Organic Chemistry

1. The Concept of Valence

Atoms combine in various ways to form an enormous variety of molecules. Chemists have discovered simple rules governing these combinations of atoms – rules that bring order to what would otherwise be an impossible task of rote memorization and library searching. As we will see, rules of atomic combination, combined with understanding of molecular interactions, enable us to make sense of the material universe in which we find ourselves. That is what Chemistry 12H is about.

In this supplement to Chemistry 12H, we will focus on organic chemistry, a topic with which many of you will not be familiar. We do this because the subject provides excellent examples with which we can illustrate many of the concepts that come later in the course. Think of this topic as providing a toolkit that we will draw upon throughout the next two semesters. For those of you planning to take organic chemistry next year, this approach will help prepare you for that experience. Organic chemistry is also relevant to biology and biologically-related courses, and is important in understanding polymers and new materials. For those of you not going on in chemistry, this section will provide you with some background in one of chemistry’s most important branches. It is a topic that will continually come up throughout your life, no matter what your profession.

We start by reviewing the elementary rules of covalent atomic combination which we assume you learned in an earlier course. These are the rules that refer to the number of covalent bonds an atom of each element forms as it combines with another atom of the same element or of a different element. You will most likely remember these covalent bonds as “sticks” connected to each atom in a diagram showing how the atoms are connected in a molecule. For example, the structural formula for a molecule of water is:

\[
\text{H–O–H}
\]

**structural formula for a water molecule**

Note that the oxygen atom is connected to two sticks, or covalent bonds, and each hydrogen is connected to one bond. This is the normal number of covalent bonds for each of these atoms – two for oxygen and one for hydrogen. These numbers are sometimes called the *valences* of the atoms. The normal valences for some other atoms of interest to us in this chapter are: one for fluorine (F); three for nitrogen (N), and four for carbon (C). Generally, we expect elements in the same family of the periodic table (i.e., in the same vertical column) to share the same valence. Thus, the valence for chlorine (Cl) is one because chlorine is in the same family as fluorine, that for sulfur (S) is two because it is in the same family as oxygen, etc. (You may have learned in an earlier course that the most common valence number associated with each family in the periodic table reads as follows as we go from left to right across the table: 1, 2, 3, 4, 3, 2, 1, 0.)
SAMPLE EXERCISE  Draw structural formulas for the simplest molecule you can construct from (a) oxygen and chlorine, (b) sulfur and hydrogen, (c) carbon and fluorine.

Cl−O−Cl          H−S−H
  chlorine with oxygen  sulfur with hydrogen  carbon with fluorine

The solutions to the Sample Exercise show each atom connected to each of its bonded neighbors by a *single bond*. You probably recall from earlier courses that this is not the only possibility. Some molecules involve *multiple bonds*, that is, cases where neighbors are connected by two or even three bonds. Here are two examples, resulting when a pair of oxygen atoms combine to form an oxygen molecule or when two nitrogen atoms combine to form a nitrogen molecule.

\[
\text{O}=\text{O} \quad \text{N}≡\text{N}
\]

\text{oxygen molecule (O}_2\text{)} \quad \text{nitrogen molecule (N}_2\text{)}

Observe that the rules of valence are still satisfied. Each oxygen has satisfied its valence of two and each nitrogen has satisfied its valence of three. The oxygen molecule has a *double bond* and the nitrogen molecule has a *triple bond*. The existence of this option accounts for some of the variety in molecular compounds. Oxygen, for example, can form a double bond with itself, as shown above, but can also form a single bond with itself if it can find some way to bond to another atom to satisfy its valence of two. Hydrogen peroxide is an example.

\[
\text{H−O−O−H}
\]

\text{hydrogen peroxide (H}_2\text{O}_2\text{)}

The valence requirements guides us to what is possible and exclude what is not possible. Thus, we expect NH\textsubscript{3} to be a stable molecule, but not NH\textsubscript{2}. More accurately, we are not surprised that NH\textsubscript{3} (ammonia) is stable. But if we were to discover that NH\textsubscript{2} is a stable molecule, we would be surprised and investigate to discover where our simple scheme is incorrect. All sciences proceed in this manner: we develop a scheme, or set of rules, or theory, and then make corrections or refinements or extensions on the basis of the situations where it does not work.

The rules of valence, clearly, go a long way toward making sense of the choices that atoms make when combining to form molecules. They also serve as a source of useful clues about molecular structure and bond energy. For instance, the distance between oxygen atoms is shorter in the doubly-bonded \textsubscript{O}_2 than in the singly bonded \textsubscript{H}_2\textsubscript{O}, and more energy is needed to break the double bond in \textsubscript{O}_2 than the O-O single bond in \textsubscript{H}_2\textsubscript{O}_2.
There is one more combining rule that we need before we venture into organic chemistry. It has to do with the ability of an atom to combine with others of its own kind. One can imagine bonding together oxygen atoms to form long chains, as illustrated in this structure.

\[
\text{H--O--O--O--O--O--...--O--O--O--O--O--H}
\]

**A proposed long chain of O_nH_2**

This structure satisfies the rules of valence, but the molecule shown does not exist. Chain formation between atoms of the same type does not occur to significant extents for most elements to produce stable molecules. A few elements, such as sulfur, are moderately successful at forming chains (the stable form of sulfur is a ring of eight atoms), but there is one element that is supremely successful at forming chains by bonding to itself, and that is carbon. Carbon forms bonds with itself that are very stable and that go on and on over chain lengths of tens of thousands of atoms. This is a key factor in the ability of compounds of carbon to form a limitless number of compounds. It is also the reason that carbon compounds are the natural realm for life processes, for only here is the variety of compounds available for the range of functions that nature requires (and modifies) in life forms. It was the recognition of the central role of carbon-containing compounds that led early chemists to call these compounds “organic,” and to propose that such compounds had a special life-related nature that made them somehow different from “inorganic” compounds. We now know that the rules governing carbon compounds stem from the same physical principles as those underlying all of chemistry, but the name “organic chemistry” continues as the label for the field of the chemistry of carbon-containing compounds.

The rules described above are very simple – too simple really, and we will return to explaining and refining them later in the course. For our present purposes, though, they will serve.

2. **Various Formula Conventions**

Chemists use formulas to represent molecules. Over many years, as they have learned more and more about molecules, chemists have looked for ways to encapsulate that new information into new kinds of formulas. In this section we will review the kinds of formulas that you will see throughout this course, and what those formulas tell you.

An example of the most rudimentary kind of formula is H_2O. This tells us only two things: what kinds of atoms are present in the molecule, and how many of each kind are there. It tells us nothing about the way the atoms are connected together or what the overall shape of the molecule is. Of course, you have just seen that, using the rules of valence, you could figure out that this molecule must have each hydrogen atom bonded to the oxygen, with no bond directly between the hydrogen atoms. You have seen how this can be explicitly represented in a formula:

\[
\text{H--O--H}
\]

This contains the added information about which atoms are bonded together, and also what kinds of bonds (single, double, triple) are used.
The next stage in sophistication is to show not only all of the above information, but to show the actual angles with which the bonds are attached to the atoms. For water, it is known that H-O-H angle is 105°. We indicate this as follows:

\[
\text{H} \quad \text{O} \quad \text{H}
\]

Notice that the only difference between the last two formulas for water is that one of them shows the molecule as linear and the other as bent. If you were not told that the first formula is not being used to convey information about shape, you might think that it is telling you that the water molecule is linear. Eventually, you will be expected to know enough about molecular shapes so that we will not always need to tell you whether a formula is meant to be accurate about shape. We will expect you to know, for instance, that the water molecule is bent, and that the linear representation is not telling you about shape. For the time being, however, we will have to be explicit about this when it matters.

The next level of representation arises when we worry about the actual volume taken up by a molecule. This matters when we care about how molecules pack together in liquids or solids, or when they try to get together to react. To show these so-called space-filling models, each atom is surrounded by a sphere of appropriate size, and the spheres are partially nested into each other where they bond together. A great deal of science lies behind these representations. For now, you only need to know what the pictures mean. For water, the space-filling molecular formula, or model looks like this:

The nuclear framework for water is two-dimensional. Complications arise when we try to represent shapes for three-dimensional molecules. Consider the molecule methane, CH4. The formula that shows connection but not shape looks like this:

\[
\text{H} \\
\text{H} - \text{C} - \text{H} \\
\text{H}
\]
If the molecule were square, hence planar (i.e., two-dimensional), this formula would also be correctly showing molecular shape. But the molecule is not planar. The four bonds poke out of carbon towards the corners of an imagined tetrahedron, making CH$_4$ a three-dimensional molecule. Drawing a three-dimensional molecule on a two-dimensional piece of paper requires some added artistic conventions. The correctly shaped structural formula for methane looks like this:

![Methane structural formula](https://example.com/methane_formula.png)

On the left, we show it drawn in the outline of a tetrahedron. This helps you to see that the carbon and two of the hydrogens are to be imagined to lie in the plane of the page, that one of the hydrogens lies behind the page, and that the remaining hydrogen is poking out of the page towards you. A dashed line is used to represent a bond going away from you and a heavy line, often wedge shaped, is used to represent a bond poking out at you. Ordinarily, the molecular formula is drawn without the assistance of a tetrahedron or other shape, as shown on the right.

The space-filling model for methane is shown below. It is easy to see its relation to the structure above. This convention necessarily blocks the view of those parts of the molecule facing away from you. For some of the more complex molecules you will be seeing, this can be inconvenient. However, the wonders of modern computer technology can come to the rescue here. Space-filling models are constructed by smart programs on the computer screen, and the operator then can move a mouse or turn a knob and the whole molecular image rotates around to reveal whatever we want to see. You will most likely be shown this kind of technology in lecture. If you go on in science, you may do a fair amount of working with such smart computer programs on your own.

There is one other important kind of convention you should be aware of. This is the stereoscopic molecular structure. Basically, you are given two pictures, taken from slightly different angles so that your eyes will make it look three-dimensional, as if you were looking at a three-dimensional model. This kind of viewing is crucial to understanding biochemical structures and reactions. The three-dimensional view is easiest to observe if you look at the picture through a special viewer. But most people, with a little practice, can see it without a viewer. This is a convenient skill to develop. Shown on the next page is a stereo view of a “wire” formula (i.e., showing only bonds) of yeast phenylalanine transfer RNA.

Hold the page about a foot away from your eyes in good light, and let your eyes defocus so that the two images swim together. It may take you some time to get them to swim all the way together, maybe as much as ten minutes. Once they swim together, the three-dimensional molecule should seem to pop out at you. If it does not work on the first try, give it another try or two later. If your instructor makes a viewer available to you, try using that. Then it may be easier for you to make progress without the viewer. However, do not worry if you find that you, like many others, can only see three-dimensionally with a viewer. If you ever find yourself making much use of stereo images, you will have your own viewer.
These days, people can put on special glasses and look at special computer screens to see three-dimensional molecules moving around. You are fortunate to live in an age where you do not need to rely completely on imagination and crude drawings of molecules, but can see highly accurate, three-dimensional, animated images.

3. Some Examples of Organic Molecules

We have referred to the enormous numbers and wide range of types of organic molecules. Before taking a systematic look, we present some examples to give you the flavor of this field, and to present some more examples of conventions for molecular formulas.

Octane. Octane contains only the elements carbon and hydrogen, and is a component of gasoline. The “oct” in the name indicates that there are eight carbons in the molecule (octo is Latin for “eight”). We will look more carefully at naming conventions later. Some of the ways this molecule might be represented are shown below:

\[
\begin{align*}
C_8H_{18} & \quad \text{H--C--C--C--C--C--C--C--H} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{CH}_3(\text{CH}_2)_6\text{CH}_3
\end{align*}
\]

Formulas for octane

The first of these is simply a compositional formula. It doesn’t tell us how the atoms are connected together. The second shows us the connectivity of the atoms but not the molecular shape. The third shows molecular shape. The fourth is a symbolic formula that shows the composition and sequence of the molecule. Each CH\text{2} group is understood to be linked to the
group on either side of it in the list. The fifth is a shorthand version of the fourth. The sixth is a space-filling version, showing more realistically the structure and volume of octane. The seventh is an extremely convenient shorthand formula. It is created from the third formula by suppressing all the symbols for carbon and all of the hydrogens attached to carbons as well as the C−H bonds. The representations shown above suggest that the octane molecule is shaped like a log, or a loaf of Italian bread. However, you should realize that some molecules are very flexible, and writhe about like excited worms. Octane is such a molecule, and a space-filling version of the molecule in one of its less-extended orientations is shown below:

![Octane coiled up](image)

Later, you will be shown how to tell whether a molecule is rigid or flexible and subject to writhing. Octane serves here as an example to alert you to the existence of the possibility of molecular flexibility.

**Formic Acid.** This is a fairly simple molecule, containing only five atoms. It is the compound that gives an ant its sting. (The Latin word for “ant” is *formica.*) If you crush an ant and smell it, the acrid odor is that of formic acid. As the name implies, this compound is an acid. We will have a great deal to say about acids at various points in Chemistry 12 and 13. Five ways in which the formula for formic acid might be represented are:

![Formulas for formic acid](image)

The second of these formulas gives information about the connection sequence, but requires some knowledge from the reader. A naïve reading of the formula HCOOH is that the bonding pattern is H−C−O−O−H, but this would violate the valence rule for carbon, which needs four bonds. The third formula shows the actual bonding pattern, but is more cumbersome to insert in a line of print. COOH is an example of one of the few patterns of symbols where the reader is expected to recognize that the actual connection scheme is not exactly the same as what is shown. As such cases come up, we will highlight them for you. They are very few in number, and easy to recognize with the help of valence rules. The fourth formula above is the streamlined version resulting from suppression of carbon symbols and C−H bonds. Note that double bonds continue to be shown explicitly as well as hydrogens attached to anything other than carbon. Formic acid is the common name for this compound. We will later see that there is a systematic naming system for organic molecules. The systematic name for formic acid is *methanoic acid.* At this point, we don’t expect you to remember either of these names or even
the formula for this compound. What we do want you to remember from this and the previous examples is (1) how to interpret these formulas, (2) that the same compound may have several names, (3) that aspects of everyday life, such as ant bites or gasoline, can be related to the existence of specific compounds, (4) that some molecules can writhe about and change their shape significantly without actually breaking any bonds.

A Few More Examples. Now that you have seen a bit more about formula conventions, we can show some more complex molecules with interesting properties. Carvone, \( \text{C}_{10}\text{H}_{14}\text{O} \), is what gives oil of spearmint its characteristic taste and odor:

![Carvone](image)

Notice that this molecule has a ring of carbons. Ring structures are very common in organic chemistry, especially rings of six connected atoms.

Cholesterol, \( \text{C}_{27}\text{H}_{46}\text{O} \) is a molecule of great interest to health-concerned people. It is produced in the liver and may form deposits in the arteries.

![Cholesterol](image)
Cholesterol contains a series of four rings, one of them a five-membered ring. This ring pattern is characteristic of a whole family of compounds called steroids. Two other steroids are the male sex hormone testosterone and the female sex hormone estradiol, both of which are shown below.

![Testosterone, C₁₉H₂₈O₂](image1)

![Estradiol, C₁₈H₂₄O₂](image2)

Caffeine, C₈H₁₀O₂N₄, is an example of a two-ring compound with a few noncarbon atoms participating in the ring structure.

![Caffeine](image3)

Putrescine, C₄H₁₂N₂, accounts in part for the bad odor of rotting meat, while 3-methylbutane-1-thiol, C₅H₁₂S, accounts for the odor of the defensive blast given off by a skunk.

![Putrescine](image4)

![3-methylbutane-1-thiol](image5)

Teflon™, (CF₂CF₂)ₙ, is a polymer, which means that the molecules are extremely long.

![Polytetrafluoroethylene (Teflon™)](image6)

The value of \( n \) in the above formula is typically about 25,000. This material tends to have little attraction for other substances, which makes it convenient as a coating for cookware or for bullets designed for maximum penetration. Teflon is the commercial name for this polymer. Its systematic name is polytetrafluoroethylene.
These examples give you a very small glimpse of the world of organic chemistry and hint at the tremendous variety of compounds and properties that chemists deal with. Fortunately, a systematic treatment of organic chemistry is possible. We will now describe some of the knowledge that has been discovered and systematized over the last two centuries.

**SAMPLE EXERCISE** Write out a structural formula for caffeine, based on the abbreviated formula above. Show all atoms and bonds, but do not worry about shape.

![Caffeine structural formula]

4. **Some Hydrocarbons**

We have already encountered two molecules, methane (CH₄) and octane (C₈H₁₈), containing only atoms of hydrogen and carbon. Such molecules are called hydrocarbons. Even with only two elements to work with, we can find an enormous variety of molecules while still satisfying the rules of valence. Many of these molecules are found in nature, others have been synthesized by clever chemists, and some are thought to be too unstable to exist. We begin our systematic approach to organic chemistry with a discussion of hydrocarbons.

**Unbranched alkanes.** We described octane earlier as a chain of eight carbon atoms linked together with single bonds, with all of the other carbon valences being satisfied through single bonds to hydrogen atoms. It is quite easy to see that this kind of prescription can be followed for six carbons, or twenty, or two hundred. If we try it for only two, three, or four carbons, we obtain the molecules shown below.

- **Ethane, C₂H₆**
- **Propane, C₃H₈**
- **Butane, C₄H₁₀**

Comparing these molecules with each other and with octane, C₈H₁₈, it is clear that any hydrocarbon of this type will have two hydrogens for each carbon present, plus two more hydrogens to cap the ends of the molecule. Thus, for 20 carbons, we would expect 42 hydrogens, and we don’t need to draw out the molecular structure to know this. A general formula for this class of hydrocarbons, then, is CₙH₂ₙ₊₂, where n can be any positive integer.

In the case where n is one, the molecule is methane, CH₄, which used to be called marsh gas, and is the primary compound in natural gas (used for fuel). Here we have no linking of carbon atoms, but the molecule still fits the general prescription insofar as being a hydrocarbon,
having only single bonds, satisfying carbon’s valence of four, and having the formula C\(_n\)H\(_{2n+2}\). Hence, methane is the first member of this family. Ethane is the second member, and propane is the third. Propane is also widely used as a fuel gas and is stored in steel tanks which you have seen outside of some houses or trailers. The fourth member of the family is butane. Again, you may have heard of this as a fuel for cigarette lighters. Butane is also a gas at room temperature.

Notice that all of these compounds are named with a suffix “ane.” This is not a coincidence. Chemists did not *discover* that ethane is named ethane. (“Hi, I have two carbons, and my name is ethane.”) The “ane” suffix is the code that chemists have agreed to use to carry the information that the molecule belongs in this hydrocarbon family. The name “octane” informs us that it has its carbons linked together with single bonds and that it is a hydrocarbon of formula C\(_n\)H\(_{2n+2}\). Furthermore, the name tells us that \(n=8\), through the use of the prefix “oct.” The prefix code names for the value of \(n\), from one to ten are listed below. You should learn these.

<table>
<thead>
<tr>
<th>Number of carbons</th>
<th>Prefix</th>
<th>Example for alkane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Meth</td>
<td>Methane</td>
</tr>
<tr>
<td>2</td>
<td>Eth</td>
<td>Ethane</td>
</tr>
<tr>
<td>3</td>
<td>Prop</td>
<td>Propane</td>
</tr>
<tr>
<td>4</td>
<td>But</td>
<td>Butane</td>
</tr>
<tr>
<td>5</td>
<td>Pent</td>
<td>Pentane</td>
</tr>
<tr>
<td>6</td>
<td>Hex</td>
<td>Hexane</td>
</tr>
<tr>
<td>7</td>
<td>Hept</td>
<td>Heptane</td>
</tr>
<tr>
<td>8</td>
<td>Oct</td>
<td>Octane</td>
</tr>
<tr>
<td>9</td>
<td>Non</td>
<td>Nonane</td>
</tr>
<tr>
<td>10</td>
<td>Dec</td>
<td>Decane</td>
</tr>
</tbody>
</table>

The family we have been describing has an unlimited number of members, since \(n\) has no upper limit. We need a name for the whole family. How about hydrocarbon? This won’t do because, as we shall see, there are many other ways to make compounds containing only hydrogen and carbon. Members of this family are hydrocarbons, but not all hydrocarbons are members of this family. The generic prefix that is used to name a particular family of hydrocarbons is “alk.” So we are talking about molecules in the alkane family. But we are going to see soon that we can have molecules that have the formula C\(_n\)H\(_{2n+2}\) but do not have all of their carbons linked in a simple chain; the chain can be branched. The name alkane refers to the whole C\(_n\)H\(_{2n+2}\) family, branched or unbranched, having only single bonds. The name *straight-chain alkanes* refers to the sub-family we have been talking about.

There is one more bit of terminology we should mention here. We keep mentioning the fact that we are discussing molecules having only single bonds. We could include some double or triple bonds in the chain, but that would require us to remove some hydrogen atoms. (If a carbon already has four bonds, and we change a single bond to a double one, the carbon will have five bonds unless we remove a bond to something else.) Another way to describe this is to say that we have used the valences of carbon to attach the maximum possible number of hydrogens to the carbon chain. The carbon skeleton is saturated with hydrogens. For this reason, we also refer to these molecules as *saturated hydrocarbons*.
We will be looking at both physical and chemical properties of organic compounds. Physical properties include such things as boiling point, melting point, density, solubility in water or in other liquids, odor, taste and color. These are properties that can be measured or observed without transforming the substance into a different substance. Chemical properties generally concern chemical reactivity. Does the material burn in oxygen? Does it react with an acid? Does it form a new substance when mixed with chlorine? The answers to such questions, whether yes or no, are chemical properties, and they require us to at least attempt to change the material in the process of measuring the property.

The alkanes (both branched and straight-chain) are not very chemically reactive, compared to many other kinds of organic compounds. We will see examples later that this means that, if an organic molecule has a saturated hydrocarbon part and different kind of part, for example a double bond, then a reaction can take place at the double bond without doing anything to the saturated hydrocarbon part. In other words, organic and biochemists see lots of reactions where saturated hydrocarbon sections are present, but just “go along for the ride,” with the real chemical action taking place in other parts of the molecules. You will soon come to appreciate the importance of this for classifying families of reactions.

However, just because they are not very reactive does not mean that the alkanes are near or at the lowest-energy situation for hydrogen and carbon. We know that methane, propane, butane, and octane are common fuels, which means that they combine with oxygen to produce a good deal of heat. Such reactions are called combustion. If there is adequate oxygen present, combustion of hydrocarbons produces water, carbon dioxide, and heat. The equation for the complete combustion of propane is:

\[ C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \]

If insufficient oxygen is present for complete combustion, incomplete combustion can occur. As a general rule, the oxygen is first used to form water from the hydrogen, and secondarily to oxidize the carbon. Therefore, the octane burning in an automobile engine that is running “rich” (meaning there is excess gasoline for the amount of air present) will produce water, and some carbon monoxide (CO) along with the carbon dioxide. When a kerosene lamp is burned with inadequate air, water and some carbon (seen as soot) are produced, along with some carbon monoxide and carbon dioxide.

The message we get from these observations is that an alkane plus oxygen is not nearly as stable as water plus carbon monoxide or carbon dioxide, because much energy is released when the former converts to the latter. And yet alkanes can coexist with oxygen indefinitely, reacting only after a spark or flame initiates the process. We can only conclude that the process of partially breaking the bonds in the alkane molecules, thereby allowing new bonds to form, requires too much energy to occur at room temperature. In short, alkanes are rather unreactive, not because they already enjoy the best bonding situation, but because they resist breaking their existing bonds in order to form still stronger ones.
Chemists like to picture the reaction situation described above with a simple diagram, sketched below:

![Energy diagram](image)

The vertical coordinate is energy; moving up means energy is absorbed, and moving down means it is released. The horizontal coordinate represents the progress of the reaction; reactants are at the left, and products are at the right. For the alkane-plus-oxygen reaction, we know that heat is given off, so we know that the products are lower in energy than the reactants. That means that the finishing point at the right is lower than the starting point on the left. But significant energy is needed to make the reaction take place. This is represented by drawing a hill in the reaction energy curve. The hill represents the amount of energy that the reactants must absorb in order to partially break the old bonds before beginning to form the new bonds. All that energy, and more, is regained when the new bonds form. Any chemist can tell at a glance from such a sketch whether a reaction will or will not give off significant heat, and also whether a reaction will take place spontaneously or with difficulty.

The above discussion should make you realize, perhaps for the first time, that chemistry involves much more than simply remembering facts and equations, like “alkanes are not very reactive,” or “alkanes burn in oxygen to produce water and carbon dioxide.” It involves seeking a detailed picture of what occurs at the molecular level when a reaction takes place, and being able to infer information about molecular processes from such things as the inability of alkanes to combust without an ignition source of some kind. Only through understanding at this level can scientists design more efficient fuels and engines, better materials, and compounds that can cure diseases.

The physical properties of straight-chain alkanes, and the way these change as we proceed up the series, is interesting and revealing. Most books list a few of these for the reader in an efficient paragraph or two. However, our strategy is to get you to dig these out for yourself from tabulated data you will find at the end of this chapter. You will be asked to find trends and generalizations regarding melting point, boiling point, density, and solubility in water. As you pick out and evaluate such data and try to find ways to make sense of it, you will be operating on an intellectual level much more representative of scientific pursuit than would be the case if we prepackaged conclusions for you.
Branched alkanes. Consider the two structural formulas shown below.

\[ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \]
\[ \text{H} - \text{C} - \text{C} - \text{H} \]

Are these different compounds? No. Both are “straight-chain” hydrocarbons because both have the same connection scheme – a carbon with a second carbon attached and then a third carbon attached to the second and fourth carbon attached to the third. We chose to draw the carbons in a straight line in the formula on the left and in a bent line on the right, but that doesn’t signify a real difference. This is a flexible molecule that is writhing about so no particular orientation of the chain is uniquely correct. Therefore, both of these formulas should be viewed as proper representations of butane.

Now consider another formula:

\[ \text{H} - \text{C} - \text{C} - \text{H} \]
\[ \text{H} - \text{C} - \text{H} \]

This one really is different from the other two, because the connection pattern of the carbons is different. Here we have a carbon with a second one attached, and then two carbons attached to the second; there is a branching at the second carbon. Notice that, no matter which end we start at, the longest chain we can find has only three carbons. There is no way this branched molecule can turn into the unbranched version by writhing around. Only if we break a C–C bond and a C–H bond and reconnect the pieces can we turn the branched into the unbranched molecule. Therefore, we recognize the branched molecule as a different compound than the unbranched one. They will have different boiling and melting points, and different densities, even though they share the same compositional formula, C$_4$H$_{10}$.

We have two different compounds made up of 4 carbons and 10 hydrogens. These two are said to be structural isomers of each other. (*Iso* means “same” and *mer* means “part.”) C$_4$H$_{10}$ is the first member of the alkane family to have structural isomers and there are only two of them. C$_5$H$_{12}$ occurs as three structural isomers, C$_6$H$_{14}$ as five, C$_7$H$_{16}$ as nine, C$_8$H$_{18}$ as eighteen, and C$_{10}$H$_{22}$ as seventy-five. In each of these cases, one isomer is a straight-chain molecule and the others are branched in different ways. Isomers are different compounds having the same formula.
Consider the three formulas shown below for \( \text{C}_5\text{H}_{12} \):

\[
\begin{align*}
\text{CCC} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Are these different? They look different, but they are really the same molecule either bent (without breaking any bonds) or else turned so that the branching appears on the other side. All three have the pattern of a chain of four carbons with one more carbon branched off of the carbon coming just before the end of the chain.

**SAMPLE EXERCISE** Draw the structural formulas for the three structural isomers of \( \text{C}_5\text{H}_{12} \).

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

The problem immediately arises, how are we to distinguish by name between structural isomers? If we use the name “pentane” for all three of the molecules shown in the Sample Exercise, our label is ambiguous.

Various naming conventions have been used over the years. The currently accepted convention, defined by the International Union of Pure and Applied Chemistry (IUPAC), is the one we will use (to a modest extent) in this course. For alkanes, the naming rules we will use in this course are quite simple. We will start the explanation by giving the names of the three structural isomers of \( \text{C}_5\text{H}_{12} \), shown in the Sample Exercise above. From left to right, they are named pentane, 2-methylbutane, and 2,2-dimethylpropane. Comparing these names to the structures will give you a pretty clear idea of how this system works. Basically, we end the name of the structure according to the longest continuous chain of carbons present, and we modify that name with the prefixes that tell what the branches are and where they are attached. Thus, 2-methylbutane tells us that we have a four-carbon chain with a branch called “methyl” at carbon number two.

We need to say more about “methyl” and also about “carbon number two.” *Methyl* refers to a group that is like methane, except it is missing one hydrogen because it is using one bond to connect to a carbon in the continuous chain. The methyl group has the formula \( \text{CH}_3 \), but it is not a stable molecule since it doesn’t satisfy the valence of carbon. (Methyl groups can exist, but
they tend to react quickly with other molecules if they come in contact with them.) If the branch had two carbons, it would be called an ethyl group (formula C₂H₅). Any group formed by removing a hydrogen from an alkane is called an alkyl group. “Carbon number two” means the second carbon from the end of the continuous chain. The potential ambiguity here is, which end? Clearly, the compound we have called 2-methylbutane could just as easily be called 3-methylbutane by starting our numbering from the other end of the butane part. The IUPAC rule is that one should number the continuous chain so that the branching points get the lowest numbers.

Another convention we need to know is that, if the same type of branch occurs several times in the molecule, we indicate it by using a prefix: di- (two), tri- (three), tetra- (four), penta- (five), and so forth. Thus, 2,2-dimethylpropane means that there are two methyl groups present, both of which are bonded to the second carbon of the propane chain.

Finally, if there are several kinds of branch, they should appear in the name in alphabetical order. If both methyl and ethyl branches are present, the ethyl branch is listed first. If there is an ethyl and two methyl branches, then ethyl precedes dimethyl: the di, tri, tetra,…are not considered part of the name when alphabetizing.

**SAMPLE EXERCISE** Name the following alkane:

![Alkane structure](image)

We select the longest chain. (There are actually two equivalent longest chains.) It has seven carbons, so the name will end in heptane. We number from the right because this gives branches at atoms 2 and 4. If we chose the other end, the branches would be at atoms 4 and 6. The branch at 2 is a methyl and that at 4 is an ethyl. Ethyl is first, alphabetically, so the name is 4-ethyl-2-methylheptane.
SAMPLE EXERCISE  Name the following alkane:

\[
\begin{align*}
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{C} \\
&\text{C} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
\end{align*}
\]

The longest chain for this molecule has seven carbons, but we have to turn a few corners to get them all in. We have to number from the right end to keep the branching numbers lowest (2 and 4). The name is 4-ethyl-2-methylheptane. Note that this is the same name we obtained for the previous example. This indicates that these are the same molecule, even though they have been drawn differently. The systematic naming procedure helps us to avoid mistaking two superficially different structures for different molecules.

SAMPLE EXERCISE  Draw the structure of 3-ethyl-4,6,6-trimethyldecane.

\[
\begin{align*}
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
\end{align*}
\]

The three structural isomers of C₃H₁₂ shown earlier have the same numbers of hydrogen and carbon atoms and the same number of C–C and C–H bonds. However, their physical and chemical properties are not identical. For example, their boiling points are different: pentane's is 36°C, and 2,2-dimethylpropane’s is 9.5°C. The first two are liquids at room temperature and the third is a gas. For some reason, the molecules of 2,2-dimethylpropane do not stick together as strongly as those of the other isomers, and so they fly apart to form a gas at a lower temperature. Their melting points differ also. Taken in the same order, they are −130°C, −159°C, and −16.6°C. The differing amounts of attraction between molecules influences the readiness with which they allow heat to cause the molecules to become unlocked from each other and to move about. It is interesting to try to think of a reason why 2,2-dimethylpentane molecules cling together as a solid to a much higher temperature than the other isomers, and then, after liquefying, separate most easily to form a gas. You will be asked to dig out and
contemplate a few trends in connection with reading this chapter. Later on in the course you will encounter more detailed discussions of the factors influencing such attractions.

**Cycloalkanes.** It is possible for carbon to link up into rings as well as chains. When saturated hydrocarbons form rings, they are called cycloalkanes. If there are six carbons in the ring, we have cyclohexane, and so forth. Since it takes at least three carbons to make a ring, cyclopropane is the first member of this series. Cycloalkanes do not have the formula \( C_nH_{2n+2} \). We leave it as an exercise for you to figure out what the general formula is.

![Two structural formulas for cyclohexane](image)

**Some Unsaturated Hydrocarbons.** There are two ways to create organic compounds outside of the class of saturated hydrocarbons. One is to include atoms other than carbon or hydrogen, and the other is to replace one or more single \( C\)–\( C \) bonds with double or triple bonds. The latter strategy still gives hydrocarbons, but now there are fewer than the maximum possible number of hydrogens attached to the carbon skeleton, so they are called *unsaturated* hydrocarbons.

A simple example, shown below, contains two carbons attached by a double bond.

![Ethylene](image)

The common name for this compound is ethylene. It is a gas that has important industrial uses, one of which is for ripening fruit. It turns out that ethylene is given off by ripe fruit. It also causes fruit to ripen more quickly. That’s why putting very ripe fruit into a bowl with unripe fruit hastens the ripening of the latter (as well as the rottin of the former). This is the basis of the old saw: one bad apple spoils the barrel, and it is a nice example of how a product of a reaction can sometimes speed up that reaction.

We will be concerned with the way a double or triple bond affects molecular structure, the way we name compounds having multiple bonds, and the way such bonds affect reactivity.

**Doubly-bonded hydrocarbons.** Recall the straight-chain alkanes writhe about, changing shape, because groups separated by a single bond can rotate easily with respect to one another. A ball-and-stick model of such a molecule can easily be twisted about because such rotation is permitted by the model. A special feature of double bonds is that they lock the groups on each side of the bond into place. Free rotation cannot take place, and rigidity is introduced into the molecule in the locality of the double bond. In the case of ethylene, the whole molecule is in the neighborhood of the bond, and no significant movement is possible anywhere in the
molecule. On the other hand, the molecules shown below are rigid around the double bond, but still undergo writhing motions in the long alkyl chains.

![ Molecular structures](image)

Notice that this means that the two molecules shown above are not simply the same molecule in different positions as it writhes about. To get from one of these structures to the other, the molecule would have to rotate about its double bond, which it cannot do. So these are really two different molecules. They are **geometrical isomers**, which means that they have the same bonding order, but a different spatial arrangement. We will need to name these two compounds in a manner that distinguishes between them.

The geometry around the double bond is not only rigid, it is planar, with each carbon having two attached groups and the double bond orientated at about 120° with respect to each other. This is shown explicitly in for the molecule below.

![ Molecular structure](image)

The presence of a double bond in a hydrocarbon is indicated with the suffix *ene*. Thus, while the molecule having two carbons connected with a single bond is named ethane, the molecule having two carbons connected by a double bond (shown above) is named *ethene*. This is different from the older name, ethylene. (In general, you will be held responsible only for the systematic names of organic compounds. However, there are a few molecules that are so frequently referred to by their common names that you will need to know them too. Ethylene is the first of these. A summary list of common names you should know will be presented at the end of this chapter.)

The molecule shown below has a three-carbon chain and one double bond. It is named *propene*.

![ Molecular structures](image)
Note that we have drawn this in two ways. However, these are not isomers because one orientation can be reached from the other by rotating the entire molecule. Propene is a rigid molecule, except for the ability of the methyl group to rotate, a motion that does little to affect the overall shape of the molecule. Ethene and propene are the first members of the general class called alkenes.

Interesting isomeric possibilities appear when we get to four-carbon straight-chain alkenes. Shown below are three different molecules:

![Chemical structures](image)

1-butene  trans-2-butene  cis-2-butene

The systematic names of these three compounds shown in the figure illustrate the basic naming rules: the suffix “ene” signals a double bond; the prefix (“but” in these cases) indicates a four-carbon chain; an ordinal number tells us which bond is double, with bonds numbered from the end that makes this number lowest; the label trans or cis indicates, respectively, whether the chain of carbons traverses the double bond without changing its general direction or whether it gets turned around by the double bond to form a “U-shaped” curve. (i.e., it is cis if the chain enters and leaves the same side of the double bond.)

**SAMPLE EXERCISE** Name the compound having the formula shown.

![Chemical structure](image)

There are eight carbons in the chain, and we find the double bond to be in either position 3 or 5, depending on whether we number the bonds from the left or the right. Choosing the lower number and observing that the chain enters and leaves the double bond on the same side, we name this compound cis-3-octene.

We mentioned earlier that alkanes are not very reactive. The C−C and C−H bonds require significant energy to break, and there is no unused bonding capacity in such molecules to offer a potential reactant a bonding opportunity. In alkenes the situation is different. The double bond between carbons is not as strong as two single bonds. Putting this another way, each of the two bonds in the double bond is less strong than it would be if it were a single C−C bond. This means that, if one of the two bonds in the pair opens up to accept a new partner, the other can become a single C−C bond. This means that the energy gain by the second bond’s becoming single can help pay the energy cost of opening the first bond. As a result, alkenes are found to be much more reactive than alkanes, and the reactions are found to take place at the double bond.
One example of this is a reaction sometimes used as a test for the presence of a double bond in a compound. A drop of bromine, which is a red-brown liquid of considerable reactivity, is added to the compound in question. If the compound is a simple alkene, the bromine reacts with an audible “pop” and the red-brown color disappears. The reaction of bromine with trans-2-heptene is shown below:

\[ \text{Br}_2 + \text{C}_7\text{H}_{10} \rightarrow \text{C}_7\text{H}_{12} \text{Br}_2 \]

The name of the product is 2,3-dibromoheptane, which should make sense to you, based on what you have seen so far. Can you see why we not longer need the term cis or trans?

The type of reaction shown above is called an addition reaction because bromine has been added to the molecule without any other atoms being taken away.

**Triply-bonded hydrocarbons.** If a triple bond is present in a hydrocarbon, we refer to it as an alkyne. The simplest alkyne contains two carbons and is shown below:

\[ \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H} \]

**Ethyne (common name; acetylene)**

This molecule is linear, which is to say that the single and triple bonds emanating from a carbon atom come out at a 180° angle with respect to each other. Because of its linearity, the possibility for cis or trans geometrical isomerism does not come up, nor does it matter whether rotation about the triple bond is possible. Alkynes, like alkenes, are reactive at the position of the multiple bond. The only significant difference is that an alkyne can react in steps, first adding a reactant to form a product with a double bond, and then adding more reactant to form a product with only single bonds.
SAMPLE EXERCISE  Chlorine, Cl₂, reacts with 3-heptyne. Draw structures for all of the products you could expect to be formed in partial or complete addition reactions.

The structure for 3-heptyne is shown below:

![3-heptyne structure](image)

When Cl₂ adds to the triple bond to change it to a double bond, we can envision two products, shown below:

![3,4-dichloro-cis-3-heptene and 3,4-dichloro-trans-3-heptene](image)

3,4-dichloro-cis-3-heptene  
3,4-dichloro-trans-3-heptene

When another chlorine reacts with either of these heptenes, the product is:

![3,3,4,4-tetrachloroheptane](image)

3,3,4,4-tetrachloroheptane

Aromatic Hydrocarbons

A very important unsaturated hydrocarbon is shown below:

![Benzene](image)

Benzene

Notice that it consists of a ring of six carbons, each bonded to one hydrogen. The molecular structure is drawn with three single C–C bonds and three double ones. The valence rules are satisfied regardless of whether we place the double bonds as shown on the left or on the right in the figure. In either case, we should expect the whole molecule to lie in the same plane (see if you can reason this out), with the bond angles around each carbon being 120°. This molecule is named benzene.

Benzene was recognized to be a very important compound in the 1800’s, and its formula, C₆H₆, was determined quite early. But is structure was a mystery for some time since no one could figure out how to satisfy the rules of valence with six carbons and only six hydrogens. The
fact that double bonds are present was obscured by the fact that benzene does not react spontaneously with bromine the way ethane does. And the fact that a chain could bend back on itself to form a ring was also not recognized. It was a scientist named Kekulé who finally guessed the structure shown above. The failure of the double bonds to react with bromine is just one of many pieces of evidence that double bonds in benzene are much more stable than a double bond in an alkene. It is now recognized that double bonds that are conjugated, i.e., that occur in groups (double-single-double-single…), are much more stable than double bonds that are isolated from other double bonds by two or more single bonds. And when the conjugated double bonds occur in a cycle of six carbons, the stabilization is especially great.

Benzene is the simplest of a whole class of related compounds made up of rings of six with conjugated double bonds. A few more are shown below:

(Except for benzene, you are not responsible for these names. We mention them only because you may have run across some of them already. Naphthalene, for instance, is the chemical that is also called “moth balls.”)

Benzene and related molecules are called aromatic hydrocarbons. Sometimes the members having more than one ring are called “polycyclic aromatic hydrocarbons,” or PAHs. These are mentioned frequently in the popular press because some of them cause cancer (i.e., are carcinogenic), and because they occur in our environment (e.g., in a well-grilled steak, or in diesel exhaust). For our purposes in this chapter, you should remember that these compounds are planar and that they are remarkably unreactive, considering that they have double bonds. In fact, if chemical tricks are used to force benzene to react with say, chlorine, the product is not the addition product resulting from changing double bonds to single ones. Rather, it is the molecule C₆Cl₆, shown below:

Notice that the benzene has reacted in a manner to preserve its double bonds. Such a reaction is called a substitution reaction, rather than an addition reaction, since chlorine atoms actually substitute for the hydrogens instead of simply adding to the parent compound.

Hexachlorophene kills bacteria, and was an ingredient in some toothpastes and topical disinfectants until recently, when it was recognized to be slightly carcinogenic. The suffix “phene” is often used to indicate the presence of a benzene ring.
5. **Functional Groups**

So far we have looked at hydrocarbons, molecules that contain only carbon and hydrogen. The alkanes we found to be relatively unreactive. By introducing one or more multiple bonds we created new classes of compounds – the alkenes and alkynes – with different chemical properties. A relatively small change in one part of a hydrocarbon can result in large changes in its behavior.

We will now look at some new classes of compounds that result from the introduction of atoms other than carbon and hydrogen. We will consider only two such atoms, oxygen and nitrogen. But you will see that with this apparently small extension we will be able to describe many of the molecules that are fundamental to biology and others that are on the constantly growing list of important synthetic materials. Before you read further, look again at a periodic table and review the locations of carbon, nitrogen, and oxygen.

The new classes of compounds we will consider are characterized by specific arrangements or groups of atoms. These groups cause the molecule containing them to have special and specific chemical and physical properties. For this reason they are called functional groups. Double and triple bonds may be thought of as functional groups.

5.1 **Alcohols**

If we replace one (or more) of the hydrogen atoms in a hydrocarbon with a hydroxyl group, −OH, we get an alcohol. For instance, if we replace one hydrogen in methane, CH₄, with an OH group we get H₃COH, or CH₃OH. This compound is called methyl alcohol or methanol. If we do the same with ethane we get ethyl alcohol or ethanol. When we make these substitutions we immediately see striking changes. Methane and ethane are both gases at room temperature; methanol and ethanol are liquids. Hydrocarbons are only slightly soluble in water. Methanol and ethanol are **miscible** in water; that is, they dissolve in water in any and all proportions. Some similarities remain: both ethanol and methanol burn readily in the presence of adequate oxygen to give water and carbon dioxide.

The naming of alcohols is simple. The last letter in the name of the alkane is changed to −ol. If necessary a prefix numeral is used to show which carbon in the carbon chain contains the −OH group. There are, for instance, two structural isomers of propanol. CH₃CH₂CH₂OH is 1-Propanol and CH₃CHOHCH₃ is 2-Propanol. Some of alcohols were shown earlier on page O.8-O.9 of these notes. Look through your own collection of personal-care products (medicines, hair-care materials, toothpaste, deodorant, etc.) and see how many of them contain compounds whose names have the −ol ending or the word “alcohol.” Ordinary rubbing alcohol, for instance, is largely 2-Propanol and water.

At this point you should read section 19.2 of your textbook through the material on alcohols. We have already mentioned the combustion reaction of alcohols. As we consider other functional groups we will see some other important reactions of alcohols.

5.2 **Ethers, aldehydes, and ketones**

Read about these functional groups in sections 19.3-19.5 of your textbook. You should be able to recognize these functional groups as well as the carbonyl group. Look at each of these groups carefully and convince yourself that the valence rules discussed earlier are obeyed in all of them.
5.3 Carboxylic acids and esters

You should recall that the simplest definition of an acid is a compound which, when dissolved in water, produces some hydrogen ion, $H^+(aq)$. (The symbol “aq” here means “aqueous” and means that the ion is in water solution.) Thus, nitric acid, $HNO_3$, is an acid because in water it gives hydrogen ions and nitrate ions:

$$HNO_3 \rightarrow H^+(aq) + NO_3^-(aq)$$

Nitric acid is called a strong acid because this ionization reaction in water is complete; all of the nitric acid goes to ions.

Organic acids are described in section 19.6 of your text; you should read this material. One of the most common organic (or carboxylic) acids is acetic acid, $CH_3COOH$. The structural formula is:

![Acetic Acid Structure](image)

It is an acid because in water it gives hydrogen ions and acetate ions:

$$CH_3COOH \rightarrow H^+(aq) + CH_3COO^-(aq)$$

Note that it is the hydrogen on the carboxyl group, $-COOH$, that comes off; the hydrogens on the methyl group are not acidic. Acetic acid is called a weak acid because only a small fraction of the acetic acid molecules in aqueous solution form ions; most of them remain as unionized molecules. Acetic acid is familiar to you as the acid in vinegar. It will be mentioned and used as an example throughout the course so you should know its structural formula.

Why does the $-OH$ in a carboxylic acid tend to release its hydrogen as an ion in water while the $-OH$ in an alcohol does not? This is an interesting question which we will discuss later in the course after we have learned more about the structures of molecules and ions.

Organic acids and alcohols can react to form esters. They are described on pages 996-997 of your textbook. The reaction is called a condensation reaction because two molecules – acid and alcohol – condense into one molecule, the ester, with the elimination of a small molecule, water.

5.4 Amines and amides

Many important industrial and biological organic molecules contain nitrogen as well as carbon and hydrogen. Amines and amides are two of the major classes of nitrogen-containing organic molecules. They are described in section 19.8 of your textbook.

To understand the chemical behavior of amines, let’s start with ammonia, $NH_3$. Ammonia itself is a gas at room temperature and it readily dissolves in water, where it acts as a base. Remember that the simplest definition of a base is a compound that produces hydroxide ion, $OH^-$ in water. Sodium hydroxide, $NaOH$, is a strong base. When dissolved in water it ionizes completely:
NaOH $\rightarrow$ Na$^+(aq) + $ OH$^-(aq)$

Ammonia is a weak base. When dissolved in water a small amount goes to form ions:

$$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+(aq) + \text{OH}^-(aq)$$

If we replace one (or more) of the hydrogens in ammonia with an alkyl group we create an amine. For example, CH$_3$CH$_2$NH$_2$ is ethylamine. Many drugs – prescription, over-the-counter, and illegal – contain the amine functional group. Look, for example, at the ingredients of medications for colds and allergies.

We will discuss the amide functional group in the following sections. You should be able to identify it and, as with the other groups, you should verify that it satisfies the valence rules.

6. Polymers

Polymers are molecules made up of long chains of repeating units. They are of fundamental importance as synthetic materials, such as plastics, and in biological systems. We will first discuss synthetic polymers and will refer to section 19.9-19.12 of your textbook. Then we will look at some of the biological polymers discussed in 19.13-19.15.

You should review these:

- organic chemistry
- biochemistry
- alkanes, alkenes, alkynes
- aromatic hydrocarbons
- structural isomer
- alkyl group
- cycloalkanes
- geometrical isomers
- addition reaction
- functional group
- alcohol, ether, carbonyl group,
- aldehyde, ketone
- ester, saponification
- amine, amide
- protein, amino acid
- carbohydrate

<table>
<thead>
<tr>
<th>List of Common Names</th>
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<tbody>
<tr>
<td>ethylene</td>
</tr>
<tr>
<td>acetylene</td>
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<tr>
<td>formaldehyde</td>
</tr>
<tr>
<td>acetaldehyde</td>
</tr>
<tr>
<td>benzene</td>
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</tbody>
</table>
PROBLEMS

1. Draw formulas for the simplest molecules you can construct from the following atoms. Be sure the rules of valence are satisfied. Don’t worry about bond angles.

   (a) carbon and oxygen

   (b) hydrogen and chlorine

2. Carbon combines with oxygen to form two different compounds, carbon monoxide (CO) and carbon dioxide (CO₂). Based on valence rules, which compound would you predict to be the more stable?

3. In Section 3, a formula is shown for carvone. Write the formula out in a manner such that all the atomic symbols are shown explicitly. What is the molecular mass of this compound in amu?

4. How many hydrogen atoms are present in a noncyclic saturated hydrocarbon having (a) 123 carbon atoms? (b) a molecular mass of 842 amu? (Assume that carbon and hydrogen atoms weigh exactly 12 and 1 amu, respectively.)

5. Brown, LeMay, and Bursten, Problem 25.18(a).

6. Sometimes all of the isomers for a noncyclic saturated hydrocarbon are named as a group with the name of the straight-chain member. For example, all of the molecules having the formula C₆H₁₄ can be collectively referred to as hexane. When only the straight chain isomer is meant, it is often referred to as n-hexane (for normal hexane). Draw structures for as many isomers of hexane as you can. Name them using the IUPAC rules. Which one is n-hexane?

7. Diamond and graphite are two forms of pure carbon having different bonding arrangements. It is known that, if diamond converts to graphite, a small amount of heat is released. But diamond is extremely stable at room temperatures, and exists indefinitely with no tendency to convert to graphite. Sketch the qualitative reaction energy curve that corresponds to this situation.

8. At room temperature, the molecule for a methyl fragment, CH₃, reacts whenever it encounters another methyl fragment, forming ethane and giving off a large amount of energy. Sketch the qualitative reaction curve that corresponds to this situation. What does this curve imply about the ease with which an ethane molecule can break up into two methyl groups?

9. Write all the isomers you can having the formula C₆H₁₂. (Don’t forget cycles.)
10. How many carbon atoms are in the longest continuous chain of carbon atoms in each of the following?

(a) butane  
(b) 2-methylpropane  
(c) 2,2-dimethyloctane  
(d) 2,3-dimethylpentane  
(e) 2,2,5,5-tetramethylhexane

11. What is the relationship between each of the following pairs of structures? Are they totally different molecules (i.e., which do not have the same molecular formula), are they isomers, or are they two drawings of the same compound?

(a) C₄H₁₀  
(b)  
(c)  
(d)  
(e) 

12. Name each of the following compounds:

(a) (CH₃CH₂CH₂)₂CHCH₃  
(b) CH₃(CH₂)₅CH(CH₃)₂  
(c)
13. To each of these questions, involving pairs of molecules answer Yes or No.

(a) Is A an isomer of B?

(b) Is C an isomer of D?

(c) Is E an isomer of F?

(d) Is G an isomer of H?
(e) Is I an isomer of J?

\[
\begin{align*}
\text{I:} & \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{C} - \text{H} \\
& \quad \text{H} - \text{C} - \text{H} \\
\text{J:} & \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{C} - \text{H} \\
& \quad \text{H} - \text{C} - \text{H}
\end{align*}
\]

(f) Is K an isomer of L?

\[
\begin{align*}
\text{K:} & \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} \\
\text{L:} & \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}
\end{align*}
\]

(g) Is M and isomer of N?

\[
\begin{align*}
\text{M:} & \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} \\
\text{N:} & \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{H} - \text{H} - \text{H} \\
& \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}
\end{align*}
\]

14. Brown, LeMay, and Bursten, Problem 25.19. All parts except (c) and (e).

15. Draw the structural formula for 1,3-dimethylcyclooctane. Do not worry about bond angles.

16. What general formula applies for a cyclic hydrocarbon having n carbon atoms? What about a cyclic hydrocarbon to which a methyl group is attached, having a total of n carbons?

17. Write a structural formula for each of the following compounds:

(a) 2,2-dimethylhexane

(b) butylcyclopentane

(c) 4-ethylheptane
18. Give the molecular formula of an alkane, an alkyne, and an aromatic hydrocarbon that in each case contains six carbon atoms. Which are saturated and which are unsaturated hydrocarbons?

19. Figure out the general formula for simple alkenes and alkynes. Is it the case that any molecule having a formula that fits the general rule for alkenes must therefore be an alkene?

20. Explain why 2-butene exists as cis-trans isomers, whereas 2-butyne does not. Can 1-butyne exist as cis-trans isomers?

21. Write a balanced equation for the complete combustion of each of the following in oxygen:
   
   (a) pentane
   (b) cyclopropane
   (c) 2-butene
   (d) 1-butyne

22. Give the compositional formula for each of the following. (see p. O.6)
   
   (a) an alkane with eight carbon atoms
   (b) an alkene with six carbon atoms and one double bond
   (c) an alkyne with five carbon atoms and one triple bond
   (d) a cycloalkane containing a six-membered ring of carbon atoms

23. Generally it is much easier to go from a name to a molecular structure than vice versa. Even though you wouldn’t be able to name the following compounds from their structures, you should be able to guess how to draw their structures from their names.

   (a) 1,3-butadiene
   (b) 1,3-hexadien-5-yne

24. Polycyclic aromatic hydrocarbons have the property that the double bonds may be placed in more than one way, always satisfying the rules of valence. Show that this is true for naphthalene, anthracene, phenanthrene, and pyrene. In each case, figure out the maximum number of possible arrangements that exists.

25. In the section called “Doubly-bonded Hydrocarbons,” (p. O.18) the first drawing shows two molecules. Name them.

26. Draw a structural formula for CH₂Cl₂, not worrying about molecular shape. If this molecule were planar, with bond angles of 90°, how many isomers would there be? If it is tetrahedral, with bond angles of 109.5°, how many isomers are there?

27. If benzene were to react with chlorine via an addition reaction instead of a substitution reaction, what would be the compositional formula of the product?
28. HCl can add to a double or triple bond, just as Cl₂ can, except now an H becomes attached to the carbon at one end of the bond and a Cl to the carbon on the other end. Draw as many isomers as you can for the intermediate and final products of the addition of HCl to 2-pentyne.

29. Methylanthracene is anthracene with a hydrogen replaced by a methyl group. How many isomers of methylanthracene are there?

30. Benzene has compositional formula C₆H₆. Do all polycyclic aromatic hydrocarbons have the formula CₙHₙ?

31. Write the structural formulas for each of the following noncyclic compounds containing three carbon atoms.

(a) a primary alcohol
(b) a secondary alcohol
(c) an aldehyde
(d) a ketone
(e) a carboxylic acid
(f) an ether
(g) an amide
(h) a primary amine

32. Identify the functional groups in each of the following compounds:

(a) \[
\begin{array}{c}
\text{CH₃CCH₂CH₃} \\
\text{O}
\end{array}
\]

(b) \[
\begin{array}{c}
\text{CH₃C=O} \\
\text{OH}
\end{array}
\]

(c) \[
\begin{array}{c}
\text{CH₂CH₂CH₃} \\
\text{OH}
\end{array}
\]

(d) \[
\begin{array}{c}
\text{CH₃OCCH₂CH₃} \\
\text{O}
\end{array}
\]

(e) \[
\begin{array}{c}
\text{H₂NCCH₃} \\
\text{O}
\end{array}
\]

(f) \[
\begin{array}{c}
\text{CH₃CH₂NH(CH₃)}
\end{array}
\]
33. Identify the functional groups in each of the following compounds:

(a) \[
\begin{array}{c}
\text{H}_2\text{N} \\
\text{O} \\
\text{C} \xrightarrow{\text{HO}} \\
\text{OH}
\end{array}
\]

(b) \( \text{CH}_2=\text{CH} \xrightarrow{\text{CH}_2\text{OH}} \)

(c) \( \text{CH}_3\xrightarrow{\text{O}} \text{CH} \xrightarrow{\text{NHCH}_3} \)

(d) \( \text{CH}_3\xrightarrow{\text{CH}_3\xrightarrow{\text{C}} \xrightarrow{\text{O}}} \)

(e) \( \text{HC} \xrightarrow{\text{CH}_2\text{CH}_3} \)

(f) \( \text{HC} \xrightarrow{\text{C}} \xrightarrow{\text{HO}} \text{CH}_2\text{OH} \)

34. To which class or classes of compounds does each of the following compounds belong?

(a) \( \text{CH}_3 \)

(b) \( \text{HCONH}_2 \)

(c) \( (\text{CH}_3)_2\text{C}=\text{CH}_2 \)

(d) \( \text{CH}_3\text{COOCH}_2\text{CH}_3 \)

(e) \( \text{CH}_3\text{COCH}_2\text{CH}_3 \)

(f) \( \text{H}_3\text{CC}=\text{CCH}_3 \)

(g) \( (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3 \)

(h) \( \text{CH}_3\text{CH}_2\text{NH}_2 \)

35. To which class or classes of compounds does each of the following compounds belong?

(a) \( (\text{CH}_3)_2\text{CHCH}_2\text{OH} \)

(b) \( \text{CH}_3\text{OCH}_2\text{CH}_3 \)

(c) \( (\text{CH}_3)_2\text{CHCl} \)

(d) \( \text{CH}_3\text{CH}_2\text{I} \)

(e) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \)

(f) \( \text{CH}_3\text{CH}_2\text{CHO} \)

(g) \( \text{HO} \xrightarrow{\text{CH}_3} \)

(h) \( \text{CH}_2\text{OH} \)
36. The functional groups in each of the following pairs of classes of compounds are often confused. What do the members of each pair have in common and what is different about them?

(a) an amine and an amide  
(b) an aldehyde and a ketone  
(c) a carboxylic acid and an ester  
(d) an ether and a ketone

37. Write the complete structural formula for a piece of the polymer chain from the polymerization of H₂C=CHF that contains four monomer units.

38. You have seen three isomers of C₄H₈ in the section on doubly-bonded hydrocarbons. Can you find any more? How would you name these?

39. The Medicine Cabinet: The following organic compounds are found in common over-the-counter drugs that you may have used. Their common name is given along with their structure. Using the table on the next two pages, decide which of the compounds are

(a) amines  
(b) amides  
(c) alcohols  
(d) ethers  
(e) esters  
(f) ketones  
(g) carboxylic acids
## The Medicine Cabinet

<table>
<thead>
<tr>
<th>Common Name(s)</th>
<th>Activity (uses)</th>
<th>Lewis Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenhydramine hydrochloride (Benadryl, Benocten)</td>
<td>Antihistamine</td>
<td><img src="image1" alt="Lewis Structure" /></td>
</tr>
<tr>
<td>Acetaminophen (Tylenol, Tempra, Panadol, etc.)</td>
<td>Analgesic</td>
<td><img src="image2" alt="Lewis Structure" /></td>
</tr>
<tr>
<td>Acetylsalicylic acid (aspirin, Bayer, Excedrin, etc.)</td>
<td>Analgesic</td>
<td><img src="image3" alt="Lewis Structure" /></td>
</tr>
<tr>
<td>Camphor</td>
<td>Moth repellant</td>
<td><img src="image4" alt="Lewis Structure" /></td>
</tr>
<tr>
<td>Glycerin (glycerol)</td>
<td>Hand lotions</td>
<td><img src="image5" alt="Lewis Structure" /></td>
</tr>
<tr>
<td>Sodium Benzoate</td>
<td>Preservative</td>
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<tr>
<td>Ibuprofen (Motrin)</td>
<td>Anti-inflammatory</td>
<td><img src="image7" alt="Lewis Structure" /></td>
</tr>
<tr>
<td>Substance</td>
<td>Category</td>
<td>Molecular Structure</td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Oxybenzone</td>
<td>Sunscreen agent</td>
<td><img src="image1" alt="Molecular Structure" /></td>
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<tr>
<td>Phenylpropanolamine</td>
<td>Decongestant</td>
<td><img src="image2" alt="Molecular Structure" /></td>
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<tr>
<td>Phenylpropanolamine</td>
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<td><img src="image3" alt="Molecular Structure" /></td>
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<tr>
<td>Brompheniramine</td>
<td>Antihistimine</td>
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<td>Dramamine</td>
<td>Antinauseant</td>
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</tr>
<tr>
<td>Aspartame</td>
<td>Sweetener</td>
<td><img src="image6" alt="Molecular Structure" /></td>
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</table>
The following questions require that you refer to the Data Table at the end of the problems section (pp. O.41-O.42).

40. Liquid water has a density of about 1.0 g/mL at 20°C. The water molecule consists of two atoms of mass 1 amu and one atom of mass 16 amu.
   (a) Devise a crude model from which to predict what you might expect for the density of C_{30}H_{62}. (The measured density at 20°C is 0.81 g/mL.)
   (b) From the tabulated density of C_{30}H_{62}, use your simple model to predict the densities of the straight-chain alkanes having n=5-10, and 20. Compare your results with the tabulated values.
   (c) In a sentence or two, explain why these hydrocarbons are all less dense than water, and what the factor is that appears to dominate the questions of the relative densities of liquid compounds of different composition.
   (d) How would you expect the density of ethanol to compare to that of water?
   (e) How should the density of CCl_{4} compare to that of water? These two liquids are not very soluble in each other. When they are poured together, which one would you expect to float on top?

41. (a) Compare the boiling points given in the data tabulation on pp. O.41-O.42 for the straight-chain alkanes. What generalization can you make? What boiling points would you predict for C_{11}H_{24}, C_{12}H_{26}, and C_{13}H_{28}?
   (b) Compare the melting points for the same molecules as in part (a). What generalization applies here? Estimate the melting points for the same three compounds as in part (a).
   (c) Do these two generalizations seem compatible? Explain your thinking.

42. (a) Which would you predict to be more water soluble, benzene or cyclohexane? Defend your choice.
   (b) Predict whether bromoethane should be a gas or a liquid at room temperature. Defend your choice.

43. Which kind of substituent appears most effective at promoting solubility in water? Which seems least effective? (see table on pp. O.41-O.42)
   (a) −CH_{2}−
   (b) −OH
   (c) =O
   (d) −N−H
   (e) −O−
   (f) −F
44. Can you make any summary statement about the solubilities of alkanes in water as their molecular mass increases? (see table on pp O.41-O.42)

45. Do molecules of similar molecular mass but from different families (e.g., alkanes, alcohols, etc.) have the same (or similar) melting points, boiling points, densities, or solubilities?

46. Do structural isomers have the same physical properties?

47. Bromoethane is more than five times as soluble in water as fluoromethane, by weight. But each molecule of bromomethane is much heavier than a molecule of fluoromethane. Decide from the data whether or not more molecules of bromomethane than fluoromethane dissolve in a given amount of water. Based on the data, what can you conclude about the water solubility imparted to a molecule by H, F, Cl, Br and I?
### Some Physical Properties of Organic Compounds

<table>
<thead>
<tr>
<th>Name</th>
<th>MW g/mol</th>
<th>Melting Point °C</th>
<th>Boiling Point °C</th>
<th>Density at 20 °C (g/mL) (if condensed)</th>
<th>Solubility in Water at 25 °C g/100g H₂O</th>
</tr>
</thead>
</table>

#### 1. Some Alkanes, CₙH₂ₙ₊₂

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<td>16.043</td>
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<tr>
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<td>-89</td>
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<td>-</td>
<td>0.0061</td>
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<td>36</td>
<td>0.626</td>
<td>0.0038</td>
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<td>0.660</td>
<td>0.0013</td>
</tr>
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#### 2. Some Isomers of Hexane

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#### 3. Some Alkenes

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#### 4. Some Alkynes

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<td>Name</td>
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<td>Boiling Point °C</td>
<td>Density at 20°C (g/mL) (if condensed)</td>
<td>Solubility in Water at 25°C g/100g H₂O</td>
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<td>5. Some Halogenated Alkanes</td>
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<td>-95</td>
<td>40</td>
<td>1.3266</td>
<td>1.98</td>
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<tr>
<td>CHCl₃</td>
<td>119.378</td>
<td>-64</td>
<td>61</td>
<td>1.4832</td>
<td>0.76</td>
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<tr>
<td>CCl₄</td>
<td>153.823</td>
<td>-23</td>
<td>77</td>
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<td>0.079</td>
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<tr>
<td>6. Some Alcohols</td>
<td></td>
<td></td>
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<tr>
<td>Methanol</td>
<td>32.042</td>
<td>-94</td>
<td>65</td>
<td>0.7914</td>
<td>Total</td>
</tr>
<tr>
<td>Ethanol</td>
<td>44.069</td>
<td>-117</td>
<td>78</td>
<td>0.7892</td>
<td>Total</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>60.096</td>
<td>-126</td>
<td>97</td>
<td>0.8035</td>
<td>Total</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>74.122</td>
<td>-90</td>
<td>117</td>
<td>0.8098</td>
<td>8.06</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>88.149</td>
<td>-79</td>
<td>138</td>
<td>0.8144</td>
<td>2.82</td>
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<tr>
<td>1-Hexanol</td>
<td>102.176</td>
<td>-47</td>
<td>157</td>
<td>0.8136</td>
<td>0.62</td>
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<tr>
<td>1-Heptanol</td>
<td>116.203</td>
<td>-34</td>
<td>176</td>
<td>0.8219</td>
<td>0.174</td>
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<tr>
<td>1-Octanol</td>
<td>130.230</td>
<td>-17</td>
<td>195</td>
<td>0.8270</td>
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<tr>
<td>1-Nonanol</td>
<td>144.256</td>
<td>-6</td>
<td>213</td>
<td>0.8273</td>
<td>0.013</td>
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<tr>
<td>1-Decanol</td>
<td>158.283</td>
<td>7</td>
<td>231</td>
<td>0.8297</td>
<td>0.0037</td>
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<td>7. Various Compounds Having Five Heavy Atoms</td>
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<td>Pentane CH₃CH₂CH₂CH₂CH₃</td>
<td>72.14</td>
<td>-130</td>
<td>36</td>
<td>0.626</td>
<td>0.0038</td>
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<tr>
<td>1-Pentene CH₂=CHCH₂CH₂CH₃</td>
<td>70.13</td>
<td>-138</td>
<td>33</td>
<td>0.6405</td>
<td>0.0148</td>
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<tr>
<td>1-Pentyne CH≡CCH₂CH₂CH₃</td>
<td>68.12</td>
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<td>40</td>
<td>0.6901</td>
<td>0.0786</td>
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<tr>
<td>1-Butanol CH₃CH₂CH₂CH₂OH</td>
<td>74.12</td>
<td>-90</td>
<td>117</td>
<td>0.8098</td>
<td>8.06</td>
</tr>
<tr>
<td>Diethylether C₂H₅−O−C₂H₅</td>
<td>74.12</td>
<td>-116</td>
<td>34</td>
<td>0.7138</td>
<td>6.57</td>
</tr>
<tr>
<td>Butanal CH₃CH₂CH₂Ọ</td>
<td>72.12</td>
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<td>75</td>
<td>0.8170</td>
<td>9.13</td>
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<tr>
<td>Methyl ethyl ketone O</td>
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<td>79</td>
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<td>Propanoic acid O</td>
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<td>141</td>
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</tr>
<tr>
<td>Methyl acetate O</td>
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<td>-98</td>
<td>57</td>
<td>0.9330</td>
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<tr>
<td>1-Butylamine CH₃CH₂CH₂CH₂NH₂</td>
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<td>-49</td>
<td>78</td>
<td>0.7414</td>
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</tr>
<tr>
<td>Diethylamine H</td>
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<td>56</td>
<td>0.7056</td>
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