CHAPTER 10. CARBON AND HYDROCARBONS: ENERGY FROM FOSSILS AND MUCH MORE

Carbon Compounds and Organic Chemistry

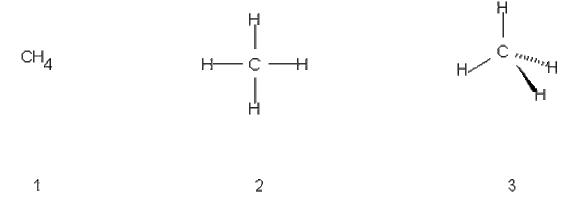
Chemists were using the term "organic" long before the word was applied to food production. Today organic foods are generally understood to have been grown without pesticides or industrially produced fertilizers, and since 2002 the US Department of Agriculture has had standards defining what the term means for various categories of foods. To chemists, **organic compounds** mean those compounds containing the element carbon. Originally chemists believed that, since living organisms were composed largely of complex carbon-containing molecules, these organic compounds could be produced only within living organisms. In 1828 the German chemist Friedrich Wohler caused a sensation by producing the compound urea, found in urine, by heating the compound ammonium cyanate, thus producing urea without a living organism. Until that time the theory of **vitalism** had been widely accepted; scientists believed that there was a special vital force within living things that enabled them to produce the complex organic molecules. Now the synthesis, or manufacture, of organic compounds in the laboratory is commonplace. Vitamin C, for instance, is found naturally in fruits and vegetables; the same exact chemical structure can be made in the laboratory.

Organic chemistry, the study of the compounds of carbon, is one of the most important branches of chemistry. The chemistry of our bodies, of plants and animals, of foods and drugs, fuels and fibers, is largely the chemistry of carbon compounds. It is no accident that the most complex molecules in our world are made from the carbon atom. Carbon atoms four covalent (electronsharing) bonds; hence they can bond to one another in small molecules, form chains of thousands of carbon atoms, or form rings and interlocking rings. Carbon atoms can form covalent bonds with other atoms like oxygen, hydrogen, and nitrogen as well as with other carbon atoms; the possibilities for organic structures are endless. There are millions of known organic compounds, and more are being made and discovered daily.

Hydrocarbons

Most organic compounds, in addition to containing carbon, also contain hydrogen. The hydrocarbons are a class of organic compounds that contain only hydrogen and carbon. They are a very important class of organic compounds, though they are the simplest. Studying their structures is a good introduction to the complex world of organic molecules.

Inspecting Table 10-1, you will see that what at first appears to be a lengthy list of rather complicated molecules is really a rather simple series, with each compound on the list having one more carbon than the on preceding it. In order to have a good understanding of the structure of these compounds, look first at the simplest one, methane, CH₄. We have already studied its bonding, and even made its structure from gumdrops and toothpicks.. The carbon atom has four valence electrons and each hydrogen has one; the carbon and hydrogen atoms share electrons in four covalent bonds. Here you see its formula (1), its stick diagram (2), and an attempt at showing the 3D structure (3).



Notice that the same bonding pattern prevails throughout this series of hydrocarbons. The fact that each carbon forms four covalent bonds and each hydrogen can form only one determines the structure of the hydrocarbons. If there are two carbons, for instance, there must be six hydrogens in order for each carbon to form a total of four single covalent bonds. In this homologous series of hydrocarbons called the **alkanes**, the number of hydrogens is always twice the number of carbons plus two more.

NAME	FORMULA	BOILING POINT, *C	STRUCTURAL FORMULA	USE
Methane	CH4	-162		Principal component in natural gas
Ethane	C ₂ H ₆	- 88.5	H H $H - C - C - H$ $H H$ $H H$	Minor component in natural gas
Propane	C ₃ H ₈	- 42	H H H H $H - C - C - C - H$ $H H H$	Bottled gas
n-Butane	C4H10	0	$ \begin{array}{c} H & H & H & H \\ H - C - C - C - C - C - H \\ H & H & H & H \end{array} $	for fuel
a-Pentane	C ₆ H ₁₂	36	$ \begin{array}{c} H H H H H H \\ H H H H H H \\ H - C - C - C - C - C - H \\ H H H H H H \\ H H H H H \\ \end{array} $	
n-Hexane	C6H14	69	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	
-Heptane	C ₇ H ₁₆	98	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Some components of gasoline
o-Octane	C _a H ₁₈	126	$\begin{array}{c} H \\ H $	
Nonane	C₂H₂∞	151	$\begin{array}{c} H & H & H & H & H & H & H & H & H \\ H & I & I & I & I & I & I & I & I \\ H & C & -C & -C & -C & -C & -C & -C & -$	
o-Decane	C10H22	174	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Found in kerosene

Table 10-1 The First Ten Straight-Chain Saturated Hydrocarbons

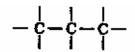
from Jones et al., "Chemistry and Society"

Note: Figures from other texts are chosen to approximate desired content and style.

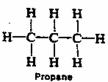
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Problem example 11-1: Draw the structure for the alkane with three carbons, called propane.

Notice that since hydrogen forms only one covalent bond, it cannot be placed between two other atoms. Draw the three carbons together in a row with single bonds between them. Then complete the bonds to carbon by drawing a total of three bonds to each carbon.



Finally, fill in the hydrogen atoms to which the carbons are bonded.



Problem example 11-2. Give the condensed structural formula for propane.

Just as methane can be written as CH_4 , other hydrocarbons may be represented by showing the number of hydrogens bonded to each carbon without drawing all the bonds. For propane, the formula is

CH₃CH₂CH₃

As we saw in Chapter 5, methane is not a flat molecule but a tetrahedral one. The hydrocarbons, and other organic molecules in which carbon atoms have four single bonds, are threedimensional molecules with each carbon atom tetrahedrally bonded. Chemists often use **molecular models** (Fig. 11-1) to show the space-filling properties of these molecules in a way that no twodimensional drawing can accomplish.

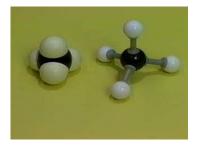


Fig. 11-1: some models of methane CH₄

Petroleum Refining

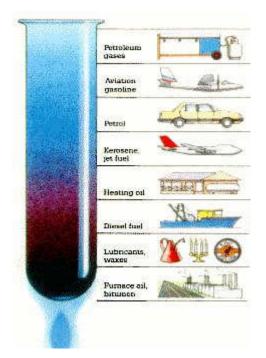
Petroleum, found in natural deposits underground, is largely a mixture of hydrocarbons, the decomposed residue of microscopic creatures that lived millions of years ago. Along with coal, which is largely carbon, the hydrocarbons are called "fossil fuels" because of their prehistoric origins. After the petroleum is removed from the ground it is processed in oil refineries to separate the various components. The crude oil is heated in the absence of oxygen at the bottom of the apparatus, called a fractional distillation column. The hydrocarbons with the lowest molecular weights rise to the top of the column to form the lightest fraction. Heavier hydrocarbon molecules condense into liquid as they rise up the column; the heavier the molecules, the lower down the column they will tend to condense. Hence the hydrocarbon molecules are distributed by molecular weight over the length of the column, and the column can be tapped at various points to drain off hydrocarbon fractions of desired molecular weight range.

Methane, or natural gas, is the lightest of the hydrocarbons, with only one carbon atom, and is in the gaseous state at room temperature. Some natural fossil fuel formations are largely natural gas; often methane gas is found in natural formations along with liquid petroleum. Methane is one of the most common household fuels. Commercial natural gas usually contains also some ethane gas, with two carbon atoms, and perhaps a trace of higher molecular-weight gases. Propane, with three carbon atoms, and butane, with four, are also in the gaseous state at room temperature. They are commercially sold as LPG, or liquefied petroleum gas, contained in high-pressure cylinders as a portable fuel source.

The next, heavier fraction, with between five and twelve carbon atoms, has the very useful property of being in the liquid state at room temperature; it is used for gasoline. The kerosene fraction is somewhat heavier, with between twelve and fifteen carbons. Heating oil and diesel oil are taken from the next, heavier, fraction, with between fifteen and eighteen carbons, and lubricating oils and greases made from the fraction with eighteen to twenty carbons. Demand for these fractions varies with the season of the year; more gasoline is used by consumers during the summer months, while during the winter the demand for heating oil rises sharply. Further refining processes are used on these liquid petroleum fractions to change the molecular weight distribution which is obtained directly from the distillation column. **Cracking** is a process in which heavier hydrocarbons (fifteen to eighteen

carbons) are broken down into gasoline-sized molecules by the use of catalysts, high temperature, and high pressure. Through **polymerization** light hydrocarbons can be reacted to form molecules of gasoline range, or a heavier mix created to produce heating oil.

http://www.world-petroleum.org/education/petref/index.html



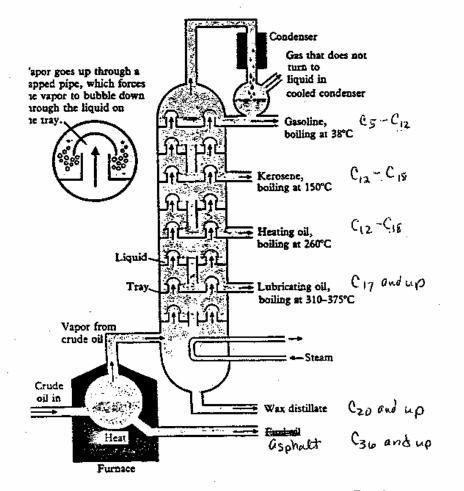


Fig. 10-2. A Distillation Column for Separating Petroleum Fractions

This version from Manahan. "General Applied Chemistry"

Note: Figures from other texts are chosen to approximate desired content and style.

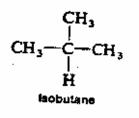
Structural Isomers

For hydrocarbons of four or more carbons, another structural consideration arises beyond simply the number of carbon atoms. So far we have considered only the possibility of joining the carbon atoms in a long chain, as in this chain formation of the four-carbon hydrocarbon butane; this structure is called is called normal or *n*-butane.

CH3-CH2-CH2-CH3

Normal butane

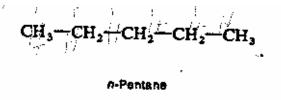
But another possibility exists in which each of the four carbons has four single covalent bonds. We call this branched structure isobutane. Notice that isobutane has the same number of carbons and hydrogens as *n*-butane.



Compounds like this which have the same molecular formula but different structures are called **structural isomers**. As the number of carbons in a hydrocarbon increases, the number of possible isomers increases rapidly. Pentane, with five carbons, has three possible isomers.

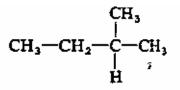
Problem example 11-3: Write structures for the three isomers of pentane.

The simplest isomer to draw is **n**-pentane, in which all the carbons are joined in a straight line.

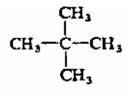


Drawing the isomer in the form below may look different on two-dimensional paper, but is simple another way to draw a straight-chain isomer. Looking at a molecular model, you would be able to tell that \mathbf{n} -pentane can bend to form this shape.

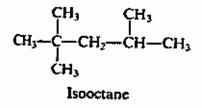
In order to draw a second isomer of pentane, draw five carbons with a branched chain. Notice that one of the carbons is bonded to three other carbons.



For a third isomer, draw the carbon atoms so that one of them is bonded to four other carbons:



Octane, the eight-carbon chain which is one of the principal components of gasoline, has eighteen possible structural isomers. Not all isomers of octane perform equally well in gasoline formulations. Isooctane is the name given to this highly branched isomer which burns especially smoothly without causing the engine to "knock."



Gasoline mixtures are rated by **octane number**, which compares the combustion properties of the mixture to that of isooctane; a rating of 100 refers to pure isooctane; an octane rating of 0 is given to pure *n*-heptane, which burns very poorly. An octane rating of 90, for instance, performs like a mixture of 90% isooctane and 10% *n*-heptane. A refining technique called **catalytic reforming** can be used to change the chain structure of hydrocarbons into branched or cyclic forms which will perform better in gasoline engines, thus increasing the octane number of the product.

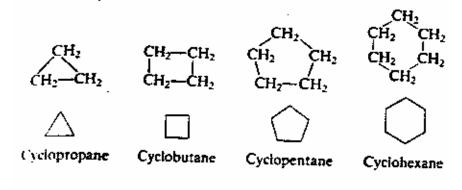
Unsaturated Hydrocarbons

All the hydrocarbons we have discussed so far have featured only single covalent bonds, with one shared electron pair between any two atoms; these are referred to as **saturated** hydrocarbons. Hydrocarbons with two or more carbons may also have one or more double or triple bonds between carbons; any such hydrocarbon is called **unsaturated**. Here are some simple unsaturated hydrocarbons.



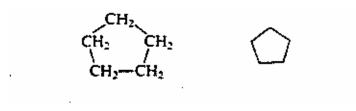
Hydrocarbons can also form ring structures, both simple and complex; these are called **cyclic** hydrocarbons. Often when drawing a cyclic compound, the C symbols for the carbon atoms are omitted; each of the points on the geometric structures is understood to represent a carbon. The

hydrogen atoms are omitted entirely; you simply have to remember that each carbon forms four covalent bonds, and "fill in the blanks" in your mind to see how many hydrogen atoms are present at each carbon position.



Problem example 11-4: Draw the structure of cyclopentane.

Cyclopentane has 5 carbons like pentane, and the carbons are connected up to form a circle. Cyclopentane can be drawn in two ways. showing all the atoms with the five carbons joined to form a cyclic structure, or with the carbon atoms represented by the points of a pentagon, with the hydrogen atoms omitted entirely :



Coal and Coal Tar Derivatives

The liquid hydrocarbons are a convenient source of energy, readily usable in automobile engines and home heating systems, and natural gas is a clean fuel that is inexpensively delivered through pipelines. But coal, a solid fossil fuel that is mostly carbon, with varying amounts of water, sulfur, and nitrogen present, is by far the world's most abundant fossil fuel. Anthracite, or hard coal, is the most desirable form of coal, with the highest carbon content and the lowest amounts of sulfur and nitrogen; United States reserves of anthracite coal are found in the Western states. Bituminous, or soft coal, reserves, abundant in the Appalachian region of the Eastern United States, have higher levels of these impurities. When the coal is burned or oxidized to produce heat energy, the sulfur and nitrogen are oxidized as well, and the resultant sulfur and nitrogen oxides are an important source of air pollution and ultimately of harmful acid precipitation. Coupled with the expense and difficulty of transporting the solid fuel over long distances, environmental concerns have discouraged the increased use of coal as a fossil fuel source.

Solid coal can be processed to produce other forms of combustible material called **synfuels**; these products can be in gaseous or liquid form and can be treated to reduce pollution-forming products. Although several forms of the synfuels are now in commercial use, none have gained popularity in this country because natural gas and oil are currently less expensive. However, processing bituminous coal to produce high-carbon **coke** is a very old process that is still in use. Among the by-products of this process are **coal gas**, a mixture of hydrogen, methane, and carbon monoxide; and **coal tar**, a black, viscous liquid. By fractional distillation coal tar can be separated into many components, including a group of hydrocarbons which early came to be called aromatic because of the pleasant odors of many of them and their related compounds. (The name remains to this day, even though many of the "aromatic" compounds have been found to be foul-smelling!)

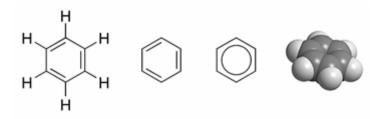
Benzene: A Structural Puzzle Becomes a Chemical Staple

The chemical structure of the aromatic compounds was a puzzle to chemists, and a major scientific debate centered around the structure of the aromatic compound **benzene**, which was known to contain six carbon atoms and six hydrogen atoms. The latter part of the nineteenth century was filled with ferment and controversy among organic chemists as they struggled to prove just which of the possible structures which correspond to the molecular formula C_6H_6 represented the true structure of benzene. The structure which turned out to be the correct one was first visualized by the German chemist August Kekule in 1865. The moment of inspiration, now a famous part of scientific history was described by him in a passage with which the student may identify, at least in its earlier portion:

"I was sitting writing at my textbook, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformations; long rows, sometimes more closely fitted together; all twisting and turning in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I woke;...I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth."

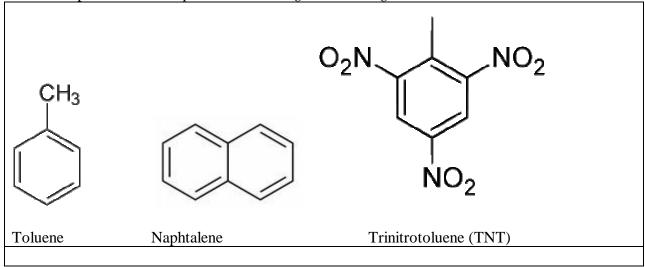
The insight that led Kekule to envision the cyclic structure for benzene was correct, but much

laboratory experimentation and scientific reasoning had to follow before organic chemists had a full picture of the structure of benzene. Instead of behaving as a molecule normally would if it featured alternating double and single bonds, benzene seems to have equivalent bonds all around the ring, and benzene compounds react differently from normal double-bonded or single-bonded compounds. Sometimes benzene rings are written with alternating double and single bonds; this is helpful, for instance, in showing that each carbon in the ring can bond to only one other atom, since it has the equivalence of three bonds already. The double bonds can be written in either of the two possible positions. As with other cyclic carbon compounds, the hydrogen atoms are usually omitted when the ring structure is drawn in order to make a simpler picture of the molecule. Often benzene and its compounds are written with a circle in the middle of the six-member ring, to indicate the equivalence of all its bonds. Thus all three of the structures and the molecular model below are ways of representing the benzene molecule.



Benzene is only the simplest compound of the aromatic family; numerous structures are possible using the benzene ring as a building block. One simple example is toluene, or methylbenzene, found in cans of spray paint as a volatile solvent. Two aromatic rings are fused together in naphthalene, which is often used as a moth repellant.

Fig. 11-3: Labeled structural diagrams of toluene, naphthalene, and trinitrotoluene. Caption: *Some compounds containing benzene rings*.



Aromatic compounds have been used by chemists as starting materials for products that have turned out to have a wide variety of uses. Toluene, for instance, is used to make trinitrotoluene, or TNT, an explosive. Coal tar aromatics are a major source of dyes of many brilliant colors. As a matter of fact, it was the discovery of the first man-made dye, mauve or aniline purple, as a substitute for natural dyes such as indigo, that first sparked the interest in aromatic structures. At one point after its discovery in 1856, mauve became so popular it was twice as expensive as platinum. No wonder chemists suddenly became so interested in the structure of these coal tar compounds! In the next chapter we will look more closely at the possible structures when other types of atoms are joined to the basic hydrocarbon structures, and we will learn that the aromatics are the gateway to the manufacture of many of the powerful drugs we take for granted today.

Fossil Fuels as Chemical Feedstocks

Our society depends on coal, oil, and natural gas as major sources of energy through heir combustion reactions. They power our factories and power plants and serve as the energy basis for our transportation. But the importance to us of the fossil fuels extends far beyond their energy uses. They provide the chemical **feedstocks**, or raw materials, from which chemists make many of the materials which are part of our everyday lives. Fibers for textiles, plastics for building materials and household products, detergents, paints, and even drugs are made from chemical building blocks which originate in the fossil fuels. Not only the chemical industry, but the building, automobile, and pharmaceutical industries, to name only a few, depend upon the availability of these substances. Shortages or price increases in chemical feedstocks are passed on directly to these other industries. Even food production is dependent on petroleum products, because they are used to make the fertilizers that are essential to modern agriculture. Today we are very dependent on the fossil fuels for energy to heat our homes, power our transportation, and produce the basic materials for our everyday lives. What, then, is the prospect for fossil fuel supplies in the coming decades?



Drugs, paints, toys, and detergents are only a few of the petroleum-derived products we use.

Fossil Fuels: A Nonrenewable Energy Source

Since the fossil fuels took millions of years in formation, they will not be easily replaced. It as if we were given a limited amount of money to spend, but absolutely no prospect of having any more after that was gone. Are we spending this limited capital wisely?

For a very long time, human beings made no withdrawals from the fossil energy bank. Early man discovered fire, but burned wood, which is a renewable resource, since new trees will eventually grow to replace harvested ones. Windmills and waterwheels were discovered as civilizations developed, but these, too, relied on renewable sources of energy. With the coming of the Industrial Revolution demands for energy sources suddenly began to grow rapidly. Early steam engines used wood as fuel, but soon the concentrated and reliable energy provided by coal became the standard energy source for steamships, locomotives, and factories as our modern industrial world was born. In 1850 the industrialized nations used wood to provide 91% of commercial energy; by 1900, 73% of commercial energy was provided by coal, with oil and natural gas providing 7%. The discovery and popularization of the internal combustion engine created a demand for oil in the twentieth century; today oil is our most popular source of energy, with natural gas second, followed by coal, renewable energy sources, and nuclear power.

Unfortunately, our available energy resources do not correspond well to our energy needs. Coal, the least utilized fossil fuel, is the most abundant, both in terms of world resources and United States reserves. Oil, the most-used fuel, is lowest in reserves world-wide. And its concentration in a few countries makes its supply dependent on the political stability of these countries, as we have seen in recent years. Our fossil fuel reserves are not limitless. And, as we have learned in our study of hydrocarbons, they provide not only fuel sources, but the raw materials for medicines, fertilizers, and the daily necessities of our modern lives. Hence, if we can find energy alternatives to our fossil fuels, we can save the fossil fuels for use as raw materials. Switching to alternative fuels may be a challenge, but having to do without our basic chemical feedstocks would be an even worse problem.

CONCEPTS TO UNDERSTAND FROM CHAPTER 10

Organic compounds are those which contain the element carbon.

<u>Vitalism</u>, the idea that only living things produce organic compounds, was disproven when Wohler synthesized urea from ammonium cyanate.

The unique ability of carbon to form single and multiple covalent bonds with itself or other elements to create countless molecular structures makes organic chemistry an important branch of chemistry.

<u>Hydrocarbons</u>, containing only hydrogen and carbon, are important both as fuels and as building blocks to form other organic compounds.

<u>Saturated</u> hydrocarbons contain only single bonds. <u>Unsaturated</u> hydrocarbons contain one or more double, or, more rarely, triple bonds.

Compounds with the same molecular formula but different structures are called structural isomers.

FACTS TO LEARN FROM CHAPTER 10

<u>Fossil fuels</u>: coal, oil, and natural gas, are made of ancient living matter changed chemically over time into carbon and hydrocarbons.

In <u>petroleum refining</u>, crude oil, a mixture of hydrocarbons, is separated into hydrocarbon fractions by molecular weight. The crude oil is heated, and the fractions are drawn from a distilling column.

Coal. made mostly from carbon, is the world's most abundant fossil fuel.

Oil is the most widely used fossil fuel.

Solid coal can be processed to form other forms of combustible material called <u>synfuels</u>. These products can be in gaseous or liquid form, and can be used to reduce pollution-forming byproducts of coal combustion.

Coal tar, a by-product of coke production, is a source of aromatic compounds. These compounds, which feature benzene rings, are important chemical building blocks for drugs, dyes, and other synthetic products.

You should be able to recognize the names of the first ten straight-chain hydrocarbons (Table 11-1).

SKILLS TO LEARN FROM CHAPTER 10

After reading this chapter, you should be able to:

Draw structural formulas for any straight-chain or cyclic alkanes for which you are given the name and molecular formula.

Draw structural isomers for butane, and recognize structural isomers for other alkanes.

Name	Date

CHAPTER 10 PROBLEMS

10-1. Draw the structure of the naphthalene molecule (Fi. 11-3), writing in a C where each carbon atom occurs and an H where each hydrogen atom occurs. How many carbon atoms are in the naphthalene molecule ? How many hydrogen atoms?

10-2. Fill in the blanks in the following table for the homologous alkane series.

Name	<u>Formula</u>
Methane	
Ethane	
	C_3H_8
	C_4H_{10}
	C_5H_{12}
Hexane	

10-3. Give complete structures for the following compounds:

a. <u>iso</u>-butane

b. cyclobutane

c. <u>n</u>-butane

10-4. Give complete structures for the following compounds:

a. <u>n</u>-hexane

b. another isomer of hexane

c. cyclohexane

10-5. Draw the structure of an unsaturated compound with the formula C_4H_8 .

10-6. Match each compound with the appropriate phrase by placing the correct letter in the blank.

C ₈ H ₁₈	a. Found in heating oil
CH ₄	b. Found in LPG
C ₆ H ₆	c. Found in coal tar
$\C_{10}H_8$	d. Found in gasoline
C ₃ H ₈	e. Found in natural gas
C ₁₆ H ₃₄	f. Found in mothballs

10-7. Which has the higher boiling point, $C_{11}H_{24}$ or $C_{12}H_{26}$?

10-8. Which hydrocarbon rises higher in a fractional distillation column, octane or decane?

10-9. What is a chemical feedstock?

10-10. Why can the double bonds of benzene be written in either of two positions?

10-11. Which is the most abundant fossil fuel?

Which is the most heavily used?

10-12. When an oil spill occurs, "refined" petroleum that has been processed in a refinery disappears faster than crude oil. Why do you think this is so?

10-13. An unsaturated hydrocarbon can be converted to a saturated hydrocarbon by reacting it with hydrogen in a reaction called hydrogenation. Write a balanced equation for the formation of ethane by the hydrogenation of ethylene. Hint: what are the starting materials? What is the final product? Is the equation balances as written?

10-14. A rise in the price of oil is usually followed months later by a rise in the price of carpeting. Why is this so?

10-15. Purple dye was very costly for centuries. In some countries only royalty was permitted to wear the precious color purple. Now it is common. Why?