 and 2**). Consider this molecule as having six unbonded valence electrons distributed around a 6-carbon-atom ring, forming a strong hexagonal structure.

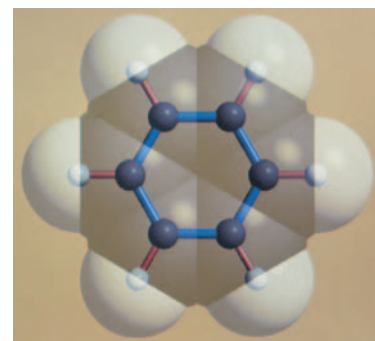


Figure 1 Although Loschmidt and others had proposed several hypotheses for the structure of benzene (C_6H_6), Kekulé championed a hexagon model. The evidence from structural isomers and chemical reactions and the logical consistency of this model with the bonding capacities of carbon and hydrogen led to the acceptance of the hexagon hypothesis (model) by the chemistry community.

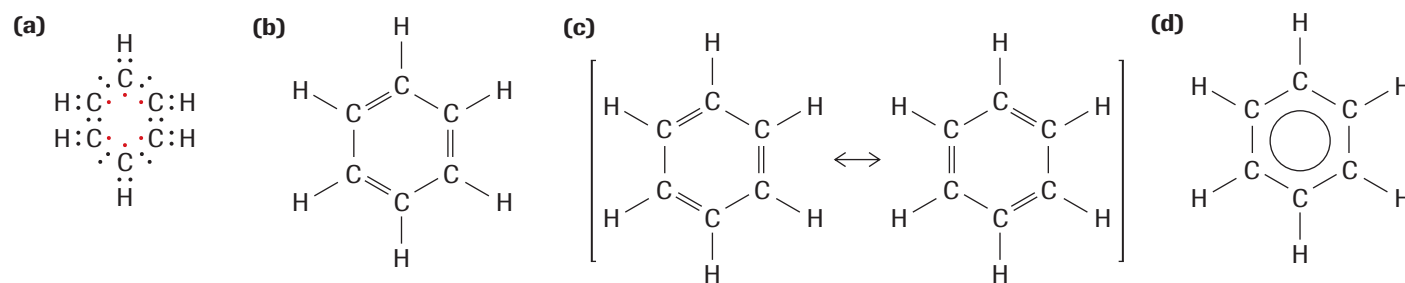
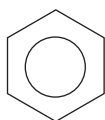
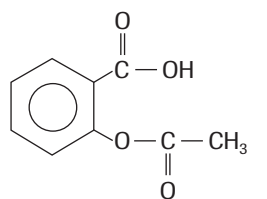


Figure 2

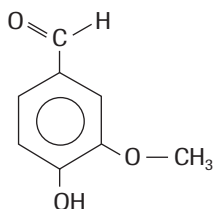
A progressive series of models of benzene: **(a)** agrees with the evidence but is not consistent with the theory that carbon forms four bonds with other atoms; **(b)** disagrees with the evidence but is consistent with the four-bond theory for carbon; **(c)** is closer to the evidence and is consistent with the four-bond theory; **(d)** represents a new theory that agrees with the evidence; and **(e)** is a line structural formula that represents the new theory—the sharing of six valence electrons among six carbon atoms.

(e)





Aspirin®
(ASA, acetylsalicylic acid)



vanillin

Figure 4

Common aromatic compounds include Aspirin® and vanillin. Vanillin is one of the flavour molecules in vanilla. You will notice that many aromatic molecules are often depicted using a condensed structural formula except for the benzene ring, which is shown as a line structural formula. This combination is commonly used by chemists.

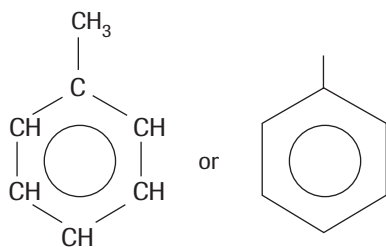
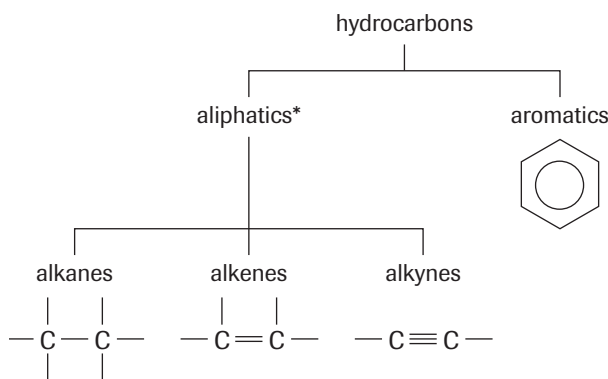


Figure 5

Methylbenzene ($C_6H_5CH_3(l)$), commonly known as toluene, is a solvent used in glues and lacquers. It is toxic to humans but is preferred to benzene as a solvent because benzene is both toxic and carcinogenic.

Figure 6

Three isomers of diethylbenzene. The *o*-, *m*-, and *p*- classical nomenclature is described in the Learning Tip on the next page.



*includes cyclo compounds of each family

Figure 3

Aliphatic and aromatic hydrocarbons

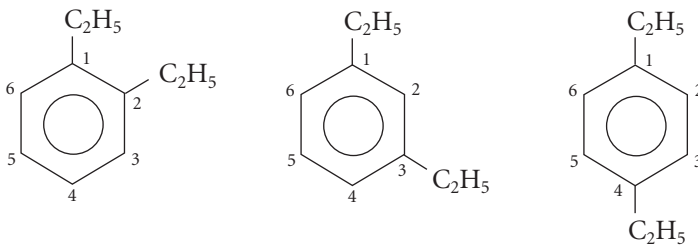
Based on the evidence of the properties of benzene, this structure must be particularly stable. The reactions of benzene are similar to those of alkanes—benzene behaves chemically like a saturated hydrocarbon (an alkane). Since 1865, hydrocarbons were classified as aliphatic or aromatic (**Figure 3**). For our purposes, aromatic compounds contain the benzene ring, which is represented by a hexagon with an inscribed circle. Structures of all aromatic compounds include bonding similar to that in the benzene ring (**Figure 4**).

Naming Aromatics

Simple aromatics are usually named as relatives of benzene. If an alkyl group is bonded to a benzene ring, it is named as an alkylbenzene (**Figure 5**). The alkyl group is considered a substitute for a hydrogen atom. Since all of the carbon atoms of benzene are equivalent to each other, no number is required in the names of compounds of benzene that contain only one addition.

When two hydrogen atoms of the benzene ring have been substituted, three isomers are possible. These isomers are named as alkylbenzenes, using the lowest possible pair of numbers to indicate the locations of the two alkyl groups on the benzene ring. The numbering starts at one of the substituents and goes clockwise or counterclockwise to obtain the lowest possible pair of numbers (**Figure 6**).

For some larger molecules, it is more convenient to consider the benzene ring as a branch. In such molecules, the benzene ring is called a **phenyl group**, $-C_6H_5$. For example, the compound in **Figure 7** is named 2-phenylpentane, according to the naming system for branched alkanes (page 368). Either naming system for aromatic compounds is acceptable; choose the more convenient method for the compound in question.



1,2-diethylbenzene
(*o*-diethylbenzene)

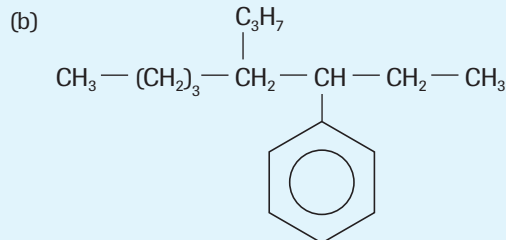
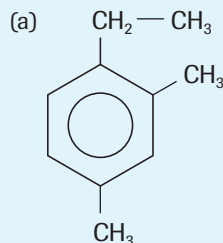
1,3-diethylbenzene
(*m*-diethylbenzene)

1,4-diethylbenzene
(*p*-diethylbenzene)

When drawing a structural formula from a name, carbon 1 can be designated anywhere on the benzene ring. The numbering 1 to 6 can be done clockwise or counterclockwise: The molecules do not know which way is up.

COMMUNICATION example

Write IUPAC names for the following aromatic hydrocarbons:



Solution

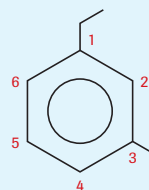
- (a) 1-ethyl-2,4-dimethylbenzene (b) 3-phenyl-4-propyloctane

When drawing a structural formula for an aromatic compound, always look at the end of the given name to identify the parent chain. Is the parent chain benzene or an aliphatic compound? Draw the parent chain first, then consider the placement of the branches.

SAMPLE problem 9.3

Draw the line structural formula for 1-ethyl-3-methylbenzene.

First, draw the benzene ring, and then add an ethyl group to any C atom of the ring; this C atom automatically becomes C 1 in the numbering system. Finally, add a methyl group to C 3, which can be clockwise or counterclockwise from C 1.



Note that, for line structural formulas, no hydrogen atoms are shown and the end of any line segment denotes a carbon atom.

SUMMARY Naming Aromatic Hydrocarbons

1. If an alkyl branch is attached to a benzene ring, the compound is named as an alkylbenzene. Alternatively, the benzene ring may be considered as a branch of a large molecule; in this case, the benzene ring is called a phenyl branch.
2. If more than one alkyl branch is attached to a benzene ring, the branches are numbered using the lowest numbers possible, starting with one of the branches. Given a choice between two sets of lowest numbers, choose the set that is in both numerical and alphabetical order. See Sample Problem 9.3.



WWW WEB Activity

Web Quest—West Nile Denial

In this Web Quest, investigate traditional and modern mosquito repellents, and create a brochure to help people in the prairie provinces reduce the risk of contracting West Nile Virus.

www.science.nelson.com

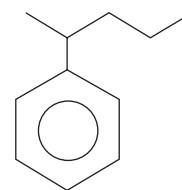


Figure 7

A line structural formula for 2-phenylpentane

Learning Tip

You may encounter a naming system—known as the classical system—for benzene rings with two substituted groups. The 1,2-, 1,3-, and 1,4-arrangements are denoted by the prefixes ortho- (*o*), meta- (*m*), and para- (*p*), respectively. These names, such as *o*-dimethylbenzene, are still used in industry, and you may encounter them in other references.

DID YOU KNOW?

VOCs

Volatile organic compounds (VOCs) are gases and vapours, such as benzene, that are released throughout the petroleum refining processes. Petrochemical plants (see Chapter 10), plastics manufacturing, and the distribution and burning of gasoline all release VOCs into the atmosphere. Some VOCs, like benzene, are carcinogens. Other VOCs react in sunlight with nitrogen oxides from automobile exhaust to form ground-level ozone, a component of smog.



LAB EXERCISE 9.A

Report Checklist

- | | | |
|---|---------------------------------|--|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (2, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input type="radio"/> Evidence | |

Chemical Properties of Aliphatics and Aromatics

Comparing chemical properties of different classes of hydrocarbons can be difficult in a high school chemistry laboratory. Many hydrocarbons are volatile organic compounds (VOCs), some are carcinogenic (such as benzene), and many are flammable. In this investigation, the properties of aliphatics are compared to those of aromatics by reporting the evidence for the reaction of a cycloalkane, a cycloalkene, and an aromatic with potassium permanganate, a strong oxidizing agent. When completing the Prediction, provide a theoretical justification.

Purpose

The purpose of this investigation is to test the generalization that aromatic hydrocarbons react like saturated rather than unsaturated hydrocarbons.

Problem

What is the order of reaction rate for cyclohexane, cyclohexene, and benzene?

Design

Each of cyclohexane, cyclohexene, and benzene is mixed vigorously with aqueous potassium permanganate in a fumehood. Evidence for a reaction is a change in the purple colour of the aqueous potassium permanganate.

Evidence

Cyclohexane

- Initially, no changes were observed in the mixture.
- After 5 min, the colour changed from purple to grey-purple.

Cyclohexene

- The colour of the mixture immediately changed to green.
- After 5 min, a brown precipitate formed.

Benzene

- Initially, no changes were observed in the liquid.
- After 5 min, the colour was still the same.



LAB EXERCISE 9.B

Report Checklist

- | | | |
|---|---------------------------------|--|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (2, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input type="radio"/> Evidence | |

Boiling Points of Sample Aliphatics and Aromatics

Most of the hydrocarbons with smaller molecules, such as methane, ethane, propane, and butane, are gases at SATP. Hydrocarbons with medium-sized molecules (C_5 – C_{18}) are found to be liquids. We often fail to appreciate how easy it is to transport and dispense these liquid hydrocarbons. We can explain the relative boiling points of hydrocarbons theoretically with the concept of London forces. Evaluate the ability of the concept of London forces to predict the relative boiling points of different classes of hydrocarbons. (According to philosophers of science, in this lab exercise, you are testing the *predictive* power of a scientific concept.)

Purpose

The purpose of this lab exercise is to test the ability of the concept of London forces to predict the relative boiling points of aliphatic and aromatic hydrocarbons.

Problem

What is the relative order of boiling points of simple C_6 alkane, alkene, cycloalkane, cycloalkene, and aromatic hydrocarbons?

Design

The boiling points of hexane, hexene, cyclohexane, cyclohexene, and benzene are obtained from *Lange's Handbook of Chemistry, 13th Edition*.

Evidence

Table 1 Boiling Points of C_6 Aliphatics and Aromatics

Hydro-carbon	Hexane	Hex-1-ene	Cyclo-hexane	Cyclo-hexene	Benzene
Boiling point ($^{\circ}C$)	68.7	63.5	80.5	83.0	80.10

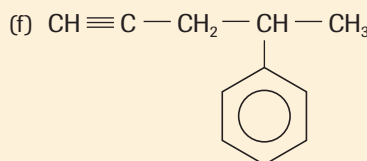
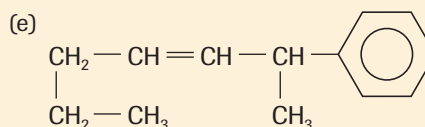
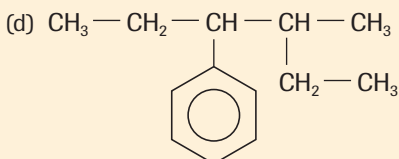
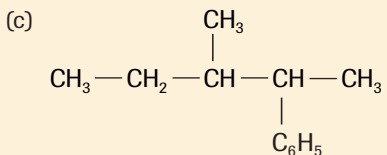
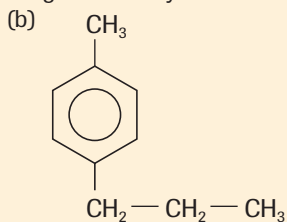
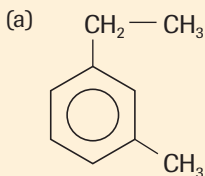
Section 9.4 Questions

- State the name and chemical formula of the simplest aromatic compound. In your own words, describe what is unusual about its structure.
- There are over 4000 dehydrators at natural gas well sites throughout Canada. The older technology allowed for emissions of benzene, methylbenzene (toluene), ethylbenzene, and the three dimethylbenzenes (xylenes). Newer technologies have been invented to reduce these emissions. Draw line structural formulas for each of these six aromatic compounds.
- Draw a combination of line and condensed structural formulas for the following aromatics:
 - 1,2,4-trimethylbenzene
 - 1-ethyl-2-methylbenzene
 - 3-phenylpentane
 - 3-methyl-1-phenylbutane
- The isomers of dimethylbenzene, commonly called xylenes, are used as solvents for adhesives (**Figure 8**). Write alternative IUPAC names and draw structural formulas for the three xylene isomers.
 - 1,4-dimethylbenzene
 - 1,3-dimethylbenzene
 - 1,2-dimethylbenzene

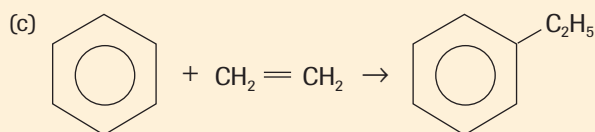
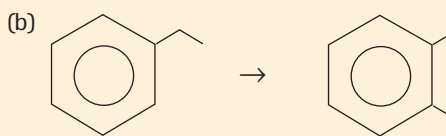
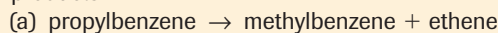


Figure 8
Isomers of dimethylbenzene, known as xylenes, are used as solvents.

- Write IUPAC names for the following aromatic hydrocarbons:



- Aromatics can also take part in various chemical refining reactions. For each of the following reactions, draw a structural formula equation. Include all reactants and products.



- Classify each of the following hydrocarbons as aromatic or aliphatic.
 - 2,3-dimethylhexane
 - $\text{CH}_3\text{—CH}_2\text{—CH(C}_6\text{H}_5\text{)—CH}_3$
 - 1,2-dimethylcyclohexane
 - 3-methyl-2-pentyne
 - 1,3-dimethylbenzene
 - 2-phenyl-3-hexene
- Classify each of the following hydrocarbons as saturated or unsaturated.
 - $\text{C}_2\text{H}_4(\text{g})$
 - $\text{CH}_3\text{—(CH}_2\text{)}_4\text{—CH}_3$
 - $\text{C}_6\text{H}_5\text{CH}_3(\text{l})$
 - $\text{C}_3\text{H}_4(\text{g})$
 - $\text{CH}_3\text{—(CH}_2\text{)}_2\text{—CH}_3$
 - $\text{C}_6\text{H}_6(\text{l})$
- Why is benzene not called 1,3,5-cyclohexatriene, to communicate three double bonds in a hexagon?
- In Lab Exercise 9.B, you compared the boiling points of hexane, hex-1-ene, cyclohexane, cyclohexene, and benzene. Test the ability of the concept of London forces to explain the relative order of the boiling points of these C_6 hydrocarbons. Did the London-force concept or your understanding of it need to be revised to provide an acceptable explanation? (According to philosophers of science, in this question, you are testing the explanatory power of a scientific concept.)
- Even though the use of benzene as a solvent was banned in Canada several decades ago, people's exposure to benzene has not stopped. A Materials Safety Data Sheet (MSDS) is the source of chemical safety information. List some common sources of benzene exposure and identify some short-term and long-term health effects.

9.5 Crude Oil Refining



Figure 1
Pump jacks are found over oil wells in many parts of Alberta. This one is near Cochrane, Alberta.

Crude oil is pumped from the ground by thousands of pump jacks throughout Alberta (**Figure 1**). The crude oil then enters a pipeline through which it is shipped to an oil refinery. If the oil has to travel a long distance, pumping stations are situated along the way to assist the movement of the oil. Much of the oil in Alberta is exported to other provinces and other countries for refining. Some of the oil is refined in Alberta.

Crude oil throughout the world is classified on the basis of viscosity, hydrocarbon composition, and sulfur content. (Viscosity is a measure of how well a liquid pours: low-viscosity liquids pour like water, whereas high-viscosity liquids pour like molasses or liquid honey.) For example, light crude oil has a lower viscosity and requires less refining than heavy or high-viscosity crude oil. While some types of crude oil are best suited for gasoline production, other types of crude oil may be better suited for jet fuel, diesel fuel, home heating, motor oil, and asphalt end products (**Figure 2**). Most crude oil is separated into a variety of components that differ according to the percentage of each component obtained. This separation can involve both physical and chemical processes.

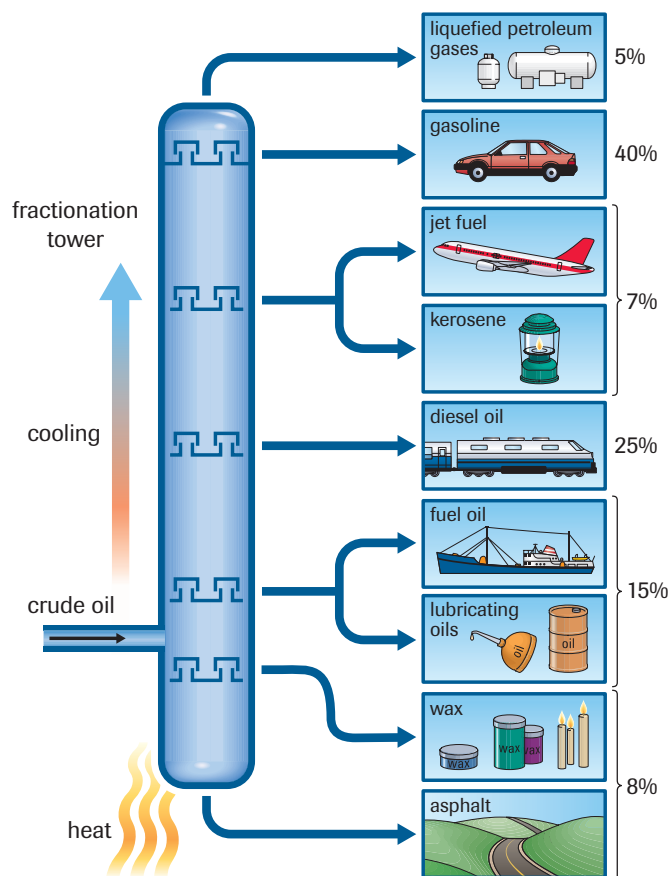


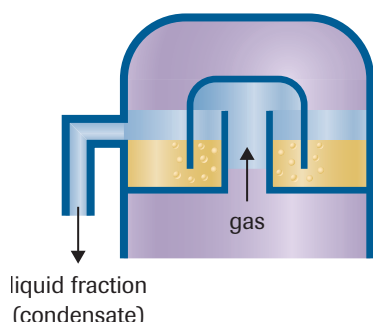
Figure 2
A fractional distillation (fractionation) tower contains trays positioned at various levels. Heated crude oil enters near the bottom of the tower. The bottom of the tower is kept hot, and the temperature gradually decreases toward the top of the tower. The concentration of components with lower boiling points increases from the bottom to the top of the tower. The percentage distributions shown vary with the type of crude oil and with seasonal demands.

Physical Processes in Oil Refining

Crude oil is a complex mixture of hundreds of thousands of compounds. Some of these compounds boil at temperatures as low as 20 °C. The least volatile components of crude oil, however, boil at temperatures above 400 °C. Chemical engineers take advantage of the differences in boiling points to physically separate the components. This technological process is called *fractional distillation*, or **fractionation**.

Any substance with a boiling point above 25 °C is a liquid or solid at SATP. Chemical engineers have found that, when crude oil is heated to 500 °C in the absence of air, most of its constituent compounds vaporize. The compounds with boiling points higher than 500 °C remain as mixtures called asphalts and tars. The vaporized components of the crude oil rise and gradually cool in a metal tower (**Figure 2**). The technological design is very ingenious: To get from one level to the next, the vapours have to force their way through the liquid in the next tray. Bubble caps, which were used in the past, illustrate the contact between liquid and vapour (**Figure 3**). Currently, valve trays, which are more efficient, are used in distillation columns. When the temperature of the liquids in the trays in the higher parts of the tower is below the boiling points of the vaporized compounds, the substances in the vapour begin to condense. Those substances with high boiling points condense in the lower, hotter trays of the tower, whereas those with lower boiling points condense in the cooler trays near the top of the tower. Side streams are withdrawn from various locations along the column. These various streams are called **fractions**. Some typical fractions and their properties are listed in **Table 1**.

Chemists have an explanation for the boiling points of these fractions. They have found that the fractions with the lowest boiling points generally contain the smallest molecules. Chemists explain that the low boiling points are due to small molecules,

**Figure 3**

The vaporized components are forced to bubble through the liquids condensed in each tray. Any gas with its condensation point (boiling point) greater than the temperature of the liquid in the tray will condense. The liquid in each tray continuously overflows into the draining tube and the liquid mixture is piped from the fractionation tower.

Table 1 Fractional Distillation of Crude Oil

Boiling point range of fraction (°C)	Number of carbon atoms per molecule	Fraction (intermediate product)	Products
below 30	1 to 5	gases; LPGs	gaseous fuels for cooking and for heating homes
30 to 90	5 to 6	naphthas	dry-cleaning solvents, naphtha gas, camping fuel
30 to 200	5 to 12	straight-run gasoline	automotive gasoline
175 to 275	12 to 16	kerosene	diesel, jet, and kerosene fuels; cracking stock* (raw materials for fuel and petrochemical industries)
250 to 375	15 to 18	light gas or fuel oil	furnace oil; cracking stock
over 350	16 to 22	heavy gas oil	lubricating oils; cracking stock
over 400	18 and up	greases	lubricating greases; cracking stock
over 450	20 and up	paraffin waxes	candles, waxed paper, cosmetics, polishes; cracking stock
over 500	26 and up	unvaporized residues	asphalts and tars for roofing and paving

* Cracking stock is feedstock (raw material) that is, for example, hydrocracked to make smaller molecules that are more in demand; e.g., gasoline molecules.

which have fewer electrons and weaker London forces compared with large molecules. The fractions with higher boiling points are found to contain much larger molecules. Some typical fractions are shown in **Table 1**. Recall from Chapter 3 that London forces are also dependent on the shape of the molecules; that is, on whether the molecule is branched. Since these molecules are hydrocarbons, chemists explain that dipole–dipole and hydrogen bonding are not involved.

Other Physical Processes in Oil Refining

In addition to fractional distillation, there are several other physical processes that are used to treat fractions before and/or after chemical processing. Several of these physical processes are *solvent extractions*—a solvent is added to selectively dissolve and remove an impurity or to separate some useful products from a mixture. Dewaxing is a simple process of cooling a mixture to precipitate the larger wax fraction.

DID YOU KNOW?

Naphthas

Like all of the fractions listed in Table 1, naphtha is a mixture with varying composition (including aliphatic and aromatic hydrocarbons). The mixture depends on the source of the hydrocarbon (e.g., light or heavy crude, bitumen, or coal) or customer demand. Naphtha, for example, may be petroleum naphtha with more aliphatic character, or bitumen naphtha with more aromatic character. What defines it as naphtha is the boiling point range over which it is collected in the fractionator.

CAREER CONNECTION



Petroleum Engineer

Petroleum engineers apply their knowledge of chemistry to the discovery, recovery, and processing of oil and gas deposits.

Rob Manuel is a petroleum engineer. He combines his Western scientific world view with his Aboriginal world view (he grew up on the Upper Nicola Indian Band Reserve) to bring a “different way of thinking to the table.” Find out about the education petroleum engineers require for the kind of work they do.

www.science.nelson.com





INVESTIGATION 9.3 Introduction

Report Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input type="radio"/> Evaluation (1, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Fractional Distillation (Demonstration)

Fractional distillation is a process used commercially to separate components (fractions) of petroleum using boiling point differences.

Purpose

The purpose of this investigation is to use the concept and technique of fractional distillation to separate two hydrocarbon components from a liquid mixture.

Problem

What is the percent by volume of each of the two hydrocarbon components?

Design

A mixture of the two liquids is heated in a fractional distillation apparatus while the temperature is measured at regular intervals in a fume hood.

To perform this investigation, turn to page 402.

DID YOU KNOW?

Oil Recovery

The recovery of oil can be enhanced by the use, for example, of water or of carbon dioxide. Recent research has shown that carbon dioxide can be captured from large industries and transported by pipeline to oil wells. The recovery of the oil from underground increases from about 25% to about 40%. The carbon dioxide used in this application helps reduce emissions and helps meet Kyoto targets.

Practice

- State some similarities and differences between the operation of a fractionation tower and a laboratory-scale distillation apparatus.
- Why is crude oil heated in the absence of air in the fractionation tower?
 - Write chemical equations to represent the vaporization of pentane and of octane at the bottom of a fractionation tower.
 - Write chemical equations to represent the condensation of pentane and of octane in a bubble-cap tray of a fractionation tower.
 - Which of pentane and octane has a higher boiling point, and why?
 - Which of pentane and octane is removed in a higher bubble tray of the fractionation tower?
- Feedstock is raw or semi-processed material that is fed into a chemical process to produce a more valuable product. Cracking stock is feedstock that is cracked into smaller or more branched hydrocarbons. List the different fractions that are used as cracking stock. Suggest some reasons why so many fractions are used for this purpose.
- What percentage of petroleum is used as fuel? What is the major type of fuel that makes up this category?
- Straight-run gasoline is gasoline that comes straight from a crude-oil, fractional distillation tower. There are various kinds of crude oil, including light, heavy, and synthetic. Some kinds of oil provide a greater percentage of straight-run gasoline than others.
 - Describe the straight-run gasoline fraction compared to other crude oil fractions.
 - Write balanced chemical equations for the complete combustion of the pentane and octane components of straight-run gasoline while driving a hybrid (gasoline and electric) automobile.
- Crude oil is a solution of many, many hydrocarbons, including hydrocarbons that are solids, liquids, and gases as pure substances.
 - Explain how this mixture can be a solution.
 - Water is part of the mixture when extracting crude oil from oil wells. Use intermolecular forces concepts to explain why water would or would not be a solute in the crude oil solution.
- Use the information in this section to add to your collection of statements, pro and con, from a variety of perspectives on the resolution that the burning of fossil fuels should be reduced.

Chemical Processes in Oil Refining

The refining of crude oil can be divided into two main types of processes: physical processes, such as fractionation and solvent extraction, and chemical processes, such as cracking and reforming (Figure 4). These chemical processes are necessary because the fractional distillation of crude oil does not produce enough of the hydrocarbons that are in demand (particularly the gasoline fraction) and produces too much of the heavier fractions. Compared to gasoline and diesel, there is limited market demand for fuel oil, lubricating oils, greases, and waxes. Notice that all of these fractions (Table 1, page 387) contain larger molecules than those typically found in gasoline (C_5 to C_{12}).

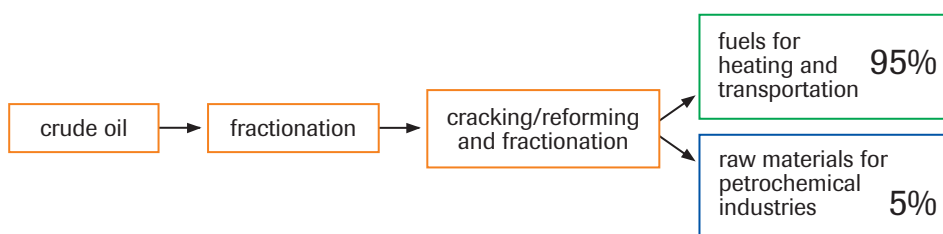


Figure 4

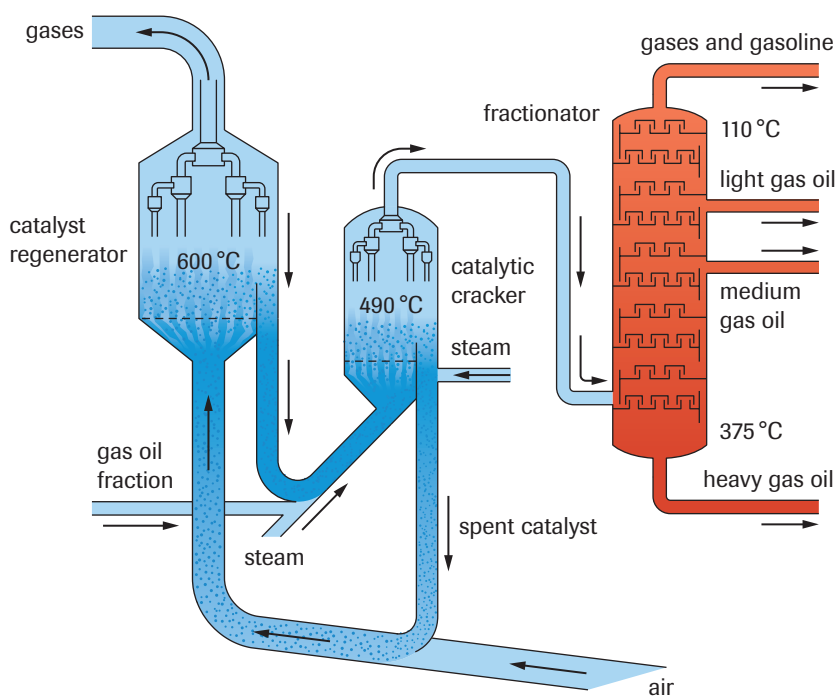
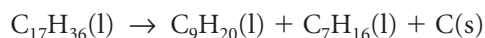
Only 5% of the original mass of crude oil is used as starting chemicals (called feedstock) in the manufacture of solvents, greases, plastics, synthetic fibres, and pharmaceuticals.

www.science.nelson.com



Cracking

Cracking is a chemical process in which larger molecules are broken down with heat and/or catalysts to produce smaller molecules. In the early 1900s, cracking was accomplished using only high temperatures and pressures in a process called *thermal cracking*. This process is fairly effective, but is messy and wasteful because it produces large quantities of solid coke (carbon). Thermal cracking is still used today, but to a limited extent. By 1937, basic research and technological development produced a new improved cracking technique called *catalytic cracking* (Figure 5). This process breaks apart larger molecules, but the presence of a catalyst, along with less severe reaction conditions, produces more desirable fractions and less residual materials such as tar, asphalt, and coke. (You will learn more about the uses of catalysts in chemical processes in Chapter 12.) A typical reaction equation might be



CAREER CONNECTION



The Petroleum Industry

The Petroleum Human Resources Council of Canada has been set up to handle the huge demand for employees in the areas of exploration, development, production, service industries, pipeline transmission, gas processing, and the mining, extracting, and upgrading of heavy oil and bitumen. Find out more about the Petroleum HR Council, the seven human resource issues it has identified, and the strategies it has developed to address any one of these issues. If you were interested in working in this field, how might the Petroleum HR Council's work benefit you?

www.science.nelson.com



Figure 5

For catalytic cracking, the gas oil fraction, for example, enters the central vessel, is catalytically cracked, and then fractionated again in the column on the right. The catalyst is recycled into the vessel on the left. The catalyst is regenerated when the coke is burned off of it in the left vessel.

DID YOU KNOW?

Ammolite Gems and Ammonite Fossils

Ammolite (**Figure 6(a)**) is one of only three organic gemstones, besides pearl and amber, but contains traces of up to a dozen metals. The highly supported hypothesis is that ammolite comes from the shells of ammonites—squid-like creatures that lived about 75 Ma ago in the Bearpaw Sea that ran north to south through the middle of Alberta (**Figure 6(b)**). Aboriginal peoples, ranchers, and prospectors have found ammolite along the banks of the St. Mary River, south of Lethbridge, Alberta. Ammolite is the only uniquely Canadian gem, and has been mined and refined in Alberta since the 1980s.

Ammolite is also known as aapoak (Blackfoot for small, crawling stone) and buffalo stone (also named by the Blackfoot of southern Alberta). The latter name comes from the Blackfoot legend about a princess who found an ammolite gemstone that brought prosperity (in the form of a buffalo herd) back to the Blackfoot. Since then, the Blackfoot have regarded ammolite as a sign of prosperity.

(a)



(b)

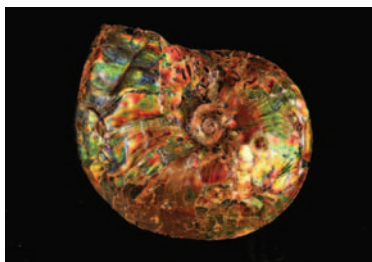
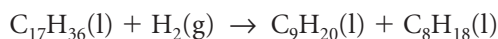


Figure 6

(a) An ammolite gem and (b) an ammonite fossil

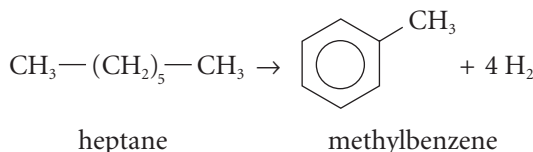
The history of oil refining is a story of continuous technological development to meet societal needs for various petroleum products, in particular, gasoline. In 1960, another improvement, called hydrocracking, helped meet this demand. **Hydrocracking** is a combination of catalytic cracking and hydrogenation and is used for heavier feedstocks, particularly those containing complex aromatic compounds. During the hydrogenation process, no coke (carbon) is produced. A simplified hydrocracking reaction equation would be



Catalytic Reforming and Alkylation

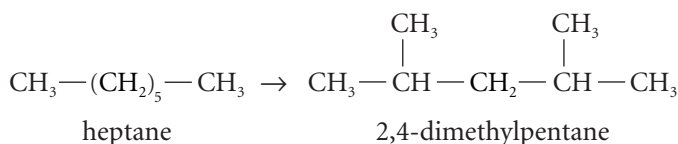
Cracking reactions are like decomposition reactions because the main objective is to break larger molecules into smaller ones. Both the fractionation process and the cracking process produce large quantities of light fractions such as gases and naphthas (**Table 1**, page 387), as well as molecules whose structures are not suitable for our needs. For example, there might be too few branches on the molecules to produce a sufficiently high-quality gasoline. The chemical process of reforming and alkylation rearranges the bonding in molecules to improve the quality of the gasoline.

Catalytic reforming is the chemical process involved in converting molecules in a naphtha (gasoline) fraction into aromatic gasoline molecules. These aromatic molecules have better burning properties than the original aliphatic (non-aromatic) molecules. For example, heptane does not burn well in internal combustion (car) motors. If the heptane is converted into methylbenzene, the gasoline burns better in car motors. All reforming is now done with the use of catalysts to increase the rate of the reaction, and is, therefore, often called catalytic reforming. Hydrogen, a by-product of catalytic reforming, is usually recycled in other processes, such as hydrocracking.



Alkylation

Another way of improving the quality of gasoline is to increase the branching of the molecules in a process called *alkylation*. This process is also called isomerization because it converts a molecule into a branched isomer. For example, heptane can be converted into 2,4-dimethylpentane, a molecule that burns better in an internal combustion motor.



WWW WEB Activity

Canadian Achievers—Karl Chuang

Karl Chuang studied chemical engineering at the University of Alberta in the 1970s. Today, he is a top distillation expert in Canada and one of the best in the world. He has developed distillation technologies that are used in refineries around the world.

What are Dr. Chuang's current research interests?

www.science.nelson.com



SUMMARY

Gasoline and diesel fuel are high-demand crude oil fractions. More of each of these fractions can be made by cracking heavier fractions. Also, molecules that burn better in internal combustion motors can be made by chemical processes (e.g., catalytic reforming and alkylation) controlled by chemical engineers.

Catalytic cracking: larger molecules \rightarrow smaller molecules + carbon

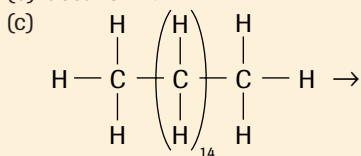
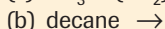
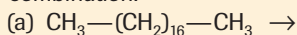
Hydrocracking: larger molecule + hydrogen \rightarrow smaller molecules

Catalytic reforming: aliphatic molecule \rightarrow aromatic molecule + hydrogen

Alkylation (isomerization): aliphatic molecule \rightarrow more branched molecule

Practice

- Why are chemical processes necessary in oil refining, in addition to the physical process of fractionation?
- Write a condensed structural formula equation for each of the following catalytic cracking reactions. Assume that unbranched alkanes are produced, in addition to carbon (coke). There are many possible product combinations. Predict one combination.



- Compare hydrocracking and catalytic reforming. In what way are they complementary?
- High-quality gasoline requires chains of C_5 to C_{12} molecules, branching within the molecules, and some aromatic molecules. For each of these three requirements, identify the physical and/or chemical process that accomplishes the requirement.
- Since crude oil contains many alkanes, unwanted hydrocracking reactions are common in the first stage of oil refining during fractionation. The hydrogen is a product of thermal cracking. For each of the following word equations representing hydrocracking reactions, write a balanced condensed structural formula equation:
 - hexane + hydrogen \rightarrow ethane + butane
 - 2-methylpentane + hydrogen \rightarrow propane + propane
 - 2,2-dimethylbutane + hydrogen \rightarrow ethane + methylpropane
- After initial fractional distillation, catalytic reforming and alkylation reactions increase the yield of desirable products, such as compounds whose molecules have aromatic character and more branches. Complete each of the following equations. Draw condensed structural formulas when IUPAC names are given, and write IUPAC names when condensed structural formulas are given.
 - $\text{CH}_3 - \text{CH}_2 - \text{CH}_3 + \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \rightarrow$
 $\text{CH}_3 - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{CH}(\text{CH}_3) - \text{CH}_3$
 - octane \rightarrow 1,3-dimethylbenzene + hydrogen
 - $\text{CH}_3 - (\text{CH}_2)_3 - \text{CH}_3 \rightarrow \text{C}_3\text{H}_5(\text{C}_2\text{H}_5) + \text{H}_2$
 - decane \rightarrow 3-ethyl-2-methylheptane

DID YOU KNOW?

Transportation Fuels

About 50% of crude oil processed in Canadian refineries is used as transportation fuels—gasoline, diesel fuel, jet fuel, and fuel oil for ships and locomotives. The demand keeps increasing, although, for example, the decreasing demand for fuel oil for heating homes (in Eastern Canada) has allowed more of the fuel-oil supply to be used as a transportation fuel.

DID YOU KNOW?

Oil Sands Discovery

In 1719, a Cree named Wa-pa-su took a sample of Athabasca oil sands to the Hudson Bay Post in Fort Churchill. Aboriginal peoples used the tarry substance, mixed with tree sap, to waterproof their canoes and other items.

Extension

14. Benzene and other aromatic hydrocarbons have a low H:C ratio (close to 1:1). Chemical engineers have invented two processes to increase this ratio to about 2:1.
 - (a) Explain how the 1:1 hydrogen-to-carbon ratio is derived for aromatics.
 - (b) What classes of hydrocarbons have H:C ratios close to 2:1?
 - (c) Describe how hydrocracking works to improve the H:C ratio of aromatics from approximately 1:1 to approximately 2:1.
15. For economic and efficiency reasons, crude oil refining technologies have moved from thermal cracking to catalytic cracking. Both catalytic cracking and hydrocracking employ catalysis. Chemical engineers who are designing modern refineries are increasingly moving toward hydrocracking over straight catalytic cracking. What is an advantage of hydrocracking over catalytic cracking?

Case Study

Octane Number

Hydrocracking, alkylation, and catalytic reforming reactions produce not only more gasoline, but also convert low-grade gasoline into higher-grade gasoline. At gas stations, you see the grades displayed on the gas pumps, for example, as Regular and Super or as a specific number, such as 88 and 98. The numbers, 88 and 98, represent the octane rating (number) of the gasoline.

Low-octane gasoline, with long straight-chain molecules, burns quickly. Fuel is supposed to ignite in the cylinder as a result of a spark. The spark is timed to ignite the fuel when the piston is close to the top of its “up stroke” (see **Figure 7**). Sometimes the mixture auto-ignites as a result of the pressure in the cylinder, rather than burning when the spark is produced. If the fuel ignites earlier, high-performance vehicle engines lose some of their efficiency. They sometimes produce a knocking or pinging sound. High-performance gasoline engines require high-octane fuel, which contains more branched-chained and aromatic hydrocarbons. Higher-octane gasoline resists spontaneous (high-pressure, no-spark) auto-ignition of excess fuel. The engine runs more smoothly, and is less likely to be damaged or lose efficiency.

Russell Marker, a chemist, assigned 2,2,4-trimethylpentane (an isomer of octane) an octane number of 100, and heptane (a straight-chain alkane) an octane number of zero. These chemicals were chosen for comparison due to their similar boiling points and enthalpies of vaporization (**Table 2**).

In addition to using high-octane gasoline to reduce knocking in high-performance engines, an additive (octane booster) can be used. From the 1920s until the 1970s, the most common additive was tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4(\text{l})$. Because lead deactivated the catalysts in the catalytic converters installed in cars starting in 1972, tetraethyl lead was removed from gasoline by the 1990s.

Several ingredients have replaced the tetraethyl lead, such as dibromoethene (ethylene dibromide, EDB), dichloroethene (ethylene chloride, EDC), and 2-methyl-2-methoxypropane (methyl tertiary butyl ether, MTBE). Each substitute has had its own problems.

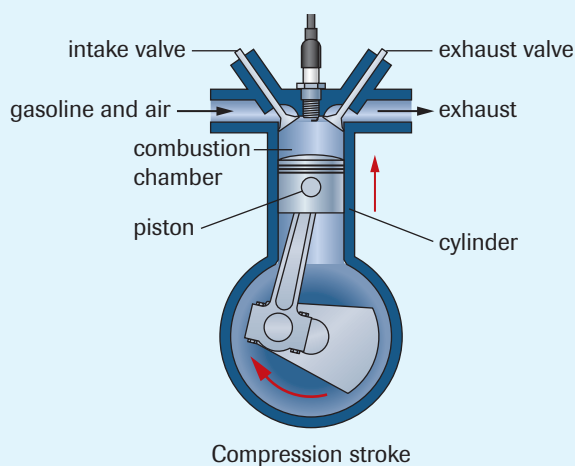


Figure 7

Engine knock in an internal combustion engine is caused by auto-ignition of excess fuel occurring between carefully timed sparks.

Table 2 Octane Rating Reference Scale

Chemical	Boiling point (°C)	Octane rating
heptane $\text{CH}_3 - (\text{CH}_2)_5 - \text{CH}_3$	98.4	0
2,2,4-trimethylpentane $\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	99.3	100

Case Study Questions

- As they relate to octane rating of gasoline, why are alkylation and catalytic reforming reactions carried out?
- Predict the reaction products in a word equation, and then write a structural formula equation for each of the following gasoline reactions. Recall that complete combustion involves a reaction with oxygen to produce the most common oxides.
 - octane + oxygen \rightarrow
 - 2,2,4-trimethylpentane + oxygen \rightarrow
 - heptane + oxygen \rightarrow
 - methylbenzene (toluene) + oxygen \rightarrow
- Knocking occurs when compression ignites fuel during the power stroke that did not ignite initially from the spark provided by the spark plug (**Figure 7**). Write line structural formulas for the following hydrocarbons in the internal combustion engine.
 - 1,3-dimethylbenzene enters the cylinder through the intake port of the cylinder.
 - 2,3-dimethylbutane is ignited by a spark from the spark plug at the top of the compression stroke.
 - Hexane is ignited by heat and high pressure before completion of the compression stroke.
 - Decane (an excess/unreacted hydrocarbon) exits through the exhaust port of the cylinder.

Sulfur in Gasoline

Many organic compounds incorporate sulfur in their molecules. Sulfur in gasoline is a pollution problem. When the gasoline is burned, sulfur emissions reduce air quality and can also decrease the pH of rain, resulting in acid deposition. **Table 3** presents typical emissions found in the exhaust of a well-tuned automobile with a catalytic converter.

Besides contributing to the problem of acid deposition, sulfur dioxide causes problems even before leaving the exhaust pipe of an automobile. Sulfur dioxide and sulfur atoms in unburned fuel tend to reduce the effectiveness of the catalytic converter. (You will learn more about the catalytic converter in Chapter 12.) This reduced effectiveness increases the quantity of other pollutants, such as carbon monoxide and nitrogen oxides, that make their way through the exhaust system and into the air.

Research indicates that refined gasoline has a typical average sulfur content of 340 ppm, although the range is from 30 ppm to 1000 ppm. Some jurisdictions have legislated a sulfur content as low as 30 ppm.

The technology that scientists and engineers have created to reduce the sulfur content in gasoline is a process called hydrogenation or hydrotreating. Hydrogen gas (likely obtained by catalytic reforming of crude oil fractions) reacts with sulfur atoms in gasoline molecules to produce hydrogen sulfide gas. The $\text{H}_2\text{S}(\text{g})$ is then converted to sulfur and water in a Claus converter (**Figure 8**).

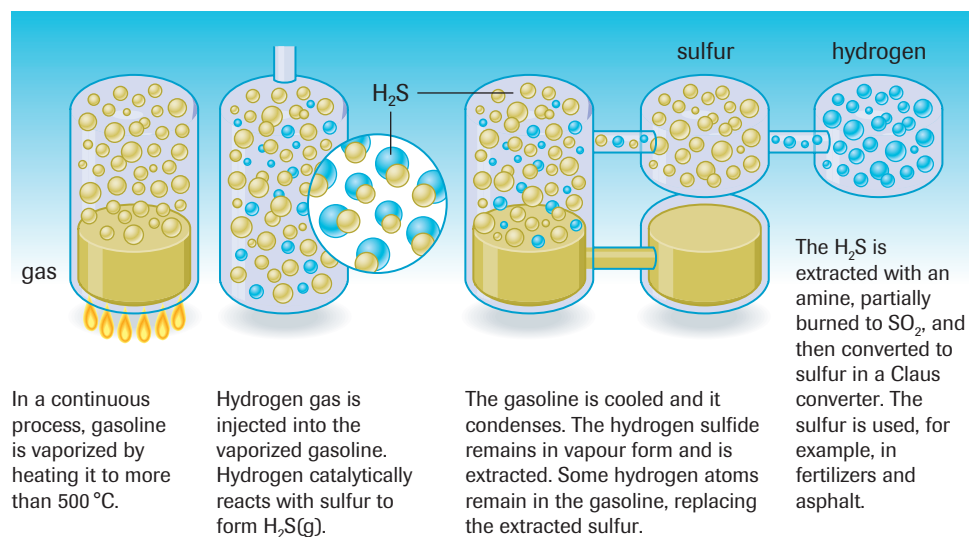


Table 3 Typical Gasoline Automobile Exhaust

Gas	Volume (%)
carbon dioxide	9
oxygen	4
hydrogen	2
carbon monoxide	4–9
hydrocarbons	< 0.2
aldehydes	0.004
nitrogen oxides	0.05–0.4
sulfur dioxide	0.006
ammonia	0.0006
nitrogen, etc.	$\approx 75^*$

* The approximate 75% includes, for example, water vapour that condenses into a vapour trail on a cold winter day.

Figure 8

To achieve the federally mandated goal of sulfur reduction in gasoline, suppliers needed to invest in new or additional desulfurization equipment, another step in the refining process. Refineries in Alberta have upgraded to reduce sulfur content in their products. Alberta oil refineries include

- Ft. Saskatchewan (Shell)
- Edmonton (PetroCanada)
- Edmonton (Imperial Oil)

DID YOU KNOW?

Sulfur Compounds

There are many organic compounds that contain sulfur. They have traditionally been identified by the use of suffixes:

thiol indicates $R-S-H$

thio represents $R=S$

sulfide communicates $R-S-R$

(R represents a hydrocarbon chain.)

Practice

16. There are many possible sulfur-bearing organic compounds in gasoline. Write a condensed structural formula equation to communicate the hydrogenation (hydrotreating) of sulfur to hydrogen sulfide for the following sulfur compounds. (You are not required to name organic compounds of sulfur.) For example, nonanethiol: $CH_3-(CH_2)_7-SH(l) + H_2(g) \rightarrow H_2S(g) + CH_3-(CH_2)_6-CH_3(l)$
- (a) $S=CH-CH_2-CH(C_6H_5)-CH_3$
(b) methylphenylsulfide ($CH_3SC_6H_5$)
(c) thio-2-butylbenzene ($SCHCH_2CH(C_6H_5)CH_3$)
17. Researchers have predicted that the price of gasoline must increase by 1–3 ¢/L in order to finance the further refining of gasoline to decrease the sulfur content to 30 ppm.
- (a) Would you be willing to pay the extra price? Why or why not?
(b) What alternatives do we have to using sulfur-containing gasoline for fueling our transportation needs?

INVESTIGATION 9.4 Introduction

Bitumen from Oil Sands

In 1920, Canadian Karl Clark invented the hot water and caustic soda, $NaOH(s)$, recovery process for extracting bitumen from oil sands. In 1923, Clark and associates at the Alberta Research Council set up a pilot project in the basement of the power plant at the University of Alberta. After decades of work, the first economically feasible world-scale plant for the extraction of bitumen from oil sands was opened in 1967 near Fort McMurray by what is now Suncor Energy.

Recent advances in bitumen extraction have called into question the need for caustic soda. This investigation involves testing the old process.

Purpose

The purpose of this investigation is to test the need for caustic soda in the extraction of bitumen from oil sands.

To perform this investigation, turn to page 403. 

Report Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 2, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Problem

What is the percentage, by mass, of bitumen in an oil sands sample?

Design

The volume of caustic soda solution added to a hot water and oil sands mixture is systematically varied. Each research group uses a different volume of caustic soda and reports the percentage mass of bitumen obtained to the other groups.

INVESTIGATION 9.5 Introduction

Solvent Extraction

Solvent extraction of bitumen from oil sands has significant importance for the development of the oil sands chemical industry in Alberta. Some in-situ bitumen extraction processes use a solvent. Most, if not all, of the surface mining bitumen extractions use a solvent to assist with bitumen extraction during the hot-water extraction process. This investigation asks you to predict which of water, propan-2-ol (an alcohol), or naphtha (a distillation fraction) is the best solvent for bitumen.

Purpose

The purpose of this investigation is to test solubility theory to predict which solvents can be used to dissolve bitumen.

To perform this investigation, turn to page 404. 

Report Checklist

- | | | |
|---|--|---|
| <input type="radio"/> Purpose | <input checked="" type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input checked="" type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 2, 3) |
| <input type="radio"/> Hypothesis | <input checked="" type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Problem 1

Which of water, propan-2-ol, or naphtha is the best solvent for extracting bitumen from oil sands?

Problem 2

Which of water, propan-2-ol, or naphtha is the best solvent for extracting bitumen from water?

Case Study

The Athabasca Oil Sands

World technology at present is utterly dependent on energy from burning fuels derived from petroleum. We know that oil resources are finite, and that oil production must, inevitably at some point, reach a peak and then decline. In the continental United States (the world's biggest oil consumer), production peaked in 1970. The world's production peak is predicted at various times by different specialists in this area, but few predict it later than the mid-21st century, and some argue that it is already here. Alberta has a huge and growing interest in this area because Alberta's oil reserves are very large.

The special case in Alberta is that the reserves are mostly not liquid crude oil, but rather bitumen—a tarry residue coating the sand grains of the immense Athabasca and other oil sand deposits (**Figure 9**). Mining oil sand and then separating bitumen from the sand (**Figure 10**) is a huge operation, involving equipment and processes on a massive scale (**Figure 11**).



Figure 9
Bitumen permeates this sample of “oil sand.”



Figure 10
Chemical engineering is required to extract bitumen from oil sands (left) and then convert bitumen (right) into synthetic crude oil.



Bitumen Extraction

As indicated in Investigation 9.4, Karl Clark used controlled experiments to develop the caustic hot water process for bitumen extraction from oil sands. He and others found that oil sand is typically 84% sand, 12% bitumen, and 4% water. Further research has shown that the sand particles are surrounded by a thin layer of water and then a thicker layer of bitumen (**Figure 12**).

Experience shows that if the oil sand dries out, the hot water process for extracting bitumen from the sand does not work: The water layer disappears and the bitumen sticks very tightly to the sand.

A current technology is to have the initial separation occur in a hydrotransport pipeline that simultaneously carries the oil sands and caustic hot water, and separates the bitumen from the sand. At the plant, the mixture is physically separated by density in a large conical vessel into bitumen froth, water, and sand. The bitumen froth, created by blowing air into the mixture, floats to the top and is skimmed off.



Figure 11
The complex processes in this refinery eventually produce a valuable “synthetic” crude oil product.

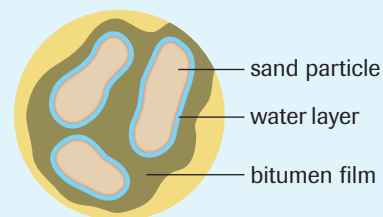


Figure 12
Close examination of oil sand shows a sand particle surrounded by water and bitumen.

Many technological advances for bitumen extraction have occurred through research over the last couple of decades, and many more creative advances for bitumen extraction and upgrading are likely to occur in the next couple of decades.

The transforming of bitumen into useful liquid synthetic crude oil, however, is where the chemistry of organic reactions comes into play, in a reaction system that has great importance for Alberta, Canada, and the world.

Bitumen is about 20% alkanes and cycloalkanes in the form of very complex branched chains; and about 80% aromatic compounds with multiple rings, forming many complex structures, from rather small to extremely large molecular sizes. Converting the bitumen into a useful product begins either with a process called coking or with hydrocracking. Both of these processes increase the hydrogen-to-carbon (H/C) ratio of bitumen. Coking removes carbon and hydrocracking adds hydrogen.

Bitumen Upgrading: Coking

Coking involves spraying bitumen onto a bed of hot (500 °C) coke particles. Coke is a material like charcoal, with a very high carbon content. Coking vaporizes the smaller molecular substances in bitumen, and causes thermal cracking in the larger molecular substances. (No catalyst is present, so the cracking is caused by high-temperature collisions.) The cracking produces many new substances that then vaporize. The process also causes some of the substances in the original bitumen to convert to solid, granular coke. When the hot vapour leaves the coking vessel and is cooled, much of it condenses to liquid that can be separated into fractions, just as is done with crude oil.

Bitumen Upgrading: Hydrocracking

Molecules in a sample of bitumen have a molar mass of 500–800 g/mol and an H/C ratio of less than one. Similar to coking, hydrocracking breaks the large aromatic molecules in bitumen into smaller aromatic and aliphatic molecules (increasing the H/C ratio). The aromatic character of bitumen results in a greater aromatic character to synthetic crude oil compared to conventional crude oil. Hydrocracking uses a catalyst to increase the rate of the cracking reaction at a lower temperature. As the name, hydrocracking, suggests, hydrogen is also a reactant—to increase the H/C ratio, convert unsaturated hydrocarbons to saturated hydrocarbons, and to remove, for example, nitrogen and sulfur impurities.

Bitumen Upgrading: Hydrotreating

Hydrotreating is the process of causing reactions of the organic substances in partially upgraded (cracked) bitumen with hydrogen, at high temperature and pressure. The reactions remove impurities, particularly nitrogen and sulfur, which cause problems with the uses for synthetic crude oil. The hydrogenation reactions also convert any double or triple carbon-carbon bonds in the liquids to single bonds, to make the molecules more stable (less reactive).

Case Study Questions

- Use solubility theory to explain
 - the natural existence of oil sands as separate layers of bitumen and then water next to the sand
 - the reason for choosing water as the liquid for extracting bitumen from oil sands
 - the difficulty of separating bitumen from sand when oil sand is left standing to dry out
 - the need for a hydrocarbon solvent for extracting bitumen from oil sand that has been dried by our sun
- What is the H/C ratio of the following compounds?
 - naphthalene in bitumen (**Figure 13**)
 - methylbenzene in gasoline
 - heptane in naphtha (camping fuel)

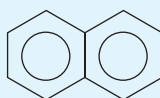


Figure 13

The molecular structure of naphthalene, a small molecule in bitumen

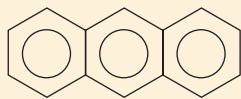
- During coking, a naphthalene, $C_{10}H_8(l)$, molecule (Figure 13) in a bitumen sample is thermally cracked into a hexane molecule and a but-2-ene molecule as products.
 - Write and balance an equation for this reaction, using any structural formula to represent each of the substances involved.
 - What is the H/C ratio for each of naphthalene, hexane, and but-2-ene?
- Consider the hydrotreating of this organic substance: $H_2NCH_2CSCH_2COOH + \text{___ } H_2(g) \rightarrow$
 - Complete a balanced chemical equation to produce the most common hydrogen compounds of N, S, and O and a saturated hydrocarbon.
 - Why is more hydrotreating needed after coking than after hydrocracking?
- For each of the following reactions of one mole of reactant, predict the product, including its structural formula and name, and state the chemical amount (in moles) of hydrogen required for complete reaction.
 - $CH_2CHCHCH_2 + \text{___ } H_2(g) \rightarrow$
 - $HCCCH_2CH_2C_6H_5 + \text{___ } H_2(g) \rightarrow$
- The oil sands are a huge source of oil for Alberta, Canada, and the world. The development of this resource will cost billions of dollars and cause environmental damage. Why are we developing the oil sands? Answer, pro and con, from a variety of perspectives and add these statements to your Exploration issue concerning the resolution that the burning of fossil fuels for heat and transportation should be significantly reduced.
- Fly through the whole process, from the initial mining of the oil sands to the final products, in this video. Prepare a flowchart to describe the oil sands process.

www.science.nelson.com

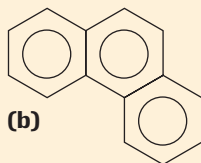


Section 9.5 Questions

- What physical property of hydrocarbons is used for fractionation?
 - What chemical theory explains the difference in the physical property used for fractionation?
- Using Table 1 (page 387), identify all products that you have used and classify them as essential, useful, convenient, or a luxury.
- Why does crude oil have to be chemically processed, in addition to being fractionated?
 - How would our technologies and/or our society be different without the invention of these processes?
- The conceptual understanding of any phenomenon in science usually starts with the creation of a classification system. Classify and write condensed structural formula equations for each of the following organic reactions. Catalysts are involved in all reactions other than combustion.
 - ethane \rightarrow ethene + hydrogen
 - hexane \rightarrow benzene + hydrogen
 - 4,4-dimethylpent-2-yne + hydrogen \rightarrow
propene + methylpropane
 - methylbenzene + oxygen \rightarrow
 - nonane \rightarrow 1-ethyl-3-methylbenzene + hydrogen
 - $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$ + hydrogen \rightarrow
nonane + octane + methane
- Predict a possible structural equation for the following reaction classes and reactants. There are many correct answers.
 - combustion of decane
 - hydrocracking of decane
 - catalytic reforming of decane
- What chemical processes are used for the upgrading of bitumen?
- What is the chemical difference between
 - bitumen and crude oil?
 - synthetic and conventional crude oil?
- Evidence gathered in the laboratory by analytical chemists indicates that the molecules in bitumen have a hydrogen-to-carbon ratio of 1:1 or less. The interpretation placed on this evidence is that the molecules are composed of multiple benzene rings (**Figure 14**).



(a)



(b)

Figure 14

Anthracene (a) and phenanthrene (b) are a couple of the smaller aromatic compounds found in bitumen and coal.

- Write the molecular formula for each molecule in Figure 14.
 - What is the H/C ratio for each of these aromatic compounds?
 - Propose a chemical reaction equation for the hydrocracking of anthracene.
- In terms of molecules, compare low-octane and high-octane gasoline. What technological processes did engineers invent to convert low-octane gasoline into high-octane gasoline?
 - Only 10–25% of the crude oil in an oil well is initially recovered using current technology. 95% of the recovered oil is burned, and only 5% is used to make useful products, such as pharmaceuticals and plastics. Some people argue that it is morally wrong for our generation to be burning this valuable chemical resource rather than giving future generations the opportunity to extract more of it using more advanced technology. Use this information (and other information from this section) to add pro and con perspective statements to the Evidence section of your Exploration (STS issue) report from page 357.

Extension

- Compare the following processes:
 - thermal cracking and catalytic cracking
 - hydrocracking and catalytic reforming
 - hydrocracking and hydrotreating
 - catalytic reforming and alkylation
- In addition to alkanes, cracking reactions may also involve alkenes, alkynes, and aromatics. For each of the following reactions, draw a structural formula equation. Include all reactants and products.
 - but-1-ene \rightarrow ethyne + ethane
 - 3-methylheptane \rightarrow but-2-ene + butane
 - 3-methylheptane \rightarrow propene + 2-methylbut-1-ene + hydrogen
 - propylbenzene \rightarrow benzene + propene
- For each of the following alkylation reactions in gasoline refining (octane boosting), draw a structural formula or write the IUPAC name for each reactant and product.
 - 2-methylpent-1-ene \rightarrow 2,3-dimethylbut-1-ene
 -



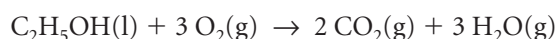
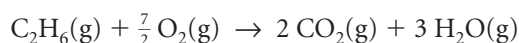
Practice

- Write chemical and structural formula equations for complete and one possible incomplete combustion reaction of butane (in a lighter).
- When automobiles burn gasoline, combustion is incomplete. Complete combustion produces carbon dioxide, a greenhouse gas. Incomplete combustion produces carbon monoxide, a toxic gas that becomes part of the airborne “chemical soup.” Write a balanced chemical equation to represent one possible incomplete combustion of each of the following gasoline components to carbon monoxide, carbon dioxide, and water vapour.
 - 3-methylhexane
 - benzene
 - cyclohexane

Evidence from combustion studies indicates that all three types of combustion reactions occur simultaneously when an organic compound is burned, albeit not in equal proportions. Comparing the equations for complete and incomplete combustion of 2,2,4-trimethylpentane, you will notice that the fuel-to-oxygen molar ratio decreases from a high of 2:25 in complete combustion, to 2:17 in the reaction producing carbon monoxide, to 2:9 in the reaction producing soot. Thus, increasing the amount of oxygen available during combustion may increase the proportion of complete combustion reactions that occur. Even a stoichiometric excess of oxygen does not guarantee that only complete combustion will take place. The larger the excess of oxygen available during combustion, however, the smaller the amount of carbon monoxide and soot that is produced.

Carbon monoxide is a toxic gas that can reach dangerous levels in a confined area (such as in a house, a car, and even in a city). Reducing carbon monoxide emissions from oil and gas furnaces, gas stoves, and vehicles helps keep atmospheric concentrations of carbon monoxide low. In some places, alcohol is added to gasoline to help reduce carbon monoxide emissions. When added to gasoline, alcohols are often called *oxygenators* because they provide additional oxygen to the combustion reaction. Oxygenators make the combustion more complete, as evidenced by the reduced quantity of carbon monoxide and soot in the exhaust of automobiles that have been tested. In fact, some jurisdictions legislate the percentage of oxygenator that must be included in gasoline.

The following two equations allow you to compare the combustion of ethane and ethanol. Note the smaller chemical amount of oxygen required to burn ethanol:



INVESTIGATION 9.6 Introduction

Complete and Incomplete Combustion

Complete combustion has several benefits over incomplete combustion. Even complete combustion can create problems for the environment, however. In this investigation, you have an opportunity to start a research program (a major experimental design) on improving combustion. This is an open entry investigation. You create it and then possibly carry it out.

Purpose

The purpose of this investigation is to create a research program to improve combustion of, for example, candle wax.

To perform this investigation, turn to page 404.

Report Checklist

- | | | |
|----------------------------------|--|--|
| <input type="radio"/> Purpose | <input checked="" type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input checked="" type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 3) |
| <input type="radio"/> Hypothesis | <input checked="" type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Problem

How can the combustion of a hydrocarbon be improved?

DID YOU KNOW?

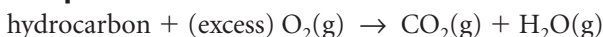
Ethanol in Gasoline

In the 1920s and 1930s, cars could be converted to run on gasoline, ethanol (from corn), or a 25% blend of ethanol with gasoline. In 2002, about 620 000 m³ of corn were used to produce ethanol for blending with gasoline in hundreds of gas stations in Canada. The importance of ethanol has returned! It takes approximately 1.5 L of ethanol to deliver the same energy as 1.0 L of regular gasoline. The percentage of carbon monoxide emissions from burning ethanol or ethanol-blended gasoline, however, is significantly reduced. Despite this drawback, some provinces now have legislation that calls for mandatory blending of ethanol in gasoline.

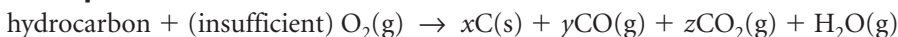
SUMMARY

Complete and Incomplete Combustion

Complete Combustion



Incomplete Combustion





(The ratio of $x:y:z$ largely depends on the proportion of oxygen available.)

Section 9.6 Questions

1. The primary reaction of the components of natural gas is combustion with oxygen from the air. The primary product of these combustion reactions is energy. List three chemical by-products of this energy-producing reaction.
2. Write molecular and condensed structural formula equations for the combustion of pentane (in winter gasoline). Assume complete combustion.
3. Evaluate, with reasoning, the statement: "Fossil fuels must contain significant quantities of nitrogen because nitrogen oxides are found in the exhaust of cars and trucks."
4. Combustion is not always complete, usually because of an insufficient supply of oxygen. Write a hypothesis, including a chemical equation, to explain the following events.
 - (a) When ethyne (acetylene) is burned in air, black soot appears.
 - (b) Deaths have occurred when charcoal briquettes (assume pure carbon) are burned inside a tent to keep campers warm on a cold night.
 - (c) Deaths have occurred when people fall asleep in the back seat of a car that has a leaky muffler.
5. Gasoline is not a mixture of pure hydrocarbons. Some of the hydrocarbon molecules are contaminated with nitrogen, sulfur, and oxygen atoms. Air pollutants, such as nitrogen dioxide and sulfur dioxide, are produced from the combustion of these molecules. Write unbalanced chemical equations to represent the complete combustion of
 - (a) $\text{C}_6\text{H}_5\text{NO}(\text{l})$
 - (b) $\text{C}_4\text{H}_8\text{S}(\text{l})$
 - (c) $\text{NHC}_3\text{H}_4\text{S}(\text{l})$
6. Canadians are among the highest producers of greenhouse gases in the world; for example, the average Albertan produces five tonnes per annum of greenhouse gases. The One-Tonne Challenge (OTC) to each Canadian is to reduce his or her greenhouse gas production by the equivalent of one tonne of carbon dioxide per year. Write pro and/or con statements from at least four perspectives concerning the resolution that GHGs should be reduced.

7. Use the information in this section to add to your list of pro and con perspective statements regarding your resolution on reducing fossil fuel consumption.

Extension

8. Evidence-based reasoning and scientific concept-based reasoning are goals of science and of science education. There are many examples of claims that gather a following even though they are based on anecdotal evidence and concepts that have not gained acceptance by the scientific community. Use the links provided to start an investigation into claims of spontaneous human combustion. What is your evaluation, based on the evidence and on accepted scientific concepts?
www.science.nelson.com 
9. Chemists communicate their research through peer-reviewed (refereed) journals. (See Appendix B.4.) Other chemists who do research on the same topic search for and read the abstract to see if they want to read the full research report. Read the abstract provided by the link below. What fuel was added to the natural gas and what effect did it have on the carbon dioxide emission?
www.science.nelson.com 



INVESTIGATION 9.1

Classifying Fossil Fuels

Alberta has many different fossil fuels. Samples of fossil fuels can be described and classified in terms of their physical properties of colour, transparency, viscosity, and density. In this investigation, the focus is on density.

Purpose

The purpose of this investigation is to use the known properties of fossil fuels to analyze the provided samples.

Problem

What are the classes of the fossil fuel samples provided?

Design

Equal-volume samples of fossil fuels are provided in sealed containers of equal mass. The mass of each sample, including the container, is determined. The fossil fuel samples are classified based upon their densities.

Report Checklist

- | | | |
|----------------------------------|--|--|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 3) |
| <input type="radio"/> Hypothesis | <input checked="" type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Materials

lab apron eye protection
equal volume samples, labelled A to G, of
heavy oil natural gas
light oil medium oil
coalbed methane bitumen
coal

Table 1 Densities of Fossil Fuels

Fossil fuel class	Density (g/cm ³)
methane	0.0007165
light crude oil	0.800–0.850
medium crude oil	0.875–0.900
heavy crude oil	0.935–1.000
bitumen	>1.000–1.075
coal	1.3–>2.0



INVESTIGATION 9.2

Structures and Properties of Isomers

Molecular models are visual representations of molecules that help us to understand some of the properties and structures of molecules. In addition to building models, this investigation asks you to consult references to obtain data gathered by chemists over many years of laboratory work.

Purpose

The purpose of this investigation is to use models and a reference, respectively, to examine the structures and physical properties of some isomers of unsaturated hydrocarbons.

Problem

What are the structures and physical properties of the isomers of C₄H₈ and C₄H₆?

Design

Structures of possible isomers are determined by means of a molecular model kit. Once each structure is named, the boiling

Report Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

and melting points are obtained from a reference such as the *CRC Handbook of Chemistry and Physics* or *The Merck Index*.

www.science.nelson.com

Materials

molecular model kits chemical reference

Procedure

1. Use the required “atoms” to make a model of C₄H₈.
2. Draw a structural formula of the model and write the IUPAC name for the structure.
3. Rearrange bonds to produce models for all other isomers of C₄H₈, including cyclic structures. Draw structural formulas and write the IUPAC name for each structure before disassembling the models.



INVESTIGATION 9.2 *continued*

- If you construct a model that contains a double C–C bond, test the restricted rotation of groups about the bond axis and the bond length.
- Repeat steps 1 to 4 for C_4H_6 .
- In a reference, find the melting point and the boiling point of each of the compounds you identified.



INVESTIGATION 9.3

Fractional Distillation (Demonstration)

Fractional distillation is a process used commercially to separate molecular components of petroleum using boiling point differences. The same technique can be used to separate components of most liquid mixtures, provided a significant boiling point difference exists. In this demonstration, the vapours of the boiling mixture rise into a fractionating column, where initially they all condense and fall back into a flask. When the temperature in the column rises sufficiently, vapours of the component with the lower boiling point pass through the column and enter a condenser, which cools and condenses the component back to a liquid for collection. The component with the higher boiling point still condenses in the fractionating column, which separates the two liquids.

Purpose

The purpose of this investigation is to use the concept and technique of fractional distillation to separate two hydrocarbon components from a liquid mixture.

Problem

What is the percent by volume of each of the two hydrocarbon components?

Design

A mixture of the two liquids is heated in a fractional distillation apparatus while the temperature is measured at regular intervals in a fume hood.

Materials

lab apron
eye protection
round-bottom distillation flask
electric heating mantle
2 small collecting flasks
stopwatch
fume hood

thermometer or temperature probe to fit column stopper
pentane, $C_5H_{12}(l)$
2-methylpropan-2-ol, $CH_3C(CH_3)_2OH$
fractionating column
stand and clamp

Report Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input type="radio"/> Evaluation (1, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

50 mL graduated cylinder
large 400–600 mL beaker
condenser with tubing and fittings

Procedure

- Obtain a 50 mL sample of the mixture of unknown composition.
- Heat the flask slowly, taking the vapour temperature at regular 30 s intervals.
- After most of the pentane has boiled off, when the column temperature rises noticeably, change collection flasks at the outflow of the condenser (**Figure 1**).
- Measure the volume of pentane collected.
- As soon as most of the alcohol has boiled off, remove the heating mantle.
- Dispose of the organic chemicals into an organic waste container.

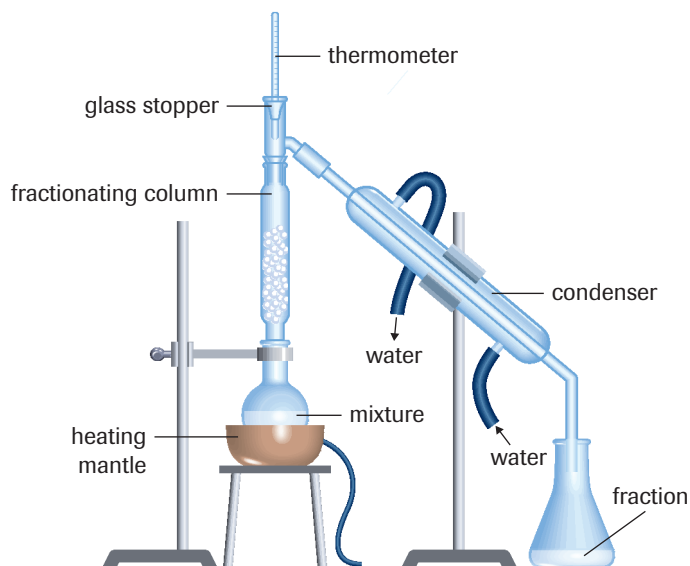


Figure 1
A fractional distillation apparatus

**INVESTIGATION 9.4****Bitumen from Oil Sands**

In 1920, Canadian Karl Clark invented the hot water and caustic soda, NaOH(s), recovery process for extracting bitumen from oil sands. In 1923, Clark and associates at the Alberta Research Council set up a pilot project in the basement of the power plant at the University of Alberta. After decades of work, the first economically feasible world-scale plant for the extraction of bitumen from oil sands was opened in 1967 near Fort McMurray by what is now Suncor Energy.

Surface mining of oil sands allows for over 90% recovery of the bitumen. This percentage compares very favourably with in-situ oil sands at 25-75%, conventional heavy oil at less than 20%, and conventional light oil at about 30%. Fortunately for the environment, over 80% of the oil sands will have to be mined in-situ rather than from a surface mine. Unfortunately, the recovery rate of in-situ operations is significantly lower using current technologies.

Recent advances in bitumen extraction have called into question the need for caustic soda. This investigation involves testing the effects of using various amounts of caustic soda (sodium hydroxide).

Purpose

The purpose of this investigation is to test the need for caustic soda in the extraction of bitumen from oil sands.

Problem

What is the percentage, by mass, of bitumen in an oil sands sample?

Design

The volume of caustic soda solution added to a hot water and oil sands mixture is systematically varied. Each research group uses a different volume of caustic soda and reports the percentage mass of bitumen obtained to the other groups.

Materials

eye protection
lab apron
ring stand
wire gauze
250 mL beaker
400 mL beaker
ring clamp
laboratory burner or hot plate
beaker tongs

Report Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 2, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

dropper bottle of 1.0 mol/L NaOH(aq)
small disposable plastic spoon
100 g of oil sands
laboratory balance
disposable clear plastic container
paper towel



Sodium hydroxide is corrosive. Avoid skin and eye contact.

Procedure

1. Add about 250 mL of tap water to the 400 mL beaker.
2. Add 0, 4, 8, and 12 (as assigned to your research group) drops of 1.0 mol/L sodium hydroxide solution to the water.
3. Heat the water to boiling.
4. Place the disposable plastic container into a paper-towel-lined 250 mL beaker (or equivalent).
5. Add a measured mass of oil sands to the disposable container and set the container on a paper towel.
6. Use the beaker tongs to pour water onto the oil sands to make a slurry.
7. Use the plastic spoon to stir the slurry for about 5 min.
8. Use the beaker tongs again to add about 100 mL more hot water to nearly fill the container.
9. Allow the contents of the container to settle.
10. Measure the mass of a double layer of paper towel.
11. Use the plastic spoon to remove the bitumen from the container onto a double layer of paper towel.
12. Dry and measure the mass of the bitumen plus paper towel.

INVESTIGATION 9.5

Solvent Extraction

Solvent extraction of bitumen from oil sands has significant importance for the development of the oil sands chemical industry in Alberta. Some in-situ bitumen extraction processes use a solvent. Most, if not all, of the surface mining bitumen extractions use a solvent to assist with bitumen extraction during the hot-water extraction process. This investigation asks you to predict which of water, propan-2-ol (an alcohol), or naphtha (a distillation fraction) is the best solvent for bitumen.

Purpose

The purpose of this investigation is to test solubility theory to predict which solvents can be used to dissolve bitumen.

Report Checklist

- | | | |
|---|--|---|
| <input type="radio"/> Purpose | <input checked="" type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input checked="" type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 2, 3) |
| <input type="radio"/> Hypothesis | <input checked="" type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Problem 1

Which of water, propan-2-ol, or naphtha is the best solvent for extracting bitumen from oil sands?

Problem 2

Which of water, propan-2-ol, or naphtha is the best solvent for extracting bitumen from water?

INVESTIGATION 9.6

Complete and Incomplete Combustion

Complete combustion has several benefits over incomplete combustion. Even complete combustion can create problems for the environment, however. In this investigation, you have an opportunity to start a research program (a major experimental design) on improving combustion. This is an open entry investigation. You create it and then possibly carry it out.

Report Checklist

- | | | |
|----------------------------------|--|--|
| <input type="radio"/> Purpose | <input checked="" type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input checked="" type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 3) |
| <input type="radio"/> Hypothesis | <input checked="" type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Purpose

The purpose of this investigation is to create a research program to improve the combustion of, for example, candle wax.

Problem

How can the combustion of a hydrocarbon be improved?

Outcomes

Knowledge

- define organic compounds, recognizing inorganic exceptions (9.1)
- identify and describe organic compounds in everyday life, as well as their origins and applications (all sections)
- name and draw structures for saturated and unsaturated aliphatic and aromatic hydrocarbons (9.2 to 9.6)
- classify organic compounds from their structural formulas (9.2 to 9.5)
- define and use the concept of structural isomerism and relate to properties of isomers (9.2 to 9.4)
- compare boiling points and solubility of organic compounds (9.2 to 9.4)
- describe fractional distillation and solvent extraction (9.1, 9.2, 9.3, 9.5)
- define, provide examples of, predict products, and write and interpret balanced equations for combustion reactions (9.1, 9.2, 9.5, 9.6)
- describe major reactions for producing energy and economically important compounds from fossil fuels (all sections)

STS

- illustrate how science and technology are developed to meet societal needs and expand human capabilities (all sections)
- describe interactions of science, technology, and society (all sections)
- illustrate how science and technology have both intended and unintended consequences (9.1, 9.2, 9.5, 9.6)

Skills

- initiating and planning: describe procedures for safe handling, storing, and disposal of materials used in the laboratory, with reference to WHMIS and consumer product labelling information (9.5)
- performing and recording: separate a mixture of organic compounds based on boiling point differences (9.5); build molecular models depicting the structures of selected organic and inorganic compounds (9.3)
- analyzing and interpreting: follow IUPAC guidelines for naming and formulas and by compiling evidence to compare the properties of structural isomers (all sections); compile and organize data to compare the properties of structural isomers (9.3); investigate sources of greenhouse gases, that is, methane, carbon dioxide, water, and dinitrogen oxide (nitrous oxide) and the issue of climate change (all sections)
- communication and teamwork: work cooperatively in addressing problems and apply skills and conventions of science in communicating information and ideas and in assessing results by preparing reports on topics related to organic chemistry (all sections)

Key Terms

9.1

organic chemistry
hydrocarbon
refining

9.2

alkane
homologous series
saturated hydrocarbon
structural isomer
alkyl branch
cycloalkane

9.3

hydrogenation

alkene
alkyne
cycloalkene
cracking
aliphatic

9.4

aromatic
phenyl group

9.5

fractionation
fraction
hydrocracking
catalytic reforming

▶ **MAKE a summary**

1. Create a concept map starting with “Fossil Fuels” in the centre of a page. Include all of the Key Terms, Key STS, and Key Skills, as well as any other information you think may be useful in studying for a test on this chapter.
2. Refer back to your answers to the Starting Points questions at the beginning of this chapter. How has your thinking changed?

▶ **Go To**

www.science.nelson.com



The following components are available on the Nelson Web site. Follow the links for *Nelson Chemistry Alberta 20–30*.

- an interactive Self Quiz for Chapter 9
- additional Diploma Exam-style Review questions
- Illustrated Glossary
- additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

www.science.nelson.com 

DO NOT WRITE IN THIS TEXTBOOK.

Part 1

- Organic chemistry is defined as the study of
 - all carbon compounds
 - all carbon compounds except cyanide
 - all carbon compounds except oxides and ionic compounds
 - compounds produced by living organisms
- Chemists have developed classification systems for the compounds they study. The empirical classification of hydrocarbons is based on
 - physical properties only
 - chemical properties only
 - physical and chemical properties
 - physical and chemical properties and empirically determined molecular formulas
- Hydrocarbons that contain a benzene ring in their molecules are called
 - aromatics
 - alkanes
 - alkenes
 - alkynes

Use this information to answer questions 4 to 6.

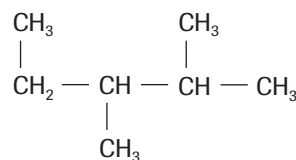
- hex-1-ene
- hex-1-yne
- 1,2-dimethylbenzene
- hex-2-ene
- 2-methylpent-2-ene
- benzene
- cyclohexane
- cyclohexene
- methylbenzene

4. The alkenes are
NR _____

5. The aromatics are
NR _____

6. The isomers of C₆H₁₂ are
NR _____

7. The IUPAC name for the following hydrocarbon is

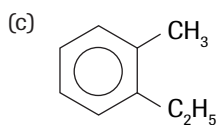
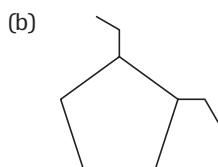
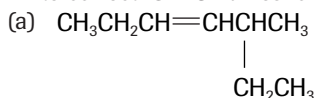


- 3,4-dimethylpentane
 - 2,3-dimethylpentane
 - 1,2,3-trimethylbutane
 - 4,5,6-trimethylbutane
- Differences in boiling points are the basis of
 - catalytic cracking
 - solvent extraction
 - catalytic reforming
 - fractional distillation
 - The natural gas used by consumers to heat their homes contains mostly
 - methane
 - ethane
 - propane
 - butane
 - For a related series of hydrocarbons, such as unbranched alkanes, a property that decreases as molar mass increases is
 - boiling point
 - melting point
 - volatility
 - viscosity
 - The change in boiling point of alkanes with increasing molar mass is primarily due to increasing
 - London forces
 - dipole-dipole forces
 - covalent bonds
 - hydrogen bonds
 - Separating the components of natural gas can involve all of the following processes *except*
 - fractionator
 - Claus converter
 - condenser
 - amine scrubber
 - The technology of cracking and reforming hydrocarbons was developed primarily to meet the societal demand for
 - asphalt for paving highways
 - lubricating oils for machines
 - gasoline for automobiles
 - propane for home heating
 - The chemical reaction that produces coke is
 - combustion
 - catalytic reforming
 - catalytic cracking
 - alkylation

15. Identify the missing product in the following catalytic cracking reaction: $C_{17}H_{36}(l) \rightarrow C_8H_{18}(l) + \text{_____} + C(s)$
- $CH_3C(CH_3)_2(CH_2)_3CH_3(l)$
 - $C_8H_{16}(l)$
 - $C_9H_{18}(l)$
 - $C_6H_5(CH_3)_2(l)$

Part 2

16. Write correct IUPAC names for the following structures:



17. Draw a structural formula for each of the following compounds, and write the IUPAC name for each:
- ethylene
 - propylene
 - acetylene
 - toluene, the toxic solvent used in many glues
 - the three isomers of xylene (dimethylbenzene), used in the synthesis of other organic compounds such as dyes
18. Using your knowledge of elements and compounds, **explain** why carbon forms more compounds than all other elements combined.
19. List some examples of carbon-containing compounds that are not classified as organic. What do these compounds have in common?
20. State the name and formula of the simplest member of each of the four hydrocarbon families and include one important use of each.
21. Can a molecular formula for an aliphatic hydrocarbon be used to predict the specific family to which it belongs? **Explain**, using examples and noting limitations.
22. **Compare** the physical processes of distillation and solvent extraction.
23. Draw a line structural formula for each hydrocarbon.
- 2-methylnonane
 - methylcyclopentane
 - hex-3-yne
 - 1,2,4-trimethylbenzene
 - 4-propyloctane
 - 2-phenylpropane
 - 3-methylpent-2-ene

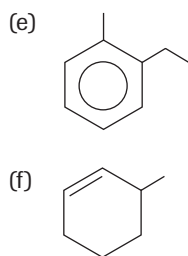
- 1,4-diethylbenzene
- 5-ethyl-2-methylhept-2-ene
- 4-methylpent-2-yne

24. Classify each hydrocarbon in question 23 into its family of hydrocarbons and **identify** which ones are saturated and which ones are unsaturated.
25. Draw structural formulas and write the IUPAC names for all the isomers of C_4H_8 .
26. In addition to alkanes, cracking reactions may also involve alkenes, alkynes, and aromatics. For each of the following reactions, draw a condensed structural formula equation. (You may draw a line structural formula for benzene.) Include all reactants and products.
- but-1-ene \rightarrow ethyne + ethane
 - 3-methylheptane \rightarrow but-2-ene + butane
 - 3-methylheptane \rightarrow
propene + 2-methylbut-1-ene + hydrogen
 - propylbenzene \rightarrow methylbenzene + ethene
27. Classify the reaction type and write condensed structural formula (except for benzene) equations for the following organic reactions.
- ethane \rightarrow ethene + hydrogen
 - but-2-ene + hydrogen \rightarrow butane
 - 4,4-dimethylpent-2-yne + hydrogen \rightarrow
propene + methylpropane
 - methylbenzene + (excess) oxygen \rightarrow
 - decane \rightarrow 2,2,4-trimethylheptane
 - octane \rightarrow 1,3-dimethylbenzene
 - nonane \rightarrow propane + pentane + carbon
28. Camping fuel is composed of alkanes with five or six carbon atoms per molecule. Name the following hydrocarbons found in this light naphtha fuel.

- $\begin{array}{c} CH_3 \\ | \\ CH_3 - CH - CH_2 - CH_3 \end{array}$
- $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$
- $\begin{array}{c} CH_3 \\ | \\ CH_3 - CH - CH_2 - CH_2 - CH_3 \end{array}$
- $(CH_3)_4C(l)$
- $(CH_3)_2CHCH(CH_3)_2(l)$

29. Write IUPAC names for the following hydrocarbons.

- $CH \equiv C - CH_2 - CH_2 - CH_3$
- $CH_3 - CH = CH - CH_2 - CH_3$
- $\begin{array}{c} CH \equiv C - CH - CH_3 \\ | \\ CH_3 \end{array}$
- $\begin{array}{c} CH_3 \\ \diagup \\ CH_3 - CH = C \\ \diagdown \\ CH_3 \end{array}$



30. Coal is the most abundant fossil fuel in Alberta. The main use of coal in Alberta is to burn it to produce steam for driving turbines for turning electrical generators.
- (a) If bituminous coal has an empirical formula of $C_9H_6O(s)$, **predict** a balanced chemical equation for the complete combustion of this coal.
- (b) The sulfur and nitrogen content of coal from Alberta is relatively low, which puts Alberta coal in demand in Canada and beyond. If a coal molecule has a molecular formula of $C_{100}H_{40}O_{10}N_2S(s)$, **predict** a balanced chemical equation for the complete combustion of this molecule.
31. The safe storage and handling of hydrocarbon fuels requires knowledge of their boiling points. The trends in boiling points within a hydrocarbon family make it possible to predict boiling points that are unknown. The purpose of this activity is to **identify** the trend in the boiling points for each family, and then use the trend to **predict** the boiling point of the next member of the series. Complete the Prediction, Analysis, and Evaluation (2, 3) of the investigation report.

Problem

What are the boiling points of hexane, hex-1-ene, and hex-1-yne?

Design

For three families (classes) of aliphatic hydrocarbons, the boiling points are plotted versus the number of carbon atoms per molecule. The graphs are extrapolated to predict the boiling point of the next member of each family. The predictions are evaluated by looking up the measured values in the *CRC Handbook of Chemistry and Physics*.

Evidence

See **Table 1** below.

32. Copy and complete **Table 2**.
33. For each of the following compounds, write its structural formula, and state its origin and a technological application.
- methane
 - ethene
 - ethyne
 - 2,2,4-trimethylpentane
 - 1,2-dimethylbenzene
34. Draw condensed structural formulas for and name the structural isomers of C_5H_{10} .

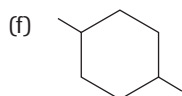
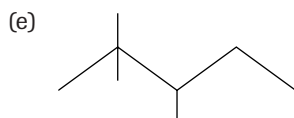
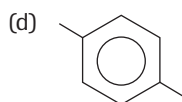
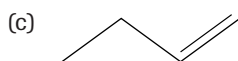
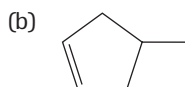
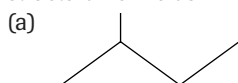
Table 1 Boiling Points of Aliphatic Hydrocarbons

Alkanes	Boiling point (°C)	Alkenes	Boiling point (°C)	Alkynes	Boiling point (°C)
ethane	-89	ethene	-104	ethyne	-84
propane	-42	prop-1-ene	-47	prop-1-yne	-23
butane	-0.5	but-1-ene	-6.3	but-1-yne	8.1
pentane	36	pent-1-ene	30	pent-1-yne	40

Table 2 Some Important Hydrocarbons

IUPAC name	Condensed structural formula	Family/Class	Common use
	$CH_3 - C \equiv C - H$	alkynes	cutting/welding torch
	$CH_2 = CH_2$		petrochemical feedstock
propene			making plastics
methylpropane			butane lighters
2,3,3-trimethylpentane			gasoline
heptane		alkane	early anesthetic
methylbenzene			solvent

35. Write the IUPAC name of each of the following line structural formulas.



36. Complete the Design, Materials, and Procedure for the following investigation report.

Purpose

The purpose of this investigation is to use the properties of organic and inorganic chemicals to identify unknown chemicals.

Problem

Which of the chemicals provided is organic and which is inorganic?

37. Solvent extraction is used in chemical research and in the chemical industry to separate chemical components of a mixture. Researchers have found solvents that work best in specific situations. **Explain** the effectiveness of the solvent in each of the following processes.

- Naphtha is used to extract bitumen from a water, sand, and bitumen mixture.
- Toluene (methylbenzene) is used to separate asphaltenes (large aromatic molecules) from bitumen.
- Water does not dissolve bitumen but is used to extract it from oil sands.

38. **Outline** the major processes used in the refining of crude oil. Your response should include

- DE**
- some details of the physical and chemical changes at each stage of the process
 - chemical reaction equations to illustrate some of the chemical changes
 - a consideration of the impact of crude oil refining from several perspectives

39. Mining and oil development, due to their extractive nature, inevitably leave an environmental footprint, even before drilling occurs. For example, in its search for oil in the Edmonton area, Anadarko Petroleum has tested seismic lines near the Kehewin Cree people's reserve. Despite the assertion by Anadarko officials that the band will be consulted before drilling, some of the Aboriginal residents say the search itself may ruin traditional hunting grounds. Research this issue or another similar dispute from the perspective of the energy company, a local Aboriginal band, and an environmentalist. On what specific issues do these groups agree and disagree?

www.science.nelson.com

Extension

40. Some natural gas is sold without the hydrocarbon components being fractionated.

- DE**
- Write a balanced chemical equation for the burning of natural gas containing the smallest four alkanes (see Table 1, page 363). Include a realistic mole ratio of the hydrocarbons in the balanced chemical equation.
 - Why is it that more and more of the natural gas being burned is nearly pure methane, even though it is expensive to remove the other components?
 - Why do some importers, such as the U.S., insist that the natural gas *not* be fractionated?
 - At one time in the past, the second-largest hydrocarbon component of natural gas that was most difficult to remove was not removed. Identify the component, and speculate as to why it was not removed and why the situation has changed.

41. Do a literature/media/Internet search for information on methane trapped in the Arctic ice of Canada. Present your findings in an innovative manner.

42. Quite often in the media, you hear or read stories about "proven oil reserves." The most quoted source of this information is the U.S. Department of Energy. What is meant by the term "proven oil reserves"? Does the Middle East really have most of the oil in the world? What influence do politics and science have in determining oil reserves? Are the media giving a true picture of the world's oil reserves? Investigate these questions and present your findings, with illustrations and graphs, in a short article suitable for publication in a daily newspaper or on a Web page.

www.science.nelson.com

43. Cracking and reforming of crude oil are very complex chemical processes. Read about catalytic reforming and then list some of the other kinds of processes involved, such as polymerization.

www.science.nelson.com









44. In 1992, the International Institute for Sustainable Development (IISD) published the report *Our Responsibility to the Seventh Generation*. This report highlights the value of Indigenous knowledge and contributions to sustainable development. The report includes, for example, the quotation "We cannot simply think of our survival; each new generation is responsible to ensure the survival of the seventh generation."

- What is the definition of sustainable development provided in this report?
- In the Overview of the report starting on page 7, what are the one or two most prominent perspectives presented in the first three chapters? (See Appendix D.1.)

www.science.nelson.com

Hydrocarbon Derivatives, Organic Reactions, and Petrochemicals

► In this chapter

-  Exploration: Burning Fossil Fuels
-  Investigation 10.1: Substitution and Addition Reactions
-  Lab Exercise 10.A: Synthesis of an Organic Halide
-  Investigation 10.2: Isomers of Butanol
-  Web Activity: Cellulosic Ethanol
-  Lab Exercise 10.B: Explaining Physical Property Trends
-  Biology Connection: Natural Esters
-  Investigation 10.3: Synthesis of an Ester
-  Investigation 10.4: Testing with Models
-  Web Activity: Teflon—Healthy or Hazardous?
-  Web Activity: Recycling Plastics
-  Biology Connection: Correlation versus Cause and Effect
-  Web Activity: Molecular Modelling
-  Investigation 10.5: Preparing Nylon 6,10 (Demonstration)
-  Explore an Issue: Natural or Artificial Polymers?
-  Biology Connection: Glycogen
-  Mini-Investigation: Starch and Cellulose
-  Web Activity: Cellulose Acetate

Alberta's resources contribute to making this province one of the best places in the world to live and work. Alberta's resource wealth includes a diverse, well-educated population, an environment that brings tourists in all seasons, and petroleum reserves. You may not realize it, but all of these resources depend on organic chemicals and the reactions that this unique class of chemicals can undergo.

When the price of natural gas, crude oil, and gasoline increases, the price of almost everything else likewise increases—evidence for the strong connection between fossil fuels and many other products. Chemicals that are produced from petroleum are called *petrochemicals*. Petrochemicals include plastics, asphalt shingles, paints, dyes, cosmetics, antifreezes, lubricants, adhesives, carpets, pesticides, fertilizers, and pharmaceuticals.


Much of the petrochemical industry in Alberta is located near Sherwood Park, Fort Saskatchewan, and Red Deer. Both natural gas and crude oil are the raw materials that, when refined, supply the petrochemical feedstock. Ninety-five percent of refined crude oil and natural gas is burned. The other five percent is used as petrochemical *feedstock*. Feedstock is a variety of chemical substances used in the chemical processes to produce petrochemicals. The end products are in demand by industry, commerce, and consumers.

Some of the main petrochemical feedstocks derived from natural gas are methane, ethane, propane, and butane. The main feedstocks from crude oil are naphtha and gas oil. Organic reactions convert these hydrocarbon feedstocks to petrochemicals. In this chapter, you will learn how to describe, explain, and predict organic reactions. As with any undertaking, there are risks and benefits to the development of petrochemical industries in Alberta. Throughout this chapter, you are asked to adopt a multiperspective view and to gather information for and against this industrial development.

STARTING Points

Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.

1. What reactions, other than combustion and cracking, do organic compounds undergo?
2. List some important consumer, commercial and/or industrial petrochemical products of organic reactions.
3. What are polymers? Give some specific examples.

 Career Connection:
Chemical Engineer; Chemical Employee

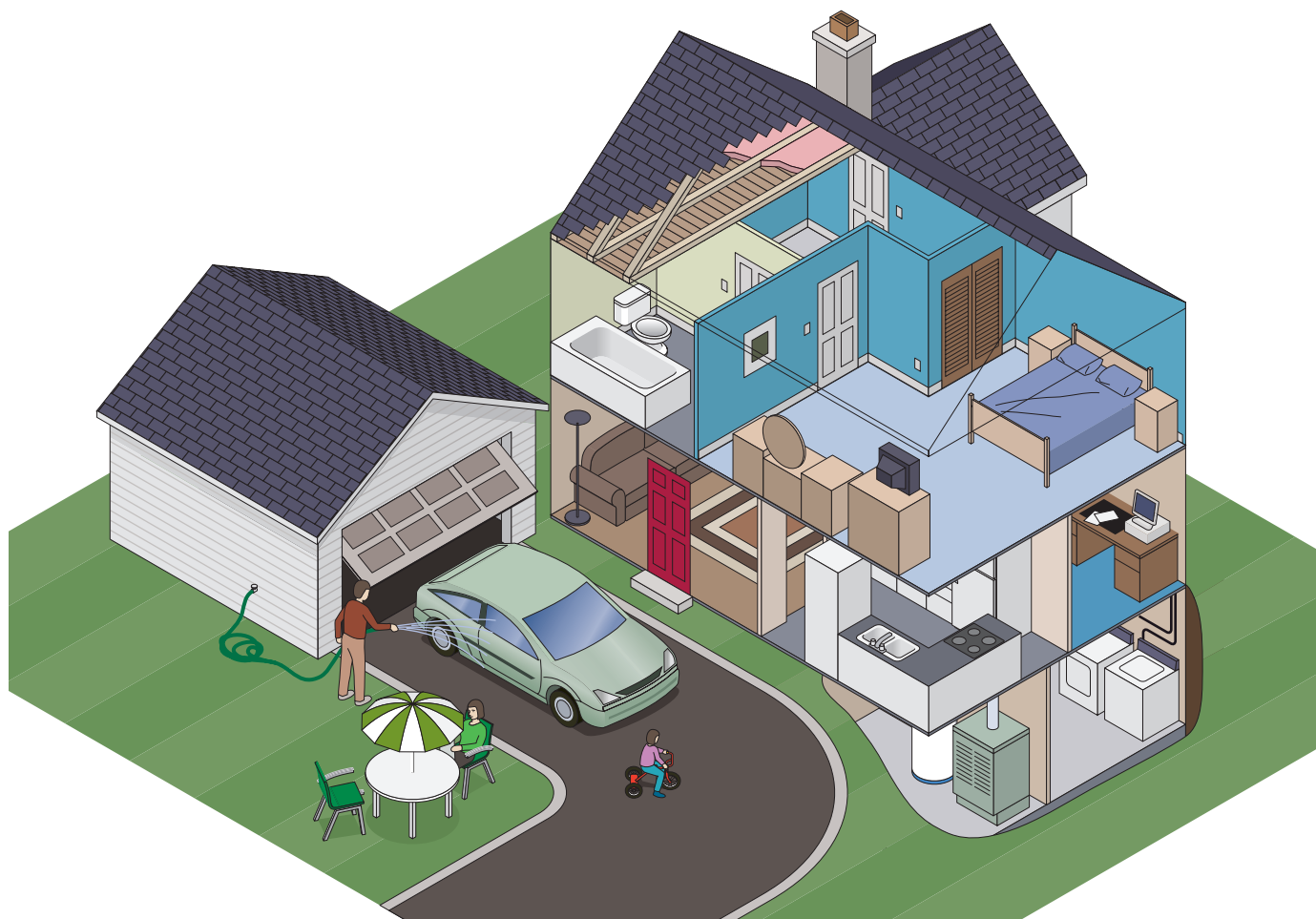


Figure 1

Chemicals from petroleum—petrochemicals—are everywhere around us. There are at least twenty different petrochemical products in this illustration, such as synthetic fabrics in bedding, countertops, rugs, vinyl flooring, garden hose, chairs, and siding. What are some other examples?

► Exploration

Burning Fossil Fuels

This Exploration continues from Chapter 9. In this chapter (which looks at the production of petrochemicals from petroleum), the emphasis is on the second, boldfaced, statement below.

Scientists agree that fossil fuels are a nonrenewable, finite resource. Fossil fuels in Alberta include coal, natural gas, crude oil, oil sands, and heavy oil. Studies have indicated that about 95% of the fossil fuels used in Alberta are used for energy production, including natural gas and propane for home heating, and gasoline and diesel fuel for cars, trucks, and buses. The evidence indicates that about 5% of fossil fuels are converted into petrochemicals (such as plastics) through technologies based on chemical reactions. Two issues related to burning fossil fuels for energy production are

- whether we should be burning a very valuable resource at the rate that we are
- **whether we should be saving more of this resource for petrochemical use in the future**

Issue Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Issue | <input checked="" type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Resolution | <input checked="" type="radio"/> Evidence | <input checked="" type="radio"/> Evaluation |

Resolution: We should be saving more fossil fuels for future use as petrochemicals.

While progressing through Chapter 10, complete the Design, Evidence, Analysis, and Evaluation components of this second issue report. Specific to this chapter, the evidence includes a list of important organic reactions that produce valued petrochemicals.

Governments, industry, and citizens alike speak of sustainable development. The United Nations Commission on Environment and Development defines sustainable development as development that meets the needs of the present without compromising the ability of future generations to meet their own needs. Keep this concept in mind while completing this unit-long exploration.

10.1 Petrochemicals in Alberta

CAREER CONNECTION

Chemical Engineer

The chemical industry is Canada's most knowledge-based industry. About 30% of workers in the chemical industry have university degrees. The salaries in the chemical industry are, as expected, among the highest in Canada. What types of chemical industries employ chemical engineers?

www.science.nelson.com



The petrochemical industry in Alberta is a secondary and tertiary industry that takes raw materials, such as crude oil and natural gas, and feedstocks, such as ethane, and converts them into value-added chemicals. This industry is an important economic and social addition to the fossil fuel, agriculture, and tourism industries of Alberta. The petrochemical industry in Alberta exports to other parts of Canada and the world. **Figure 1** depicts the raw materials, feedstock, and primary petrochemicals that start the chemical processes you will learn about in this chapter.

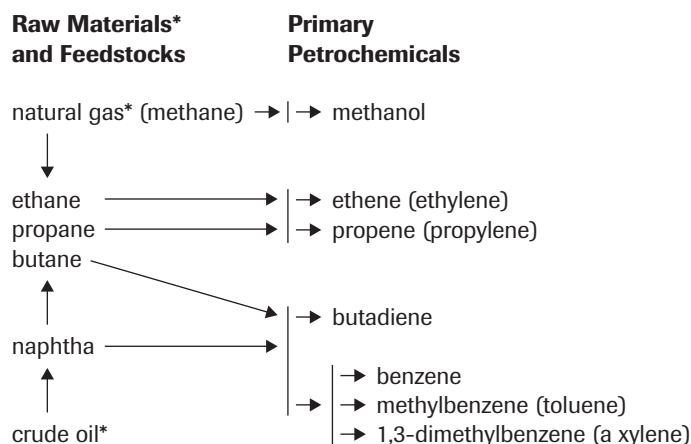


Figure 1
The sources of primary petrochemicals

Some of these primary petrochemicals have immediate uses, but most of them undergo further chemical reactions to produce chemical derivatives. For example, methanol has an immediate use as a fuel and as a windshield washer fluid and gas line antifreeze. Xylene is a chemical name that you find listed as an ingredient of solvents found in a hardware or lumber store. Ethene may be used directly for helping to ripen some varieties of fruits, but most of this primary petrochemical is used in chemical processes to produce polymers, such as polyethene.

Practice

- The following chemicals are feedstocks for a petrochemical industry. Draw full structural formulas for each.

(a) methane	(c) propane
(b) ethane	(d) butane
- Naphtha is a distillation fraction from crude, heavy, or synthetic oil.
 - What range of hydrocarbons is expected to be found in naphtha?
 - In what technological application(s) is naphtha burned?
- The following chemicals are primary petrochemicals in a petrochemical industry. Draw line structural formulas for each:

(a) methanol	(e) benzene
(b) ethene	(f) methylbenzene
(c) propene	(g) 1,3-dimethylbenzene
(d) buta-1,3-diene (CH ₂ CHCHCH ₂ (g))	

DID YOU KNOW?

A Keystone Industry

The chemical industry uses natural raw materials from the earth, water, and air to manufacture everyday products. The chemical industry produces more than 70 000 chemical products, including papers, pesticides, cleaning compounds, cosmetics, toiletries, paints, pharmaceuticals, and safe water.

Primary Petrochemicals

Chemical engineers use the primary petrochemicals in **Figure 1** to produce the intermediates and derivatives in **Figure 2**. Notice the extensive petrochemical industry that can be created from a few basic chemical building blocks—from primary petrochemicals obtained from crude oil and natural gas. Many new compounds can be made by adding other substituents (such as chlorine and oxygen), changing the bonding, or joining small molecules together. You will learn about polymers (listed mostly in the last column of Figure 2) in Section 10.5.

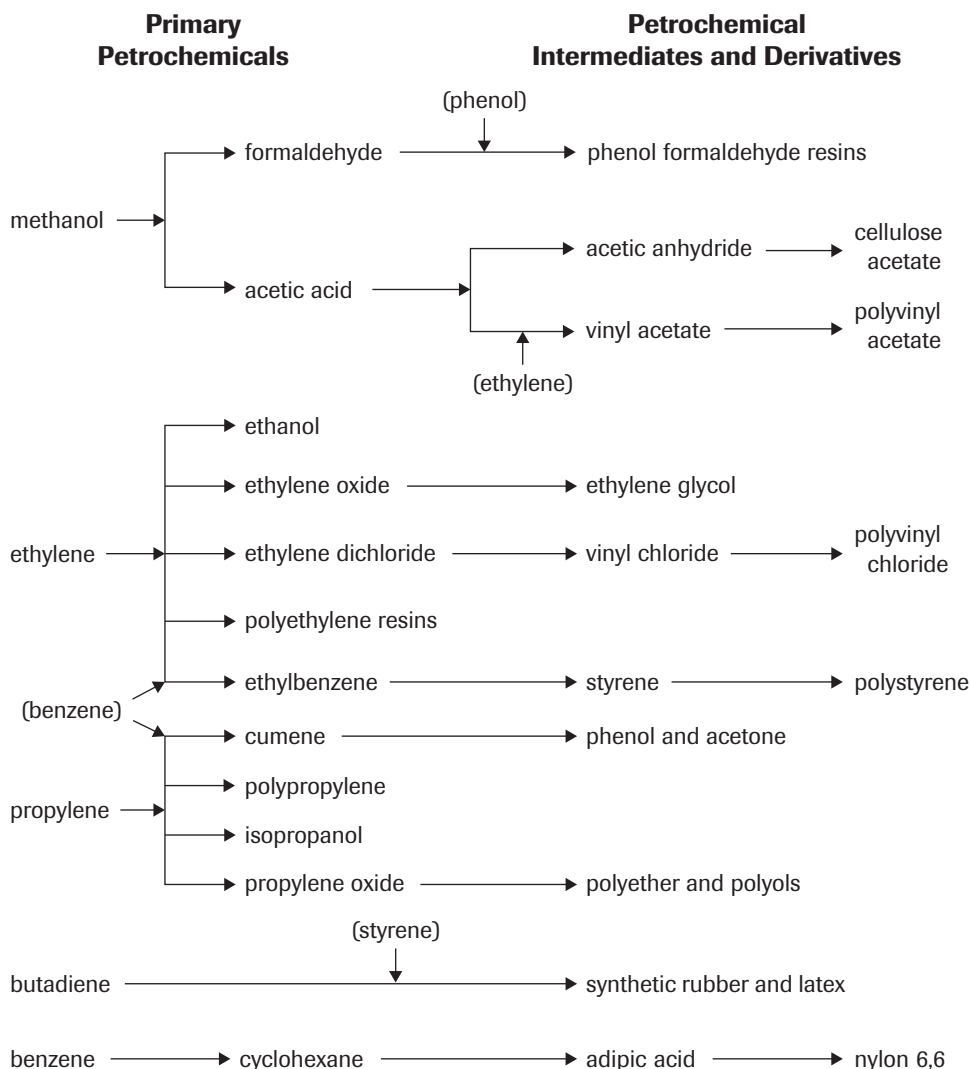


Figure 2

This figure, provided by industry, communicates primary petrochemicals, intermediates, and derivatives. You do not have to memorize this figure, or the common industrial names (except acetic acid, ethylene, and propylene). Most of these common names are translated into systematic IUPAC names in the exercise below.

DID YOU KNOW?

Natural Gas Consumption

Chemical operators account for over half of the natural gas consumption in Alberta. This consumption includes the extraction and refining of fossil fuels, as well as the processing of refined fossil fuels into petrochemicals. As oil sands projects multiply, the consumption of natural gas by industry is likely to increase significantly. Most of the natural gas is used for heat and power. Only about 5% is converted directly into petrochemicals.

Practice

4. Draw structural formulas for the following list of intermediate, reagent, and derivative chemicals from **Figure 2**. Follow the bonding capacity of each element. The molecular formula is not given if you should know it. You might want to reconstruct Figure 2 in your notebook using full structural formulas. The chemicals marked with an asterisk (*) are ones that you will know by the end of this chapter.

- formaldehyde is methanal, $\text{HCHO}(\text{l})$
- phenol is hydroxybenzene, $\text{C}_6\text{H}_5\text{OH}(\text{s})^*$
- acetic acid is ethanoic acid, $\text{CH}_3\text{COOH}(\text{l})^*$
- acetic anhydride is $(\text{CH}_3\text{CO})_2\text{O}(\text{l})$

DID YOU KNOW?

Largest in Canada

After food production, the petrochemical industry is the second largest manufacturing sector in Alberta. Alberta is Canada's largest petrochemical producing area. The availability of energy, feedstock, and a highly educated population give Alberta an advantage over other regions in Canada.

- (e) vinyl acetate is $\text{CH}_2\text{CHOOCCH}_3(\text{l})$
- (f) ethanol
- (g) ethylene oxide is $(\text{CH}_2)_2\text{O}(\text{g})$
- (h) ethylene glycol is 1,2-dihydroxyethane, $\text{CH}_2\text{OHCH}_2\text{OH}(\text{l})^*$
- (i) ethylene dichloride is 1,2-dichloroethane, $\text{CH}_2\text{ClCH}_2\text{Cl}(\text{l})$
- (j) vinyl chloride is chloroethene, $\text{C}_2\text{H}_3\text{Cl}(\text{g})^*$
- (k) ethylbenzene (a full and line structural formula hybrid is okay for (k) and (l))
- (l) styrene is vinylbenzene (phenylethene)*
- (m) cumene is 2-phenylpropane
- (n) acetone is propan-2-one, $\text{CH}_3\text{COCH}_3(\text{l})$
- (o) isopropanol is propan-2-ol, $\text{CH}_3\text{CHOHCH}_3(\text{l})^*$
- (p) propylene oxide is $\text{CH}_3\text{CHOCH}_2(\text{l})$
- (q) cyclohexane
- (r) adipic acid is 1,4-hexanedioic acid, $\text{HOOC}(\text{CH}_2)_4\text{COOH}(\text{s})$

5. All of the chemicals in question 4 are involved in organic chemical reactions. Choose any two of the reactions from **Figure 1** or **Figure 2** and hypothesize a balanced chemical equation for the reactions; e.g., methanol to acetic acid, ethene to ethanol, ethene to styrene, and/or benzene to cyclohexane.
6. Polymers are long-chain molecules that can be made into plastics and synthetic fabrics. List six chemicals from Figure 2 that you think might be classified as polymers (e.g., polyethylene).
7. In 2002, Statistics Canada listed the sales of chemicals in Canada, in billions of dollars (**Table 1**). Create a pie chart to represent the percent sales for each category.
8. Use a reference to find the basic physical properties of two of the chemicals listed in **Figure 1** or **Figure 2**; e.g., styrene, ethylene dichloride, acetic acid, vinyl chloride, and/or formaldehyde.

Table 1 Chemical Sales in Canada

Chemical	Sales (G\$)
basic*	20.2
soaps	1.8
fertilizers	2.5
paints	2.0
toiletries	1.3
pharmaceuticals	7.5
adhesives	0.6
inks	0.4
other	3.9

* basic chemicals and resins (for plastics)

Ethene and Its Derivatives

About 5% of our fossil fuels is used to produce petrochemicals. The economic importance of petrochemicals lies in the fact that basic raw materials are processed and reprocessed many times. For example, **Figure 3** shows the numbers of jobs in various industries that rely on petrochemicals. Ethene (ethylene) is one of the most important petrochemicals. For every 11 jobs involved in the manufacture of ethylene, 116 jobs are created in manufacturing the intermediate, vinyl chloride (chloroethene), 600 jobs in manufacturing the plastic polyvinyl chloride (PVC), and about 6000 jobs in manufacturing other commercial and consumer products, such as pipes and tiles.

As you learned in Chapter 9, ethene is produced in Alberta by cracking ethane that is extracted from natural gas (page 378). At one time, we burned the ethane in the natural gas without removing it. The natural gas that is burned now in consumer, commercial, and industrial settings, however, is likely to have had the ethane (and propane and butane) extracted. These gases are extracted as liquids and are called natural gas liquids (NGLs) or liquefied petroleum gases (LPGs). The remaining natural gas contains mostly methane.

In **Figure 2**, ethene (ethylene) is shown as undergoing reactions to produce ethanol, ethylene oxide, ethylene dichloride, polyethylene resins, and ethylbenzene. You will study some of these reactions, and others, in the pages that follow. **Table 2** gives the locations of some of the chemical plants that produce products related to ethane and ethene.

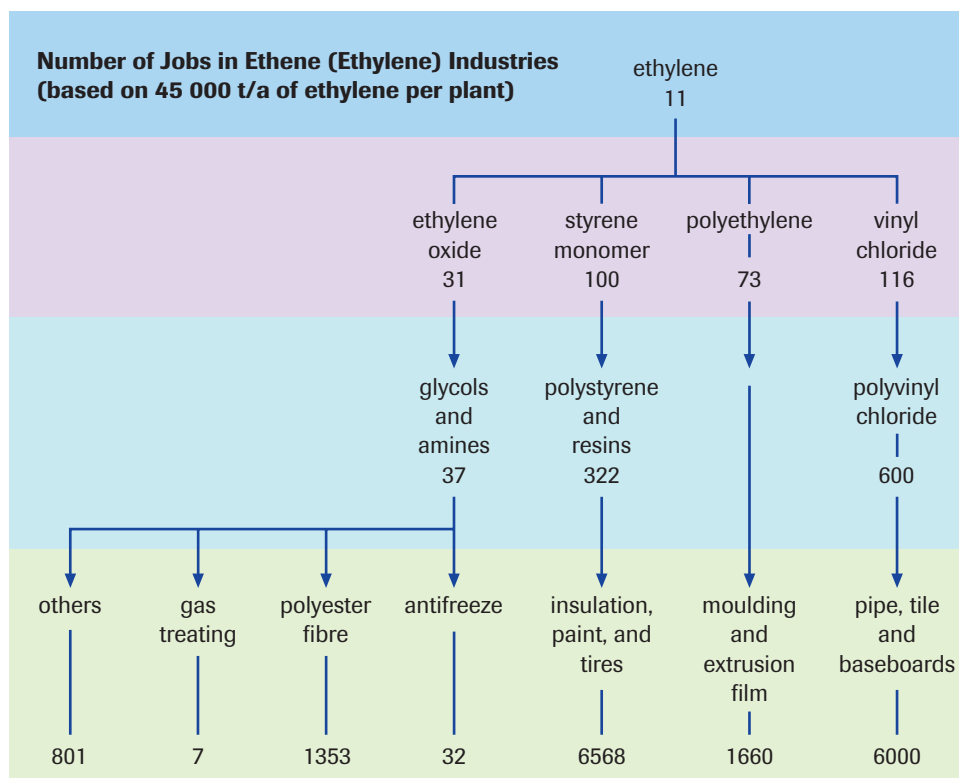


Figure 3

Number of jobs in ethene industries, based on 45 000 t/a of ethene per plant. This is called a multiplier effect. For every 11 jobs in the ethene plant, there are thousands of jobs created elsewhere.

Table 2 Alberta Chemical Operations

Chemical	Owner	Location in Alberta
ethane	Taylor NGL	Joffre (east of Red Deer)
	ATCO/Altagas	Edmonton
	Inter Pipeline (IPL)	Cochrane (west of Calgary)
	ATCO, EnCana, IPL, BP Canada, and Duke	Empress (6 plants straddling gas pipelines, northeast of Medicine Hat)
ethylene (ethene)	Dow Chemical	Fort Saskatchewan
	Nova Chemicals	Joffre (3 plants)
polyethylene	Dow Chemical	Prentiss (northeast of Red Deer), Fort Saskatchewan
	AT Plastics	Edmonton
	Nova Chemicals	Joffre (east of Red Deer)
styrene	Shell Chemicals	Scotford (east of Edmonton)
polystyrene	Dow Chemical	Fort Saskatchewan
vinyl chloride	Dow Chemical	Fort Saskatchewan
polyvinyl chloride	Oxy Vinyls	Fort Saskatchewan
ethylene glycol	Dow Chemical	Fort Saskatchewan, Prentiss
	Shell Chemical	Scotford (east of Edmonton)
ethylene dichloride	Dow Chemical	Fort Saskatchewan

CAREER CONNECTION



Chemical Employees

According to Statistics Canada, the chemical industry in Alberta employs 8000 full-time people directly. Each job in the chemical industry creates 2.5 additional jobs in the local economy; e.g., engineers, scientists, technologists, and trades and support personnel.

Research a chemical career that you might be interested in at the Alberta Learning Information Service (ALIS) Web site. Report on the type and years of education required, and the expected salary.

www.science.nelson.com



Learning Tip

You are not expected to learn the names of the chemical companies nor their locations in Alberta. **Table 2** provides specific evidence that over 50% of Canada's petrochemical capacity is in Alberta. **Table 2** serves to reinforce the point that Alberta is a major petrochemical centre in Canada and could become a major centre in the world. All of the chemicals mentioned in **Table 2** are presented in greater detail later in this chapter.



The End of Oil?

Are we close to running out of easily available petroleum resources, or do we have enough to meet our needs for centuries? Which would be the “better” scenario? Two writers voice their perspectives on the topic. Either way, you may be worried.

www.science.nelson.com



SUMMARY

Petrochemicals

- The petrochemical industry in Alberta and Canada contributes significantly to our economy.
- There are risks and benefits associated with every chemical—natural or manufactured.
- Ethane is obtained from natural gas, is cracked into ethene, and then the ethene is converted by chemical reactions into many other petrochemicals.
- Petrochemicals include plastics, paints, dyes, cosmetics, antifreezes, adhesives, carpets, fertilizers, and pharmaceuticals.
- There are many well-paying careers in the petrochemical industry.

Section 10.1 Questions

1. The chemicals listed in **Table 2**, Alberta Chemical Operations, are also listed in **Table 3**, along with the formulas of the chemicals involved. Many industry publications use common or alternative names for products. From the molecular formula provided, draw the structural formula. You will learn more about naming these compounds later in this chapter.

Table 3 Alberta Chemical Operations—Names and Formulas

Chemical	Alternative name(s)	Molecular formula
(a) ethane*	ethyl hydride	CH ₃ CH ₃
(b) ethylene	ethene*	CH ₂ CH ₂
(c) polyethylene	polyethene*	(CH ₂ CH ₂) _n
(d) styrene	vinylbenzene* or phenylethene*	CH ₂ CHC ₆ H ₅
(e) polystyrene	polyphenylethene* or Styrofoam®	(CH ₂ CHC ₆ H ₅) _n
(f) vinyl chloride	chloroethene*	CH ₂ CHCl
(g) polyvinyl chloride	PVC, polychloroethene*, or polychloroethylene	(CH ₂ CHCl) _n
(h) ethylene glycol	ethane-1,2-diol* or 1,2-dihydroxyethane	CH ₂ OHCH ₂ OH
(i) ethylene dichloride	1,2-dichloroethane*	CH ₂ ClCH ₂ Cl

Note: The *n* is an indication that the structure repeats itself in a chain *n* units long. For this exercise, draw a full structural formula where *n* = 3.

*preferred (IUPAC) name

2. **Figure 3**, on the previous page, illustrates the job multiplier effect that results from creating ethene from ethane.
 - (a) For every 11 jobs in an ethene plant, how many potential jobs are created by using ethene?

- (b) Alberta citizens and petrochemical companies have objected to the export of natural gas from which ethane has not been removed. Why?
- (c) As the cost of natural gas increases, the value of ethane as a heating fuel increases. Consequently, the ethane may be burned as part of natural gas rather than being removed. How does burning ethane in natural gas affect the cost of ethane to petrochemical plants, the cost of products produced from ethene, and the number of jobs in the ethene industry?

3. Create a graph of your choice to communicate the relative quantities of petrochemicals produced in Canada (**Table 4**). Follow the link below to update the data from Statistics Canada.

Table 4 Petrochemical Production in Canada, 2004

Petrochemical	Production (Mt)
benzene	10
ethene (ethylene)	57
buta-1,3-diene	3
butenes (butylenes)	3
propene (propylene)	11
methylbenzene (toluene)	3
dimethylbenzenes (xylenes)	4
phenylethene (styrene)	9

www.science.nelson.com



4. Use the information above and from your own research to continue gathering perspective statements concerning the statement that we should be saving more fossil fuels for petrochemical use in the future.

Organic Halides and Addition and Substitution Reactions

10.2

Chemists divide organic compounds into two main classes: hydrocarbons and hydrocarbon derivatives. As you learned in Chapter 9, hydrocarbons contain only carbon and hydrogen atoms. **Hydrocarbon derivatives** are molecular compounds of carbon, usually hydrogen, and at least one other element. (See the diagram of organic compound families in Chapter 9, **Figure 3** on page 382.) For ease of classification, such compounds are named as if they had been produced by the modification of a hydrocarbon molecule. The hydrocarbon-derivative families studied in this chapter are organic halides, alcohols, carboxylic acids, esters, and polymers.

Organic Halides

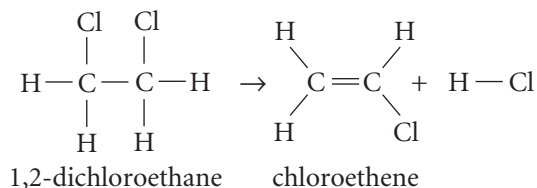
Organic halides are organic compounds in which one or more hydrogen atoms have been replaced by halogen (group 17) atoms. The functional group for organic halides is the halogen atom. A **functional group** is a characteristic arrangement of atoms within a molecule that determines the most important chemical and physical properties of a class of compounds. Organic halides include many common products, such as freons (chlorofluorocarbons) used in refrigerators and air conditioners, and Teflon® (polytetrafluoroethylene), used in cookware and labware.

Many organic halides are toxic and many are also carcinogenic, so their benefits must be balanced against potential hazards. Two such compounds are the insecticide DDT (dichlorodiphenyltrichloroethane) and PCBs (polychlorinated biphenyls), used in electrical transformers. PCBs are no longer being produced but are still in circulation. DDT is banned in many countries but is still being produced in some countries, such as China.

According to solution theory, organic halides are solvents that can dissolve nonpolar hydrocarbons and/or polar hydrocarbons. Organic halide molecules may be polar or nonpolar, or they may have a relatively nonpolar hydrocarbon end and a polar halide end.

IUPAC nomenclature for halides follows the same format as that for branched-chain hydrocarbons. The branch is named by shortening the halogen name to *fluoro-*, *chloro-*, *bromo-*, or *iodo-* (**Table 1**). For example, $\text{CHCl}_3(\text{l})$ is trichloromethane (chloroform), an important solvent, and $\text{C}_6\text{H}_5\text{Br}(\text{l})$ is bromobenzene, an additive to motor oils.

When translating IUPAC names for organic halides into full structural formulas, draw the parent chain and add branches at locations specified in the name. For example, 1,2-dichloroethane indicates that this compound has a two-carbon (eth-), single bonded parent chain (-ane), with one chlorine atom on each carbon (1,2-dichloro-). 1,2-dichloroethane is a liquid organic halide produced by Dow Chemical in Fort Saskatchewan. 1,2-dichloroethane is used to produce chloroethene, which in turn is used to produce polyvinyl chloride (PVC).



DID YOU KNOW?

Alkyl Halides

Organic halides are also known as alkyl halides and halogenated hydrocarbons. The term alkyl halides does not include aryl (aromatic) halides, such as bromobenzene. The more general term, organic halides, is used in this chapter.

Learning Tip

Each of the classes of hydrocarbon derivatives studied in this chapter is associated with a type of chemical reaction. For example,

- organic halides undergo addition and substitution reactions
- alcohols undergo elimination reactions
- carboxylic acids and esters are involved in esterification reactions

Try to use this organization to help you learn these concepts.

Table 1 Halide Functional Groups

Chemical symbol	Prefix
— F	fluoro
— Cl	chloro
— Br	bromo
— I	iodo

DID YOU KNOW?

Ozone Depletion

In 1982, a 30% decrease in the ozone layer—referred to as an ozone “hole”—was noticed for the first time by a team of British researchers working in Halley Bay, Antarctica. The British team’s results surprised American researchers who had been measuring ozone levels by weather satellite since 1978. American satellite data are transmitted to Earth and are automatically processed by computers before scientists examine them. The Americans had not noticed the decrease in ozone levels because their computers were programmed to reject low measurements as invalid anomalies. The British scientists had also been monitoring atmospheric concentrations of chlorofluorocarbons (CFCs) and they raised the possibility that the decreasing ozone levels and the increasing CFC concentrations in the atmosphere were related. Since 1982, American computers processing total ozone mapping spectrophotometer (TOMS) data no longer reject low values, and alarming depletions of 60% to 70% in ozone levels over Antarctica have been detected.

The ozone layer has now stopped shrinking because of the measures we have taken to reduce our use of CFCs, but it will take many years to regenerate.

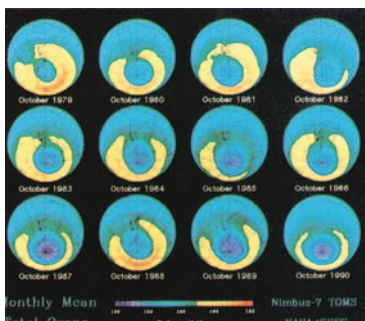


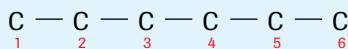
Figure 1

These NASA satellite photos show ozone levels over Antarctica as measured by the ozone-detecting device called TOMS. Look for recent photos on the Internet.

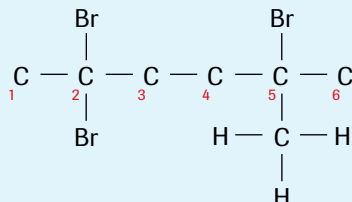
SAMPLE problem 10.1

Draw a structural formula for 2,2,5-tribromo-5-methylhexane.

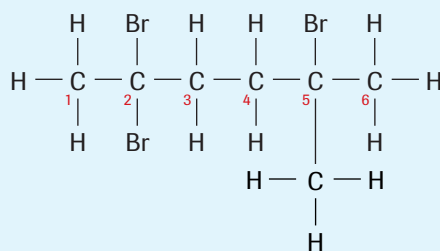
First, draw and number the parent alkane chain, the hexane:



Next, add two Br atoms to carbon 2, one Br atom to carbon 5, and a methyl group to carbon 5.

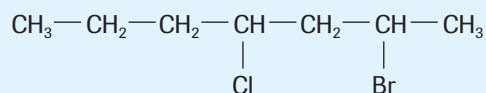


Finally, complete the bonding by adding H atoms to the C atoms.



COMMUNICATION example 1

Write the IUPAC name for the organic halide



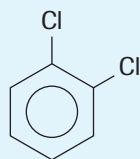
Solution

This compound is 2-bromo-4-chloroheptane.

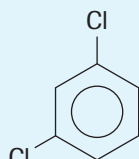
COMMUNICATION example 2

Draw line structural formulas for the three isomers of dichlorobenzene. Name the isomers.

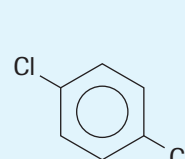
Solution



1,2-dichlorobenzene



1,3-dichlorobenzene



1,4-dichlorobenzene

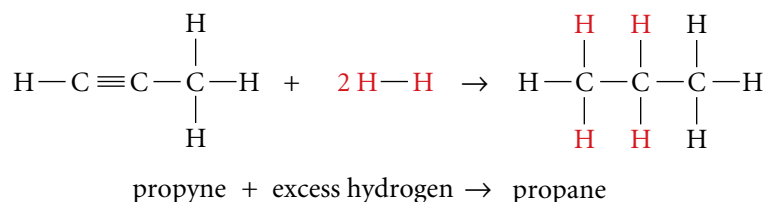
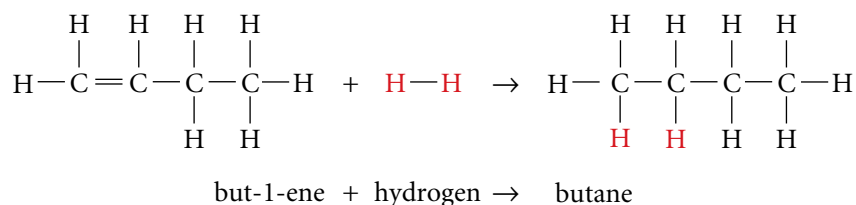
Practice

1. Draw a structural formula for each of the following organic halides:
 - (a) 1,2-dichloroethane (solvent for rubber)
 - (b) tetrafluoroethene (used in the manufacture of Teflon)
 - (c) 1,2-dichloro-1,1,2,2-tetrafluoroethane (refrigerant)
 - (d) 1,4-dichlorobenzene (moth repellent)

2. Write IUPAC names for each of the formulas given.
- | | |
|--|---|
| (a) CHI_3 (antiseptic) | (c) CH_2Cl_2 (paint remover) |
| (b) $\text{CH}_2 = \underset{\begin{array}{c} \\ \text{CH}_3 \end{array}}{\text{C}} - \text{CH}_2\text{Cl}$
(insecticide) | (d) $\text{CH}_2\text{Br} - \text{CHBr} - \text{CH}_2\text{Br}$ (soil fumigant) |
| | (e) $\text{C}_6\text{H}_5\text{Cl(l)}$ (insoluble in water) |
| | (f) $\text{C}_6\text{H}_5 - \text{CH} = \text{CH}_2$ (monomer) |
3. Use your knowledge of intermolecular forces to predict, with reasoning,
- the relative boiling points of ethene and chloroethene
 - the relative solubility of ethene and chloroethene in water
4. Chlorofluorocarbons (CFCs) are organic halides that have chlorine or fluorine atoms present. Until the 1990s, chlorofluorocarbons (CFCs) were used as refrigerants, foaming agents, and aerosol sprays. Besides depleting the ozone layer, CFCs are excellent absorbers of thermal infrared (IR) radiation; in other words, they are greenhouse gases (GHGs). Provide structural formulas for the following CFCs.
- | | |
|---|--|
| (a) $\text{CCl}_4(\text{l})$ | (c) $\text{CFCl}_3(\text{l})$ |
| (b) $\text{CH}_3\text{CCl}_3(\text{l})$ | (d) $\text{CF}_2\text{ClCFCl}_2(\text{l})$ |
5. Hydrochlorofluorocarbons (HCFCs) have hydrogen and fluorine atoms present, in addition to chlorine atoms. HCFCs were used as a temporary replacement for CFCs in the 1990s. HFCs (hydrofluorocarbons) are replacing both CFCs and HCFCs. Draw structural formulas for these HCFCs.
- | | |
|--|---|
| (a) $\text{CHF}_2\text{Cl(l)}$ | (c) $\text{CHF}_3(\text{l})$ |
| (b) $\text{CH}_3\text{CFCl}_2(\text{l})$ | (d) $\text{CF}_3\text{CH}_2\text{F(l)}$ |

Addition Reactions

Unsaturated hydrocarbons react with small diatomic molecules, such as bromine and hydrogen. This type of reaction is an **addition reaction**. Addition reactions usually occur in the presence of a catalyst. Recall from Section 9.3 that addition of a sufficient quantity of hydrogen, called *hydrogenation*, converts unsaturated hydrocarbons to saturated ones. This reaction requires a catalyst.



It seems logical that the addition of halogen or hydrogen halide molecules to the carbons of a double or triple bond would be an effective method of preparing halides. Experiment supports this expectation. Chemists explain the rapid rate of these reactions by the concept that a compound with a carbon-carbon double or triple bond can become more stable by achieving an octet of electrons in a tetrahedral structure of single bonds. For example, ethene reacts with chlorine, producing 1,2-dichloroethane. 1,2-dichloroethane is used as a solvent for fats, oils, and particularly for rubber. It is also

+ EXTENSION

CFCs, HFCs, and the Ozone Layer

As a result of Nobel Prize research on stratospheric ozone depletion by a group of chemists, CFCs were phased out of production, worldwide. Find out what the CFCs were being used for, and what follow-up agreements are in the works.

www.science.nelson.com 

Learning Tip

Recall that, for IUPAC nomenclature of substitution groups on a hydrocarbon chain, list the substituents in alphabetical order; e.g., 2-bromo-4-chloroheptane (as in Communication Example 1).

+ EXTENSION

Reactions of Hydrocarbons with Bromine

Watch a video in which bromine, dissolved in an inert solvent, is added to pentane and pent-1-ene in two dishes. Do these two hydrocarbons react in the same way?

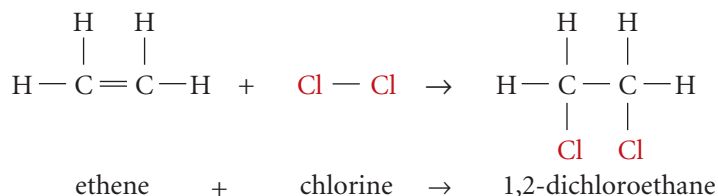
www.science.nelson.com 

DID YOU KNOW?

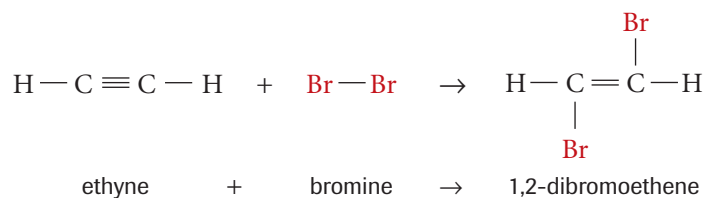
Ethylene Dichloride

Why is ethylene dichloride the classical name for 1,2-dichloroethane? You can, perhaps, see the reason in the reaction equation for the production of 1,2-dichloroethane. Ethylene dichloride is produced from ethylene—it is a dichloride from (not of) ethylene. The name, ethylene dichloride, is misleading, which is why its IUPAC name is 1,2-dichloroethane.

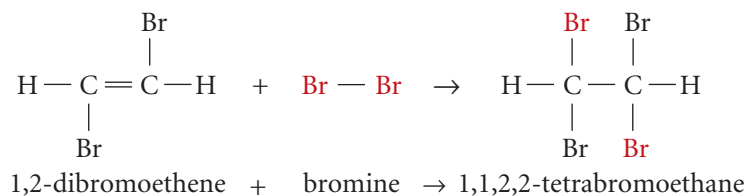
used as a fumigant. More importantly for the Alberta chemical industry, 1,2-dichloroethane is used in huge quantities to produce chloroethene, a monomer used to produce the polymer PVC. (See the last equation on page 417 for the next step.)



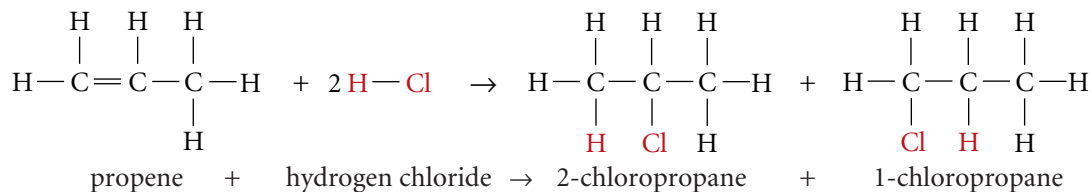
The addition of halogens to alkynes results in alkenes or alkanes. For example, the initial reaction of ethyne with bromine produces 1,2-dibromoethene.



Since addition reactions involving multiple bonds are very rapid, the alkene product, 1,2-dibromoethene, can easily undergo a second addition step to produce 1,1,2,2-tetrabromoethane. Excess bromine promotes this second step.



The addition of hydrogen halides (HF, HCl, HBr, or HI) to unsaturated compounds can produce structural isomers, since the hydrogen halide molecules can add in different orientations. If you were to create the hypothesis that the addition might occur equally with orientations of H—Cl and Cl—H, then you would predict the following reaction.



A laboratory test of this prediction would provide evidence to falsify this prediction. Only a tiny proportion of 1-chloropropane is produced compared to the 2-chloropropane.

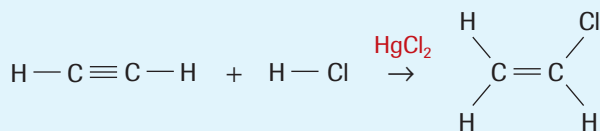
Learning Tip

The general formula for an organic halide is R—X, where X is a halogen atom, the functional group.

► COMMUNICATION example 3

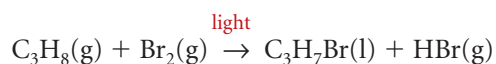
Chloroethene (vinyl chloride) is made industrially in Alberta from a two-step reaction starting with ethene. An alternative method is to react ethyne (acetylene) with limited hydrogen chloride in the presence of a HgCl_2 catalyst. Write a structural formula equation to communicate this alternative reaction.

Solution

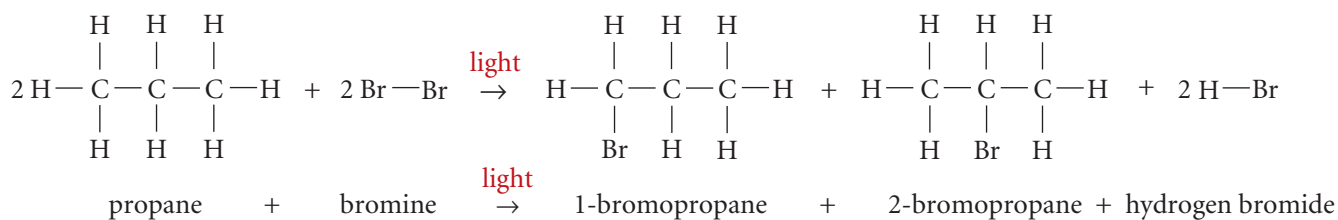


Substitution Reactions

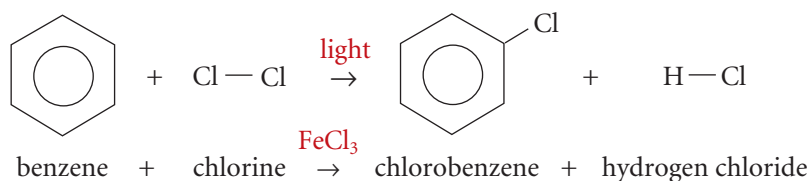
According to laboratory work, another reaction that produces organic halides is a **substitution reaction**. The theoretical description of substitution reactions is that they involve breaking a carbon–hydrogen bond in an alkane or aromatic ring and replacing the hydrogen atom with another atom or group of atoms. These reactions often occur slowly at room temperature, indicating that very few of the molecular collisions at room temperature are energetic enough to break carbon–hydrogen bonds. Electromagnetic radiation (light) may be necessary for the substitution reaction to proceed at a noticeable rate. Consider the following example, the reaction of propane with bromine vapour:



In this reaction, a hydrogen atom on the propane molecule is substituted with a bromine atom. Propane contains hydrogen atoms bonded in two different locations—those on an end-carbon atom and those on the middle-carbon atom—so two different products are formed, in unequal proportions.



Laboratory evidence indicates that benzene rings are stable structures and, like alkanes, react slowly with halogens, even in the presence of light. For example, the reaction of benzene with chlorine is shown to produce chlorobenzene and hydrogen chloride. As with alkanes, further substitution can occur in benzene rings until all hydrogen atoms are replaced by halogen atoms in the presence of excess halogens.



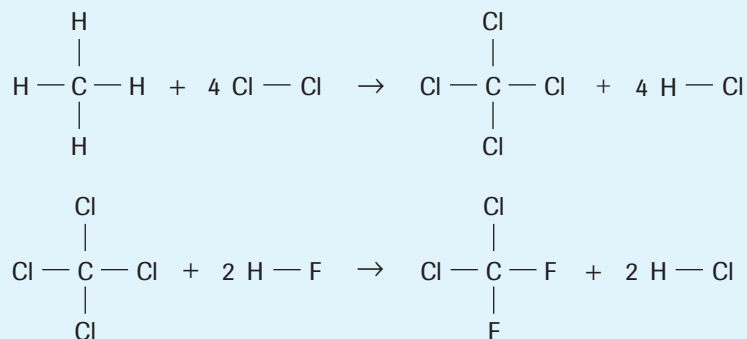
The reaction of benzene and chlorine is so slow that it requires light and a catalyst such as FeCl_3 . This reaction produces HCl , as evidenced by wet blue litmus turning red

in or above the reaction mixture. This evidence dictates the reaction equation given above, and leads to the interpretation that this reaction is a substitution reaction.

► COMMUNICATION example 4

CFCs were used until the 1990s as refrigerants (for refrigerators and air conditioners) and to create bubbles in plastic foams (used as foam insulation, foam trays, and cartons). CFC-12, which is pure CF_2Cl_2 , was made by reacting carbon tetrachloride with gaseous hydrogen fluoride. The carbon tetrachloride was produced by reacting methane with chlorine. Draw structural formula equations to represent these two reactions.

Solution



INVESTIGATION 10.1 Introduction

Report Checklist

Substitution and Addition Reactions

Substitution and addition reactions are two common classes of organic reactions. Substitution reactions are common to saturated hydrocarbons. Addition reactions are common to unsaturated (alkene and alkyne) hydrocarbons. In general, substitution reactions are slower and addition reactions are faster.

Purpose

The purpose of this investigation is to test the generalization that addition reactions are faster than substitution reactions.

- | | | |
|---|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 2, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Problem

Which compound reacts faster with aqueous bromine: cyclohexane or cyclohexene?

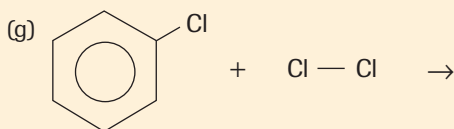
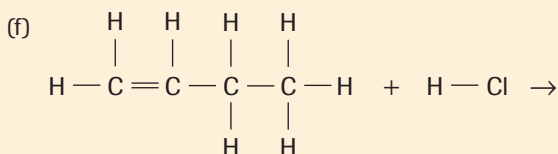
Design

Aqueous bromine is added to samples of cyclohexane and cyclohexene in both the presence and absence of light.

To perform this investigation, turn to page 461.

► Practice

- The halide derivatives of hydrocarbons form a wide variety of useful products. Draw structural formulas for the following examples:
 - 1,2-dimethylbenzene (solvent)
 - 1,1,1-trichloroethane (a banned CFC)
- Classify each of the following reactions as substitution or addition reactions. Predict all possible products for only the initial reaction. Complete the word equation and the structural formula equation in each case. Assume that light is present in all cases and catalysts are used as required.
 - trichloromethane + chlorine \rightarrow
 - propene + bromine \rightarrow
 - ethylene + hydrogen iodide \rightarrow
 - ethane + chlorine \rightarrow
 - $\text{Cl} - \text{C} \equiv \text{C} - \text{Cl} + \text{F} - \text{F}$ (excess) \rightarrow

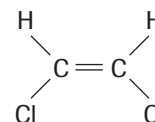


8. Classify and write balanced full structural formula equations for each of the following organic reactions. Assume that light is present in all cases and catalysts are used as required.
- (a) propane + chlorine \rightarrow 1-chloropropane + 2-chloropropane + hydrogen chloride
- (b) propene + bromine \rightarrow 1,2-dibromopropane
- (c) benzene + iodine \rightarrow iodobenzene + hydrogen iodide
- (d) 2-butene + hydrogen chloride \rightarrow 2-chlorobutane
- (e) bromobenzene + chlorine \rightarrow
9. The synthesis of an organic compound typically involves a series of reactions, for example, some substitutions and some additions.
- (a) Design an experiment beginning with a hydrocarbon to prepare 1,1,2-trichloroethane.
- (b) Why do chemists and chemical engineers invent chemical processes?
- (c) What other perspectives, besides scientific and technological, can be taken into account when inventing a new technology?
10. Test the explanatory power of intermolecular force theory by explaining why the two organic halide isomers, 1-bromopropane and 2-bromopropane, have different boiling points: 71 °C and 59 °C, respectively.
11. Petrochemicals are chemicals produced from petroleum (assume hydrocarbons) and from other petrochemicals, such as organic halides. Use your list of perspectives to classify the following statements about petrochemicals. (See STS Problem Solving in Appendix D.)
- (a) Many human lives have been saved by the use of organic halide pesticides.
- (b) Organic halides are used successfully as refrigerants and foaming agents.
- (c) Research is on-going to find a replacement for CFCs and HCFCs.
- (d) Farmers have saved considerable money by using organic halide pesticides.
- (e) Getting elected may depend on promising that controls will be placed on the use of organic halides.
- (f) There is a need for laws to control the release of organic halides.
- (g) There are claims that workers in the past were not informed about the toxic or carcinogenic character of organic halides with which they worked.
- (h) Communities have acted together to recycle petrochemical products.

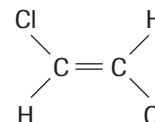
DID YOU KNOW?

Cis and Trans Isomerism

There is always a new concept to learn that extends what you have already learned. This applies to research chemists as much as it applies to you as a student. One example for you at this point is the introduction of evidence for the existence of *cis* and *trans* isomers, in addition to the structural isomers that you know about. Examples of *cis* and *trans* isomers are 1,2-dichloroethene, shown below as structural formulas.



cis-1,2-dichloroethene



trans-1,2-dichloroethene

Cis isomers involve special bonding on the same side of the double bond. *Trans* isomers have the special bonding across the double bond. See more on *cis* and *trans* isomerism in relation to transfats in Sections 10.4 and 10.5.



LAB EXERCISE 10.A

Synthesis of an Organic Halide

1,2-dichloroethane is also commonly called ethylene dichloride. Chemical engineers have invented ways to convert ethane to ethene to 1,2-dichloroethane to chloroethene to the plastic PVC (polyvinylchloride). Finding economically and environmentally sound ways to manufacture chemicals is the task of chemists and chemical engineers. Your task is to propose a reaction series for at least two different ways to manufacture 1,2-dichloroethane (ethylene dichloride) from hydrocarbons.

Report Checklist

- | | | |
|---|---------------------------------|----------------------------------|
| <input checked="" type="radio"/> Purpose | <input type="radio"/> Design | <input type="radio"/> Analysis |
| <input checked="" type="radio"/> Problem | <input type="radio"/> Materials | <input type="radio"/> Evaluation |
| <input checked="" type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input type="radio"/> Evidence | |

SUMMARY

Organic Halides

Properties

Organic halides

- may be polar or nonpolar molecules or may have a relatively nonpolar (hydrocarbon) end and a polar (halide) end
- have higher boiling points than similar hydrocarbons
- have very low solubility in water but higher solubility (especially for small molecules) than similar hydrocarbons
- are typically good solvents for organic materials such as fats, oils, waxes, gums, resins, and/or rubber

Preparation

Addition reactions with halogens or hydrogen halides

- alkenes and alkynes \rightarrow organic halides
e.g., $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$

Substitution reactions with halogens

- alkanes and aromatics $\xrightarrow{\text{light}}$ organic halides
e.g., $\text{CH}_3-\text{CH}_2\text{Cl} + \text{Cl}_2 \xrightarrow{\text{light}} \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} + \text{H}-\text{Cl}$

Section 10.2 Questions

1. Addition and substitution reactions typically require catalysts to produce a reasonable rate of reaction in a chemical plant. Substitution reactions occur (slowly) in the laboratory due to the presence of light. Design an experiment to test the last statement.
2. Organic halides include alkyl halides and halogenated hydrocarbons. Draw line structural formulas for the following organic halides.
 - (a) 1,4-dichlorobenzene (moth repellent)
 - (b) 1-bromo-4-methylbenzene (chemical reagent)
 - (c) 1,2-dibromoethane (suspected carcinogen)
 - (d) chloroethene (to produce PVC)
3. The relative boiling points of three halogen substituted ethane compounds are:
chloroethane: 12.3 °C
bromoethane: 38.2 °C
iodoethane: 72.3 °C
 - (a) Explain the relative boiling points of these organic halides.
 - (b) Predict whether these compounds are more soluble in water or in ethanol.
4. Classify and write full structural formula equations for the following organic reactions:
 - (a) propane + chlorine \rightarrow
1-chloropropane + 2-chloropropane + hydrogen chloride
 - (b) propene + bromine \rightarrow 1,2-dibromopropane
 - (c) benzene + iodine \rightarrow iodobenzene + hydrogen iodide

Extension

5. Shortly after the connection was made between the "hole" in the ozone layer and the release of chlorofluorocarbons,

many manufacturers stopped using CFCs as propellants in aerosol cans.

- (a) Research what alternatives were developed, and the effectiveness of each in the marketplace. Are the alternatives still in use? Have any of them been found to cause problems?
- (b) Design a product (one that must be sprayed under pressure) and its packaging. Plan a marketing strategy that highlights the way in which your product is sprayed from the container.

www.science.nelson.com



6. Use the information in this section and from your own research to continue gathering perspective statements concerning the statement that we should be saving more fossil fuels for petrochemical use in the future.
7. Long-term replacements for CFCs and HCFCs include hydrofluorocarbons (HFCs), which have no chlorine atoms. HFCs are now being used in refrigerators, automobile air conditioners, aerosol cans, and as foaming agents. Draw the structural formula for $\text{CH}_2\text{FCF}_3(\text{l})$ (also called HFC-134a).
8. Why are some organic halides toxic whereas others are not? And why are some organisms affected more than others? Find out, using the following key words: bioaccumulation, fat soluble, food chain. Report on your findings in a short article for a popular science magazine or Web site.

www.science.nelson.com



Alcohols

Alcohols have many consumer, commercial, and industrial applications. They have very different properties compared to their hydrocarbon cousins with the same number of carbon atoms, such as relatively high solubility in water and clean burning properties. Chemists first classified alcohols by their empirical properties and their empirically determined formulas. Laboratory work showed that **alcohols** all contain one or more **hydroxyl groups**, $-\text{OH}$. The $-\text{OH}$ group is the functional group for alcohols.

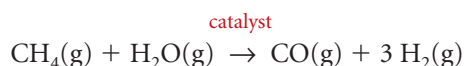
Alcohols have characteristic empirical properties that can be explained theoretically by the presence of a hydroxyl ($-\text{OH}$) functional group attached to a hydrocarbon chain. Alcohols boil at much higher temperatures than do hydrocarbons of comparable molar mass. Chemists explain that alcohol molecules, because of the $-\text{OH}$ functional group, form hydrogen bonds (see Section 3.4, page 111) and, thus, liquid alcohols are less volatile than similar hydrocarbons. Shorter-chain alcohols are very soluble in water because of their size, polarity, and hydrogen bonding.

Because the hydrocarbon portion of the molecule of long-chain alcohols is non-polar, larger alcohols are less soluble in water and are good solvents for non-polar molecular compounds as well. (See the Solubility in Water Generalizations, Chapter 5, page 222.) Alcohols are frequently used as solvents in organic reactions because they are effective for both polar and non-polar compounds. Alcohols are also used as starting materials in the synthesis of other organic compounds.

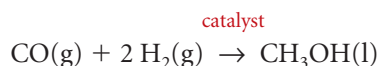
Methanol and Ethanol

Two of the most common alcohols are methanol, $\text{CH}_3\text{OH}(\text{l})$, and ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$. Increasingly, one of the most important technological applications of alcohols is as a gasoline additive. Alcohol is added to gasoline in some jurisdictions, such as Manitoba, to increase the octane number, reduce harmful emissions (such as carbon monoxide), and conserve crude oil (see Chapter 9, page 399). The alcohols typically added are ethanol and methanol. These alcohols (as pure substances) have octane numbers of 113 and 108, respectively. They are often called oxygenators because they provide oxygen to the combustion reaction. The result is that less carbon monoxide is released in the exhaust. The combustion reaction of gasoline is, therefore, more complete.

An old method for manufacturing methanol involved decomposing and distilling the cellulose in wood, which is how it got its alternative name: wood alcohol. The modern method of preparing methanol involves two major processes. First, methane reacts catalytically with water (steam) to produce carbon monoxide and hydrogen:



Next, carbon monoxide and hydrogen react at high temperature and pressure in the presence of a catalyst:



A common consumer use of alcohols (including methanol) is as antifreezes (**Figure 2** on the next page).

Methanol is toxic to humans. Drinking even small amounts of it or inhaling the vapour for prolonged periods can lead to blindness or death. All alcohols are not the same. Methanol is even added to non-beverage ethanol to denature it. Denatured ethanol is toxic.

DID YOU KNOW?

Ethanol in Alberta

At the time of writing, there are only three chemical plants in Alberta that produce ethanol from grain. The API Grain Processing Plant in Red Deer, Alberta produces industrial alcohol and Highwood Distillers in High River, Alberta produces beverage alcohol. There is also a large plant near the Alberta-Saskatchewan border at Lloydminster. In future, there will likely be more and more ethanol plants in western Canada to supply this gasoline additive. Grain-based ethanol plants are adding another significant market for grain farmers (**Figure 1**).



Figure 1

Grain is a source of ethanol, used as a gasoline additive to reduce GHG emissions.

Learning Tip

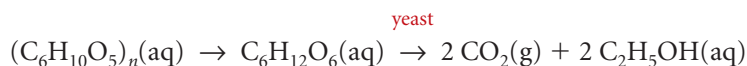
The general formula for an alcohol is R-OH . The alcohol functional group is the $-\text{OH}$ (hydroxyl) group.

Figure 2

Alcohols available to consumers as antifreezes include, from left to right, gas line antifreeze (methanol), windshield de-icer (methanol), windshield washer antifreeze (methanol), and radiator and recreation vehicle antifreezes (ethane-1,2-diol and propane-1,2-diol).



Ethanol can be prepared by the fermentation of sugars from starch, such as corn and grains; hence its alternative name—grain alcohol. In the fermentation process, enzymes produced by yeast cells act as catalysts in the breakdown of sugar (glucose) molecules:



In terms of industrial applications, ethanol is an important synthetic organic chemical. It is a solvent in lacquers, varnishes, perfumes, and flavourings, and is a raw material in the synthesis of other organic compounds.

Some oil companies in Alberta put ethanol in gasoline, for example, as a winter additive, for increased vaporization, and as a gas line antifreeze. Currently there is no legislation requiring ethanol in gasoline in Alberta.

There is an increasing number of ethanol plants being built in western Canada to produce ethanol as a gasoline additive. Provincial legislation to include 10% ethanol in gasoline, and tax incentives, will accelerate the expansion of the ethanol industry.

DID YOU KNOW?

Fill Up with Methanol

Alcohols have many uses, one of the more recent being a fuel for motor vehicles. The problem with methanol as a pure fuel for cars is that it is less volatile than the hydrocarbons that make up gasoline, and the low volatility makes it difficult to ignite. In our cold Canadian winters, there is little methanol vapour in the engine and an electrical spark is insufficient to start the car. Canadian scientists are investigating a variety of dual ignition systems, one of which is a plasma jet igniter that is 100 times more energetic than conventional ignition systems.

Practice

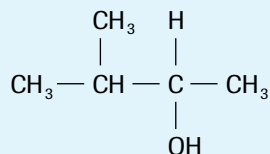
1. Chemical engineers have introduced alcohol into gasoline to play multiple roles. Describe at least three of these roles.
2. Write pro and con statements from social, political, and economic perspectives relative to the resolution that legislation should require the addition of alcohol to gasoline (gasohol) in Alberta.
3. Write the chemical equations for
 - (a) photosynthesis to produce glucose
 - (b) the conversion of glucose to starch
 - (c) the fermentation of starch to glucose
 - (d) the fermentation of glucose to ethanol
4. Volatile compounds evaporate or vaporize relatively easily. Volatile organic compounds (VOCs) can cause atmospheric smog. For molecules of the same molar mass, list hydrocarbons, organic halides, and alcohols, in general, in order of increasing volatility.

Naming Alcohols

Simple alcohols are named from the alkane of the parent chain. The *-e* is dropped from the end of the alkane name and is replaced with *-ol*. For example, the simplest alcohol, with one carbon atom, has the IUPAC name “methanol.” The number of carbon atoms in the alcohol is communicated by the standard prefixes: *meth-*, *eth-*, *prop-*, etc. Single bonds between the carbon atoms are communicated by the “an” in the middle of the name, for example, ethanol rather than ethenol.

▶ SAMPLE problem 10.2

Write the IUPAC name for the following alcohol.



- Identify the longest continuous carbon chain on which the alcohol functional group—the hydroxyl ($-\text{OH}$) group—is located; e.g., four carbon atoms.
- Write the prefix for the name to indicate the number of carbons in the longest chain; e.g., “but” for a four-carbon chain.
- Add an “an” to the prefix to indicate that all of the carbon–carbon bonds are single bonds; e.g., “butan-”.
- Number the carbon chain from the end nearest the hydroxyl group; e.g., 1–4 from the right (in this case).
- If necessary, add the locant (number) for the hydroxyl group to the name; e.g., “butan-2”.
- Complete the parent name with “-ol” to indicate that the compound is an alcohol; e.g., “butan-2-ol”.
- Indicate the presence of any substituent as a prefix; e.g., “methylbutan-2-ol”.
- If necessary, add the locant (number) to indicate the location of the substituent; e.g., “3-methylbutan-2-ol”.
- Double-check to make sure that the numbers are necessary to differentiate this compound from a similar compound; e.g., 2-methyl-1-butanol.

The name of this alcohol is 3-methylbutan-2-ol.

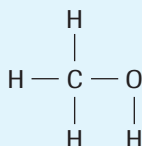
▶ COMMUNICATION example 1

Due to their physical and chemical properties, alcohols have many technological applications. Provide the molecular and structural formulas for alcohols (a) and (b), and the molecular and condensed formulas for alcohols (c) and (d).

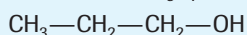
- (a) methanol (race car fuel) (c) propan-1-ol (solvent for organic compounds)
 (b) ethanol (gasoline additive) (d) butan-1-ol (used for manufacturing rayon)

Solution

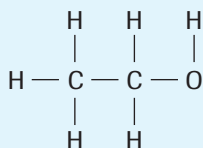
(a) methanol: $\text{CH}_3\text{OH}(\text{l})$



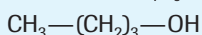
(c) propan-1-ol: $\text{C}_3\text{H}_7\text{OH}(\text{l})$



(b) ethanol: $\text{C}_2\text{H}_5\text{OH}(\text{l})$



(d) butan-1-ol: $\text{C}_4\text{H}_9\text{OH}(\text{l})$



Learning Tip

The nomenclature of alcohols is very similar to that of alkanes and alkenes. Look for the longest continuous chain, including the functional group in the case of alkenes and alcohols. Identify the location of any functional group and any substituent(s). Communicate all of this information in the format specified by IUPAC. For example,

- 2-methylbutane
- 2-methylbut-2-ene
- 2-methylbutan-2-ol

Try drawing the structural formula for each of the above compounds.

Learning Tip

The carbon atoms can be numbered from either end of the chain, whichever gives a lower number for the location of the hydroxyl group.

DID YOU KNOW?

Alcohol Poisoning

Like other short-chain alcohols, ethanol is poisonous, and a concentration of only 0.40% in the blood can cause death. According to Canadian law, individuals whose blood alcohol levels are greater than 0.08% are considered impaired. Driving while impaired is a serious threat to the driver, the passengers, and anyone else on or near the road.

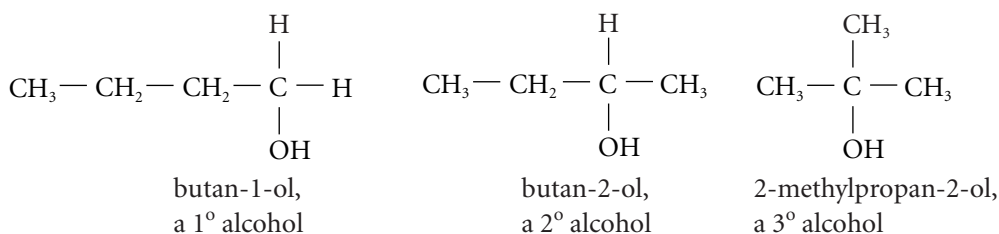
Primary, Secondary, and Tertiary Alcohols

By convention, when we write the molecular formula or the condensed structural formula (rather than the structural formula) for alcohols, we write the -OH group at the end, for example, $\text{C}_2\text{H}_5\text{OH}$ or $\text{CH}_3\text{-CH}_2\text{-OH}$ for ethanol.

The position of the -OH group can vary, however, and make alcohols quite different, in terms of their chemical and physical properties. For example, the 1 in propan-1-ol indicates that the hydroxyl group is bonded to a carbon atom at the end of the carbon chain, that is, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (1) rather than $\text{CH}_3\text{CHOHCH}_3$ (1).

Structural models of alcohols with four or more carbon atoms suggest that three structural types of alcohols exist.

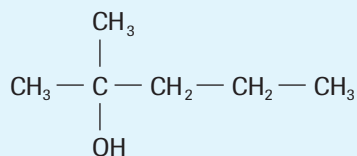
- *primary* (1°) *alcohols*, in which the carbon atom carrying the -OH group is bonded to one other carbon atom, as in $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (1), butan-1-ol
- *secondary* (2°) *alcohols*, in which the carbon atom carrying the -OH group is bonded to two other carbon atoms, as in $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$ (1), butan-2-ol
- *tertiary* (3°) *alcohols*, in which the carbon atom carrying the -OH group is bonded to three other carbon atoms, as in $(\text{CH}_3)_3\text{COH}$ (1), 2-methylpropan-2-ol



When naming alcohols with more than two carbon atoms, we indicate the position of the hydroxyl group. For example, there are two isomers of propanol, $\text{C}_3\text{H}_7\text{OH}$: propan-1-ol is used as a solvent for lacquers and waxes, as a brake fluid, and in the manufacture of propanoic acid; propan-2-ol, or isopropanol, is sold as rubbing alcohol and is used to manufacture oils, gums, and acetone. (The prefix *iso-* indicates that the hydroxyl group is bonded to the central carbon atom.) Both isomers of propanol are toxic to humans if taken internally.

▶ SAMPLE problem 10.3

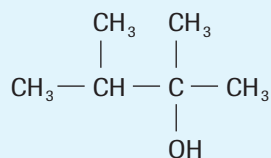
Name the following alcohol from its condensed structural formula and indicate whether it is a primary, secondary, or tertiary alcohol.



1. Identify the longest C chain. Since it is five Cs long, the alcohol is a pentanol.
2. Look at where the hydroxyl groups are attached. An -OH group is located on the second C atom, so the alcohol is a pentan-2-ol.
3. Look to see where any other group(s) are attached. A methyl group is located on the second C atom, so the alcohol is 2-methylpentan-2-ol.
4. Since the second C atom, to which the OH is attached, is attached to three other carbon atoms, the alcohol is a tertiary alcohol.

► COMMUNICATION example 2

The following alcohol is used as a toxic denaturant for ethanol, as an octane booster in gasoline, as a paint remover, and for manufacturing perfumes. Name this alcohol from its condensed structural formula.

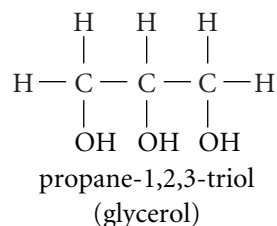
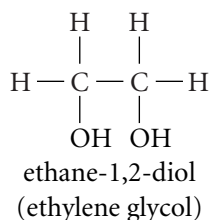


Solution

This tertiary alcohol is 2,3-dimethylbutan-2-ol.

Polyalcohols

Alcohols that contain more than one hydroxyl group are called *polyalcohols*; their names indicate the number and positions of the hydroxyl groups. For example, 1,2-ethanediol (ethylene glycol) is used as antifreeze for car radiators. Propane-1,2,3-triol (glycerol) is safe to consume, in limited quantities. It is a base material in many cosmetics and functions as a moisturizer in foods such as chocolates. Glycerol, also called glycerin and glycerine, is sold in drugstores. Fats and oils are derived from glycerol.



DID YOU KNOW?

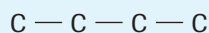
Glycerol: An Everyday Polyalcohol

The moisturizing effect of glycerol (propane-1,2,3-triol) is related to its multiple hydroxyl groups, each capable of hydrogen bonding with water molecules. When glycerol, commonly sold as glycerine in drugstores, is added to a soap bubble solution, the soap film formed contains more fixed water molecules and thus does not readily disintegrate from drying out (evaporation of water molecules).

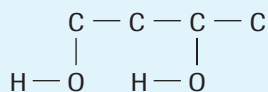
► SAMPLE problem 10.4

Draw a structural formula for butane-1,3-diol or 1,3-dihydroxybutane.

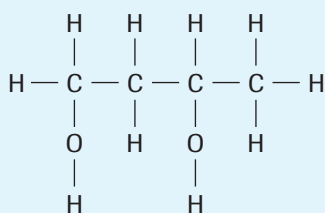
First, write the C skeleton for the parent molecule, butane.



Next, attach an OH group to the first and third C atoms.



Finally, complete the remaining C bonds with H atoms.



Learning Tip

Ask your teacher whether you will need to learn about cycloalcohols or aromatic alcohols. If so, ask about how complex the ones you need to know will be.

Cyclic and Aromatic Alcohols

Chemists have discovered alcohols whose parent compounds are cycloalkanes, cycloalkenes, and benzene. These compounds can become very complex quickly, so you only need to know some of the simplest examples:

- $C_6H_{11}OH(l)$ is cyclohexanol
- $C_6H_5OH(s)$ is phenol (an aromatic alcohol)

You may have heard of phenols when chemists talk about the odour and taste of spring run-off water. The phenols come from the decaying plant matter over which the water runs. Phenols are slightly soluble in water, more soluble in benzene, and very soluble in alcohols.

DID YOU KNOW?

Grape Expectations

The cosmetics industry has developed a line of “anti-aging” creams that purport to make the skin look younger. The active ingredient is listed as polyphenols (extracted from grape seeds and skins (**Figure 3**), and also from olives). Manufacturers claim that these compounds, described as antioxidants, reverse signs of aging in the skin.



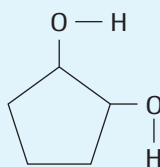
Figure 3

Grapes contain polyphenols—antioxidants that can be made into cosmetics.

COMMUNICATION example 3

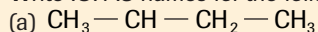
Draw a line structural formula for cyclopentane-1,2-diol.

Solution

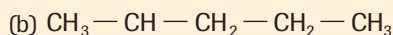
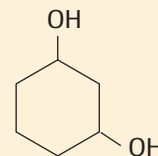


Practice

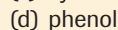
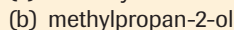
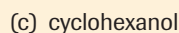
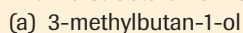
5. Write IUPAC names for the following compounds:



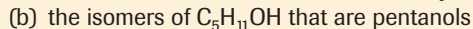
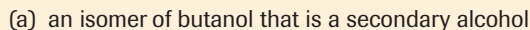
(c)



6. Draw a structural formula for

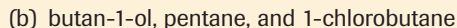
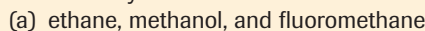


7. Draw line structural formulas and name:



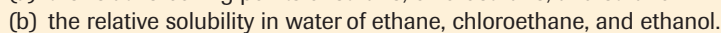
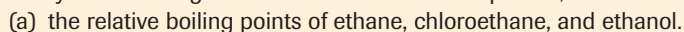
8. Explain briefly why methanol has a higher boiling point than methane.

9. Predict the order of increasing boiling points for the following compounds, and give reasons for your answer.



10. Glycerol is more viscous than water, and can lower the freezing point of water. When added to biological samples, it helps to keep the tissues from freezing, thereby reducing damage. From your knowledge of the molecular structure of glycerol, suggest reasons to account for these properties of glycerol.

11. Use your knowledge of intermolecular forces to predict, with reasoning,



12. Methanol is produced from methane from natural gas in a two-step process. Write a molecular formula equation to communicate each of the following steps:
 (a) Methane reacts with water to produce carbon monoxide and hydrogen.
 (b) Carbon monoxide and hydrogen then react to produce methanol.
13. Ethanol can be produced by a two-step chemical process. Communicate the process using structural formula equations.
 (a) Ethane from natural gas is cracked to produce ethene.
 (b) Ethene reacts with water in an addition reaction to produce ethanol.
14. Only a few of the simpler alcohols are used in combustion reactions. Alcohol-gasoline mixtures, known as gasohol, are the most common examples. Write a balanced chemical equation, using structural formulas, for the complete combustion of each of the following alcohols:
 (a) ethanol (in gasohol)
 (b) methanol (in gas line antifreeze, **Figure 4**)
15. Ethanol is a beverage alcohol. Calculate the volume of ethanol in each of the drinks in (a), (b), and (c):
 (a) 355 mL of beer (5.0% ethanol by volume)
 (b) 150 mL of wine (12% ethanol by volume)
 (c) 45 mL of rum (40% ethanol by volume)
 (d) How does the quantity of ethanol compare for each of these standard-size drinks?
16. Why is industrial (and school) ethanol denatured (made toxic with, for example, methanol)? Include an economic and a societal perspective in your answer.
17. Alcohols have varying physical properties that may be attributed to intermolecular bonding. Test intermolecular bonding theories by predicting the relative boiling points of the alcohols listed below. Support your prediction with reasoning, based on intermolecular bonding theories. Collect the evidence from a named reference source such as the *CRC Handbook of Chemistry and Physics* or the Internet. Complete Step 2 of an Evaluation.

Purpose

The purpose of this investigation is to test intermolecular bonding theories.

Problem

What are the relative boiling points of butan-1-ol, methanol, propan-1-ol, and ethanol?

**Figure 4**

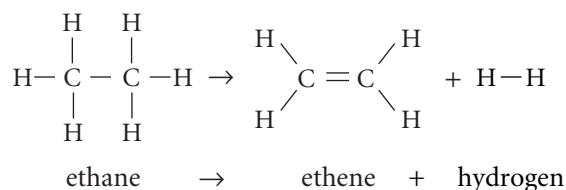
Methanol, sold as methyl hydrate, is used throughout Canada as gas line antifreeze and windshield washer fluid.

Elimination Reactions

The production of alkenes is a very important laboratory and industrial reaction. As you know from Section 10.1, ethene is the cornerstone of the Alberta petrochemical industry. As you will learn in Section 10.5, alkenes are necessary to produce one of the two main classes of polymers. Besides cracking reactions mentioned in Chapter 9 and reviewed below, elimination reactions are a primary source of alkenes—derived from either alcohols or alkyl halides.

Producing Ethene by Cracking Ethane

As indicated in Chapter 9, chemical engineers have devised several methods for producing ethene on an industrial scale. Over time, high-temperature steam cracking of ethane, as illustrated below, became the preferred technological process. As you can see, molecules of hydrogen are “eliminated” from the ethane.



Learning Tip

Recall that the ethane to ethene reaction is called cracking, although it is quite different from cracking that involves breaking carbon-carbon bonds. Sometimes tradition determines the name of something against usual reasoning. This process is also sometimes called elimination or dehydrogenation.



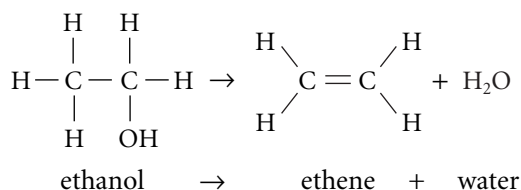
Figure 5

A gas generator produces ethene, which speeds the ripening of fruits such as bananas. Ethanol reacts in the gas generator in the presence of an acid catalyst—an elimination reaction.

In review, ethane is cracked into ethene in a world-scale plant at, for example, Joffre, east of Red Deer, Alberta. The ethane used in the cracking process in Alberta comes from natural gas.

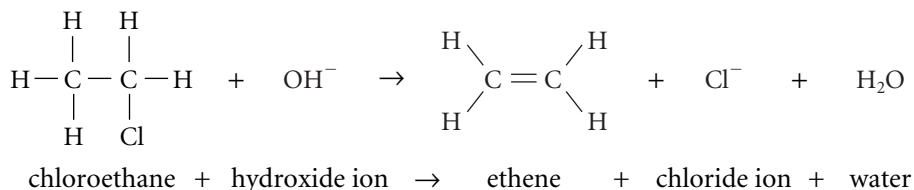
Producing Ethene by Elimination Reactions

Ethene was discovered serendipitously in the 17th century by heating ethanol in the presence of sulfuric acid (as a catalyst). Eventually, chemists experimented with many catalysts other than sulfuric acid and found that aluminium oxide and phosphoric acid were effective in this reaction (Figure 5).



This reaction, called an **elimination reaction**, involves eliminating atoms and/or groups of atoms from adjacent carbon atoms in an organic molecule. In the case of the synthesis of ethene from ethanol, a hydrogen atom and a hydroxyl group on adjacent carbon atoms are eliminated, forming water as a by-product. This particular kind of elimination reaction is also called *dehydration*, because of the apparent removal of water from the alcohol.

Another example of an elimination reaction is the dehydrohalogenation (removal of hydrogen and halogen atoms) of an organic halide to produce an alkene. Ethene can, for example, be produced in the laboratory by reacting chloroethane with potassium hydroxide:



In this reaction, a hydrogen atom and a halogen atom are eliminated from the alkyl halide to produce the alkene plus a halide ion and a water molecule.

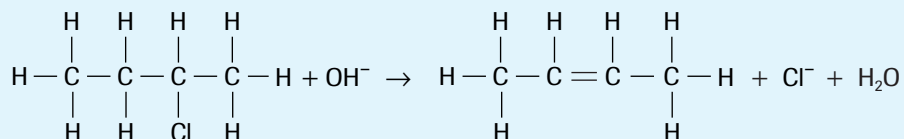
Chemists have identified other elimination reactions and other ways to synthesize ethene and other alkenes. Research has indicated, however, that the above two methods (starting with ethanol or chloroethane) are the best choices for the laboratory. From an industrial perspective, the cracking of abundant fossil fuel alkanes to produce alkenes is the preferred method.

► COMMUNICATION example 4



The elimination of a halide ion from an organic halide is the most common method for preparing a specific alkene in the laboratory. Write a structural formula equation for the preparation of but-2-ene from 2-chlorobutane, in the presence of a strong base.

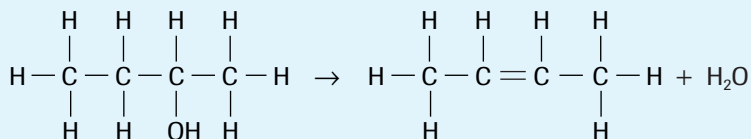
Solution



► COMMUNICATION example 5

The elimination of the elements of a water molecule from an alcohol is the second most common method for preparing a specific alkene in the laboratory. Write a structural formula equation for the preparation of but-2-ene from butan-2-ol, in the presence of a catalyst.

Solution



► Practice

- Write a structural formula equation to represent the synthesis of ethene by reacting bromoethane with a strong base.
- Alkenes can be manufactured by three different chemical processes. Write structural formula equations for each of the following hypothetical chemical processes:
 - Butane is cracked into but-2-ene.
 - 1-chlorobutane undergoes an elimination reaction in a strongly basic solution to produce but-1-ene, chloride ions, and water.
 - butan-1-ol undergoes an elimination reaction to produce but-1-ene and water.
- Write structural formula equations for the synthesis of propene by three different processes.
- Chemical engineers face many difficulties during the technological design of ethane cracking plants (Figure 6). Suggest a different solution to each of the following problems encountered when ethane is thermally cracked:
 - 40% of the ethane remains uncracked after coming from the ethane cracker
 - ethyne (acetylene) is produced in addition to ethene
 - hydrogen and methane are produced



Figure 6

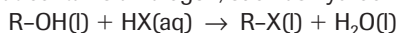
Alberta is Canada's top producer of petrochemicals and home to the world's two largest ethane-based processing plants—at Joffre, east of Red Deer, and Fort Saskatchewan, northeast of Edmonton. This photo shows the largest of the three ethylene plants located at the Joffre site. Significant infrastructure supports the Joffre site facilities: feedstock pipelines, an ethane extraction plant, and a cogeneration power plant.



INVESTIGATION 10.2 Introduction

Isomers of Butanol

Organic halides have many uses, but they are not commonly found in nature. Organic halides must, therefore, be synthesized from other compounds. On an industrial scale, organic halides are produced by addition and substitution reactions of hydrocarbons. A common laboratory-scale process is the halogenation of alcohols in which the hydroxyl group of the alcohol is replaced by a halogen. This reaction requires the presence of a strong acid that contains a halogen, such as hydrochloric acid.



Organic halides have much lower solubilities in water compared with their corresponding alcohols.

Purpose

The purpose of this investigation is to test a personal hypothesis about the relative reactivity of the alcohol isomers of butan-1-ol.

To perform this investigation, turn to page 462.

Report Checklist

- | | | |
|---|--|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input checked="" type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 2, 3) |
| <input checked="" type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Problem

What is the difference in reactivity, if any, of the alcohol isomers of butan-1-ol with concentrated hydrochloric acid?

Design

Samples of butan-1-ol, butan-2-ol, and 2-methylpropan-2-ol are mixed with concentrated hydrochloric acid. Evidence of reaction is obtained by looking for a low-solubility organic halide product (cloudy mixture).

SUMMARY Alcohols and Elimination Reactions

Alcohols

Functional group:

–OH, hydroxyl group

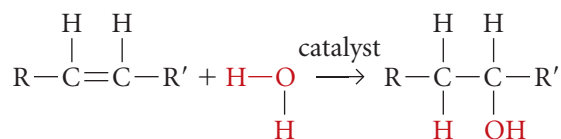
Naming alcohols:

- Drop the “e” from the alkane name and add “ol”; e.g., ethane becomes ethanol.
- If necessary, add a number (or numbers) to communicate where the hydroxyl group(s) is (are) located; e.g., propan-1-ol and propan-2-ol.
- If the alcohol has two or three hydroxyl groups, it is a diol or a triol, respectively; e.g., ethane-1,2-diol and propane-1,2,3-triol. For diols and triols, do not drop the “e” from the alkane name.

Preparation:

Addition reactions with water

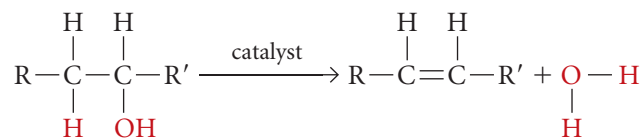
- alkenes + water → alcohols



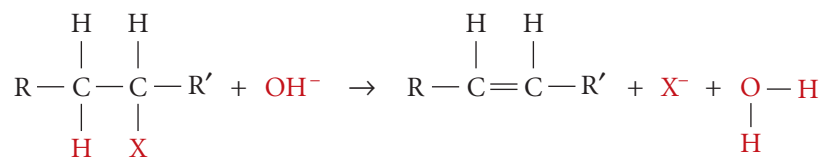
(R and R' can be the same or different alkyl groups. Isomers often result.)

Elimination Reactions

- alcohols → alkenes + water



- organic halides + OH[−] → alkenes + halide ion + water



Learning Tip

The types of organic reactions that you are responsible for learning to this point in the unit are:

1. photosynthesis and respiration
2. hydrocracking
3. catalytic reforming
4. complete and incomplete combustion
5. substitution
6. addition
7. elimination

WEB Activity

Web Quest—Cellulosic Ethanol

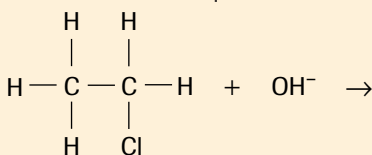
This Web Quest focuses on the technological, environmental, and ecological impacts of building a cellulosic ethanol plant. In the past, ethanol was widely used as a fuel, only to be replaced by abundant and inexpensive gasoline. What are the issues with creating and using cellulosic ethanol? Does it have the potential to provide a realistic alternative to gasoline? You will examine the cellulosic ethanol plant from the point of view of a consulting firm, and present your supported conclusions to the community.

www.science.nelson.com



Section 10.3 Questions

- Write structural formulas and IUPAC names for all saturated alcohols with four carbon atoms and one hydroxyl group.
- Explain why the propane that is used as fuel in a barbecue is a gas at room temperature, but propan-2-ol, used as rubbing alcohol, is a liquid at room temperature.
- Draw the structural formulas and write the IUPAC names of the two alkenes that are formed when hexan-2-ol undergoes an elimination reaction in the presence of an acid catalyst.
- Write an equation using structural formulas to show the production of each of the following alcohols from an appropriate alkene:
 - butan-2-ol
 - methylpropan-2-ol
- A major use of organic halides is in the preparation of unsaturated compounds. Predict the products of the following elimination reaction. Write a word equation and a structural formula equation.



- Classify and write structural formula equations for the following catalyzed organic reactions:
 - ethene + water \rightarrow ethanol
 - butan-2-ol \rightarrow but-1-ene + but-2-ene + water
 - ethene + hypochlorous acid ($\text{HOCl}(\text{aq})$) \rightarrow 2-chloroethanol
 - cyclohexanol + oxygen \rightarrow
- Draw structural formulas to represent the elimination reaction of 2-chloropentane to form an alkene. Include reactants, reaction conditions, and all possible products and their IUPAC names.
- The nomenclature of organic compounds is similar across classes of compounds. Name the following alkanes, alkenes, and alcohols.
 - $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$
 - $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_3$
 - $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
 - $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}_2$
 - $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$
 - $\text{CH}_3-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$
 - $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{OH}$
 - $\text{CH}_3-\text{C}(\text{CH}_3)(\text{OH})-\text{CH}_3$
- Draw line structural formulas for the following alcohols.
 - propan-2-ol
 - phenol (hydroxybenzene)
 - propane-1,2,3-triol (glycerol)
 - cyclohexanol
- Complete the Hypothesis (including reasoning), Analysis, and Evaluation (2, 3) for the following investigation report:

Purpose

The purpose of this investigation is to test a hypothesis concerning the relative boiling points and solubility of alcohols. Assume that solubility means in water.

Problems

- What is the trend in boiling points for C_1-C_6 primary alcohols?
- What is the trend in solubility for C_1-C_6 primary alcohols?

Evidence

Table 1 Boiling Points and Solubilities of Various Alcohols

Alcohol	Boiling point ($^{\circ}\text{C}$)	Solubility (mL/100 mL)
methanol	65	miscible
ethanol	78	miscible
propan-1-ol	97	miscible
butan-1-ol	117	9.1
pentan-1-ol	138	3.0
hexan-1-ol	157	slight

- Use the information in this section and from your own research to continue gathering perspective statements concerning the statement that we should be saving more fossil fuels for petrochemical use in the future.

Extensions

- Alcohols have gained increased popularity as an additive to gasoline, as a fuel for automobiles. "Gasohols" may contain up to 10% methanol and ethanol, and are considered more environmentally friendly than gasoline alone.
 - Write balanced chemical reaction equations for the complete combustion of methanol and ethanol.
 - When small amounts of water are present in the gasoline in the gas lines of a car, the water may freeze and block gasoline flow. Explain how using a gasohol would affect this problem.

www.science.nelson.com 

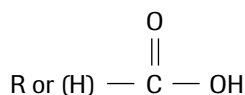
- Radiator antifreeze and coolant is ethane-1,2-diol (ethylene glycol). Ethylene glycol is usually mixed 50:50 with water for use in the radiator. Large quantities of this chemical product are produced near Fort Saskatchewan and Scotford, Alberta. Ethene reacts with oxygen in one reactor to produce ethylene oxide ($\text{C}_2\text{H}_4\text{O}(\text{g})$). The ethylene oxide then reacts with water in a second reactor to produce ethylene glycol.
 - Write structural formula equations for these reactions.
 - Explain why ethylene glycol is a better choice as a radiator antifreeze and coolant than ethanol.
 - Explain why methanol, rather than ethylene glycol, is used as a windshield wiper antifreeze.
 - Which is more toxic, methanol or ethylene glycol?
 - Use a reference to find the freezing point of a 50:50 mixture of ethylene glycol and water.

www.science.nelson.com 

10.4 Carboxylic Acids, Esters, and Esterification Reactions

Learning Tip

The general formula for a carboxylic acid is



The functional group for carboxylic acids is the carboxyl group, $-\text{COOH}$.



Figure 1

Tracking dogs, with their acute sense of smell, are trained to identify odours in police work. As carboxylic acids have distinctive odours, the dogs may follow the characteristic blend of carboxylic acids in a person's sweat. Trained dogs are also used to seek out illegal drug laboratories by the odour of acetic acid. Acetic acid is formed as a byproduct when morphine, collected from opium poppies, is treated to produce heroin.

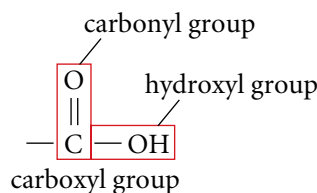
Figure 2

- (a) Most ants and ant larvae are edible and are considered quite delicious. They have a vinegary taste because they contain methanoic acid, HCOOH , commonly called formic acid. In some countries, large ants are squeezed directly over a salad to add the tangy ant juice as a dressing.
- (b) This ball-and-spring model represents the evidence chemists have collected on methanoic acid.

Natural products and processes involve a wide variety of organic chemicals. In this section, you will learn what chemists and chemical engineers have discovered about some organic products and processes. Chemists, like you, started off learning the basics of organic chemistry—just as you have learned about inorganic chemistry. The study of most topics in science begins with classification based on the physical and chemical properties of the chemicals involved. Nomenclature—providing names for the classes of chemicals and for individual chemicals—usually follows quickly after the classification process. The parallel process is most often the creation of theories to explain the properties of each of the classes of compounds.

Carboxylic Acids

The family of organic compounds known as **carboxylic acids** contain the **carboxyl group**, $-\text{COOH}$, which includes both the carbonyl and hydroxyl functional groups.



Note that, because the carboxyl group involves three of the carbon atom's four bonds, the carboxyl group is always at the end of a carbon chain or branch.

Chemists explain the characteristic properties of carboxylic acids by the presence of the carboxyl group. Carboxylic acids occur naturally in citrus fruits, crabapples, rhubarb, and other foods characterized by the sour, tangy taste of acids. Carboxylic acids also have distinctive odours (Figure 1).

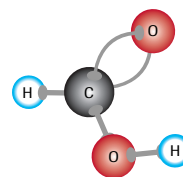
As we might predict from the structure of carboxylic acids, the molecules of these compounds are polar and form hydrogen bonds both with each other and with water molecules. These acids exhibit the same solubility behaviour as alcohols. The smaller members (one to four carbon atoms) of the acid series are miscible with water, whereas larger ones are virtually insoluble. Aqueous solutions of carboxylic acids have the properties of acids; a litmus test can distinguish these compounds from other hydrocarbon derivatives. The smaller carboxylic acids are all liquids at room temperature. The dicarboxylic acids (even the small ones) are solids at room temperature, as are the larger-molecule carboxylic acids.

Carboxylic acids are named by replacing the *-e* ending of the corresponding alkane name with *-oic*, followed by the word "acid." The first member of the carboxylic acid family is methanoic acid, HCOOH , commonly called formic acid (Figure 2). Methanoic acid is used in removing hair from hides and in coagulating and recycling rubber.

(a)



(b)

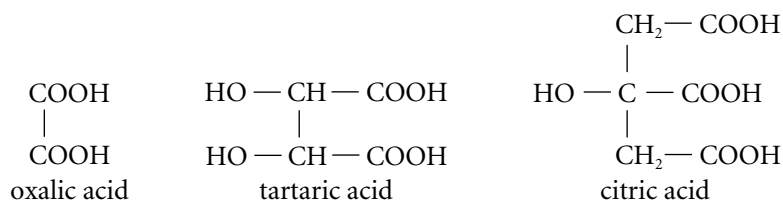


Ethanoic acid, $\text{CH}_3\text{COOH}(\text{l})$, commonly called acetic acid, is the compound that makes vinegar taste sour (**Figure 3(a)**). Wine vinegar and cider vinegar are produced naturally when sugar in fruit juices is fermented first to alcohol, and then to ethanoic acid. This acid is employed extensively in the textile dyeing process and as a solvent for other organic compounds.

glucose \rightarrow ethanol \rightarrow ethanoic acid (acetic acid)

fruit juice \rightarrow wine \rightarrow vinegar

Some acids contain two or three carboxyl groups. For example, oxalic acid, used in commercial rust removers and in copper and brass cleaners, consists of two carboxyl groups bonded together. Oxalic acid (**Figure 3(b)**) occurs naturally in rhubarb, tartaric acid occurs in grapes, and citric acid occurs in citrus fruits. Due to the extra hydrogen bonding, all three of these acids are solids as pure substances at room temperature.



You do not have to memorize these names and condensed structural formulas, or those of any other polycarboxylic acids. However, you should recognize that they are carboxylic acids (from the carboxyl functional groups). You should also recognize that multiple hydrogen bonding is possible, which increases the melting and boiling points and solubility in water of these compounds.



Figure 3

Oxalic acid (**(b)**), found in rhubarb, differs from pure acetic (ethanoic) acid, $\text{CH}_3\text{COOH}(\text{l})$ (**(a)**), in that its molecule contains an additional carboxyl group. This increased polarity and hydrogen bonding explain why oxalic acid is a solid while pure acetic acid is a liquid at the same temperature.



LAB EXERCISE 10.B

Report Checklist

Explaining Physical Property Trends

Many physical properties of organic compounds can be understood using knowledge of the functional groups present and of intermolecular forces. Complete the Analysis and Evaluation of the investigation report.

Purpose

The purpose of this investigation is to use your knowledge of organic structures and intermolecular forces to explain some physical properties of alcohols and carboxylic acids.

Evidence

Table 1 Boiling Points and Solubilities of Various Alcohols and Carboxylic Acids

Alcohol	Boiling point (°C)	Solubility in water (g/100 mL)	Carboxylic acid	Boiling point (°C)	Solubility in water (g/100 mL)
methanol	65	miscible	methanoic acid	101	miscible
ethanol	79	miscible	ethanoic acid	118	miscible
propan-1-ol	97	miscible	propanoic acid	141	miscible
butan-1-ol	117	8.0	butanoic acid	164	miscible
pentan-1-ol	137	2.7	pentanoic acid	186	2.4

- | | | |
|----------------------------------|---------------------------------|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input type="radio"/> Evidence | |

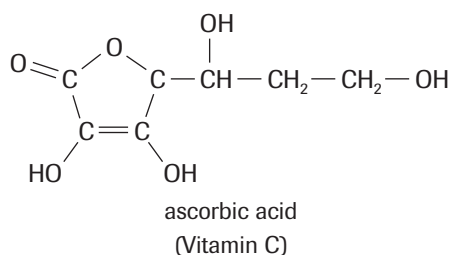
Problem

What is the explanation for the trends in boiling points and solubilities in water within and between series of simple alcohols and carboxylic acids?

DID YOU KNOW?

Water-Soluble Vitamins

With its many polar hydroxyl groups, vitamin C (ascorbic acid) is highly water-soluble. The water-soluble vitamins are not stored in the body; rather, they are readily excreted in the urine. It is, therefore, important that we include these vitamins in our daily diet. Although taking too much vitamin C is not dangerous, taking excessive amounts is truly sending money down the drain.



Learning Tip

The technological applications of the following chemicals should be memorized as common knowledge:

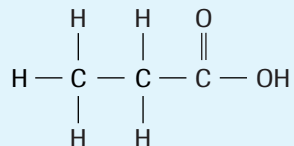
CH ₄ (g)	natural gas
C ₃ H ₈ (g)	barbecue fuel
C ₄ H ₁₀ (g)	lighter fluid
C ₈ H ₁₈ (l)	in gasoline
C ₂ H ₄ (g)	polyethylene monomer
C ₂ H ₂ (g)	cutting torch fuel
C ₆ H ₆ (l)	in gasoline
CH ₃ OH(l)	gasoline antifreeze
C ₂ H ₅ OH(l)	beverage alcohol
CH ₂ OHCH ₂ OH	radiator antifreeze
CH ₃ COOH(l)	in vinegar

SAMPLE problem 10.5

Write the IUPAC name and the full structural formula for propanoic acid.

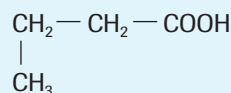
The prefix *propan-* indicates that the acid contains three C atoms; the end C atom is in the carboxyl group.

The structural formula for propanoic acid is



COMMUNICATION example 1

What is the IUPAC name for this carboxylic acid, which has an unpleasant, rancid odour?



Solution

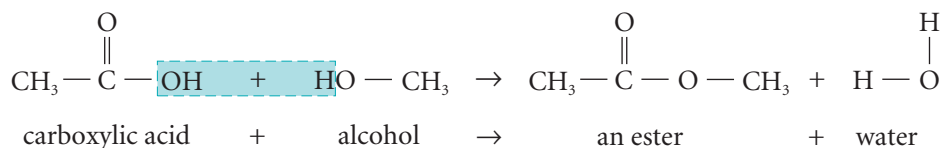
This condensed structural formula represents butanoic acid.

Practice

1. Draw a structural formula for each of the following compounds:
 - (a) octanoic acid
 - (b) benzoic acid
 - (c) ethanoic (acetic) acid
2. Give IUPAC and, if applicable, common names for these molecules:
 - (a) $\begin{array}{c} \text{O} \\ || \\ \text{H} - \text{C} - \text{OH} \end{array}$
 - (b) HOOC — CH₂ — CH₂ — CH₂ — CH₃
 - (c) CH₃ — CH₂ — CH₂ — CH₂ — CH₂ — COOH

Esterification Reactions

Carboxylic acids undergo a variety of organic reactions. In a **condensation reaction**, a carboxylic acid combines with another reactant, forming two products—an organic compound and a compound such as water. For example, a carboxylic acid can react with an alcohol, forming an **ester** and water. This type of condensation reaction is known as an **esterification reaction**.

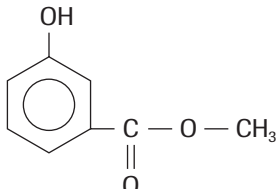


Esters

The **ester functional group**, $-\text{COOR}$, is similar to that of an acid, except that the hydrogen atom of the carboxyl group has been replaced by a hydrocarbon branch. Esters occur naturally in many plants and are responsible for some of the odours of fruits and flowers. Esters are often added to foods to enhance aroma and taste. Other commercial applications include cosmetics, perfumes, synthetic fibres, and solvents.

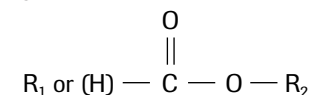
The odour of food strongly influences its flavour. Artificial flavourings are made by mixing synthetic esters to give the approximate odour (such as raspberry or banana) of the natural substance. For artificial fruit flavours, organic acids are usually added to give the sharp taste characteristic of fruit. Artificial flavours can only approximate the real thing, because it would be too costly to include all the components of the complex mixture of compounds present in the natural fruit or spice. **Table 2** shows the main esters used to create the odours of certain artificial flavours. The names are covered next.

Table 2 Odours of Selected Esters

Odour	Name	Formula
apple	methyl butanoate	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{COO}-\text{CH}_3$
apricot	pentyl butanoate	$\text{CH}_3-(\text{CH}_2)_2-\text{COO}-(\text{CH}_2)_4-\text{CH}_3$
banana	3-methylbutyl ethanoate	$\text{CH}_3-\text{COO}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_3$
cherry	ethyl benzoate	$\text{C}_6\text{H}_5-\text{COO}-\text{CH}_2-\text{CH}_3$
orange	octyl ethanoate	$\text{CH}_3-\text{COO}-(\text{CH}_2)_7-\text{CH}_3$
pineapple	ethyl butanoate	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{COO}-\text{CH}_2-\text{CH}_3$
red grape	ethyl heptanoate	$\text{CH}_3-(\text{CH}_2)_5-\text{COO}-\text{CH}_2-\text{CH}_3$
rum	ethyl methanoate	$\text{H}-\text{COO}-\text{CH}_2-\text{CH}_3$
wintergreen	methyl salicylate	

Learning Tip

The general formula for an ester is



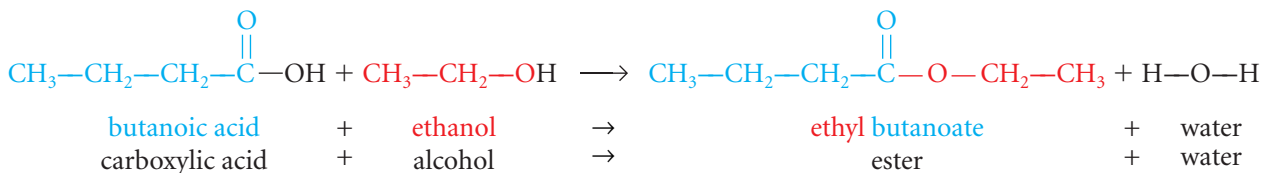
where R_2 is the alkyl branch from the alcohol and R_1 (or H) is from the acid.

Learning Tip

Note that the names for esters have a space between the prefix and the principal group, for example, ethyl butanoate. These “organic salts” are named like inorganic salts; e.g., sodium chloride.

Naming and Preparing Esters

Esters are organic “salts” formed from the reaction of a carboxylic acid and an alcohol. Consequently, the name of an ester has two parts. The first part is the name of the alkyl group from the alcohol used in the esterification reaction. The second part comes from the acid. The ending of the acid name is changed from *-oic acid* to *-oate*. For example, in the reaction of ethanol and butanoic acid, the ester formed is ethyl butanoate, an ester with a banana odour. A strong acid catalyst, such as $\text{H}_2\text{SO}_4(\text{aq})$, is used to increase the rate of this organic reaction, along with some careful heating.



Learning Tip

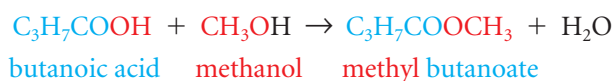
Note the colour coding of the reactant segments that show the movement of the O atoms and that also assist with naming the ester.

DID YOU KNOW?

Radioactive Tracing

Radioactive tracing can be used by medical personnel to trace the movement of chemicals in your body. Chemists use a similar approach to trace the movement of atoms in a chemical reaction. For example, if the O atom in propan-1-ol is manipulated to be radioactive (O-18), and the resulting ester is radioactive, then the radioactive O-18 atom has moved to the ester. The hydroxyl (–OH) group from the acid, therefore, must move to the water. Radioactive tracing is not important for predicting the products, but it provides chemists with deeper theoretical understanding.

The general formula of an ester is written as RCOOR'. When read from left to right, RCO– comes from the carboxylic acid, and –OR' comes from the alcohol. Hence, CH₃COOCH₂CH₂CH₃ is propyl ethanoate. Note that, for an ester, the acid is the first part of its formula as drawn, but is the second part of its name.



SAMPLE problem 10.6

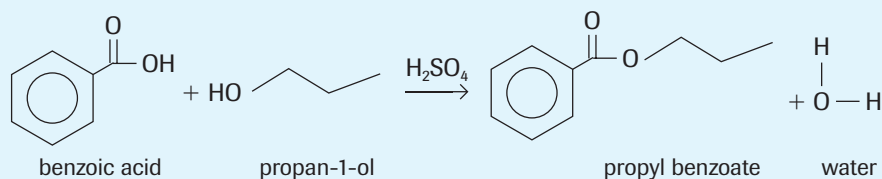
Draw a line structural formula equation and write the IUPAC name for the ester formed in the reaction between propan-1-ol and benzoic acid.

To name the ester:

- The first part of the name comes from the alcohol: propyl.
- The second part of the name comes from the acid: benzoate.
- The IUPAC name of the ester is propyl benzoate.

To draw the line structural formula:

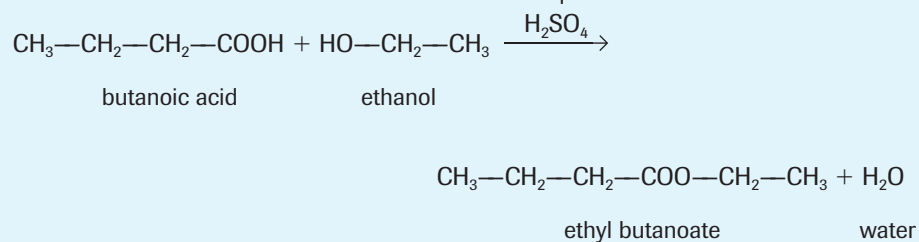
- Draw structural formulas of the reactants and complete the condensation reaction.



SAMPLE problem 10.7

Write a condensed structural formula equation for the esterification reaction to produce the ester CH₃CH₂CH₂COOCH₂CH₃. Write IUPAC names for each reactant and product.

First, identify the acid (four carbons—butanoic acid) and the alcohol (two carbons—ethanol) that may be used in the synthesis of the ester. Then write condensed structural formulas and include the conditions in the chemical equation.



COMMUNICATION example 2

Name the ester CH₃COOCH₃ and the acid and alcohol from which it can be prepared.

What conditions are necessary?

Solution

The ester is methyl ethanoate, and it can be prepared from methanol and ethanoic acid.

A strong acid catalyst, such as H₂SO₄(aq), is required, along with some heating.

Practice

- Write a structural formula equation to illustrate the synthesis of each of the following esters from an alcohol and an acid. Refer to **Table 2** and identify the odour of each ester formed.
 - ethyl methanoate
 - ethyl benzoate
 - methyl butanoate
 - 3-methylbutyl ethanoate
- Name each of the following esters, and the acids and alcohols from which they could be prepared:
 - $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$
 - $\text{HCOOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 - $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$
- Name the carboxylic acid and alcohol required to produce each of the following ester odours:
 - apricot
 - orange
- The graph in **Figure 4** communicates evidence gathered for the boiling points of straight-chain carboxylic acids, methyl esters, and alkanes. (Methyl esters are prepared with methanol and their names begin with “methyl.”) The boiling points are plotted against the molar masses of these organic compounds. The scientific purpose of this task is to test the explanatory power of the intermolecular force theories known to you.

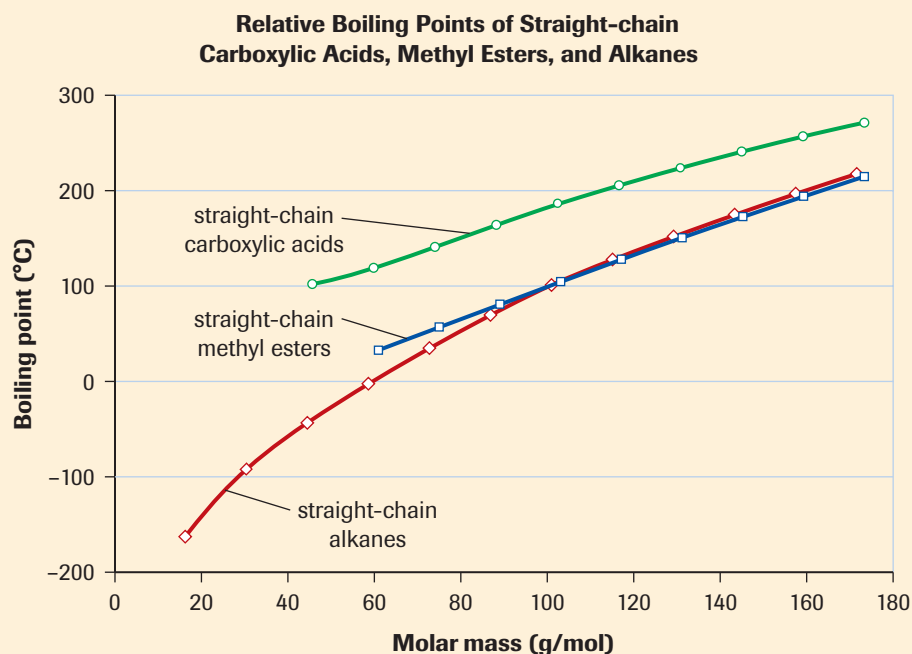


Figure 4

Boiling points of straight-chain carboxylic acids, methyl esters, and alkanes

- Explain the same upward trend in boiling points of the three classes of straight-chain organic compounds.
- Explain the relatively close boiling point values for the alkanes and the methyl esters.
- Explain the difference in boiling points for carboxylic acids versus alkanes and methyl esters with the same molar masses.

BIOLOGY CONNECTION



Natural Esters

Esters occur naturally. Beeswax, for example, is a natural ester containing chains 40–46 carbon atoms long. Plants' leaves are coated in waxy esters to minimize water loss; insects and animals may also have a surface coating (including skin) that includes esters. Chemical analysis of the coating on leaves shows that these natural esters (sometimes called wax esters) contain 34–62 carbon atoms. Of the natural waxes present on the surface of apples, for example, about 18% are esters.

www.science.nelson.com



Learning Tip

You will find it helpful to memorize the functional groups for the classes of organic compounds that you have studied. A short summary (with the functional group in parentheses) is:

alkenes; e.g., $\text{CH}_2=\text{CH}_2$
(double bond)

alkynes; e.g., $\text{CH}\equiv\text{CH}$
(triple bond)

aromatics; e.g., $\text{C}_6\text{H}_5-\text{CH}_3$
(benzene ring(s))

organic halides; e.g., CH_3-Cl ;
 $\text{R}-\text{X}$
($\text{X}=\text{F}, \text{Cl}, \text{Br}$ and/or I)

alcohols; e.g., CH_3-OH ;
 $\text{R}-\text{OH}$ (hydroxyl group, $-\text{OH}$)

carboxylic acids; e.g.,
 CH_3-COOH ; $\text{R}(\text{H})-\text{COOH}$
(carboxyl group, $-\text{COOH}$)

esters; e.g., $\text{CH}_3-\text{COO}-\text{C}_2\text{H}_5$;
 $\text{R}^1(\text{H})\text{COOR}^2$
(ester group, $-\text{COOC}-$)

R is a hydrocarbon chain/group. R(H) means that the R can be an H.

- (d) Do your intermolecular force theories pass the test of being able to explain the relative boiling points of these straight-chain compounds? Give reasons for your answer.
- (e) Why is the test restricted to comparing straight-chain compounds?
- (f) Predict the position of the line representing the boiling point of alcohols, placed on this same set of axes.
- (g) Referenced values of boiling points for some straight-chain alcohols include 64 °C for methanol, 97 °C for propan-1-ol, 138 °C for pentan-1-ol, and 176 °C for heptan-1-ol. Is your prediction in (f) verified or falsified? If falsified, critique your prediction and/or the hypothesis upon which you based your prediction.
7. What are some pros and cons, from at least two perspectives, for using artificial flavouring (manufactured esters) instead of natural flavours?



INVESTIGATION 10.3 Introduction

Report Checklist

Synthesis of an Ester

Purpose

The purpose of this investigation is to use the esterification generalization and diagnostic tests to synthesize and observe the properties of two esters.

Problem

What are some physical properties of ethyl ethanoate (ethyl acetate) and methyl salicylate?

To perform this investigation, turn to page 463. 

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input type="radio"/> Evaluation |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Design

The esters are produced by the reaction of appropriate alcohols and acids, using sulfuric acid as a catalyst. The solubility and the odours of the esters are observed.



INVESTIGATION 10.4 Introduction

Report Checklist

Testing with Models

Molecular models, either physical or electronic, are based on empirically known molecular structures. These models can then be considered as representing evidence collected in a variety of experiments. Recall stereochemical formulas from Chapter 3.

Purpose

The purpose of this investigation is to test stereochemical formula equations by using molecular models.

Problem

What are the stereochemical formula equations for the following reactions?

- (a) methane undergoes complete combustion
 (b) ethane is cracked into ethene
 (c) propane reacts with chlorine

To perform this investigation, turn to page 464. 

- | | | |
|---|--|--|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input type="radio"/> Analysis |
| <input type="radio"/> Problem | <input checked="" type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (2, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

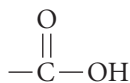
- (d) but-2-ene reacts with water
 (e) ethanol eliminates water to produce ethene
 (f) chloropropane undergoes an elimination reaction with hydroxide ions to produce propene, a chloride ion, and water
 (g) ethanol reacts with methanoic acid

Design

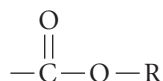
Physical or electronic models of the reactants and products for each reaction are constructed. The bonding and shapes of the molecules from the models are compared with the predictions.

SUMMARY**Carboxylic Acids, Esters, and Esterification****Functional groups**

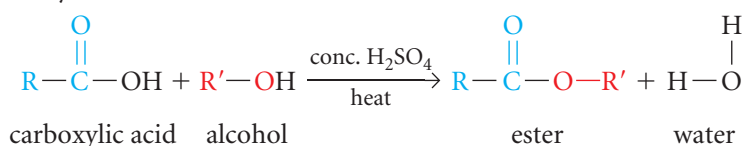
- carboxylic acid: $-\text{COOH}$ carboxyl group



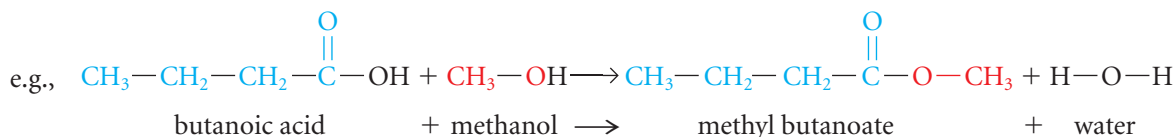
- ester: $-\text{COOR}$ alkylated carboxyl group

**Esterification reaction**

carboxylic acid + alcohol \rightarrow ester + water



(For esterification, R can be replaced by an H, but R' cannot be replaced by an H.)

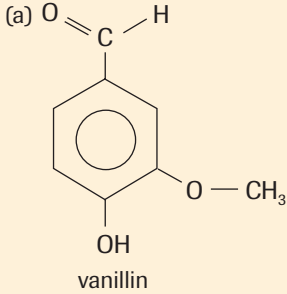
**Learning Tip**

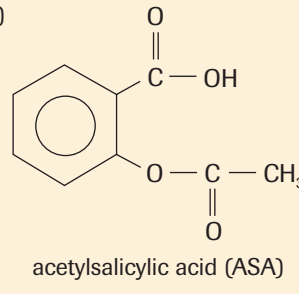
Evidence of high boiling points and solubility indicates that, of the classes of organic compounds studied in this section, the following classes exhibit hydrogen bonding:

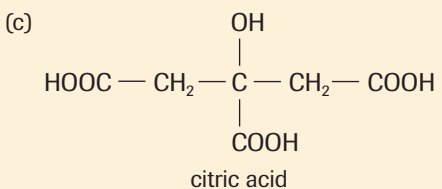
alcohols $\text{R}-\text{OH}$
 carboxylic acids $\text{R or H}-\text{COOH}$

Esters, R^1COOR^2 , do not exhibit hydrogen bonding.

Section 10.4 Questions

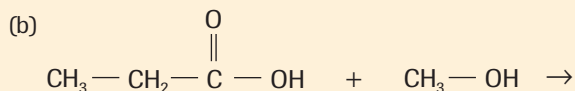
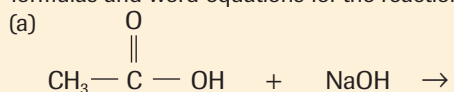
- Prepare a table with the headings: Family, General Formula, and Naming System. Complete the table for the following organic families:
 - alcohols
 - carboxylic acids
 - esters
- In what way is the functional group of an ester different from that of a carboxylic acid? How does this difference account for any differences in properties?
- Design an experimental procedure for the synthesis of an ester, given ethanol and acetic acid. Describe the steps in the procedure, the safety equipment required, and the precautions needed in the handling and disposal of the materials.
- Esters are often referred to as organic salts, and the esterification reaction is sometimes considered a neutralization reaction. An ester is similar, in some ways, to an ionic compound.
 - Use chemical formulas and equations to identify similarities and differences between esters and inorganic salts.
 - Design an investigation to determine which of two unlabelled pure samples provided to you is an ester and which is an ionic compound. List several diagnostic tests.
- Many organic compounds have more than one functional group in a molecule. Copy the following structural formulas. Circle and label the functional groups for an alcohol, a carboxylic acid, and/or an ester. Suggest either a source or a use for each of these substances.
 - 

vanillin
 - 

acetylsalicylic acid (ASA)
 - 

citric acid

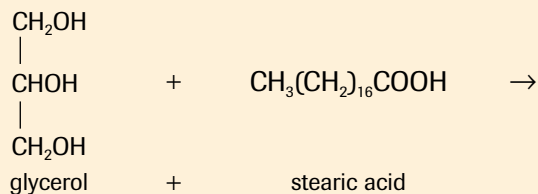
6. Carboxylic acids, like inorganic acids, can be neutralized by bases. Carboxylic acids also undergo organic reactions. Classify the following reactions as neutralization or esterification. Write the complete condensed structural formulas and word equations for the reactions.



(c) benzoic acid + potassium hydroxide \rightarrow

(d) ethanol + methanoic acid \rightarrow

7. Fats and oils are naturally occurring esters that store chemical energy in plants and animals. Fatty acids, such as octadecanoic acid (also known as stearic acid), typically combine with propane-1,2,3-triol, known as glycerol, to form fat, a triester. Complete the following chemical equation by predicting the structural formula for the ester product.



8. Classify the chemicals and write a complete balanced structural formula equation for each of the following predicted organic reactions. Where possible, classify the reactions and name the compounds as well. Assume that catalysts are used where required (for most of the reactions).
- (a) $\text{C}_2\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{HBr}$
- (b) $\text{C}_3\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_3\text{H}_6\text{Cl}_2$
- (c) $\text{C}_6\text{H}_6 + \text{I}_2 \rightarrow \text{C}_6\text{H}_5\text{I} + \text{HI}$
- (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{OH}^- \rightarrow$
 $\text{CH}_3\text{CH}_2\text{CHCH}_2 + \text{H}_2\text{O} + \text{Cl}^-$
- (e) $\text{C}_3\text{H}_7\text{COOH} + \text{CH}_3\text{OH} \rightarrow \text{C}_3\text{H}_7\text{COOCH}_3 + \text{H}_2\text{O}$
- (f) $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$
- (g) $\text{C}_6\text{H}_5\text{CH}_3 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
9. Complete the Prediction, Materials, Analysis, and Evaluation (2, 3) of the investigation report.

Purpose

The purpose of this investigation is to test the esterification reaction generalization.

Problem

What is the product of the reaction between benzoic acid and ethanol?

Design

Small quantities of benzoic acid and ethanol are mixed. A few drops of sulfuric acid catalyst are added. The mixture is heated and the product is tested for odour and solubility.

Evidence

The odour of cherries is observed.

The product has low solubility in water.

10. Bees build honeycomb cells from beeswax. Qualitative chemical analysis indicates that beeswax is an ester formed from mainly C_{26} and C_{28} straight-chain carboxylic acids and C_{30} and C_{32} straight-chain primary alcohols.
- (a) Write a molecular formula equation for the formation of beeswax from the C_{26} carboxylic acid and the C_{32} alcohol.
- (b) Use a molecular formula equation to represent the synthesis of beeswax from the C_{28} carboxylic acid and the C_{30} alcohol.
11. Use the information in this section and from your own research to continue gathering perspective statements concerning the statement that we should be saving more fossil fuels for petrochemical use in the future.

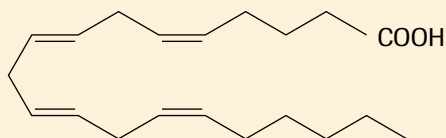
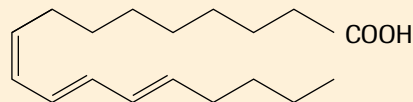
Extension

12. Tannic acid, originally obtained from the wood and bark of certain trees, has for centuries been used to “tan” leather.
- (a) Give the structural formula for tannic acid.
- (b) What effect does tannic acid have on animal hides? Explain your answer with reference to the chemical reactions that take place.

www.science.nelson.com



13. Transfats are formed when glycerol reacts with a carboxylic acid that has at least one double bond with a *trans* orientation. In a *trans* orientation, the hydrogen atoms are across the double bond from one another (compared to a *cis* orientation, where the hydrogens are on the same side of the double bond).
- (a) Identify the number of *cis* and *trans* orientations found in the following two carboxylic acids. (See *cis* and *trans* isomers on page 423.)



- (b) Transfats have been removed from most foods. What is the issue?

www.science.nelson.com



Polymerization Reactions— Monomers and Polymers

10.5

If you take a look around you, you will likely find that you are surrounded by plastic products of many shapes and sizes. They may include pens, buttons, buckles, and parts of your shoes, chair, and lamp. There are plastic components in your calculator, telephone, computer, sporting equipment, and even the building in which you live. What are plastics and what makes them such desirable and versatile materials?

Plastics belong to a group of substances called **polymers**: large molecules made by linking together many smaller molecules, called **monomers**, much like paper clips in a long chain. Different types of small molecules form links in different ways, by either addition or condensation reactions. The types of small units and linkages can be manipulated to produce materials with desired properties such as strength, flexibility, high or low density, transparency, and chemical stability. As consumer needs change, new polymers are designed and manufactured.

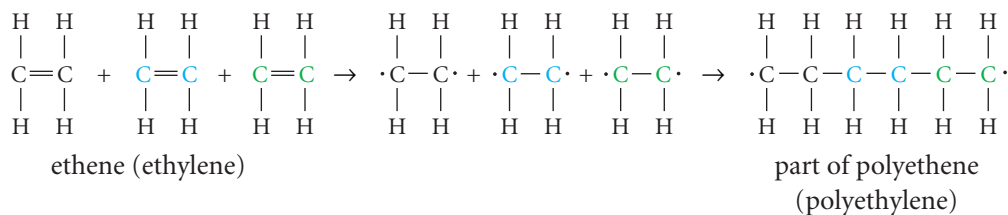
Plastics are synthetic polymers, but many natural polymers have similar properties recognized since early times. Amber from tree sap, and tortoise shell, for example, can be processed and fashioned into jewellery or ornaments. Rubber and cotton are plant polymers, and wool and silk are animal polymers that have been shaped and spun into useful forms. In fact, our own cells manufacture several types of polymers—molecules so large and varied that they make us the unique individuals we are. Proteins and carbohydrates are all very different natural polymers.

Polymerization is the formation of polymers from the reaction of monomer subunits. These compounds have long existed in nature but were only synthesized by technological processes in the 20th century. They have molar masses up to millions of grams per mole.

Addition Polymers



Many plastics are produced by the polymerization of alkenes. For example, polyethene (polyethylene) is made by polymerizing ethene molecules in a reaction known as **addition polymerization**. Polyethylene is used to make plastic insulation for wires, and containers such as plastic milk bottles (**Figure 1**), refrigerator dishes, and laboratory wash bottles. Addition polymers are formed when monomer units join each other in a process that involves the rearranging of electrons in double or triple bonds in the monomer. The polymer is the only product formed.



The monomers form dimers (from two monomers) and trimers (from three monomers), and continue reacting to form polymers (from many monomers, dimers, and trimers).

Polypropylene, polyvinyl chloride (PVC), Plexiglas, polystyrene (Styrofoam®), and natural rubber are also addition polymers. The production process for polypropylene is illustrated in **Figure 2**.

+ EXTENSION



CBC **radiONE**

QUIRKS & QUARKS

Plastics Under Pressure

Most plastics need to be heated and melted during recycling, but that same heat is damaging to the plastic, and degrades it into a less useful material. Researchers may have a solution to the problem: a new plastic that can be reformed under pressure instead of heat, and can be recycled many times. This technology could make recycling cheaper and much more environmentally friendly.

www.science.nelson.com

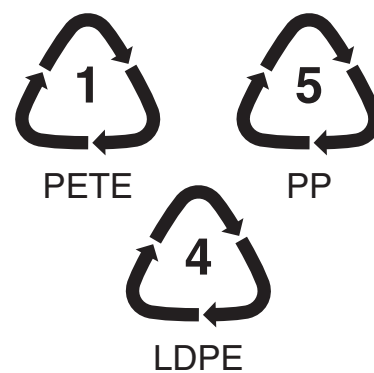


Figure 1

For recycling purposes, plastics (especially containers) are coded with a symbol for the type of plastic incorporated.

1. polyethylene terephthalate (PETE)
2. high-density polyethylene (HDPE)
3. polyvinyl chloride (PVC)
4. low-density polyethylene (LDPE)
5. polypropylene (PP)
6. polystyrene (PS)
7. other or mixtures

Look for these symbols on plastic products and, of course, recycle the product when you are finished with it.

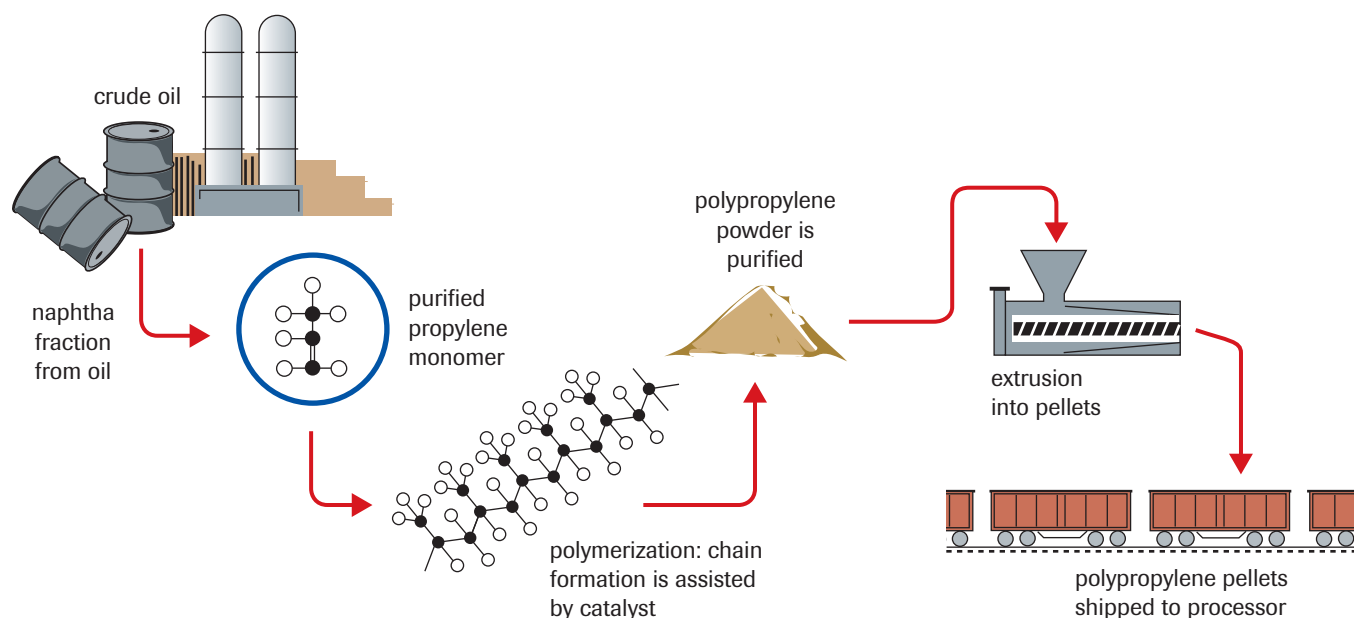


Figure 2

The production of polypropylene from crude oil



Figure 3

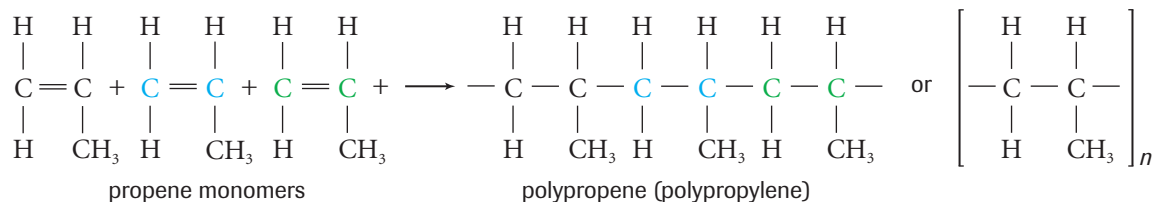
Polypropylene rope is one of many petrochemical products.

Other Addition Polymers: Carpets, Raincoats, and Insulated Cups

There are hundreds of different industrial polymers, all with different properties, and formed from different reactants.

Polypropene

Propene also undergoes addition polymerization, producing polypropene, commonly called polypropylene. You may have used polypropylene rope (**Figure 3**), or walked on polypropylene carpet.



The polymerization reaction in the formation of polypropene is very similar to that of polyethene. The propene molecule can be considered as an ethene molecule with the substitution of a methyl group in place of a hydrogen atom. The polymer formed contains a long carbon chain, with methyl groups attached to every other carbon atom in the chain.

Polyvinyl Chloride

Ethene molecules with other substituted groups produce other polymers. For example, polyvinyl chloride, commonly known as PVC, is an addition polymer of chloroethene. A common name for chloroethene is vinyl chloride. PVC is used as insulation for electrical wires and as a coating on fabrics used for raincoats and upholstery materials (Figure 4).

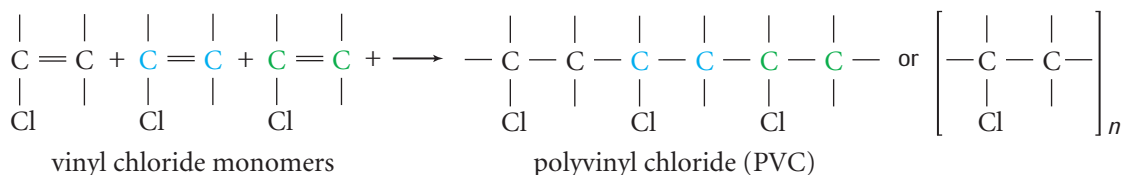
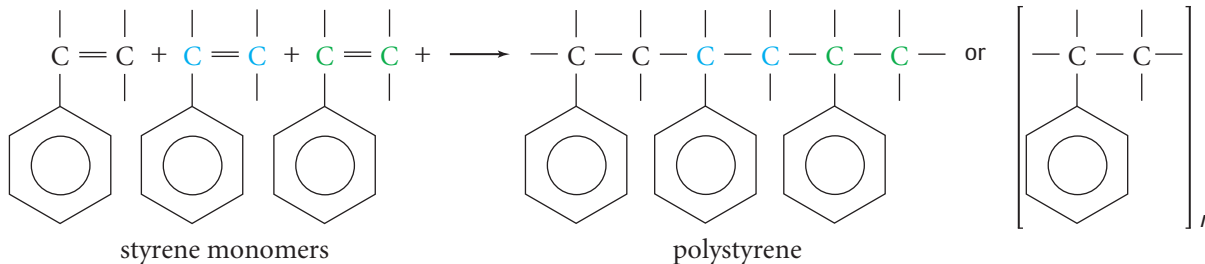


Figure 4
Polychloroethene or polyvinyl chloride is used for upholstery.

Polystyrene

When a benzene ring is attached to an ethene molecule, the molecule is vinyl benzene, commonly called styrene. An addition polymer of styrene is polystyrene, often used to make cups and containers. Look for the recycle symbol with a 6 and PS.



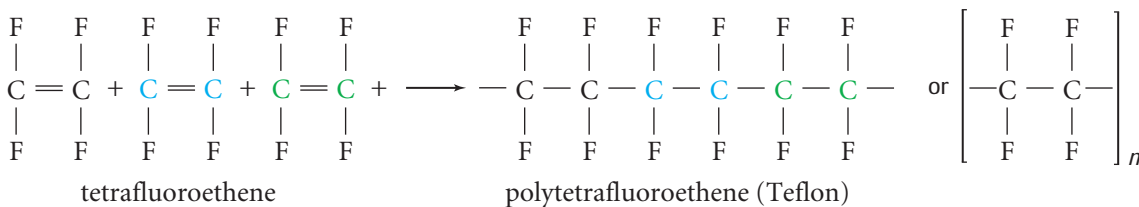
Teflon

Teflon® is the common name for an addition polymer with nonstick properties that are much desired in cookware (Figure 5).

The monomer used to synthesize Teflon is the simple molecule tetrafluoroethene, $\text{F}_2\text{C}=\text{CF}_2$, an ethene molecule in which all hydrogen atoms are replaced with fluorine atoms. The absence of carbon–hydrogen bonds and the presence of the very strong carbon–fluorine bonds make Teflon highly unreactive with almost all reagents. It is this unreactivity that allows it to be in contact with foods at relatively high temperatures without “sticking.” The inert (unreactive) nature of Teflon makes it a very useful polymer in a wide variety of applications. There is, however, some controversy about its safety, as you will discover in the following Web Activity.



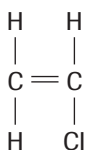
Figure 5
The invention of Teflon has made life easier in many ways.



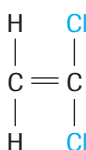
DID YOU KNOW?

Addition Monomers

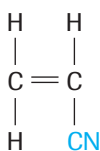
Ethene and its double-bonded derivatives are monomers for polymers with a wide variety of properties. Some of these monomers include:



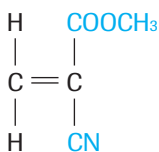
monomer of PVC



monomer of Saran™ wrap



monomer of acrylic



monomer of instant glue

WWW WEB Activity

Web Quest—Teflon: Healthy or Hazardous?

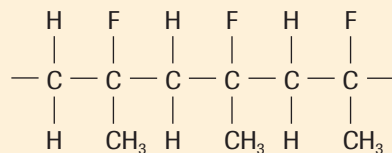
Cooks used to coat pots and pans with butter or oil to keep food from sticking, but the result was greasy high-fat food. The invention of Teflon®, a non-stick cooking surface, changed all this. Recently, concern has been growing regarding the possibility that Teflon® releases toxic chemicals if it gets too hot. Research the pros and cons of Teflon®, and decide for yourself if the risks are worth the benefits.

www.science.nelson.com 

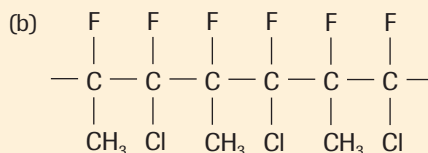
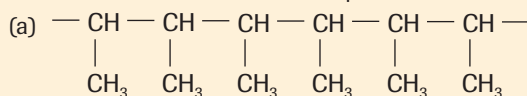
Practice

1. Draw a structural formula of three repeating units of
 - (a) a polymer of 1-butene
 - (b) a polymer of vinyl fluoride
 - (c) a polymer of chlorofluoroethene
 - (d) Predict the properties of the polymer in (c) in terms of solubility in organic solvents, rigidity, and resistance to heating.

2. Draw a structural formula of the monomer of the following polymer:



3. What monomer could be used to produce each of these polymers?



4. What functional group(s), if any, must be present in a monomer that undergoes an addition polymerization reaction?
5. Addition polymers may be produced from two different monomers, called co-monomers. Saran™, the polymer used in a brand of food wrap, is made from the monomers vinyl chloride and 1,1-dichloroethene. Draw structural formulas for each monomer, and for three repeating units of the polymer, with alternating co-monomers.
6.
 - (a) What are the typical properties of a plastic?
 - (b) What types of bonding would you expect to find within and between the long polymer molecules?
 - (c) Explain the properties of plastics by referring to their bonding.
7. Polymerization is a term used for a crude-oil refining process that converts small alkenes into gasoline-sized molecules. The polymerization process is controlled to produce dimers and trimers only (not large polymers), using phosphoric acid as a catalyst. Provide a structural formula equation for the reaction of
 - (a) three molecules of ethene
 - (b) propene and 1-butene
 - (c) 1-butene and 2-butene
8. Find out from your community recycling facility what types of plastic products are accepted for recycling in your area. If there are some plastics that are not accepted, find out the reason. Summarize your findings in a well-organized table.



Case Study—Recycling Plastics

Much of the plastic we use today is collected. We sometimes think of collecting as "recycling," but true recycling only happens if the plastic is used to make a product similar to the original one. How is recycling done? Investigate several Web sites and gather information to write a procedure for processing recycled plastic. Also, collect some pros and cons from multiple perspectives concerning the use of plastics.

www.science.nelson.com



Condensation Polymers

Some polymers, including the synthetic fibres nylon and polyester, and natural polymers like proteins and DNA, are produced by **condensation polymerization** reactions. These reactions involve the formation of a small molecule (such as H_2O , NH_3 , or HCl) from the functional groups of two different monomer molecules. The small molecule is said to be "condensed out" of the reaction. The monomer molecules bond at the site where atoms are removed from their functional groups. To form a condensation polymer, the monomer molecules must each have at least two functional groups, one on each end.

Comparing Natural with Synthetic Polymers

Research chemists have found that Nature has many well-designed molecular structures that are polymers. Many synthetic condensation polymers are structural analogs of the nutrient molecules found in foods: they have structures similar to those of lipids (fats and oils), proteins, and carbohydrates. Over the next few pages, there is a classification and description of some of these natural polymers: proteins and carbohydrate polymers. Most of us recognize these classes of compounds as categories of foodstuffs. Food labels usually list the mass of fat, protein, and carbohydrate per serving.

A synthetic compound that has a similar chemical structure to a naturally occurring substance is called a structural analog. For example, nylon is a structural analog of protein, but not a functional analog (**Figure 6**). Functional analogs are synthetic compounds that perform the same function as a naturally occurring substance but do not necessarily have similarities in chemical structure. For example, synthetic sweeteners are functional analogs of sweet carbohydrates: sugars. Chemists who study natural chemicals in order to prepare synthetic copies are called natural-product chemists.

Natural Product (food nutrient molecules)	Lipids	Proteins	Carbohydrates
	↓	↓	↓
Structural Analog (synthetic polymers)	Polyesters	Nylon	Cellulose Polymers

Lipids and Polyesters

Lipids (fats and oils) are formed by esterification reactions between glycerol (propane-1,2,3-triol) and fatty acids (long-chain carboxylic acids). Since glycerol has three hydroxyl ($-\text{OH}$) groups, three molecules of fatty acid can react with each glycerol molecule to form a tri-ester. This reaction is a condensation reaction that is not, strictly speaking, a polymerization reaction: The largest molecule formed is a tri-ester.

DID YOU KNOW?

Photodegradable Polymers

James Guillet (1927–2005), a Canadian green-chemist, used his fascination with photosynthesis to inspire his study of the photochemistry of synthetic systems. While on holidays in the Bahamas, he was disturbed by the quantity of plastic litter and realized that, with his knowledge, he could "make it disappear." Guillet registered three patents for photodegradable polymers in 1970. Unfortunately, his invention was not widely embraced. Self-interests lobbied against his "human-made plastics."

DID YOU KNOW?

Aboriginal Technologies

Aboriginal peoples used many natural materials to create useful technologies. For example, Aboriginal peoples invented the birch-bark canoe, seal-skin kayak, rawhide and willow snowshoes, and animal skin tips. The natural polymers, such as cellulose and protein, in these Aboriginal technologies have, in some cases, been replaced by synthetic polymers.

Figure 6

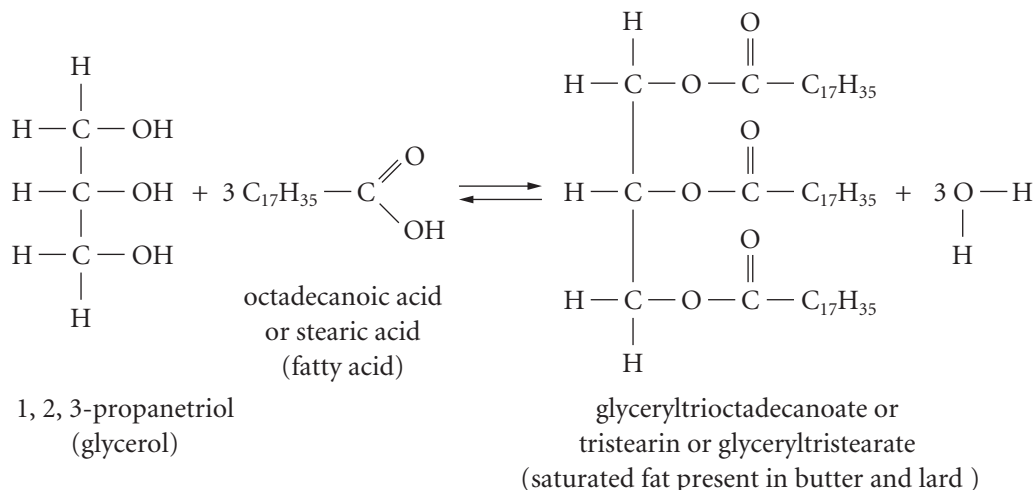
Food nutrients and their synthetic structural analogs are an example of natural product chemistry, where chemists copy and modify the structure of chemicals found in nature.

Learning Tip

You are not required to learn the names of carboxylic acids beyond ten carbons. You also do not have to name the triesters representing fats and oils. You should, however, learn the general structures of

- polyalcohols (especially propane-1,2,3-triol),
- saturated and unsaturated fatty acids, and
- triester fats and oils.

glycerol + saturated fatty acid \rightleftharpoons saturated fat present in lard and butter + water



BIOLOGY CONNECTION

Correlation versus Cause and Effect

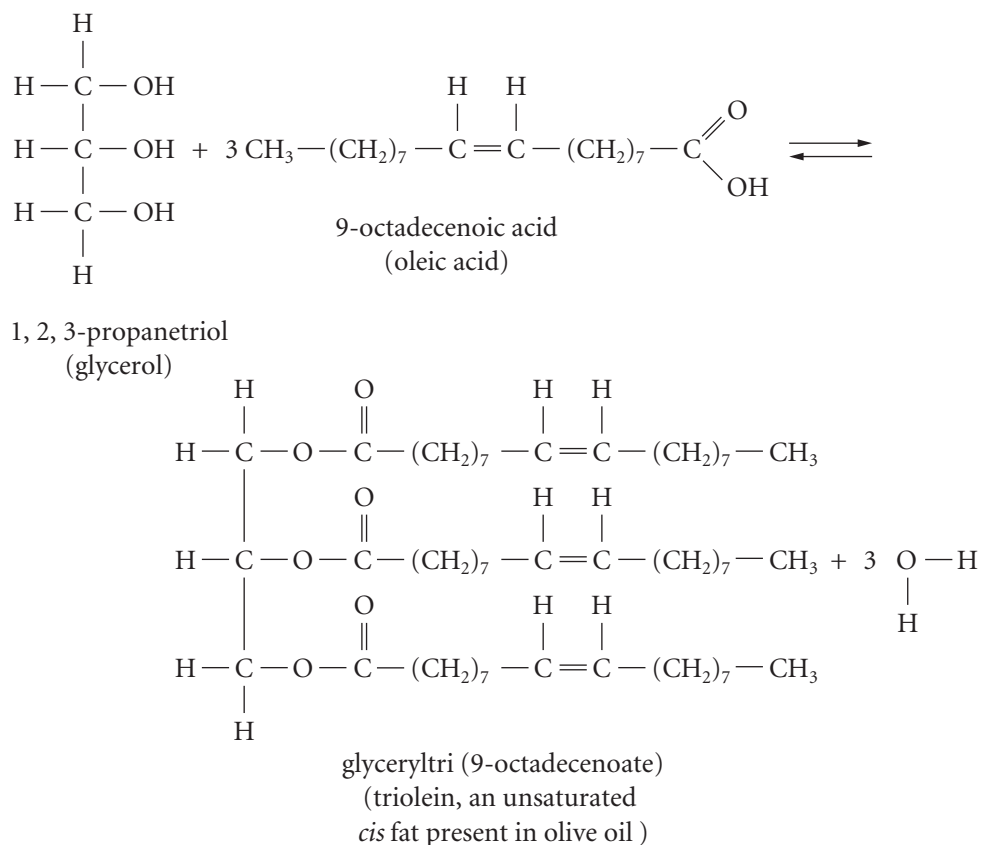
Many biochemistry studies related to food are correlational studies. These studies look for a correlation (relationship) between two variables (without being able to control all other variables—as a cause-effect study would). For example, scientists found a strong correlation between saturated fats (and transfats), and artery and heart diseases. Chemists responded with creative solutions (Figure 7).



Figure 7

Butter and margarine are examples of saturated and unsaturated fats (lipids). There are many criteria that can be used to evaluate which is the best product.

glycerol + unsaturated fatty acid \rightleftharpoons unsaturated oil present in olive oil + water



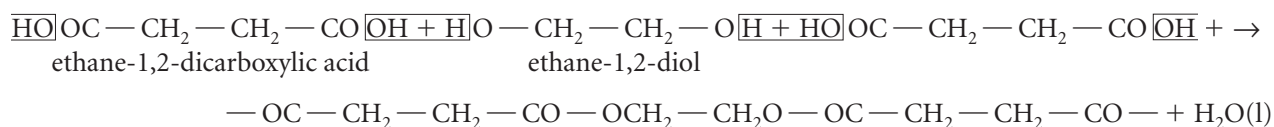
At one time, unsaturated fats were considered to be healthier in the diet than saturated fats and oils. Unsaturated oils are generally liquids at room temperature. To change the oil into a solid (such as margarine), the unsaturated fat is partially hydrogenated to remove some of the double bonds and increase the melting point. Subsequent research showed that, although unsaturated fats were healthier, the hydrogenation process created unhealthy transformed fats (called transfats or trans fatty acids). Chemist used their creative thinking to then solve the transfat problem.

Practice

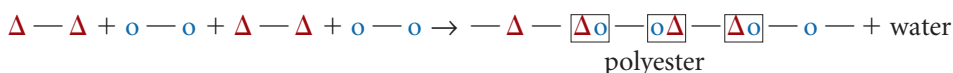
- Unsaturated lipids are generally more liquid (i.e., oils), and saturated lipids are generally more solid (i.e., fats). Create a hypothesis to explain the difference between the melting points of unsaturated versus saturated lipids.
- The fatty acid $C_{19}H_{39}COOH$ reacts with glycerol, $C_3H_5(OH)_3$, to produce peanut oil. Write a structural formula equation to communicate this reaction.
- The fatty acid $CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$ is hydrogenated. Write a structural formula equation for this chemical reaction.

Polyesters

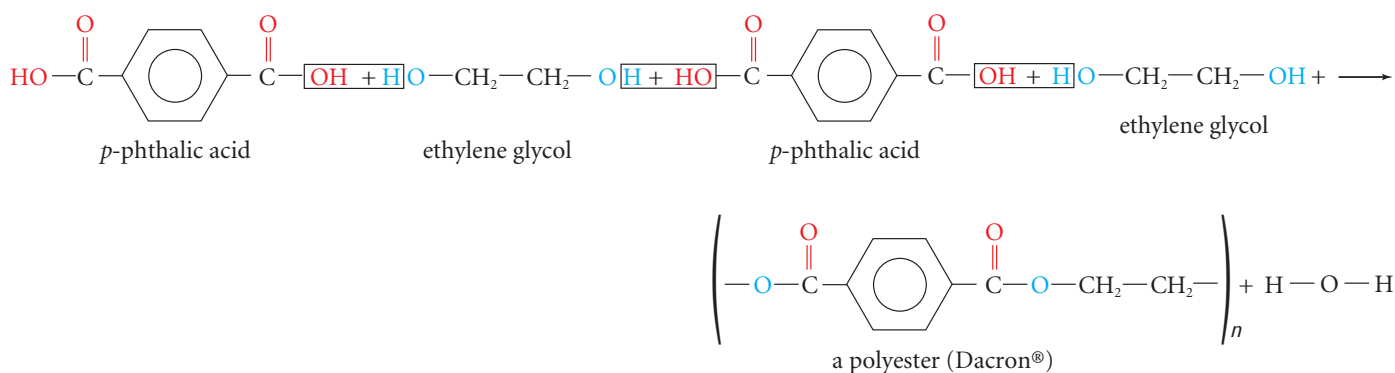
When a carboxylic acid reacts with an alcohol in an esterification reaction, a water molecule is eliminated and a single ester molecule is formed. The two reactant molecules are linked together into a single ester molecule. This esterification reaction can be repeated to form not just one ester molecule, but many esters joined in a long chain, a **polyester**. This is accomplished using a dicarboxylic acid (an acid with a carboxyl group at each end of the molecule), and a diol (an alcohol with a hydroxyl group at each end of the molecule). Ester linkages can then be formed end to end between alternating acid molecules and alcohol molecules.



If we were to depict the acid with the symbol $\Delta - \Delta$, the alcohol with $o - o$, and the ester linkage with $\boxed{o\Delta}$, we could represent the polymerization reaction like this:



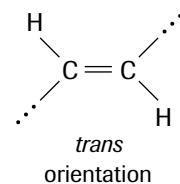
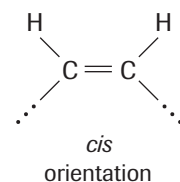
Dacron[®], another polyester, is made from *p*-phthalic acid (p-dibenzoic acid) and ethane-1,2-diol (ethylene glycol). Note the two carboxyl groups in the dicarboxylic acid and the two hydroxyl groups in the polyalcohol that start the chain reaction.



DID YOU KNOW?

Transfat

A transfat has a double bond where the hydrogen atoms are on the opposite side of the double bond. *Trans* means across, so the hydrogen atoms are across the double bond from one another.



DID YOU KNOW?

Amines and Amides

Two classes of organic compounds that are not studied in detail in this textbook are amines and amides. The simplest amines have the -NH_2 (amino) functional group, as in R-NH_2 . The simplest amides have the -CONH_2 functional group in a molecule of R-CONH_2 . A polyamide may be formed naturally or technologically by repeatedly reacting a carboxyl group with an amino group. The -CONH- group is called an amide (or peptide) linkage. Proteins and nylon are polymers that are called polyamides. Protein polymers are specifically called polypeptides.

Practice

12. Draw a structural formula equation to show a repeating unit of a condensation polymer formed from the following compounds:
 $\text{HOOC-CH}_2\text{-CH}_2\text{-COOH}$ and $\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$
13. What functional groups must be present to form a polyester?
14. How are the reactions to form fats and to form polyesters similar and different?

WEB Activity

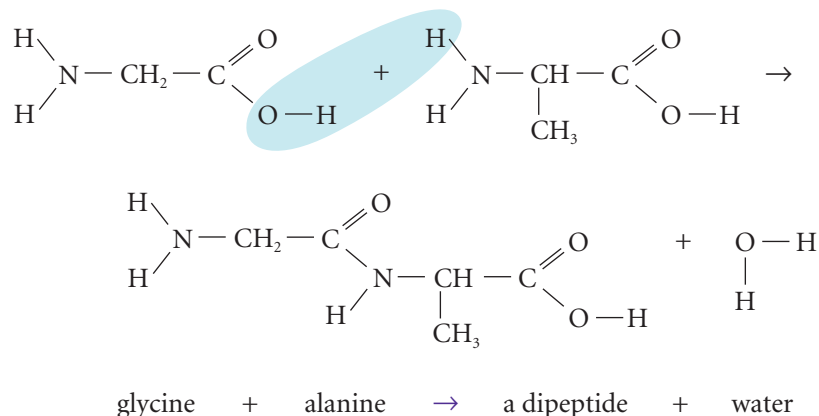
Simulation—Molecular Modelling

Molecular modelling has become more of a computer activity than a physical activity. Chemists routinely use interactive models to better understand how the shapes of compounds affect their properties. Check out some of the molecular modelling Web sites.

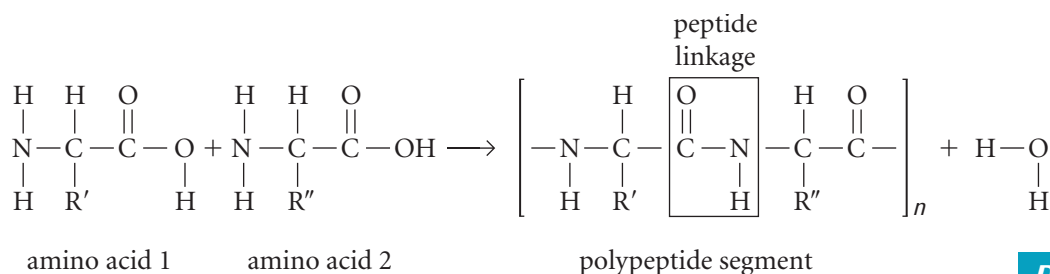
www.science.nelson.com 

Proteins and Nylon

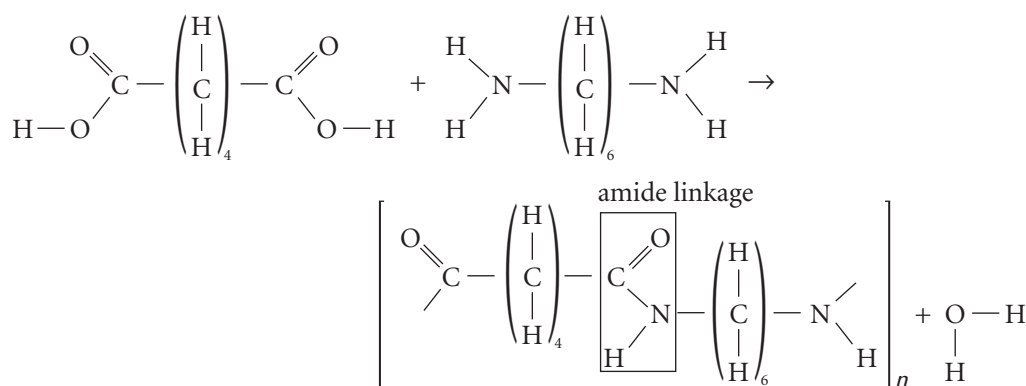
Proteins are a fundamental structural material in plants and animals. Scientists estimate that there are more than ten billion different proteins in living organisms on Earth. Remarkably, all of these proteins are constructed from only about 20 amino acids. Through a reaction that involves the carboxyl group and the amine (-NH_2) group, amino acids polymerize into peptides (short chains of amino acids) or proteins (long chains of amino acids). The condensation reaction of the amino acids glycine and alanine illustrates the formation of a dipeptide. Condensation polymerization produces a protein, with a molar mass tens of thousands to millions of grams per mole—thousands of monomers long.



The dipeptide reacts with itself or with more glycine and/or alanine. Of course, other amino acids may be present to produce an even more complex peptide. The polypeptide produced by polymerization is a protein with peptide (-CONH-) linkages. The following general equation illustrates the formation of a protein from amino acids.



Many synthetic polymers, such as nylon, form in similar ways to proteins. Nylon is a synthetic condensation polymer. For both the natural polymer (protein) and the synthetic polymer (nylon), the polymer forms by the reaction of a carboxyl group ($-\text{COOH}$) with a $-\text{NH}_2$ group with amide linkages ($-\text{CONH}-$). Polymers with amide linkages are called **polyamides**. Amide linkages in proteins are called peptide linkages and the polymers are called **polypeptides**.



1,6-hexanedioic acid + 1,6-diaminohexane \rightarrow part of the nylon 6,6 polymer chain + water



INVESTIGATION 10.5 Introduction

Report Checklist

Preparing Nylon 6,10 (Demonstration)

Nylon was considered the “miracle” fibre when it was discovered in 1935. At the time, nylon was unique because it was the first synthetic fibre produced from petrochemicals. It initiated an entire new world of manufactured fibres. In this demonstration, sebacyl chloride, $\text{COCl}(\text{CH}_2)_8\text{COCl}(\text{l})$, reacts with 1,6-diaminohexane to produce one type of nylon. For the prediction, write a condensed or line structural formula equation showing the formation of the polymer.

Purpose

The purpose of this demonstration is to use your knowledge of condensation polymerization to explain the formation of a nylon polymer.

To perform this investigation, turn to page 464.

- | | | |
|---|---|----------------------------------|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input type="radio"/> Evaluation |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Problem

How does the combination of sebacyl chloride and 1,6-diaminohexane form the polymer known as nylon 6,10?

Design

A solution of 1,6-diaminohexane is carefully poured on top of an aqueous solution of sebacyl chloride. The nylon that forms at the interface of the two layers is slowly pulled out of the mixture using forceps.

Nylon was synthesized as a substitute for silk, a natural polyamide whose structure nylon mimics. The onset of the Second World War speeded up nylon production to make parachutes, ropes, cords for aircraft tires, and even shoelaces for army boots. It is the $-\text{CONH}$ groups that make nylon such a strong fibre. When spun, the long polymer

DID YOU KNOW?

Nylon

Nylon was designed in 1935 by Wallace Carothers, a chemist who worked for DuPont; the name *nylon* is a contraction of New York and London.

DID YOU KNOW?

Pulling Fibres

When a polymer is to be made into a fibre, the polymer is first heated and melted. The molten polymer is then placed in a pressurized container and forced through a small hole, producing a long strand, which is then stretched (**Figure 8**). The process, called extrusion, causes the polymer chains to orient themselves lengthwise along the direction of the stretch. Covalent or hydrogen bonds form between the chains, giving the fibres added strength.

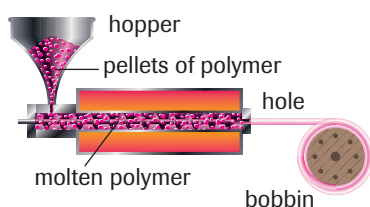
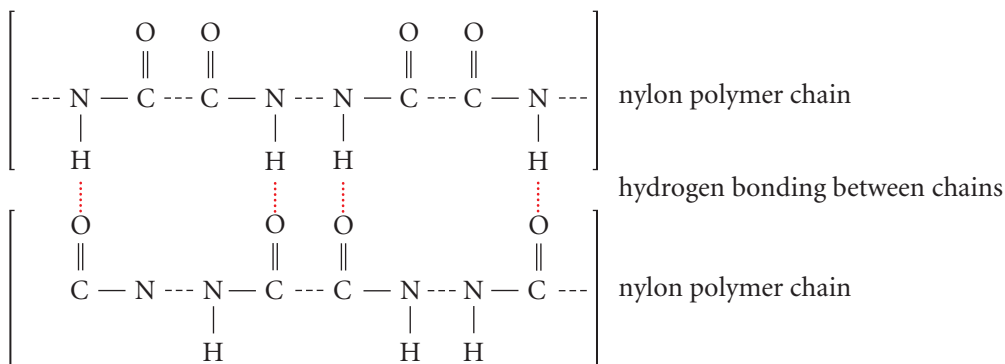


Figure 8
Making a polymer

chains line up parallel to each other, and the $-\text{CONH}$ groups form hydrogen bonds with $-\text{CONH}$ groups on adjacent chains.

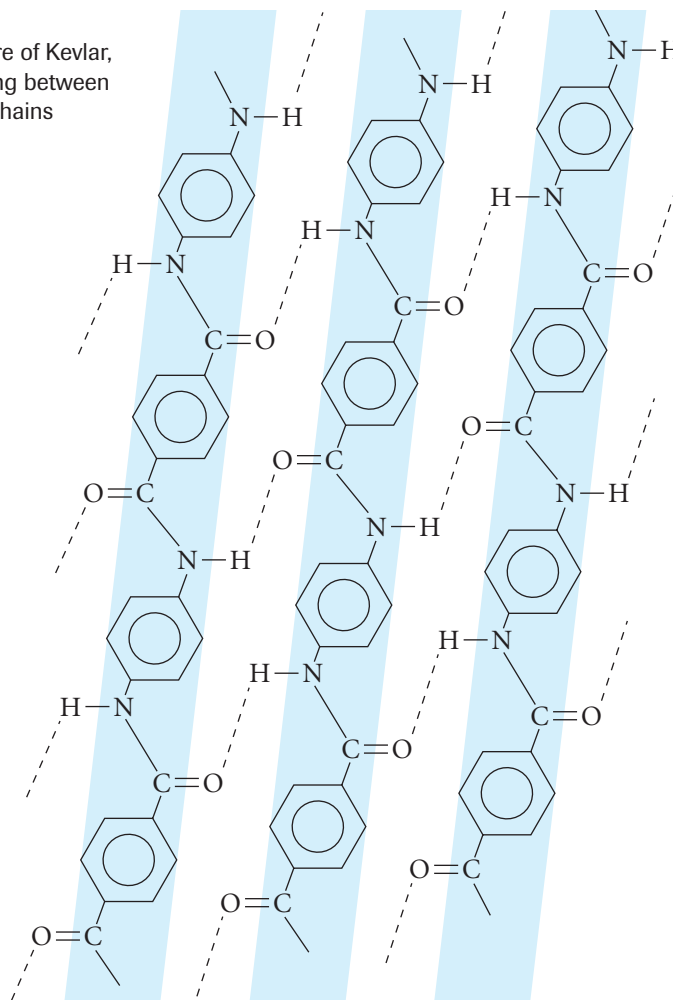


Kevlar

To illustrate the effect of hydrogen bonding in polyamides, consider a polymer with very special properties. It is stronger than steel and heat resistant, yet is lightweight enough to wear. This material is called Kevlar® (**Figure 9**) and is used to make products such as aircraft, sports equipment, protective clothing for firefighters, and bulletproof vests for police officers. What gives Kevlar these special properties? The polymer chains form a strong network of hydrogen bonds holding adjacent chains together in a sheet-like structure. The sheets are in turn stacked together to form extraordinarily strong fibres. When woven together, these fibres are resistant to damage, even that caused by a speeding bullet.

Figure 9

The chemical structure of Kevlar, with hydrogen bonding between the shaded polymer chains



DID YOU KNOW?

Paintball: A Canadian Invention

The sport of paintball was invented in Windsor, Ontario. Paintballs were first used to mark cattle for slaughter and trees for harvesting, using oil-based paints in a gelatin shell. When recreational paintball use demanded a water-based paint, the water-soluble gelatin shell was modified by adjusting the ratio of the synthetic and natural polymers used.

Practice

- What kind of polymerization does the formation of a polyamide (natural or synthetic) involve?
- Provide one example each of a natural and of a similar synthetic condensation polymer.
- Draw a structural formula representation of the nylon 6,8 monomer, formed by reacting $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ and $\text{HOOC}(\text{CH}_2)_6\text{COOH}$.



EXPLORE an issue

Issue Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Issue | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Resolution | <input checked="" type="radio"/> Evidence | <input checked="" type="radio"/> Evaluation |

Natural or Artificial Polymers?

From the time your grandparents were babies to the time you were born, diapers have been made entirely of polymers. Cotton cloth diapers were, and still are, made of cellulose, a natural polymer. Nowadays, disposable diapers, made mainly of synthetic polymers, are a popular choice. Which is better for the baby? How do they affect our environment? The typical disposable diaper has many components, mostly synthetic plastics, that are designed with properties particularly desirable for its function.

- Polyethylene film:** The outer surface is impermeable to liquids, to prevent leakage. It is treated with heat and pressure to appear cloth-like for consumer appeal.
- Hot melts:** Different types of glue are used to hold components together. Some glues are designed to bond elastic materials.
- Polypropylene sheet:** The inner surface at the leg cuffs is designed to be impermeable to liquids and soft to the touch. The main inner surface is designed to be porous, to allow liquids to flow through and be absorbed by the bulk of the diaper.

- Polyurethane, rubber, and Lycra:** Any or all of these stretchy substances may be used in the leg cuffs and the waist-band.
- Cellulose:** Basically processed wood pulp, this natural polymer is obtained from pine trees. It forms the fluffy filling of a diaper, absorbing liquids into the capillaries between the fibres.
- Polymethylacrylate:** This crystalline polymer of sodium methylacrylate absorbs water through osmosis and hydrogen bonding. The presence of sodium ions in the polymer chains draws water that is held between the chains. The presence of water results in attractions between the chains and causes the formation of a gel (**Figure 10**).

Manufacturers claim that grains of sodium polymethylacrylate can absorb up to 400 times their own mass in water. If sodium ions are present in the liquid, they act as contaminants, reducing absorbency because the attraction of water to the polymer chains is diminished. Urine always contains sodium ions, so the absorbency of diapers for urine is actually less than the advertised maximum.

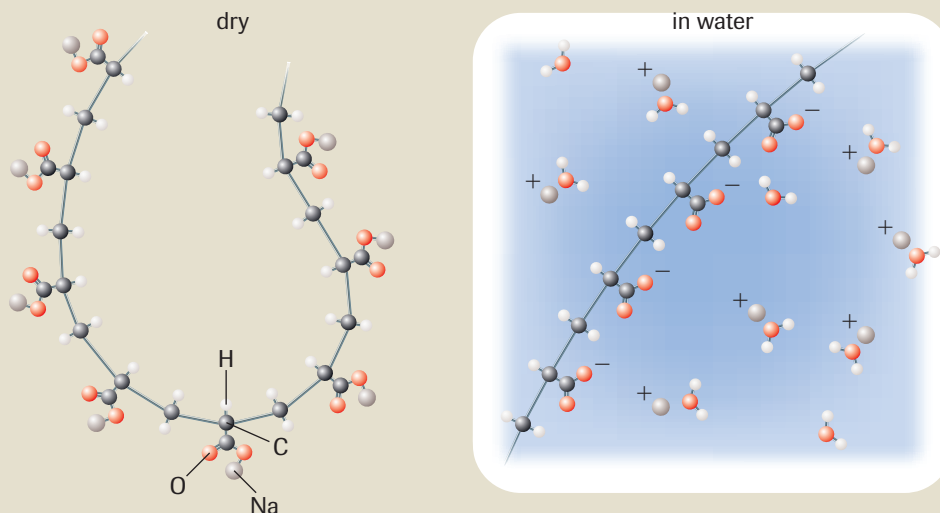


Figure 10
Polymethylacrylate

Proponents of natural products argue that disposable diapers pose a long-term threat to our environment, filling waste disposal sites with non-biodegradable plastics for future centuries. The industry has developed some new “biodegradable” materials—a combination of cellulose and synthetic polymers, for example. Some of these materials have proven too unstable to be practical, while others appear to biodegrade in several years, which gives the diapers a reasonable shelf life. The energy and raw materials needed to manufacture the huge quantity of disposable diapers used is also of concern. Diaper manufacturers and their supporters argue, however, that using the natural alternative—cloth diapers—consumes comparable amounts of energy in the laundry. In addition, the detergents used in the cleaning process are themselves non-biodegradable synthetic compounds made from petroleum products.

Issue

Do cloth diapers pose less of a threat to the environment than disposable diapers?

Resolution

Consumers should return to using cloth diapers in order to protect the environment.

Design

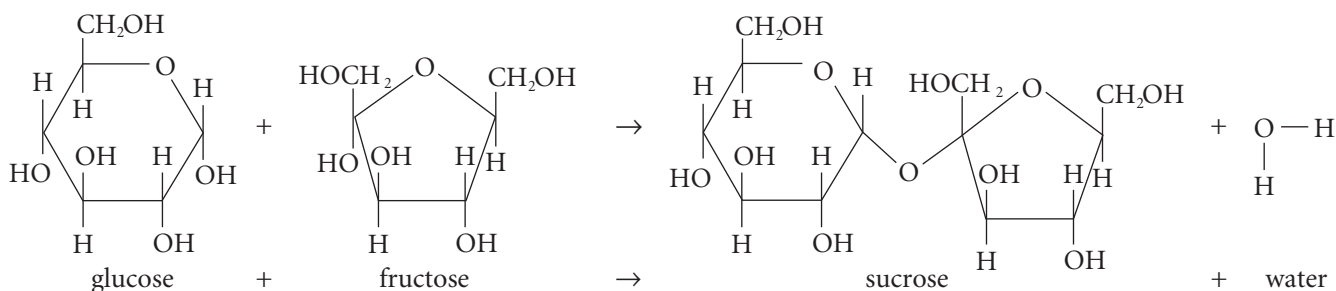
Within small groups, research the pros and cons of using cloth diapers. Gather information from a wide variety of perspectives.

www.science.nelson.com



Carbohydrates and Cellulose Acetate

The monomers of carbohydrates—compounds with the general formula $C_x(H_2O)_y$ —are simple sugar molecules. The sugar monomers undergo a condensation polymerization reaction in which a water molecule is formed, and the monomers join together to form a larger molecule. For example, the sugar monomers glucose and fructose can form sucrose (table sugar) and water. Both starch and cellulose consist of long chains of glucose molecules. Simple sugar monomers are sometimes called monosaccharides; dimers are called disaccharides; and polymers are called polysaccharides.



DID YOU KNOW?

Maple Sugar and Corn

Canadian Aboriginal peoples introduced Europeans to maple sugar. Sugar (a disaccharide) can be obtained from sugar cane (from South America) and sugar beets (from southern Alberta). The greatest contribution of Aboriginal agriculture is corn—one of the most prolific and widespread crops in human history—from which we obtain corn syrup.

Starch for Energy; Cellulose for Support

Starchy foods such as rice, wheat, corn, and potatoes provide us with readily available energy. They are also the main method of energy storage for the plants that produce them, as seeds or tubers. Starches are polymers of glucose, in either branched or unbranched chains; they are, thus, polysaccharides.

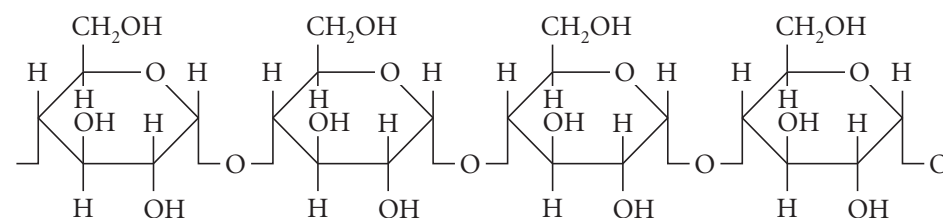
We have, in our digestive tracts, very specific enzymes. One breaks down starch. However, the human digestive system does not have an enzyme to break down the other polymer of glucose: cellulose. Cellulose is a straight-chain, rigid polysaccharide with glucose–glucose linkages different from those in starch or glycogen. It provides structure and support for plants, some of which tower tens of metres in height. Wood is mainly cellulose; cotton fibres and hemp fibres are also cellulose. Indeed, it is because cellulose is indigestible that whole grains, fruits, and vegetables are good sources of dietary fibre.

It is the different glucose–glucose linkages that make cellulose different from starch. When glucose forms a ring structure, the functional groups attached to the ring are fixed in a certain orientation above or below the ring. Our enzymes are specific to the

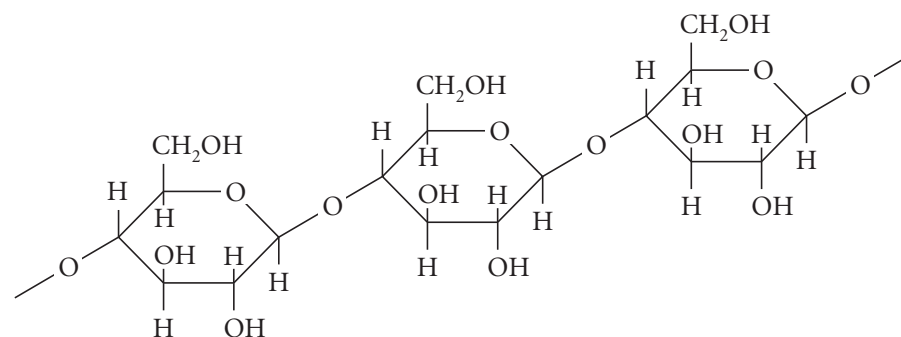
orientation of the functional groups, and cannot break the glucose–glucose linkages found in cellulose. Herbivores such as cattle, rabbits, termites, and giraffes rely on some friendly help to do their digesting: They have specially developed stomachs and intestines that house enzyme-producing bacteria or protozoa to aid in the breakdown of cellulose.

In starch, glucose monomers are added at angles that lead to a helical structure, which is maintained by hydrogen bonds between -OH groups on the same polymer chain (**Figure 11(a)**). The single chains are sufficiently small to be soluble in water. Thus, starch molecules are both mobile and soluble—important properties in their role as readily available energy storage for the organism.

In cellulose, glucose monomers are added to produce linear polymer chains that can align side by side, favouring interchain hydrogen bonding (**Figure 11(b)**). These interchain links produce a rigid structure of layered sheets of cellulose. This bulky and inflexible structure not only imparts exceptional strength to cellulose; it also renders it insoluble in water. It is, of course, essential for plants that their main building material does not readily dissolve in water.



(a) starch



(b) cellulose

Figure 11

The difference in linkages between glucose monomers gives very different three-dimensional structures.

(a) In starch, the polymer takes on a tightly coiled helical structure.

(b) In cellulose, the linked monomers can rotate, allowing formation of straight fibres.

mini Investigation *Starch and Cellulose*

Use a molecular model kit and/or a computer program to construct and/or investigate molecular models of glucose, sucrose, starch, and cellulose.

www.science.nelson.com



BIOLOGY CONNECTION

Glycogen

Animals also produce a starch-like substance, called glycogen, that performs an energy storage function. Glycogen is stored in the muscles as a ready source of energy, and also in the liver, where it helps to regulate blood glucose levels.

www.science.nelson.com



DID YOU KNOW?

Cotton—A Natural Polymer

North American Aboriginal peoples made extensive use of cotton for clothing. This technology was exported to Europe, where it contributed to starting the industrial revolution in Britain. Cotton is a natural carbohydrate (cellulose) polymer. There are now regenerated (manufactured) fibres from cellulose, such as cellulose acetate and cellulose nitrate. In 1850, long-fibre cotton comprised over 50% of Britain's exports. The mechanization and infrastructure developed for processing cotton, and the resulting capital gained, helped to fuel and shape the Industrial Revolution.

DID YOU KNOW?

The Centre of the Chocolate

Sucrose, a disaccharide, is slightly sweeter than glucose but only half as sweet as fructose. The enzyme sucrase, also called invertase, can break sucrose down into glucose and fructose—a mixture that is sweeter and more soluble than the original sucrose. The centres of some chocolates are made by shaping a solid centre of sucrose and invertase, and coating it with chocolate (Figure 12). Before long, the enzyme transforms the sucrose centre into the sweet syrupy mixture of glucose and fructose.



Figure 12

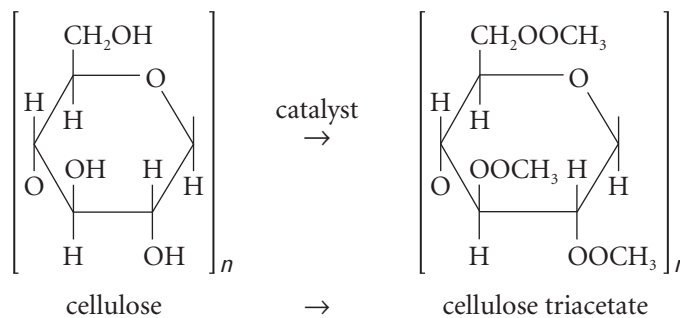
Invertase breaks sucrose down to glucose and fructose in some chocolates.

Practice

- Identify the functional groups present in a molecule of glucose and in a molecule of fructose.
- Describe several functions of polysaccharides and how their molecular structures serve these functions in plants.
- Compare the following pairs of compounds, referring to their structure and properties:
 - sugars and starch
 - starch and cellulose
- What are the distinctive features of carbohydrate molecules that, given a structural formula, would allow you to classify them as carbohydrates?
- Explain in terms of molecular structure why sugars have a relatively high melting point compared with hydrocarbons of comparable size.
- Describe, and then explain, the relative solubility of glucose, starch, and cellulose in water.

Cellulose Acetates—Structural Analogs of Polysaccharides

Chemists have researched and developed polymers that are modifications of natural polymers. These natural–synthetic polymers are called **biopolymers**. For example, starch and cellulose have been made into synthetic polymers. An example is cellulose triacetate. Cellulose, a polysaccharide, is modified by reacting it with acetic acid, $\text{CH}_3\text{COOH}(\text{l})$, and acetic anhydride, $(\text{CH}_3\text{CO})_2\text{O}(\text{l})$, with sulfuric acid as a catalyst.



Cellulose triacetate is a polymer that is used in fabrics such as permanently pleated garments, textured knits, and sportswear. There are other, similar, cellulose acetates.

WEB Activity

Case Study—Cellulose Acetate

This activity leads you through an exploration of the historical and current work done by polymer chemists to use natural polymers to produce synthetic polymers with desired characteristics and applications.

www.science.nelson.com

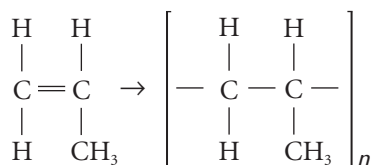


SUMMARY *Polymers—Plastics, Fibres, and Food*

Polymers are a common part of our everyday world and include natural polymers (lipids (triesters), proteins, and carbohydrates) and synthetic polymers (e.g., nylon, cellulose acetate, and polyesters). For the structural formula equations of these polymers, see previous pages.

Addition Polymers

Synthetic Addition Polymer (e.g., polypropene)



Condensation Polymers (Structural Analogs)

Polyesters

- Natural “Polyester” (e.g., butter):
glycerol + fatty acid \rightarrow fat or oil + water
e.g., $\text{C}_3\text{H}_5(\text{OH})_3 + 3 \text{C}_{17}\text{H}_{35}\text{COOH} \rightarrow \text{C}_3\text{H}_5(\text{OCC}_{17}\text{H}_{35})_3 + 3 \text{H}_2\text{O}$
- Synthetic Polyester (e.g., Dacron)
dicarboxylic acid + polyalcohol \rightarrow polyester + water
e.g., $\text{HOOC} - \text{CC}_6\text{H}_4 - \text{COOH} + \text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH} \rightarrow$
 $[-\text{OOC} - \text{C}_6\text{H}_4 - \text{COO} - \text{CH}_2 - \text{CH}_2 -]_n + n \text{H}_2\text{O}$

Polyamides

- Natural (proteins; polypeptides):
amino acid + amino acid + ... \rightarrow protein + water
e.g., $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH} + \text{H}_2\text{N} - \text{CH}(\text{CH}_3) - \text{COOH} \rightarrow$
 $[-\text{NH} - \text{CH}_2 - \text{CONH} - \text{CH}(\text{CH}_3) - \text{CO}-]_n + n \text{H}_2\text{O}$
- Synthetic (e.g., nylon 6,6):
dicarboxylic acid + di-amine \rightarrow nylon + water
e.g., $\text{HOOC} - (\text{CH}_2)_4 - \text{COOH} + \text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2 \rightarrow$
 $[-\text{OC} - (\text{CH}_2)_4 - \text{CON} - (\text{CH}_2)_6 - \text{NH}-]_n + n \text{H}_2\text{O}$

Polysaccharides

- Natural (e.g., starch):
glucose + glucose \rightarrow starch + water
glucose + glucose \rightarrow cellulose + water
(The glucose molecules that polymerize to produce starch or cellulose have slightly different stereochemical formulas.)
 $\text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow [-\text{C}_6\text{H}_{10}\text{O}_5-]_n + n \text{H}_2\text{O}$
- Synthetic (e.g., cellulose triacetate):
cellulose + acetic acid + acetic anhydride \rightarrow cellulose acetate + ...
 $[-\text{C}_6\text{H}_{10}\text{O}_5-]_n + \text{CH}_3\text{COOH} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow [-\text{C}_6\text{H}_7\text{O}_5(\text{OCH}_3)_3-]_n + \dots$

Learning Tip

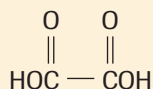
Try to equate the classification of condensation polymers with the three food groups when organizing your knowledge of polymers:

- polyesters include **lipids** and polyester fabrics
- polyamides include **proteins** and polyamide fabrics
- polysaccharides include **carbohydrates** and, for example, cellulose acetate.

Chemists create classification systems to help them organize their knowledge. Use the same approach to your advantage.

Section 10.5 Questions

1. Teflon®, made from tetrafluoroethene monomer units, is a polymer that provides a non-stick surface on cooking utensils. Write a structural formula equation to represent the formation of polytetrafluoroethene.
2. Polyvinyl chloride, or PVC plastic, has numerous applications. Write a structural formula equation to represent the polymerization of chloroethene (vinyl chloride).
3. Using a molecular model kit, construct models of the following monomers and polymers:
 - (a) starch
 - (b) polyvinyl chloride
 - (c) nylon
 - (d) polypropene
 - (e) a polyester
 - (f) cellulose acetate
4. As with most consumer products, the use of polyethylene has benefits and problems. What are some beneficial uses of polyethylene and what problems result from these uses? Suggest alternative substances for each application.
5. Use the information in this section and from your own research to continue gathering perspective statements concerning the statement that we should be saving more fossil fuels for petrochemical use in the future.
6. The first nylon product that was introduced to the public, in 1937, was a nylon toothbrush called Dr. West's Miracle-Tuft toothbrush. Earlier toothbrush bristles were made of hair from animals such as boar. From your knowledge of the properties of nylon, suggest some advantages and drawbacks of nylon toothbrushes compared with their natural counterparts.
7. Oxalic acid is a dicarboxylic acid found in rhubarb and spinach. Its structure is shown below.



Draw three repeating units of the condensation polymer made from oxalic acid and ethan-1,2-diol.

8. What is the synthetic polymer analog of each of the following foods?
 - (a) pasta
 - (b) meat
 - (c) butter
9. Suppose that two new polymers have been designed and synthesized for use as potting material for plants.
 - (a) List and describe the properties of an ideal polymer to be used to hold and supply water and nutrients for a plant over an extended period of time.
 - (b) Design an experiment to test and compare the two polymers for the properties you listed. Write a brief description of the procedures followed, and possible interpretations of experimental results.
10. When we purchase a product, we may want to consider not only the source of its components, but also the requirements for its use and maintenance. In your opinion, how valid is the use of the terms "organic," "natural," and "chemical" in the promotion of consumer goods?
11. Starch and cellulose have the same caloric value when burned, but very different food values when eaten by humans. Explain.
12. Explain why the sugars in a maple tree dissolve in the sap but the wood in the tree trunk does not.
13. Many consumer products are available in natural or synthetic materials: paper or plastic shopping bags, wood or plastic lawn furniture, cotton or polyester clothing. Choose one consumer product and list the advantages and disadvantages of the natural and synthetic alternatives, with particular reference to structure and properties of the material used as it relates to the function of the product.
14. Classify the type of polymerization for each of the following polymers:
 - (a) polyethenes
 - (b) polyesters
 - (c) polyamides
 - (d) polysaccharides
15. Research or use what you know to write a combination of a word, molecular formula, and structural formula equation for each of the following chemical transformations:
 - (a) starch (from grain) to glucose to ethanol
 - (b) cellulose (from aspen trees) to glucose to methanol

Extension

16. Alkyd (oil-based) paint is a polyester formed by reacting glycerol ($\text{CH}_2\text{OHCHOHCH}_2\text{OH}$) with 1,2-benzenedicarboxylic acid ($\text{C}_6\text{H}_4(\text{COOH})_2$). Communicate this reaction using a structural formula equation.
17. What functional group(s), if any, must be present in a monomer of a condensation polymer?
18. In an attempt to reduce body weight, many Canadians are considering low-carbohydrate or low-sugar diets. Based on your knowledge of the chemistry of carbohydrates and sugars, comment on which of these diets might be more effective.
19. Natural rubber is made from resin produced by the rubber tree, *Hevea brasiliensis*.
 - (a) Research the history of the use of rubber by Aboriginal peoples long before Europeans came to the Americas.
 - (b) Research the commercial invention, production, and use of natural rubber, and the circumstances that stimulated the development of synthetic rubber.
 - (c) Write a brief report on your findings.
20. Raymond Lemieux, from Lac La Biche, Alberta, was the first chemist to artificially synthesize sucrose (in 1953). Consult the biographical information of Lemieux. Describe his interest in science and one of his other accomplishments (other than the synthesis of sucrose).

www.science.nelson.com



www.science.nelson.com





INVESTIGATION 10.1

Substitution and Addition Reactions

Substitution and addition reactions are two common classes of organic reactions. Substitution reactions are common to saturated hydrocarbons. Addition reactions are common to unsaturated (alkene and alkyne) hydrocarbons. In general, substitution reactions are slower and addition reactions are faster.

Purpose

The purpose of this investigation is to test the generalization that addition reactions are faster than substitution reaction.

Problem

Which compound reacts faster with aqueous bromine: cyclohexane or cyclohexene?

Design

Aqueous bromine is added to samples of cyclohexane and cyclohexene in both the presence and absence of light.

Materials

lab apron
 eye protection
 4 small test tubes with stoppers
 test tube rack (or beaker)
 aluminium foil (approx. 10 cm × 10 cm)
 dropper bottles of
 cyclohexane
 cyclohexene
 aqueous bromine



Cyclohexane and cyclohexene are flammable. Work in a well-ventilated area. Keep away from sparks or flames.



Bromine is toxic and corrosive. Avoid skin and eye contact. Wash hands thoroughly when finished.



Report Checklist

- | | | |
|---|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 2, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Procedure

1. Add 20 drops of cyclohexane to each of two test tubes and stopper immediately.
2. Cover one of the test tubes up to the rim with aluminium foil.
3. Repeat steps 1 and 2 using cyclohexene and two more test tubes.
4. For each of the four test tubes: remove the stopper briefly to add 10 drops of aqueous bromine.
5. Placing a thumb or finger on the stopper, briefly shake each test tube.
6. Record your observations immediately and again after several minutes. (You will need to momentarily slide the covered test tubes out of the foil to observe.)
7. Dispose of the contents of all test tubes into labelled waste containers.

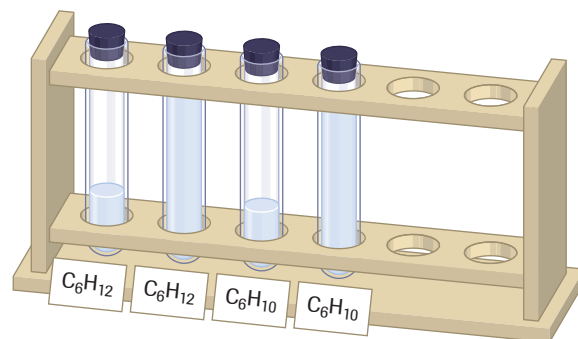


Figure 1

Set-up for reactions of cyclohexane and cyclohexene with and without light



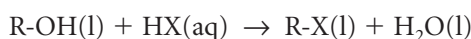
INVESTIGATION 10.2

Report Checklist

- | | | |
|---|--|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input checked="" type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (1, 2, 3) |
| <input checked="" type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Isomers of Butanol

Organic halides have many uses, but they are not commonly found in nature. Organic halides must, therefore, be synthesized from other compounds. On an industrial scale, organic halides are produced by addition and substitution reactions of hydrocarbons. A common laboratory-scale process is the halogenation of alcohols in which the hydroxyl group of the alcohol is replaced by a halogen. This reaction requires the presence of a strong acid that contains a halogen, such as hydrochloric acid.



Organic halides have much lower solubilities in water compared with their corresponding alcohols.

Purpose

The purpose of this investigation is to test a personal hypothesis about the relative reactivity of the alcohol isomers of butan-1-ol.

Problem

What is the difference in reactivity, if any, of the alcohol isomers of butan-1-ol with concentrated hydrochloric acid?

Design

Samples of butan-1-ol, butan-2-ol, and 2-methylpropan-2-ol are mixed with concentrated hydrochloric acid. Evidence of reaction is obtained by looking for a low-solubility organic halide product (cloudy mixture).



Concentrated hydrochloric acid is corrosive and the vapour is very irritating to the respiratory system. Avoid contact with skin, eyes, clothing, and the lab bench. Wear eye protection, gloves, and a laboratory apron.



All three alcohols are highly flammable. Do not use near an open flame.

Procedure

1. Add two drops each of butan-1-ol, butan-2-ol, and 2-methylpropan-2-ol into separate small labelled test tubes in a test-tube rack.
2. In the fume hood, add 10 drops of concentrated HCl(aq) to each of the three isomers in the test tubes.
3. Stopper and swirl each of the test tubes gently and cautiously.
4. Back at your laboratory bench, observe the test tubes over a period of a few minutes. Look for cloudiness in the water layer—an indication of the formation of an organic halide.
5. Dispose of the contents of all test tubes in the fume hood into a labelled waste container.

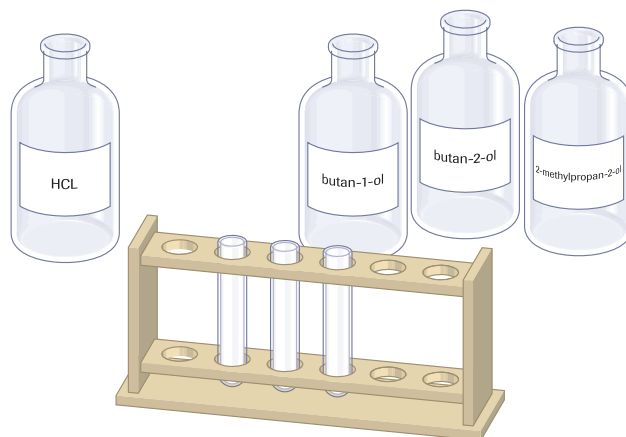


Figure 2

Set-up for testing the reactivity of three butanol isomers



INVESTIGATION 10.3

Synthesis of an Ester

Purpose

The purpose of this investigation is to use the esterification generalization and diagnostic tests to synthesize and observe the properties of two esters.

Problem

What are some physical properties of ethyl ethanoate (ethyl acetate) and methyl salicylate?

Design

The esters are produced by the reaction of appropriate alcohols and acids, using sulfuric acid as a catalyst. The solubility and the odours of the esters are observed.

Materials

lab apron
 eye protection
 dropper bottles of ethanol, methanol, glacial ethanoic (acetic) acid, and concentrated sulfuric acid
 vial of salicylic acid (2-hydroxybenzoic acid)
 two 25 × 250 mm test tubes
 250 mL beaker or polystyrene cup
 two 50 mL beakers
 two 10 mL graduated cylinders
 laboratory scoop
 balance
 hot plate or hot tap water
 thermometer
 ring stand with test tube clamp



Concentrated ethanoic and sulfuric acids are dangerously corrosive. Protect your eyes, and do not allow the acids to come into contact with skin, clothes, or lab desks.



Both methanol and ethanol are flammable; do not use near an open flame.



Excessive inhalation of the products may cause headaches or dizziness. Use your hand to waft the odour from the beaker toward your nose. The laboratory should be well ventilated.

Procedure

1. Add about 5 mL of ethanol and 6 mL of ethanoic acid to one of the test tubes.
2. Ask your teacher to add 8 to 10 drops of concentrated sulfuric acid to the mixture.

Report Checklist

- | | | |
|----------------------------------|---|---|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input checked="" type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input type="radio"/> Evaluation |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

3. Set up a hot water bath using the 250 mL beaker. (The temperature of the water should not exceed 70 °C.)
4. Clamp the test tube so that the reaction mixture is completely immersed in hot water (**Figure 3**).
5. As a safety precaution to block any eruption of the volatile mixture, invert a 50 mL beaker above the end of the test tube (**Figure 3**).
6. After the reaction mixture heats for about 10 min, rinse the second 50 mL beaker with cold tap water and add about 30 mL of cold water to this beaker.
7. Cool the test tube by running cold tap water on the outside of the tube.
8. Pour the contents of the test tube into the cold water in the 50 mL beaker. Observe and smell the mixture carefully, using the correct technique for smelling chemicals.
9. Repeat steps 1 to 7, using 3.0 g of salicylic acid, 10 mL of methanol, and 20 drops of sulfuric acid.
10. Dispose of all mixtures into the sink with lots of cold running water.

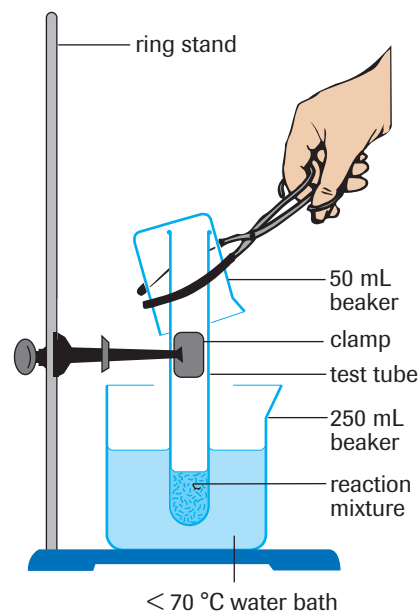


Figure 3
Set-up for synthesis of an ester



INVESTIGATION 10.4

Report Checklist

- | | | |
|---|--|--|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input type="radio"/> Analysis |
| <input type="radio"/> Problem | <input checked="" type="radio"/> Materials | <input checked="" type="radio"/> Evaluation (2, 3) |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Testing with Models

Molecular models, either physical or electronic, are based on empirically known molecular structures. These models can then be considered as representing evidence collected in a variety of experiments.

Purpose

The purpose of this investigation is to test stereochemical formula (see Chapter 3) equations by using molecular models.

Problem

What are the stereochemical formula equations for the following reactions?

- methane undergoes complete combustion
- ethane is cracked into ethene
- propane reacts with chlorine
- but-2-ene reacts with water
- ethanol eliminates water to produce ethene

- chloropropane undergoes an elimination reaction with hydroxide ions to produce propene, a chloride ion, and water
- ethanol reacts with methanoic acid

Design

Physical or electronic models of the reactants and products for each reaction are constructed. The bonding and shapes of the molecules from the models are compared with the predictions.



INVESTIGATION 10.5

Report Checklist

- | | | |
|---|---|----------------------------------|
| <input type="radio"/> Purpose | <input type="radio"/> Design | <input type="radio"/> Analysis |
| <input type="radio"/> Problem | <input type="radio"/> Materials | <input type="radio"/> Evaluation |
| <input type="radio"/> Hypothesis | <input type="radio"/> Procedure | |
| <input checked="" type="radio"/> Prediction | <input checked="" type="radio"/> Evidence | |

Preparing Nylon 6,10 (Demonstration)

Nylon was considered the “miracle” fibre when it was discovered in 1935. At the time, nylon was unique because it was the first synthetic fibre produced from petrochemicals. It initiated an entire new world of manufactured fibres. In this demonstration, sebacyl chloride, $\text{COCl}(\text{CH}_2)_8\text{COCl}(\text{l})$, reacts with 1,6-diaminohexane to produce one type of nylon. For the prediction, write a condensed or line structural formula equation showing the formation of the polymer.

Purpose

The purpose of this demonstration is to use your knowledge of condensation polymerization to explain the formation of a nylon polymer.

Problem

How does the combination of sebacyl chloride and 1,6-diaminohexane form the polymer known as nylon 6,10?

Design

A solution of 1,6-diaminohexane is carefully poured on top of an aqueous solution of sebacyl chloride. The nylon that forms at the interface of the two layers is slowly pulled out of the mixture using forceps.



The reactants and solvent used are irritants. Use a fume hood for this demonstration.

Outcomes

Knowledge

- identify and describe significant organic compounds in daily life, demonstrating generalized knowledge of their origins and applications (all sections)
- name and draw structural, condensed structural and line diagrams and formulas for organic halides, alcohols, carboxylic acids, and esters (all sections)
- identify types of compounds from their functional groups, given the structural formula and name the functional groups (10.2, 10.3, 10.4)
- compare, both within a homologous series and between compounds with different functional groups, the boiling points and solubility of examples of alcohols and carboxylic acids (10.3, 10.4)
- define, illustrate, and provide examples of simple addition, substitution, elimination, and esterification (condensation) reactions (10.2, 10.3, 10.4, 10.5)
- predict products and write and interpret balanced equations for the above reactions (10.2, 10.3, 10.4, 10.5)
- define, illustrate, and give examples of monomers, polymers, and polymerization in living and non-living systems (10.5)
- relate the reactions described above to major reactions for producing economically important compounds from fossil fuels (all sections)

STS

- illustrate how science and technology are developed to meet societal needs and expand human capabilities (all sections)
- describe interactions of science, technology, and society (all sections)
- illustrate how science and technology have both intended and unintended consequences (10.5)

Skills

- initiating and planning: predict the ester formed from an alcohol and an organic acid (10.4); describe procedures for safe handling, storing and disposal of materials used in the laboratory, with reference to labelling information (10.2, 10.3, 10.4, 10.5); design an experiment to compare the properties of organic to inorganic compounds (10.4)
- performing and recording: build molecular models depicting the structures of selected organic and inorganic compounds (10.4); perform an experiment to investigate the reactions of organic compounds (10.2, 10.3, 10.4, 10.5)
- analyzing and interpreting: follow appropriate IUPAC guidelines in writing the names and formulas of organic compounds (all sections); compile and organize data to compare the properties of structural isomers (10.3); interpret results of a test to distinguish between a saturated and an unsaturated aliphatic using aqueous bromine solution (10.2); use appropriate chemical symbols and nomenclature in writing organic chemical reactions (all sections); use models to illustrate polymerization (10.5)

- work cooperatively in addressing problems and apply the skills and conventions of science in communicating information and ideas and in assessing results (10.3, 10.4, 10.5)

Key Terms

10.2

hydrocarbon derivative
organic halide
functional group
addition reaction
substitution reaction

10.3

alcohol
hydroxyl group
elimination reaction

10.4

carboxylic acid
carboxyl group

condensation reaction
ester
esterification reaction
ester functional group

10.5

polymer
monomer
polymerization
addition polymerization
condensation polymerization
polyester
polyamide
polypeptide

▶ **MAKE a summary**

1. Draw a map of Alberta and indicate at least one location where each of the following chemicals is produced: ethane, ethene, ethylene glycol, methanol, polyethene, polyvinyl chloride, styrene, urea. For each chemical, indicate the reaction type and illustrate the reaction with a structural formula equation.
2. Refer back to your answers to the Starting Points questions at the beginning of this chapter. How has your thinking changed?

▶ **Go To**

www.science.nelson.com



The following components are available on the Nelson Web site. Follow the links for *Nelson Chemistry Alberta 20–30*.

- an interactive Self Quiz for Chapter 10
- additional Diploma Exam-style Review questions
- illustrated Glossary
- additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

www.science.nelson.com 

DO NOT WRITE IN THIS TEXTBOOK.

Part 1

- There are arguments pro and con from a variety of perspectives for saving our fossil fuels for petrochemical production for generations to come. Which of the following statements is *not* classified correctly?
 - economic: We need the corporate profit and individual salaries now.
 - legal: It isn't right for us to be burning these irreplaceable fossil fuels.
 - ethical: This resource doesn't just belong to us; it belongs to future generations.
 - social: Families and communities need the resource development now.
- The organic compound ethane-1,2-diol is manufactured in Alberta from the primary petrochemical
 - ethene
 - propene
 - methanol
 - benzene
- The type of chemical reaction that involves breaking a carbon-hydrogen bond and replacing the hydrogen atom with another atom or group of atoms is called
 - addition
 - substitution
 - condensation
 - esterification

Use the names of these organic compounds to answer questions 4 and 5.

- gasoline additive, ethanol
- glycerol, propane-1,2,3-triol
- PVC monomer, chloroethene
- organic solvent, ethyl ethanoate
- pineapple odour, ethyl butanoate
- radiator antifreeze, ethane-1,2-diol
- wintergreen odour, methyl salicylate
- banana odour, 3-methylbutyl ethanoate
- used to manufacture acetone, propan-2-ol

4. In numerical order, the alcohols are **NR** ____, ____, ____, and ____.

5. In numerical order, the esters are **NR** ____, ____, ____, and ____.

- Chemists were initially surprised that the reaction of benzene and chlorine to form chlorobenzene and hydrogen chloride is an example of a(n)
 - addition reaction
 - elimination reaction
 - esterification reaction
 - substitution reaction
- Chemists predict, based on a generalization, that the reaction between methanol and propanoic acid produces water and
 - propanol
 - propyl methanoate
 - methyl propanoate
 - methanoic acid
- A generalization supported by laboratory evidence suggests that bromine and propene react to produce
 - 1-bromopropane
 - 2-bromopropane
 - 1,1-dibromopropane
 - 1,2-dibromopropane

There are more compounds of carbon than compounds of all other elements combined. Use this short list of carbon compounds to answer questions 9 to 12.

- | | |
|------------------|-------------------|
| 1. butanoic acid | 6. methylpropane |
| 2. butan-1-ol | 7. octan-1-ol |
| 3. ethanoic acid | 8. propanoic acid |
| 4. ethanol | 9. pentanoic acid |
| 5. hexan-1-ol | |

9. From lowest to highest, the order of boiling points of the **NR** alcohols is ____, ____, ____, and ____.

10. From lowest to highest, the order of solubility of the **NR** alcohols is ____, ____, ____, and ____.

11. From lowest to highest, the order of solubility of the acids **NR** is ____, ____, ____, and ____.

12. The two compounds that must react to form ethyl **NR** butanoate are ____ and ____.

13. The functional group, —COOH, is characteristic of

- esters
- alcohols
- aromatics
- carboxylic acids

14. Which of the following substances is an addition polymer?

- protein
- polyester
- polypropylene
- polysaccharide

Part 2

15. **Identify** the category, and draw a line structural formula, for each of the following organic compounds.
- triiodomethane
 - 1,2-difluoroethene
 - propane-1,2,3-triol
 - 2-methylpropan-2-ol
 - propanoic acid
 - methyl butanoate
 - phenol
 - 1,3-dibromobenzene
 - benzoic acid
 - ethyl benzoate
16. Complete the following word equations and draw complete structural formula equations for each of the following organic reactions.
- butane + chlorine \rightarrow
 - but-1-ene + hydrogen chloride \rightarrow
 - chloroethane + hydroxide ion \rightarrow
 - benzene + fluorine \rightarrow
 - benzoic acid + ethanol \rightarrow
 - propene + bromine \rightarrow
 - propan-1-ol + ethanoic acid \rightarrow
17. Alcohols, carboxylic acids, and esters are generally more soluble in water than the corresponding alkanes. Draw structural formulas for simple 3-carbon molecules from each of these families and **explain** why they are more soluble in water than propane.
18. **Explain** the difference between addition and condensation polymers. Your response should include

DE

- characteristics of the monomers
- products of the polymerization reaction

19. **Identify** what special precautions must be taken when working with and disposing of organic compounds.
20. Because of side reactions in organic reactions, the yield of desired product is often low, and is usually expressed as a % yield. Complete the Analysis of the investigation report.

Problem

What is the percent yield in the esterification reaction between pentanol and butanoic acid to form pentyl butanoate?

Design

An excess of pentanol reacts with a measured mass of butanoic acid in the presence of a sulfuric acid catalyst. The product is separated from the reaction mixture by fractional distillation.

Evidence

mass of butanoic acid reacted = 2.00 g
mass of pentyl butanoate provided = 1.32 g

21. **Design** an experiment to distinguish alkanes from alkenes. Assume the hydrocarbons are in the liquid phase.

22. Write IUPAC names for the following organic compounds.
- $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CHF—CH}_2\text{F}$
 - $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{OH}$
 - $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—COOH}$
 - $\text{CH}_3\text{—CH}_2\text{—COO—CH}_2\text{—CH}_3$
 - $\text{CH}_2\text{OH—CHOH—CH}_2\text{OH}$
 - $\text{CH}_3\text{—CH}_2\text{—COOH}$
 - $\text{CH}_3\text{—CH}_2\text{—COO—CH}_2\text{—CH}_2\text{—CH}_3$
 - $\text{CH}_3\text{—CHBr—CH}_2\text{—CH}_2\text{Br}$
23. Draw a line structural formula for each of the following aromatic compounds.
- 1,4-dichlorobenzene
 - benzoic acid
 - phenol
 - methyl benzoate
 - 1,2,3-tribromobenzene
 - ethyl benzoate

Use the following information to answer questions 24 to 26.

The field of polymer chemistry has blossomed since Carothers' discovery of nylon in 1935. Thousands of new polymers have now been developed, including Teflon, polystyrene, polypropylene, and polyvinyl chloride.

Polymers have been very beneficial in many ways. They have also, however, introduced problems for many societies around the world.

24. (a) **Identify** the class of synthetic polymers into which all of the named compounds (above) fall.
DE (b) Name and draw structural formulas for the monomers used to produce each of the four polymers.
(c) What feature do these monomers have in common? **Explain** how this enables polymerization to occur. **Illustrate** your explanation with a structural formula reaction equation.
25. **Explain** why the monomers used to produce condensation polymers must be bifunctional (have two functional groups).
26. **Compare** the impacts of polymers on two different societies: one urban and relatively wealthy; one rural and relatively poor. Your response should include
- a variety of perspectives
 - benefits and drawbacks of the development of synthetic polymers
 - suggestions for alternatives to synthetic polymers
 - an answer to the question: On balance, do synthetic polymers benefit humanity?
-
27. Consider the Resolution in the Exploration that began this chapter. Respond to the Resolution with the production and use of polymers in mind.

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

www.science.nelson.com



DO NOT WRITE IN THIS TEXTBOOK.

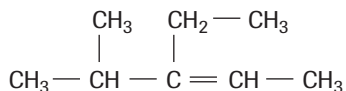
Part 1

- Alberta refines and manufactures many organic compounds. The Alberta product that is not considered an organic compound is
 - gas line antifreeze, $\text{CH}_3\text{OH}(\text{l})$
 - vinegar, $\text{CH}_3\text{COOH}(\text{aq})$
 - limestone, $\text{CaCO}_3(\text{s})$
 - natural gas, $\text{CH}_4(\text{g})$
- Which one of the following organic compounds is *least* likely obtained from a natural gas well?
 - methane
 - ethane
 - propane
 - benzene
- There are many organic compounds that are important in daily life. Match the compounds listed with the applications.

1	gasoline additive
2	plastic wrap
3	barbecue fuel
4	natural sweetener

When the common applications for propane, ethanol, sucrose, and polyethylene are listed in order, the order is __, __, __, and __.

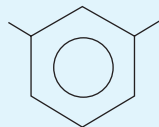
- The IUPAC name for the following possible component of gasoline is



- 2-methyl-3-ethylpent-3-ene
 - 3-ethyl-4-methylpent-2-ene
 - 2-methyl-3-ethylpent-2-ene
 - 2,3,3-trimethylpent-2-ene
- The boiling points, from smallest to largest members of an aliphatic family
 - increase
 - decrease
 - stay relatively constant
 - increase initially, and then decrease

Use this information to answer questions 6 and 7.

Xylenes are important aromatics used in a variety of applications, such as solvents and as raw materials for the production of polyester fibres, dyes, and insecticides. The structure of one particular xylene is



- The IUPAC name for this xylene is
 - 1,3-dimethylcyclohexane
 - ethylbenzene
 - 2,6-dimethylbenzene
 - 1,3-dimethylbenzene
 - A structural isomer of this xylene is
 - octane
 - ethylcyclohexane
 - ethylbenzene
 - 1,3-dimethylhex-1-ene
-
- Which one of the following technological processes is *not* used to physically separate organic compounds from a mixture?
 - solubility
 - hydrocracking
 - solvent extraction
 - fractional distillation
 - The most likely reaction between an alkene and chlorine is
 - addition
 - combustion
 - elimination
 - substitution
 - Which of the following organic reactions is most likely to produce an alkene?
 - $\text{C}_3\text{H}_6 + \text{Cl}_2 \rightarrow$
 - $\text{C}_4\text{H}_8 + \text{H}_2 \rightarrow$
 - $\text{CH}_3(\text{CH}_2)_2\text{COOH} + \text{CH}_3(\text{CH}_2)_2\text{OH} \rightarrow$
 - $\text{CH}_2\text{ClCH}_3 + \text{OH}^- \rightarrow$
 - Which of the following chemical equations represents a catalytic reforming reaction?
 - $\text{C}_6\text{H}_6 + \text{I}_2 \rightarrow \text{C}_6\text{H}_5\text{I} + \text{HI}$
 - $\text{CH}_3(\text{CH}_2)_5\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + 4 \text{H}_2$
 - $\text{C}_2\text{H}_5\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$
 - $2 \text{C}_4\text{H}_{10} + 13 \text{O}_2 \rightarrow 8 \text{CO}_2 + 10 \text{H}_2\text{O}$

Use this information to answer questions 12 to 15.

Scientists create classification systems to help them organize their knowledge and develop generalizations to make predictions. Classify the following organic reactions as requested.

- $C_3H_6 + Cl_2 \rightarrow C_3H_6Cl_2$
- $CH_3CH_2ClCH_3 + OH^- \rightarrow CH_3CHCH_2 + H_2O + Cl^-$
- $C_3H_8 \rightarrow C_3H_6 + H_2$
- $C_3H_8 + Br_2 \rightarrow CH_3CHBrCH_3 + HBr$
- $C_{12}H_{26} + H_2 \rightarrow C_7H_{16} + C_5H_{12}$
- $C_2H_5OH \xrightarrow{H^+} C_2H_4 + H_2O$
- $C_8H_{18} + H_2 \rightarrow 2 C_4H_{10}$
- $C_4H_8 + H_2 \rightarrow C_4H_{10}$
- $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

12. In numerical order, the substitution reactions are

NR _____

13. In numerical order, the addition reactions are

NR _____

14. In numerical order, the hydrocracking reactions are

NR _____

15. In numerical order, the elimination reactions are

NR _____

Use this information to answer questions 16 to 19.

The most severe test of a generalization is its ability to predict. Predict the correct reaction product(s) for each organic reaction below. Some of the reactions have only one product. You may use the same number more than once.

- | | |
|--------------------|----------------------|
| 1. 1-chloropropane | 5. carbon dioxide |
| 2. 2-chloropropane | 6. hydrogen chloride |
| 3. prop-1-ene | 7. water vapour |
| 4. propan-2-ol | |

16. propane + chlorine \rightarrow _____ + _____

NR

17. propene + hydrogen chloride \rightarrow _____ + _____

NR

18. propane + oxygen \rightarrow _____ + _____

NR

19. propene + steam \rightarrow _____ + _____

NR

Part 2

- Describe**, in words or using a chart, how you would classify an organic compound given its structural formula. Include all classes of organic compounds discussed in this unit.
- Design** an experiment to distinguish pure organic compounds from pure inorganic compounds. Include as many different methods as possible.
- Fossil fuels are of major importance to Alberta. List the different kinds of fossil fuels found in Alberta. For each kind, state one or two major uses.

Use this information to answer questions 23 to 26.

Dow Chemical Canada Inc. (**Figure 1**) has extensive chemical operations in Prentiss and Fort Saskatchewan, Alberta. The major products produced are: hydrochloric acid, Styrofoam® (extruded polyphenylethene (polystyrene) insulation), vinyl chloride monomer (chloroethene), 1,2-dichloroethane, sodium hydroxide, chlorine, ethylene (ethene), and polyethylene. The sites are also home to MEGlobal Canada, which produces ethylene glycol (ethane-1,2-diol).



Figure 1
Dow Chemical Canada Inc.

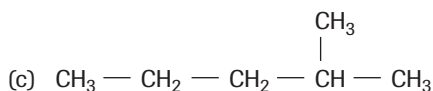
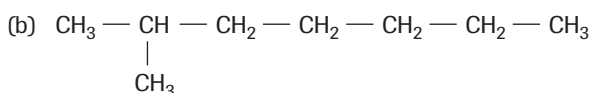
- Classify each of the products produced by Dow Chemical as organic or inorganic.
- Draw full structural formulas for as many of the organic products produced at Dow Chemical's sites as possible. Circle functional groups and identify the organic family.
- Suggest a possible chemical reaction for the production of 1,2-dichloroethane using only the substances produced by Dow Chemical.
- Some of the substances produced by Dow Chemical are intermediates used to manufacture other substances, and some substances may show up in final products. From the list given, **identify** any substances that consumers are able to buy in stores. For each of these substances, state a typical use.

Use this information to answer questions 27 to 29.

Catalytic reforming is an important process in the modern oil refining industry. Catalytic reforming is used to produce aromatics to improve the quality of gasoline and as a starting material for the petrochemical industry. An overview of the catalytic reforming process is

C_6 to C_8 alkanes (naphtha feedstock) \rightarrow cycloalkanes/enes (intermediates) \rightarrow simple aromatics (final products)

27. Write the IUPAC name for each of the following hydrocarbons in a naphtha feedstock:

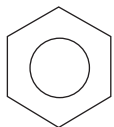


28. Draw a line structural formula for each of the following intermediates from catalytic reforming:

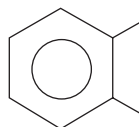
- (a) cyclohexane
 (b) 1-methylcyclopentene
 (c) 1,2-dimethylcyclohexane

29. Write the IUPAC name for each of the following aromatic products from catalytic reforming:

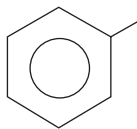
(a)



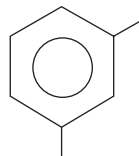
(c)



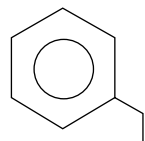
(b)



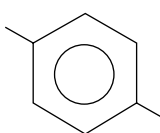
(d)



(e)



(f)

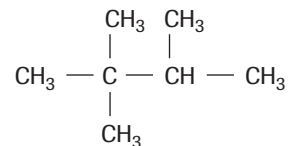
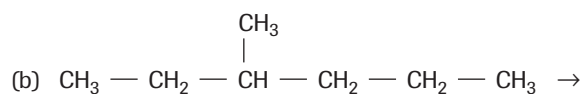
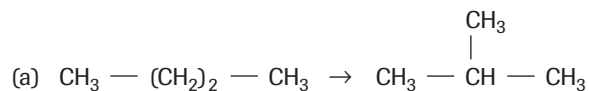


Use this information to answer questions 30 to 32.

Many new technologies are being developed for oil refining. One example is alkylation (isomerization). This process is used to produce more branching in alkanes and also to produce isomers of simple aromatics.

30. Using your knowledge of the term “isomers,” **describe**, in your own words, the process of alkylation (isomerization).

31. For each of the following isomerization reaction equations, write IUPAC names or draw condensed structural formulas as required:



- (c) heptane \rightarrow 2,4-dimethylpentane
 (d) octane \rightarrow 2-methyl-3-ethylpentane

32. What chemical process increases the octane rating by increasing the aromatic character of the gasoline?

33. The following compounds contain molecules that have approximately the same number of electrons: chloroethene, ethanoic acid, propan-1-ol, and butane.

- (a) Draw a full structural formula of each molecule.
 (b) Using the theoretical rules of intermolecular bonding, arrange these substances in order of increasing boiling points. Briefly explain the order.
 (c) **Predict** which substances would likely have a high solubility in water and which would have a low solubility. **Justify** your answer.

34. For each of the following reactions of one mole of an organic reactant, **predict** the chemical amount of hydrogen required for a complete reaction:

- (a) $CH_2=CH-CH=CH_2 + H_2 \rightarrow$
 (b) $CH\equiv C-CH_2-CH_2-C_6H_5 + H_2 \rightarrow$
 (c) $C_7H_{14} + H_2 \rightarrow$

35. Cycloalkanes have structural isomers that are alkenes.

Design an experiment to distinguish between an alkene and a cycloalkane that are structural isomers of each other. Provide the Design, including diagnostic tests.

Problem

Which sample of $C_6H_{12}(l)$ is an alkene isomer, and which is a cycloalkane isomer?

Use this information to answer questions 36 and 37.

Petroleum products with double and triple bonds can polymerize, and form waxy deposits that plug pipe systems and pipelines. One purpose of hydrotreating is to remove multiple bonds to stabilize the liquids, so that polymerization in pipes does not occur.

36. Write a structural formula equation for the addition polymerization of ethene (ethylene) molecules, showing how two molecules can attach to each other and have a free bond at each end for further attachments.
37. Write a structural formula for a section of a polymer of propene (propylene) showing at least four monomer units in the section.
38. Suggest a reaction equation or a sequence of reaction equations to synthesize each of the following organic compounds:
- ethanol (common solvent; component of alcoholic beverages and gasohol)
 - propene (monomer for polypropylene plastic)
 - dichlorodifluoromethane (CFC-12, a refrigerant)
 - Teflon® polymer
 - ethyl ethanoate (solvent)
39. For each of the following reactions, draw structural formulas for all reactants and products, name the products, and classify the reaction type.
- cyclohexane + chlorine \rightarrow
 - 2-phenylpropane + oxygen \rightarrow
 - 2,3-dimethylbut-2-ene + hydrogen chloride \rightarrow
 - octane \rightarrow ethylbenzene
 - butan-1-ol + methanoic acid \rightarrow
 - 2-bromohexane + hydroxide ion \rightarrow
 - decane + hydrogen \rightarrow butane + hexane
40. (a) Given that octane has a density of 0.70 kg/L and assuming that gasoline is octane, **predict** the volume of octane that will produce 1.0 t of carbon dioxide by complete combustion in an automobile engine.
- (b) How far could you drive a typical car on that much gasoline? (Assume 10 L/100 km.)

41. Copy and complete **Table 1**.

Table 1 Some Important Organic Compounds

IUPAC name	Condensed structural formula	Organic family	Common use
	$\text{CH}_2 = \text{CH}_2$		
ethane-1,2-diol			
tetrachloroethene			degreaser for metal components
	$\text{CH}_3 - (\text{CH}_2)_6 - \text{CH}_3$		
ethyl ethanoate			fingernail polish solvent
methylbenzene			gasoline component; solvent
			vinegar
		alkyne	welding and cutting torch

42. Side reactions and byproducts are common for organic reactions. The yield of a product is often expressed as a % yield. Complete the Analysis of the investigation report.

Problem

What is the percent yield in the initial substitution reaction between methane and chlorine?

Design

A quantity of methane reacts with chlorine gas. The products of the reaction are separated by condensation of the gaseous products into separate fractions.

Evidence

mass of methane reacted = 1.00 kg
mass of chloromethane produced = 2.46 kg

43. Fossil fuels come with various physical and chemical properties. As a result of these properties, they are refined by different processes and used in different ways.
- List the fossil fuels of Alberta, from most dense to least dense.
 - Describe** two differences between the refining of natural gas and the refining of crude oil.
 - Evaluate**, with reasoning and evidence, the statement: "Gasoline must contain significant quantities of nitrogen because nitrogen oxides are found in the exhaust of cars and trucks."
44. Methane is produced naturally by a number of sources and becomes part of the hydrocarbon component in the atmosphere of Earth. Human technologies also contribute to atmospheric hydrocarbons.
- Identify** two natural sources and two technological sources of atmospheric methane.
 - Methane is a greenhouse gas. **Define** a greenhouse gas.
 - Identify** some other greenhouse gases and their sources.
 - Describe** actions you can take to reduce the quantity of hydrocarbon molecules that you may allow to escape into the atmosphere.

www.science.nelson.com



45. Copy and complete **Table 2**.

Table 2 Common Monomers

IUPAC name	Chemical formula	Polymer name	Type of polymer
tetrafluoroethene		Teflon®	
benzene-1,4-dicarboxylic acid		Dacron®	
ethane-1,2-diol			
chloroethene		PVC	
benzene-1,3-dicarboxylic acid		alkyd resin	
propane-1,2,3-triol			
phenylethene		styrene	
amino acids		proteins	
1,1-dichloroethene		Saran®	
glucose		starch	
propene		polypropylene	

Use this information to answer questions 46 to 49.

Greenhouse gas (GHG) emissions from internal combustion engines in transportation vehicles are a major concern for environmental chemists. Statistics Canada gathers data over time to provide citizens and scientists with information such as that presented in **Table 3**. Use this table, or a more recent one from StatsCan, to answer the following questions.

Table 3 Greenhouse Gas Emissions by Road Transportation Source

Transportation source	CO ₂ (kt) 1990	CO ₂ (kt) 2001	CH ₄ (kt) 1990	CH ₄ (kt) 2001	N ₂ O (kt) 1990	N ₂ O (kt) 2001	CO ₂ ¹ (kt) 1990	CO ₂ ¹ (kt) 2001	Change %
Gasoline automobiles	51 600	46 400	9.0	4.6	6.3	7.3	53 700	48 700	-9.3
Light duty gasoline trucks	20 400	36 400	4.0	4.8	4.2	9.0	21 800	39 400	80.7
Heavy duty gasoline vehicles	2 990	3 930	0.4	0.6	0.4	0.6	3 140	4 130	31.5
Motorcycles	225	236	0.2	0.2	0.0	0.0	230	242	5.2
Diesel automobiles	657	583	0.0	0.0	0.0	0.0	672	596	-11.3
Light duty diesel trucks	577	629	0.0	0.0	0.0	0.0	591	643	8.8
Heavy duty diesel vehicles	24 300	38 200	1.2	1.9	0.7	1.1	24 500	38 600	57.6
Propane and natural gas vehicles	2 160	1 100	1.7	1.7	0.0	0.0	2 210	1 140	-48.4
Transportation total	103 000	127 000	16.0	14.0	12.0	19.0	107 000	134 000	25.2

¹CO₂-equivalent emissions are the weighted sum of all greenhouse gas emissions. The following global warming potentials are used as the weights: CO₂ = 1; CH₄ = 21; N₂O = 310.

46. **Identify** the top three road transportation sources for each of carbon dioxide, methane, and nitrous oxide.
47. **Identify** the road transportation source that had the greatest increase and greatest decrease in carbon-dioxide-equivalent emissions over the period.

48. **Determine** the percentage contribution of the chemical with the largest contribution to GHG emissions in each year presented.
49. List, in increasing weighted order, the least to the most individually problematic chemicals as greenhouse gases.

50. Who owns what? Traditional Aboriginal environmental views are generally that resources are gifts and that land cannot be owned, whereas Canadian law allows for ownership and exploitation of the land and its resources. Even ownership is subject to change as laws change, however. Who should change their views or practices? Is there a compromise that can or should be considered? Consider the issue from several perspectives. Briefly state your views relative to the fossil fuel industry.

51. Sulfur in gasoline is a pollution problem. Research indicates that refined gasoline may contain anywhere from 30 ppm to 1000 ppm sulfur content. Some jurisdictions have legislated a maximum sulfur content at 30 ppm, which adds one to three cents per litre to the cost of gasoline.

(a) Nonanethiol, $\text{CH}_3(\text{CH}_2)_8\text{SH}(\text{l})$, is one of many possible sulfur-containing components of gasoline. Write the balanced chemical equation for the complete combustion of this compound.

(b) Briefly **describe** the pollution problems that sulfur in gasoline causes.

(c) Are you willing to pay the extra price for low-sulfur gasoline? **Justify** your answer.

52. Oil sands extraction and upgrading requires chemical engineers to use many chemical concept. The concepts presented in this unit get you started on understanding the chemistry of the oil sands.

Solubility is an important concept used in the oil sands industry. The following three processes are technological applications of solubility.

- Water is used to separate the bitumen from the sand.
- When oil sands dry, the water layer between the bitumen and the sand is removed and the hot-water separation of the bitumen from the sand is no longer possible.
- Naphtha is used to dilute the bitumen for transportation.

Another technological process used by the oil sands industry is the thermal coking of bitumen to crack large hydrocarbon molecules into smaller molecules and coke (carbon). Many of the products of coking are hydrotreated to remove sulfur, nitrogen, and multiple bonds from the molecules.

- (a) Use the concept of solubility to **explain** why the three processes, listed above, work.
- (b) Draw line structural formulas for the following products of coking.
- ethylbenzene
 - 4-methylhex-2-ene
 - 6-ethyl-2,3,5-trimethyloctane
- (c) Draw structural formulas to complete the following catalyzed hydrotreating reactions.
- $2,4,5\text{-trimethyloct-2-ene} + \text{hydrogen} \rightarrow$
 - $\text{hept-3-yne} + \text{excess hydrogen} \rightarrow$

53. Complete the Exploration of the two issues identified at the beginning of Chapters 9 and 10. Decide on the type of report and complete this report. (See Appendix D.2.)

54. Review the focusing questions on page 352. Using the knowledge you have gained from this unit, briefly **outline** a response to each of these questions.

Extension

55. Ethene has many uses, including the ripening of fruit and vegetables. List six examples of fruit and vegetables that you eat, along with ethylene production by the fruit or vegetable, and the ethylene sensitivity of the fruit or vegetable.

www.science.nelson.com



56. Alberta has an extensive chemical industry that is the second-largest manufacturing industry in the province, producing about ten billion dollars' worth of products annually. List the four main segments of the Alberta chemical industry. Which one is the largest of the four? What is the main basis of this segment? **Describe** some employment opportunities in the Alberta petrochemical industry.

57. BP Amoco has a linear alpha olefin (LAO) plant in Joffre, Alberta that is producing 250 kt of LAO annually. What are LAOs? Write the IUPAC name and draw the structural formula for a few simple LAOs. **Describe** some major applications for small, medium, and large LAOs.

www.science.nelson.com



58. Research matters. Research is at the heart of all advances and innovations in science and engineering. Search the Internet for information on E10 and E85 ethanol blends, oxydiesel, and/or P-series fuels to gain an understanding of the current research programs involving gasohols.

www.science.nelson.com



59. In-situ oil sands processes include steam-assisted gravity drainage (SAGD) and hydrocarbon-gas injection (e.g., Vapex). In hydrocarbon-gas injection, propane and/or butane is injected (with or without steam) into the oil sands seam. The hydrocarbon acts as a solvent to reduce the viscosity of and extract the bitumen. The bitumen solution is collected in a recovery pipe below the injection pipe. View and/or find an animation to view this process.

Outline several advantages of the hydrocarbon gas process over the SAGD process.

www.science.nelson.com



60. Solvent extraction can be used to remove waxes from crude oil. Two solvents may be used: toluene (methylbenzene), which dissolves the hydrocarbon-oil, and methyl ethyl ketone ($\text{CH}_3\text{COC}_2\text{H}_5$), which dissolves the ester-wax but precipitates it when the temperature is dropped. **Explain**, using structural formulas and solubility theory, the solubility of hydrocarbon oil in toluene and the solubility of wax in methyl ethyl ketone.

www.science.nelson.com

