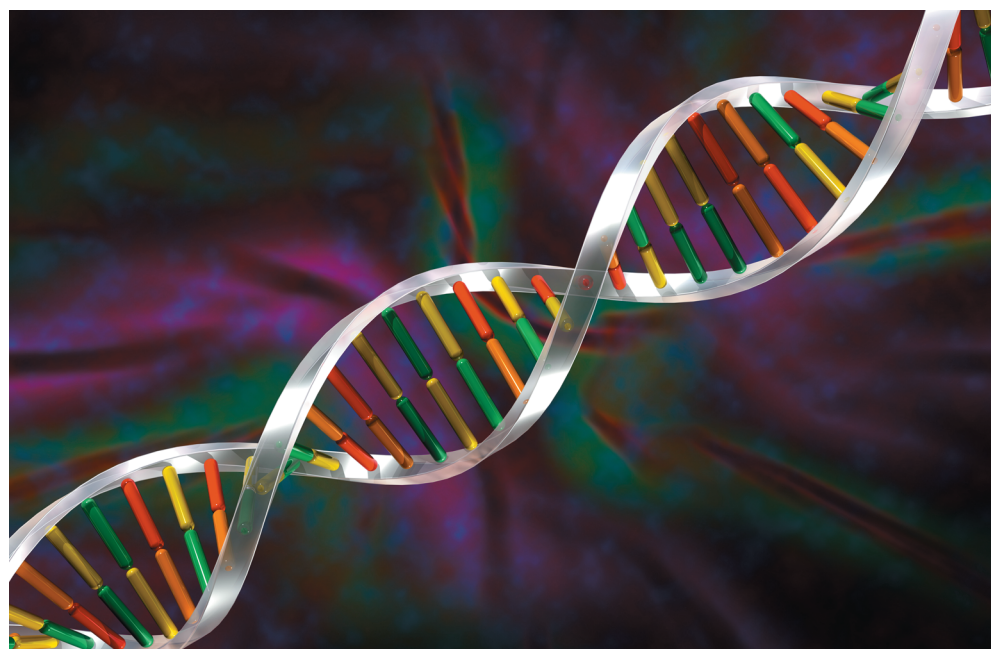


21

The Chemistry of the Nucleic Acids

a double helix



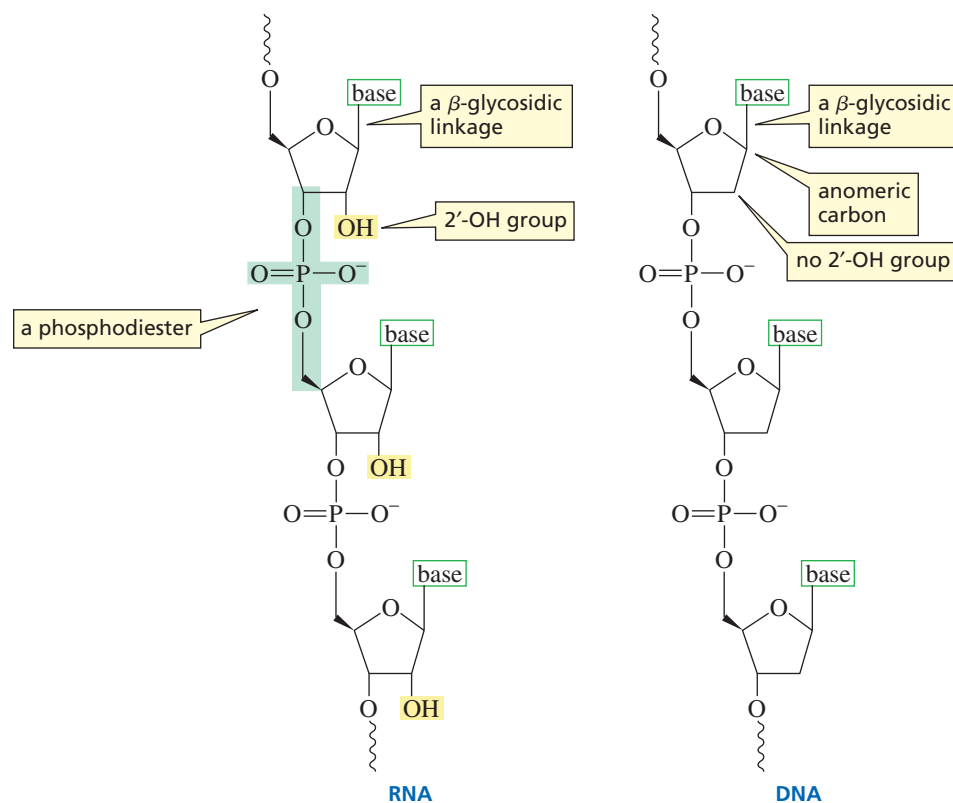
We have studied two of the three major kinds of biopolymers: polysaccharides in Chapter 16 and proteins in Chapter 17. Now in this chapter, we will look at the third kind of biopolymer—nucleic acids. There are two types of nucleic acids: deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA encodes an organism's entire hereditary information and controls the growth and division of cells. In all organisms (except certain viruses), the genetic information stored in DNA is transcribed into RNA. This information can then be translated for the synthesis of all the proteins needed for cellular structure and function.

DNA was first isolated in 1869 from the nuclei of white blood cells. Because it was found in the nucleus and was acidic, it was called *nucleic acid*. Eventually, scientists found that the nuclei of all cells contain DNA, but not until it was shown in 1944 that DNA could be transferred from one species to another, along with inheritable traits, did they realize that DNA is the carrier of genetic information. In 1953, James Watson and Francis Crick described the three-dimensional structure of DNA—the famed double helix.

21.1 NUCLEOSIDES AND NUCLEOTIDES

Nucleic acids are chains of five-membered-ring sugars linked by phosphate groups. Notice that the linkages are **phosphodiester**s (Figure 21.1). In RNA, the five-membered-ring sugar is D-ribose. In DNA, it is 2'-deoxy-D-ribose (D-ribose without an OH group in the 2'-position).

The anomeric carbon of each sugar is bonded to a nitrogen of a heterocyclic compound in a β -glycosidic linkage. (Recall from Section 16.6 that a β -linkage is one in which the substituent on C-1 of the furanose ring points up.) Because the heterocyclic compounds are amines, they are commonly referred to as **bases**.

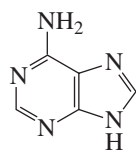


▲ **Figure 21.1**

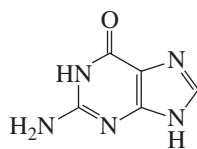
Nucleic acids consist of a chain of five-membered-ring sugars linked by phosphate groups. Each sugar (D-ribose in RNA, 2'-deoxy-D-ribose in DNA) is bonded to a heterocyclic amine (a base) in a β-glycosidic linkage.

The vast differences in heredity between different species and between different members of the same species are determined by the sequence of the bases in DNA. Surprisingly, there are only four bases in DNA: two are substituted purines (adenine and guanine), and two are substituted pyrimidines (cytosine and thymine).

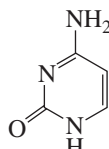
bases in DNA and RNA



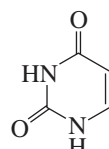
adenine



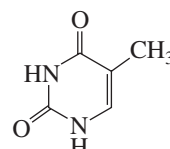
guanine



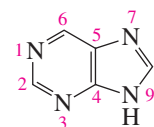
cytosine



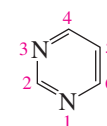
uracil



thymine



purine

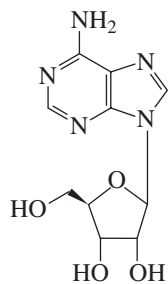


pyrimidine

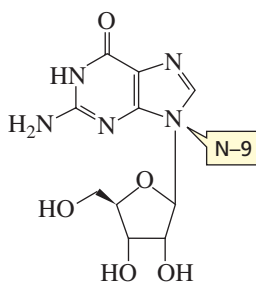
RNA also contains only four bases. Three (adenine, guanine, and cytosine) are the same as those in DNA, but the fourth base in RNA is uracil instead of thymine. Notice that thymine and uracil differ only by a methyl group. (Thymine is 5-methyluracil.) The reason DNA contains thymine instead of uracil is explained in Section 21.10.

The anomeric carbon of the furanose ring is bonded to purines at N-9 and to pyrimidines at N-1. A compound containing a base bonded to D-ribose or to 2'-deoxy-D-ribose is called a **nucleoside**. The ring positions of the sugar component of a nucleoside are indicated by primed numbers to distinguish them from the ring positions of the base. This is why the sugar component of DNA is referred to as 2'-deoxy-D-ribose.

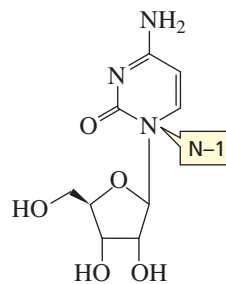
nucleosides in RNA



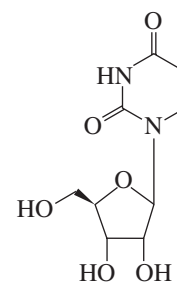
adenosine



guanosine



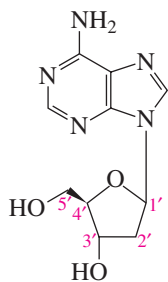
cytosine



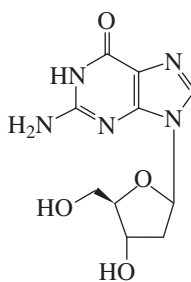
uridine

Nucleoside = base + sugar

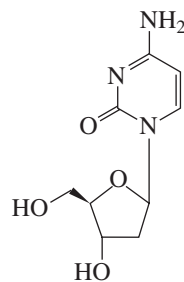
nucleosides in DNA



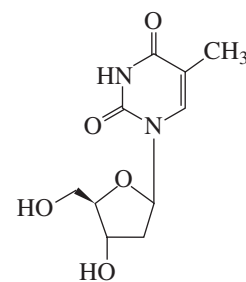
2'-deoxyadenosine



2'-deoxyguanosine



2'-deoxycytidine

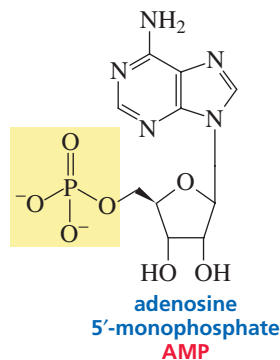
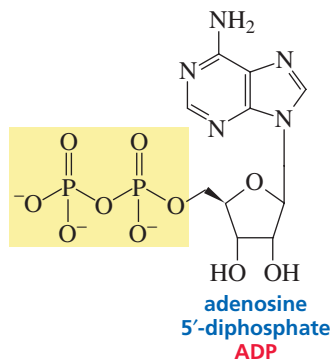
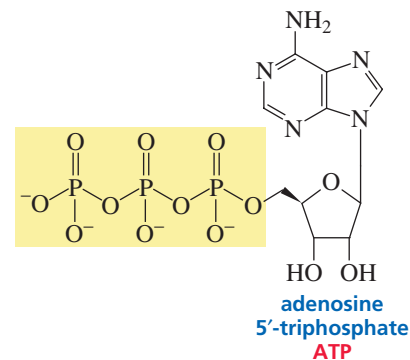


thymidine

A **nucleotide** is a nucleoside with an OH group of the sugar bonded in an ester linkage to phosphoric acid. The nucleotides of RNA are more precisely called **ribonucleotides**, and those of DNA are called **deoxyribonucleotides**.

A nucleotide can exist as a monophosphate, a diphosphate, or a triphosphate. Nucleotides are named by adding *monophosphate*, *diphosphate*, or *triphosphate* to the name of the nucleoside.

nucleotides of adenosine

adenosine
5'-monophosphate
AMPadenosine
5'-diphosphate
ADPadenosine
5'-triphosphate
ATPNucleotide = base + sugar +
phosphate

The names of the nucleotides are abbreviated (A, G, C, T, U—followed by MP, DP, or TP, depending on whether it is a monophosphate, diphosphate, or triphosphate—with a d in front if it contains 2'-deoxy-D-ribose instead of D-ribose: for example, ATP, dATP).

Notice the difference in the base names and their corresponding nucleoside (or nucleotide) names in Table 21.1. For example, adenine is the base, whereas adenosine is the nucleoside (or nucleotide); similarly, cytosine is the base, whereas cytidine is the nucleoside (or nucleotide), and so forth. Because uracil is found only in RNA, it is shown attached to D-ribose but not to 2'-deoxy-D-ribose; because thymine is found only in DNA, it is shown attached to 2'-deoxy-D-ribose but not to D-ribose.

Table 21.1 The Names of the Bases, the Nucleosides, and the Nucleotides

Base	Ribonucleoside	Deoxyribonucleoside	Ribonucleotide	Deoxyribonucleotide
Adenine	Adenosine	2'-Deoxyadenosine	Adenosine 5'-phosphate	2'-Deoxyadenosine 5'-phosphate
Guanine	Guanosine	2'-Deoxyguanosine	Guanosine 5'-phosphate	2'-Deoxyguanosine 5'-phosphate
Cytosine	Cytidine	2'-Deoxycytidine	Cytidine 5'-phosphate	2'-Deoxycytidine 5'-phosphate
Thymine	—	Thymidine	—	Thymidine 5'-phosphate
Uracil	Uridine	—	Uridine 5'-phosphate	

The Structure of DNA: Watson, Crick, Franklin, and Wilkins

James D. Watson was born in Chicago in 1928. He graduated from the University of Chicago at the age of 19 and received a Ph.D. three years later from Indiana University. In 1951, as a postdoctoral fellow at Cambridge University, Watson worked on determining the three-dimensional structure of DNA.

Francis H. C. Crick (1916–2004) was born in Northampton, England. Originally trained as a physicist, Crick did research on radar during World War II. After the war, deciding that the most interesting problem in science was the physical basis of life, he entered Cambridge University to study the structure of biological molecules by X-ray analysis. He was a graduate student when he carried out his portion of the work that led to the proposal of the double helical structure of DNA. He received a Ph.D. in chemistry in 1953.

Rosalind Franklin (1920–1958) was born in London. She graduated from Cambridge University and studied X-ray diffraction techniques in Paris. In 1951, she returned to England and accepted

a position to develop an X-ray diffraction unit in the biophysics department at King's College. Her X-ray studies showed that DNA was a helix with the sugars and phosphate groups on the outside of the molecule. Tragically, Franklin never protected herself from her X-ray source and died without knowing the role her work had played in determining the structure of DNA, and without being recognized for her contribution.

Watson and Crick shared the 1962 Nobel Prize in Physiology or Medicine with Maurice Wilkins for determining the double-helical structure of DNA. Wilkins (1916–2004), who contributed X-ray studies that confirmed the double-helical structure, was born in New Zealand to Irish immigrants and moved to England six years later with his parents. He received a Ph.D. from Birmingham University. During World War II, he joined other British scientists who were working with American scientists on the development of the atomic bomb. He returned to England in 1945 and, having lost interest in physics, turned his attention to biology.



Francis Crick (left) and James Watson (right)



Rosalind Franklin

PROBLEM 1

Draw the structure for each of the following:

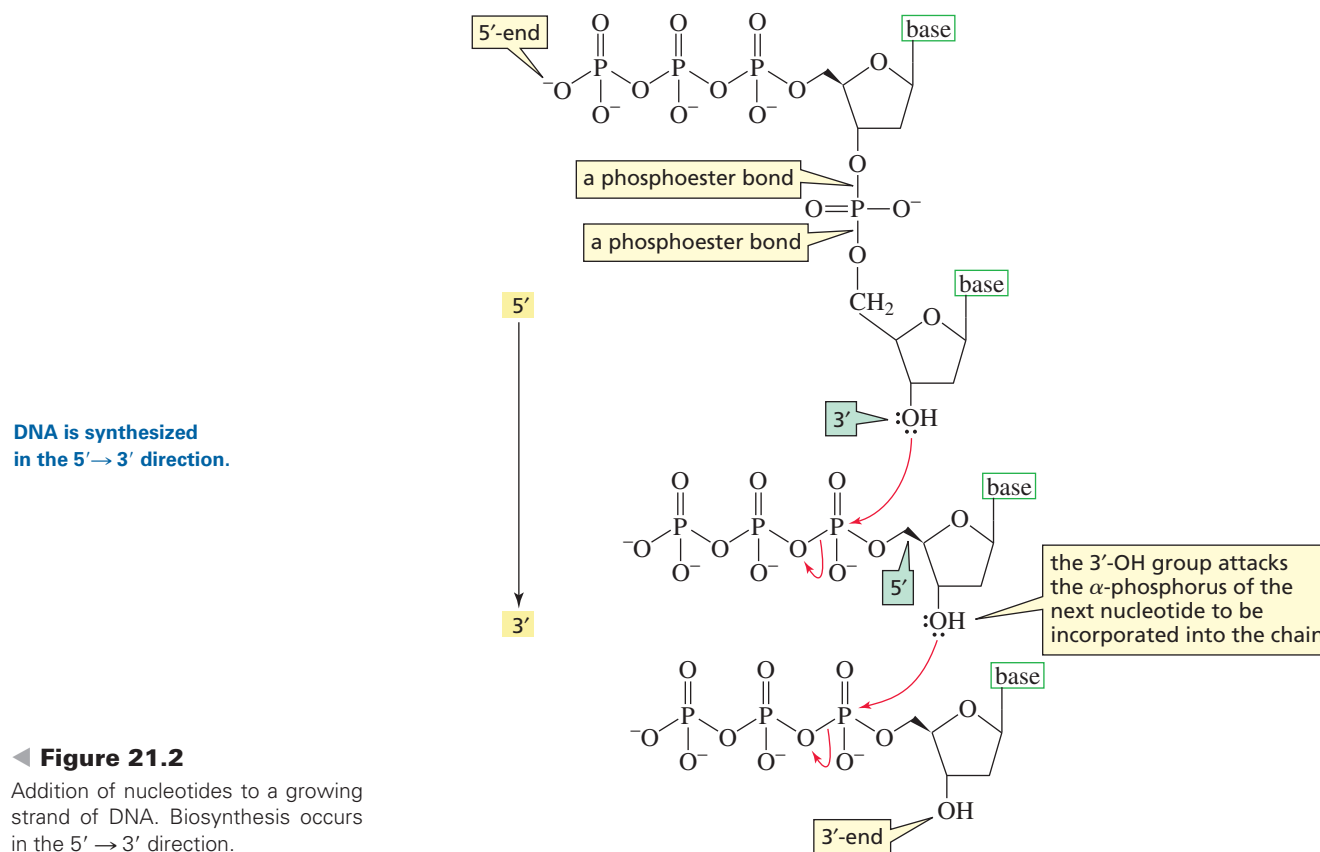
- | | | |
|---------|---------|-------------------------------|
| a. dCDP | c. dUMP | e. guanosine 5'-triphosphate |
| b. dTTP | d. UDP | f. adenosine 5'-monophosphate |

21.2 NUCLEIC ACIDS ARE COMPOSED OF NUCLEOTIDE SUBUNITS

Nucleic acids are composed of long strands of nucleotide subunits (Figure 21.1). A **dinucleotide** contains two nucleotide subunits, an **oligonucleotide** contains 3–10 subunits, and a **polynucleotide** contains many subunits. DNA and RNA are polynucleotides.

Nucleoside triphosphates are the starting materials for the biosynthesis of nucleic acids. DNA is synthesized by enzymes called *DNA polymerases*; RNA is synthesized by enzymes called *RNA polymerases*. The nucleotides are linked as a result of an S_N2 reaction (Section 8.1): the 3'-OH group of one nucleoside triphosphate attacks the

α -phosphorus of another nucleoside triphosphate, breaking a phosphoanhydride bond and eliminating pyrophosphate (Figure 21.2). Thus, the phosphodiester joins the 3'-OH group of one nucleotide and the 5'-OH group of the next nucleotide, and the growing polymer is synthesized in the 5' \rightarrow 3' direction. In other words, new nucleotides are added to the 3'-end. Pyrophosphate is subsequently hydrolyzed, which makes the reaction irreversible (Section 20.2). Irreversibility is important if the genetic information in DNA is to be preserved. RNA strands are biosynthesized in the same way, using ribonucleoside triphosphates instead of 2'-deoxyribonucleoside triphosphates.



The **primary structure** of a nucleic acid is the sequence of bases in the strand. By convention, the sequence of bases is written in the 5' → 3' direction (the 5'-end is on the left). Remember that the nucleotide at the 5'-end of the strand has an unlinked 5'-triphosphate group, and the nucleotide at the 3'-end has an unlinked 3'-hydroxyl group.



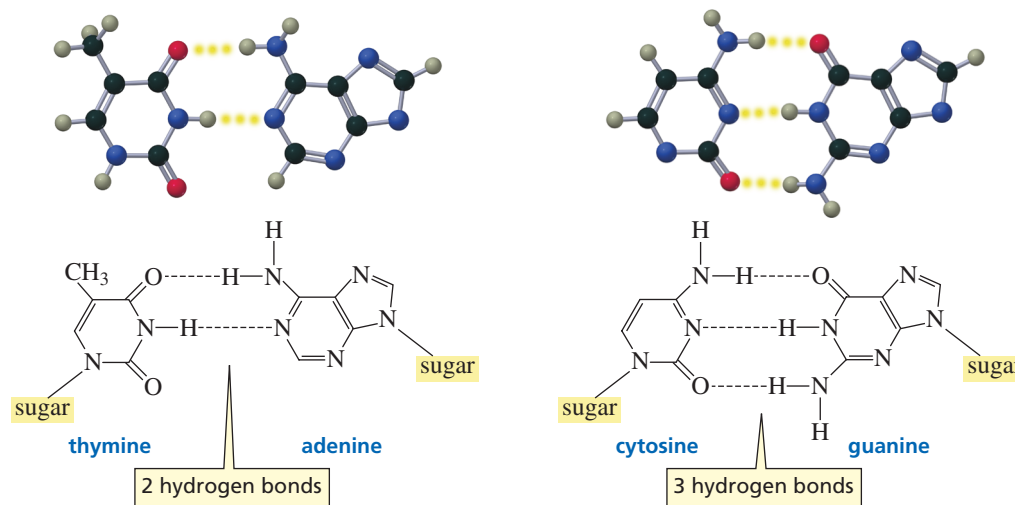
21.3 THE SECONDARY STRUCTURE OF DNA—THE DOUBLE HELIX

Watson and Crick, with the aid of Rosalind Franklin's X-ray data, concluded that DNA consists of two strands of nucleotides, with the sugar-phosphate backbone on the outside and the bases on the inside. The strands are antiparallel (they run in opposite directions) and are held together by hydrogen bonds between the bases on one strand and the bases on the other strand (Figure 21.3).

Adenine (A) always pairs with thymine (T), and guanine (G) always pairs with cytosine (C). This means the two strands are *complementary*: where there is an A in one strand, there is a T in the opposing strand; and where there is a G in one strand, there is a C in the other strand (Figure 21.3). Thus, if you know the sequence of bases in one strand, you can figure out the sequence of bases in the other strand.

Why does A pair with T? Why does G pair with C? First of all, the width of the double-stranded molecule is relatively constant, so a purine must pair with a pyrimidine. If the larger purines paired, the strands would bulge; if the smaller pyrimidines paired, the strands would have to pull in to bring the two pyrimidines close enough to form hydrogen bonds. But what causes A (a purine) to pair with T (a pyrimidine) rather than with C (the other pyrimidine)?

The base pairing is dictated by hydrogen bonding. Adenine forms two hydrogen bonds with thymine but would form only one hydrogen bond with cytosine. Guanine forms three hydrogen bonds with cytosine but would form only one hydrogen bond with thymine (Figure 21.4).



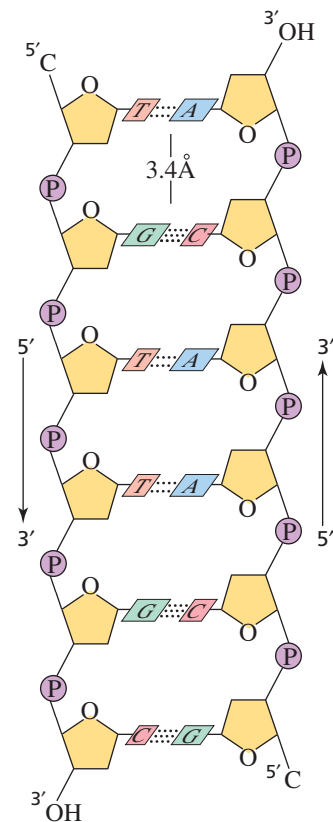
▲ **Figure 21.4**

Base pairing in DNA: adenine and thymine form two hydrogen bonds; cytosine and guanine form three hydrogen bonds.

The two antiparallel DNA strands are not linear but are twisted into a helix around a common axis (Figure 21.5a). The base pairs are planar and parallel to each other on the inside of the helix (Figure 21.5b). The secondary structure is, therefore, known as a **double helix**. The double helix resembles a circular staircase: the base pairs are the rungs, and the sugar–phosphate backbones are the handrails (see pages 628 and 629). The negatively charged phosphates repel nucleophiles, thereby preventing cleavage of the phosphodiester bonds.

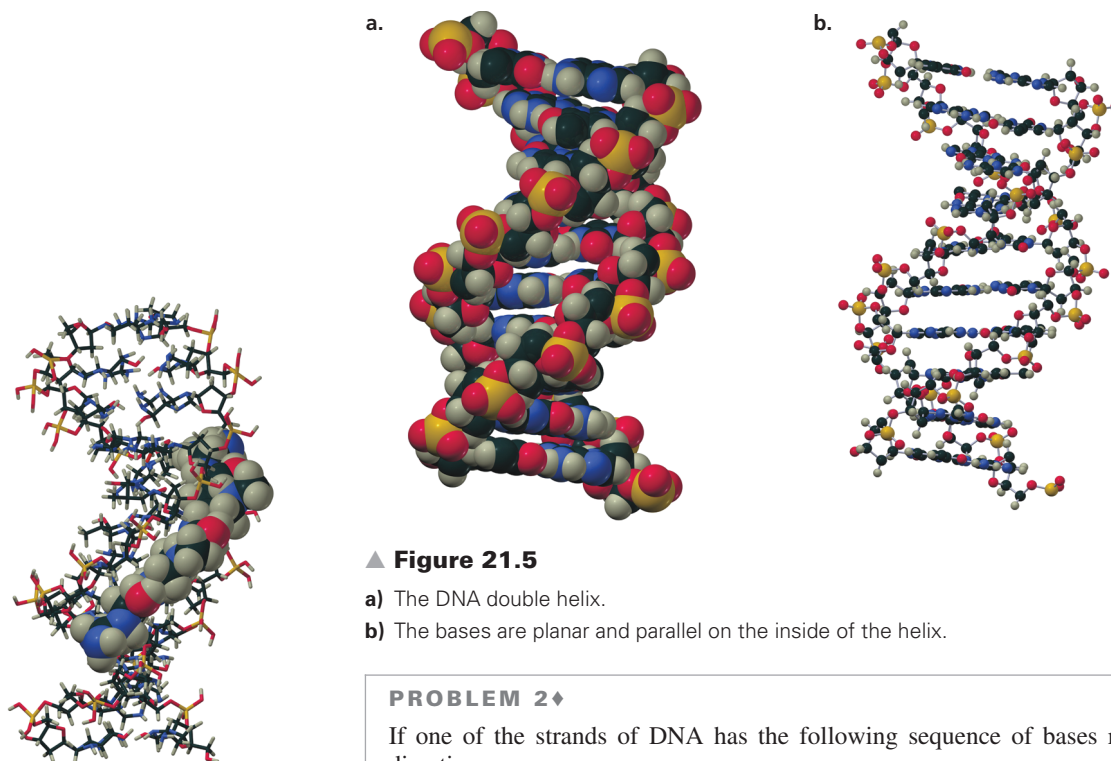
Hydrogen bonding between base pairs is just one of the forces holding the two strands of the DNA double helix together. The bases are planar aromatic molecules that stack on top of one another, each pair slightly rotated with respect to the next pair, like a partially spread-out hand of cards. In this arrangement, there are favorable van der Waals interactions between the mutually induced dipoles of adjacent pairs of bases. These interactions, known as **stacking interactions**, are weak attractive forces, but when added together they contribute significantly to the stability of the double helix.

There are two different alternating grooves in a DNA helix; a **major groove** and a narrower **minor groove**. Proteins and other molecules can bind to the grooves. The hydrogen-bonding properties of the functional groups facing into each groove determine what kind of molecules will bind to the groove. For example, netropsin is an antibiotic that works by binding to the minor groove of DNA (Figure 21.6).



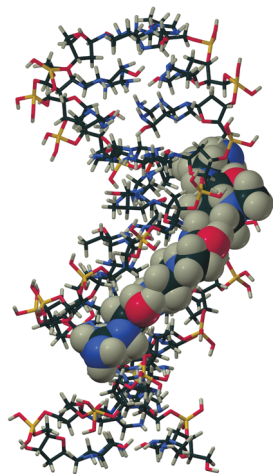
▲ **Figure 21.3**

The sugar–phosphate backbone of DNA is on the outside and the bases are on the inside; As pair with Ts and Gs pair with Cs. The two strands are antiparallel—that is, they run in opposite directions.

▲ **Figure 21.5**

a) The DNA double helix.

b) The bases are planar and parallel on the inside of the helix.

▲ **Figure 21.6**

The antibiotic netropsin bound in the minor groove of DNA.

PROBLEM 2♦

If one of the strands of DNA has the following sequence of bases running in the 5' → 3' direction,

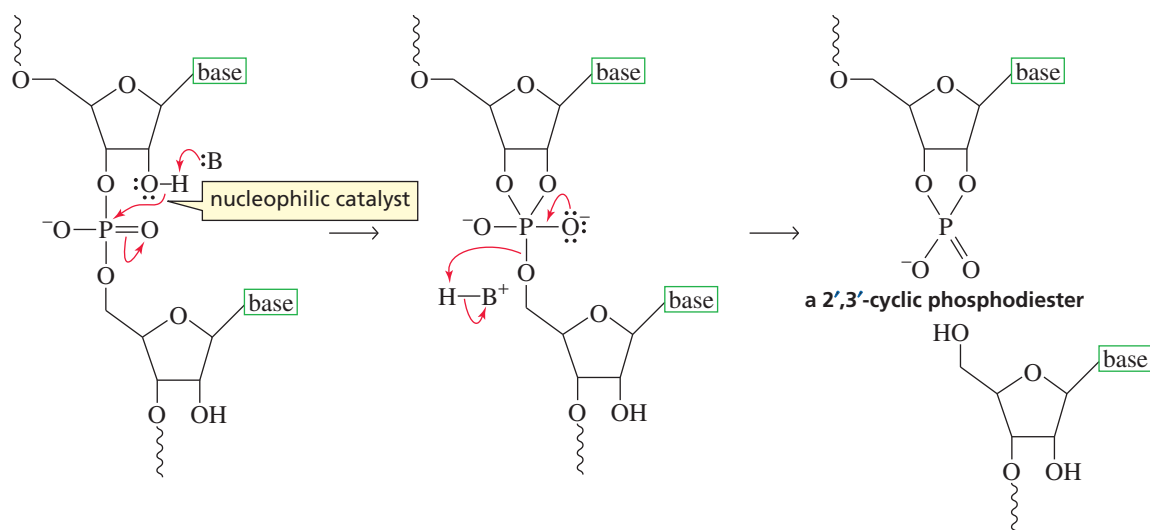


a. what is the sequence of bases in the complementary strand?

b. what base is closest to the 5'-end in the complementary strand?

21.4 WHY DNA DOES NOT HAVE A 2'-OH GROUP

Unlike DNA, RNA is not stable, because the 2'-OH group of ribose acts as a nucleophilic catalyst for the cleavage of RNA (Figure 21.7). This explains why the 2'-OH group is absent in DNA. DNA must remain intact throughout the life span of a cell in order to preserve the genetic information. Easy cleavage of DNA would have disastrous consequences for the cell and for life itself. RNA, in contrast, is synthesized as it is needed and is degraded once it has served its purpose.

▲ **Figure 21.7**

Catalysis of RNA cleavage by the 2'-OH group. RNA undergoes cleavage 3 billion times faster than DNA.

PROBLEM 3

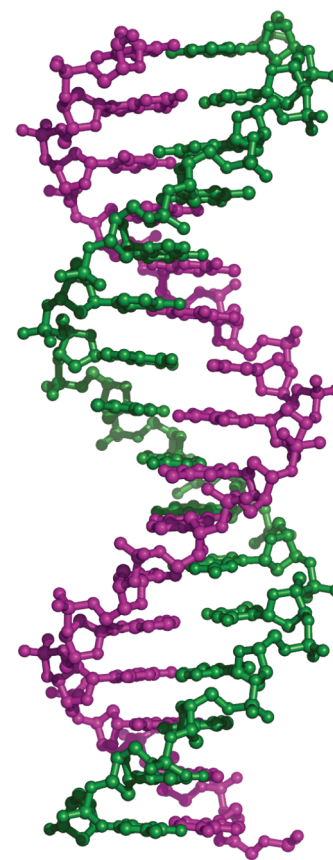
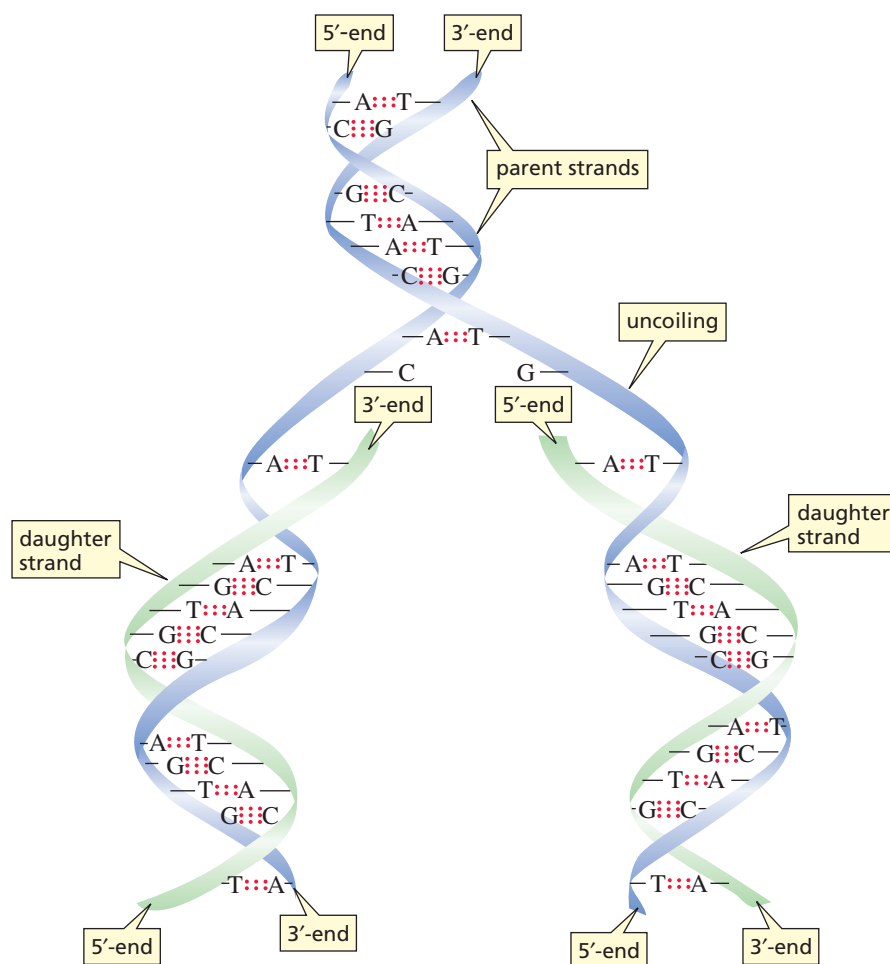
The 2',3'-cyclic phosphodiester that is formed (Figure 21.7) when RNA is cleaved reacts with water, forming a mixture of nucleotide 2'- and 3'-phosphates. Propose a mechanism for this reaction.

21.5 THE BIOSYNTHESIS OF DNA IS CALLED REPLICATION

The genetic information of a human cell is contained in 23 pairs of chromosomes. Each chromosome is composed thousands of **genes** (segments of DNA). The total DNA from a human cell—the **human genome**—contains 3.1 billion base pairs.

Part of the excitement created by Watson and Crick's proposed structure for DNA was due to the fact that the structure immediately suggested how DNA is able to pass on genetic information to succeeding generations. Because the two strands are complementary, both carry the same genetic information. Thus, when organisms reproduce, DNA molecules can be copied using the same base-pairing principle that is fundamental to their structure—that is, each strand can serve as the template for the synthesis of a complementary new strand (Figure 21.8). The new (daughter) DNA molecules are identical to the original (parent) molecule, so they contain all the original genetic information. The synthesis of identical copies of DNA is called **replication**.

All the reactions involved in nucleic acid synthesis are catalyzed by enzymes. The synthesis of DNA takes place in a region of the molecule where the strands have started to separate. Because a nucleic acid can be synthesized only in the 5' → 3' direction, only the daughter strand on the left in Figure 21.8 is synthesized continuously in a single piece



DNA

▲ **Figure 21.8**

Replication of DNA. The green daughter strand on the left is synthesized continuously in the 5' → 3' direction; the green daughter strand on the right is synthesized discontinuously in the 5' → 3' direction.

(because it is synthesized in the $5' \rightarrow 3'$ direction). The other daughter strand needs to grow in a $3' \rightarrow 5'$ direction, so it is synthesized discontinuously in small pieces. Each piece is synthesized in the $5' \rightarrow 3'$ direction, and the fragments are joined together by an enzyme called DNA ligase (see Figure 17.10 on page 573). Each of the two new molecules of DNA—called daughter molecules—contains one of the original parent strands (blue strand in Figure 21.8) plus a newly synthesized strand (green strand). This process is called **semiconservative replication**.

PROBLEM 4

Using a dark line for the original parental DNA and a wavy line for DNA synthesized from parental DNA, show what the population of DNA molecules would look like in the fourth generation. (Parental DNA is the first generation.)

21.6 DNA AND HEREDITY

If DNA contains hereditary information, there must be a method to decode that information. The decoding occurs in two steps.

1. The sequence of bases in DNA provides a blueprint for the synthesis of RNA; the synthesis of RNA from a DNA blueprint is called **transcription** (Section 21.7).
2. The sequence of bases in RNA determines the sequence of amino acids in a protein; the synthesis of a protein from an RNA blueprint is called **translation** (Section 21.9).

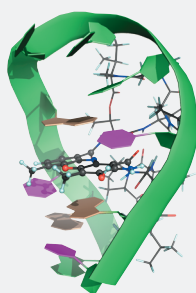
Do not confuse transcription and translation: these words are used just as they are used in English. Transcription (DNA to RNA) is copying *within the same language*—in this case the language of nucleotides. Translation (RNA to protein) is *changing to another language*—the language of amino acids. First, we will look at transcription.

Transcription: DNA \rightarrow RNA

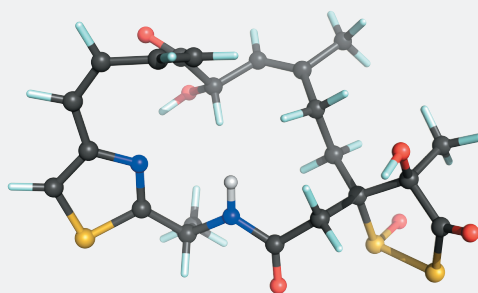
Translation: mRNA \rightarrow protein

Natural Products That Modify DNA

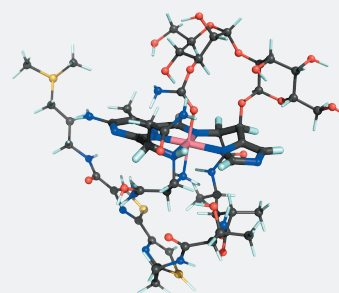
More than three-quarters of clinically approved anticancer drugs are natural products—compounds derived from plants, marine organisms, or microbes—that interact with DNA. Because cancer is characterized by the uncontrolled growth and proliferation of cells, compounds that interfere with the replication or transcription of DNA stop the growth of cancer cells. These drugs can interact with DNA by binding between the base pairs (called intercalation) or by binding to either its major or minor groove. The three anticancer drugs discussed here were isolated from *Streptomyces* bacteria found in soil.



actinomycin D



leinamycin



bleomycin

Because intercalating compounds become sandwiched between the stacked bases in DNA, they are planar and often aromatic. Their binding to DNA is stabilized by stacking interactions with neighboring base pairs. Actinomycin D is an example of an intercalator. When this drug binds to DNA, it distorts the double helix, inhibiting both the replication and transcription of DNA. Actinomycin D has been used to treat a variety of cancers.

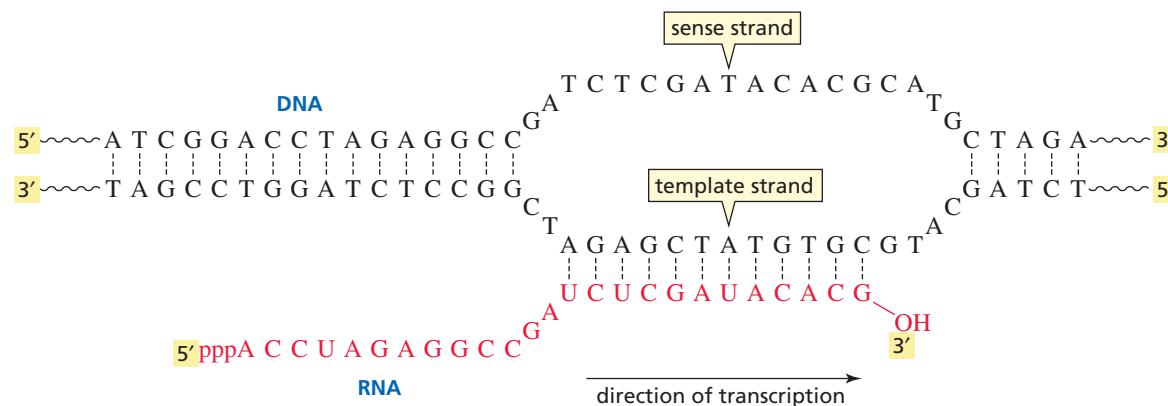
Drugs that bind to the major and minor grooves of DNA do so by a combination of hydrogen bonding, van der Waals interactions, and electrostatic attractions—the same forces proteins use to bind their substrates. Leinamycin is an example of an anticancer drug that binds to the major groove. Once leinamycin is bound, it alkylates the N-7 position of a purine ring.

Bleomycin binds to the minor groove of DNA. Once in the minor groove, it uses a bound iron atom to remove a hydrogen atom from DNA, the first step in cleaving DNA. This drug has been approved for the treatment of Hodgkin lymphoma.

21.7 THE BIOSYNTHESIS OF RNA IS CALLED TRANSCRIPTION

Transcription starts when DNA unwinds at a particular site—called a *promoter site*—to form two single strands. One of the strands is called the **sense strand**. The complementary strand is called the **template strand**. In order for RNA to be synthesized in the 5' → 3' direction, the template strand is read in the 3' → 5' direction (Figure 21.9). The bases in the template strand specify the bases that need to be incorporated into RNA, following the same base-pairing principle used in the replication of DNA. For example, each guanine in the template strand specifies the incorporation of a cytosine into RNA, and each adenine in the template strand specifies the incorporation of a uracil into RNA. (Recall that in RNA, uracil is used instead of thymine.) Because both RNA and the sense strand of DNA are complementary to the template strand, RNA and the sense strand of DNA have the same base sequence, except that RNA has a uracil wherever the sense strand has a thymine. Just as there are promoter sites in DNA that signal where to start RNA synthesis, there are sites signaling that no more bases should be added to the growing RNA chain.

RNA is synthesized in the 5' → 3' direction.



▲ **Figure 21.9**

Transcription: using DNA as a blueprint for the synthesis of RNA.

Until recently, it was thought that only about 2% of the DNA in our cells was used to make proteins and the rest had no informational content. However, our knowledge about DNA has been greatly expanded since the first human genome was sequenced in 2000. The biological purpose of about 80% of the DNA in the human genome had now been identified, and future experiments are expected to identify the purpose of the rest.

Apparently, a large amount of DNA is for the purpose of regulation. There are about 150 types of human cells, and each one carries the DNA that codes for 21,000 proteins. But only a subset of these is activated in a particular cell. For example, the gene that makes hair is not activated in a cell that makes insulin and vice versa.

It is now known that there are about 30,000 additional genes that are a blueprint for RNA that is not subsequently translated to make proteins. Instead, the RNA is used for regulation. In other words, these RNA strands appear to be the switches that turn genes on and off. The enormous number of switches has surprised scientists. Now the problem is to find out how these switches work.

PROBLEM 5♦

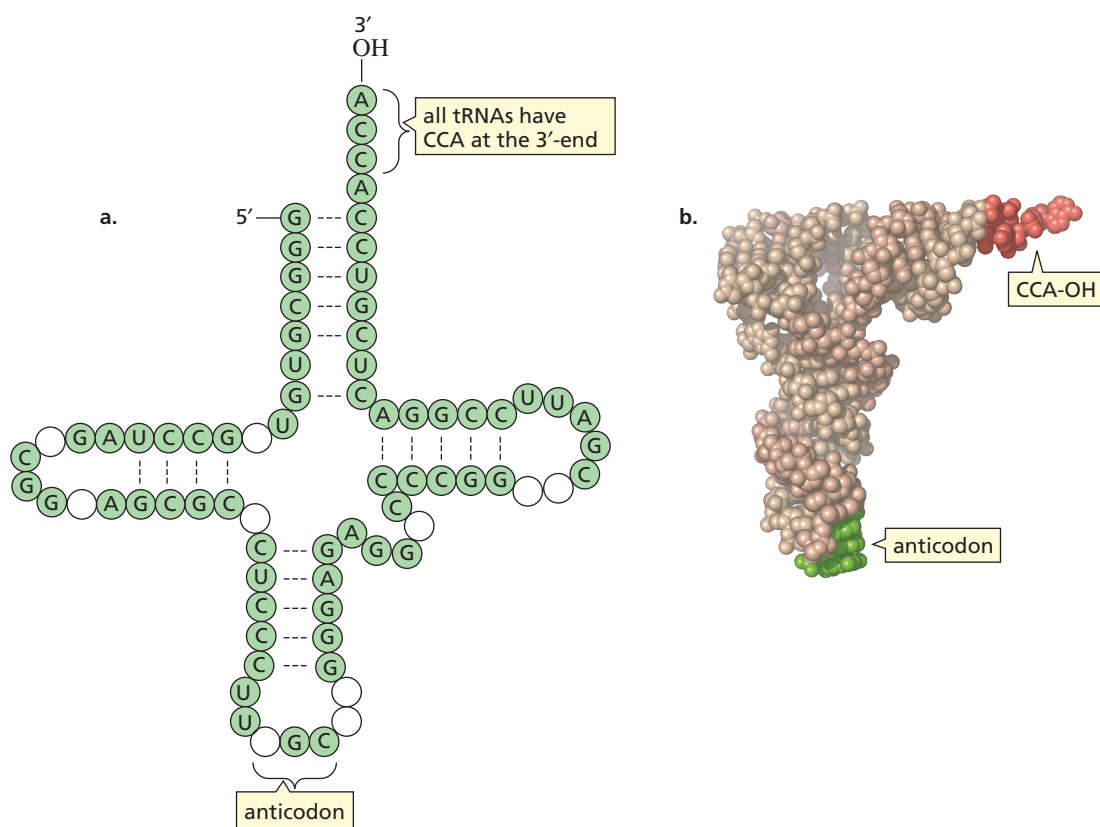
Why do both thymine and uracil specify the incorporation of adenine?

21.8 THE RNAs USED FOR PROTEIN BIOSYNTHESIS

RNA molecules are much shorter than DNA molecules and are generally single-stranded. While DNA molecules have billions of base pairs, RNA molecules rarely have more than 10,000 nucleotides. There are several kinds of RNA. The RNAs used for protein biosynthesis are as follows:

- **messenger RNA (mRNA)**, whose sequence of bases determines the sequence of amino acids in a protein
- **ribosomal RNA (rRNA)**, a structural component of ribosomes, which are the particles on which the biosynthesis of proteins takes place
- **transfer RNA (tRNA)**, the carrier of amino acids used for protein synthesis

tRNA molecules are much smaller than mRNA or rRNA molecules. A tRNA contains only 70–90 nucleotides. The single strand of tRNA is folded into a characteristic cloverleaf structure, with three loops and a little bulge next to the right-hand loop (Figure 21.10a). There are at least four regions with complementary base pairing. The three bases at the bottom of the loop directly opposite the 5'- and 3'-ends are called an **anticodon**. All tRNAs have a CCA sequence at the 3'-end (Figures 21.10a and 21.10b).



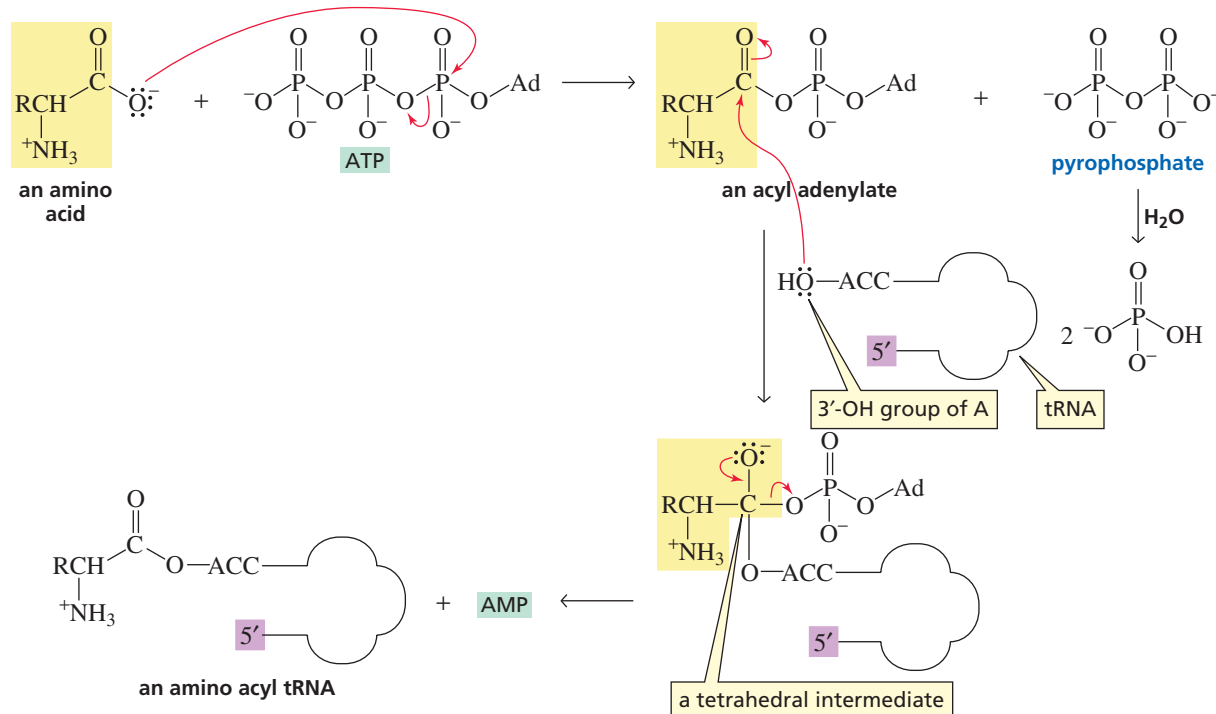
▲ **Figure 21.10**

- a)** A transfer RNA: compared with other RNAs, tRNA contains a high percentage of unusual bases (shown as empty circles). These bases result from enzymatic modification of the four normal bases.
b) A transfer RNA: the anticodon is green; the CCA at the 3'-end is red.

Each tRNA can carry an amino acid bound as an ester to its terminal 3'-OH group. The amino acid will be inserted into a protein during protein biosynthesis. Each tRNA can carry only one particular amino acid. A tRNA that carries alanine is designated as tRNA^{Ala}.

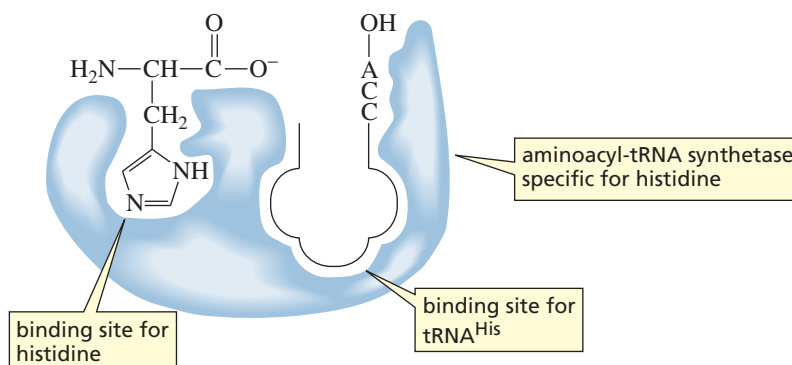
The attachment of an amino acid to a tRNA is catalyzed by an enzyme called aminoacyl-tRNA synthetase. The mechanism for the reaction is shown here.

MECHANISM FOR THE ATTACHMENT OF AN AMINO ACID TO A tRNA



- The carboxylate group of the amino acid is activated by forming an acyl adenylate; now the amino acid has a good leaving group (Section 11.16).
- The pyrophosphate that is eliminated is subsequently hydrolyzed, ensuring the irreversibility of the phosphoryl transfer reaction (Section 19.1).
- Notice that the second and third steps are the two steps of a nucleophilic acyl substitution reaction (Section 11.4). The 3'-OH group of tRNA adds to the carbonyl carbon of the acyl adenylate, forming a tetrahedral intermediate.
- The aminoacyl tRNA is formed when AMP is eliminated from the tetrahedral intermediate.

All the steps take place at the active site of the enzyme. Each amino acid has its own aminoacyl-tRNA synthetase. Each synthetase has two specific binding sites, one for the amino acid and one for the tRNA that will carry that amino acid (Figure 21.11).



► **Figure 21.11**

An aminoacyl-tRNA synthetase has a binding site for the amino acid and a binding site for the tRNA that will carry that amino acid. In this example, histidine is the amino acid, and tRNA^{His} is the tRNA.

21.9 THE BIOSYNTHESIS OF PROTEINS IS CALLED TRANSLATION

A protein is biosynthesized from its N-terminal end to its C-terminal end by a process that reads the bases along the mRNA strand in the 5' → 3' direction. The amino acid that is to be incorporated into a protein is specified by a three-base sequence called a **codon**. The bases are read consecutively and are never skipped. The three-base sequences and the amino acid that each sequence codes for are known as the **genetic code** (Table 21.2). A codon is written with the 5'-nucleotide on the left. For example, the codon UCA on mRNA codes for the amino acid serine, whereas CAG codes for glutamine.

Table 21.2 The Genetic Code					
5'-Position	Middle position				3'-Position
	U	C	A	G	
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	Stop	Stop	A
	Leu	Ser	Stop	Trp	G
C	Leu	Pro	His	Arg	U
	Leu	Pro	His	Arg	C
	Leu	Pro	Gln	Arg	A
	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
	Ile	Thr	Asn	Ser	C
	Ile	Thr	Lys	Arg	A
	Met	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G

Because there are four bases and the codons are triplets, 4³ (or 64) different codons are possible. This is many more than are needed to specify the 20 different amino acids, so all the amino acids—except methionine and tryptophan—have more than one codon. It is not surprising, therefore, that methionine and tryptophan are the least abundant amino acids in proteins. Actually, 61 of the codons specify amino acids, and three codons are stop codons. **Stop codons** tell the cell to “stop protein synthesis here.”

PROBLEM 6♦

If methionine is always the first amino acid incorporated into an oligopeptide, what oligopeptide is coded for by the following stretch of mRNA?

5'—G—C—A—U—G—G—A—C—C—C—G—U—U—A—U—U—A—A—A—C—A—C—3'

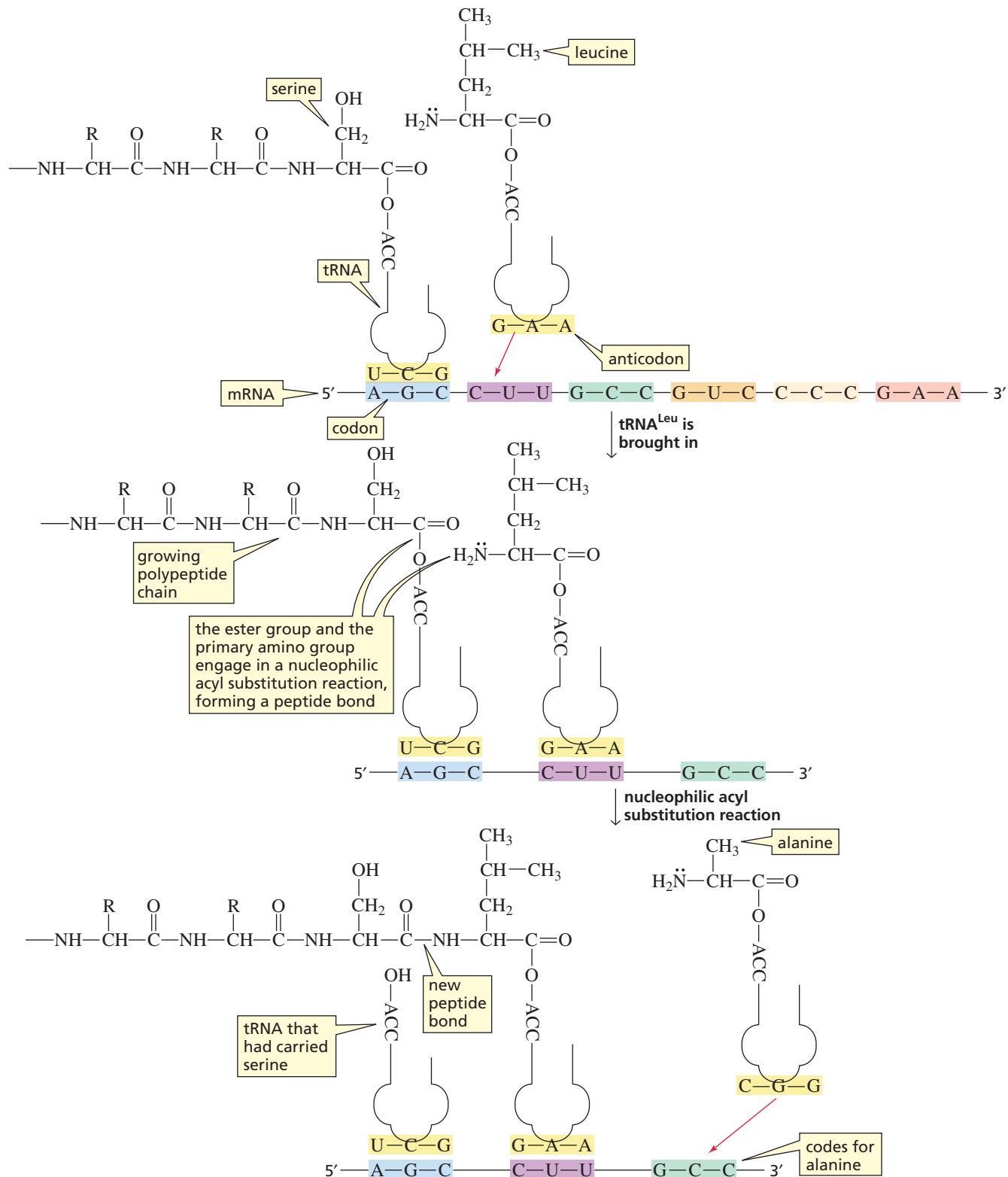
PROBLEM 7♦

Four Cs occur in a row in the segment of mRNA shown in Problem 6. What oligopeptide would be formed from the mRNA if one of the four Cs were cut out of the strand?

PROBLEM 8

UAA is a stop codon. Why does the UAA sequence in the segment of mRNA in Problem 6 not cause protein synthesis to stop?

How the information in mRNA is translated into a polypeptide is shown in Figure 21.12. In this figure, serine, specified by the codon AGC, was the last amino acid incorporated into the growing polypeptide chain.



▲ **Figure 21.12**

Translation: the sequence of bases in mRNA determines the sequence of amino acids in a protein.

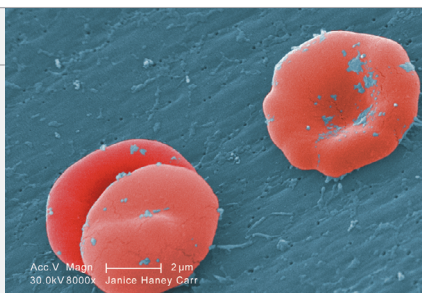
- Serine was specified by the AGC codon in mRNA because the anticodon of the tRNA that carries serine is GCU (3'-UCG-5'). (Remember that a base sequence is read in the 5' → 3' direction, so the sequence of bases in an anticodon must be read from right to left.)
- The next codon, CUU, signals for a tRNA with an anticodon of AAG (3'-GAA-5'). That particular tRNA carries leucine. The amino group of leucine reacts in an enzyme-catalyzed nucleophilic acyl substitution reaction with the ester on the adjacent serine-carrying tRNA, displacing the tRNA that brought in serine (Section 11.4).
- The next codon (GCC) specifies a tRNA that carries alanine. The amino group of alanine will react in an enzyme-catalyzed nucleophilic acyl substitution reaction with the ester group on the adjacent leucine-carrying tRNA to displace the tRNA that brought in leucine.

Subsequent amino acids are brought in one at a time in the same way, with the codon in mRNA specifying the amino acid to be incorporated by complementary base pairing with the anticodon of the tRNA that carries that amino acid.

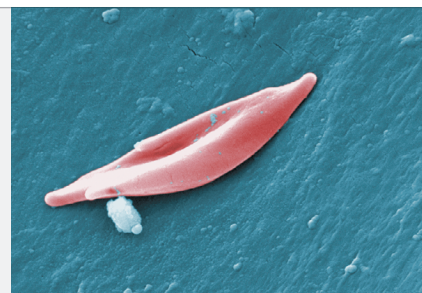
A protein is biosynthesized in the N-terminal → C-terminal direction

Sickle Cell Anemia

Sickle cell anemia is an example of the damage that can be caused by a change in a single base of DNA (Problem 57 in Chapter 17). It is a hereditary disease caused when a GAG triplet becomes a GTG triplet in the sense strand of a section of DNA that codes for the β -subunit of hemoglobin (Section 17.13). As a consequence, the mRNA codon becomes GUG—which signals for incorporation of valine—rather than GAG, which would have signaled for incorporation of glutamate. The change from a polar glutamate to a nonpolar valine is sufficient to change the shape of the deoxyhemoglobin molecule. The change in shape stiffens the cells, making it difficult for them to squeeze through capillaries. Blockage of capillaries causes severe pain and can be fatal.



normal red blood cells



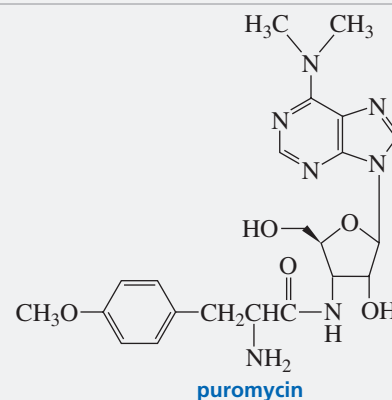
sickle red blood cell

Antibiotics That Act by Inhibiting Translation

Puromycin is a naturally occurring antibiotic, one of several that acts by inhibiting translation. It does so by mimicking the 3'-CCA-aminoacyl portion of a tRNA, fooling the enzyme into transferring the growing peptide chain to the NH_2 group of puromycin rather than to the NH_2 group of the incoming 3'-CCA-aminoacyl tRNA. As a result, protein synthesis stops. Because puromycin blocks protein synthesis in eukaryotes as well as in prokaryotes, it is poisonous to humans and, therefore, is not a clinically useful antibiotic. To be clinically useful, an antibiotic must affect protein synthesis only in prokaryotic cells.

Clinically useful antibiotics Mode of action

Tetracycline	Prevents the aminoacyl-tRNA from binding to the ribosome
Erythromycin	Prevents the incorporation of new amino acids into the protein
Streptomycin	Inhibits the initiation of protein synthesis
Chloramphenicol	Prevents the new peptide bond from being formed



PROBLEM 9♦

A change in which base of a codon would be least likely to damage a protein? _____

PROBLEM 10♦

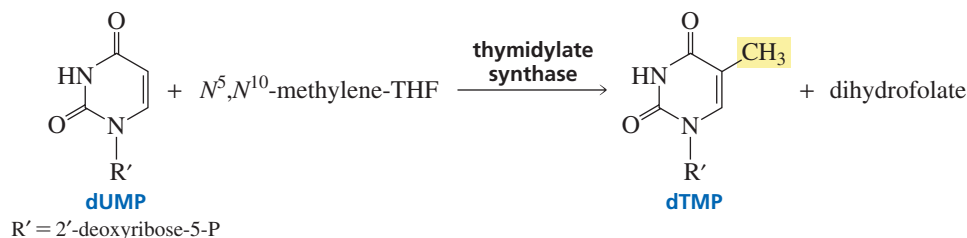
Write the sequences of bases in the sense strand of DNA that resulted in the mRNA in Problem 6. _____

PROBLEM 11

List the possible codons on mRNA that specify each amino acid in Problem 6 and the anticodon on the tRNA that carries that amino acid. _____

21.10 WHY DNA CONTAINS THYMINE INSTEAD OF URACIL

In Section 18.13, we saw that dTMP is formed by methylating dUMP, with coenzyme N^5,N^{10} -methylenetetrahydrofolate supplying the methyl group.

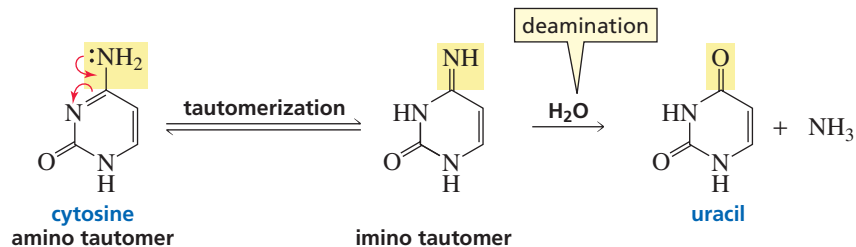


Because the incorporation of the methyl group into uracil oxidizes tetrahydrofolate to dihydrofolate, dihydrofolate must be reduced back to tetrahydrofolate to prepare the coenzyme for another catalytic reaction. The reducing agent is NADPH.



The NADP^+ formed in this reaction has to be reduced back to NADPH by NADH. Every NADH formed in a cell can result in the formation of 2.5 ATPs (Section 19.3). Therefore, reducing dihydrofolate comes at the expense of ATP formation. This means that the synthesis of thymine is energetically expensive, so there must be a good reason for DNA to contain thymine instead of uracil.

The presence of thymine instead of uracil in DNA prevents potentially lethal mutations. Cytosine can tautomerize to form an imine (Section 13.3), which can be hydrolyzed to uracil (Section 12.8). The overall reaction is called a **deamination** because it removes an amino group.

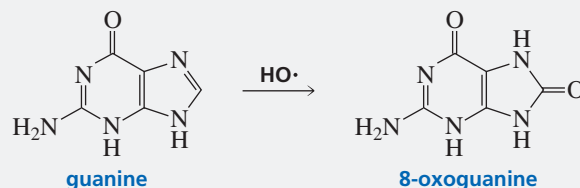


If a C in DNA is deaminated to a U, the U will specify incorporation of an A into the daughter strand during replication instead of the G that would have been specified by C, and all the progeny of the daughter strand would have the same mutated chromosome. Fortunately, there is an enzyme that recognizes a U in DNA as a “mistake” and replaces it with a C before an incorrect base can be inserted into the daughter strand. The enzyme cuts out the U and replaces it with a C. If Us were normally found in DNA, the enzyme would not be able to distinguish between a normal U and a U formed by deamination of a cytosine. Having Ts in place of Us in DNA allows the Us that are found in DNA to be recognized as mistakes.

Unlike DNA that replicates itself, RNA is continually degraded and then resynthesized from the DNA template, so any mistake in RNA does not survive for long. Therefore, changing a C to a U in RNA could lead to some copies of a defective protein, but most would not be defective. Thus, it is not worth incurring the loss of ATP to incorporate Ts into RNA.

Antibiotics Act by a Common Mechanism

Recently, it has been found that three different classes of antibiotics (a β -lactam, a quinolone, and an aminoglycoside) all kill bacteria in the same way. The antibiotics trigger the production of hydroxide radicals. The hydroxide radicals oxidize guanines to 8-oxoguanines. The cell is able to recognize 8-oxoguanines as mistakes and replace them with guanines. However, if there are too many 8-oxoguanines in DNA, the cell's repair mechanism becomes overwhelmed. Then, instead of cutting out the 8-oxoguanines, it breaks the DNA strand, which leads to cell death.



PROBLEM 12♦

Adenine can be deaminated to hypoxanthine, and guanine can be deaminated to xanthine. Draw structures for hypoxanthine and xanthine.

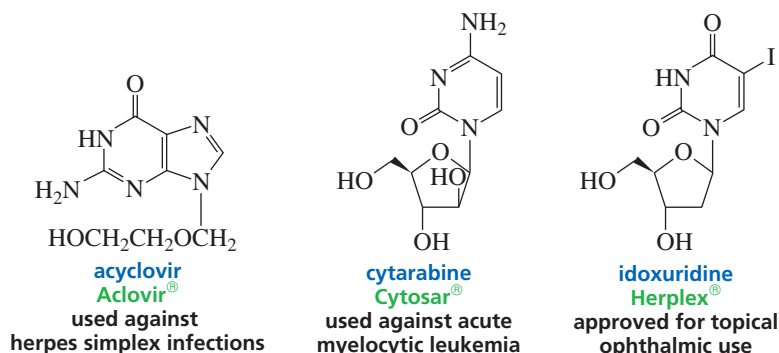
PROBLEM 13

Explain why thymine cannot be deaminated.

21.11 ANTIVIRAL DRUGS

Relatively few clinically useful drugs have been developed for viral infections. The slow progress of this endeavor is due to the nature of viruses and the way they replicate. Viruses are smaller than bacteria and consist of nucleic acid—either DNA or RNA—surrounded by a coat of protein. Some viruses penetrate the host cell; others merely inject their nucleic acid into the cell. In either case, the viral nucleic acid is transcribed by the host and is integrated into the host genome.

Most **antiviral drugs** are analogues of nucleosides, interfering with the virus's nucleic acid synthesis. In this way, they prevent the virus from replicating. For example, acyclovir, the drug used against herpes viruses, has a three-dimensional shape similar to that of guanine. Therefore, acyclovir can fool the virus into incorporating the drug instead of guanine into its DNA. Once this happens, the DNA strand can no longer grow because acyclovir lacks a ribose with a 3'-OH group.



Cytarabine, used for acute myelocytic leukemia, competes with cytosine for incorporation into viral DNA. Cytarabine contains an arabinose rather than a ribose (Table 16.1). Because the 2'-OH group is in the β -position, the bases in cytarabine-modified DNA are not able to stack properly (Section 21.3).

Idoxuridine is approved (in the United States) only for the topical treatment of ocular infections, although it is used for herpes infections in other countries. Idoxuridine has an iodo group in place of the methyl group of thymine and is incorporated into DNA in place of thymine. Chain elongation can continue because idoxuridine has a 3'-OH group, but the resulting DNA is more easily broken and is also not transcribed properly. (See also the description of AZT on page 644.)

Influenza Pandemics

Every year we face an outbreak of influenza (the flu). Most of the time it is a virus that is already present in the population and, therefore, can be controlled by flu shots. But every once in awhile, a new influenza virus appears, which can cause a worldwide pandemic because it is not affected by any immunity a person may have to older strains of influenza and can, therefore, spread rapidly and infect a large number of people. And almost no effective antiviral drugs are available for the flu. (See Tamiflu in Section 18.2.)

The Russian flu of 1889–1890 was the first of the flu pandemics. It killed about 1 million people. The Spanish flu that broke out in 1918–1919 killed over 50 million people worldwide. The Asian flu of 1956–1958 killed about 2 million people before a vaccine was developed in 1957 to contain it. The Hong Kong flu of 1968–1969—so called because it affected 15% of the population of Hong Kong—had a much lower death rate—only about 750,000 people died—because people who had had the Asian flu had some immunity. Because this was the last worldwide pandemic, public health officials worry that another may occur soon.

Recent flu outbreaks that have been causes for concern are the avian flu (bird flu), discovered in 1997, and the swine flu, discovered in 2009. The avian flu was linked to chickens, but it was subsequently transmitted to hundreds of people, 60% of whom died. The swine flu is a respiratory disease of pigs, but it has been known to affect people. There are concerns that either of these flus could become a worldwide pandemic.

The carbohydrates attached to the surface of the viral protein account for the biggest difference in virus strains. The symptoms caused by viruses that bind primarily to sugars in the nose and throat are not as severe as those caused by viruses that bind to sugars deep in the lungs.

21.12 HOW THE BASE SEQUENCE OF DNA IS DETERMINED

In June 2000, two teams of scientists (one from a private biotechnology company and one from the publicly funded Human Genome Project) announced that they had completed the first draft of the sequence of the 3.1 billion base pairs in human DNA. This was an enormous accomplishment.

Clearly, DNA molecules are too large to sequence as a unit. Therefore, DNA is first cleaved at specific base sequences, and the resulting DNA fragments are then sequenced individually.

restriction endonuclease	recognition sequence
<i>AluI</i>	AGCT TCGA
<i>FnuDI</i>	GGCC CCGG
<i>PstI</i>	CTGCAG GACGTC

The enzymes that cleave DNA at specific base sequences are called **restriction endonucleases**, and the DNA fragments they produce are called **restriction fragments**. Several hundred restriction endonucleases are now known; a few examples, the base sequence that each recognizes, and the point of cleavage in that base sequence are shown in the margin.

The base sequences that most restriction endonucleases recognize are *palindromes*. A palindrome is a word or a group of words that reads the same forward and backward. “Toot” and “race car” are examples of palindromes, as is “Was it a car or a cat I saw?” A restriction endonuclease recognizes a piece of DNA in which *the template strand is a palindrome of the sense strand*. In other words, the sequence of bases in the template strand (reading from right to left) is identical to the sequence of bases in the sense strand (reading from left to right).

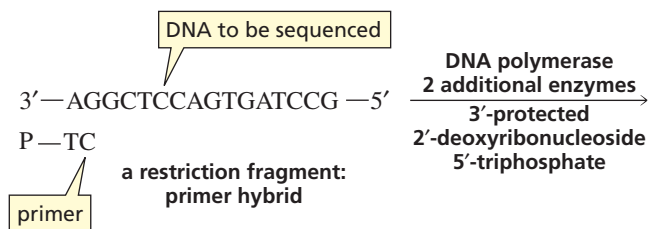
PROBLEM 14♦

Which of the following base sequences would most likely be recognized by a restriction endonuclease?

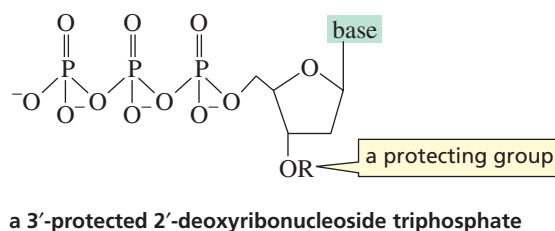
- | | | |
|-----------------|-----------------|------------------|
| A ACGCGT | C ACGGCA | E ACATCGT |
| B ACGGGT | D ACACGT | F CCAACC |

A currently used technique to determine the sequence of bases in DNA is an automated procedure called **pyrosequencing**. In this method, a small piece of DNA primer is added to the restriction fragment whose sequence is to be determined. Nucleotides are then added to the primer by base pairing with the restriction fragment. This method detects the identity of each base that adds to the primer.

Pyrosequencing requires DNA polymerase—the enzyme that adds nucleotides to a strand of DNA—and two additional enzymes that cause light to be emitted when pyrophosphate is detected.



Pyrosequencing also requires the four 2'-deoxyribonucleoside 5'-triphosphates, each with a protected 3'-OH group.



The restriction fragment:primer hybrid is attached to a solid support in a column. The solid support is similar to the one used in ion-exchange chromatography (see Figure 17.4). The steps involved in pyrosequencing are as follows:

- The enzymes and one of the four 3'-protected 2'-deoxyribonucleoside 5'-triphosphates (for example, 3'-protected dATP) are added to the column.
- The reagents are washed from the solid support.
- The process is repeated with a different 3'-protected 2'-deoxynucleoside 5'-triphosphate (for example, 3'-protected dGTP).
- The process is repeated with 3'-protected dCTP, and then repeated again with 3'-protected dTTP.

- The sequencer keeps track of which of the four nucleotides caused light to be observed—in other words, which nucleotide released pyrophosphate as a result of being added to the primer.
- The protecting group on the 3'-OH is removed.

The steps are repeated to determine the identity of the next nucleotide that adds to the primer. Pyrosequencing can determine the base sequence of a restriction fragment with as many as 500 nucleotides.

When a human genome can be rapidly sequenced at a reasonable cost, the era of personalized medicine can begin. We will then understand what makes people more susceptible to certain diseases and why drugs work differently on different people. Eventually, drugs will be prescribed based on a patient's genetic profile.

21.13 GENETIC ENGINEERING

Genetic engineering (also called genetic modification) is the insertion of a segment of DNA into the replicating DNA of a host cell so that the segment of DNA is replicated along with the DNA of the host cell. Genetic engineering has many practical applications. For example, replicating the DNA that codes for human insulin makes it possible to synthesize large amounts of the protein (Section 17.8).

Agriculture is benefiting from genetic engineering as crops are being produced with new genes that increase their resistance to drought and insects. For example, genetically engineered cotton crops are resistant to the cotton bollworm, and genetically engineered corn is resistant to the corn rootworm. Genetically modified organisms (GMOs) have been responsible for a nearly 50% reduction in agricultural chemical sales in the United States. Recently, corn has been genetically modified to boost ethanol production, apples have been genetically modified to prevent them from turning brown when they are cut, and soybeans have been genetically modified to prevent trans fats from being formed when soybean oil is hydrogenated (Section 5.6).

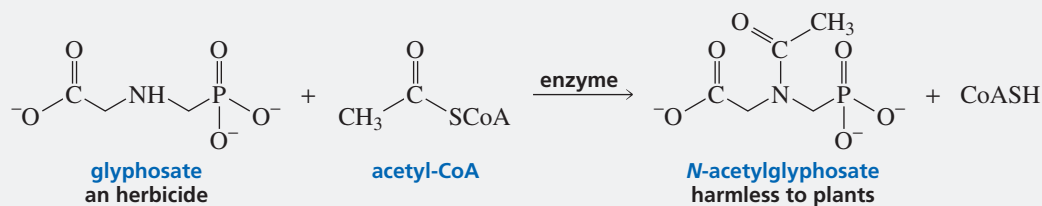
Resisting Herbicides

Glyphosate, the active ingredient in a well-known herbicide called Roundup, kills weeds by inhibiting an enzyme that plants need to synthesize phenylalanine and tryptophan, amino acids they require for growth. Corn and cotton have been genetically engineered to tolerate the herbicide. Then, when fields are sprayed with glyphosate, the weeds are killed but the crops are not.

These crops have been given a gene that produces an enzyme that uses acetyl-CoA to acetylate glyphosate in a nucleophilic acyl substitution reaction (Section 11.16). Unlike glyphosate, *N*-acetylglyphosate does not inhibit the enzyme that synthesizes phenylalanine and tryptophan.



Corn genetically engineered to resist the herbicide glyphosate by acetylating it.



Using Genetic Engineering to Treat the Ebola Virus

Plants have long been a source of drugs—morphine, digitoxin, and codeine are just a few examples (Section 9.10). Now scientists are attempting to obtain drugs from plants by biopharming. Biopharming uses genetic engineering techniques to produce drugs in crops such as corn, rice, tomatoes, and tobacco. To date, the only biopharmed drug approved by the Food and Drug Administration (FDA) is one that is manufactured in carrots and used to treat Gaucher's disease.

An experimental drug that was used to treat a handful of patients with Ebola, the virus that is spreading throughout West Africa, was obtained from genetically engineered tobacco plants. The tobacco plants were infected with three genetically engineered plant viruses that are harmless to humans and animals but have structures similar to that of the Ebola virus. As a result of being infected, the plants produced antibodies to the viruses. The antibodies were isolated from the plants, purified, and then used to treat the patients with Ebola.

The experimental drug had been tested in 18 monkeys who had been exposed to a lethal dose of Ebola. All 18 monkeys survived, whereas the three monkeys in the control group died. Typically, drugs go through rigorous testing on healthy humans prior to being administered to infected patients (see page 201). With the recent Ebola cases, the FDA made an exception because it feared that the drug might be these patients' only hope. Five of the seven people given the drug survived. Currently, it takes about 50 kilograms of tobacco leaves and about 4–6 months to produce enough drug to treat one patient.



tobacco plants

SOME IMPORTANT THINGS TO REMEMBER

- **Deoxyribonucleic acid (DNA)** encodes an organism's hereditary information and controls the growth and division of cells.
- A **nucleoside** contains a base bonded to D-ribose or to 2'-deoxy-D-ribose. A **nucleotide** is a nucleoside with an OH group of the sugar bonded to phosphoric acid by an ester linkage.
- **Nucleic acids** are composed of long strands of nucleotide subunits linked by phosphodiester bonds. These linkages join the 3'-OH group of one nucleotide to the 5'-OH group of the next nucleotide.
- DNA contains 2'-deoxy-D-ribose, whereas RNA contains D-ribose. The difference in the sugars causes DNA to be stable and RNA to be easily cleaved.
- The **primary structure** of a nucleic acid is the sequence of bases in its strand. DNA contains **A, G, C, and T**; RNA contains **A, G, C, and U**.
- The presence of **T** instead of **U** in DNA prevents mutations caused by tautomerization and imine hydrolysis of **C** to form **U**.
- DNA is double-stranded. The strands run in opposite directions and are twisted into a double helix, giving DNA a major groove and a minor groove.
- The bases are confined to the inside of the helix, and the sugar and phosphate groups are on the outside. The strands are held together by hydrogen bonds between bases of opposing strands as well as by **stacking interactions**.
- The two strands—one is called a **sense strand** and the other a **template strand**—are complementary: **A** pairs with **T**, and **G** pairs with **C**.
- DNA is synthesized in the 5' → 3' direction by a process called **semiconservative replication**.
- The sequence of bases in DNA provides the blueprint for the synthesis (**transcription**) of RNA. RNA is synthesized in the 5' → 3' direction by reading the bases along the DNA template strand in the 3' → 5' direction.
- The RNAs used in protein biosynthesis are messenger RNA, ribosomal RNA, and transfer RNA.
- Each three-base sequence of mRNA—a **codon**—specifies the particular amino acid to be incorporated into a protein. The codons and the amino acids they specify are known as the **genetic code**.
- Protein synthesis (**translation**) proceeds from the N-terminal end to the C-terminal end by reading the bases along the mRNA strand in the 5' → 3' direction.

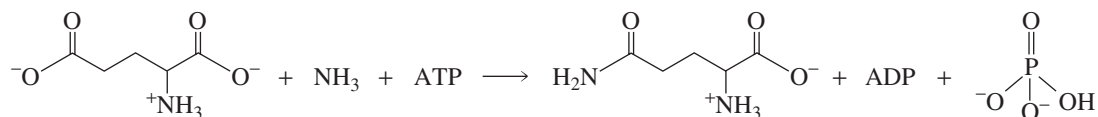
- A tRNA carries the amino acid bound as an ester to its terminal 3'-position.
- Cytosines can be deaminated to uracils. **Deamination** is a reaction that removes an amino group.
- **Restriction endonucleases** cleave DNA at specific palindromes, forming **restriction fragments**.
- **Pyrosequencing** is a method used to determine the sequence of bases in the restriction fragments.
- A large amount of a particular protein can be synthesized by **genetic engineering**.
- The human genome contains 3.1 billion base pairs.

PROBLEMS

15. Draw structures for the following:
 a. guanosine-5'-monophosphate b. cytidine-5'-diphosphate c. dAMP d. thymidine
16. What nonapeptide is coded for by the following fragment of mRNA?
 5'—AAA—GUU—GGC—UAC—CCC—GGA—AUG—GUG—GUC—3'
17. What is the sequence of bases in the template strand of DNA that codes for the mRNA in Problem 16?
18. What is the sequence of bases in the sense strand of DNA that codes for the mRNA in Problem 16?
19. What would be the C-terminal amino acid if the codon at the 3'-end of the mRNA in Problem 16 underwent the following mutations?
 a. The first base is changed to A. c. The third base is changed to A.
 b. The second base is changed to A. d. The third base is changed to G.
20. What would be the base sequence of the segment of DNA responsible for the biosynthesis of the following hexapeptide?

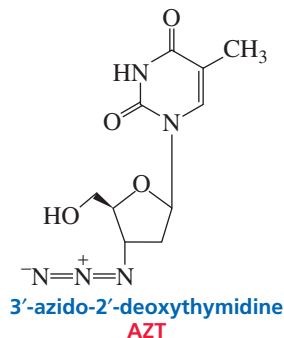
Gly-Ser-Arg-Val-His-Glu

21. Propose a mechanism for the following reaction:



22. A segment of DNA has 18 base pairs. It has 7 cytosines in the segment.
 a. How many thymines are in the segment? b. How many guanines are in the segment?
23. Match the codon with the anticodon:
- | | | | | | | | | |
|-------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Codon: | AAA | GCA | CUU | AGG | CCU | GGU | UCA | GAC |
| Anticodon: | ACC | CCU | UUU | AGG | UGA | AAG | GUC | UGC |
24. Using the single-letter abbreviations for the amino acids in Table 17.2, write the sequence of amino acids in a tetrapeptide represented by the first four different letters in your first name. Do not use any letter twice. (Because not all letters are assigned to amino acids, you might have to use one or two letters in your last name.) Write one of the sequences of bases in mRNA that would result in the synthesis of that tetrapeptide. Write the sequence of bases in the sense strand of DNA that would result in formation of that fragment of mRNA.
25. Indicate whether each functional group of the five heterocyclic bases in nucleic acids can function as a hydrogen bond acceptor (A) or a hydrogen bond donor (D).
26. Using the A and D designations in Problem 25, indicate how base pairing would be affected if the bases existed in the enol form.
27. Which of the following pairs of dinucleotides are present in equal amounts in DNA?
 A CC and GG B CG and GT C CA and TG D CG and AT E GT and CA F TA and AT
28. If an mRNA contained only U and G in random sequence, what amino acids would be present in the protein when the mRNA is translated?
29. Why is the codon a triplet rather than a doublet or a quartet?

30. Human immunodeficiency virus (HIV) is the retrovirus that causes AIDS. AZT was one of the first drugs designed to interfere with retroviral DNA synthesis. When cells take up AZT, they convert it to AZT-triphosphate. Explain how AZT interferes with DNA synthesis.



31. The amino acid sequences of peptide fragments obtained from a normal protein were compared with those obtained from the same protein synthesized by a defective gene. They were found to differ in only one peptide fragment. Their amino acid sequences are shown here:

Normal: Gln-Tyr-Gly-Thr-Arg-Tyr-Val

Mutant: Gln-Ser-Glu-Pro-Gly-Thr

- a. What is the defect in DNA?
 - b. It was later determined that the normal peptide fragment is an octapeptide with a C-terminal Val-Leu. What is the C-terminal amino acid of the mutant peptide?
32. Which cytosine in the following sense strand of DNA could cause the most damage to the organism if it were deaminated?

A—T—G—T—C—G—C—T—A—A—T—C

33. 5-Bromouracil, a highly mutagenic compound (that is, a compound that causes changes in DNA), is used in cancer chemotherapy. When administered to a patient, it is converted to the triphosphate and incorporated into DNA in place of thymine, which it resembles sterically. Why does it cause mutations? (*Hint:* The bromo substituent increases the stability of the enol tautomer.)
34. Why does DNA not unravel completely before replication begins?
35. The first amino acid incorporated into a polypeptide chain during its biosynthesis in prokaryotes is *N*-formylmethionine. Explain the purpose of the formyl group. (*Hint:* The ribosome has a binding site for the growing peptide chain and a binding site for the incoming amino acid.)

Answers to Selected Problems

CHAPTER 1

- 1-1. 8 + 8, 8 + 9, 8 + 10
 1-2. a. 3 b. 5 c. 6 d. 7
 1-3. 7
 1-4. a. C 2 and 4; Si 10 and 4 b. O 2 and 6; S 10 and 6 c. N 2 and 5; P 10 and 5
 1-5. a. 1 b. 4s
 1-6. a. Cl—CH₃ b. H—OH c. H—F d. Cl—CH₃
 1-7. a. KCl b. Cl₂
 1-9. a. $\delta^- \text{HO}-\delta^+ \text{H}$ c. $\delta^+ \text{H}_3\text{C}-\delta^- \text{NH}_2$ e. $\delta^- \text{HO}-\delta^+ \text{Br}$ g. $\delta^+ \text{I}-\delta^- \text{Cl}$
 b. $\delta^- \text{F}-\delta^+ \text{Br}$ d. $\delta^+ \text{H}_3\text{C}-\delta^- \text{Cl}$ f. $\delta^- \text{H}_3\text{C}-\delta^+ \text{Li}$ h. $\delta^+ \text{H}_2\text{N}-\delta^- \text{OH}$
 1-10. a. LiH and HF b. Its hydrogen has the greatest electron density.
 1-11. a. oxygen b. oxygen c. oxygen d. hydrogen
 1-14. a. CH₃CH₂OH CH₃OCH₃
 b. CH₃CH₂CH₂OH $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ CH₃CH₂OCH₃
 1-15. a. CH₃CH₂ $\ddot{\text{N}}\text{H}_2$ c. CH₃CH₂ $\ddot{\text{O}}\text{H}$ e. CH₃CH₂ $\ddot{\text{C}}\text{I}:$
 b. CH₃ $\ddot{\text{N}}\text{HCH}_3$ d. CH₃ $\ddot{\text{O}}\text{CH}_3$ f. $\text{H}\ddot{\text{O}}\ddot{\text{N}}\text{H}_2$
 1-16. a. CH₃CH₂CH₂Cl c. $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3$
 b. $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$ d. CH₃CH₂C \equiv N
 1-17. a. Cl b. O c. N d. C and H
 1-19. The C—C bonds are formed by *sp*³–*sp*³ overlap; the C—H bonds are formed by *sp*³–*s* overlap.
 1-23. a. 120° b. 120° c. 107.3°
 1-24. the nitrogen
 1-25. most = water; least = methane
 1-27. a. relative lengths: Br₂ > Cl₂; relative strengths: Cl₂ > Br₂
 b. relative lengths: CH₃Br > CH₃Cl > CH₃F; relative strengths: CH₃F > CH₃Cl > CH₃Br
 1-28. a. 1. C—I 2. C—Cl 3. H—Cl b. 1. C—Cl 2. C—C 3. H—F
 1-30. σ
 1-33. a. 109.5° b. 107.3° c. 109.5° d. 109.5°
 1-36. a and d

CHAPTER 2

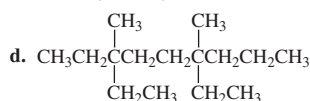
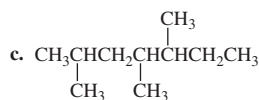
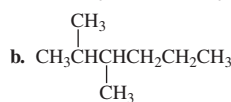
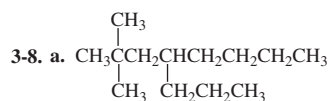
- 2-1. CO₂ and CCl₄
 2-2. a. Cl[−] + ⁺NH₄ b. HO[−] + NH₃
 2-3. a. 1. ⁺NH₄ 2. HCl 3. H₂O 4. H₃O⁺ b. 1. [−]NH₂ 2. Br[−] 3. NO₃[−] 4. HO[−]
 2-4. a. 5.2 b. 3.4 × 10^{−3}
 2-5. weaker
 2-7. a. basic b. acidic c. basic
 2-8. a. CH₃CH₂ $\overset{+}{\text{O}}\text{H}_2$ c. $\text{CH}_3\text{C}(\text{OH})=\text{OH}$ e. $\text{CH}_3\text{CH}_2\text{C}(\text{OH})=\text{OH}$
 b. CH₃CH₂OH d. CH₃CH₂ $\overset{+}{\text{N}}\text{H}_3$
 2-10. 40, 15, 5, 10
 2-11. a. CH₃COO[−] b. [−]NH₂ c. H₂O
 2-12. CH₃NH[−] > CH₃O[−] > CH₃NH₂ > $\text{CH}_3\text{C}(\text{O})\text{O}^{\ominus}$ > CH₃OH

- 2-13. acid
 2-16. HO[−], CH₃NH₂, HC \equiv C[−]
 2-17. [−]CH₃ > [−]NH₂ > HO[−] > F[−]
 2-18. CH₃CH₂[−] > H₂C=CH[−] > HC \equiv C[−]
 2-19. the one on the right
 2-21. F[−] > Cl[−] > Br[−] > I[−]
 2-22. a. oxygen b. H₂S c. CH₃SH
 2-23. a. HBr b. CH₃CH₂CH₂ $\overset{+}{\text{O}}\text{H}_2$ c. the one on the right d. CH₃CH₂CH₂SH
 2-24. a. I[−] b. F[−] c. F[−]
 2-25. a. HO[−] b. NH₃ c. CH₃O[−] d. CH₃O[−]
 2-26. a. CH₃OCH₂CH₂OH b. CH₃CH₂CH₂ $\overset{+}{\text{O}}\text{H}_2$
 c. CH₃CH₂OCH₂CH₂OH d. CH₃CH₂C(=O)OH
 2-27. a. $\text{CH}_3\text{C}(\text{F})\text{CO}^{\ominus}$ b. $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}^{\ominus}$ c. BrCH₂CH₂C(=O)[−] d. CH₃CH₂C(=O)CH₂O[−]
 2-30. $\text{CH}_3\text{S}(\text{OH})_2$ forms a more stable base because the electrons left behind when the proton is removed are shared by 3 oxygens.
 2-31. a. CH₃COO[−] b. CH₃CH₂ $\overset{+}{\text{N}}\text{H}_3$ c. H₂O d. Br[−]
 e. ⁺NH₄ f. [−]C \equiv N g. NO₂[−] h. NO₃[−]
 2-32. a. 1. neutral 2. neutral 3. charged 4. charged 5. charged 6. charged
 b. 1. charged 2. charged 3. charged 4. charged 5. neutral 6. neutral
 c. 1. neutral 2. neutral 3. neutral 4. neutral 5. neutral 6. neutral
 2-34. b. >12.7 c. ≤2.8
 2-35. a. CH₃COO[−] + H⁺ \rightleftharpoons CH₃COOH
 b. CH₃COOH + HO[−] \rightleftharpoons CH₃COO[−] + H₂O
 2-37. a. CH₃O[−] + H₂O b. NH₃ + H₂O c. CH₃NH₂ + H₂O d. CH₃COO[−] + H₂O

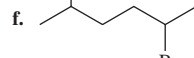
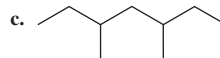
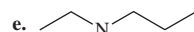
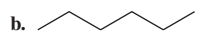
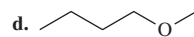
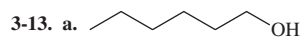
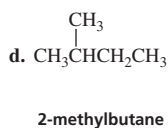
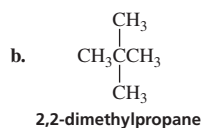
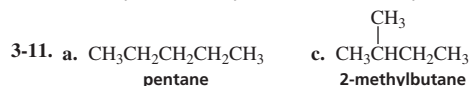
CHAPTER 3

- 3-1. a. 36 hydrogens b. 36 carbons
 3-3. a. *n*-propyl alcohol or propyl alcohol b. butyl methyl ether
 c. *n*-propylamine or propylamine
 3-4. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$ $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$ $\text{CH}_3\text{C}(\text{Br})(\text{CH}_3)_2$
 butyl bromide isobutyl bromide sec-butyl bromide tert-butyl bromide
 or *n*-butyl bromide
 3-5. a. $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{F}$ b. $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{F}$ c. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHI}$
 d. $\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{CH}_3$ e. $\text{CH}_3\text{C}(\text{CH}_3)(\text{NH}_2)\text{CH}_2\text{CH}_3$ f. CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂Br
 3-6. a. ethyl methyl ether b. ethylpropylamine c. sec-butylamine
 d. *n*-butyl alcohol or butyl alcohol e. isobutyl bromide
 f. sec-butyl chloride
 3-7. a. $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ b. $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$
 2-methylbutane 2,2-dimethylpropane

A-2 Answers to Selected Problems



- 3-10. a. 2,2,4-trimethylhexane b. 2,2-dimethylbutane c. 2,2,5-trimethylhexane
d. 5-ethyl-4,4-dimethyloctane e. 3,3-diethylhexane f. 2,5-dimethylheptane



- 3-14. a. $C_{10}H_{20}O$ b. $C_{10}H_{20}O_2$

- 3-16. a. 1-ethyl-2-methylcyclopentane b. ethylcyclobutane c. 1-ethyl-3-methylcyclohexane d. 3,6-dimethyldecane e. heptane f. 1-bromohexane

- 3-17. a. same b. same

- 3-18. a. *sec*-butyl chloride, 2-chlorobutane b. cyclohexyl bromide, bromocyclohexane c. isohexyl chloride, 1-chloro-4-methylpentane d. isopropyl fluoride, 2-fluoropropane

- 3-19. a. tertiary b. tertiary c. primary

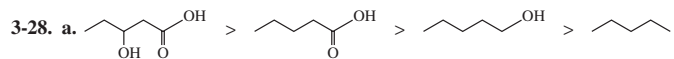
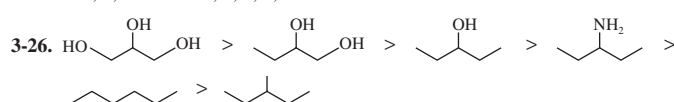
- 3-20. a. methylpropylamine, secondary b. trimethylamine, tertiary c. diethylamine, secondary d. butyldimethylamine, tertiary

- 3-22. a. 104.5° b. 107.3° c. 104.5°

- 3-23. pentane

- 3-24. a. O-H covalent bond b. O-H covalent bond

- 3-25. a. 1, 4, 5 b. 1, 2, 4, 5, 6



- 3-29. ethanol

- 3-30. hexethal

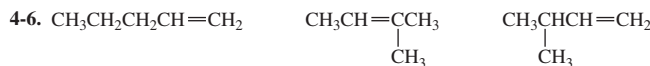
- 3-35. isopropylhexane

- 3-36. a. cis b. trans c. cis d. trans

CHAPTER 4

- 4-1. a. $CH_3CH_2CH_2OH$ b. CH_3CHOH c. $CH_3CH_2OCH_3$ d. 7

- 4-3. a. 5 b. 4 c. 4 d. 6



- 4-7. a. $-I > -Br > -OH > -CH_3$

- b. $-OH > -CH_2Cl > -CH=CH_2 > -CH_2CH_2OH$

- 4-8. Z

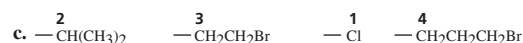
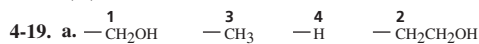
- 4-11. a. (*E*)-2-heptene b. (*Z*)-3,4-dimethyl-2-pentene

- c. (*Z*)-1-chloro-3-ethyl-4-methyl-3-hexene

- 4-13. b and d

- 4-14. a, c, and f

- 4-16. a, c, and f



- 4-20. a. (*R*)-2-bromobutane b. (*R*)-1,3-dichlorobutane

- 4-21. a. *R* b. *R* c. *R* d. *R*

- 4-22. a. identical b. enantiomers c. enantiomers

- 4-23. a. 0 b. +79. c. -79

- 4-24. a. levorotatory b. dextrorotatory

- 4-27. a. *S* b. *R* c. *R* d. *S*

- 4-28. +6.7

- 4-29. a. -24 b. 0

- 4-30. do not know

- 4-31. a. enantiomers b. identical c. diastereomers

- 4-32. a. 8 b. $2^8 = 256$

- 4-34. A, C, E

- 4-35. a. diastereomers b. enantiomers c. identical d. constitutional isomers

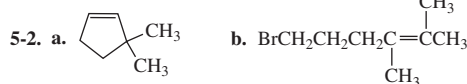
- 4-38. A = identical, B = enantiomer, C = diastereomer, D = identical

- 4-39. B, D, and F

- 4-42. the one on the left

CHAPTER 5

- 5-1. a. 2 b. 4



- c. $CH_3CH_2OCH=CH_2$ d. $CH_2=CHCH_2OH$

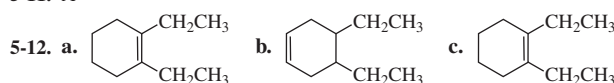
- 5-3. a. 4-methyl-2-pentene b. 2-chloro-3,4-dimethyl-3-hexene

- c. 1-bromocyclopentene d. 1,5-dimethylcyclohexene

- e. 1-bromo-4-methyl-3-hexene f. 1-bromo-2-methyl-1,3-pentadiene

- 5-4. electrophiles: $CH_3\dot{C}HCH_3$; nucleophiles: H^- , CH_3O^- , $CH_3C\equiv CH$, NH_3

- 5-11. A



- 5-13. *cis*-3,4-dimethyl-3-hexene > *trans*-3-hexene > *cis*-3-hexene > *cis*-2,5-dimethyl-3-hexene

- 5-14. decreasing; increasing

- 5-15. a. a and b b. b c. c

- 5-18. a. first step b. revert to reactants c. second step

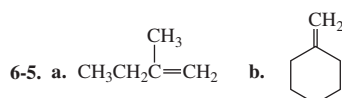
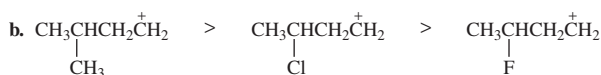
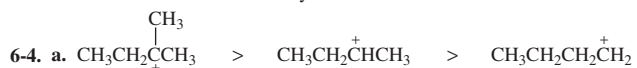
- 5-19. a. 1 b. 2 c. $C \rightarrow D$ d. $C \rightarrow B$ e. $C \rightarrow D$ f. $B \rightarrow C$ g. $C \rightarrow B$

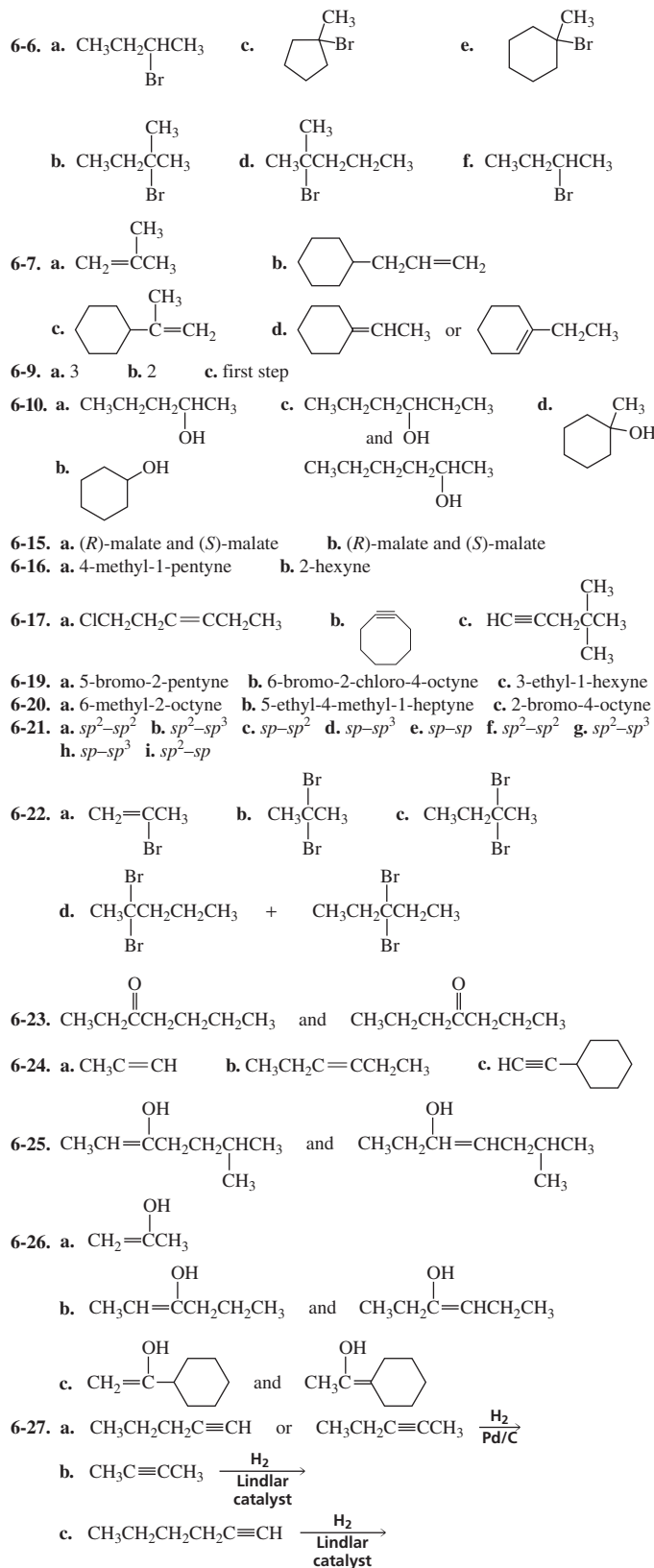
- 5-20. ΔG^\ddagger

CHAPTER 6

- 6-2. a. 0 b. ethyl cation because of hyperconjugation

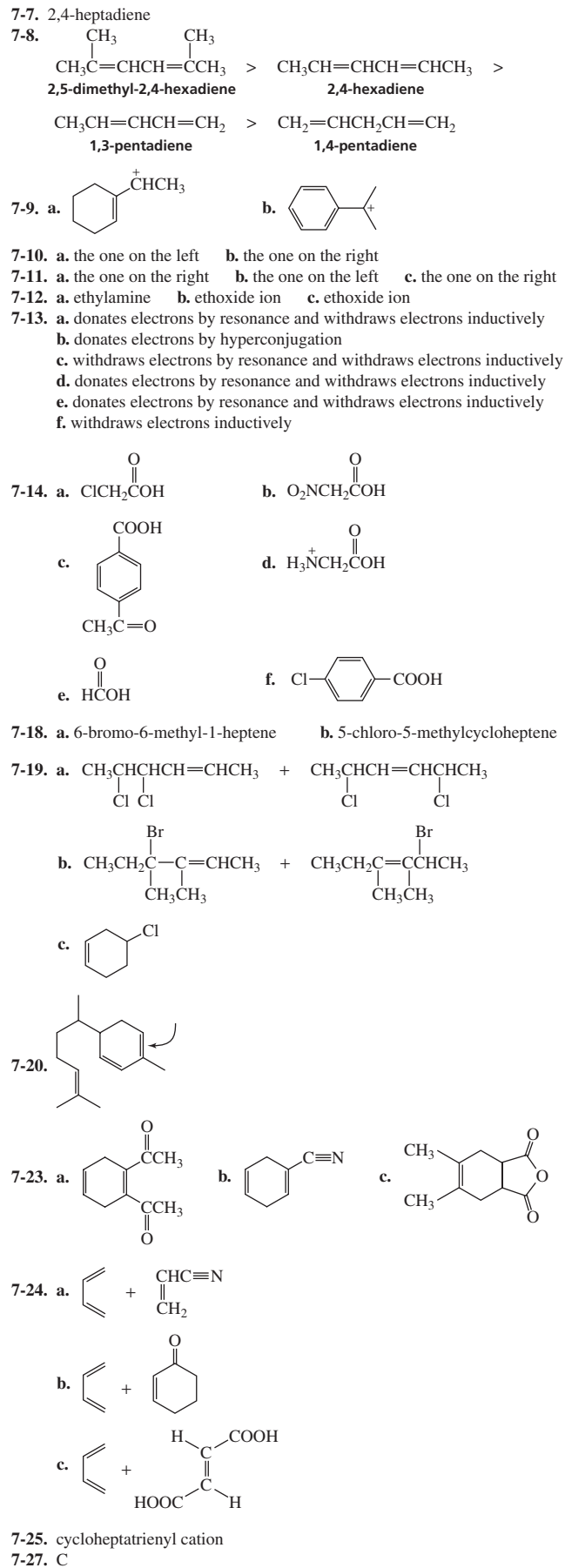
- 6-3. a. 1. 3 2. 3 3. 6 b. *sec*-butyl cation





CHAPTER 7

- 7-4. a. all are the same length b. 2/3 of a negative charge
- 7-5. the dianion > the monoanion > the neutral compound
- 7-6. acetate ion

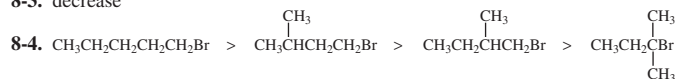


A-4 Answers to Selected Problems

CHAPTER 8

8-2. a. tripled b. half as fast.

8-3. decrease



8-5. a. 2-methoxybutane b. (S)-2-methoxybutane c. (R)-3-hexanol d. 3-pentanol

8-7. a. 1-bromo-2-methylbutane b. 2-bromopropane c. 2-bromobutane

d. 1-bromo-2-phenylethane

8-8. a. $\text{CH}_3\text{CH}_2\text{Br} + \text{HO}^-$ b. $\text{CH}_3\text{CH}_2\text{Cl} + \text{CH}_3\text{O}^-$

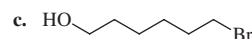
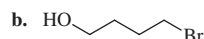
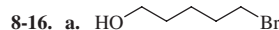
8-11. a. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ b. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_3$ c. $\text{CH}_3\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Br}^-$
d. $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$

8-12. a. (R)-3-methoxy-3-methylhexane + (S)-3-methoxy-3-methylhexane

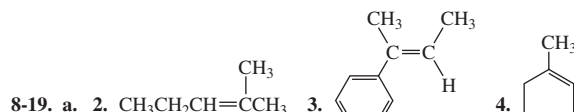
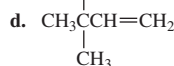
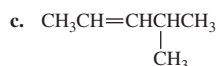
b. 3-methoxy-3-methylpentane

8-13. 2-iodo-2-methylpentane > 2-bromo-2-methylpentane > 2-chloro-2-methylpentane > 3-chloropentane

8-15. a and b



8-18. a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$ b. $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$



b. the same as in an E2

8-20. a. *tert*-butyl bromide b. *tert*-butyl bromide

8-21. a. B b. B c. B d. A

8-23. a. 1-bromopropane b. 1-iodo-1-methylcyclohexane

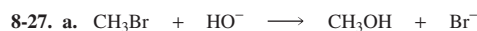
c. 2-bromo-2-methylbutane

8-24. a. primarily substitution b. substitution and elimination

c. substitution and elimination e. only elimination

8-25. it would increase

8-26. a. decrease b. decrease c. increase



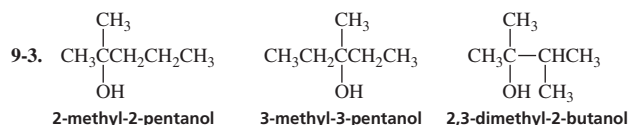
8-29. a. 50% water/50% ethanol b. *tert*-butyl alcohol, *tert*-butyl ethyl ether, and 2-methylpropene in 50% water/50% ethanol; *tert*-butyl ethyl ether and 2-methylpropene in ethanol.

CHAPTER 9

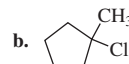
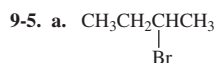
9-2. a. 1-pentanol b. 4-methylcyclohexanol c. 5-methyl-2-hexanol

d. 3-ethyl-1-hexanol e. 5-chloro-2-methyl-2-pentanol

f. 2,6-dimethyl-4-octanol



9-4. no lone pair



9-8. $3^\circ > 1^\circ > 2^\circ$

9-9. B

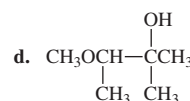
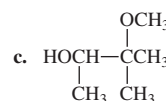
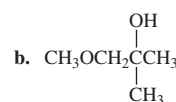
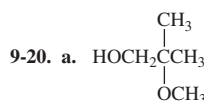
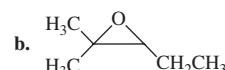
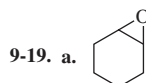
9-12. (E)-3,4-dimethyl-3-hexene (major) + (Z)-3,4-dimethyl-3-hexene

9-13. a. 3-ethyl-2,4-dimethyl-3-hexene b. (E)-3-ethyl-2,4-dimethyl-3-hexene

9-14. a. 3-pentanone a. no reaction a. 1-pentanal

9-15. a. 2-butanol b. benzyl alcohol c. 1-butanol

9-16. a. 1. methoxyethane 2. ethoxyethane 3. 4-methoxyoctane 4. 1-propoxybutane
b. no c. 1. ethyl methyl ether 2. diethyl ether 3. none 4. butyl propyl ether



9-21. noncyclic ether

9-24. the one on the right

9-25. The first one is too insoluble; the second is too reactive; the third is too unreactive.

CHAPTER 10

10-1. B, C, E

10-3. $m/z = 57$

10-5. a. C_5H_{12} b. $\text{C}_6\text{H}_{12}\text{O}$

c. $\text{C}_5\text{H}_{10}\text{O}_2$

d. $\text{C}_6\text{H}_{12}\text{NO}$

10-6. C_6H_{14} , $\text{C}_5\text{H}_{10}\text{O}$, $\text{C}_4\text{H}_6\text{O}_2$

10-7. 2,6-dimethylheptane

10-8. 1-bromopropane

10-10. C_6H_{14}

10-11. a. yes b. no

10-14. a. IR b. UV

10-15. a. 2000 cm^{-1} b. $8\text{ }\mu\text{m}$

10-16. a. $\text{C}\equiv\text{C}$ b. $\text{C}-\text{H}$ stretch c. $\text{C}=\text{N}$ d. $\text{C}=\text{O}$

10-17. a. carbon-oxygen stretch of a phenol b. carbon-oxygen double-bond stretch of a ketone c. $\text{C}-\text{N}$ stretch of aniline

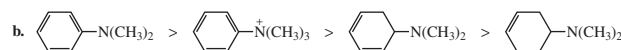
10-18. sp^3

10-19. $\text{C}-\text{O}$ bond of pentanoic acid has partial double bond character

10-20. ethanol dissolved in carbon disulfide

10-21. tertiary amine

10-24. methyl vinyl ketone



10-26. a. left = purple; right = blue b. They would be the same color.

10-27. yellow and blue

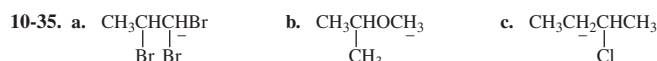
10-28. monitor increase in absorption at 340 nm

10-29. 5.0

10-31. a. 2 b. 1 c. 1 d. 3 e. 3 f. 3

10-33. to the right of the TMS signal

10-34. a. in each structure, it is the proton(s) on the carbon on the right-hand side of the structure b. in each structure, it is the protons on the methyl group on the left-hand side of the structure

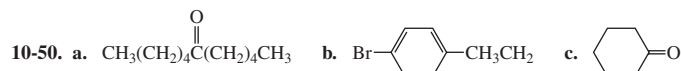
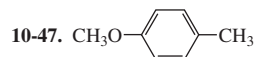


10-38. The compounds have different integration ratios: 2:9, 1:3, and 2:1

10-39. B

10-40. first spectrum = 1-iodopropane

10-42. a. 2-chloropropanoic acid b. 3-chloropropanoic acid



CHAPTER 11

11-1. a. benzyl acetate b. isopentyl acetate c. methyl butyrate

11-2. a. potassium butanoate, potassium butyrate b. isobutyl butanoate, isobutyl butyrate c. pentanoyl chloride, valeryl chloride

d. 5-methylhexanoic acid, methylcaproic acid e. propanamide, propionamide f. *N,N*-dimethylhexanamide, *N,N*-dimethylcaproamide

11-4. B

11-5. In an alcohol because there is no electron delocalization.

11-6. a. sodium acetate b. no reaction

11-7. a. new b. no reaction c. mixture of two

11-8. a. no reaction b. sodium acetate c. no reaction d. no reaction

11-16. a. isopropyl butyrate b. ethyl acetate

11-18. a. propoxide ion b. H^+ would destroy the nucleophilicity of the amine; HO^- and RO^- would provide the wrong nucleophile

11-20. a. butyrate ion and iodomethane b. acetate ion and 1-iodooctane

11-21. 2 and 5

11-23. $B > C > A$

11-24. a. butanenitrile, propyl cyanide b. 4-methylpentanenitrile, isopentyl cyanide

11-25. a. 1-bromopropane b. 1-bromo-2-methylpropane c. 1-bromopentane

11-28. a. acetyl chloride and butyrate ion b. butyryl chloride and acetate ion

11-29. a. butanoyl chloride and ethylamine b. ethanoyl chloride and dimethylamine

11-30. a. propanoic acid + phosphorus trichloride followed by phenol
b. acetic acid + phosphorus trichloride followed by ethylamine
c. propanoic acid + phosphorus trichloride followed by acetate ion

CHAPTER 12

12-3. a. 4-heptanone, dipropyl ketone b. 2-methyl-4-heptanone, isobutyl propyl ketone c. 4-ethylhexanal, γ -ethylcaproaldehyde

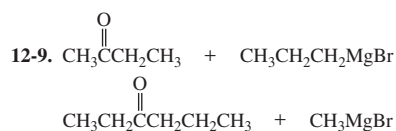
12-4. if elsewhere would not be a ketone

12-5. a. 2-heptanone b. chloromethyl phenyl ketone

12-6. a. ethane + hydroxide ion b. ethane + methoxide ion
c. ethane + CH_3NH d. ethane + acetylide ion

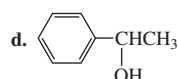
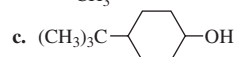
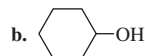
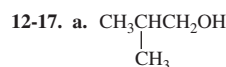
12-7. C

12-8. a. 2-butanol b. 2-methyl-2-pentanol c. 1-methylcyclohexanol

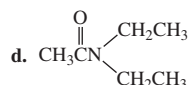
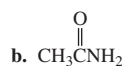
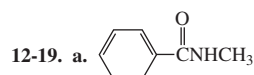


12-10. a. two; (*R*)-3-methyl-3-hexanol and (*S*)-3-methyl-3-hexanol
b. one; 2-methyl-2-pentanol

12-14. B and D



12-18. a. 1-butanol and ethanol b. benzyl alcohol + methanol. c. 1-pentanol



12-23. a. 1, 5, 6 b. 2, 3, 4

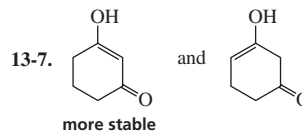
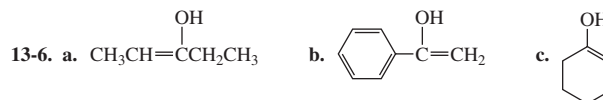
CHAPTER 13

13-2. a. the one on the left b. the one on the right

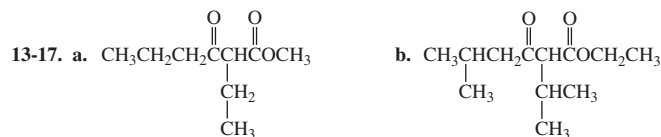
13-3. no competition for electron delocalization onto oxygen

13-4. The proton on the nitrogen is more acidic than the proton on the α -carbon.

13-5. HO^- will react with the acyl chloride to form a carboxylate ion.



13-13. a. butanal b. 3-pentanone



13-18. A, B, and D

13-20. A and D

13-23. a. 3 b. 7

CHAPTER 14

14-3. 6

14-4. the one on the third carbon from the left

14-5. a. 3 b. 1 c. 3 d. 5 e. 5 f. 4

14-7. chlorination

14-9. 5

14-10. a. D b. B

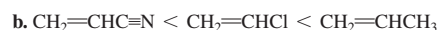
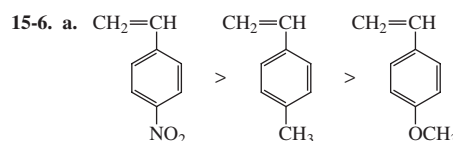
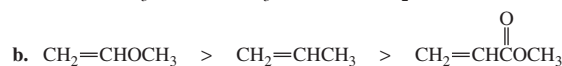
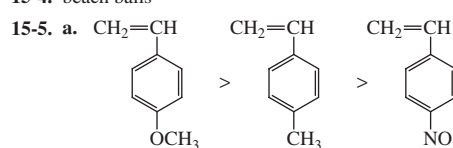
14-11. 4

CHAPTER 15

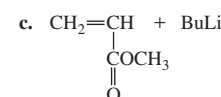
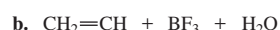
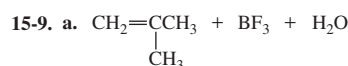
15-1. a. $CH_2=CHCl$ b. c. $CF_2=CF_2$



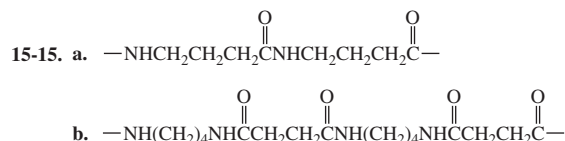
15-4. beach balls



15-8. The carbocation would be unstable because of the electron withdrawing ester group.



A-6 Answers to Selected Problems

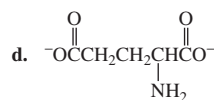
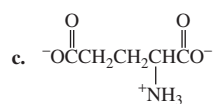
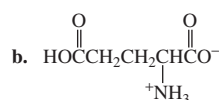
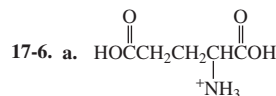


CHAPTER 16

- 16-1. D-Ribose is an aldopentose. D-Sedoheptulose is a ketoheptose. D-Mannose is an aldohexose.
- 16-3. a. enantiomers b. diastereomers
- 16-4. a. D-ribose b. L-talose c. L-allose d. L-ribose
- 16-5. D-psicose
- 16-6. a. $2^4 = 16$ b. $2^5 = 32$ c. none
- 16-7. D-psicose
- 16-11. a. the OH group at C-2 b. the OH group at C-2, C-3, and C-4
c. the OH group at C-3 and C-1
- 16-13. a. propyl β -D-alloside b. α -D-talose
- 16-14. A protonated amine is not a nucleophile.
- 16-15. -74.2
- 16-16. a. amylose has α -1,4'-glycosidic linkages; cellulose has β -1,4'-glycosidic linkages b. amylopectin has 1,6'-glycosidic linkages that create branches; amylose doesn't have branches c. glycogen has more branches than amylopectin d. chitin has an N-acetylamino group instead of an OH group at the 2-position.
- 16-17. a. From those with type A, B, or AB blood.
b. To those with type A, B, or O blood.

CHAPTER 17

- 17-2. Ile
- 17-4. because of the electron-withdrawing ammonium group



- 17-7. a. 5.43 b. 10.76 c. 5.68 d. 2.98
- 17-8. a. Asp b. Arg
- 17-9. 2-methylpropanal
- 17-10. Leucine and isoleucine have similar polarities and pI values, so they show up as one spot.
- 17-13. a. L-Ala and D-Ala, L-Asp and D-Asp, L-Glu and D-Glu
b. L-Ala, L-Asp, L-Glu
- 17-14. a. leucine b. methionine
- 17-15. a. alanine b. isoleucine c. leucine
- 17-19. the bonds on either side of the α -carbon
- 17-21. Edman's reagent would release two amino acids in approximately equal amounts.
- 17-22. Gly-Arg-Trp-Ala-Glu-Leu-Met-Pro-Val-Asp
- 17-24. a. His-Lys, Leu-Val-Glu-Pro-Arg, Ala-Gly-Ala
b. Leu-Gly-Ser-Met-Phe-Pro-Tyr, Gly-Val
- 17-26. Leu-Tyr-Lys-Arg-Met-Phe-Arg-Ser
- 17-28. a. cigar-shaped protein b. subunit of a hexamer

CHAPTER 18

- 18-1. ~ 1
- 18-2. NAM
- 18-4. Arginine forms a direct hydrogen bond; lysine forms an indirect hydrogen bond.
- 18-5. 2, 3, and 4
- 18-7. 2
- 18-12. a. 7 b. 3 isolated from 2 others
- 18-13. N-5 is a stronger base because the lone pair on N-5, unlike the lone pair on N-1, cannot be delocalized onto an oxygen.
- 18-23. a. alanine b. aspartate
- 18-24. the one on the right
- 18-25. If the nitrogen is not protonated, it will be a poorer source for electron delocalization.
- 18-26. The hydrogen bond formed by the OH group weakens the bond to the α -carbon.
- 18-30. In THF, a carbonyl group is at C-4, and the bond between C-3 and C-4 is a single bond; in aminopterin, an amino group is at C-4, and the bond between C-3 and C-4 is a double bond.

CHAPTER 19

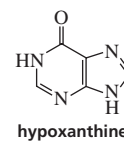
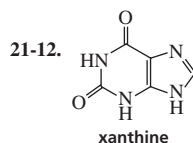
- 19-1. eight
- 19-2. seven
- 19-3. The β -carbon has a partial positive charge.
- 19-5. a. conversion of glucose to glucose-6-phosphate; conversion of fructose-6-phosphate to fructose-1,6-bisphosphate
b. conversion of 1,3-bisphosphoglycerate to 3-phosphoglycerate; conversion of phosphoenolpyruvate to pyruvate
- 19-7. two
- 19-8. acetaldehyde reductase
- 19-9. a ketone
- 19-11. pyruvate
- 19-13. a secondary alcohol
- 19-14. citrate and isocitrate
- 19-15. succinyl
- 19-16. a. 1 b. $1 + 5 = 6$
- 19-17. a. glycerol kinase b. phosphatidic acid phosphatase

CHAPTER 20

- 20-2. glycerol tripalmitate
- 20-10. The two halves are synthesized in a head-to-tail fashion and then joined together in a tail-to-tail linkage.
- 20-14. The reaction of dimethylallyl pyrophosphate and isopentenyl pyrophosphate is an S_N1 reaction.
- 20-15. two 1,2-hydride shifts; two 1,2-methyl shifts

CHAPTER 21

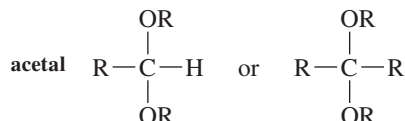
- 21-2. a. $3'\text{—C—C—T—G—T—T—A—G—A—C—G—5'}$ b. guanine
- 21-5. Thymine and uracil have the hydrogen bond donor and the hydrogen bond acceptor in the same place.
- 21-6. Met-Asp-Pro-Val-Ile-Lys-His
- 21-7. Met-Asp-Pro-Leu-Leu-Asn
- 21-9. the third base
- 21-10. $5'\text{—G—C—A—T—G—G—A—C—C—C—G—T—T—A—T—T—A—A—C—A—C—3'}$



- 21-14. A

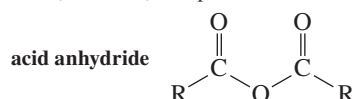
Glossary

absorption band a peak in a spectrum that occurs as a result of the absorption of energy.



achiral (optically inactive) an achiral molecule has a conformation identical to (superimposable upon) its mirror image.

acid (Brønsted) a species that loses a proton.



acid–base reaction a reaction in which an acid donates a proton to a base or accepts a share in a base's electrons.

acid catalyst a catalyst that increases the rate of a reaction by donating a proton.

acid-catalyzed reaction a reaction catalyzed by an acid.

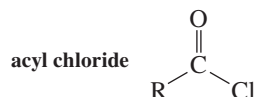
acid dissociation constant a measure of the degree to which an acid dissociates in solution.

active site a pocket or cleft in an enzyme where the substrate is bound.

acyclic noncyclic.

acyl adenylate a carboxylic acid derivative with AMP as the leaving group.

acyl–enzyme intermediate an intermediate formed when an amino acid residue of an enzyme is acetylated.



acyl group a carbonyl group bonded to an alkyl group or to an aryl group.

acyl phosphate a carboxylic acid derivative with a phosphate leaving group.

acyl pyrophosphate a carboxylic acid derivative with a pyrophosphate leaving group.

1,2-addition (direct addition) addition to the 1- and 2-positions of a conjugated system.

1,4-addition (conjugate addition) addition to the 1- and 4-positions of a conjugated system.

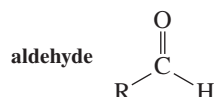
addition polymer (chain-growth polymer) a polymer made by adding monomers to the growing end of a chain.

addition reaction a reaction in which atoms or groups are added to the reactant.

adrenal cortical steroids glucocorticoids and mineralocorticoids.

alcohol a compound with an OH group in place of one of the hydrogens of an alkane (ROH).

alcoholysis reaction with an alcohol.



aldol addition a reaction between two molecules of an aldehyde (or two molecules of a ketone) that connects the α -carbon of one with the carbonyl carbon of the other.

aldol condensation an aldol addition followed by the elimination of water.

aldose a polyhydroxyaldehyde.

aliphatic a nonaromatic organic compound.

alkaloid a natural product, with one or more nitrogen heteroatoms, found in the leaves, bark, or seeds of plants.

alkane a hydrocarbon that contains only single bonds.

alkene a hydrocarbon that contains a double bond.

alkylation reaction a reaction that adds an alkyl group to a reactant.

alkyl halide a compound with a halogen in place of one of the hydrogens of an alkane.

alkyl substituent (alkyl group) formed by removing a hydrogen from an alkane.

alkyne a hydrocarbon that contains a triple bond.

allene a compound with two adjacent double bonds.

allosteric activator a compound that activates an enzyme when it binds to a site on the enzyme (other than the active site).

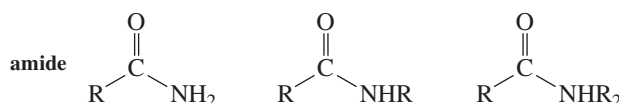
allosteric inhibitor a compound that inactivates an enzyme when it binds to a site on the enzyme (other than the active site).

allyl group $\text{CH}_2=\text{CHCH}_2-$

allylic carbon an sp^3 carbon adjacent to a vinylic carbon.

allylic cation a species with a positive charge on an allylic carbon.

alternating copolymer a copolymer in which two monomers alternate.



amine a compound with a nitrogen in place of one of the hydrogens of an alkane (RNH_2 , R_2NH , R_3N).

amine inversion the configuration of an sp^3 hybridized nitrogen with a non-bonding pair of electrons that rapidly turns inside out.

amino acid an α -aminocarboxylic acid. Naturally occurring amino acids have the L configuration.

amino acid analyzer an instrument that automates the ion-exchange separation of amino acids.

amino acid residue a monomeric unit of a peptide or protein.

aminolysis reaction with an amine.

amino sugar a sugar in which one of the OH groups is replaced by an NH_2 group.

anabolic steroids steroids that aid in the development of muscle.

anabolism reactions that living organisms carry out in order to synthesize complex molecules from simple precursor molecules.

androgens male sex hormones.

angle strain the strain introduced into a molecule as a result of its bond angles being distorted from their ideal values.

angstrom unit of length; 100 picometers = 10^{-8} cm = 1 angstrom.

anion-exchange resin a positively charged resin used in ion-exchange chromatography.

anionic polymerization chain-growth polymerization in which the initiator is a nucleophile; the propagation site, therefore, is an anion.

anomeric carbon the carbon in a cyclic sugar that is the carbonyl carbon in the open-chain form.

anomers two cyclic sugars that differ in configuration only at the carbon that is the carbonyl carbon in the open-chain form.

antibiotic a compound that interferes with the growth of a microorganism.

antibodies compounds that recognize foreign particles in the body.

anticodon the three bases at the bottom of the middle loop in tRNA.

anti conformer the most stable of the staggered conformers.

antigens compounds that can generate a response from the immune system.

antisense strand (template strand) the strand in DNA that is read during transcription.

antiviral drug a drug that interferes with DNA or RNA synthesis in order to prevent a virus from replicating.

applied magnetic field the externally applied magnetic field.

aramide an aromatic polyamide.

arene oxide an aromatic compound that has had one of its double bonds converted to an epoxide.

aromatic a cyclic and planar compound with an uninterrupted ring of p orbital-bearing atoms containing an odd number of pairs of π electrons.

aryl group a benzene or a substituted-benzene group.

asymmetric center an atom bonded to four different atoms or groups.

G-2 Glossary

atactic polymer a polymer in which the substituents are randomly oriented on the extended carbon chain.

atomic number the number of protons (or electrons) that the neutral atom has.

atomic orbital an orbital associated with an atom.

atomic weight the average mass of the atoms in the naturally occurring element.

axial bond a bond of the chair conformation of cyclohexane that is perpendicular to the plane in which the chair is drawn (an up–down bond).

back-side attack nucleophilic attack on the side of the carbon opposite the side bonded to the leaving group.

basal metabolic rate the number of calories that would be burned if one stayed in bed all day.

base¹ a species that gains a proton.

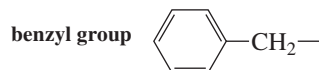
base² a purine or a pyrimidine in DNA and RNA.

base catalyst a catalyst that increases the rate of a reaction by removing a proton.

base peak the peak with the greatest abundance in a mass spectrum.

basicity the tendency of a compound to share its electrons with a proton.

bending vibration a vibration that does not occur along the line of the bond. It results in changing bond angles.



benzylic carbon an sp^3 hybridized carbon bonded to a benzene ring.

benzylic cation a compound with a positive charge on a benzylic carbon.

bifunctional molecule a molecule with two functional groups.

bile acids steroids that act as emulsifying agents so that water-insoluble compounds can be digested.

bimolecular reaction (second-order reaction) a reaction whose rate depends on the concentration of two reactants.

biochemistry (biological chemistry) the chemistry of biological systems.

biodegradable polymer a polymer that can be broken into small segments by an enzyme-catalyzed reaction.

bioorganic compound an organic compound found in biological systems.

biopolymer a polymer that is synthesized in nature.

biosynthesis synthesis in a biological system.

biotin the coenzyme required by enzymes that catalyze carboxylation of a carbon adjacent to an ester or a keto group.

block copolymer a copolymer in which there are regions (blocks) of each kind of monomer.

boat conformation the conformation of cyclohexane that roughly resembles a boat.

boiling point the temperature at which the vapor pressure from a liquid equals the atmospheric pressure.

bond length the internuclear distance between two atoms at minimum energy (maximum stability).

bond order the number of covalent bonds shared by two atoms.

bond strength the energy required to break a bond homolytically.

brand name (proprietary name, trade name) identifies a commercial product and distinguishes it from other products. It can be used only by the owner of the registered trademark.

Brønsted acid a species that loses a proton.

Brønsted base a species that gains a proton.

buffer a weak acid and its conjugate base.

carbanion a compound containing a negatively charged carbon.

carbocation a species containing a positively charged carbon.

carbocation rearrangement the rearrangement of a carbocation to a more stable carbocation.

carbohydrate a sugar or a saccharide. Naturally occurring carbohydrates have the D configuration.

α -carbon a carbon bonded to a leaving group or adjacent to a carbonyl carbon.

β -carbon a carbon adjacent to an α -carbon.

carbon acid a compound containing a carbon that is bonded to a relatively acidic hydrogen.

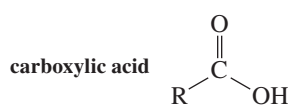
carbonyl carbon the carbon of a carbonyl group.

carbonyl compound a compound that contains a carbonyl group.

carbonyl group a carbon doubly bonded to an oxygen.

carbonyl oxygen the oxygen of a carbonyl group.

carboxyl group COOH



carboxylic acid derivative a compound that is hydrolyzed to a carboxylic acid.

carboxyl oxygen the single-bonded oxygen of a carboxylic acid or an ester.

carotenoid a class of compounds (a tetraterpene) responsible for the red and orange colors of fruits, vegetables, and fall leaves.

catabolism reactions that living organisms carry out in order to break down complex molecules into simple molecules and energy.

catalyst a species that increases the rate at which a reaction occurs without being consumed in the reaction. Because it does not change the equilibrium constant of the reaction, it does not change the amount of product that is formed.

catalytic hydrogenation the addition of hydrogen to a double or a triple bond with the aid of a metal catalyst.

cation-exchange resin a negatively charged resin used in ion-exchange chromatography.

cationic polymerization chain-growth polymerization in which the initiator is an electrophile; the propagation site, therefore, is a cation.

cephalin a phosphoacylglycerol in which the second OH group of phosphate has formed an ester with ethanolamine.

cerebroside a sphingolipid in which the terminal OH group of sphingosine is bonded to a sugar residue.

chain-growth polymer (addition polymer) a polymer made by adding monomers to the growing end of a chain.

chain transfer a growing polymer chain reacts with a molecule XY in a manner that allows X to terminate the chain, leaving behind Y to initiate a new chain.

chair conformation the conformation of cyclohexane that roughly resembles a chair. It is the most stable conformation of cyclohexane.

chemically equivalent protons protons with the same connectivity relationship to the rest of the molecule.

chemical shift the location of a signal in an NMR spectrum. It is measured downfield from a reference compound (most often, TMS).

chiral (optically active) a chiral molecule has a nonsuperimposable mirror image.

chiral center a tetrahedral atom bonded to four different groups.

cholesterol a steroid that is the precursor of all other animal steroids.

chromatography a separation technique in which the mixture to be separated is dissolved in a solvent and the solvent is passed through a column packed with an absorbent stationary phase.

cis fused two cyclohexane rings fused together such that if the second ring were considered to be two substituents of the first ring, one substituent would be in an axial position and the other would be in an equatorial position.

cis isomer the isomer with the hydrogens on the same side of the double bond or cyclic structure.

cis–trans isomers geometric isomers.

citric acid cycle (Krebs cycle) a series of reactions that converts the acetyl group of acetyl-CoA into two molecules of CO₂.

Claisen condensation a reaction between two molecules of an ester that connects the α -carbon of one with the carbonyl carbon of the other and eliminates an alkoxide ion.

α -cleavage homolytic cleavage of an alpha substituent.

codon a sequence of three bases in mRNA that specifies the amino acid to be incorporated into a protein.

coenzyme a cofactor that is an organic molecule.

coenzyme A a thiol used by biological organisms to form thioesters.

coenzyme B₁₂ the coenzyme required by enzymes that catalyze certain rearrangement reactions.

coil conformation (loop conformation) that part of a protein that is highly ordered, but not in an α -helix or a β -pleated sheet.

common name nonsystematic nomenclature.

competitive inhibitor a compound that inhibits an enzyme by competing with the substrate for binding at the active site.

complete racemization the formation of a pair of enantiomers in equal amounts.

complex carbohydrate a carbohydrate containing two or more sugar molecules linked together.

concerted reaction a reaction in which all the bond-making and bond-breaking processes occur in one step.

condensation polymer (step-growth polymer) a polymer made by combining two molecules while removing a small molecule (usually water or an alcohol).

condensation reaction a reaction combining two molecules while removing a small molecule (usually water or an alcohol).

conducting polymer a polymer that can conduct electricity.

configuration the three-dimensional structure of a particular atom in a compound. The configuration is designated by *R* or *S*.

configurational isomers stereoisomers that cannot interconvert unless a covalent bond is broken. Cis–trans isomers and optical isomers are configurational isomers.

conformation the three-dimensional shape of a molecule at a given instant that can change as a result of rotations about σ bonds.

conformers different conformations of a molecule.

conjugate acid a species accepts a proton to form its conjugate acid.

conjugate addition 1,4-addition to an α,β -unsaturated carbonyl compound.

conjugate base a species loses a proton to form its conjugate base.

conjugated double bonds double bonds separated by one single bond.

constitutional isomers (structural isomers) molecules that have the same molecular formula but differ in the way their atoms are connected.

contributing resonance structure (resonance contributor, resonance structure) a structure with localized electrons that approximates the structure of a compound with delocalized electrons.

copolymer a polymer formed from two or more different monomers.

coupled protons protons that split each other. Coupled protons have the same coupling constant.

coupled reaction an endergonic reaction followed by an exergonic reaction.

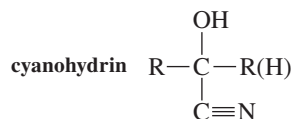
covalent bond a bond created as a result of sharing electrons.

crossed aldol addition an aldol addition in which two different aldehydes or ketones are used.

crossed Claisen condensation a Claisen condensation in which two different esters are used.

cross-linking connecting polymer chains by intermolecular bond formation.

C-terminal amino acid the terminal amino acid of a peptide (or protein) that has a free carboxyl group.



cycloalkane an alkane with its carbon chain arranged in a closed ring.

deamination loss of ammonia.

decarboxylation loss of carbon dioxide.

dehydration loss of water.

dehydrogenase an enzyme that carries out an oxidation reaction by removing hydrogen from the substrate.

dehydrohalogenation elimination of a proton and a halide ion.

delocalization energy (resonance energy) the extra stability a compound achieves as a result of having delocalized electrons.

delocalized electrons electrons that are shared by more than two atoms.

denaturation destruction of the highly organized tertiary structure of a protein.

deoxygenation removal of an oxygen from a reactant.

deoxyribonucleic acid (DNA) a polymer of deoxyribonucleotides.

deoxyribonucleotide a nucleotide in which the sugar component is D-2'-deoxyribose.

deoxy sugar a sugar in which one of the OH groups has been replaced by an H.

detergent a salt of a sulfonic acid.

dextrorotatory the enantiomer that rotates polarized light in a clockwise direction.

diastereomer a configurational stereoisomer that is not an enantiomer.

1,3-diaxial interaction the interaction between an axial substituent and the other two axial substituents on the same side of the cyclohexane ring.

Diels–Alder reaction a [4 + 2] cycloaddition reaction.

diene a hydrocarbon with two double bonds.

dienophile an alkene that reacts with a diene in a Diels–Alder reaction.

β -diketone a ketone with a second carbonyl group at the β -position.

dimer a molecule formed by the joining together of two identical molecules.

dinucleotide two nucleotides linked by phosphodiester bonds.

dipeptide two amino acids linked by an amide bond.

dipole–dipole interaction an interaction between the dipole of one molecule and the dipole of another.

dipole moment (μ) a measure of the separation of charge in a bond or in a molecule.

direct addition 1,2-addition to an α,β -unsaturated carbonyl compound (addition to the carbonyl carbon).

disaccharide a compound containing two sugar molecules linked together.

disproportionation transfer of a hydrogen atom by a radical to another radical, forming an alkane and an alkene.

dissociation energy the amount of energy required to break a bond, or the amount of energy released when a bond is formed.

disulfide bridge a disulfide ($-\text{S}-\text{S}-$) bond in a peptide or protein.

DNA (deoxyribonucleic acid) a polymer of deoxyribonucleotides.

doping adding or removing electrons from a polymer with conjugated double bonds.

double bond a σ bond and a π bond between two atoms.

doublet an NMR signal split into two peaks.

doublet of doublets an NMR signal split into four peaks of approximately equal height. Caused by splitting a signal into a doublet by one hydrogen and into another doublet by another (nonequivalent) hydrogen.

drug a compound that reacts with a biological molecule, triggering a physiological effect.

drug resistance biological resistance to a particular drug.

eclipsed conformation a conformation in which the bonds on adjacent carbons are aligned as viewed looking down the carbon–carbon bond.

E conformation the conformation of a carboxylic acid or carboxylic acid derivative in which the carbonyl oxygen and the substituent bonded to the carbonyl oxygen or nitrogen are on opposite sides of the single bond.

Edman's reagent phenyl isothiocyanate. A reagent used to determine the N-terminal amino acid of a polypeptide.

effective magnetic field the magnetic field that a proton “senses” through the surrounding cloud of electrons.

E isomer the isomer with the high-priority groups on opposite sides of the double bond.

electromagnetic radiation radiant energy that displays wave properties.

electronegative element an element that readily acquires an electron.

electronegativity tendency of an atom to pull electrons toward itself.

electron sink site to which electrons can be delocalized.

electrophile an electron-deficient atom or molecule.

electrophilic addition reaction an addition reaction in which the first species that adds to the reactant is an electrophile.

electrophilic aromatic substitution a reaction in which an electrophile substitutes for a hydrogen of an aromatic ring.

electrophilic catalysis catalysis in which the species that facilitates the reaction is an electrophile.

electrophoresis a technique that separates amino acids on the basis of their pI values.

electrostatic attraction attractive force between opposite charges.

electrostatic catalysis stabilization of a charge by an opposite charge.

elimination reaction a reaction that involves the elimination of atoms (or molecules) from the reactant.

enantiomers nonsuperimposable mirror-image molecules.

endergonic reaction a reaction with a positive ΔG° .

endopeptidase an enzyme that hydrolyzes a peptide bond that is not at the end of a peptide chain.

endothermic reaction a reaction with a positive ΔH° .

enediol rearrangement interconversion of an aldose and one or more ketoses.

enkephalins pentapeptides synthesized by the body to control pain.

enolization keto–enol interconversion.

enthalpy the heat given off ($-\Delta H^\circ$) or the heat absorbed ($+\Delta H^\circ$) during the course of a reaction.

entropy a measure of the freedom of motion in a system.

enzyme a protein that is a catalyst.

epimerization changing the configuration of an asymmetric center by removing a proton from it and then reprotonating the molecule at the same site.

epimers monosaccharides that differ in configuration at only one carbon.

epoxidation formation of an epoxide.

epoxide an ether in which the oxygen is incorporated into a three-membered ring.

epoxy resin substance formed by mixing a low-molecular-weight prepolymer with a compound that forms a cross-linked polymer.

equatorial bond a bond of the chair conformer of cyclohexane that juts out from the ring in approximately the same plane that contains the chair.

G-4 Glossary

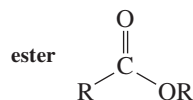
equilibrium constant the ratio of products to reactants at equilibrium or the ratio of the rate constants for the forward and reverse reactions.

E1 reaction an elimination reaction with a unimolecular transition state.

E2 reaction an elimination reaction with a bimolecular transition state.

essential amino acid an amino acid that humans must obtain from their diet because they cannot synthesize it at all or cannot synthesize it in adequate amounts.

essential oils fragrances and flavorings isolated from plants that do not leave residues when they evaporate. Most are terpenes.



estrogens (estrone and estradiol) female sex hormones.

ether a compound containing an oxygen bonded to two carbons (ROR).

exergonic reaction a reaction with a negative ΔG° .

exopeptidase an enzyme that hydrolyzes a peptide bond at the end of a peptide chain.

exothermic reaction a reaction with a negative ΔH° .

fat a triester of glycerol that exists as a solid at room temperature.

fatty acid a long-chain carboxylic acid.

feedback inhibitor a compound that inhibits a step at the beginning of the pathway for its biosynthesis.

fibrous protein a water-insoluble protein in which the polypeptide chains are arranged in bundles.

Fischer projection a method of representing the spatial arrangement of groups bonded to an asymmetric center. The asymmetric center is the point of intersection of two perpendicular lines; the horizontal lines represent bonds that project out of the plane of the paper toward the viewer, and the vertical lines represent bonds that point back from the plane of the paper away from the viewer.

flavin adenine dinucleotide (FAD) a coenzyme required in certain oxidation reactions. It is reduced to FADH_2 , which forms 1.5 ATPs in oxidative phosphorylation when it is oxidized back to FAD.

formal charge the number of valence electrons – (the number of nonbonding electrons + $1/2$ the number of bonding electrons).

free energy of activation (ΔG^\ddagger) the true energy barrier to a reaction.

frequency the velocity of a wave divided by its wavelength (in units of cycles/s).

Friedel–Crafts acylation an electrophilic substitution reaction that puts an acyl group on a benzene ring.

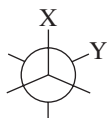
Friedel–Crafts alkylation an electrophilic substitution reaction that puts an alkyl group on a benzene ring.

functional group the center of reactivity in a molecule.

furanose a five-membered-ring sugar.

furanoside a five-membered-ring glycoside.

gauche X and Y are gauche to each other in this Newman projection:



gauche conformer a staggered conformer in which the largest substituents are gauche to each other.

gauche interaction the interaction between two atoms or groups that are gauche to each other.

gene a segment of DNA.

generic name a commercially nonrestricted name for a drug.

gene therapy a technique that inserts a synthetic gene into the DNA of an organism that is defective in that gene.

genetic code the amino acid specified by each three-base sequence of mRNA.

genetic engineering insertion of a segment of DNA into the DNA of a replicating host cell.

geometric isomers cis–trans (or *E,Z*) isomers.

Gibbs standard free-energy change (ΔG°) the difference between the free-energy content of the products and the free-energy content of the reactants at equilibrium under standard conditions (1 M, 25 °C, 1 atm).

globular protein a water-soluble protein that tends to have a roughly spherical shape.

gluconeogenesis the synthesis of D-glucose from pyruvate.

glycolysis (glycolytic cycle) the series of reactions that converts D-glucose into two molecules of pyruvate.

glycoprotein a protein that is covalently bonded to a polysaccharide.

glycoside the acetal of a sugar.

N-glycoside a glycoside with a nitrogen instead of an oxygen at the glycosidic linkage.

glycosidic bond the bond between the anomeric carbon and the alcohol in a glycoside.

α -1,4'-glycosidic linkage a linkage between the C-1 oxygen of one sugar and the C-4 of a second sugar with the oxygen atom of the glycosidic linkage in the axial position.

β -1,4'-glycosidic linkage a linkage between the C-1 oxygen of one sugar and the C-4 of a second sugar with the oxygen atom of the glycosidic linkage in the equatorial position.

genetically modified organism (GMO) insertion of a gene into the DNA of a species.

graft copolymer a copolymer that contains branches of a polymer of one monomer grafted onto the backbone of a polymer made from another monomer.

Grignard reagent the compound that results when magnesium is inserted between the carbon and halogen of an alkyl halide (RMgBr , RMgCl).

ground-state electronic configuration a description of which orbitals the electrons of an atom or molecule occupy when all of the electrons of atoms are in their lowest-energy orbitals.

half-chair conformation the least stable conformation of cyclohexane.

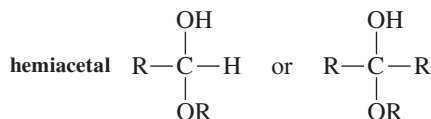
halogenation reaction with halogen (Br_2 or Cl_2).

Haworth projection a way to show the structure of a sugar; the five- and six-membered rings are represented as being flat.

head-to-tail addition the head of one molecule is added to the tail of another.

heat of hydrogenation the heat ($-\Delta H^\circ$) released in a hydrogenation reaction.

α -helix the backbone of a polypeptide coiled in a right-handed spiral with hydrogen bonding occurring within the helix.



heptose a monosaccharide with seven carbons.

hexose a monosaccharide with six carbons.

high-energy bond a bond that releases a great deal of energy when it is broken.

homolytic bond cleavage (homolysis) breaking a bond with the result that each of the atoms gets one of the bonding electrons.

homopolymer a polymer that contains only one kind of monomer.

hormone an organic compound synthesized in a gland and delivered by the bloodstream to its target tissue.

human genome the total DNA of a human cell.

hybrid orbital an orbital formed by mixing (hybridizing) orbitals.

hydrated water has been added to a compound.

hydration addition of water to a compound.

hydride ion a negatively charged hydrogen.

1,2-hydride shift the movement of a hydride ion from one carbon to an adjacent carbon.

hydrocarbon a compound that contains only carbon and hydrogen.

α -hydrogen usually, a hydrogen bonded to the carbon adjacent to a carbonyl carbon.

hydrogenation addition of hydrogen.

hydrogen bond an unusually strong dipole–dipole attraction (5 kcal/mol) between a hydrogen bonded to O, N, or F and the nonbonding electrons of an O, N, or F of another molecule.

hydrogen ion (proton) a positively charged hydrogen.

hydrolysis reaction with water.

hydrophobic interactions interactions between nonpolar groups. These interactions increase stability by decreasing the amount of structured water (increasing entropy).

hyperconjugation delocalization of electrons by overlap of carbon–hydrogen or carbon–carbon σ bonds with an empty p orbital.

imine (Schiff base) $\text{R}_2\text{C}=\text{NR}$

induced-dipole–induced-dipole interaction an interaction between a temporary dipole in one molecule and the dipole the temporary dipole induces in another molecule.

induced-fit model a model that describes the specificity of an enzyme for its substrate: the shape of the active site does not become completely complementary to the shape of the substrate until after the enzyme binds the substrate.

inductive electron donation donation of electrons through σ bonds.

inductive electron withdrawal withdrawal of electrons through a σ bond.
informational strand (sense strand) the strand in DNA that is not read during transcription; it has the same sequence of bases as the synthesized mRNA strand (with a U, T difference).

infrared radiation electromagnetic radiation familiar to us as heat.

infrared spectroscopy uses infrared energy to provide a knowledge of the functional groups in a compound.

infrared (IR) spectrum a plot of percent transmission versus wavenumber (or wavelength) of infrared radiation.

initiation step the step in which radicals are created, or the step in which the radical needed for the first propagation step is created.

interchain disulfide bridge a disulfide bridge between two cysteine residues in different peptide chains.

intermediate a species formed during a reaction and that is not the final product of the reaction.

intermolecular reaction a reaction that takes place between two molecules.

internal alkyne an alkyne with the triple bond not at the end of the carbon chain.

intrachain disulfide bridge a disulfide bridge between two cysteine residues in the same peptide chain.

intramolecular reaction a reaction that takes place within a molecule.

inversion of configuration turning the configuration of a carbon inside out like an umbrella in a windstorm, so that the resulting product has a configuration opposite that of the reactant.

ion-dipole interaction the interaction between an ion and the dipole of a molecule.

ion-exchange chromatography a technique that uses a column packed with an insoluble resin to separate compounds on the basis of their charges and polarities.

ionic bond a bond formed through the attraction of two ions of opposite charges.

isoelectric point (pI) the pH at which there is no net charge on an amino acid.

isolated double bonds double bonds separated by more than one single bond.

isomers nonidentical compounds with the same molecular formula.

isoprene rule rule expressing the head-to-tail linkage of isoprene units.

isotactic polymer a polymer in which all the substituents are on the same side of the fully extended carbon chain.

isotopes atoms with the same number of protons but different numbers of neutrons.

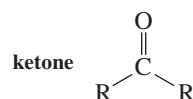
IUPAC nomenclature systematic nomenclature of chemical compounds.

Kekulé structure a model that represents the bonds between atoms as lines.

keto-enol tautomerism (keto-enol interconversion) interconversion of keto and enol tautomers.

keto-enol tautomers a ketone and its isomeric α,β -unsaturated alcohol.

β -keto ester an ester with a second carbonyl group at the β -position.



ketose a polyhydroxyketone.

kinase an enzyme that puts a phosphate group on its substrate.

kinetic control when a reaction is under kinetic control, the relative amounts of the products depend on the rates at which they are formed.

kinetic product the product that is formed the fastest.

kinetic resolution separation of enantiomers on the basis of the difference in their rate of reaction with an enzyme.

kinetics the field of chemistry that deals with the rates of chemical reactions.

kinetic stability chemical reactivity, indicated by ΔG^\ddagger . If ΔG^\ddagger is large, the compound is kinetically stable (not very reactive). If ΔG^\ddagger is small, the compound is kinetically unstable (highly reactive).

Krebs cycle (citric acid cycle, tricarboxylic acid cycle, TCA cycle) a series of reactions that convert the acetyl group of acetyl-CoA into two molecules of CO_2 .

λ_{max} the wavelength at which there is maximum UV/Vis absorbance.

lead compound the prototype in a search for other biologically active compounds.

leaving group the group that is displaced in a nucleophilic substitution reaction.

Le Châtelier's principle states that if an equilibrium is disturbed, the components of the equilibrium will adjust in a way that will offset the disturbance.

lecithin a phosphoacylglycerol in which the second OH group of phosphate has formed an ester with choline.

levorotatory the enantiomer that rotates polarized light in a counterclockwise direction.

Lewis structure a model that represents the bonds between atoms as lines or dots and the valence electrons as dots.

lipid a water-insoluble compound found in a living system.

lipid bilayer two layers of phosphoacylglycerols arranged so that their polar heads are on the outside and their nonpolar fatty acid chains are on the inside.

lipoate a coenzyme required in certain oxidation reactions.

living polymer a nonterminated chain-growth polymer that remains active. This means that the polymerization reaction can continue upon the addition of more monomer.

localized electrons electrons that are restricted to a particular locality.

lock-and-key model a model that describes the specificity of an enzyme for its substrate: the substrate fits the enzyme as a key fits a lock.

lone-pair electrons (nonbonding electrons) valence electrons not used in bonding.

loop conformation (coil conformation) that part of a protein that is highly ordered, but not in an α -helix or β -pleated sheet.

magnetic resonance imaging (MRI) NMR used in medicine. The difference in the way water is bound in different tissues produces a variation in signal between organs as well as between healthy and diseased tissue.

major groove the wider and deeper of the two alternating grooves in DNA.

mass number the number of protons plus the number of neutrons in an atom.

mass spectrometry provides a knowledge of the molecular weight, molecular formula, and certain structural features of a compound.

mass spectrum a plot of the relative abundance of the positively charged fragments produced in a mass spectrometer versus their m/z values.

materials science the science of creating new materials to be used in place of known materials such as metal, glass, wood, cardboard, and paper.

mechanism-based inhibitor (suicide inhibitor) a compound that inactivates an enzyme by undergoing part of its normal catalytic mechanism.

mechanism of a reaction a description of the step-by-step process by which reactants are changed into products.

melting point the temperature at which a solid becomes a liquid.

membrane the material that surrounds a cell in order to isolate its contents.

mercaptan (thiol) the sulfur analog of an alcohol (RSH).

meso compound a compound that contains asymmetric centers and a plane of symmetry.

metabolism reactions that living organisms carry out in order to obtain the energy and to synthesize the compounds they require.

methine hydrogen a tertiary hydrogen.

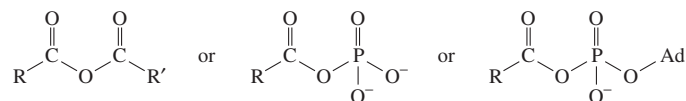
methylene group a CH_2 group.

1,2-methyl shift the movement of a methyl group with its bonding electrons from one carbon to an adjacent carbon.

micelle a spherical aggregation of molecules, each with a long, hydrophobic tail and a polar head, arranged so that the polar head points to the outside of the sphere.

minor groove the narrower and more shallow of the two alternating grooves in DNA.

mixed anhydride an anhydride formed from two different acids.



mixed triacylglycerol a triacylglycerol in which the fatty-acid components are different.

molecular ion (parent ion) peak in the mass spectrum with the greatest m/z .

molecular orbital an orbital associated with a molecule.

molecular recognition the recognition of one molecule by another as a result of specific interactions; for example, the specificity of an enzyme for its substrate.

monomer a repeating unit in a polymer.

monosaccharide (simple carbohydrate) a single sugar molecule.

monoterpene a terpene that contains 10 carbons.

MRI scanner an NMR spectrometer used in medicine for whole-body NMR.

multiplet an NMR signal split into more than seven peaks.

multiplicity the number of peaks in an NMR signal.

mutarotation a slow change in optical rotation to an equilibrium value.

mutase an enzyme that transfers a group from one position to another.

$N + 1$ rule an ^1H NMR signal for a hydrogen with N equivalent hydrogens bonded to an adjacent carbon is split into $N + 1$ peaks. A ^{13}C NMR signal for a carbon bonded to N hydrogens is split into $N + 1$ peaks.

natural-abundance atomic weight the average mass of the atoms in the naturally occurring element.

natural product a product synthesized in nature.

neurotransmitter a compound that transmits nerve impulses.

nicotinamide adenine dinucleotide (NAD⁺) a coenzyme required in certain oxidation reactions. It is reduced to NADH, which forms 2.5 ATPs in oxidative phosphorylation when it is oxidized back to NAD⁺.

nicotinamide adenine dinucleotide phosphate (NADP⁺) a coenzyme that is reduced to NADPH, which is used as a reducing agent in anabolic reactions.

nitration substitution of a nitro group (NO₂) for a hydrogen of a benzene ring.

nitride a compound that contains a carbon–nitrogen triple bond (RC≡N).

NMR spectroscopy the absorption of electromagnetic radiation to determine the structural features of an organic compound. In the case of NMR spectroscopy, it determines the carbon–hydrogen framework.

node that part of an orbital in which there is zero probability of finding an electron.

nominal mass mass rounded to the nearest whole number.

nonbonding electrons (lone-pair electrons) valence electrons not used in bonding.

noncovalent interaction an interaction between atoms (or molecules) that is weaker than a covalent bond.

nonpolar covalent bond a bond formed between two atoms that share the bonding electrons equally.

normal alkane (straight-chain alkane) an alkane in which the carbons form a contiguous chain with no branches.

N-phthalimidomalonate ester synthesis a method used to synthesize an amino acid that combines the malonate ester synthesis and the Gabriel synthesis.

N-terminal amino acid the terminal amino acid of a peptide (or protein) that has a free amino group.

nucleic acid the two kinds of nucleic acid are DNA and RNA.

nucleophile an electron-rich atom or molecule.

nucleophilic acyl substitution reaction a reaction in which a group bonded to an acyl or aryl group is substituted by another group.

nucleophilic addition reaction a reaction that involves the addition of a nucleophile to a reagent.

nucleophilic catalysis (covalent catalysis) catalysis that occurs as a result of a nucleophile forming a covalent bond with one of the reactants.

nucleophilic catalyst a catalyst that increases the rate of a reaction by acting as a nucleophile.

nucleophilicity a measure of how readily an atom or a molecule with a pair of nonbonding electrons attacks an atom.

nucleophilic substitution reaction a reaction in which a nucleophile substitutes for an atom or a group.

nucleoside a heterocyclic base (a purine or a pyrimidine) bonded to the anomeric carbon of a sugar (D-ribose or D-2'-deoxyribose).

nucleotide a heterocycle attached in the β-position to a phosphorylated ribose or deoxyribose.

observed rotation the amount of rotation observed in a polarimeter.

octet rule states that an atom will give up, accept, or share electrons in order to achieve a filled shell. Because a filled second shell contains eight electrons, this is known as the octet rule.

oil a triester of glycerol that exists as a liquid at room temperature.

olefin an alkene.

oligomer a protein with more than one peptide chain.

oligonucleotide 3 to 10 nucleotides linked by phosphodiester bonds.

oligopeptide 3 to 10 amino acids linked by amide bonds.

oligosaccharide 3 to 10 sugar molecules linked by glycosidic bonds.

open-chain compound an acyclic compound.

operating frequency the frequency at which an NMR spectrometer operates.

optical isomers stereoisomers that contain chirality centers.

optically active rotates the plane of polarized light.

optically inactive does not rotate the plane of polarized light.

orbital the volume of space around the nucleus in which an electron is most likely to be found.

orbital hybridization mixing of orbitals.

organic compound a compound that contains carbon.

organic synthesis preparation of organic compounds from other organic compounds.

organometallic compound a compound containing a carbon–metal bond.

oxidation loss of electrons by an atom or a molecule.

β-oxidation a series of four reactions that removes two carbons from a fatty acyl-CoA.

oxidation reaction a reaction in which the number of C—H bonds decreases or the number of C—O, C—N, or C—X (X = a halogen) increases.

oxidative phosphorylation a series of reactions that converts a molecule of NADH and a molecule of FADH₂ into 2.5 and 1.5 molecules of ATP, respectively.

oxyanion a compound with a negatively charged oxygen.

paraffin an alkane.

parent hydrocarbon the longest continuous carbon chain in a molecule.

parent ion (molecular ion) peak in the mass spectrum with the greatest *m/z*.

partial hydrolysis a technique that hydrolyzes only some of the peptide bonds in a polypeptide.

pentose a monosaccharide with five carbons.

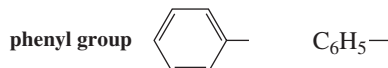
peptide polymer of amino acids linked together by amide bonds. A peptide contains fewer amino acid residues than a protein does.

peptide bond the amide bond that links the amino acids in a peptide or protein.

peroxyacid a carboxylic acid with an OOH group instead of an OH group.

perspective formula a method of representing the spatial arrangement of groups bonded to an asymmetric center. Two bonds are drawn in the plane of the paper; a solid wedge is used to depict a bond that projects out of the plane of the paper toward the viewer, and a hatched wedge is used to represent a bond that projects back from the plane of the paper away from the viewer.

pH the pH scale is used to describe the acidity of a solution ($\text{pH} = -\log[\text{H}^+]$).



pheromone a compound secreted by an animal that stimulates a physiological or behavioral response from a member of the same species.

phosphatase an enzyme that removes a phosphate group from its substrate.

phosphatidic acid a phosphoacylglycerol in which only one of the OH groups of phosphate is in an ester linkage.

phosphoacylglycerol (phosphoglyceride) a compound formed when two OH groups of glycerol form esters with fatty acids and the terminal OH group forms a phosphate ester.

phosphoanhydride bond the bond holding two phosphoric acid molecules together.

phospholipid a lipid that contains a phosphate group.

phosphoryl transfer reaction the transfer of a phosphate group from one compound to another.

photosynthesis the synthesis of glucose and O₂ from CO₂ and H₂O.

pi (π) bond a bond formed as a result of side-to-side overlap of *p* orbitals.

pinacol rearrangement rearrangement of a vicinal diol.

pK_a describes the tendency of a compound to lose a proton ($\text{pK}_a = -\log K_a$, where *K_a* is the acid dissociation constant).

plane of symmetry an imaginary plane that bisects a molecule into mirror images.

plasticizer an organic molecule that dissolves in a polymer and allows the polymer chains to slide by each other.

β-pleated sheet the backbone of a polypeptide that is extended in a zigzag structure with hydrogen bonding between neighboring chains.

polar covalent bond a covalent bond between atoms of different electronegativities.

polarimeter an instrument that measures the rotation of polarized light.

polarized light light that oscillates only in one plane.

polyamide a polymer in which the monomers are amides.

polycarbonate a step-growth polymer in which the dicarboxylic acid is carbonic acid.

polyester a polymer in which the monomers are esters.

polymer a large molecule made by linking monomers together.

polymer chemistry the field of chemistry that deals with synthetic polymers; part of the larger discipline known as materials science.

polymerization the process of linking up monomers to form a polymer.

polynucleotide many nucleotides linked by phosphodiester bonds.

polypeptide many amino acids linked by amide bonds.

polysaccharide a compound containing more than 10 sugar molecules linked together.

polyunsaturated fatty acid a fatty acid with more than one double bond.

polyurethane a polymer in which the monomers are urethanes.

porphyrin ring system consists of four pyrrole rings joined by one-carbon bridges.

primary alcohol an alcohol in which the OH group is bonded to a primary carbon.

primary alkyl halide an alkyl halide in which the halogen is bonded to a primary carbon.

primary alkyl radical a radical with the unpaired electron on a primary carbon.

primary amine an amine with one alkyl group bonded to the nitrogen.

primary carbocation a carbocation with the positive charge on a primary carbon.

primary carbon a carbon bonded to only one other carbon.

primary hydrogen a hydrogen bonded to a primary carbon.

primary structure (of a nucleic acid) the sequence of bases in a nucleic acid.

primary structure (of a protein) the sequence of amino acids in a protein.

promoter site a short sequence of bases at the beginning of a gene.

propagating site the reactive end of a chain-growth polymer.

propagation step in the first of a pair of propagation steps, a radical (or an electrophile or a nucleophile) reacts to produce another radical (or an electrophile or a nucleophile) that reacts in the second to produce the radical (or the electrophile or the nucleophile) that was the reactant in the first propagation step.

prostacyclin a lipid, derived from arachidonic acid, that dilates blood vessels and inhibits platelet aggregation.

protecting group a reagent that protects a functional group from a synthetic operation that it would otherwise not survive.

protein a polymer containing 40 to 4000 amino acids linked by amide bonds.

proton a positively charged hydrogen (H^+); a positively charged particle in an atomic nucleus.

proton-decoupled ^{13}C NMR spectrum a ^{13}C NMR spectrum in which all the signals appear as singlets because there is no coupling between the nucleus and its bonded hydrogens.

proton transfer reaction a reaction in which a proton is transferred from an acid to a base.

protoporphyrin IX the porphyrin ring system of heme.

pyranose a six-membered-ring sugar.

pyranoside a six-membered-ring glycoside.

pyridoxal phosphate the coenzyme required by enzymes that catalyze certain transformations of amino acids.

pyrosequencing a technique used to determine the sequence of bases in a polynucleotide by detecting the identity of each base that adds to a primer.

quartet an NMR signal split into four peaks.

quaternary structure a description of the way the individual polypeptide chains of a protein are arranged with respect to each other.

racemic mixture (racemate) a mixture of equal amounts of a pair of enantiomers.

radical an atom or a molecule with an unpaired electron.

radical chain reaction a reaction in which radicals are formed and react in repeating propagating steps.

radical inhibitor a compound that traps radicals.

radical initiator a compound that creates radicals.

radical polymerization chain-growth polymerization in which the initiator is a radical; the propagation site is, therefore, a radical.

radical reaction a reaction in which a new bond is formed by using one electron from one reagent and one electron from another reagent.

radical substitution reaction a substitution reaction that has a radical intermediate.

random coil the conformation of a totally denatured protein.

random copolymer a copolymer with a random distribution of monomers.

random screen (blind screen) the search for a pharmacologically active compound without any information about what chemical structures might show activity.

rate constant a measure of how easy or difficult it is to reach the transition state of a reaction (to get over the energy barrier to the reaction).

rate-determining step (rate-limiting step) the step in a reaction that has the transition state with the highest energy.

R configuration after assigning relative priorities to the four groups bonded to an asymmetric center, if the lowest-priority group is on a vertical axis in a Fischer projection (or pointing away from the viewer in a perspective formula), an arrow drawn from the highest-priority group to the next-highest-priority group goes in a clockwise direction.

reaction coordinate diagram describes the energy changes that take place during the course of a reaction.

reactivity-selectivity principle states that the greater the reactivity of a species, the less selective the species will be.

recombinant DNA DNA that has been incorporated into a host cell.

reduction reaction a reaction in which the number of C—H bonds increases or the number of C—O, C—N, or C—X (X = a halogen) decreases.

reduction gain of electrons by an atom or a molecule.

reductive amination the reaction of an aldehyde or a ketone with ammonia or with a primary amine in the presence of a reducing agent (H_2 , Pd/C).

reference compound a compound added to a sample whose NMR spectrum is to be taken. The positions of the signals in the NMR spectrum are measured from the position of the signal given by the reference compound.

regioselective reaction a reaction that leads to the preferential formation of one constitutional isomer over another.

regulatory enzyme an enzyme that can be turned on and off.

relative configuration the configuration of a compound relative to the configuration of another compound.

relative rate obtained by dividing the actual rate constant by the rate constant of the slowest reaction in the group being compared.

replication the synthesis of identical copies of DNA.

resolution of a racemic mixture separation of a racemic mixture into the individual enantiomers.

resonance a compound with delocalized electrons is said to have resonance.

resonance contributor (resonance structure, contributing resonance structure) a structure with localized electrons that approximates the true structure of a compound with delocalized electrons.

resonance electron donation donation of electrons through p orbital overlap with neighboring π bonds.

resonance electron withdrawal withdrawal of electrons through p orbital overlap with neighboring π bonds.

resonance energy (delocalization energy) the extra stability associated with a compound as a result of its having delocalized electrons.

resonance hybrid the actual structure of a compound with delocalized electrons; it is represented by two or more structures with localized electrons.

restriction endonuclease an enzyme that cleaves DNA at a specific base sequence.

restriction fragment a fragment that is formed when DNA is cleaved by a restriction endonuclease.

retro Diels-Alder reaction a reverse Diels-Alder reaction.

retrosynthesis (retrosynthetic analysis) working backward (on paper) from the target molecule to available starting materials.

retrovirus a virus whose genetic information is stored in its RNA.

rf radiation radiation in the radiofrequency region of the electromagnetic spectrum.

ribonucleic acid (RNA) a polymer of ribonucleotides.

ribonucleotide a nucleotide in which the sugar component is D-ribose.

ribosome a particle composed of about 40% protein and 60% RNA on which protein biosynthesis takes place.

ring-expansion rearrangement rearrangement of a carbocation in which the positively charged carbon is bonded to a cyclic compound and, as a result of rearrangement, the size of the ring increases by one carbon.

ring-flip (chair-chair interconversion) the conversion of the chair conformer of cyclohexane into the other chair conformer. Bonds that are axial in one chair conformer are equatorial in the other.

ring-opening polymerization a chain-growth polymerization that involves opening the ring of the monomer.

RNA (ribonucleic acid) a polymer of ribonucleotides.

rule of 13 allows possible molecular formulas to be determined from the m/z value of the molecular ion.

saponification hydrolysis of an ester (such as a fat) under basic conditions.

saturated hydrocarbon a hydrocarbon that is completely saturated (i.e., contains no double or triple bonds) with hydrogen.

Schiff base (imine) $R_2C=NR$

S configuration after assigning relative priorities to the four groups bonded to an asymmetric center, if the lowest-priority group is on a vertical axis in a Fischer projection (or pointing away from the viewer in a perspective formula), an arrow drawn from the highest-priority group to the next-highest-priority group goes in a counterclockwise direction.

secondary alcohol an alcohol in which the OH group is bonded to a secondary carbon.

secondary alkyl halide an alkyl halide in which the halogen is bonded to a secondary carbon.

secondary alkyl radical a radical with the unpaired electron on a secondary carbon.

secondary amine an amine with two alkyl groups bonded to the nitrogen.

secondary carbocation a carbocation with the positive charge on a secondary carbon.

secondary carbon a carbon bonded to two other carbons.

secondary hydrogen a hydrogen bonded to a secondary carbon.

secondary structure of a protein a description of the conformation of the backbone of a protein.

secondary structure of DNA the double helix.

semiconservative replication the mode of replication that results in a daughter molecule of DNA having one of the original DNA strands plus a newly synthesized strand.

sense strand (informational strand) the strand in DNA that is not read during transcription; it has the same sequence of bases as the synthesized mRNA strand (with a U and T difference).

separated charges a positive and a negative charge that can be neutralized by the movement of electrons.

sesquiterpene a terpene that contains 15 carbons.

shielding phenomenon caused by electron donation to the environment of a proton. The electrons shield the proton from the full effect of the applied magnetic field. The more a proton is shielded, the farther to the right its signal appears in an NMR spectrum.

sigma (σ) bond a bond with a cylindrically symmetrical distribution of electrons.

simple carbohydrate (monosaccharide) a single sugar molecule.

simple triacylglycerol a triacylglycerol in which the fatty acid components are the same.

single bond a σ bond.

singlet an unsplit NMR signal.

skeletal structure shows the carbon-carbon bonds as lines and does not show the carbon-hydrogen bonds.

S_N1 reaction a unimolecular nucleophilic substitution reaction.

S_N2 reaction a bimolecular nucleophilic substitution reaction.

soap a sodium or potassium salt of a fatty acid.

solvation the interaction between a solvent and another molecule (or ion).

solvolysis reaction with the solvent.

specific rotation the amount the plane of polarization of plane-polarized light will be rotated by a compound with a concentration of 1.0 g/mL in a sample tube 1.0 dm long.

spectroscopy study of the interaction of matter and electromagnetic radiation.

sphingolipid a lipid that contains sphingosine.

sphingomyelin a sphingolipid in which the terminal OH group of sphingosine is bonded to phosphocholine or phosphoethanolamine.

spin-coupled ¹³C NMR spectrum a ¹³C NMR spectrum in which each signal of a carbon is split by the hydrogens bonded to that carbon.

spin coupling the atom that gives rise to an NMR signal is coupled to the rest of the molecule.

spin decoupling the atom that gives rise to an NMR signal is decoupled from the rest of the molecule.

spin-spin coupling the splitting of a signal in an NMR spectrum described by the $N + 1$ rule.

α -spin state nuclei in this spin state have their magnetic moments oriented in the same direction as the applied magnetic field.

β -spin state nuclei in this spin state have their magnetic moments oriented opposite the direction of the applied magnetic field.

splitting diagram a diagram that describes the splitting of a set of protons.

squalene a triterpene that is a precursor of steroid molecules.

stacking interactions van der Waals interactions between the mutually induced dipoles of adjacent pairs of bases in DNA.

staggered conformation a conformation in which the bonds on one carbon bisect the bond angle on the adjacent carbon when viewed looking down the carbon-carbon bond.

step-growth polymer (condensation polymer) a polymer made by combining two molecules while removing a small molecule (usually water or an alcohol).

stereochemistry the field of chemistry that deals with the structures of molecules in three dimensions.

stereogenic center (stereocenter) an atom at which the interchange of two substituents produces a stereoisomer.

stereoisomers isomers that differ in the way their atoms are arranged in space.

steric effects effects due to the fact that groups occupy a certain volume of space.

steric hindrance refers to bulky groups at the site of a reaction that make it difficult for the reactants to approach each other.

steric strain (van der Waals strain, van der Waals repulsion) the repulsion between the electron cloud of an atom or a group of atoms and the electron cloud of another atom or group of atoms.

steroid a class of compounds that contains a steroid ring system.

stop codon a codon at which protein synthesis is stopped.

straight-chain alkane (normal alkane) an alkane in which the carbons form a continuous chain with no branches.

Strecker synthesis a method used to synthesize an amino acid: an aldehyde reacts with NH₃, forming an imine that is attacked by cyanide ion. Hydrolysis of the product gives an amino acid.

stretching frequency the frequency at which a stretching vibration occurs.

stretching vibration a vibration occurring along the line of a bond.

structural isomers (constitutional isomers) molecules that have the same molecular formula but differ in the way their atoms are connected.

structural protein a protein that gives strength to a biological structure.

α -substituent a substituent on the side of a steroid ring system opposite that of the angular methyl groups.

β -substituent a substituent on the same side of a steroid ring system as that of the angular methyl groups.

α -substitution reaction a reaction that puts a substituent on an α -carbon in place of an α -hydrogen.

substrate the reactant of an enzyme-catalyzed reaction.

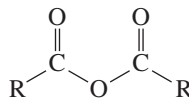
subunit an individual chain of an oligomer.

suicide inhibitor (mechanism-based inhibitor) a compound that inactivates an enzyme by undergoing part of its normal catalytic mechanism.

sulfide (thioether) the sulfur analog of an ether (RSR).

sulfonation substitution of a hydrogen of a benzene ring by a sulfonic acid group (SO₃H).

symmetrical anhydride an acid anhydride with identical R groups:



symmetrical ether an ether with two identical substituents bonded to the oxygen.

syndiotactic polymer a polymer in which the substituents regularly alternate on both sides of the fully extended carbon chain.

synthetic polymer a polymer that is not synthesized in nature.

systematic nomenclature nomenclature based on structure.

target molecule desired end product of a synthesis.

tautomerism interconversion of tautomers.

tautomers rapidly equilibrating isomers that differ in the location of their bonding electrons.

template strand (antisense strand) the strand in DNA that is read during transcription.

terminal alkyne an alkyne with the triple bond at the end of the carbon chain.

termination step the step in which two radicals combine to produce a molecule in which all the electrons are paired.

terpene a lipid, isolated from a plant, that contains carbon atoms in multiples of five.

terpenoid a terpene that contains oxygen.

tertiary alcohol an alcohol in which the OH group is bonded to a tertiary carbon.

tertiary alkyl halide an alkyl halide in which the halogen is bonded to a tertiary carbon.

tertiary alkyl radical a radical with the unpaired electron on a tertiary carbon.

tertiary amine an amine with three alkyl groups bonded to the nitrogen.

tertiary carbocation a carbocation with the positive charge on a tertiary carbon.

tertiary carbon a carbon bonded to three other carbons.

tertiary hydrogen a hydrogen bonded to a tertiary carbon.

tertiary structure a description of the three-dimensional arrangement of all the atoms in a protein.

tetraene a hydrocarbon with four double bonds.

tetrahedral bond angle the bond angle (109.5°) formed by adjacent bonds of an sp^3 hybridized carbon.

tetrahedral carbon an sp^3 hybridized carbon; a carbon that forms covalent bonds by using four sp^3 hybridized orbitals.

tetrahedral intermediate the intermediate formed in a nucleophilic acyl substitution reaction.

tetrahydrofolate (THF) the coenzyme required by enzymes that catalyze reactions that donate a group containing a single carbon to their substrates.

tetraterpene a terpene that contains 40 carbons.

tetrose a monosaccharide with four carbons.

thermal cracking using heat to break a molecule apart.

thermodynamic control when a reaction is under thermodynamic control, the relative amounts of the products depend on their stabilities.

thermodynamic product the most stable product.

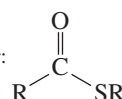
thermodynamics the field of chemistry that describes the properties of a system at equilibrium.

thermodynamic stability indicated by ΔG° . If ΔG° is negative, the products are more stable than the reactants. If ΔG° is positive, the reactants are more stable than the products.

thiamine pyrophosphate (TPP) the coenzyme required by enzymes that catalyze a reaction that transfers an acyl group to a substrate.

thin-layer chromatography a technique that separates compounds on the basis of their polarity.

thioester the sulfur analogue of an ester:



thioether (sulfide) the sulfur analog of an ether (RSR).

thiol (mercaptan) the sulfur analog of an alcohol (RSH).

titration curve a plot of pH versus added equivalents of hydroxide ion.

trademark a registered name, symbol, or picture.

trade name (proprietary name, brand name) identifies a commercial product and distinguishes it from other products.

transamination a reaction in which an amino group is transferred from one compound to another.

transcription the synthesis of mRNA from a DNA blueprint.

transesterification reaction the reaction of an ester with an alcohol to form a different ester.

trans fused two cyclohexane rings fused together such that if the second ring were considered to be two substituents of the first ring, both substituents would be in equatorial positions.

transimination the reaction of a primary amine with an imine to form a new imine and a primary amine derived from the original imine.

trans isomer the isomer with the hydrogens on opposite sides of the double bond or cyclic structure; the isomer with identical substituents on opposite sides of the double bond.

transition state the highest point on a hill in a reaction coordinate diagram. In the transition state, bonds in the reactant that will break are partially broken and bonds in the product that will form are partially formed.

translation the synthesis of a protein from an mRNA blueprint.

triacylglycerol the compound formed when the three OH groups of glycerol are esterified with fatty acids.

triene a hydrocarbon with three double bonds.

trigonal planar carbon an sp^2 hybridized carbon.

triose a monosaccharide with three carbons.

tripeptide three amino acids linked by amide bonds.

triple bond a σ bond plus two π bonds.

triplet an NMR signal split into three peaks.

triterpene a terpene that contains 30 carbons.

twist-boat conformation (skew-boat conformation) a conformation of cyclohexane.

ultraviolet light electromagnetic radiation with wavelengths ranging from 180 to 400 nm.

unimolecular reaction a reaction whose rate depends on the concentration of one reactant.

unsaturated hydrocarbon a hydrocarbon that contains one or more double or triple bonds.

unsymmetrical ether an ether with two different substituents bonded to the oxygen.

urethane a compound with a carbonyl group that is both an amide and an ester.

UV/Vis spectroscopy the absorption of electromagnetic radiation in the ultraviolet and visible regions of the spectrum; used to determine information about conjugated systems.

valence electron an electron in an unfilled shell.

van der Waals forces (London forces) induced-dipole–induced-dipole interactions.

vector sum takes into account both the magnitudes and the directions of the bond dipoles.

vinyl group $\text{CH}_2=\text{CH}-$

vinyl carbon a carbon in a carbon–carbon double bond.

vinyl cation a compound with a positive charge on a vinyl carbon.

vinyl polymer a polymer in which the monomers are ethylene or a substituted ethylene.

visible light electromagnetic radiation with wavelengths ranging from 400 to 780 nm.

vitamin a substance needed in small amounts for normal body function that the body cannot synthesize at all or cannot synthesize in adequate amounts.

vitamin KH_2 the coenzyme required by the enzyme that catalyzes the carboxylation of glutamate side chains.

vulcanization heating rubber with sulfur to increase its hardness while maintaining its flexibility.

wave equation an equation that describes the behavior of each electron in an atom or a molecule.

wavelength distance from any point on one wave to the corresponding point on the next wave (usually in units of μm or nm).

wavenumber the number of waves in 1 cm.

wax an ester formed from a long-chain carboxylic acid and a long-chain alcohol.

wedge-and-dash structure a method of representing the spatial arrangement of groups. Wedges are used to represent bonds that point out of the plane of the paper toward the viewer, and dashed lines are used to represent bonds that point back from the plane of the paper away from the viewer.

Williamson ether synthesis formation of an ether from the reaction of an alkoxide ion with an alkyl halide.

Ziegler–Natta catalyst an aluminum–titanium initiator that controls the stereochemistry of a polymer.

Z isomer the isomer with the high-priority groups on the same side of the double bond.

zwitterion a compound with a negative charge and a positive charge on non-adjacent atoms.



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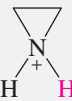
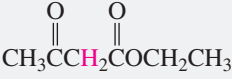
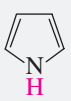




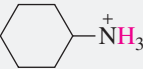
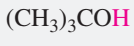
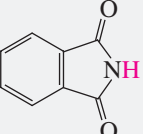
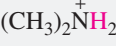
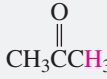

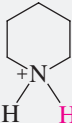

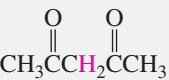

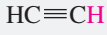

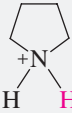
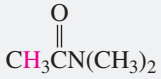
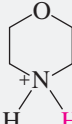


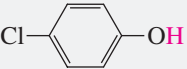

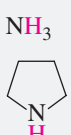




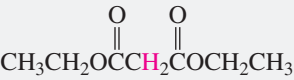
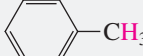
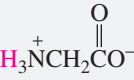


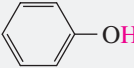
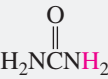
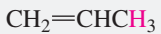
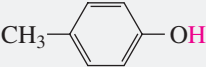
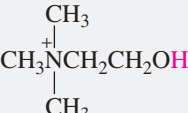
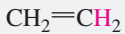






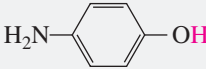




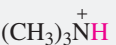
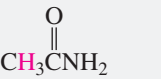
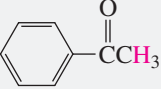
Zwitterion, 555, 556, 578

pK _a Values					
Compound	pK _a	Compound	pK _a	Compound	pK _a
<chem>CH3C#N[H+]</chem>	-10.1	<chem>O=[N+]([O-])c1ccc([NH3+])cc1</chem>	1.0	<chem>CC(=O)Oc1ccc(C)cc1</chem>	4.3
<chem>I</chem>	-10	<chem>[H+]c1ccncc1</chem>	1.0	<chem>COc1ccc(C(=O)O)cc1</chem>	4.5
<chem>HBr</chem>	-9	<chem>ClC(=O)O</chem>	1.3	<chem>[NH3+]c1ccccc1</chem>	4.6
<chem>CC(=O)O</chem>	-8	<chem>[H]S(=O)(=O)([O-])[O-]</chem>	2.0	<chem>CC(=O)O</chem>	4.8
<chem>CC(=O)O</chem>	-7.3	<chem>[H]P(=O)([O-])[O-]</chem>	2.1	<chem>c1ccc2c(c1)c(c[nH+]2)</chem>	4.9
<chem>HCl</chem>	-7	<chem>[H]c1nc2c(ncn2)[nH+]1</chem>	2.5	<chem>CC(=O)O</chem>	5.1
<chem>c1ccc(S(=O)(=O)O)cc1</chem>	-6.5	<chem>FCC(=O)O</chem>	2.7	<chem>CC(=O)O</chem>	5.2
<chem>CC(=O)O</chem>	-6.5	<chem>ClCC(=O)O</chem>	2.8	<chem>[NH3+]c1ccc(C)cc1</chem>	5.3
<chem>CC(=O)O</chem>	-6.1	<chem>BrCC(=O)O</chem>	2.9	<chem>CC(=O)O</chem>	5.5
<chem>H2SO4</chem>	-5	<chem>ICCC(=O)O</chem>	3.2	<chem>CC(=O)O</chem>	5.9
<chem>[H+]c1cc[nH+]1</chem>	-3.8	<chem>HF</chem>	3.2	<chem>CC(=O)O</chem>	6.0
<chem>CC(=O)O</chem>	-3.6	<chem>[H]NO2</chem>	3.4	<chem>CC(=O)O</chem>	6.4
<chem>CC(=O)O</chem>	-2.4	<chem>O=[N+]([O-])c1ccc(C(=O)O)cc1</chem>	3.4	<chem>CC(=O)O</chem>	6.8
<chem>CC(=O)O</chem>	-2.5	<chem>O=C</chem>	3.8	<chem>CC(=O)O</chem>	7.0
<chem>[H3O+]</chem>	-1.7	<chem>Brc1ccc([NH3+])cc1</chem>	3.9	<chem>CC(=O)O</chem>	7.1
<chem>HNO3</chem>	-1.3	<chem>BrC(=O)O</chem>	4.0	<chem>CC(=O)O</chem>	7.2
<chem>CC(=O)O</chem>	-1.2	<chem>c1ccccc1C(=O)O</chem>	4.2	<chem>CC(=O)O</chem>	7.8
<chem>CC(=O)O</chem>	0.0				
<chem>F3CC(=O)O</chem>	0.2				
<chem>Cl3CC(=O)O</chem>	0.64				
<chem>[OH-]</chem>	0.79				

^apK_a values are for the red H in each structure

(continued)

pK_a Values (continued)

Compound	pK _a	Compound	pK _a	Compound	pK _a
	8.0		10.7		~17
	8.1		10.7		17
	8.2		10.7		18
	8.3		10.7		20
	8.6		11.1		24.5
	8.9		11.0		25
	9.1		11.3		30
	9.3		11.6		35
	9.4		12.3		36
	9.4		12.4		40
	9.5		13.3		41
	9.8		13.5		43
	10.0		13.7		43
	10.2		13.9		44
	10.2		14.4		46
	10.2		15.5		60
	10.3		15.7		> 60
	10.5		16.0		
	10.6		16		
			16.0		

Periodic Table of the Elements

[illegible]

^aThe labels on top (1A, 2A, etc.) are common American usage. The labels below these (1, 2, etc.) are those recommended by the International Union of Pure and Applied Chemistry.

The names for elements 113, 115, 117, and 118 have not yet been decided.

Atomic weights in brackets are the masses of the longest-lived or most important isotope of radioactive elements. The names for elements 113, 115, 117, and 118 have not yet been decided.