INTERCHAPTER F

Saturated Hydrocarbons

Interference of light through a thin film of oil. Oil is composed of a complex mixture of hydrocarbons. The oil-derived fossil fuels propane, butane, and octane are examples of saturated hydrocarbons.

At one time chemists divided all compounds into two classes: inorganic and organic. Inorganic compounds were classified as those that could be obtained from minerals and other inanimate sources, whereas organic compounds were those obtained from living or once-living sources. For many years it was believed that organic compounds contained some sort of vital force and that it was possible to synthesize organic compounds only from other organic compounds, which also contained this vital force. This belief, called *vitalism,* was put to rest in 1829 when the German chemist Friedrich Wöhler synthesized the organic compound urea, which occurs in urine, directly from inorganic starting materials. Since then, chemists have synthesized millions of organic compounds in the laboratory from simpler inorganic and organic substances.

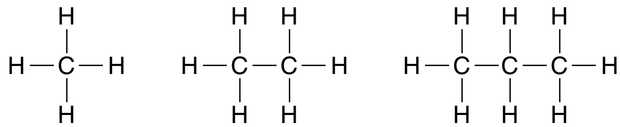
Chemists still classify compounds as either inorganic or organic, but now **organic compounds** are considered to be simply a class of compounds containing carbon atoms. Carbon atoms are unusual in that they can form long covalently bonded chains and rings. The vast majority of all known compounds, and particularly almost all biologically important compounds, are organic compounds. In this interchapter we shall begin to introduce a variety of organic compounds and their characteristic reactions. We shall continue this introduction in the next two Interchapters, discussing unsaturated hydrocarbons in Interchapter G and aromatic hydrocarbons, such as benzene, in Interchapter H. We then look at the chemistry of some important classes of organic compounds in some of the later Interchapters; namely, alcohols, aldehydes, and ketones in Interchapter P, carboxylic acids in Interchapter R, and synthetic and natural polymers in Interchapters S and T.

Figure F.1 Natural gas compressor station in Belarus.

F-1. Alkanes Are Hydrocarbons That Contain Only Single Bonds

Compounds that consist of only carbon and hydrogen atoms are called **hydrocarbons.** Methane, $CH_4(g)$, ethane, $C_2H_6(g)$, and propane, $C_3H_8(g)$, the first three members of the series of hydrocarbons called the **alkanes**, are hydrocarbons that contain only carbon-carbon single bonds. The alkanes have the general formula C_nH_{2n+2}, where $n = 1, 2, 3 \ldots$.

Natural gas consists primarily of methane, with small quantities of ethane and propane (Figures F.1 and F.2). The Lewis formulas of these molecules are



CH_4, methane C_2H_6, ethane C_3H_8, propane

The chemical formulas of ethane and propane are often written as CH_3CH_3 and $CH_3CH_2CH_3$, respectively. Such formulas, which can be thought of as abbreviations of the above Lewis formulas, are called **condensed structural formulas.**

In alkane molecules, the arrangement of the four bonds about each atom is tetrahedral. All the H–C–H, H–C–C, and C–C–C bond angles in these molecules are close to the ideal tetrahedral bond angle of 109.5°. In addition, the H–C bond lengths are all equal (109 pm) and the C–C bond lengths are all equal (153 pm). Each of the four bonds from a carbon atom is connected to a different atom (there are no double or triple bonds). It is not possible to bond any additional atoms directly to carbon atoms in alkane molecules. The bonding about each carbon atom is said to be **saturated,** so alkanes are called **saturated hydrocarbons.**

The fourth member of the alkane series is butane, $C_4H_{10}(g)$. Butane is interesting because there are two

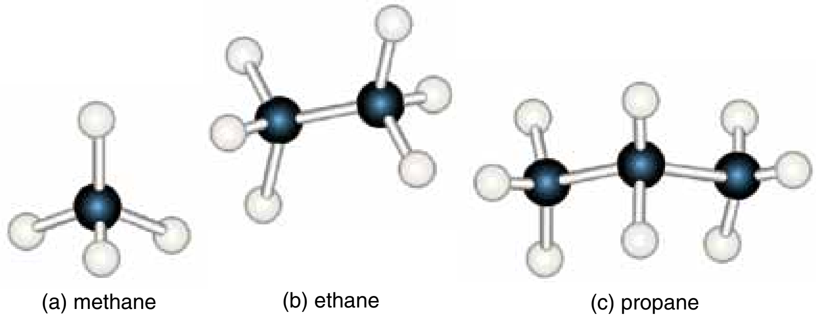
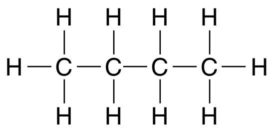


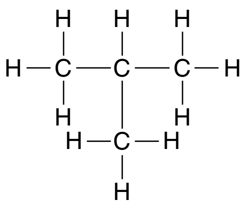
Figure F.2 Ball-and-stick models of (a) methane, CH_4, (b) ethane, CH_3CH_3, and (c) propane, $CH_3CH_2CH_3$. The hydrogen atoms in a methane molecule are at the vertices of a regular tetrahedron. Each of the carbon atoms in the molecules ethane and propane is surrounded by a tetrahedral array of atoms. The carbon-hydrogen bond lengths (109 pm) in the molecules ethane and propane are the same as that in a methane molecule, and the H–C–H and H–C–C bond angles are close to the ideal tetrahedral bond angle of 109.5°.

different types of butane molecules (Figure F.3). The Lewis formulas for the two forms of butane are



n-butane

and



isobutane

and their condensed structural formulas are

$CH_3CH_2CH_2CH_3$
n-butane

and

CH_3CHCH_3
  |
CH_3
isobutane

The straight-chain molecule, that is, the one not containing any branches, is called normal butane, written *n*-butane; and the branched molecule is called isobutane (Figure F.4). (These are the common names of these compounds; we shall learn to assign systematic names to organic compounds in Section F-3). It is important to realize that *n*-butane and isobutane are different compounds, with different physical and chemical properties. For example, the boiling point of *n*-butane is –0.5°C and that of isobutane is –11.73°C. Compounds that have the same molecular formula but different structures are called **structural isomers.**

As we shall see in Chapter 9, rotation can occur about carbon-carbon single bonds in a molecule. Because there is rotation about carbon-carbon single bonds, the formula

$CH_2CH_2CH_3$
|
CH_3

does *not* represent a third isomer of butane. It simply represents four carbon atoms joined in a chain and is just a somewhat misleading way of writing the structural formula for an *n*-butane molecule.

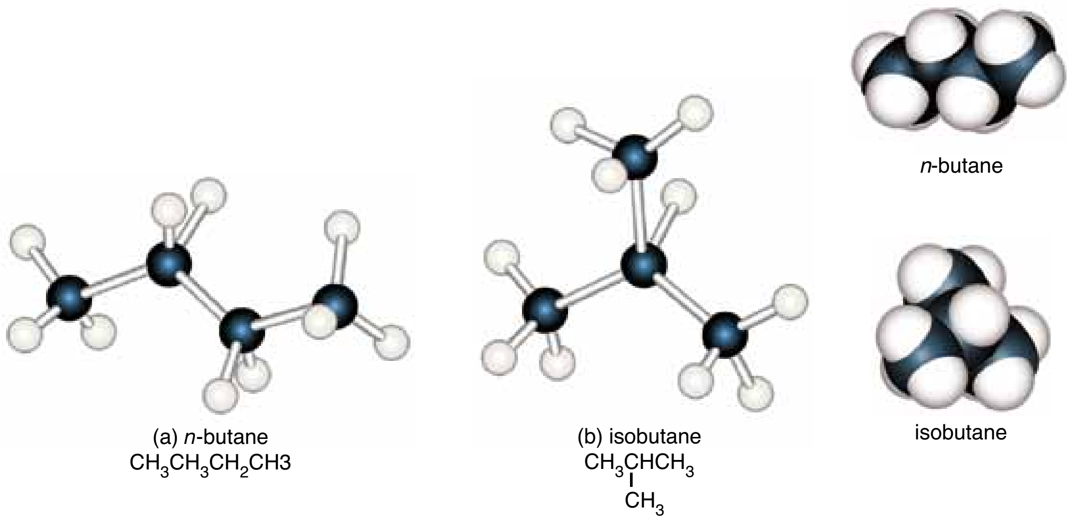
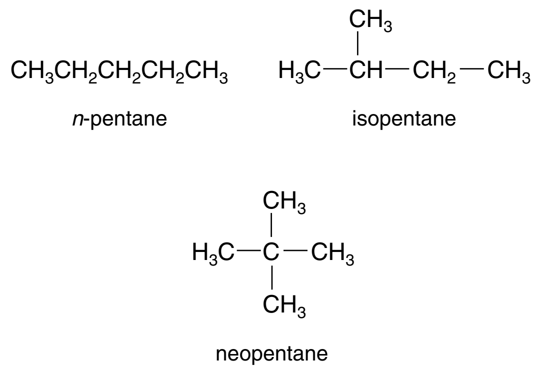


Figure F.3 Ball-and-stick and space-filling models of the molecules (a) *n*-butane and (b) isobutane. As in ethane and propane molecules, the bonds about each carbon atom are tetrahedrally oriented.

After butane, the alkanes are assigned systematic names that indicate the number of carbon atoms in the molecule. For example, $C_5H_{12}(l)$ is called pentane. The prefix *penta-* indicates that there are five carbon atoms, and the ending *-ane* denotes an alkane. The names of the first 10 straight-chain alkanes are given in Table F.1. The first four *n*-alkanes are gases at room temperature (20°C), whereas *n*-pentane through *n*-decane are liquids at room temperature. Higher alkanes are waxy solids at room temperature.

The number of structural isomers increases very rapidly as the number of carbon atoms in an alkane increases. For example, there are three structural isomers of pentane (Figure F.5):



(Note that all three isomers have the molecular formula C_5H_{12}.) Hexane has 5 structural isomers, heptane has 9, octane has 18, nonane has 35, and decane has 75 (Table F.1).

Figure F.4 A mixture of *n*-butane and isobutane is used in lighter fluid.

All the normal straight-chain alkanes through $C_{33}H_{68}(s)$, as well as many branched-chain hydrocarbons, have been isolated from petroleum. Table F.2 lists common hydrocarbons obtained from petroleum. A few alkanes occur elsewhere in nature. For example, the skin of an apple contains the C_{27} and C_{29} *n*-alkanes. These waxes are responsible for the waxy feel of an apple when it is polished. Long- chain saturated hydrocarbons often form part of the protective coating on leaves and fruits. Similar hydrocarbons are found in beeswax (Figure F.6). Apparently, the major function of these waxes in fruits is to retard water loss.

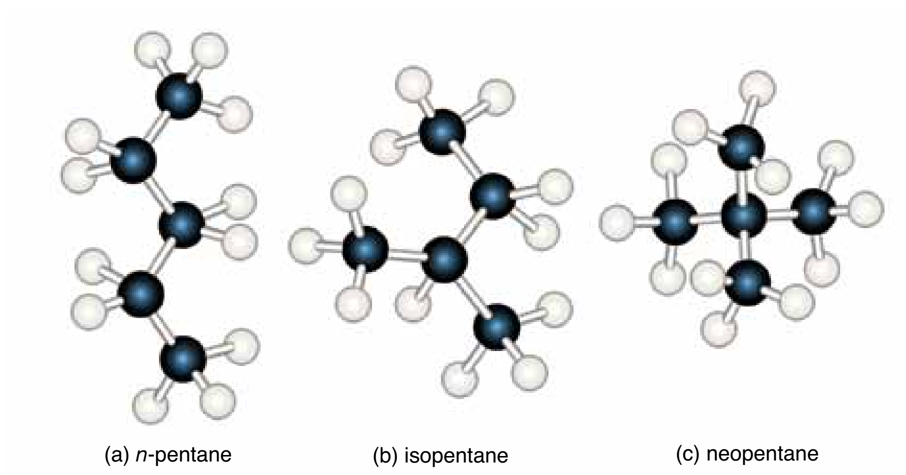


Figure F.5 Ball-and-stick models of the three structural isomers of pentane: (a) *n*-pentane, (b) isopentane, and (c) neopentane.

TABLE F.1 The first 10 straight-chain alkanes

Name*	Molecular formula	Structural formula	Structural isomers	Melting point/°C	Normal boiling point/°C	
methane	CH_4	CH_4	1	–182.47	–161.48	gases at 20°C and 1 bar
ethane	C_2H_6	CH_3CH_3	1	–182.79	88.6	
propane	C_3H_8	$CH_3CH_2CH_3$	1	–187.63	–42.1	
n-butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	2	–138.3	–0.5	
n-pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3	–129.67	36.06	liquids at 20°C and 1 bar
n-hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5	–95.35	68.73	
n-heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9	–90.55	98.4	
n-octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18	–56.82	125.67	
n-nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35	–53.46	150.82	
n-decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75	–29.6	174.15	

*The prefix *n*-, which indicates the "normal" or straight-chain isomer of the molecule, is dropped in the IUPAC or systematic nomenclature.

TABLE F.2 Common petroleum products

Product	Alkanes present	Boiling range/°C
natural gas	C_1	–162
liquefied petroleum gas (LPG), propane, butane	C_3–C_4	–42 to 0
petroleum ether (solvent)	C_5–C_7	30 to 98
gasoline	C_5–C_{10}	36 to 175
kerosene, jet fuel	C_{10}–C_{18}	175 to 275
diesel fuel	C_{12}–C_{20}	190 to 330
fuel oil	C_{14}–C_{22}	230 to 360
lubricating oil	C_{20}–C_{30}	above 350
mineral oil (refined)	C_{20}–C_{30}	above 350
		Melting range/°C
petroleum jelly	C_{22}–C_{40}	40 to 60
paraffin	C_{25}–C_{50}	50 to 65

Figure F.6 Bees produce high-formula-mass hydrocarbons that are the major components of beeswax.

F-2. Alkanes Are Not Very Reactive

Alkanes can be heated for long periods in strong acids or strong bases with no appreciable reaction. Nor do they react with reactive reagents such as $KMnO_4(s)$ or $NaH(s)$. We can write these nonreactions of the alkanes as

$$\left.\begin{array}{l}\text{alkane + strong acid [e.g., } H_2SO_4(aq)] \rightarrow \\ \text{alkane + strong base [e.g., } KOH(aq)] \rightarrow \\ \text{alkane + reactive reagent [e.g., } KMnO_4(aq)] \rightarrow\end{array}\right\} \text{no reaction}$$

The alkanes do burn in oxygen, however, to produce carbon dioxide and water. These combustion reactions generate energy as heat and constitute the basis for the use of hydrocarbons as heating fuels (Figure F.7). The equation for the combustion of propane, for example, is

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

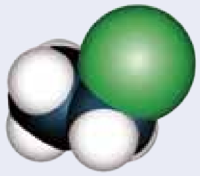
The alkanes also can react with $F_2(g)$, $Cl_2(g)$, and $Br_2(l)$, although a mixture of an alkane and chlorine will remain unreacted indefinitely in the dark. If such a mixture is heated or exposed to the ultraviolet radiation in sunlight, however, a reaction occurs in which one or more of the hydrogen atoms in the alkane are replaced by chlorine atoms. Such a reaction is called a **substitution reaction** because the alkane hydrogen atoms are substituted by chlorine atoms. For example,

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{uv}} CH_3Cl(g) + HCl(g)$$

where uv denotes ultraviolet radiation. The product in this case can be considered to be a **derivative** of methane and therefore is named chloromethane. The function of the ultraviolet radiation is to break the bond in the $Cl_2(g)$ molecule and produce free chlorine atoms. The chlorine atoms are free radicals—hence, highly reactive—and react with methane. Recall from Chapter 7 that a free radical is a species with an unpaired electron.

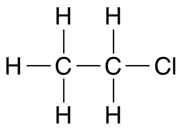
An alkane in which hydrogen atoms are replaced by halogen atoms is called an **alkyl halide**. Alkyl halides are named by prefixing the stem of the name

Figure F.7 Propane gas is sold in tanks and is used to heat homes, cook food on gas grills, and to power some alternative-fuel vehicles that run on liquefied propane gas or LPG.



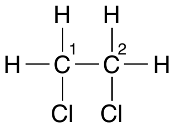
chloroethane

of the attached halogen atoms to the name of the alkane. For example, the molecule

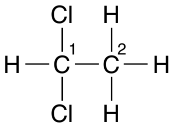


is called chloroethane. (For simplicity, we do not show the lone pair electrons on the chlorine atom). Chloroethane is also sometimes called by its older common name, ethyl chloride; the CH_3CH_2– group is called an ethyl group (Table F.3). Chloroethane is used as a topical anesthetic and acts by evaporative cooling.

If two of the hydrogen atoms in an ethane molecule are replaced by chlorine atoms, two distinct products result:

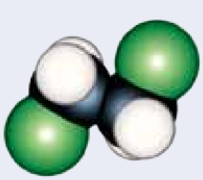


1,2-dichloroethane

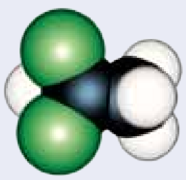


1,1-dichloroethane

These compounds provide another example of structural isomerism. We must distinguish between these two dichloroethanes. We can do this by numbering the carbon atoms along the alkane chain and designating which carbon atoms have attached chlorine atoms. Here, the dichloroethane molecule shown on the left is called 1,2-dichloroethane and the one shown on the right is called 1,1-dichloroethane. Atoms or groups of atoms that replace a hydrogen atom bonded to a carbon atom are called **substituents.** Thus, the two chlorine atoms are the substituents in the **disubstituted** ethane molecules shown here.



1,2-dichloroethane



1,1-dichloroethane

TABLE F.3 Common substituent groups

Group	Name*
$-CH_3$	methyl
$-CH_3CH_2$	ethyl
$-CH_3CH_2CH_2$	propyl
$CH_3\underset{\mid}{C}HCH_3$	isopropyl
–F	fluoro
–Cl	chloro
–Br	bromo
–I	iodo
$-NH_2$	amino
$-NO_2$	nitro
$-C_6H_5$ (benzene ring)	phenyl

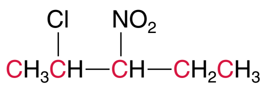
*Groups that are derived from alkanes are called **alkyl groups.** The first four groups here are alkyl groups; they are named by dropping the *-ane* ending from the name of the alkane and adding *-yl.*

F-3. Alkanes and Substituted Alkanes Can Be Named Systematically According to IUPAC Rules

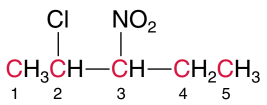
Structural isomerism leads to an enormous number of alkanes and substituted alkanes. Consequently, it is necessary to have a systematic method of naming alkanes and their derivatives simply and unambiguously. A system of nomenclature for organic molecules has been devised and is used by chemists throughout the world. This system, which has been recommended by the International Union of Pure and Applied Chemistry (IUPAC), makes the structure apparent from the name of the compound. The names of organic compounds derived from these rules are called the **systematic names** or **IUPAC names** of compounds. In some cases an older or **common name** such as isobutane or neopentane may still be in general use, but in computer databases and modern handbooks compounds are now listed by their systematic names. Thus, it is possible to find all the information on a particular compound by applying these systematic naming rules to its structural formula. We shall use the IUPAC names of compounds, giving the common name in parentheses, except in a few noted cases where the common name is still the one preferred in general usage.

The **IUPAC nomenclature** rules for alkanes and their derivatives are as follows:

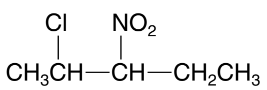
1. For straight-chain alkanes, use the names in Table F.1 *without* the *n* prefix. For example, the straight-chain alkane containing eight carbon atoms is called octane.
2. To name a branched or a substituted alkane, first identify the longest chain (the main chain) of consecutive carbon atoms in the molecule. Name this main chain according to rule 1. For example, the main chain in the following molecule has five carbon atoms (shown in red):



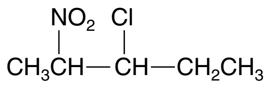
   Because there are five carbon atoms in the main chain, this substituted alkane is named as a substituted pentane.
3. Number the carbon atoms in the main chain consecutively, starting at the end that assigns the *lowest* number to the first substituent. For our substituted pentane, we have



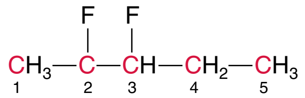
   We number the carbon atoms from left to right so that the attached groups are on the carbon atoms numbered 2 and 3, in this case. If we were to number (incorrectly) the chain from right to left, the carbon atoms with attached groups would be 3 and 4.
4. Name the groups attached to the main chain according to Table F.3 and indicate their position along the chain by writing the number of the carbon atom to which they are attached. The substituted alkane we are using as our example is named 2-chloro-3-nitropentane. Punctuation is important in assigning IUPAC names. Numbers are separated from letters by hyphens, and the name is written as one word.
5. When two or more different groups are attached to the main chain, list them in alphabetical order. For example, as we just saw, the molecule



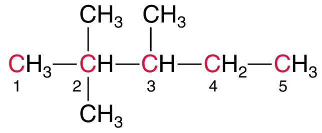
   is called 2-chloro-3-nitropentane, but



   is called 3-chloro-2-nitropentane.
6. When two or more identical groups are attached to the main chain, use prefixes such as *di-*, *tri-*, or *tetra-*. For example, the molecule

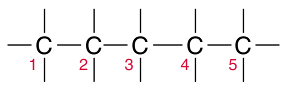


   is 2,3-difluoropentane. Note that the numbers are separated by commas. Every attached group must be named and numbered, even if two identical groups are attached to the same carbon atom. For example, the IUPAC name for the molecule

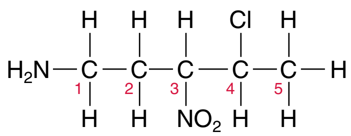


   is 2,2,3-trimethylpentane.

Working backwards, we can use Table F.3 to write structural formulas of molecules. For example, to write the structural formula of a 1-amino-4-chloro-3-nitropentane molecule, we first draw a five-carbon pentane backbone so that each carbon atom has a total of four single bonds,



Next we add the listed substituents, placing hydrogen atoms at the remaining sites to get



or, more compactly,

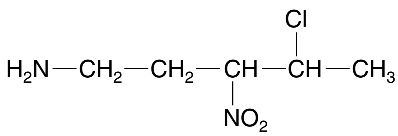
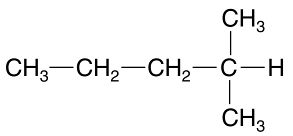


Table F.4 lists a few other examples for you to practice with if you wish.

TABLE F.4 Some structural formulas and their corresponding IUPAC names

Structural formula	IUPAC name
$CH_3—CH(CH_3)—CH_3$	2-methylpropane (isobutane)
$CH_3—CH(CH_3)—CH_2CH_3$	2-methylbutane (isopentane)
$CH_3CH_2CH_2NH_2$	1-aminopropane
$CH_3—CH(NH_2)—CH_3$	2-aminopropane
$H_3C—CH(NO_2)—C(CH_3)_2—CH_3$	2,2-dimethyl-3-nitrobutane
$CH_3—CH(Cl)—CH(CH_3)—CH_3$	2-chloro-3-methylbutane

We'll finish this Interchapter with an example that often tricks beginning students. Determine the IUPAC name of



The IUPAC name is 2-methylpentane. Do you see why? Why are 4-methylpentane and 1,1-dimethylbutane incorrect IUPAC names?

TERMS YOU SHOULD KNOW

organic compound *F1*
hydrocarbon *F1*
alkane *F1*
condensed structural formula *F1*
saturated *F1*
saturated hydrocarbon *F1*
structural isomer *F2*
substitution reaction *F5*
derivative *F5*
alkyl halide *F5*
substituent *F6*
disubstituted *F6*
systematic name *F6*
IUPAC name *F6*
common name *F6*
IUPAC nomenclature *F7*

QUESTIONS

F-1. What are the advantages of using the IUPAC system of nomenclature over the older system of common names?

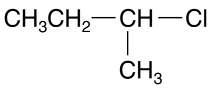
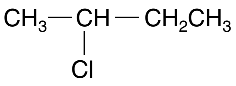
F-2. What is a substitution reaction?

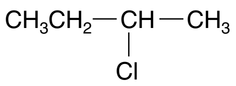
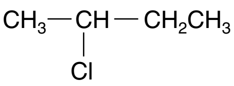
F-3. Complete and balance the following equations (if no reaction occurs, then write "no reaction"):

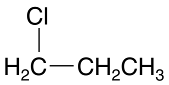
(a) $C_5H_{12}(g) + O_2(g) \longrightarrow$
(b) $C_2H_6(g) + Cl_2(g) \xrightarrow{\text{dark}}$
(c) $C_4H_{10}(g) + H_2SO_4(aq) \longrightarrow$
(d) $CH_4(g) + Cl_2(g) \xrightarrow{\text{uv}}$
(e) $C_2H_6(g) + KOH(aq) \longrightarrow$
(f) $C_3H_8(g) + KMnO_4(aq) \longrightarrow$
(g) $C_5H_{12}(g) + HCl(aq) \longrightarrow$

F-4. Which of the following pairs of molecules are identical and which are different?

(a) $ClCH_2CH_2CH_3$ and $CH_3CH_2CH_2Cl$

(b)  and 

(c)  and 

(d)  and $CH_3CH_2CH_2Cl$

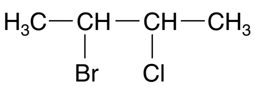
F-5. Give the IUPAC names of isopentane and neopentane.

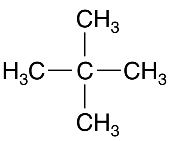
F-6. There are five structural isomers of hexane that each have the chemical formula C_6H_{14}. Write the Lewis formula of each of these five isomers. Assign each of them an IUPAC name.

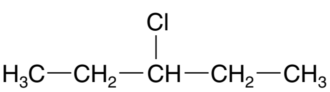
F-7. If you substitute a chlorine atom for a hydrogen atom in *n*-hexane, how many possible isomers do you get? Give IUPAC names for all these isomers.

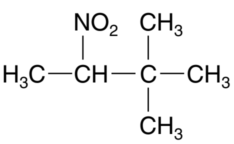
F-8. One class of saturated hydrocarbons, called cycloalkanes, has the general formula C_nH_{2n}. Write the Lewis formula of cyclopropane (C_3H_6), cyclobutane (C_4H_8), and cyclohexane (C_6H_{12}).

F-9. Give IUPAC names for the following compounds:

(a) 

(b) 

(c) 

(d) 

F-10. Explain why the following names are incorrect. Give the correct IUPAC name for each.

(a) 4-methylpentane

(b) 2-ethylbutane

(c) 2-dimethylpropane

(d) 2,3-dichloropropane

(e) 1,1,3-trimethylpropane

F-11. Write the Lewis formula for each of the following substituted alkanes:

(a) 2,3-dimethylbutane

(b) 2,2,3-trimethylbutane

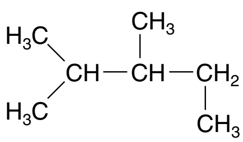
(c) 2-nitropropane

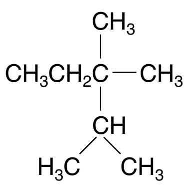
(d) 1,1,2,2-tetrachlorobutane

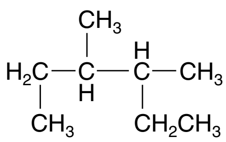
F-12. In enumerating the monochlorosubstituted isomers of propane, we listed 1-chloropropane and 2-chloropropane but not 3-chloropropane. Why not?

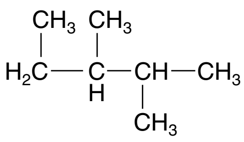
F-13. A cylinder is labeled "PENTANE." When the gas inside the cylinder is monochlorinated, five isomers of formula $C_5H_{11}Cl$ result. Was the gas pure *n*-pentane, pure isopentane, pure neopentane, or a mixture of two or all three of these?

F-14. Consider the following structures:

(1) 

(2) 

(3) 

(4) 

Indicate which of these formulas represent(s)

(a) the same compound

(b) an isomer of octane

(c) a derivative of hexane

(d) the one with the most methyl groups