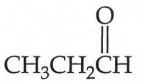
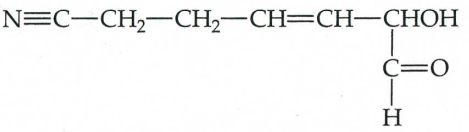
EXERCISES

Introduction to Organic Compounds; Hydrocarbons

25.7 Predict the ideal values for the bond angles about each carbon atom in the propanal molecule. Indicate the hybridization of orbitals for each carbon.



25.8 Identify the carbon atom(s) in the structure shown that has (have) each of the following hybridizations: **(a)** sp^3, **(b)** sp, **(c)** sp^2.



25.9 List five elements that are commonly found in organic compounds. Which ones are more electronegative than carbon?

25.10 CQ Organic compounds containing C—O and C—Cl bonds are more reactive than simple alkane hydrocarbons. Considering the comparative values of C—H, C—C, C—O, and C—Cl bond energies (Table 8.4), why is this so?

25.11 **(a)** What is the difference between a straight-chain and branched-chain alkane? **(b)** What is the difference between an alkane and an alkyl group? **(c)** Why are alkanes said to be saturated?

25.12 What structural features help us identify a compound as **(a)** an alkane, **(b)** a cycloalkane, **(c)** an alkene, **(d)** an alkyne, **(e)** a saturated hydrocarbon, **(f)** an aromatic hydrocarbon?

25.13 Give the molecular formula of a hydrocarbon containing five carbon atoms that is **(a)** an alkane, **(b)** a cycloalkane, **(c)** an alkene, **(d)** an alkyne. Which are saturated and which are unsaturated hydrocarbons?

25.14 Give the molecular formula of a cyclic alkane, a cyclic alkene, a linear alkyne, and an aromatic hydrocarbon that in each case contains six carbon atoms. Which are saturated and which are unsaturated hydrocarbons?

25.15 CQ Give the general formula for any dialkene, that is, a straight-chain hydrocarbon with two double bonds along the chain.

25.16 CQ Give the general formula for any cyclic alkene, that is, a cyclic hydrocarbon with one double bond.

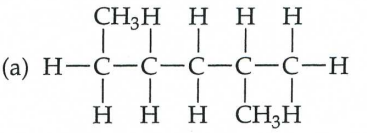
25.17 CQ Draw all the possible noncyclic structural isomers of C_5H_{10}. Name each compound.

25.18 CQ Write the condensed structural formulas for as many alkenes and alkynes as you can think of that have the molecular formula C_6H_{10}.

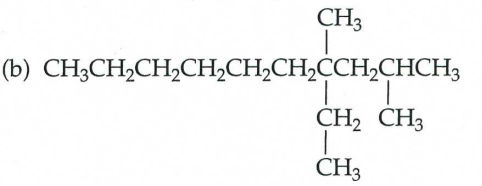
25.19 What are the approximate bond angles **(a)** about carbon in an alkane, **(b)** about a doubly bonded carbon atom in an alkene, **(c)** about a triply bonded carbon atom in an alkyne?

25.20 What are the characteristic hybrid orbitals employed by **(a)** carbon in an alkane, **(b)** carbon in a double bond in an alkene, **(c)** carbon in the benzene ring, **(d)** carbon in a triple bond in an alkyne?

25.21 Draw the structural formula or give the name, as appropriate, for the following:



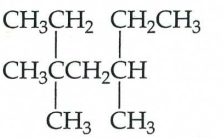
(a)



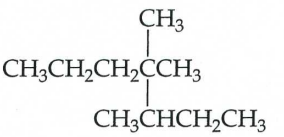
(b)

(c) 3-methylhexane
(d) 4-ethyl-2,2-dimethyloctane
(e) methylcyclohexane

25.22 Draw the structural formula or give the name, as appropriate, for the following:



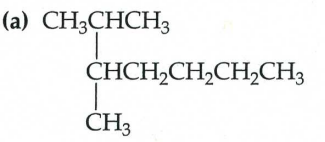
(a)



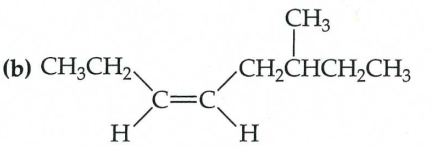
(b)

(c) 2,5-dimethylnonane
(d) 3-ethyl-4,4-dimethylheptane
(e) 1-ethyl-4-methylcyclohexane

25.23 Name the following compounds:



(a)



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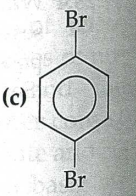
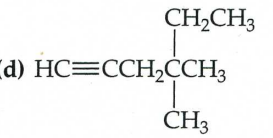


(c)



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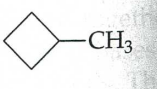
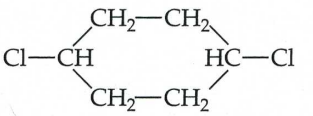
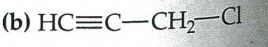


(e)

25.24 Name the following compounds:

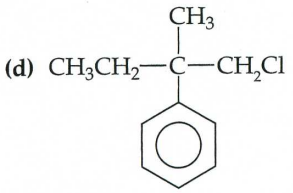


(a)



(b)

(c)

(d) 

(e) *cis*-$CH_2{=}CH{-}CH{=}CH{-}CH_2Cl$

25.25 Why is geometric isomerism possible for alkenes, but not for alkanes and alkynes?

25.26 Using butene as an example, distinguish between structural and geometric isomers.

25.27 Indicate whether each of the following molecules is capable of geometrical (cis-trans) isomerism. For those that are, draw the structures: **(a)** 1,1-dichloro-1-butene, **(b)** 2,4-dichloro-2-butene, **(c)** 1,4-dichlorobenzene, **(d)** 4,5-dimethyl-2-pentyne.

25.28 Draw all the distinct geometric isomers of 2,4-hexadiene.

25.29 What is the octane number of a mixture of 35% heptane and 65% isooctane?

25.30 Describe two ways in which the octane number of a gasoline consisting of alkanes can be increased.

Reactions of Hydrocarbons

25.31 **(a)** What is the difference between a substitution reaction and an addition reaction? Which one is commonly observed with alkenes, and which one with aromatic hydrocarbons? **(b)** Using condensed structural formulas, write the balanced equation for the addition reaction of 2,4-dimethyl-2-pentene with Br_2. **(c)** Write a balanced chemical equation for the substitution reaction of Cl_2 with *para*-dichlorobenzene in the presence of $FeCl_3$ as a catalyst.

25.32 Using condensed structural formulas, write a balanced chemical equation for each of the following reactions: **(a)** hydrogenation of cyclohexene; **(b)** addition of H_2O to *trans*-2-pentene using H_2SO_4 as a catalyst (two products); **(c)** reaction of 2-chloropropane with benzene in the presence of $AlCl_3$.

25.33 CQ **(a)** When cyclopropane is treated with HI, 1-iodopropane is formed. A similar type of reaction does not occur with cyclopentane or cyclohexane. How do you account for the reactivity of cyclopropane? **(b)** Suggest a method of preparing ethylbenzene, starting with benzene and ethylene as the only organic reagents.

25.34 CQ **(a)** One test for the presence of an alkene is to add a small amount of bromine and look for the disappearance of the brown color. This test does not work for detecting the presence of an aromatic hydrocarbon. Explain. **(b)** Write a series of reactions leading to *para*-bromoethylbenzene, beginning with benzene and using other reagents as needed. What isomeric side products might also be formed?

25.35 Describe the intermediate that is thought to form in the addition of a hydrogen halide to an alkene, using cyclohexene as the alkene in your description.

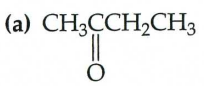
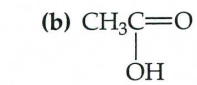
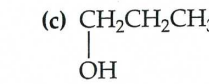
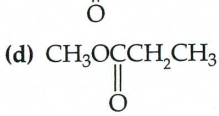
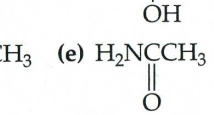
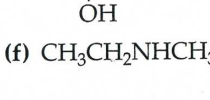
25.36 CQ The rate law for addition of Br_2 to an alkene is first order in Br_2 and first order in the alkene. Does this fact prove that the mechanism of addition of Br_2 to an alkene proceeds in the same manner as for addition of HBr? Explain.

25.37 CQ The molar heat of combustion of gaseous cyclopropane is −2089 kJ/mol; that for gaseous cyclopentane is −3317 kJ/mol. Calculate the heat of combustion per CH_2 group in the two cases, and account for the difference.

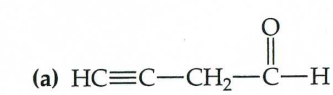
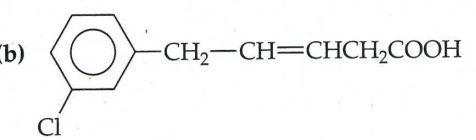
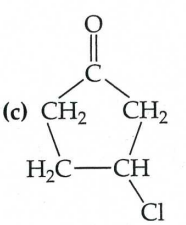
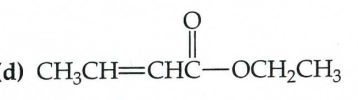
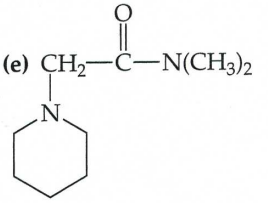
25.38 CQ The heat of combustion of decahydronaphthalene ($C_{10}H_{18}$) is −6286 kJ/mol. The heat of combustion of naphthalene ($C_{10}H_8$) is −5157 kJ/mol. (In both cases $CO_2(g)$ and $H_2O(l)$ are the products.) Using these data and data in Appendix C, calculate the heat of hydrogenation of naphthalene. Does this value provide any evidence for aromatic character in naphthalene?

Functional Groups and Chirality

25.39 Identify the functional groups in each of the following compounds:

(a) 
(b) 
(c) 
(d) 
(e) 
(f) 

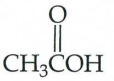
25.40 Identify the functional groups in each of the following compounds:

(a) 
(b) 
(c) 
(d) 
(e) 

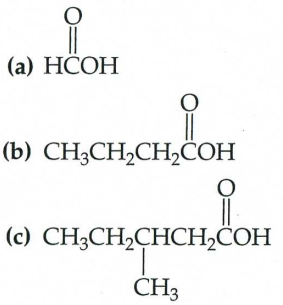
25.41 Give the structural formula for **(a)** an aldehyde that is an isomer of acetone, **(b)** an ether that is an isomer of 1-propanol.

25.42 **(a)** Give the empirical formula and structural formula for a cyclic ether containing four carbon atoms in the ring. **(b)** Write the structural formula for a straight-chain compound that is a structural isomer of your answer to part (a).

25.43 The IUPAC name for a carboxylic acid is based on the name of the hydrocarbon with the same number of carbon atoms. The ending *-oic* is appended, as in ethanoic acid, which is the IUPAC name for acetic acid,



Give the IUPAC name for each of the following acids:



25.44 Aldehydes and ketones can be named in a systematic way by counting the number of carbon atoms (including the carbonyl carbon) that they contain. The name of the aldehyde or ketone is based on the hydrocarbon with the same number of carbon atoms. The ending *-al* for aldehyde or *-one* for ketone, is added as appropriate. Draw the structural formulas for the following aldehydes or ketones: **(a)** propanal, **(b)** 2-pentanone, **(c)** 3-methyl-2-butanone, **(d)** 2-methylbutanal.

25.45 Draw the condensed structure of the compounds formed by condensation reactions between **(a)** benzoic acid and ethanol, **(b)** ethanoic acid and methylamine, **(c)** acetic acid and phenol. Name the compound in each case.

25.46 Draw the condensed structures of the esters formed from **(a)** butanoic acid and methanol, **(b)** benzoic acid and 2-propanol, **(c)** propanoic acid and dimethylamine. Name the compound in each case.

25.47 Write a balanced chemical equation using condensed structural formulas for the saponification (base hydrolysis) of **(a)** methyl propionate, **(b)** phenyl acetate.

25.48 Write a balanced chemical equation using condensed structural formulas for **(a)** the formation of butyl propionate from the appropriate acid and alcohol, **(b)** the saponification (base hydrolysis) of methyl benzoate.

25.49 CQ Would you expect pure acetic acid to be a strongly hydrogen-bonded substance? How do the melting and boiling points of the substance (see the "Chemistry at Work" box on pp. 1088–1089 for data) support your answer?

25.50 CQ Acetic anhydride is formed from acetic acid in a condensation reaction that involves the removal of a mole of water from between two acetic acid molecules. Write the chemical equation for this process, and show the structure of acetic anhydride.

25.51 Write the condensed structural formula for each of the following compounds: **(a)** 2-butanol, **(b)** 1,2-ethanediol, **(c)** methyl formate, **(d)** diethyl ketone, **(e)** diethyl ether.

25.52 Write the condensed structural formula for each of the following compounds: **(a)** 3,3-dichlorobutyraldehyde, **(b)** methyl phenyl ketone, **(c)** *para*-bromobenzoic acid, **(d)** methyl-*trans*-2-butenyl ether, **(e)** *N*, *N*-dimethylbenzamide.

25.53 Draw the structure for 2-bromo-2-chloro-3-methylpentane, and indicate any chiral carbons in the molecule.

25.54 Does 3-chloro-3-methylhexane have optical isomers? Why or why not?

Proteins

25.55 **(a)** What is an α-amino acid? **(b)** How do amino acids react to form proteins?

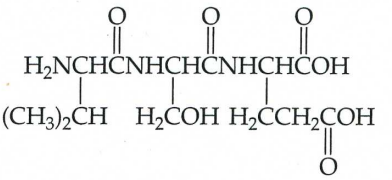
25.56 CQ What properties of the side chains (R groups) of amino acids are important in affecting the amino acid's overall biochemical behavior? Give examples to illustrate your reply.

25.57 Draw the two possible dipeptides formed by condensation reactions between serine and lysine.

25.58 Write a chemical equation for the formation of methionyl glycine from the constituent amino acids.

25.59 **(a)** Draw the condensed structure of the tripeptide Ile-Ala-Cys. **(b)** How many different tripeptides can be made from the amino acids serine and phenylalanine? Give the abbreviations for each of these tripeptides, using the three-letter codes for amino acids.

25.60 **(a)** What amino acids would be obtained by hydrolysis of the following tripeptide?



(b) How many different tripeptides can be made from the amino acids glycine, serine, and glutamic acid? Give the abbreviation for each of these tripeptides, using the three-letter codes for amino acids.

25.61 Describe the primary, secondary, and tertiary structures of proteins.

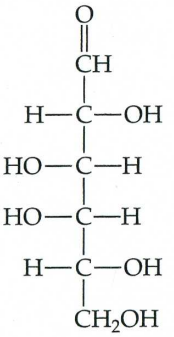
25.62 CQ Describe the role of hydrogen bonding in determining the α-helix structure of a protein.

Carbohydrates

25.63 In your own words, define the following terms: **(a)** carbohydrate, **(b)** monosaccharide, **(c)** disaccharide.

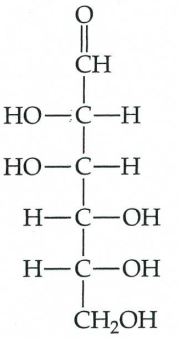
25.64 What is the difference between α-glucose and β-glucose? Show the condensation of two glucose molecules to form a disaccharide with an α linkage; with a β linkage.

25.65 The structural formula for the linear form of galactose is as follows:



(a) How many chiral carbons are present in the molecule? **(b)** Draw the structure of the six-member-ring form of this sugar.

25.66 The structural formula for the linear form of D-mannose is as follows:



(a) How many chiral carbons are present in the molecule? **(b)** Draw the structure of the six-member-ring form of this sugar.

25.67 What is the empirical formula of glycogen? What is the unit that forms the basis of the glycogen polymer? What form of linkage joins these monomeric units?

25.68 What is the empirical formula of cellulose? What is the unit that forms the basis of the cellulose polymer? What form of linkage joins these monomeric units?

Nucleic Acids

25.69 Describe a nucleotide. Draw the structural formula for deoxycytidine monophosphate, analogous to deoxyadenylic acid, in which cytosine is the organic base.

25.70 A nucleoside consists of an organic base of the kind shown in Section 25.11, bound to ribose or deoxyribose. Draw the structure for deoxyguanosine, formed from guanine and deoxyribose.

25.71 Write a balanced chemical equation using condensed formulas for the condensation reaction between a mole of deoxyribose and a mole of doubly ionized phosphoric acid, HPO_4^{2-}.

25.72 CQ A nucleotide undergoes hydrolysis under neutral conditions to yield 1 mol of $H_2PO_4^-$ and an organic product. The same starting material undergoes hydrolysis under acidic conditions to yield thymine and deoxribose-monophosphate. Draw the structure of the unknown substance.

25.73 CQ When samples of double-stranded DNA are analyzed, the quantity of adenine present equals that of thymine. Similarly, the quantity of guanine equals that of cytosine. Explain the significance of these observations.

25.74 CQ Imagine a single DNA strand containing a section with the following base sequence: A, C, T, C, G, A. What is the base sequence of the complementary strand?

Additional Exercises

25.75 Draw the condensed structural formulas for two molecules with the formula C_3H_4O.

25.76 How many structural isomers are there for a five-member straight carbon chain with one double bond? For a six-member straight carbon chain with two double bonds?

25.77 CQ There are no known stable cyclic compounds with ring sizes of seven or less that have an alkyne linkage in the ring. Why is this? Could a ring with a larger number of carbon atoms accommodate an alkyne linkage? Explain how you would use ball-and-stick molecular models to try to answer this question.

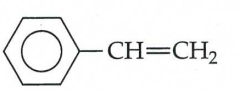
25.78 CQ Draw the condensed structural formulas for the cis and trans isomers of 2-pentene. Can cyclopentene exhibit cis-trans isomerism? Explain.

25.79 CQ Although there are silicon analogs of alkanes, silicon analogs of alkenes or alkynes are virtually unknown. Why is this?

25.80 CQ Explain why *trans*-1,2-dichloroethene has no dipole moment, whereas *cis*-1,2-dichloroethene has a dipole moment.

25.81 CQ Write the structural formulas for as many alcohols as you can think of that have empirical formula C_3H_6O.

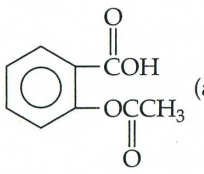
25.82 CQ How many molecules of HBr would you expect to react readily with each molecule of styrene?

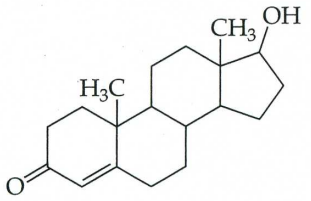


[25.83] CQ Dinitromethane, $CH_2(NO_2)_2$, is a dangerously reactive substance that decomposes readily on warming. On the other hand, dichloromethane is relatively unreactive. Why is the nitro compound so reactive compared to the chloro compound? [*Hint:* Consider the oxidation numbers of the atoms involved and the possible products of decomposition.]

25.84 Identify each of the functional groups in the following molecules:

(a) $CH_2{=}CH{-}O{-}CH{=}CH_2$ (an anesthetic)

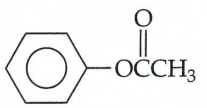
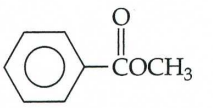
(b)  (acetylsalicylic acid, aspirin)

(c)  (testosterone, a male sex hormone)

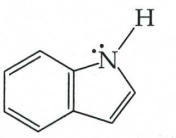
25.85 Write a condensed structural formula for each of the following: **(a)** an acid with the formula $C_4H_8O_2$, **(b)** a cyclic ketone with the formula C_5H_8O, **(c)** a dihydroxy compound with formula $C_3H_8O_2$, **(d)** a cyclic ester with formula $C_5H_8O_2$.

25.86 **CQ** Although carboxylic acids and alcohols both contain an —OH group, one is acidic in water and the other is not. Explain the difference.

25.87 Give the condensed formulas for the carboxylic acid and the alcohol from which each of the following esters is formed:

(a)  **(b)** 

[25.88] **CQ** Indole smells rather terrible in high concentrations but has a pleasant floral-like odor when highly diluted. It has the following structure:



Indole is a planar molecule. The nitrogen is a very weak base, with a K_b of 2×10^{-12}. Explain how this information indicates that the indole molecule is aromatic in character.

25.89 Locate the chiral carbon atoms, if any, in each of the following substances:

(a) $HOCH_2CH_2\overset{\overset{O}{\|}}{C}CH_2OH$ **(b)** $HOCH_2\overset{\overset{OH}{|}}{C}H\overset{\overset{O}{\|}}{C}CH_2OH$

(c) $HO\overset{\overset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}HCHC_2H_5$ (NH_2 on the second carbon)

25.90 Draw the condensed structural formula of each of the following tripeptides: **(a)** Val-Gly-Asp, **(b)** Phe-Ser-Ala.

25.91 **CQ** Glutathione is a tripeptide found in most living cells. Partial hydrolysis yields Cys-Gly and Glu-Cys. What structures are possible for glutathione?

25.92 Starch, glycogen, and cellulose are all polymers of glucose. What are the structural differences among them?

25.93 Monosaccharides can be categorized in terms of the number of carbon atoms (pentoses have five carbons and hexoses have six carbons) and according to whether they contain an aldehyde (*aldo-* prefix, as in aldopentose) or ketone group (*keto-* prefix, as in ketopentose). Classify glucose and fructose (Figure 25.28) in this way.

25.94 **CQ** Write a complementary nucleic acid strand for the strand GGTACT, using the concept of complementary base pairing.

Integrative Exercises

25.95 **CQ** Explain why the boiling point of ethanol (78°C) is much higher than that of its isomer, dimethyl ether (−25°C), and why the boiling point of CH_2F_2 (−52°C) is far above that of CF_4 (−128°C).

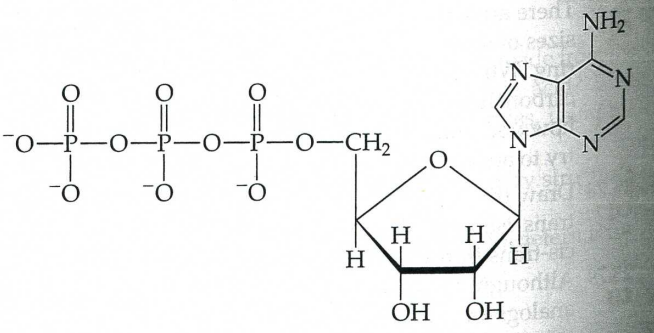
[25.96] An unknown organic compound is found on elemental analysis to contain 68.1% carbon, 13.7% hydrogen, and 18.2% oxygen by mass. It is slightly soluble in water. Upon careful oxidation it is converted into a compound that behaves chemically like a ketone and contains 69.7% carbon, 11.7% hydrogen, and 18.6% oxygen by mass. Indicate two or more reasonable structures for the unknown.

25.97 **CQ** An organic compound is analyzed and found to contain 66.7% carbon, 11.2% hydrogen, and 22.1% oxygen by mass. The compound boils at 79.6°C. At 100°C and 0.970 atm, the vapor has a density of 2.28 g/L. The compound has a carbonyl group and cannot be oxidized to a carboxylic acid. Suggest a structure for the compound.

[25.98] An unknown substance is found to contain only carbon and hydrogen. It is a liquid that boils at 49°C at 1 atm pressure. Upon analysis it is found to contain 85.7% carbon and 14.3% hydrogen by mass. At 100°C and 735 torr, the vapor of this unknown has a density of 2.21 g/L. When it is dissolved in hexane solution and bromine water is added, no reaction occurs. What is the identity of the unknown compound?

25.99 The standard free energy of formation of solid glycine is −369 kJ/mol, whereas that of solid glycylglycine is −488 kJ/mol. What is $\Delta G°$ for the condensation of glycine to form glycylglycine?

25.100 **CQ** One of the most important molecules in biochemical systems is adenosine triphosphate (ATP), for which the structure is

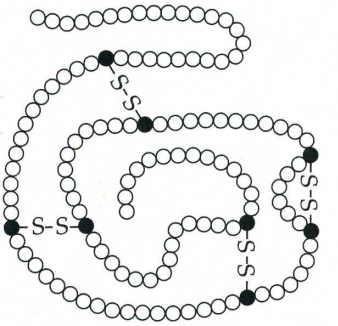


ATP

ATP is the principal carrier of biochemical energy. It is considered an energy-rich compound because the hydrolysis of ATP to yield adenosine diphosphate (ADP) and inorganic phosphate is spontaneous under aqueous biochemical conditions. **(a)** Write a balanced equation for the reaction of ATP with water to yield ADP and inorganic phosphate ion. [*Hint:* Hydrolysis reactions are just the reverse of condensation reactions (Section 22.8).] **(b)** What would you expect for the sign of the free-energy change for this reaction? **(c)** ADP can undergo further hydrolysis. What would you expect for the product of that reaction?

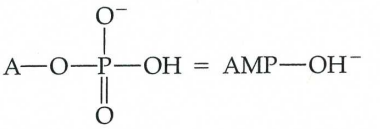
25.101 CQ A typical amino acid with one amino group and one carboxylic acid group, such as alanine [Figure 25.23(a)], can exist in water in several ionic forms. **(a)** Suggest the forms of the amino acid at low pH and at high pH. **(b)** Amino acids are reported to have two pK_a values, one in the range of 2 to 3 and the other in the range of 9 to 10. Alanine, for example, has pK_a values of about 2.3 and 9.6. Using species such as acetic acid and ammonia as models, suggest the origin of the two pK_a values.

[25.102] CQ The protein ribonuclease A in its native, or most stable, form is folded into a compact globular shape. **(a)** Does the native form have a lower or higher free energy than the denatured form, in which the protein is an extended chain? **(b)** What is the sign of the entropy change in going from the denatured to the folded form? **(c)** In the folded form the ribonuclease A has four —S—S— bonds that bridge between parts of the chain, as shown in the accompanying figure. What effect do you predict that these four linkages have on the free energy and entropy of the folded form as compared with a hypothetical folded structure that does not possess the four —S—S— linkages? Explain. **(d)** A gentle reducing agent converts the four —S—S— linkages to eight —S—H bonds. What effect do you predict this would have on the tertiary structure and entropy of the protein?



Native ribonuclease A

25.103 The monoanion of adenosine monophosphate (AMP) is an intermediate in phosphate metabolism:



where A = adenosine. If the pK_a for this anion is 7.21, what is the ratio of $[AMP—OH^-]$ to $[AMP—O^{2-}]$ in blood at pH 7.4?

eMEDIA EXERCISES

These exercises make use of the interactive objects available online in OneKey or the Companion Website, and on your Accelerator CD. Access to these resources comes in your MediaPak.

25.104 Use the **Boiling Point** activity (*25.2*) to plot the boiling points of the first six straight-chain alkanes (methane, ethane, propane, butane, pentane, and hexane) and their corresponding alcohols. **(a)** For a given number of carbons, which has the higher boiling point, the alkane or the alcohol? Use intermolecular forces to explain this observation. **(b)** Does the difference in boiling point for an alkane and its corresponding alcohol get smaller or larger as the number of carbons increases? **(c)** Using your observation from part (b), describe how the relative importance of hydrogen bonding and London dispersion forces changes with increasing length of a carbon chain. Which type of interaction contributes more significantly to the *overall* intermolecular forces for small molecules, and which for large molecules?

25.105 Plot the boiling points of at least five different alcohols and their corresponding amines (example: *tert*-butanol and *tert*-butylamine), using the **Boiling Point** activity (*25.2*). **(a)** Based on the boiling points, which functional group (alcohol or amine) appears to contribute more significantly to hydrogen bonding? Explain. **(b)** Draw Lewis structures of both alcohol and amine functional groups. Use the Lewis structures to support the conclusion that one functional group exhibits more significant hydrogen bonding than the other.

25.106 Watch the **Chirality** animation (*25.7*) and answer the following question. What conditions are required for a carbon in an organic molecule to be chiral?

25.107 The **Optical Activity** animation (*25.7*) illustrates the behavior of optically active molecules. **(a)** What conditions are necessary for an organic molecule to be optically active? **(b)** What is a *racemic mixture*, and why does it not rotate plane-polarized light? **(c)** Do cis and trans isomers of dichloroethene exhibit optical activity? Explain.

25.108 Exercise 25.59(b) asks for the number of and abbreviations for the tripeptides that can be made from the amino acids serine and phenylalanine. Using information from the **Proteins and Amino Acids** animation (*25.9*) and amino acid structural formulas in Figure 25.23, draw the structures for each of the tripeptides in your answer to Exercise 25.59(b).